Mineralogical Characterisation of the Rockliden Antimony-Bearing Volcanic-Hosted Massive Sulphide Deposit, Sweden

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Division of Geosciences and Environmental Engineering
Department of Civil, Environmental and Natural Resources Engineering
Luleå University of Technology

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ABSTRACT

Rockliden is a polymetallic Zn-Cu volcanic-hosted massive sulphide (VHMS) deposit. It is located in north-central Sweden about 150 km south of the Skellefte ore district. Two major challenges to mining and production were identified soon after Rockliden was discovered in the 1980’s. Firstly, the geographic distance to Boliden’s main ore deposits and existing concentrator in the Skellefte district will set additional financial and logistic constrains for the processing of the ore. Secondly, the locally high Sb grade in the ore potentially lowers the quality of the Cu-Pb concentrate sent to the Cu smelter. To face the second challenge to mining and production, it is necessary to use information from three disciplines: ore geology, mineral processing and process metallurgy. The three disciplines build the geometallurgical framework of the Rockliden ore characterisation. The purpose of this investigation is to outline which mineralogical factors are the cause of the elevated Sb content in the Cu-Pb concentrate. Determining such factors will help to predict the Sb content of this product and thus outline the tools required before decisions may be reached with regard to selection between various processing alternatives for the Rockliden ore. Hydrometallurgical treatment of the Cu-Pb concentrate has previously been studied by Awe (2013) and it was found that alkaline sulphide leaching can be used to lower the Sb content.

A qualitative characterisation of the ore forms the main focus of this licentiate thesis. Minerals have been identified and their chemical composition has been obtained with micro-analytical tools (SEM/EDS & EPMA/WDS) to study the mineralogical distribution of major (e.g. Zn, Cu, Fe), penalty (e.g. Sb) and bonus (e.g. Ag) metals. Furthermore, mineral textures and associations have been studied in ore samples by optical microscopy and SEM/BSE imaging. Ore types are preliminary classified based on the sulphide mineralogy, i.e. the relative content of pyrite, pyrrhotite, magnetite, sphalerite and chalcopyrite estimated by reflected light microscopy. As sphalerite and chalcopyrite form the main Cu- and Zn-bearing minerals at Rockliden, the content of these two minerals can be approached with element-to-mineral conversion based on standard drill core assays (including S, Cu, Zn, Pb, As, Sb and Ag). The mineralogy of Sb-bearing minerals is complex and a single thin section can contain more than three different Sb-bearing phases. Thus, the element-to-mineral conversion is not applicable in directly calculating the modal mineralogy of the Sb-bearing mineral fraction based on drill core assays. Additionally, it is shown that the mineral association of the Sb-bearing minerals is complex. Products from initial flotation tests have been studied and the preliminary conclusion is that the complex intergrowths with various minerals influence the distribution of Sb-bearing minerals between the flotation products. Thus, a more detailed petrographic study on the massive sulphides and their host rocks was conducted. The sulphide and non-sulphide mineralogy of the host rocks and ore types are shown to be variable. It is also shown that the host rock types can be distinguished based on their trace element geochemistry, supporting the geological classification based on drill core logging.

Based on petrographic and mineralogical observations done in this study, potential process-relevant rock-intrinsic factors are outlined. However, to evaluate the impact of such parameters on the beneficiation process, these parameters have to be quantified throughout the Rockliden deposit and this is the focus of continued studies. SEM-based automated mineralogy tools will be essential in measuring the important parameters such as modal mineralogy and mineral liberation. Quantitative
information will then be used in a larger framework to build a geometallurgical model usable for production planning.
ACKNOWLEDGEMENT

The Rockliden ore characterisation project is part of the work package 1 (Geometallurgy and 4D geological modelling) of the Centre of Advance Mining and Metallurgy (CAMM). Funding and financial support for the Rockliden project by CAMM, Boliden Mineral AB and ALS Piteå is acknowledged.

Christina Wanhainen and Pertti Lamberg do have my gratitude for their supervision, their scientific guidance, patience in listening and input of ideas. Jag vill tacka Christina för uppmärksam handledning, bra granskning och bra strukturering av alla projektetidéer. Haluan kiittää Pertti Lamberg hänen jakamistaan runsaista ideoistaan tälle hankkeelle. Also, I would like to thank my supervisors at Boliden, Jonas Lasskogen and Nils-Johan Bolin, for all assistance, suggestions, talks and contributions; and all the others who have supported me in many ways: Pär Weihe and Jan Rosenkranz (LTU), Heir Raat, Benny Mattsson, Rodney Allen, Pia Fagerström, Andreas Berggren, Peter Markström, Rolf Danielsson and Gunnar Agmalm (Boliden). Financial support for research exchange and discussions within ProMinNET (research network for Process Mineralogy and Geometallurgy, funded by Nordforsk) are appreciated.

Ulla-Britt Lundström and all the other personnel in the Boliden drill core archive for their help with finding and mounting drill cores which made it possible to obtain samples in an efficient way. Additionally to colleagues at Luleå University of Technology (Sweden) the following persons are thanked for assistance with SEM/EDS and EPMA/WDS analysis: Saku Varpenius and Leena Palmu (Center of Microscopy and Nanotechnology, Oulu University, Finland), Kurt Aasly and Kjetil Eriksen (Department of Materials Science and Engineering, NTNU Trondheim, Norway).

Also, I would like to thank my colleague Riia Chmielowski who helped out with language check whenever needed and Milan Vnuk for his last-minute help in formatting the licentiate thesis. I appreciate all the help and support which I received from my colleagues and friends at the ore geology, mineral processing and process metallurgy department; also their kindness and openness which made it easy to communicate across borders between different disciplines. Special thanks to Tobias Bauer, Abdul Mwanga and Samuel Awe for teaching me many things about their disciplines, and also to those friends passing by my office and accompanying me while travelling for data collection.

My family reserves my heartfelt thanks; my brothers for their endurance in waiting for an often busy sister and my parents for all their support on my way moving to the north.

With my journey through this PhD project, I hope that this part of work will give us awareness of our responsibility in taking care of all the earth’s resources (Psalm 24, 1).
List of Appended Papers


Conference Contributions:


General Abbreviations and Definitions

Abbreviations
AAS – Atomic Absorption Spectroscopy
BSE – Back Scattered Electrons
EDS – Energy-Dispersive X-ray Spectroscopy
EPMA – Electron Probe Micro-Analyzer
ICP-AES – Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS – Inductively Coupled Plasma Mass Spectrometry
LA-ICP-MS – Laser Ablation ICP-MS
SEM – Scanning Electron Microscopy
VHMS – Volcanic-Hosted Massive Sulphide deposit
WDS – Wavelength-Dispersive X-Ray Spectroscopy
XRF – X-Ray Fluorescence

Nomenclature (as used in this thesis)
Ore – rocks in the assessable part of the earth crust from which minerals can be profitably extracted (e.g. Robb 2005). In this study the economic aspect is not taken into account and the term ore comprises massive sulphide material and its immediate adjacent host rock which possibly would be mined together at Rockliden (theoretical mining blocks, or smallest mineable unit (SMU)).

Texture – this term will not be used in a strict petrographic sense (e.g. Vinx 2005). Within this study it comprises both micro structures (scalar mineral information, such as average diameter of mineral grains) and textures (vector mineral information, such as mineral orientation towards a given coordinate system). In the context of mineral processing performance, it includes all process-relevant petrographic information such as mineral assemblage, abundance, association, distribution, grain size, orientation, shape and grain boundary relationship (Butcher 2010; Walters and Kojovic 2006).
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1 Introduction

1.1 Practical Challenges to Mining and Production

The Rockliden volcanic-hosted massive sulphide (VHMS) Zn-Cu polymetallic deposit was discovered by Boliden Mineral AB in the 1980s (Raat and Årebück 2009). After initial beneficiation tests, the project was put on hold. It was found that the antimony (Sb) content of the Rockliden ore was high, ca. 0.2 wt\% in the upper part of the deposit (< 300m below surface) and such high Sb contents potentially lowers the quality of the Cu-Pb concentrate (Bolin 2010). Depending on the contract with the Cu smelters, a concentration higher than ca. 0.2 wt\% Sb causes penalties as it affects the smelting and refining process and influences the properties of metallic copper, e.g. lowers the conductivity (Awe et al 2012; Biswas and Davenport 1994; Knorr et al 1986; Larouche 2001; Navarro and Alguacil 2002; etc.). Several Sb minerals are known from Rockliden, including tetrahedrite, bournonite, Pb-Sb sulphosalts and gudmundite (Bolin 2010). Lager (1989) found that the behaviour of Sb in the laboratory flotation tests is dependent on the Sb mineralogy and the liberation distribution of the Sb-bearing minerals. However, there is only little previously available information on the mineralogical distribution of Sb and the 3D distribution of Sb-bearing minerals in the Rockliden ore (cf. Depauw 2009; Karup-Møller and Makovicky 1980a).

Resource delineation drilling restarted at Rockliden in 2007 and resources have increased since then (Raat and Årebück 2009). Currently, the inferred mineral resource of Rockliden is 3.53 Mt at 4.2 wt\% Zn, 1.9 wt\% Cu, 0.7 wt\% Pb and 71 g/t Ag (New Boliden 2013). It is important for the production planning to have a better understanding on the variation and complexity of mineralogy in the Rockliden ore and how this will affect the quality of the flotation products. The need for this information has led to the initialisation of the Rockliden ore characterisation and geometallurgical case study. Thus this PhD project focuses on the trace, penalty (e.g. Sb, As, Hg, Bi) and bonus (e.g. Ag, Sn), elements and their host- and associated minerals.

1.2 Antimony – Applications, Mineralogy and Metallurgy

Antimony (Sb) has several applications in form of metallo-organic and inorganic compounds, for example as flame retardants and Sb-based catalysts and alloys, to increase strength and hardness of Pb (Anderson 2012; Buttermann and Carlin 2004; Masters 2005). Given its usage, it has been defined as critical raw material for the modern society (Anderson 2012; European Commission 2010). The world market of Sb is dominated by China (Anderson 2012; Masters 2005).

The Chinese Sb resources are comprised mostly of stibnite, associated with pyrite, arsenopyrite, and jamesonite (Buttermann and Carlin 2004; Tian-cong 1988, table 1.1). Volcanic-hosted massive sulphide (VHMS) deposits, such as Rockliden, are not a primary source for Sb (Galley et al 2007). Generally, VHMS deposits are known to contain a wide range of elements beside the base-metal
elements (Cu, Zn, Pb, table 1.1) and they are referred to as polymetallic (e.g. Herzig and Hannington 1995). Given the wide range of elements contained in VHMS deposits, the mineralogy is complex. This is also true for the Sb mineralogy which is similarly complex in VHMS and vein type deposits (table 1.2). An example of vein deposit is the Sunshine mine, Idaho, USA, where Pb-Ag-Zn-Cu-Sb sulphides have been mined from tetrahedrite-rich quartz-siderite veins (Anderson 1940; Wavra et al 1994).

At the Sunshine mine, Sb has been extracted via alkaline sodium sulphide leaching and recovered by electrowinning at the antimony plant (Anderson et al 1991). Comparatively, the recovery of Sb from Sb-rich parts of the VHMS deposits in the Skellefte district and Rockliden can be considered under favourable economic circumstances. Thus far no similar projects are known where Sb is under consideration for removal or recovery from a VHMS deposit via unconventional hydro- and electrometallurgical process options (Bolin, pers. comm., 2013-09-19). However, laboratory flotation tests were done for the separation and enrichment of Sb-bearing minerals (tetrahedrite-tennantite) during scavenger flotation for Neves-Corvo ore, Portugal (Byrne et al 1995).

1.3 The Process Mineralogical and Geometallurgical Context of this Study

Process Mineralogy

Process Mineralogy is a branch of applied mineralogy (Petruk 2000). It aims to understand the variations in the metallurgical performance related to the mineralogy and petrography of ore (Jackson et al 2011); and to solve problems in any part of the process chain by collecting mineralogical information (Petruk 2000). Rock-intrinsic process-relevant parameters, such as texture (mineral grade, grain size, mineral association, etc.) and rock strength (hardness, abrasion, etc.) need to be identified and measured (Walters and Kojovic 2006). The collection of quantitative mineralogical data involves classical mineral analytical tools (Petruk 2000). Especially, SEM-based automated techniques are of use in mineralogically complex ores (Sutherland and Gottlieb 1991) such as the Rockliden ore. To evaluate the impact of rock-intrinsic process-relevant parameters, quantitative data has to be collected from a reasonable number of samples (Lamberg 2011). Further, the process mineralogical approach in itself has no direct spatial context and a large number of ore samples might need to be analysed in order to build a geometallurgical model for an entire ore deposit (Jackson et al 2011; Lamberg 2011).
Table 1.1. Sb grades in polymetallic (VHMS) deposits.

<table>
<thead>
<tr>
<th>Deposit</th>
<th>reference</th>
<th>Size (ore body, etc.)</th>
<th>S / wt%</th>
<th>Zn / wt%</th>
<th>Cu / wt%</th>
<th>Pb / wt%</th>
<th>As / wt%</th>
<th>Sb / g/t</th>
<th>Ag / g/t</th>
<th>Au / g/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maranda, Murchison (South Africa)</td>
<td>Schwarz-Schampera et al (2010)</td>
<td>ca. 1.8 Mt</td>
<td>21.0</td>
<td>23.6</td>
<td>4.2</td>
<td>0.0</td>
<td>0.0</td>
<td>51.3</td>
<td>77.4</td>
<td>0.1</td>
</tr>
<tr>
<td>LCZ (Letaba, Platveld), Murchison (South Africa)</td>
<td>Schwarz-Schampera et al (2010)</td>
<td>with LCZ</td>
<td>20.4</td>
<td>23.8</td>
<td>2.3</td>
<td>0.0</td>
<td>0.03</td>
<td>5.5</td>
<td>31.7</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Rakkejaur, Skellefte district (Sweden)</td>
<td>Allen et al (1996)</td>
<td>&gt; 17 Mt</td>
<td>26.0</td>
<td>2.4</td>
<td>0.3</td>
<td>0.2</td>
<td>1.6</td>
<td>600.0</td>
<td>50.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Renström, Skellefte district (Sweden)</td>
<td>Allen et al (1996)</td>
<td>9.0 Mt</td>
<td>15.0</td>
<td>6.5</td>
<td>0.8</td>
<td>1.5</td>
<td>0.2</td>
<td>300.0</td>
<td>155.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Kristineberg, Skellefte district (Sweden)</td>
<td>Allen et al (1996)</td>
<td>20.1 Mt</td>
<td>25.0</td>
<td>3.7</td>
<td>1.0</td>
<td>0.5</td>
<td>-</td>
<td>20.0</td>
<td>35.0</td>
<td>1.0</td>
</tr>
<tr>
<td>West Maurliden, Skellefte district (Sweden)</td>
<td>Allen et al (1996)</td>
<td>6.9 Mt</td>
<td>39.0</td>
<td>3.4</td>
<td>0.2</td>
<td>0.4</td>
<td>1.2</td>
<td>1200.0</td>
<td>4.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Rockliden mineral resource, Bothnian Basin (Sweden)</td>
<td>New Boliden (2013)</td>
<td>3.53 Mt</td>
<td>-</td>
<td>4.2</td>
<td>1.9</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>71.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Trout Lake, Flin Fion-Snow Lake areas (Manitoba, Canada)</td>
<td>Petruk (2000, chapter 4)</td>
<td>3.53 Mt</td>
<td>-</td>
<td>11.8</td>
<td>4.8</td>
<td>0.5</td>
<td>0.1</td>
<td>73.4</td>
<td>52.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Hellyer, Australia</td>
<td>McArthur (1996)</td>
<td>-</td>
<td>-</td>
<td>13.8</td>
<td>0.4</td>
<td>7.1</td>
<td>1.2</td>
<td>&lt;1000</td>
<td>167.8</td>
<td>2.5</td>
</tr>
<tr>
<td>composite feed sample, Neves-Corvo (Portugal)</td>
<td>Benzaazoua et al. (2002)</td>
<td>-</td>
<td>-</td>
<td>0.9</td>
<td>8.6</td>
<td>-</td>
<td>0.4</td>
<td>1500.0</td>
<td>50.0</td>
<td>-</td>
</tr>
<tr>
<td>MC ore, Neves-Corvo (Portugal)</td>
<td>Byrne et al (1995)</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>7.4</td>
<td>-</td>
<td>0.4</td>
<td>1000.0</td>
<td>42.0</td>
<td>-</td>
</tr>
<tr>
<td>MH ore (high grade in penalty elements), Neves-Corvo (Portugal)</td>
<td>Byrne et al (1995)</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
<td>9.4</td>
<td>-</td>
<td>0.6</td>
<td>5300.0</td>
<td>129.0</td>
<td>-</td>
</tr>
<tr>
<td>Mine sample, Neves-Corvo (Portugal)</td>
<td>Byrne et al (1995)</td>
<td>-</td>
<td>35.8</td>
<td>2.9</td>
<td>18.2</td>
<td>-</td>
<td>0.8</td>
<td>7400.0</td>
<td>195.0</td>
<td>-</td>
</tr>
<tr>
<td>Black ore, Kosika and Hanakou / Kuroko (Japan)</td>
<td>Amcoiff (1984)</td>
<td>-</td>
<td>22.5</td>
<td>2.2</td>
<td>16.0</td>
<td>-</td>
<td>290.0</td>
<td>312.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Yellow ore, Kosika and Hanakou / Kuroko (Japan)</td>
<td>Amcoiff (1984)</td>
<td>-</td>
<td>2.0</td>
<td>7.4</td>
<td>0.2</td>
<td>-</td>
<td>30.0</td>
<td>36.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>modern seafloors, mid-ocean ridges, sediment-hosted polymetallic massive sulphides (e.g. Escanaba Trough)</td>
<td>Herzig and Hannington (1995)</td>
<td>-</td>
<td>11.7</td>
<td>4.3</td>
<td>0.2</td>
<td>0.0</td>
<td>100.0</td>
<td>143.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>modern seafloors, back-arc ridges, intracontinental polymetallic massive sulphides (e.g. Okinawa Trough)</td>
<td>Herzig and Hannington (1995)</td>
<td>-</td>
<td>18.4</td>
<td>2.0</td>
<td>11.5</td>
<td>1.5</td>
<td>3000.0</td>
<td>2766.0</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Eskay Creek deposit, British Columbia, Canada</td>
<td>Sherlock et al (1999)</td>
<td>-</td>
<td>1.9 Mt</td>
<td>-</td>
<td>5.2</td>
<td>0.7</td>
<td>3.2</td>
<td>-</td>
<td>2652</td>
<td>60.2</td>
</tr>
<tr>
<td>Polymetallic veins, Sunshine, Coeur d'Alene district, Idaho</td>
<td>Anderson et al (1991)</td>
<td>concentrator feed</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>4000.0</td>
<td>0.9</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

a) production and proven-probable reserves at Dec 31 1998.
Table 1.2. Common Sb minerals in polymetallic (VHMS) deposits such as tetrahedrite-tennantite (Ttr-Tnn), bournonite (Bour) and gudmundite (Gd).

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Reference</th>
<th>Ttr-Tnn</th>
<th>Ag-Sb-(Hg) minerals</th>
<th>Sb-Pb sulphosalts</th>
<th>Pb-As-Sb sulphosalts</th>
<th>Gd (and Sb-Fe minerals)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maranda &amp; LCZ (Letaba, Platveld), Murchison (South Africa)</td>
<td>Schwarz-Schampera et al (2010)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Rakkejaur, Skellefte district (Sweden)</td>
<td>Lager and Fossberg (1990)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Renström, Skellefte district (Sweden)</td>
<td>Duckworth and Rickard (1993)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Kristineberg, Skellefte district (Sweden)</td>
<td>Hannington et al (2003)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>West Mauriden, Skellefte district (Sweden)</td>
<td>Bollin (2009)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Rockliden mineral resource, Bothnian Basin (Sweden)</td>
<td>Minz et al. (2012)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Trout Lake, Flin Fion-Snow Lake areas (Manitoba, Canada)</td>
<td>Petruk (2000, chapter 4)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>composite feed sample, Neves- Corvo (Portugal)</td>
<td>Benzaazoua et al. (2002)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Neves-Corvo (Portugal)</td>
<td>Byrne et al (1995)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>modern seafloors, mid-ocean ridges, sediment-hosted</td>
<td>Herzig and Hannington (1995 and references therein)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>polymetallic massive sulphides (e.g., Escanaba Trough)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>modern seafloors, back-arc ridges, intracontinental</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>polymetallic massive sulphides (e.g., Okinawa Trough)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hellyer, Australia</td>
<td>McArthur (1996), Grammatikopoulos et al (2006)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Eskay Creek deposit, British Columbia, Canada</td>
<td>Grammatikopoulos and Roth (2002)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Izok Lake deposit, Northwest Territories, Australia</td>
<td>Harris et al (1984)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Polymetallic veins, Sunshine, Coeur d'Alene district, Idaho</td>
<td>Anderson (1940)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

1) pyrargyrite, myargyrite, dyscrasite, etc.
2) boulangerite, meneghenite, zinckenite, falkmanite, etc.
3) jordanite, etc.
4) berthierite, etc.
5) including stibnite and kermesite (Grammatikopoulos and Roth 2002; Halbach et al 1993).
Geometallurgy

Various definitions on geometallurgy have been formulated, highlighting different aspects of the holistic view concerning all of the steps involved in the beneficiation of valuable minerals and extraction of metals from an ore deposit (Jackson et al 2011). Within this study an engineering view is used. This means that a definition of ore types is based on rock-intrinsic parameters relevant to the processing of the ore, and thus differs from a genetic classification traditionally chosen in geology (e.g. Robb 2005). Geometallurgy aims to link both quantitative geological and metallurgical information to create a spatially-based (3D) model, i.e. combining predictive processing models which are based on a geological model (Lamberg 2011). The linked information is to be applied in the mining industry, e.g. in production management, in the form of geometallurgical programs. Geometallurgical programs could, for example, help to convert currently uneconomic deposits into viable economic operations (Dunham et al 2011).

A geometallurgical program consists of several steps covering the entire processing chain of an ore (Lamberg 2011 and references therein). Before setting the scope of a geometallurgical program, its framework and the stages of 6 dimensions should be considered (Jackson et al 2011). These dimensions include: process span, response knowledge, variability knowledge, spatial knowledge, application of the program, and project phase. A critical aspect is the dimension of the process span as several mineralogical and metallurgical processes might be involved to extract minerals and metals from a deposit (Jackson et al 2011). Here it becomes important to identify which beneficiation and metallurgical extraction processes can be covered by the mining company applying a geometallurgical program or whether it is required that the products, like concentrates, are sold on the open market (Lager 1989). At the Boliden Mineral AB, company-owned facilities cover the whole process chain from mining of mineral deposits, via mineral extraction in beneficiation plants (e.g. concentrator in Boliden and Garpenberg) to metal extraction in metallurgical plants (Cu smelter and Zn plant, e.g. at Rönnskär and Kokkola) (Bolin et al 2003; Ikumapayi 2013; New Boliden 2013; Rao et al 1997). This situation allows in-house evaluation of unconventional process solutions like alkaline sulphide leaching in a hydrometallurgical plant, as exemplified in figure 1.1 for the production of copper (Cu).

![Fig. 1.1. Simplified process chain showing unconventional process solutions for the extraction of Cu from a mineralogical complex massive sulphide ore such as Rockliden.](image-url)
The ore processing chain, outlined in figure 1.1, sets also the framework for the Rockliden ore characterisation and geometallurgical research project. It should be noted that it is not the purpose to optimise the processes or parts of the processing chain in the Rockliden case study. Exemplified by the full-scale process development at the Garpenberg concentrator (Bergslagen District, southern Sweden), Bolin et al (2003) pointed out that variations in the complex sulphide ore are often underestimated. In the Rockliden case study, focus is set on ore characterisation and variability testing (cf. Lamberg 2011). The aims of the project are described below.

1.4 Objectives and Structure of the Project

To face the mineralogical challenges related to compositional and textural complexity of the ore from the Rockliden VHMS deposit, the project is divided in two main parts (Fig. 1.2), which generally cover step one and two of the mineralogical approach recommended by the geometallurgy research group of Luleå University of Technology. The mineralogical approach is described in more detail by Lund (2013).

First part (Objective 1): Ore Characterisation and Geological Modelling

Ore characterisation is a critical part of geometallurgical projects and provides, in combination with the geological model, the basis for the geometallurgical approach (Lamberg 2011; Lund 2013). On the deposit-scale, the geometry of the Rockliden ore body is rather complex. A classical geological model, estimating the 3D distribution of different host rocks and outlining the massive sulphide bodies, is currently under construction at the Exploration Department (Boliden Mines, Lasskogen, pers. com.). On a micro-scale, the mineralogy of the ore is complex and thus emphasis in the first part of this project was put on conducting a detailed mineralogical characterisation of the ore. This includes collection of information on petrography and the application of geochemical discrimination tools for the host rocks and the ore. It further provides an insight in the variation of the mineralogy especially regarding base-metals as well as bonus- and penalty-element-bearing minerals in the massive sulphide ore.


A confined number of samples are collected from drill core intervals with relatively high grades of Sb and Ag in order to be able to trace the penalty elements in form of their minerals and particles through the process. In studies on the flotation behaviour of Sb-bearing minerals in the massive sulphide ore at Neves-Corvo (Byrne et al 1995) and in studies on the Hg mineralogy of the Eskay Creek VHMS deposit (Grammatikopoulos and Roth 2002), naturally Sb- and Hg-spiked feed material was used for similar reasons. New extraction tests, also called variability testing (cf. Lamberg 2011), are planned for the second part of this study. The most recently collected Rockliden drill core samples will be treated in laboratory flotation tests, and all products will be

---

1 based on the observations and results from the first part of this study (objective 1)
documented in terms of metal content and metal distribution related to the mineralogy of the ore samples. Mainly, automated mineralogical (SEM-based) tools will be used to document the flotation distribution of locked and unlocked critical-element-bearing minerals derived from different ore types. The aim is to quantify and verify rock- and ore-intrinsic parameters which can be related to a variation in the process-response, i.e. the Sb content in the flotation products. Further, it is aimed to collect quantitative data throughout the ore deposit in order to evaluate spatial variation of the ore-intrinsic process-relevant parameters. Spatial data is intended to be used in a larger framework, i.e. by collecting this information in a structured form and by building a process-adopted geological model for the VHMS deposit at Rockliden (Fig. 1.2). Based on the geological and mineralogical variability of the ore, a complete geometallurgical model should provide tools for predicting the mineral process performance. Such information is of use in mine planning and production management, allowing for technical and economical consideration of process alternatives like roasting at the smelter (Björnberg et al 1986) or alkaline sulphide leaching in a hydrometallurgical plant and extraction of Sb by electrowinning (Awe et al 2012; Awe 2013).

Fig. 1.2. Flow chart showing the outline of the first part (black) and ideas for the second part (grey) of the PhD project (modified from Lund (2013)).
2 Materials and Methods

2.1 Drill Core Logging and Mapping

About 1500 m drill core of massive sulphides and host rock was logged by classical geological tools, i.e. using description based on macroscopic observation. The relative abundance of macroscopically distinguishable sulphide minerals such as pyrite, pyrrhotite, chalcopyrite and sphalerite were estimated and textures were documented (paper II). Recently, a 100 x 50 m² wide outcrop was mapped by Evins (2011) for structural analysis at the Rocklide site to be used in a geological model of the ore deposit. This model is currently under construction by the Boliden Mineral AB. A new surface map was constructed based on geochemical classification of samples collected from RC (KAX) drilling (Lasskogen pers. comm., 2013-09-19, map presented in paper II, table 2.1)

2.2 Preliminary Mineralogical Classification

In preparation of sampling for this study, the main sulphide mineralogy of drill core samples was calculated in the Geo module of the HSC Chemistry software (Roine 2009). A chemical assay database including S, Cu, Zn, Pb, As, and Sb, provided by Boliden Mineral AB, was converted to a simplified mineralogy of pyrite, chalcopyrite, sphalerite, galena, arsenopyrite and bournonite. The calculation is simplified; for example pyrrhotite, which is present in the ore, is included in the modal pyrite. Similarly, the bournonite includes diverse Sb-bearing minerals. Based on the total sulphide content, disseminated sulphides (< ca. 15 wt%) and massive sulphides (> 50 wt% sulphides) can be distinguished. Samples with intermediate sulphide content will be referred to as semi-massive sulphides. For additional classification the sulphide content of all samples was calculated to 100 wt%, i.e. plain sulphide fraction. Based on the sphalerite and chalcopyrite content of the sulphide fraction in the assayed drill core intervals, three preliminary classes were defined: a sphalerite-, a chalcopyrite- and a pyrite-rich class. These classes were further subdivided by their Ag- and Sb-content representing critical bonus and deleterious elements (Fig. 2.1).

Six drill cores were selected and 59 samples were collected to cover most of the preliminary defined classes throughout the vertical extent of the deposit (table 2.1). During sampling, the preliminary classification was validated with the qualitative knowledge gained from drill core logging. All 59 samples (each ca. 40 cm of quartered, mostly BQ diamond drilled core) were assayed by the ALS Minerals Division (Piteå, Sweden) for 64 major and trace elements. Chosen analytical packages comprise mostly ICP-MS and ICP-AES analytical techniques. For the ore grade samples analytical packages had to be added, including XRF and AAS techniques. Combustion furnace methods were chosen to record the total carbon and total sulphur content in the samples.
Fig. 2.1. Preliminary classification based on chemical assays and calculated mineral content (Roine 2009) of drill core material collected for this study (all samples n=59, massive sulphides n = 33).

2.3 Initial Flotation Tests

Laboratory flotation tests on three bulk samples collected from different parts of the areas designated as ore lenses within the Rockliden deposit (Fig. 3.3) were run at the Boliden laboratories (Bolin 2010). Chemical assays were done for all products and epoxy samples were prepared from the final flotation products for mineralogical studies (Fig. 4.1, table 2.1). Analytical results are compiled in paper I.

Table 2.1. Summary of samples used in this study.

<table>
<thead>
<tr>
<th>No.</th>
<th>sample type</th>
<th>experimental, analytical methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>490</td>
<td>drill core, RC drilling</td>
<td>surface mapping (Exploration Department, Boliden Mines), geochemical analysis</td>
</tr>
<tr>
<td>59</td>
<td>drill core sample (mostly ca. 40 cm quartered BQ drill core)</td>
<td>geochemical analysis and mineralogical studies (optical microscopy, SEM/BSE imaging, SEM/EDS, EPMA/WDS)</td>
</tr>
<tr>
<td>3</td>
<td>composite drill core samples (each ca. 15 to 30 kg)</td>
<td>laboratory flotation tests (2009), geochemical analysis</td>
</tr>
<tr>
<td>9</td>
<td>final products of laboratory flotation tests (2009)</td>
<td>geochemical analysis and mineralogical studies on polished epoxy moulds</td>
</tr>
</tbody>
</table>

2.4 Mineralogical Studies

To define the main mineralogy in the samples, thin sections were prepared from all drill core samples by Vancouver Petrographics Ltd, Canada. The mineralogy of thin sections from ca. 80 drill core samples and outcrop samples was studied by optical microscopy using a Nikon ECLIPSE E600 POL (Division of Geosciences and Environmental Engineering, Luleå University of Technology). The relative abundance of main opaque and sulphide minerals (pyrite, pyrrhotite,
magnetite, sphalerite and chalcopyrite) were studied in reflected light and the remaining, non-opaque, minerals such as silicates in transmitted light. Based on optical microscopy samples were selected for further micro-analytical studies by SEM/EDS and EPMA/WDS. Target minerals for EPMA/WDS studies were Sb-bearing sulphide minerals (paper I) and, mostly Fe-bearing, oxide and silicate minerals (paper II).

The Sb- and Ag-bearing minerals are minor or trace minerals (cf. Butcher 2010). Generally, they form less than 2 area% and are generally smaller than 100 μm in diameter (paper I, see also results below, table 3.5). This excludes them from being macroscopically distinguishable during drill core logging. Further, their optical properties are often similar, limiting the usage of optical microscopy. Thus, these minerals were mainly studied at the scanning electron microscope (SEM) in backscattered electron (BSE) images and by energy-dispersive X-ray spectroscopy (EDS). Most of this work was done at the Merlin SEM (FESEM - Zeiss Gemini, Luleå University of Technology, Sweden). Minor parts of the study were conducted at the following instruments: Hitachi SU6600 (FESEM, Department of Materials Science and Engineering, NTNU Trondheim, Norway) and Ultra Plus – Zeiss Gemini (FESEM, Center of Microscopy and Nanotechnology, Oulu University, Finland). The following analytical conditions were used: an acceleration voltage of 20 keV and an emission current of 0.9 to 1.1 nA. Electron microprobe/wave-length dispersive spectroscopy (EPMA/WDS) analyses were done by the JEOL JXA-8200 microanalyser at the Center of Microscopy and Nanotechnology, Oulu University, Finland. An acceleration voltage of 15 keV, an emission current of 15 to 30 nA and a beam diameter of 5 μm were used.

SEM/EDS and EPMA/WDS studies were done on polished epoxy samples from the final Cu-Pb and Zn concentrates and tailing products (Fig. 4.1) at the Research Laboratory of the Geological Survey of Finland (GTK, Helsinki; Bolin 2010). This included a search for heavy minerals (heavier than Fe-oxides) with a minimum grain size of 15 μm and the recoding of the modal composition of this heavy mineral fraction. Regarding the Sb-bearing minerals, attempts to verify modal mineralogy or evaluate mineral liberation by optical microscopy were not done. This is not only due to their similar optical properties, but also to their rather small particle sizes as the 80% passing (P80) of the feed for the laboratory test flotation was ca. 50 μm. In projects similar to this study, methods such as optical microscopy and point-counting were not found suitable based on the same reasons (Lager 1989).
3 Results

3.1 Host Rock Petrography and Silicate Mineralogy

Given the complex geometry of the Rockliden massive sulphide ore bodies (paper II), the mineralogy of the host rock will impact on the processing of the ore due to wall rock dilution. Where the massive sulphides are in straight contact with the silicate-dominated host rock, the latter might contain only disseminated sulphides with a total sulphide content of less than 15 wt%. The lithology of the Rockliden ore deposit is described in paper II. The massive sulphides are chiefly enveloped by felsic volcanic and sedimentary host rocks (paper II) which can be distinguished by their trace element geochemistry. A more detailed account on the host rock geochemistry and petrography is given in paper II. Below, the mineralogy of the host rocks including sedimentary rocks, felsic volcanic rocks, and one mafic rock unit, referred to as mafic dykes (paper II), is summarised based on optical microscopy, supported by SEM/EDS and EPMA/WDS analysis for felsic volcanic and mafic dykes.

The sedimentary host rock forms the stratigraphic top to the massive sulphides and shows very little alteration (Depauw 2009; Raat and Årebäck 2009). Petrographically they are classified as siliciclastic shales and siltstones, reaching up to fine-grained sandstones. The mineralogy of the sedimentary host rock is dominated by phyllosilicates and quartz (paper II).

Similarly to the sedimentary host rock, the felsic volcanic rocks are dominated by phyllosilicates and quartz. Additionally, they contain abundant plagioclase and alkali-feldspars, which can be distinguished by optical microscopy in the coarser grain fraction, i.e. among the phenocrysts. Moreover, the mineralogy is complicated due to (spatially) extensive alteration of the volcanic host rocks (paper II). At Rockliden, the main alteration minerals comprise sericite, chlorite and quartz, in order of increasing degree of alteration (cf. Raat and Årebäck 2009). Mineral associations found in different alteration zones are displayed in figure 3.1a to e. Locally, andalusite, calcite, epidote group minerals (Fe-rich clinozoisite, table 3.1), garnet (almandine-spessartine group, table 3.1), and Zn-rich gahnite (table 3.1), as well as traces of fluorite and anhydrite are documented in the altered volcanic rocks. Amphibole minerals (Fig. 3.1e) are found in one sample classified as a felsic volcanic rock based on its Nb/Y vs Zr/TiO₂ content (paper II; cf. Winchester and Floyd 1977). The chemical composition of these amphibole minerals differs slightly from those amphibole minerals found in the mafic dykes (Fig. 3.2). Altered volcanic rocks show locally elevated concentrations in Sb and, in addition to gudmundite, various Sb-bearing sulphosalts are documented (see subsection 3.4).
Table 3.1. Main occurrence (* in mafic dykes or felsic volcanic rocks) and chemical composition (EPMA/WDS analysis, wt%) of silicate and oxide minerals (Plg – plagioclase, Afs – alkali feldspars, Bt – biotite, Amp – amphibole (also in massive sulphides), Ep – epidote group minerals, Tit – titanite, Grt – garnet group minerals, Mgt – magnetite (analysis only for Mgt from mafic dykes), Chr – chromite (Zn-bearing), Gah – gahnite (Zn-bearing)). Modified from paper II.

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<th>V</th>
<th>K</th>
<th>Al</th>
<th>Cr</th>
<th>Sn</th>
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<td>0.11</td>
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<td>1.55</td>
<td>-</td>
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<td>0.08</td>
<td>0.06</td>
<td>-</td>
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<tr>
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<td>-</td>
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<tr>
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<td>n = 7</td>
<td>SD</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>0.27</td>
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<td>0.07</td>
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<tr>
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<tr>
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<td>-</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
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<td>0.01</td>
<td>0.62</td>
<td>0.03</td>
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</tbody>
</table>

a) statistics (LLD – lower limit of detection (EPMA/WDS analysis), AM – arithmetic mean, SD – standard deviation).
b) possibly with mineral inclusions.
Fig. 3.1. Association and textures of silicate minerals in felsic volcanic (a to e) and mafic rocks (f): a) sericite (Seri) alteration with quartz (Qtz) and minor biotite (Bt), b) quartz (Qtz) alteration zone with biotite (Bt) and gahnite (Zn-Spl), c) chlorite alteration zone with quartz (Qtz), chlorite (Chl) and biotite (Bt), d)
semi-massive sulphides with biotite (Bt), andalusite (And) and chlorite (Chl), e) amphibole (Amp) and epidote group minerals (Ep, Fe-rich clinozoisite), f) varying size of amphibole (Amp) minerals in the mafic dyke cut by fine calcite (Cal) veinlets.

Mafic dykes are dominated by amphiboles (Fig. 3.1f) and are distinguished based on their relatively high Cr and V values. Zn-rich chromite and V-Cr-rich magnetite are common trace minerals in the mafic dykes (table 3.1). The amphibole minerals represent calcic amphiboles, mostly with a chemical composition similar to hornblende or actinolite. The zoning pattern of amphiboles from the mafic dykes is rather complex, containing Fe-Al-rich rims which are not documented in amphiboles from the felsic volcanic rocks or massive sulphides (Fig. 3.2). Beside amphiboles, plagioclase, biotite and minor chlorite, titanite, ilmenite, rutile, calcite and apatite are documented in these rocks (paper II). The mafic dykes show an elevated concentration in Sb and disseminated Sb-bearing minerals such as bournonite, meneghinite and tetrahedrite are documented (paper I). In contrast to the disseminated sulphide samples from the felsic volcanic rocks, the mafic dykes contain chalcopyrite as the dominating base-metal sulphide mineral (paper II).

Fig. 3.2. Chemical zoning of amphibole (Amp) minerals: a) BSE image of an amphibole crystal in a mafic dyke, b) BSE image of an amphibole crystal in a felsic volcanic rock, c) BSE image of amphibole crystals intergrown with dolomite (Dol) in massive sulphides, d) ternary plot showing the chemical variation and clustering of EPMA/WDS analysis from rock and massive sulphide samples.
Based on calculations with HSC Chemistry (see sub-section 2.2; Roine 2009), the total sulphide content is less than 50 wt% for the non-massive sulphide samples. The border between the massive sulphides and the host rock might not be sharp in all cases. Locally, a transitional sulphide-silicate zone, termed stockwork (Depauw 2009), is documented in drill cores and is characterised by a mesh of sulphides transecting the host rock. Typically, such stockwork zones are underlying idealised VHMS ore deposits (Galley et al 2007). Samples from this zone are part of the semi-massive sulphides (15 – 50 wt% total sulphide content). The average chalcopyrite content of the (plain) sulphide fraction in these semi-massive sulphide samples is ca. 15 wt%, which is high as compared with the massive sulphides (ca. 10 wt%). It was earlier noted by Mattsson and Heeroma (1985), that chalcopyrite is the dominating base-metal sulphide of this zone. Thus, this stockwork zone is a potentially relevant Cu source at the Rockliden ore deposit, if it represents a significant part of the material to be mined.

Within the massive sulphides, besides sulphide minerals and magnetite, various other minerals were detected, such as carbonate minerals, quartz and chlorite group minerals, as well as minor amphibole and feldspar minerals (table 3.1). The carbonate minerals comprise calcite and dolomite group minerals. The Fe content of the dolomite group minerals ranges from ca. 0 up to 10 wt% (rarely reaching up to ankerite composition, SEM/EDS analysis).

3.2 Metal Zoning

There is no distinct variation in the Cu/(Cu+Zn) ratio at Rockliden, which might have been expected from a metal and mineralogical zonation, such as those typical for (bimodal-felsic) VHMS type deposits (Galley et al 2007; Mattsson and Heeroma 1985; Fig. 3.4a). The primary zoning is probably poorly preserved due to subsequent structural modification and metamorphism, suggested to be related to the deformation of the Rockliden ore deposit (Depauw 2009). It can be seen in figure 3.3c that there is not a single Cu-centre, which could be interpreted as discharge centre(s) of a hot, hydrothermal fluid in a model for a classical VHMS deposit (Hermansson 2011; Ohmoto 1996). Cu-centres appear to be rather equally distributed over the vertical extent of the Rockliden ore deposit (Fig. 3.3c). Moreover, the distribution of drill core intervals defined as chalcopyrite-dominated by the preliminary classification appear to be distributed and scattered over the 3D extent of the deposit (Fig. 3.3f).
Fig. 3.3. Metal zonation of critical trace elements and base-metals within the Rockliden massive sulphide ore body (translucent shapes): a) Sb content, b) Ag content, and c) of base-metals (Cu/(Cu+Zn) ratio calculated and modelled in Leapfrog 3D mining modelling software using a spheroidal model for kriging); and spatial distribution of preliminary classes defined with HSC Chemistry: d) Sb-rich classes, e) Ag-rich classes, f) of all sphalerite (Sp) and chalcopyrite (Ccp) dominated classes.

A mineralogical coupling might prevail, as Ag and Sb show mutual correlation coefficients compared to other elements (table 3.2). It should be noted that, generally, even a single thin section contains several Sb-bearing minerals. Differences can be seen in the 3D grade distribution of critical elements such as Sb and Ag (Fig. 3.3a and b) and the distribution of Sb- and Ag-rich drill core intervals (Fig. 3.3c and d). Variation in the Ag and Sb mineralogy on a deposit scale are indicated. It was noted that bournonite is common in the southern-central part, tetrahedrite in the northern part and gudmundite towards deeper parts of the deposit (Bolin 2010). Similar observations were made in qualitative mineralogical studies on drill core samples (paper I). However, the observations need to be quantified in order to be evaluated or verified. Also, lead
(Pb) shows high correlation coefficients with both Ag and Sb (table 3.2). However, a significant
direct mineralogical coupling of Pb and Ag has not been found so far (table 3.3 and table 3.4).

**Table 3.2.** Correlation matrix for the drill core assays available in the Boliden database (evaluated with HSC
Chemistry (Roine 2009)), all data on blue background (n = 1056) and massive sulphide drill core intervals
with total sulphides content > 50 wt% on orange background (n = 424).

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>Ag</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>As</th>
<th>S</th>
<th>Sb</th>
<th>Bi</th>
<th>Hg</th>
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</thead>
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<td>Au</td>
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<td>0.06</td>
<td>0.02</td>
<td>0.19</td>
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<td>0.14</td>
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<td>-0.15</td>
</tr>
<tr>
<td>Ag</td>
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<td>0.16</td>
<td>0.17</td>
<td>0.59</td>
<td>0.17</td>
<td>0.02</td>
<td>0.58</td>
<td>-0.06</td>
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</tr>
<tr>
<td>Zn</td>
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<td>0.40</td>
<td>1.00</td>
<td>-0.30</td>
<td>0.51</td>
<td>-0.27</td>
<td>0.05</td>
<td>0.33</td>
<td>0.57</td>
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<tr>
<td>Cu</td>
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<td>-0.29</td>
<td>0.35</td>
<td>-0.08</td>
<td>-0.22</td>
<td>-0.02</td>
<td>-0.02</td>
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<td>0.21</td>
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<td>-0.02</td>
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<td>0.02</td>
<td>-0.03</td>
<td>0.02</td>
</tr>
<tr>
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<td>0.00</td>
<td>0.65</td>
<td>0.12</td>
<td>0.22</td>
<td>1.00</td>
<td>0.26</td>
<td>0.18</td>
</tr>
<tr>
<td>Bi</td>
<td>0.00</td>
<td>0.25</td>
<td>0.75</td>
<td>0.27</td>
<td>0.26</td>
<td>0.16</td>
<td>0.59</td>
<td>0.29</td>
<td>1.00</td>
<td>-0.20</td>
</tr>
<tr>
<td>Hg</td>
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<td>0.38</td>
<td>0.21</td>
<td>0.12</td>
<td>0.35</td>
<td>0.24</td>
<td>0.26</td>
<td>0.32</td>
<td>0.04</td>
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</tr>
</tbody>
</table>

**3.3 Ore Petrography and Main Sulphide Mineralogy**

Generally, the main Fe-bearing sulphide minerals are pyrite and pyrrhotite. Thus far, SEM/EDS
studies have not indicated other elements than Fe and S to be bound within these minerals. The
relative amount of pyrite and pyrrhotite is variable. Mattsson and Heeroma (1985) estimated a
pyrite to pyrrhotite ratio of 2:1 for the upper part of the Rockliden deposit. Karup-Møller and
Makovicky (1980b) documented higher pyrite to pyrrhotite ratios, up to 20:1, in ore samples from
Rockliden and similar ratios were recorded with semi-quantitative (SEM-based) analysis in
different parts of the Rockliden ore body (Bolin 2010). In this study, it was found during drill core
logging that most of the massive sulphide ore is dominated by pyrite. However, pyrrhotite
occasionally constitutes the main Fe sulphide mineral in 1 to 2 m wide massive sulphide drill core
intersections, either isolated in host rock or marginally to massive sulphide intervals (e.g. Fig.
3.5a).

Generally, sphalerite and chalcopyrite form the main base metal sulphide minerals. Estimation of
the sphalerite and chalcopyrite content by optical microscopy shows good correlation with the
content of sphalerite and chalcopyrite calculated in HSC Chemistry (Fig. 3.4b). Thus, the overall
sphalerite to chalcopyrite ratio can be estimated to be 2:1 based on the Zn and Cu grade of the
Rockliden resource (table 1). However, just as with the main Fe-bearing minerals, the relative
content of sphalerite and chalcopyrite is variable in the massive sulphides, and based on this
variation seven base-metal groups are distinguished by optical microscopy (Po-Ccp, Po-Sp, Py, Py-
Ccp-Sp, Py+Po+Mgt-Ccp-Sp, Py-Sp-Ccp and Py-Sp). Moreover, as is mentioned in subsection 3.1,
a systematic variation in the mineralogy of the main sulphide minerals is not expected to be a
pronounced feature in the deformed Rockliden deposit. However, to study the potential
mineralogical variation, samples were taken from drill core intervals representing different
preliminary defined base-metal classes (see sub-section 2.2). The seven base-metal groups are described in the following.

Seven base-metal groups (Fig. 3.4b) are defined based on their calculated chalcopyrite (Ccp) and sphalerite (Sp) content and optically estimated pyrite (Py), pyrrhotite (Po) and magnetite (Mgt) content within the massive sulphides. In the Po-Ccp and Po-Sp group, pyrrhotite forms the main Fe-carrier (Fig. 3.5a). As pointed out above, these groups are subordinate to massive sulphide groups where pyrite is the main Fe-carrier. The Py group is characterised by dense packing of pyrite grains (Fig. 3.5b). Some samples also contain abundant magnetite or pyrrhotite and such samples are allocated to a separate group, here referred to as Py+Po+Mgt-Ccp-Sp group (Fig. 3.4b, Fig. 3.5f). An increase in the content of pyrrhotite is occasionally accompanied by chalcopyrite (Fig. 3.5b). This also marks the transition from the Py group into the Py-Ccp-Sp group (< 5 wt% Zn, Fig. 3.4b, Fig. 3.5c) and with increasing Zn content into the Py-Sp-Ccp group (> 5 wt% Zn, Fig. 3.4b, Fig. 3.5d). The Py-Sp group is characterised by a low Cu content (< 2 wt% Cu, > 5 wt% Zn, Fig. 3.4b, Fig. 3.5c).

Fig. 3.4. Distribution of main elements and minerals in the massive sulphides: a) model for undisturbed metal zoning and related mineral zoning as suggested by Mattsson and Heeroma (1985) for the upper part of the undeformed Rockliden deposit (Apy – arsenopyrite, Bour – bournonite, Ccp – chalcopyrite, Gd – gudmundite, Gn – galena, Po – pyrrhotite, Py – pyrite, Sp – sphalerite, Ttr – tetrahedrite), b) Py-Sp-Ccp ternary plot showing the base-metal groups as defined by element-to-mineral conversion and classification by optical microscopy (paper II).
Fig. 3.5. Drill core photographs and microphotographs (reflected light) of different base-metal groups distinguished by their relative content of pyrite (Py), pyrrhotite (Po), magnetite (Mgt), chalcopyrite (Ccp) and sphalerite (Sp): a) sphalerite-rich end member of the Po-dominated groups with traces of galena (Gn) and tetrahedrite (Tr), b) dense packing of pyrite grains in the Py group, c) flame texture in the Py-Ccp-Sp group, d) orientated texture of sphalerite, pyrrhotite and magnetite in the Py-Sp-Ccp group, e) pyrite grains showing atoll texture in the Py-Sp group, f) differential orientated chalcopyrite flames and magnetite seams in the Py+Po+Mgt-Ccp-Sp group. Modified from paper II.

Sphalerite is moderate in Fe content. In early microprobe studies on Rockliden ore, the Fe-content of sphalerite was found to be relatively constant with ca. 6.5 wt% (Karup-Møller and Makovicky 1980a). In this study, the Fe content of sphalerite is shown to vary between ca. 6.0 to 8.5 wt% (table 3.3). SEM/EDS analyses indicate an even larger variation in the Fe content ranging from ca. 3 to 9 wt% (average 6.5 wt%). Galena is close to its stoichiometric composition (table 3.3), but both SEM/EDS and EPMA/WDS analysis reveal that galena contains trace amounts of Se. However, galena itself is found mostly in trace amounts, and only locally as a minor mineral in the ore samples (Bolin 2010). Similar to galena, arsenopyrite is close to its stoichiometric composition, but contains trace amounts of Sb (table 3.3). Arsenopyrite is the main As-bearing mineral at Rockliden (Bolin 2010). Drill core logging and assaying revealed that the As and arsenopyrite distribution is more complex than previously proposed by Mattsson and Heeroma (1985) and this complexity might be also related to the deformation of the Rockliden deposit.

Table 3.3. EPMA/WDS analysis of sphalerite (Sp), galena (Gn) and arsenopyrite (Apy) from Rockliden.

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<th>Cu</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Zn</th>
<th>Sb</th>
<th>Cd</th>
<th>Bi</th>
<th>Sn</th>
<th>Se</th>
<th>Hg</th>
<th>Pb</th>
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</tr>
</thead>
<tbody>
<tr>
<td>-</td>
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<td>0.04</td>
<td>0.07</td>
<td>0.04</td>
<td>0.05</td>
<td>0.05</td>
<td>0.08</td>
<td>0.11</td>
<td>0.09</td>
<td>0.26</td>
<td>0.08</td>
<td>0.27</td>
<td>0.30</td>
<td>0.28</td>
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<tr>
<td>Sp</td>
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<td>7.44</td>
<td>58.47</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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</tr>
<tr>
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<td>-</td>
<td>0.16</td>
<td>0.03</td>
<td>0.11</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>0.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

a) statistics (LLD – lower limit of detection (EPMA/WDS analysis), AM – arithmetic mean, SD – standard deviation).

3.4 Sb Mineralogy

Tetrahedrite is the Sb-bearing mineral that is commonly found in VHMS deposits of the Skellefte district and in Rockliden (table 1.2). However, especially in the relatively Sb-rich deposits, or Sb-rich parts of them, several other Sb-bearing minerals have been detected including bournonite, meneghinite and gudmundite (Bolin 2010; Lager and Forssberg 1990; Minz et al 2013). The chemical composition of Sb-bearing minerals found at Rockliden is listed in table 3.4.
Table 3.4. Average chemical composition of the common Sb-bearing minerals at Rockliden in wt% (not shown are values for Bi, Se, Ni, Hg, and As). Modified from paper I.

<table>
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<tr>
<th>Mineral (abbreviation)</th>
<th>No. of analysis</th>
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<th>Ag wt%</th>
<th>Zn wt%</th>
<th>Cu wt%</th>
<th>S wt%</th>
<th>Fe wt%</th>
<th>Sb wt%</th>
<th>Pb wt%</th>
</tr>
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<tbody>
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<td>-</td>
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<td>0.10</td>
<td>0.06</td>
<td>0.19</td>
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</tr>
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<td>0.46</td>
<td>23.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.25</td>
<td>0.41</td>
<td>0.31</td>
<td>1.64</td>
</tr>
<tr>
<td>Meneghinite (Mene)</td>
<td>20</td>
<td>AM</td>
<td>-</td>
<td>0.44</td>
<td>1.56</td>
<td>17.36</td>
<td>0.47</td>
<td>18.72</td>
<td>60.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>-</td>
<td>0.36</td>
<td>0.29</td>
<td>0.17</td>
<td>0.26</td>
<td>0.40</td>
<td>0.69</td>
</tr>
<tr>
<td>Boulangerite (Boul)</td>
<td>8</td>
<td>AM</td>
<td>-</td>
<td>0.50</td>
<td>-</td>
<td>18.43</td>
<td>0.39</td>
<td>24.19</td>
<td>55.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>-</td>
<td>0.52</td>
<td>-</td>
<td>0.11</td>
<td>0.28</td>
<td>0.77</td>
<td>0.46</td>
</tr>
<tr>
<td>Gudmundite (Gd)</td>
<td>39</td>
<td>AM</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15.67</td>
<td>28.21</td>
<td>55.58</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.64</td>
<td>0.62</td>
<td>1.33</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Statistics (LLD – lower limit of detection (EPMA/WDS analysis), AM – arithmetic mean, SD – standard deviation).

The mineral association of the Sb-bearing minerals is suggested to be potentially relevant to their flotation distribution (paper I, see also discussion below). Thus, a summary of typical associations of Sb-bearing minerals in the ore samples are compiled in table 3.5, and illustrated in figure 3.6. Locally, it was noted that Sb-bearing minerals are situated in fractures transgressing pyrite grains in the massive sulphides. Such information might be of use when trying to deduce the relative timing of natural processes which might have affected the Rockliden ore deposit (see discussion). However, the main associations documented for the massive sulphides and for some host rock types (table 3.5) have been found partly reflected in particles from products of the laboratory flotation tests (paper I).

In addition to the Sb-bearing minerals listed in table 3.4, the following phases have also been indicated by SEM/EDS: berthierite, jamesonite (Fig. 3.6d), geocronite (Bolin 2010), as well as other Pb-Sb-bearing sulphosalts (chemically similar to robinsonite and madocite), and Pb-Sb-As-bearing minerals from the tetrahedrite-tennantite solid-solution series. These additional minerals were found mostly outside the massive sulphides, and are present locally within the altered volcanic host rocks.

Also, arsenopyrite was noted to contain some Sb (table 3.3). The maximum Sb content in arsenopyrite is 2.5 wt% detected by EPMA/WDS. SEM/BSE imaging and EDS studies revealed that elevated contents in Sb in arsenopyrite are related to concentric zoning of the mineral (Apy I, Fig. 3.6e). Some Sb is thus coupled to As in arsenopyrite. Furthermore, As-Sb are also found to be coupled in tetrahedrite. The As content was found to range from 0.5 to 1 wt% in tetrahedrite (EPMA/WDS analysis for tetrahedrite in polished thin sections).

<table>
<thead>
<tr>
<th>Sb-mineral</th>
<th>grain size [μm]</th>
<th>texture</th>
<th>association</th>
<th>rock type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trt</td>
<td>10-100</td>
<td>irregular shaped (Fig. 3.6a), grains in Sp</td>
<td>Gn, Bour, Ccp, Sp, Po, Gn</td>
<td>massive sulphides, mafic dykes</td>
</tr>
<tr>
<td>Bour</td>
<td>50-200</td>
<td>compact, but irregular shaped (Fig. 3.6b), intergrown with Ccp (Fig. 3.6a)</td>
<td>Gn, Ccp, Trt, Sp, Po</td>
<td>mafic dykes, massive sulphides</td>
</tr>
<tr>
<td>Gd</td>
<td>&lt;15 to 50</td>
<td>crystals (with inclusion: Sp, Gn, …), fine and complex intergrowths with Ccp and Po</td>
<td>Po, Sp, Gn, Apy, Ccp, Trt</td>
<td>all</td>
</tr>
<tr>
<td>Boul</td>
<td>25-75</td>
<td>elongated intergrowths with Mene (Fig. 3.6c)</td>
<td>Mene, Gn, Apy</td>
<td>mafic rocks, massive sulphides (deeper deposit parts)</td>
</tr>
<tr>
<td>Mene</td>
<td>up to 250</td>
<td>elongated grains between amphiboles</td>
<td>Apy, Gn</td>
<td>massive sulphides (deeper deposit parts)</td>
</tr>
<tr>
<td>Ant</td>
<td>1-20</td>
<td>fine, complex intergrowths, grains in Gn (Fig. 3.6f)</td>
<td>Po, (Ag-coated) Ccp, Gn, Sp (Ag-coated) Ccp</td>
<td>massive sulphides, mafic dykes</td>
</tr>
<tr>
<td>Ag-Sb&lt;sup&gt;a&lt;/sup&gt;</td>
<td>&lt;5</td>
<td>small grains or coated pores</td>
<td>Ccp</td>
<td>massive sulphides, mafic dykes</td>
</tr>
<tr>
<td>Apy</td>
<td>50-150</td>
<td>zoned crystals (concentric, Fig. 3.6e)</td>
<td>Po, Sp</td>
<td>massive sulphides</td>
</tr>
<tr>
<td>Bert&lt;sup&gt;b&lt;/sup&gt;</td>
<td>up to 250</td>
<td>intergrown with silicates</td>
<td>Py, Apy, Ccp</td>
<td>felsic volcanics</td>
</tr>
<tr>
<td>Jms&lt;sup&gt;c&lt;/sup&gt;</td>
<td>25-200</td>
<td>inclusions in Py and Apy</td>
<td>Py, Apy</td>
<td>felsic volcanics</td>
</tr>
</tbody>
</table>

<sup>a</sup> Diameter of grains is less than 5 μm, neighbouring Ccp reveals rapid coating under exposure with air, additional evaluated Hg-values were found with SEM/EDS.

<sup>b</sup> Local observation in altered volcanic rocks.

<sup>c</sup> For more detail see paper I.

The chemical variation of minerals from the tetrahedrite isotypic series is most complex among sulphosalts (Moëlo et al 2008). At Rockliden, the Ag-content in tetrahedrite is highly variable (Fig. 3.7a and b). The variation observed in tetrahedrite from the upper part of the Rockliden deposit ranges from 0 to 15 wt% (Karup-Møller and Makovicky 1980a; Mattsson and Heeroma 1985). The Ag content in tetrahedrite varies between the rock types (paper I). For example, it is found to be higher than 4 wt% and in the felsic volcanic rocks below 4 wt% (Fig. 3.7c).
Fig. 3.6. Typical associations of Sb-bearing minerals (in extent to observations shown in Fig. 3 paper I): a) complex intergrowth of galena (Gn), bournonite (Bour), chalcopyrite (Ccp), tetrahedrite (Ttr), pyrrhotite (Po) and sphalerite (Sp) in association with carbonate minerals (Dol + Cal) in a massive sulphide sample from the upper central part of the Rockliden deposit, b) bournonite (Bour) surrounding vermicular intergrowth of galena (Gn) and chalcopyrite (Ccp) which is enclosing gudmundite (Gd) in a mafic dyke sample (see subsection 3.1), c) complex intergrowth of meneghinite (Mene), boulangerite (Boul), bournonite (Bour), native antimony (Ant), galena (Gn) and sphalerite (Sp) surrounding pyrite (Py) grains in a massive sulphide sample from the lower part of the Rockliden deposit, d) berthierite (Bert) surrounding arsenopyrite and enclosed in arsenopyrite (Apy) with jamesonite (Jms) in a felsic volcanic rock sample (see subsection 3.1), e) oscillatory zoning (lighter lines with up to 2 wt% Sb) in arsenopyrite (Apy I) rimmed by Sb-poor
arsenopyrite (Apy II), f) native antimony between galena crystals (Gn) enclosed by stannite (Stnn)-hosting sphalerite (Sp) and pyrrhotite (Po).

Fig. 3.7. Variation of microanalysis (EPMA/WDS and SEM/EDS) for tetrahedrite in relation to host rock types and massive sulphide: a) Sb-Ag-Cu ternary plot, b) (Cu+Ag)-(Sb+As)-(Fe+Zn) ternary plot (with enlargement, grey box), c) distribution of Ag (wt%) in tetrahedrite.
4 Discussion and Suggested Work

4.1 Mineralogy, Mineral Chemistry and Textural Parameters

The main sulphide minerals at Rockliden are pyrite, sphalerite, pyrrhotite and chalcopyrite. Since chalcopyrite and sphalerite are the only main base-metal carriers at Rockliden, the calculation of the sphalerite and chalcopyrite content can be done based on chemical assays. This is biased locally by the presence of minor Cu-bearing phases such as bournonite. As indicated by SEM/EDS analysis, the main sulphur-bearing minerals show stoichiometric composition except for sphalerite. Sphalerite shows a rather large variation in its Fe content (6.0 to 8.5 wt% by EPMA/WDS, ca. 3 to 9 wt% by SEM/EDS). The EPMA/WDS database has to be extended in order to understand, model, and predict the Fe content in sphalerite on the scale of the Rockliden ore deposit. Knowing the Fe content of sphalerite will allow to evaluate the potential maximum Zn recovery since the Cu activation is found to be influenced by the Fe content in sphalerite (Boulton et al 2005).

Seven base-metal groups are defined based on calculation of the base-metal mineral content verified by optical microscopy (paper II). **Textural parameters** including the primary grain size of pyrite (mostly less than 0.5 mm) can be estimated by optical microscopy of thin sections from collected drill core samples (Fig. 3.5). Generally, the base-metal sulphide minerals are found interstitial to pyrite grains and locally next to magnetite grains. The grain size of sphalerite, chalcopyrite and pyrrhotite is more difficult to estimate by reflected light microscopy than that of the pyrite. The fact that these minerals often form the interstices of pyrite grains could be used to estimate their maximum grain size, as an approximation of the liberation grain size. But it should be noted that these minerals show locally complex intergrowth or lack straight grain boundaries (e.g. Fig. 3.5d and e). Such complex textures are partly related to modification of the ore due to deformation and metamorphism (paper II). Generally, textural information, such as the grain size of minerals in the ore, is critical for estimating the optimum liberation grain size (Butcher 2010), which in turn affects the flotation properties of minerals. For example, it has been shown for sphalerite that both the composition (i.e. Fe content) and grain size will control its flotation behaviour (e.g. Boulton et al 2005). Millimetre to centimetre scale textural variation in the ore such as banding (i.e. centimetre scale alternation of pyrite- and sphalerite-rich bands (cf. Mattsson and Heeroma 1985)) are unlikely to be taken into account in a block model since the texture is much finer than the smallest mineable unit (SMU), and will not survive the comminution process since the P80 for the massive sulphide material is about 50 μm. However, banding textures are documented throughout the Rockliden massive sulphide deposit (occasionally pervading several meters of drill core, paper II) and thus could become relevant to the processing of the ore. Especially, the abundance of relatively soft minerals such as sphalerite is expected to affect the comminution behaviour of the massive sulphide ore (Bolin, pers. com.). As pointed out above, only quantitative data on ore textures will reveal their relevance to the processing of the Rockliden ore and such information cannot be provided by the calculation of the modal mineral composition (McArthur 1996; Roine 2009). The detection of micro textures requires appropriate samples (thin sections, etc.) as well as advanced and time-consuming preparation and analytical techniques.
Further, a large number of samples need to be analysed to cover representatively the whole ore body with micro textural information (Lamberg 2011). Such approach might not be fully applicable in the mining industry.

**Oxidation & tarnishing effects:** Supergene alteration, i.e. oxidation, can influence the processing of a massive sulphide ore as it is known to affect the flotation behaviour of the ore minerals from the Black Mountain polymetallic base metal mine, South Africa (Williams and Holtzhausen 2001). Supergene alteration has been found locally along fault zones, restricted to 50 m below surface (Depauw 2009). However, this effect might be of low significance for the Rockliden ore body and only a high level of oxidation would significantly affect the recovery of ore minerals (Williams and Holtzhausen 2001). Tarnishing is known to occur in chalcopyrite from VHMS deposits and is related to a low Ag content or associated Ag-bearing minerals (Harris et al 1984, and references therein). Tarnishing of chalcopyrite and tetrahedrite was observed only locally in the Rockliden ore, especially in relation to small inclusions Hg-Ag-Sb-bearing sulphide inclusions (table 3.5; Minz et al 2012). This tarnishing is rarely observed and probably insignificant to the flotation behaviour of chalcopyrite.

Tetrahedrite, bournonite, meneghinite and gudmundite are the dominant Sb-bearing minerals at Rockliden. The Sb mineralogy of Rockliden seems to be similar to other VHMS deposits in the Skellefte ore district, e.g. West Mauliden and Rakkejaur (Bolin 2009; Lager and Forssberg 1990). Other Sb-bearing minerals are mostly present as sulphosalts and are minor components among the Sb-bearing sulphide mineral fraction at Rockliden as they are largely absent in the flotation products derived from bulk ore samples (Bolin 2010). However, there are differences documented in the Sb mineralogy for the VHMS deposits, listed in table 1.2. These differences are not unexpected as also the geological setting and the base-metal content are rather variable in VHMS deposits (e.g. Franklin et al 2005). For example, sulphosalts with a mixed composition along the tetrahedrite-tennantite solid-solution series are relatively abundant at Neves-Corvo compared to Rockliden (Benzaazoua et al 2002; Fig. 3.7).

The Sb-(Ag)-bearing minerals are rather small, mostly below 100 μm (table 3.5). Thus it is expected that the degree of liberation is relatively low in the flotation feed and locking of Sb-bearing minerals is expected to influence their distribution during flotation (paper I). Automated SEM/EDS studies on the products from the laboratory flotation tests (Bolin 2010) show that Sb-bearing minerals distribute partly in a non-ideal way (Fig. 4.1). Lager and Forssberg (1990) suggested that, when liberated, the (Cu-)Pb-Sb-bearing minerals, i.e. tetrahedrite, bournonite, meneghinite and boulangerite, should be found mostly in the Cu-Pb concentrate. Other Sb-bearing minerals chemically binding Fe such as gudmundite should account to the tailing products (Fig. 4.1, table 4.1). This pattern is generally reflected by the distribution of apparently (2D) liberated Sb-bearing minerals in the Rockliden laboratory flotation tests (Bolin 2010). However, it was documented by SEM/BSE imaging and EDS spot analysis, that locking with other sulphide minerals and to a minor extent with silicate minerals, can cause misplacement of Sb-bearing minerals (Fig. 4.1, see also paper I).
Fig. 4.1. Sb mineralogy of the final products from the Rockliden laboratory flotation tests, Sb-bearing minerals which are expected to be found in the flotation products (cf. Lager and Forssberg 1990) are bold and underlined (graphic is a modified and corrected version of Fig. 5 in paper I); SEM/BSE images show misplaced Sb-bearing minerals (Boul – boulangerite, Bour – bournonite, Gd – gudmundite, Mene – meneghinite, Ttr – tetrahedrite) locked with non-Sb-bearing minerals (Ccp – chalcopyrite, Gn – galena, Plg – plagioclase, Sp – sphalerite).

The absolute impact of the mineral association and locking on the flotation distribution of the Sb-bearing minerals was estimated to be relatively low at Rockliden (Karup-Møller and Makovicky 1980a). Automated SEM-based analyses, focusing on the Sb mineralogy, are planned to be conducted on products from new laboratory flotation tests (second part of the PhD project). Irrespectively of the total impact of the locking of Sb-bearing minerals at Rockliden, the effect might be significant in absolute numbers in the total production of Cu-Pb concentrates from the polymetallic massive sulphide deposits from the Skellefte ore district. The relatively small size of penalty- and bonus-element-bearing minerals and the potential locking in the flotation feed is not unique to the Rockliden ore. For example, Sb-bearing minerals from the Rakkejaure ore are also known to have small grain size ranging from 30 to 70 μm (Lager 1985). Further, physical
properties of the minerals and the contrast of these properties between associated minerals will affect the relative particle size and degree of liberation after comminution and thus effecting the flotation distribution of the minerals (Butcher 2010; Grammatikopoulos and Roth 2002; Trahar and Warren 1976; Vizcarra et al 2010; etc.). For example, the size of gudmundite was found to be less than 10 μm in flotation products from the Rakkejaure ore (Lager and Forssberg 1990). Thus, considerations done for the Rockliden mineralisation could be extended to other massive sulphide deposits of the Skellefte district. In this context it needs to be determined from which type of ore Cu-Pb concentrates with high Sb content will be produced (Fig. 1.1). Hydrometallurgical treatment of products with high Sb content could be considered as such option for the common Sb-bearing minerals exist (table 4.1).

Table 4.1. Liberation distribution of Rockliden’s Sb-bearing minerals and leaching characteristics.

<table>
<thead>
<tr>
<th>Sb-mineral</th>
<th>Combination of base-metals, bonus and penalty elements.</th>
<th>Flotation (lib. dis.)</th>
<th>Leaching characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ttr Cu, (Zn,) Sb, Ag</td>
<td>Cu-Pb Conc</td>
<td>alkaline sulphide leaching (Anderson et al 1991; Awe and Sandström 2010; Baláž and Achimovičová 2006)</td>
<td></td>
</tr>
<tr>
<td>Bour Cu, Pb, Sb</td>
<td>Cu-Pb Conc</td>
<td>thiosulphate leaching and indicated for alkaline sulphide leaching (Ficeriová et al 2005; Sandström, pers. comm. 2013-02-13)</td>
<td></td>
</tr>
<tr>
<td>Boul (&amp; Mene) Pb, Sb, Cu</td>
<td>Cu-Pb (&amp; Zn) Conc</td>
<td>alkaline sulphide leaching (Achimovičová and Baláž 2008)</td>
<td></td>
</tr>
<tr>
<td>Gd Fe, Sb</td>
<td>tailings</td>
<td>indicated for alkaline sulphide leaching (Sandström, pers. comm. 2013-02-13)</td>
<td></td>
</tr>
</tbody>
</table>

a) combination of base-metals, bonus and penalty elements.  
b) liberation distribution according to Lager (1990).  
c) potentially removable from the Cu-Pb concentrate by leaching methods.

Given the potential locking effects, the association of the Sb-bearing minerals in the Rockliden ore samples was studied in more detail. In addition to sphalerite and chalcopyrite, pyrrhotite is commonly associated with Sb-bearing minerals (table 3.5). Several Sb-bearing sulphasalts, such as meneghinite and bournonite, are suggested to be stable at higher temperatures, i.e. > ca. 200 °C, together with pyrrhotite (Mookherjee and Mishra 1984). In Dhurode, Ireland a mineral association combining galena and bournonite in symplectite intergrowth has been interpreted to have formed by hydrothermal fluids modifying the ore (Wen et al 1991). Likewise, the mineral association of (galena-)bournonite-tetrahedrite-chalcopyrite was found in base-metal veins in the Apollo Mine, Germany, where it has been interpreted to be related to mineral reactions caused by overprinting of the veins by Sb-Cu-Bi-rich hydrothermal fluids (Wagner and Cook 1997). Similarly, bournonite was interpreted to be a reaction product between tetrahedrite and galena as it occurs along the grain boundaries between the latter two phases in the polymetallic sulphide veins at Sunshine Mine, Idaho, USA (Anderson 1940). Taking the above listed chemical reactions into consideration, the mineral stabilities and the textural position of Sb-bearing minerals (e.g. association with pyrrhotite at Rockliden), it is suggested that some of the Sb-bearing minerals may have formed, or have been mobilised, during hydrothermal events modifying the Rockliden VHMS deposit. Extending this idea, it is possible that the position of these minerals in the ore body is connected to geological
structures which favour hydrothermal modification and thus the 3D distribution of such minerals may be structurally controlled. However, while such information would help to understand the distribution of Sb on a deposit scale, it would require a classical geological model, to take such structures into account.

EPMA/WDS data provides a first insight and basis for understanding the distribution of both penalty (Sb, Hg, As, etc.) and bonus (Ag) metals between different minerals. Based on the current data, it is proposed that the Ag content of tetrahedrite is related to the rock types, i.e. the tetrahedrite in the mafic volcanic rocks is richer in Ag than that in the felsic volcanic rocks. However, a systematic variation of the Ag content has not been found in the limited amount of EPMA/WDS data collected for the massive sulphide ore. Identifying and understanding systematic variations is critical as it is proposed that tetrahedrite is the main Ag carrier at Rockliden (Bolin 2009). In addition to the Ag-Sb combination in tetrahedrite, this mineral also contains arsenic (As). The As content in tetrahedrite and the Sb content in arsenopyrite are similarly low (i.e. mostly < 1 wt%), and only the dominance of both minerals in Sb- and As-bearing mineral fraction would result in a correlation between these elements. Such mineralogical coupling is unlikely as the correlation coefficient of As and Sb is low, less than 0.2 in drill core assays (table 3.2). Moreover, due to relatively complex zoning in arsenopyrite (Fig. 3.6e), the total amount of Sb bound by this mineral is challenging to quantify. The average Hg content of Rockliden’s tetrahedrite is low (below the lower limits of detection (ca. 0.3 wt% Hg) for EPMA/WDS analysis on Sb-bearing minerals in this study). However, it is known that tetrahedrite and stannite from the Neves-Corvo VHMS deposit in Portugal contain ca. 0.2 wt% Hg (Benzaazoua et al 2002). In addition to tetrahedrite and small grains of Ag-Hg(-Sb) solid solutions (table 3.5), stannite is also found by SEM/EDS analysis as a trace mineral at Rockliden. So far, no EPMA/WDS analyses were conducted on stannite and Ag-Hg(-Sb) solid solutions and the Hg content of these phases is undetermined.

Notes on the methods suggested for improvement in detecting the mineralogical distribution of penalty and bonus metals: The Hg content of analysed sphalerite grains from the Rockliden ore is mostly below the lower limit of detection for EPMA/WDS analysis (0.3 wt% Hg, table 3.3). Precise measurements, down to few ppm concentrations at spot sizes of 1 μm, can be achieved (e.g. Pownceby et al 2007). Although not reaching the low spot size of EPMA/WDS analysis (e.g. Van den Broeck 2004), LA-ICP-MS analysis can be used to monitor, for example, Hg in sphalerite if appropriate standards are available (e.g. Cook et al 2009). In addition to EPMA/WDS analysis, it is suggested to conduct LA-ICP-MS measurements on sphalerite as well as other base-metal bearing minerals to define the impact on the mineralogical distribution of Hg at Rockliden simultaneously to other trace elements such as Ag, In, Sn, Bi and Sb (e.g. Cook et al 2009; Ye et al 2011). Similar to Sb and other critical elements, the mineralogical distribution should then be related to the quantity of Hg-bearing minerals, e.g. by analysis from SEM-based automated mineralogy. In the case of the Eskay Creek VHMS deposit, the Hg content in sphalerite (locally up to 16.35 wt%) caused the Zn concentrate to be rich in Hg and this caused problems during pyrometallurgical processing as Hg will volatise into the roasting gases (Grammatikopoulos and Roth 2002; Grammatikopoulos et al 2006). However, even low concentrations of critical elements in the main base-metal bearing sulphide minerals can be significant to the mineralogical distribution of these...
elements. Due to environmental considerations, several methods were studied to remove Hg from roaster gases which were produced during the treatment of Zn concentrates with Hg content ranging from 0.001 to 0.02 wt% at the Kokkola smelter, Finland (Rastas and Poijärvi 1973). Regarding the massive sulphide ore from the Skellefte district, facilities to remove Hg exist at Boliden’s Zn plants (Bolin, pers. com., 2013-10-16). Further, facilities for the recovery of Ag will be taken into operation at Kokkola (NewBoliden 2013). Thus, studies on the mineralogical distribution of these trace elements might be of value, as it is for Sb, although the absolute concentrations of Hg and Ag are indicated to be lower than that observed for Sb. Generally, the Hg content is less than half of the Sb content at Rockliden (paper II).

The non-sulphide mineralogy is rather complex at Rockliden (see subsection 3.1 and paper II). However, several minerals occur only locally or as minor and trace components. Relatively abundant minerals that might have a direct impact on the physical and metallurgical processing of the Rockliden ore are quartz and magnetite (e.g. on comminution), chlorite, other clay and carbonate minerals (e.g. on flotation and leaching) (e.g. Butcher 2012; Williams and Holtzhausen 2001; Wills 2006). The quantification of non-sulphide minerals based on chemical assays is challenging as they combine a broad range of elements in their crystals. Generally, the calculation of the mineralogy solely based on standard drill core assays (S, Zn, Cu, Pb, As, Sb, Ag, and Au) is rather limited if the mineralogy is complex. The number of minerals is higher than the number of elements analysed on a routine basis, which does not allow a unique solution for the mineral proportion by element-to-mineral conversion (e.g. Berry et al 2011; Whiten 2008). For example, Fe-carriers are found in the sulphide (e.g., pyrite, pyrrhotite, arsenopyrite, chalcopyrite and sphalerite) and non-sulphide mineral fraction (e.g., magnetite, amphibole, chlorite and dolomite group minerals). Further, Fe-carriers such as amphibole minerals and, as a minor component, also the dolomite group minerals show complex zoning, and a sufficient large amount of (EPMA/WDS) data would be needed to account for variations in the chemical composition of such minerals on a deposit-scale or to give a statistically founded average composition.

In summary it can be stated that a good understanding of the distribution of elements in minerals is necessary and it will partly allow the calculation of the main mineralogical content from chemical assays of the ore samples. Quantitative mineralogical data can potentially be used as a predictive tool for mineral processing (cf. Benzaazoua et al 2002). As outlined above, the mineralogy of the Rockliden ore deposit is complex and a simplification is necessary in order to quantify the mineralogical data. This is also true for automated (SEM-based) mineralogical quantification as several minerals have similar grey scale levels in BSE images covering the full mineralogical range at Rockliden (Fig. 4.2). Continuous simplification of the list comprising process-relevant minerals at Rockliden might also be guided by results to be obtained from laboratory flotation test (variability testing, second part of the PhD study).
4.2 Outlook on a Process-Adapted Geological Model

It was noted during drill core logging that macroscopically observable textures, such as banding and the grain size of pyrite, vary on a centimetre to metre scale. Textures in the massive sulphides are partly related to metamorphism and deformation (see also discussion of paper II). Further, it is suggested that the 3D distribution of corresponding textural ore types is connected to the complex geometry of the Rockliden massive sulphide ore body. The 3D extent of textural features on a macroscopic scale will be challenging to determine. So far, only classical drill core logging has been used and no rapid, automated methods have been tested within this study. However, instrumentations and measurement solutions are available on the market. For example, automated hyperspectral drill core logging systems could be tested to detect macroscopic textures in the range of visual to infrared light in the massive sulphides from Rockliden (e.g. Olson Hoal et al 2013). Variation in colour of the sulphide minerals, partly due to oxidation, might complicate the distinction of the main sulphide-bearing minerals and the relatively small size of pyrite grains will rather result in longer measurement time to achieve an appropriate resolution.

Another challenge is the implementation of such data in a 3D model. In correspondence to textural information in the massive sulphide ore, lithological data represents non-additive data and is largely collected in a qualitative way by classical drill core logging (Lamberg 2011; Lund 2013; Walters and Kojovic 2006). Such data is difficult to model with classic geostatistical tools (Knight et al 2011). McArthur (1988) suggested using a stratigraphic coordinate system which would allow variography in stratigraphic layers. However, the usage of such system would require detailed knowledge about the stratigraphy and structure of the ore deposit under concern (McArthur 1988; McArthur 1996). As pointed out above the geometry of the Rockliden massive sulphide ore body seems to be complex (Depauw 2009; Raat and Årebäck 2009) showing tight, isoclinal folding and
faulting (Evins 2011). This geometry will be challenging when building a reliable model for the massive sulphide mineralisation.

Both variations of macro and micro textures in the massive sulphide bodies are likely to be blended and might become either insignificant or very difficult to control during mining and comminution of the ore. However, rock-intrinsic parameters relevant to the processing of the ore should be extracted from new laboratory flotation and comminution tests by detailed characterisation using the information compiled in this study. Options on how to implement them into a process-adopted model should be evaluated in subsequent steps.
5 Concluding Remarks

This study shows the complexity of the Rockliden ore body on a deposit scale and of its petrography and mineralogy on a macroscopic to microscopic scale. Mineralogical parameter are outlined which can influence the processing of the ore, especially when it comes to localising an increased content of trace (bonus and penalty) elements in the products of mineral processing stages. Focus is set on the sulphide mineralogy, including pyrite, pyrrhotite, chalcopyrite and sphalerite. These minerals dominate the ore and constitute the dominant host to trace minerals bearing critical elements (Sb, Ag, As, etc.). So far, all geological and mineralogical information obtained is qualitative.

The main subject of the coming work in this project is to collect quantitative information on mineralogical parameters potentially relevant to the processing of the Rockliden ore. With automated SEM-based mineralogical analysis such data for the products from laboratory flotation tests are planned to be collected. Quantitative (and reproducible) information is required to forecast their impact on the processing of the Rockliden ore. Thus, the continuing work should include an evaluation of process-relevant ore- and rock-intrinsic parameters. Furthermore, the spatial variation of the process-relevant mineralogical data is suggested to be done via linking to a geological model. However, the quantitative data usable for such linking might be limited in form of base-metal assays and partly also rock types at Rockliden. The final aim of a geometallurgical project is building a 3D model, which will be a useful tool in production planning during various stages of mining at Rockliden.
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PAPER I

Detailed Characterisation of Antimony Mineralogy in a Geometallurgical Context at the Rockliden Ore Deposit, North-Central Sweden

Friederike Minz, Nils-Johan Bolin, Pertti Lamberg and Christina Wanhainen

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Detailed characterisation of antimony mineralogy in a geometallurgical context at the Rockliden ore deposit, North-Central Sweden

Friederike Minza,⁎, Nils-Johan Bolinb, Pertti Lamberga, Christina Wanhainena

⁎ Luleå University of Technology, Department of Civil, Environmental and Natural Resources Engineering, Sweden
b Boliden, Division of Process Technology, Sweden

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1. Introduction

Antimony (Sb) has no commercial use as metal itself, but it finds application in form of metallo-organic and inorganic compounds as flame retardants, pigments, heat and radiation stabilizers for plastics and clarification of specialty glasses, as well as Sb-based catalysts and Sb alloys, to increase strength and hardness of Pb (Butterman and Carlin, 2004; Masters, 2005; Anderson, 2012).

Given its usage, it was defined as critical raw material for the modern society (Anderson, 2012; European Commission, 2010). The world's largest natural resources of Sb, such as those in China, are dominated by China although the closure of mines in the Hunan Province has caused a decrease in surplus world market of Sb is dominated by China although the closure of mines in the Hunan Province has caused a decrease in surplus.

Studies by Lager (1989) on massive sulphides from the Rakkejaur deposit (northern Sweden, Fig. 1) contain Sb as impurity element with grades commonly above 200 ppm (e.g. Rakkejaur), but generally below 2.5 wt% (Allen et al., 1996). The Sb grades at the Rockliden massive sulphide mineralisation also fall into this range (Raat and Årebäck, 2009). For this range in the Sb content pyrometallurgical methods, such as oxide volatilisation or roasting, which are normally used for production of Sb from low grade Sb-ores (5–25 wt%) (Anderson, 2012 and references therein), are not considered further. However, attempts have been made to remove Sb from As–Sb–Bi–rich sulphide concentrates by partial roasting before the material was to be sent to the smelter in Rönnskär, Skellefteå, Sweden (Björnberg et al., 1991).

The zinc–copper (Zn–Cu) volcanic-hosted massive sulphide (VHMS) deposits of the Skellefte district (northern Sweden, Fig. 1) contain Sb as impurity element with grades commonly above 200 ppm (e.g. Rakkejaur), but generally below 2.5 wt% (Allen et al., 1996). The Sb content of the Skellefte district VHMS deposits is expected to predict the Sb content of the Cu–Pb concentrate, among other process-relevant factors, and helps to forecast when the Cu–Pb concentrate has to be treated by alternative processes, such as alkaline sulphide leaching, before it is sold to the smelter.
Common Sb-bearing minerals (cf. Anderson, 2012; Butterman and Calvin, 2004). Sulphide leaching was tested successfully at the Sunshine Mine plant, Coeur d'Alene mining district, Idaho for Cu–Pb concentrates from the Rakkejaur massive sulphide deposit and Rockliden (Awe et al., 2012; Lager, 1985). Most of the mineralisation at Rockliden is found at the altered stratigraphic top of rhyolitic–dacitic volcanic rocks (Depauw, 2009; Mattsson and Heeroma, 1985). The volcanic rocks are thought to form an inlier, isolated within the metamorphosed sedimentary rocks of the Botnian Basin (Depauw, 2009; Kousa and Lundqvist, 2000). Silicification and sericitisation, and locally carbonate- and chloride-alteration, have affected the volcanic host rocks (Depauw, 2009; Raat and Årebäck, 2009). The metamorphnic grade of the volcanic and sedimentary host rocks reaches greenschist facies (Depauw, 2009), which is low compared to the regional, amphibolite facies, metamorphic grade (Kousa and Lundqvist, 2000). Folding and faulting resulted in steeply dipping mineralised zones (Fig. 1) with complex geometry (Svens, 2011; Raat and Årebäck, 2009). Additionally, NE–SW to ENE–WSW trending faults and parallel mafic dykes cross-cut the Rockliden mineralisation (Depauw, 2009). Remobilisation of Sb during the intrusion of the dykes has been suggested and some of the dykes contain about 1 wt% Sb (Depauw, 2009).

The work presented here is part of the Rockliden geometallurgical case study. Generally, geometallurgy combines all steps involved in finding and extracting metals from the earth under current economic conditions (e.g. Dunham et al., 2011; Jackson et al., 2011; Lamberg, 2011). This general description, however, implies that a broad range of aspects are considered from all involved disciplines. The Rockliden geometallurgical project focuses on understanding and gaining knowledge of the response to processes involved in extracting minerals from this deposit (cf. Jackson et al., 2011). Process-relevant, i.e. metallurgical-driver, rock-intrinsic parameters need to be identified (Walters and Kovsic, 2006; Williams, 2011). Further, the variability of these parameters should be captured over the spatial extent of the Rockliden deposit to outline domains representing homogeneous populations in terms of the parameters under consideration (cf. Jackson et al., 2011). These domains form a geometallurgical model to be built for Rockliden and to be used in forecasting the metallurgical response and furthermore in production planning and management.

Critical process-relevant parameters at Rockliden include the Sb content of the Cu–Pb concentrate, and the purpose of this work is to gain detailed knowledge of this component of response (cf. Jackson et al., 2011). This study compiles the Sb mineralogy at Rockliden and outlines controls on the Sb distribution in laboratory flotation tests. In earlier studies on the Sb mineralogy of Rockliden, bournonite, bornhitite and gudmundite were identified (Kanup-Moller and Malovicky, 1980). The list of Sb-bearing minerals was extended in this study, and additional information was collected, such as the grain size of the Sb-bearing minerals and their mineral association, i.e. their mode of occurrence in the crushed drill core material. This data was then used to qualitatively evaluate the liberation distribution of the Sb-bearing minerals as found in the flotation products from laboratory flotation tests.

### 2. Methods

Two types of samples were studied: uncrushed drill cores and flotation products from laboratory tests from three composite samples. Locations of drill core intersections are shown in Fig. 2. Prior to sample collection for mineralogical studies on uncrushed drill core samples, all Rockliden drill core assays available from the Boliden archive were evaluated to capture the variation
in Sb grades in relation to the base-metal content. Cu, Zn, Pb, As, S
and Sb assays were converted into mineral grades of pyrite, chalco-
pyrite, sphalerite, galena, arsenopyrite and bournonite using the
Geo module of the HSC Chemistry software (Roine, 2009). Since
chalcopyrite and sphalerite are the main base metal carriers at
Rockliden which need to be separated by flotation into Cu–Pb
and Zn concentrates, the drill core assays were classified based
on the chalcopyrite and sphalerite content of the plain sulphide
fraction, i.e. sulphides recalculated to 100 wt%. These preliminary
classes were further subdivided by their Ag and Sb content, since
these metals represent important bonus and penalty elements at
Rockliden. Using the preliminary classification as a guide, sixty
samples were collected from six drill cores distributed throughout
the Rockliden deposit (Fig. 2). In this paper these samples are re-
ferred to as mineralogical samples, i.e. samples which were used
to study primary features of Sb-bearing minerals as found in the
uncrushed ore. For each mineralogical sample, a polished thin sec-
tion was prepared and chemical assays were obtained from the
residual drill core material (i.e. ca. 30–50 cm length of quartered
BQ and NQ drill core per sample). The polished thin sections were
studied by optical microscopy and 15 thin sections were selected
for scanning electron microscope studies and 6 for electron micro-
scope studies (Fig. 2), emphasising those with elevated Sb or Ag
content in the chemical assays.

Laboratory batch flotation tests were run in 2009 by Boliden
Mineral AB to determine the metallurgical response of composite
samples (each composed of 15–30 kg mineralised drill core) col-
lected from three different parts of the Rockliden mineralisation
(CA, CB and CC, Fig. 2B). The three composite samples were not
characterised petrographically and mineralogically in any detail
prior to processing for this initial study. They were crushed to
minus 3.15 mm and divided by a rotary splitter into 1 kg lots.
Grinding was done in a laboratory rod mill. A laboratory flotation,
using the flow sheet shown in Figs. 2 and 5, was done in a 2.7 l cell
with a Wemco lab flotation machine. For each composite sample a
final Cu–Pb concentrate, a Zn concentrate and final tailings product
was collected, assayed and epoxy samples were prepared for
microscopic studies (Fig. 2).

Scanning electron microscope (SEM) studies were conducted at
the following instruments and institutions: Hitachi SUT6600 (FES-
SEM, NTNU Trondheim, Norway), Ultra Plus – Zeiss Gemini (FESEM,
Oulu University, Finland), Merlin – Zeiss Gemini (FESEM, Luleå
University of Technology, Sweden), and SEM (Research Laboratory,
Geological Survey of Finland (GTK, Helsinki, Finland)). Generally,

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### Fig. 2

A diagram showing the research approach. Sections (A) and (B) are viewing to the west on the Rockliden massive sulphide ore body (translucent shapes) with the
location of sampled and assayed drill core intervals (white dashed lines). (A) Samples for the mineralogical study (from six drill cores A–F). (B) Composite samples (CA, CB and
CC). Flotation sheet for the laboratory tests below graphic (B) (for more details see Fig. 5). The final products and samples used for microscopic studies are shown bold and
underlined. Abbreviation for microscopic and micro-analytical studies: BSE Back scattered electron imaging, EDS energy-dispersive X-ray spectroscopy, SEM scanning
electron microscope, EPMA electron probe microanalyzer, WDS wavelength-dispersive X-ray spectrometry.
the acceleration voltage was set to 20 keV and the emission current ranged from 0.9 to 1.1 nA for EDS (energy-dispersive X-ray spectroscopy) analysis. The following analytical conditions were chosen for wavelength-dispersive X-ray spectroscopy (WDS) analysis at the electron probe microanalyser (EPMA): acceleration voltage of 15–20 keV, emission current of 15–30 nA and a beam diameter of 1–5 μm. EPMA/WDS studies were conducted at the following facilities: JEDI JXA-8200 microanalyser (Oulu University) and electron microprobe Cameca SX100 (GTK Helsinki).

3. Results

3.1. Chemical composition of Sb-bearing minerals at Rockliden

The average composition of common Sb-bearing minerals at Rockliden is listed in Table 2. Analyses of bournonite, meneghinite, boulangerite and gudmundite are close to the stoichiometric composition (Moëlo et al., 2008). Meneghinite and boulangerite have a similar chemical composition (Table 2) and show similar grey scales in BSE images (i.e., similar mean atomic number). Thus, their distinction is challenging by automated SEM-based modal analysis and they consequently are grouped in one mineral class. The Sb content of the tetrahedrite analysed with EPMA/WDS is relatively constant, but the Ag-content varies between 0.5 and 12.5 wt% (i.e., relative high standard deviation, cf. Table 2). An increase in Ag in tetrahedrite corresponds to a concomitant decrease in Cu and vice versa, a well-known relationship between Cu and Ag in tetrahedrite (Moëlo et al., 2008). The highest Ag content (above 5 wt%) is measured in tetrahedrite from mineralogical samples referred to as mafic rocks (for explanation see next section) whereas the Ag content in tetrahedrite from massive sulphide samples tend to be lower. Arsenopyrite grains show fine-scale (1–5 μm), blotchy and concentric zoning in BSE images, which is related to variations in the Sb content (0–0.5 wt%).

Additionally, other Sb-bearing minerals and sulphosalts such as berthierite (FeSb3S8), jamesonite (Pb4Sb4S13), geocronite (Pb3Sb4As2S15), native antimony, pyrargyrite (Ag3SbS3) and miargyrite (AgSb2S5) were found in SEM/EDS study.

3.2. Characterisation of Sb-bearing minerals in Mineralogical Samples

The mineralogical samples are subdivided into (1) disseminated to semi-massive sulphides and (2) massive sulphide samples based on their total sulphide content calculated from chemical assays by element to mineral conversion (Roine, 2009). Generally, the total sulphide content of the disseminated to semi-massive sulphides is on average ca. 15 wt% and for the massive sulphide samples above 50 wt%. The average chemical compositions of the mineralogical samples are listed in Table 3. The main types are further divided into subtypes based on their dominating base metal sulphide (chalcopyrite/sphalerite) and their trace element (Ag/Sb) content, their host rock composition (mafic/felsic), and their spatial location (upper/deeper part).

Massive sulphides consist mostly of pyrite followed by sphalerite and chalcopyrite. Often sphalerite is the main base metal sulphide mineral, i.e. the Zn content is relative high compared to the Cu content (MASS, Table 3). In Sb- and Ag-poor samples impurity minerals were very rarely observed by optical microscopy. In the Ag-rich massive sulphide samples, tetrahedrite is the most common Sb-bearing mineral (Table 4). It is also the main Sb-bearing mineral in sphalerite-dominated, relative Sb-rich samples from the uppermost part of the massive sulphide mineralisation (Table 4). In these samples, tetrahedrite is often penetrated by chalcopyrite veins which contain small inclusions of native antimony (mostly <10 μm, Fig. 3D). However, relatively Sb-rich massive sulphides...

Table 2

<table>
<thead>
<tr>
<th>Descriptiona</th>
<th>Chemical subclassa</th>
<th>No. of samples</th>
<th>Cu (wt%)</th>
<th>Zn (wt%)</th>
<th>Sb (wt%)</th>
<th>Ag (wt%)</th>
<th>Pb (wt%)</th>
<th>As (wt%)</th>
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<td>DISS (musc)</td>
<td>Sp–Sb</td>
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<td>2.23</td>
<td>0.04</td>
<td>0.04</td>
<td>1.94</td>
<td>59</td>
<td>0.25</td>
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<tr>
<td>DISS (musc)</td>
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<td>3.53</td>
<td>3.12</td>
<td>0.50</td>
<td>1.00</td>
<td>253</td>
<td>5.58</td>
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<td>0.62</td>
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<tr>
<td>MASS (UP)</td>
<td>Ccp–Ag</td>
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<td>30.71</td>
<td>0.19</td>
<td>0.23</td>
<td>10.68</td>
<td>34</td>
<td>1.50</td>
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</table>

* Standard deviation.

Table 3

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<th>Descriptionb</th>
<th>Chemical subclassb</th>
<th>No. of samples</th>
<th>Cu (wt%)</th>
<th>Zn (wt%)</th>
<th>Sb (wt%)</th>
<th>Ag (wt%)</th>
<th>Pb (wt%)</th>
<th>As (wt%)</th>
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<td>MASS (UP)</td>
<td>Ccp–Ag</td>
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<td>30.71</td>
<td>0.19</td>
<td>0.23</td>
<td>10.68</td>
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<td>1.50</td>
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</table>

* a DISS: disseminated to semi-massive sulphides (acid or mafic host rock, for explanation see text), MASS: massive sulphides (from upper (UP, i.e. drillcore A, cf. Fig. 2) or deeper parts (DP) of the Rockliden deposit).

b Classes as defined by the preliminary classification (see Section 2 for explanation, Sp–Sb (or –Ag): sphalerite-dominated Sb-rich (or Ag-rich) subclass, Ccp–Ag: chalcopyrite-dominated Ag-rich subclass)
hides from the deeper part of the Rockliden deposit (below ca. 300 m depth) have gudmundite as a common Sb-bearing phase (Table 4). The grain size of gudmundite is variable and ranges from ca. 50 µm for individual grains up to 200 µm in star-shaped agglomerates (Fig. 3E and F). Gudmundite is also found as small grains (<10 µm) in complex intergrowths with chalcopyrite or Fe-sulphides (Fig. 3E).

Most of the studied disseminated to semi-massive sulphide samples are dominated by Fe–Mg-bearing silicate minerals such as amphiboles and biotite. They are referred to as mafic rocks. Four out of five studied disseminated sulphide samples are of this type (Table 3). Chalcopyrite is dominating over sphalerite in the mafic rock samples, and bournonite is the main Sb-bearing phase in these samples (DISS mafic, Table 4, Fig. 3A and B). Chalcopyrite is commonly found as inclusions or intergrowths with bournonite (Fig. 3B). The bournonite crystals are up to 200 µm in length. Except for bournonite, the abundance of Sb-bearing minerals in the mafic rock samples is rather variable, comprising tetrahedrite, meneghinite and gudmundite. Meneghinite reaches similar sizes as bournonite, whereas tetrahedrite has a diameter of ca. 50–100 µm and is commonly associated with bournonite, galena and chalcopyrite (Fig. 3C). The remaining, non-mafic, studied disseminated sample (DISS felsic, Tables 3 and 4) consists of quartz and clay minerals and has sphalerite as the main base metal carrier. This sample derives from a Sb-rich interval within the altered volcanic rocks and is referred to as felsic rock. Berthierite, jamesonite and minor jamesonite.

Table 4

<table>
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<tr>
<th>Descriptiona</th>
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<th>No.d</th>
<th>Ttr</th>
<th>Bour</th>
<th>Gel</th>
<th>Boul</th>
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<td>DISS (mafic)</td>
<td>Ccp–Ag(Sb)</td>
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<td>x</td>
<td>xx</td>
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<td>x</td>
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<td>Sp–Sb</td>
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<td></td>
<td>xxx</td>
<td>x</td>
<td></td>
<td></td>
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<tr>
<td>MASS (LP)</td>
<td>Sp–Sb</td>
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<td>(x)</td>
<td>xxx</td>
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<tr>
<td>MASS</td>
<td>Sp–Ag</td>
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<td></td>
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<tr>
<td>MASS</td>
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<td></td>
<td>xxx</td>
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<td>x</td>
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</table>

a DISS: disseminated to semi-massive sulphides (acid or mafic host rock, for explanation see text), MASS: massive sulphides (from upper (UP, i.e. drill core A, cf. Fig. 2) or deeper parts (DP) of the Rockliden deposit).
b Classes as defined by the preliminary classification (see Section 2 for explanation, Sp–Sb (or -Ag): sphalerite-dominated Sb-rich (or Ag-rich) subclass, Ccp–Ag: chalcopyrite-dominated Ag-rich subclass).
c This sample contains mainly berthierite and minor jamesonite.
d Number of mineralogical samples included.
3.3. Characterisation of Sb-bearing minerals in the flotation test products

The distribution of Sb-bearing minerals in the final flotation products of the three Rockliden composite samples is summarised in Fig. 5. Chemical analysis for the flotation products (as outlined in Fig. 5) are shown in Table 5 and the distribution of Sb-bearing minerals is further disclosed in Table 6.

In the Cu–Pb concentrates, tetrahedrite and bournonite are the major Sb-bearing phases (Table 6). The Cu–Pb concentrates of the composite samples from the upper part of the Rockliden deposit (CA and CB (cf. Fig. 2), Table 6) have a higher abundance of tetrahedrite compared to the Cu–Pb concentrate from the tests done for composite sample CC (cf. Fig. 2) taken at greater depth in the deposit (ca. 300–900 m). The Sb mineralogy of the Zn concentrates is similarly complex to the Cu–Pb concentrate, comprising bournonite, gudmundite, tetrahedrite and boulangerite (Table 6). In the tailing samples from the Rockliden flotation tests, gudmundite is the dominant Sb-bearing mineral (Table 6).

In the laboratory flotation tests the P_{50} of the flotation feed was ca. 50 μm. Although most of the sulphide minerals are liberated at this size, the Sb-bearing minerals remain partly locked with other minerals. This is not unexpected and reflects the size of Sb-bearing minerals observed in the mineralogical samples. Thus the mode of occurrence of Sb-bearing minerals in particles of the flotation products was studied more closely in BSE images.

Beside liberated mineral grains, tetrahedrite (Fig. 4A and B) and bournonite occur together with galena in binary particles from the Cu–Pb concentrates, but also with sphalerite, chalcopyrite and pyrite. Gudmundite is a minor Sb-bearing mineral in Cu–Pb concentrates (Table 6), but it occurs locked together with galena in binary particles and also in ternary particles complexly intergrown with chalcopyrite (Fig. 4B and C). In the Zn concentrates, tetrahedrite is found locked with sphalerite, galena and chalcopyrite (Fig. 4E), as well as with arsenopyrite and bournonite. In the Zn concentrate bournonite (Fig. 4D) is locked with galena, pyrite, pyrrhotite, chalcopyrite, sphalerite, boulangerite and arsensopyrite. In the tailing products, gudmundite is mostly found as liberated grains. But gudmundite as well as meneghinite occur also locked mainly with gangue minerals like chlorite, quartz, calcite and plagioclase (Fig. 4F).

4. Discussion

Microscopic studies of mineralogical samples are summarised and compared with the Sb deportment in the flotation products in Table 7. Similarities in the associations between the mineralogical samples and flotation products can be seen in this table, i.e. the mode of occurrence of Sb-bearing minerals as found in the uncrushed material apparently is reflected in particles in the flotation products. Thus reasons for the behaviour of particles during flotation can be linked to the mineral grain sizes and associations found in the primary rock and mineralised material.

Based on observations done in a limited number of thin sections on massive sulphide samples, there is an apparent change in the Sb mineralogy of the massive sulphide samples towards greater depth (>300 m below surface at the Rockliden deposit). The Sb-rich massive sulphide samples from the upper part of the deposit contain abundant tetrahedrite often with complex intergrowths of pyrrhotite-chalcopyrite-native antimony, whereas gudmundite is the main Sb-bearing mineral in the Sb-rich massive sulphide samples from greater depth. In the disseminated sulphide samples, bournonite is the common Sb-bearing phase of the mafic rocks. Mafic rocks are documented within or close to the massive sulphides throughout the 3D extent of the deposit, potentially complicating the Sb-mineralogy of composite samples and flotation products irrespectively of the depth from which these products are derived. Moreover, one sample taken from the felsic rocks (i.e. volcanic host rock of Rockliden) contains additional Sb-bearing phases,
jamesonite and gudmundite, indicating that the Sb-mineralogy of the host rocks is locally more complex.

Further, the highest Ag-values of tetrahedrite were documented in the mineralogical samples of mafic rock, indicating that the variation of Ag in tetrahedrite is partly related to different rock and mineralisation types. Also, it is known from previous studies of the Rockliden deposit that the Ag-content can be as high as 15 wt% in tetrahedrite in the north-western parts of the Rockliden deposit (Karup-Møller and Makovicky 1980; Mattsson and Heeroma, 1985) and variations might be related to even larger scale geological features. These relationships need to be understood in order to be able to predict the distribution of Sb combined

![Fig. 4](image)

**Table 7**

<table>
<thead>
<tr>
<th>Mineral and ideal chemical formula</th>
<th>Position in the ore body</th>
<th>Association in the mineralisation</th>
<th>Distribution in the flotation products</th>
<th>Association in particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedrite (Ttr), (Cu,Fe,Ag,Zn)<em>{12}Sb</em>{4}S_{13}</td>
<td>Mafic rocks, MASS (not Sp–Sb in DP)</td>
<td>Gp, Ccp, Sp, Po</td>
<td>Cu–Pb conc., Zn conc.</td>
<td>Gp, Sp, Ccp, Po, silicate minerals</td>
</tr>
<tr>
<td>Bournonite (Bour), PbCuSbS_{3}</td>
<td>Mafic rocks, MASS (only traces in Sp–Sb in DP)</td>
<td>Gp, Ccp, Ttr, Sp</td>
<td>Cu–Pb conc., Zn conc.</td>
<td>Gp, Sp, Ccp, Bour</td>
</tr>
<tr>
<td>Meneghinite (Mene), Pb_{13}CuSb_{7}S_{24}</td>
<td>Mafic rocks, MASS Sp–Sb in DP</td>
<td>Apy, Gp, silicate minerals</td>
<td>Cu–Pb conc., Zn conc.</td>
<td>Gp, silicate minerals</td>
</tr>
<tr>
<td>Boulangerite (Boul), Pb_{5}Sb_{4}S_{11}</td>
<td>Mafic rocks, MASS Sp–Sb in DP</td>
<td>Apy, Gp, silicate minerals</td>
<td>Cu–Pb conc., Zn conc.</td>
<td>Bour</td>
</tr>
<tr>
<td>Gudmundite (Gd), FeSbS</td>
<td>All</td>
<td>Po, Gp, Sp, Apy, (as small grains &lt; 10 μm with Ccp, Po, Sp) &amp; silicate &amp; carbonate minerals</td>
<td>Cu–Pb conc., Zn conc.</td>
<td>Gp, (Ccp, Sp), silicate &amp; carbonate minerals</td>
</tr>
</tbody>
</table>


Underlined are products where the Sb-bearing minerals are unexpected (cf. Lager and Forssberg, 1990).
with the economic valuable Ag in tetrahedrite and in other sulphosalts throughout the entire deposit.

The examples given above suggest that the Sb-mineralogy in the Rockliden deposit can be linked to the geology, to rock and mineralisation types. Thus it is clear that a geological model, accounting for the complex geometry of the Rockliden massive sulphide body should form the basis of a detailed 3D mineralogical map of the Sb mineralogy.

The Sb mineralogy of flotation products from Rockliden (Fig. 5) is partly consistent with the expected distribution based on the study of Lager and Forsberg (1990) on the separation of Sb minerals in flotation tests of Rakkegaur complex sulphide ore. The Sb-bearing minerals containing Cu, Ag or Pb are mainly found in the Cu–Pb concentrate and those which combine Sb with Fe or As in the tailings.

Based on studies by Lager and Forsberg (1990), it is expected that liberated tetrahedrite, bournonite, boulangerite, and meneghinite and jamesonite float readily under the conditions of the Rockliden laboratory flotation tests. These minerals should largely report to the Cu–Pb concentrate. The remaining Sb phase, gudmundite, is not expected to float in Cu–Pb and Zn flotation and therefore it should be found in the tailings. However, the mineralogical composition of the flotation products is generally more complex than expected from the liberation distribution of the Sb-bearing minerals (Fig. 5). When locked the associating minerals (cf. Table 7, Figs. 3 and 4) will influence the behaviour of complex particle depending on relative exposure proportions. Chalcopyrite- and galena-rich particles are expected to be recovered into the Cu–Pb concentrate and those which combine Sb with Fe or As in the tailings.

In order to implement the data on the Sb mineralogy into a geometallurgical model of the Rockliden deposit, the results of this study need to be quantified. The value of qualitative and quantitative mineralogical and petrographic studies has already been pointed out in case studies on process optimisation for several ore deposits (e.g. Baum et al., 2004; Letter et al., 2011). Thus, a main target for future work on Rockliden is to quantify the distribution and the mode of occurrence of Sb-bearing minerals in the ore and flotation products using automated SEM-based methods. This will also show how rigorously the Sb mineralogy can be derived, e.g. from chemical assays, or whether other methods such as diagnostic leaching must be applied to quantify the Sb mineralogy at Rockliden. Quantitative data should also be used in order to test proposed relationships between the Sb mineralogy and rock, alteration, and mineralisation types.

5. Conclusions

Since the Sb-content controls the quality of the Cu–Pb concentrates, it is important to know the distribution of Sb-bearing minerals and their mode of occurrence in the ore. This study outlines variations in the distribution of Sb-bearing minerals, which appear to be related to rock and mineralisation types found in the Rockliden Zn–Cu massive sulphide deposit. During flotation, both the chemical composition and mineral association of the Sb-bearing minerals, inherited from the primary ore material, control the distribution of these minerals. Examples are illustrated in this study. The examples given above suggest that the Sb-mineralogy in the Rockliden deposit can be linked to the geology, to rock and mineralisation types.

Fig. 5. Flow sheet of the laboratory flotation test (chemical assays are given in Table 5 for the streams with bold arrows). Tables for the final products show the abundance of tetrahedrite (Tr), bournonite (Bour), boulangerite (Boul, including meneghinite (Mene)), galena (Gd) within this study (estimations are based on quantifications done with INCA Mineral software (Oxford Instruments NanoAnalysis, 2012)). Sb-bearing minerals which are highly expected to be found in the flotation products (cf. Lager and Forsberg, 1990) are bold and underlined in the figure.
(e.g. Lamberg, 2011). The prediction needs to have good accuracy to support production management, for example to make decisions on the treatment of the flotation products, i.e. decisions on when the Cu-Pb concentrate has to be treated by unconventional process solutions such as alkaline leaching.

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References

PAPER II

Lithology and Mineralisation Types of the Rockliden Zn-Cu Massive Sulphide Deposit, North-Central Sweden

Friederike E. Minz, Jonas Lasskogen, Christina Wanhainen and Pertti Lamberg

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Lithology and Mineralisation Types of the Rockliden Zn-Cu Massive Sulphide Deposit, North-Central Sweden

F.E. Minz, J. Lasskogen, C. Wanhairen, P. Lamberg

1) Luleå University of Technology, Department of Civil, Environmental and Natural Resources Engineering

2) Boliden Mines, Exploration Department

Abstract

The Rockliden Zn-Cu volcanic-hosted massive sulphide deposit is located approximately 150 km south of the Skellefte ore district, north-central Sweden. Most of the mineralisation is found at the altered stratigraphic top of felsic volcanic rocks, along the lithological contact to sedimentary rocks. The volcanic rocks are known to cover a 25km² area and are intercalated in the metamorphosed siliciclastic sedimentary rocks of the Bothnian Basin. Rockliden was discovered in the 1980s by Boliden Mineral AB. The project was put on hold in 1985 because of the relatively high antimony grade in the massive sulphides and the resulting difficulty in handling and extracting antimony in the smelting process. Exploration drilling restarted in 2007 and resources have increased by about 50% since then. However, little is known about the variability in mineralogy and petrography of the ore material and its host rocks. Spatially extensive alteration zones are found primarily in the volcanic rocks, comprising of sericitisation, silicification and chloritisation, from distal to proximal to the massive sulphide mineralisation. Dyke-like mafic rocks transect all lithological units at the Rockliden deposit and consist dominantly of amphiboles. Ore types are distinguished based on their main sulphide mineralogy. Most massive sulphides are dominated by pyrite. Locally, pyrrhotite is found more abundant than pyrite. Chalcopyrite and sphalerite are the main base-metal sulphide minerals. Generally, sphalerite is dominating over chalcopyrite. Banding textures are related to centimetre-scale alternation of pyrite and sphalerite, locally cut by millimetre-wide magnetite seams or chalcopyrite flames. So far, systematic differences in the trace mineralogy were not found by qualitative ore characterisation. Potential process-relevant rock- and ore-intrinsic parameters are suggested to be quantified, evaluated, and implemented in a geological model providing an assisting tool in production management.
1 Introduction

The Rockliden volcanic-hosted massive sulphide (VHMS) deposit is located in the Västernorrlands Län, north-central Sweden, ca. 150 km SW of the Skellefte ore district and the nearby existing processing facilities (e.g. the smelter at Rönnskär, Fig. 1). The inferred mineral resource is 3.53 Mt with 4.2 wt% Zn, 1.9 wt% Cu, 0.7 wt% Pb and 71 g/t Ag (New Boliden, 2013). The Rockliden deposit is relatively Cu-rich compared to other Swedish VHMS deposits, e.g. Kristineberg, Renström, Maurliden and Rakkejaur (Allen et al., 1996; New Boliden, 2013). Similar to other VHMS deposits of the Skellefte ore district, the Rockliden mineralisation shows high concentrations in penalty elements such as As, Sb and Hg (Allen et al., 1996; Raat and Årebäck, 2009). Shortly after the discovery of Rockliden in the 1980s, the project was put on hold when metallurgical tests indicated a high Sb content in the Cu-Pb concentrate, thus lowering the quality of this product (Raat and Årebäck, 2009).

Exploration drilling in the Rockliden area restarted in 2007, indicating a decrease in the average Sb content towards depth and some variance in content in the strike extension, and new flotation tests were performed (Bolin, 2010; Raat and Årebäck, 2009). Today, alternative process solutions such as alkaline sulphide leaching are considered to remove Sb from the Cu-Pb concentrate and this method have been tested successfully (Awe, 2013; Bolin, 2010). To decide on when to use unconventional process solutions, it is important to know when the ore material, which potentially yields high Sb contents in the Cu-Pb concentrate, is coming into the process. Initial studies on the Sb mineralogy of Rockliden pointed towards several parameters controlling the distribution of Sb-bearing minerals during flotation and hence the Sb content of the Cu-Pb concentrate. One potential process-relevant parameter is the interlocking of penalty-element-bearing minerals with base-metal- and Fe-sulphides in mineralogical complex particles (Minz et al., 2013).

The purpose of this study is to characterise and classify the Rockliden mineralisation based on the occurrence and distribution of major sulphide minerals (i.e. pyrite, sphalerite, chalcopyrite and pyrrhotite). A detailed petrographic and mineralogical description of the different rock and mineralisation types is conducted, outlining different geological, i.e. rock-intrinsic parameters which potentially affect the processing of mineralised material. Rock-intrinsic parameters of the massive sulphides include the mineralogical composition and textural information such as grain size, orientated intergrowth and association with penalty- and bonus-element-bearing minerals (e.g. Walters and Kojovic, 2006). Studying the process response (cf. Jackson et al., 2011) of these parameters for different rock and mineralisation types is, however, not subject of this paper. Herein, the current knowledge of the local geology and mineralogy of Rockliden is compiled, which should form the background of a process-adopted geological sub-model for the Rockliden deposit (Lamberg 2011; Minz 2013). Such sub-model will provide 3D information on the rock-intrinsic process-relevant parameters, forming a basis to forecast the process-response of different rock and ore types in the Rockliden deposit.
2 Geological Setting

2.1 Regional Geology

The Rockliden massive sulphide deposit is located within the Bothnian Basin (Kousa and Lundqvist, 2000; Lundqvist et al., 1998; Welin, 1987). The basin comprises parts of the Svecofennian rocks south of the Luleå-Jokkmokk line (Weihed, 2004). It is located south of Skellefte ore district and north of the Bergslagen ore district (Kumpulainen, 2009; Fig. 1). The supracrustal rocks of the Svecofennian Domain are dominated by turbiditic meta-sedimentary rocks, and these units are referred to as the Härnö group (Kousa and Lundqvist, 2000; Kumpulainen, 2009). The thickness of the Härnö group was estimated to reach at least 10 km (Lundqvist, 1987; Lundqvist et al., 1990). It has been suggested that Archean and Proterozoic rocks bordering the Bothnian Basin form one possible source for the sedimentary infill of the basin (Claesson et al., 1993; Depauw, 2009; Patchett et al., 1987). Volcanic rocks in the Bothnian Basin are divided into basalt-andesites and fractionated basalts to rhyolites (Bergström, 2001). The latter show a more cale-alkaline trend and are regarded as volcanic arc type rocks (Bergström, 2001). Acid volcanic rocks occur locally and meta-rhyolitic to -dacitic volcanic rocks, located just 1.5 km west of Rockliden, were dated 1875 Ma (Welin, 1987). Similarly to the volcanic rocks of the Skellefte group (Allen et al., 1996; Rutland et al., 2001), different potential tectonic settings for the Rockliden volcanic rocks are suggested. Depauw (2009) proposed an active continental margin setting based on geochemical plots of Schandl and Gorton (2002) or an extensive setting within the Bothnian Basin rimmed to the south by the Bergslagen volcanic arc and to the north by the Skellefte volcanic arc.

Fig. 1. Location of the Rockliden VHMS deposit in the Bothnian Basin limited by the Bergslagen and Skellefte ore districts (Kumpulainen, 2009), south of the Luleå-Jokkmokk line (Mellqvist et al., 1999; Weihed 2004).
Peak metamorphism was reached in the Bothnian Basin during the Svecokarelian orogeny (1.9 to 1.8 Ga) and large parts of the basin were subjected to upper greenschist to upper amphibolite facies conditions, and were partly migmatised (Lundqvist et al., 1990; Weihed, 2004). Late-orogenic S-type granitoids (1.82-1.80 Ga) and post-orogenic A- to I-type Revsund granitoids (1.80-1.77 Ga) intruded into the basin (Claesson and Lundqvist, 1995; Weihed, 2004). Between 1.27-1.24 Ga the basin was intruded by mafic sills and dykes of the Central Scandinavian Dolerite Group (CSGD) (Söderlund et al., 2006).

2.2 Local Geology

The Rockliden massive sulphide deposit is found primarily at the contact between the Härnö sedimentary rocks and the Rockliden volcanic rocks (Depauw, 2009). Based on age data of Welin (1987), the Rockliden felsic volcanic rocks are located at the stratigraphic upper part of the sedimentary rocks (Depauw, 2009). They are classified as calc-alkaline rhyolites to rhyodacites and dacites (Mattsson and Heeroma, 1985) and interpreted as quartz-feldspar phryic coherent domes, tuffitic rocks, lavas and hyaloclastites, and volcanoclastic mass flows, autoclastic breccias, and agglomerates. The stratigraphic sequence of these rocks is not well understood. Metamorphosed turbiditic shales and silstones stratigraphically overlie the mineralisation and generally show a sharp contact against the massive sulphides (Depauw 2009; Mattsson and Heeroma, 1985; Raat and Årebäck, 2009). To the north and west, the Rockliden area is bordered by granitic rocks, whereas to the south and east meta-greywackes of the Härnö group are found as gneisses and migmatites (Depauw, 2009; Mattsson and Heeroma, 1985). Various mafic intrusions occur in the Rockliden area in the form of decimetre- to metre-wide sills and dykes. They mostly occur along weak zones like fault structures (Raat and Årebäck 2009). Dolerite dykes with chilled margins crosscut all rocks of the Rockliden area in a WSW-ENE to SW-NE direction (Fig. 2; Mattsson and Heeroma, 1985; Raat and Årebäck, 2009). Mafic sills and dykes, lacking distinct chilled margins, are found close to or within the mineralisation (Depauw, 2009). At deposit-scale, these mafic dykes are steeply dipping, mostly lying parallel to bedding or along the foliation of the host rocks, but they do not appear to be continuous over larger vertical distances of more than 50 m and often appear to coincide with possible fault structures (Raat and Årebäck, 2009). Additional mafic rock types are described by Mattsson and Heeroma (1985) including gabbros and basaltic rocks. Gabbros are found in outcrop 5 to 10 km west of the Rockliden deposit, trending in a NW-SE direction. Basaltic rocks are found ca. 10 km east of the Rockliden deposit. They are partly brecciated, silicified, containing disseminated pyrite and pyrrhotite (Mattsson and Heeroma, 1985).

While the metamorphic grade in large parts of the Bothnian Basin reached upper amphibolite facies conditions during the Svecokarelian orogeny (e.g. Lundqvist et al., 1998), the host rocks to the Rockliden mineralisation have reached a maximum metamorphic grade of upper greenschist conditions (Depauw, 2009). According to Raat and Årebäck (2009) and Depauw (2009), the volcanic rocks show locally impregnation of carbonate minerals and silicification in irregular shaped zones in distal parts of the massive sulphide mineralisation. Sericite alteration is the most prominent alteration type in the Rockliden volcanic footwall rocks, extending several tens to hundreds of metres into these rocks and transgressing into a strong to intense sericite-quartz
dominated alteration within tens of metres to a few metres towards the massive sulphides. A chlorite alteration zone of tens of metres to only a few decimetres width is found most proximal to the massive sulphides and contains locally neoblasts of andalusite, biotite, magnetite and red garnet (Depauw, 2009).

The contact between the altered volcanic rocks and the meta-sedimentary rocks of Rockliden is steeply dipping and the geometry of the massive sulphide bodies is complex due to deformation (Fig. 2; Depauw, 2009; Raat and Årebäck, 2009). Structural features are generally E-W trending (Evins, 2011) and related to the Svecokarelian orogeny (Depauw, 2009). Two deformation events were proposed by Mattsson and Heeroma (1985): a first folding event with N-S trending fold axis and a second event with E-W trending fold axis. However, the E-W trending fold axes are found prominent in the massive sulphides and are tight, nearly concentric in the outcrop of the massive sulphide mineralisation (Raat and Årebäck, 2009). These folds are occasionally accompanied by fold plane-parallel shear zones, locally with an apparent sinistral offset of up to 30 m (Evins, 2011). Additionally, NW-SE and NE-SW striking and steeply dipping faults transect the Rockliden area (Mattsson and Heeroma, 1985). Dextral offset was noticed at a late shear zone documented in the outcrop of the massive sulphide mineralisation (Evins, 2011).

Mattsson and Heeroma (1985) sketched an idealised mineralogical zoning for the undeformed massive sulphide mineralisation at Rockliden. Modifications of the Rockliden massive sulphides and deviations from the idealised zoning pattern are suggested to be due to deformation and
metamorphism (Depauw, 2009; Minz, 2013; Raat and Årebäck, 2009; Fig. 2c). This includes structural repetition of massive sulphide bodies and remobilisation in the ore shoots found along fault planes, as well as enrichment of galena and chalcopyrite in fold hinges and along fault zones and transformation of pyrite into pyrrhotite (Depauw, 2009; Raat and Årebäck, 2009).

3 Methods

In preparation of drill core sampling for this study, a simplified mineralogy (pyrite, chalcopyrite, sphalerite, galena, arsenopyrite and bournonite) was calculated from chemical assays (S, Cu, Zn, Pb, As, and Sb) for all drill core intervals using the Geo module of the HSC Chemistry software (Roine, 2009). The calculated pyrite content contains sulphide mineral which are not included in the list for the element-to-mineral conversion but might be present in the ore, for example pyrrhotite. Bournonite was chosen to represent the Sb-bearing minerals. Based on the sphalerite and chalcopyrite content of the plain sulphide fraction in the assayed drill core intervals three preliminary classes were defined: a sphalerite-, chalcopyrite- and pyrite-rich class. These classes were further subdivided by their Ag and Sb content representing critical bonus and deleterious elements. Boliden’s database of chemical assays on the Rockliden exploration project were imported and interpolated using spheroidal model for kriging with Leapfrog 3D modeling software (Zaparo Ltd., 2009) and qualitatively evaluated together with the preliminary classification. Based on this evaluation, six drill cores were selected and 59 samples were collected to cover the preliminary defined classes throughout the spatial extent of the deposit and to study the variability in the mineralogy of the Rockliden ore. All 59 samples were assayed by the ALS Minerals Division (Piteå, Sweden) for 64 major and minor elements. This data was plotted against geochemical reference data from the Boliden database for Rockliden host rock material.

Polished thin sections were prepared by Vancouver Petrographics Ltd (Canada) and were studied under the optical microscope (Nikon ECLIPSE E600 POL, Luleå University of Technology) to refine the HSC Chemistry based preliminary classification and to provide additional textural information. Further, mineralogical studies were continued with energy-dispersive X-ray spectroscopy (EDS) at the scanning electron microscope (SEM) and the chemical information on minerals supported by Wavelength-Dispersive X-Ray Spectroscopy (WDS) at the electron probe micro-analyser (EPMA). SEM/EDS and EPMA/WDS analysis were conducted mainly at the following instrumentation with the following settings: Merlin SEM (Zeiss Gemini, FESEM, Luleå University of Technology, Sweden) with acceleration voltage of 20 keV and emission current of 0.9 to 1.1 nA and JEOL JXA-8200 microanalyser (Center of Microscopy and Nanotechnology, Oulu University, Finland) with acceleration voltage of 15 keV, emission current of 15 to 30 nA and a beam diameter of 5 μm.
4 Results

Based on the total sulphide content (as calculated from drill core assays by Geo module of the HSC Chemistry software (Roine, 2009)), the following broad distinction can be made for the drill core samples: massive sulphides (samples with > 50 wt% total sulphide content) and disseminated to semi-massive sulphides (< 50 wt% total sulphide content). The latter group is dominated by silicon (Table 1) and hence by silicate minerals (Table 2). In the following they are referred to as host rocks and geochemical tools are employed to classify them.

As shown in figure 2, felsic volcanic and meta-sedimentary rocks form the main host to the Rockliden massive sulphide mineralisation. The felsic volcanic rocks constitute the stratigraphic footwall and will be described in more detail below. Several mafic rock types are also present, locally in close relationship and partly interfingering with the massive sulphides. Mafic rocks showing an elevated Sb content are included in this study.

4.1 Petrography and Geochemistry of Host Rocks

From drill core logging, three main rock types are distinguished comprising felsic volcanic, mafic and sedimentary host rocks to the massive sulphides. Regarding the base-metal sulphide minerals, mafic rocks tend to contain more chalcopyrite than the felsic volcanic and sedimentary rocks, both of which have higher sphalerite content (Fig. 3a, cf. Table 1). The three host rock types are described in more detail below.

Felsic Volcanic Rocks:

The unaltered felsic volcanic rocks are characterised by porphyritic textures with a varying abundance of feldspar and quartz phenocrysts. Feldspar phenocrysts range in length from 1 to 5 mm and constitute up to 10 area% in feldspar-rich units (Raat et al., 2011). Both plagioclase and alkali feldspar phenocrysts are identified. Quartz phenocrysts constitute generally less than 5 area%, with a maximum size of ca. 5 mm (Raat et al., 2011). Alignment of phyllosilicates such as sericite imposes a foliated texture on the volcanic rocks (Fig. 4b). In most cases the very fine-grained groundmass of these rocks cannot be further determined with optical microscopy (Fig. 4a and b).
<table>
<thead>
<tr>
<th>Classa)</th>
<th>No.</th>
<th>S / wt%</th>
<th>Cu / wt%</th>
<th>Zn / wt%</th>
<th>Pb / wt%</th>
<th>As / ppm</th>
<th>Au / ppm</th>
<th>Ag / ppm</th>
<th>Sb / ppm</th>
<th>Sn / ppm</th>
<th>Bi / ppm</th>
<th>Hg / ppm</th>
<th>Cd / ppm</th>
<th>In / ppm</th>
<th>Mo / ppm</th>
<th>Co / ppm</th>
<th>Ni / ppm</th>
<th>W / ppm</th>
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<tbody>
<tr>
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<td>4</td>
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<td>0.09</td>
<td>1.45</td>
<td>0.1</td>
<td>39.3</td>
<td>202.5</td>
<td>23.8</td>
<td>12.4</td>
<td>51.9</td>
<td>36.0</td>
<td>21.7</td>
<td>2.7</td>
<td>118.2</td>
<td>11.2</td>
<td>1.7</td>
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<tr>
<td>Po-Ccp/Sp</td>
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<td>26.72</td>
<td>2.96</td>
<td>13.61</td>
<td>2.29</td>
<td>0.50</td>
<td>0.0</td>
<td>120.7</td>
<td>1823.3</td>
<td>992.9</td>
<td>30.6</td>
<td>389.8</td>
<td>287.2</td>
<td>25.5</td>
<td>5.2</td>
<td>41.7</td>
<td>12.6</td>
<td>1.6</td>
</tr>
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<td>Py</td>
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<td>46.50</td>
<td>0.49</td>
<td>2.55</td>
<td>0.29</td>
<td>0.12</td>
<td>0.0</td>
<td>42.0</td>
<td>516.5</td>
<td>12.8</td>
<td>7.3</td>
<td>185.3</td>
<td>48.3</td>
<td>13.6</td>
<td>10.8</td>
<td>27.4</td>
<td>9.2</td>
<td>1.5</td>
</tr>
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| Classa) | No. | Si / wt% | Al / wt% | C / wt% | Na / wt% | K / wt% | Mg / wt% | Ca / wt% | Mn / wt% | Fe / ppm | P / ppm | Ti / ppm | Zr / ppm | Nb / ppm | Y / ppm | La / ppm | Cr / ppm | V / ppm |
|---------|-----|----------|----------|--------|----------|--------|---------|---------|---------|----------|---------|----------|----------|----------|---------|---------|---------|---------|---------|
| Py+Po+Mgt-Ccp-Sp | 4   | 2.50    | 0.20    | 0.15   | 0.02    | 0.02   | 0.80   | 0.38   | 0.03    | 42.68    | 5.0    | 0.0      | 4.1      | 1.7      | 1.5     | 1.4     | 20.5    | 4.8    |
| Po-Ccp/Sp | 6   | 4.98    | 0.78    | 1.01   | 0.11    | 0.26   | 1.24   | 2.45   | 0.08    | 28.78    | 45.0   | 0.0      | 17.8     | 4.4      | 4.9     | 5.8     | 9.3     |       |
| Py     | 2   | 0.90    | 0.15    | 0.47   | 0.02    | 0.02   | 0.49   | 0.93   | 0.05    | 41.80    | 5.0    | 0.0      | 2.2      | 1.0      | 1.2     | 0.7     | 0.5     | 5.0    |
| Py-Ccp-Sp | 8   | 2.93    | 0.11    | 0.25   | 0.00    | 0.01   | 0.55   | 0.44   | 0.04    | 38.78    | 6.3    | 0.0      | 1.2      | 0.8      | 1.1     | 0.9     | 1.4     | 4.8    |
| Py-Sp-Ccp | 5   | 3.66    | 0.27    | 0.35   | 0.03    | 0.04   | 0.96   | 0.60   | 0.04    | 35.32    | 14.0   | 0.0      | 5.2      | 1.1      | 1.6     | 1.6     | 11.4    | 7.2    |
| Py-Sp | 8   | 1.60    | 0.17    | 0.43   | 0.01    | 0.03   | 0.63   | 1.01   | 0.07    | 37.19    | 2.5    | 0.0      | 4.1      | 1.1      | 1.6     | 1.2     | 1.4     | 4.4    |
| felsic (altered) | 9   | 30.29   | 5.99    | 0.02   | 0.71    | 2.16   | 1.17   | 1.14   | 0.05    | 7.09     | 335.6 | 2538.9   | 9.1      | 30.3     | 37.0    | 21.4    | 20.7    |       |
| mafic | 7   | 21.21   | 6.05    | 0.19   | 1.48    | 0.39   | 5.67   | 5.76   | 0.14    | 7.22     | 615.7 | 3382.9   | 59.2     | 2.9      | 18.0    | 10.5    | 406.1   | 202.7 |
| sed | 3   | 30.90   | 7.40    | 0.07   | 1.76    | 1.79   | 1.65   | 1.84   | 0.02    | 3.49     | 656.7 | 2623.3   | 183.0    | 9.8      | 25.3    | 44.9    | 52.3    | 62.3  |

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b) Number of samples.

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<th>Sp</th>
<th>Ccp</th>
<th>Apy</th>
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<td>xx</td>
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<td>(x)</td>
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The volcanic rocks plot mainly in the field of rhyolites and dacites in the TAS diagram (Le Maitre et al., 1989; Fig. 3b) and are mostly found in the range of rhyolites and dacites in alteration box-plots, i.e. they plot within the lower part of the box which comprises analysis of the least altered rocks (cf. Large et al., 2001; Fig. 3d). The geochemical classification of the volcanic rocks is supported by the immobile trace element plot by Winchester and Floyd (1977), which shows two clusters within the rhyolitic-dacitic field (Fig. 3c). However, systematic differences in the mineralogical composition, i.e. potential correlation with the geochemical classification and clustering, have not been observed during drill core logging.

All studied samples have been taken close to the massive sulphide mineralisation and the felsic rocks described below are all affected by alteration. Also, those plotting in the box of least altered rocks show features of alteration such as silicification (Fig. 4b), but remnants of alkali feldspar crystals are locally preserved. The mineralogical composition of volcanic rocks plotting outside the box of least altered rocks, i.e. AI > 80 (cf. Large et al., 2001), comprises quartz and sericite (Fig. 4c) and varying amounts of phyllosilicates, partly identified as chlorite group minerals (Fig. 4d). In reference to optical microscopy, they appear to become more chlorite-rich with increasing CCPI index. Fe-rich gahnite (Table 3) is found locally in intensively altered samples (Fig. 4f). Amphibole minerals were documented in one host rock sample classified as a felsic volcanic rock (Fig. 4e). The average chemistry of these amphibole minerals is slightly different from those of the mafic dykes (described below), as they are lacking the Al-Fe-rich zones documented in the latter rocks (Minz, 2013). Locally, the altered volcanic rocks show elevated values of Sb and are transected by quartz veins or calcite veinlets (Fig. 4b). Besides gudmundite, various Sb-bearing sulphosalts were documented with SEM/EDS.

Turbiditic Sediments and Greywackes:

The siliciclastic sedimentary rocks comprise strata mainly alternating between shale and fine-grained sandstone (Fig. 5a). In contrast to the volcanic host rock, alteration is less pronounced in the sedimentary rocks. In drill cores they show decimetre up to few metres wide bleaching zones of silicification in contact with the massive sulphides. The formation of andalusite in the metamorphosed sedimentary rocks was noticed by Mattsson and Heeroma (1985). Andalusite crystals were not observed macroscopically by the authors in sedimentary rocks adjacent to massive sulphide intervals. However, primary sedimentary textures such as graded bedding, indications of soft-sediment deformation (Evins, 2011) and brittle deformation in the form of calcite and quartz veinlets are documented (Fig. 5a). In the TAS diagram and alteration box-plot (Fig. 3b and 3d), the sedimentary rocks plot together with the volcanic rocks, but they are mostly separated in Yb-La and Cr-V trace element plots (Fig. 3e and 3f) and partly separated in e.g. Al₂O₃/TiO₂-Zr/Al₂O₃ plots.
Fig. 3. Mineralogical and chemical classification of Rockliden host rocks (based on 20 host rock samples collected for this study and ca. 380 lithological reference samples from the host rock database (Exploration Department, Boliden Mines)): a) chalcopyrite(Ccp)-sphalerite(Sp)-pyrite(Py) ternary plot based on mineralogical composition of the sulphide fraction calculated with HSC Chemistry (Roine, 2009); b) chemical classification based on Le Maitre et al. (1989) with violet dots representing least altered felsic volcanic rocks (based on classification by alteration box plot), c) chemical classification based on Winchester and Floyed (1977), d) chemical classification based on alteration box plot after Large et al. (2001), e) discrimination of sedimentary rocks based on Yb-La diagram, f) discrimination of mafic rocks in

Fig. 4. Volcanic host rock and alteration types (optical microscopy, linear and crossed polarised light): a) volcanic host rock with feldspar and quartz phenocrysts, b) slightly sericite-altered rock with quartz veins (minor alteration minerals are andalusite and calcite), c) intensively sericite-altered rock, d) alteration assemblage comprising quartz (Qtz), chlorite group minerals (Chl) and biotite (Bt), e) amphibole crystals (Amp) and epidote group minerals (Ep), f) quartz (Qtz), Zn-spinel (Zn-Spl, Fe-rich gahnite) and biotite (Bt).
Fig. 5. Textures in sedimentary and mafic host rocks (transmitted light (crossed Nicols) and reflected light microscopy): a) variation in the grain size of quartz in the sedimentary rocks. Bedding is transected by calcite veinlets (Cal), b) mafic dyke with clusters of amphibole (Amp) crystals in an amphibole-biotite (Amp-Bt) dominated groundmass, c) mafic dyke with a plagioclase (Plg) amphibole groundmass and larger amphibole (Amp), biotite (Bt) and titanite (Ttn) crystals, d) Zn-rich chromite (Chr) enclosed by magnetite (Mgt) and associated with amphibole (Amp) and arsenopyrite (Apy).

**Mafic Rocks:**

Dolerite dykes are a few decimetres to metres wide and are largely aphyric (Raat and Årebäck, 2009). They have chilled margins and 1 to 5 mm long plagioclase crystals commonly with ophitic texture, and carbonate-quartz-filled amygdules in the central parts (Raat and Årebäck, 2009). Complementary mafic rock types have a similar thickness as the dolerite dykes in drill core intersections, but show no distinct chilled margins. The 3D extension of the mafic dykes is difficult to outline based on drill core information (Raat and Årebäck, 2009). To simplify, they will be referred to as mafic dykes in this paper. It should be noted that the authors do not imply a vertical to sub-vertical orientation of the mafic dykes towards the stratigraphy of the Rockliden deposit. Generally, the mafic dykes are composed of amphibole minerals, phyllosilicates such as biotite, and plagioclase forming a fine-grained groundmass (Fig. 5b). The size of amphibole minerals are in the range 50 to 500 μm (Fig. 5b and 5c) and chemically they represent hornblende, showing relatively large variation in Fe, Mg, Si and Al content (Table 3). Carbonate minerals comprise mostly calcite occurring in fractures together with quartz and chlorite group minerals. Most of the
Mafic dyke samples contain traces of rounded Zn-rich chromite grains, with ca. 9 wt% Zn, surrounded by Cr-V-rich magnetite rims or ilmenite rims (Fig. 5d, Table 3). In a Cr-V diagram the mafic dykes form a distinct cluster at Cr > 300 ppm and V > 150 ppm (Fig. 3f, Table 1). The studied mafic dyke material shows elevated concentration of Sb (Table 1), and bouronite, meneghinite and tetrahedrite are the main Sb-bearing minerals (Table 2).

### Table 3. Chemical composition of (non-stoichiometric) silicate and oxide minerals (EPMA/WDS analysis in wt% for Plg – plagioclase, Amp – amphibole, Bt – biotite, Ep – epidote group, Grt – garnet group, Mgt (mafic) – magnetite in mafic dykes, Chr – chromite, Gah – gahnite).

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1) number of analysis.
2) MS – massive sulphide samples.
3) statistics (LLD – lower limit of detection (EPMA/WDS analysis), mean – arithmetic mean, std – standard deviation).

### 4.2 Massive Sulphide Mineralisation Types

The variation in chemical assays of the massive sulphide mineralisation is shown in figure 6a and the grades of the inferred mineral resource at Rockliden (New Boliden, 2013) plot in the Zn-Pb-Cu field in the Cu-Pb-Zn ternary plot of Franklin et al. (1981). Below ca. 400 m depth of the Rockliden deposit, assayed drill core intervals plot less abundantly into the Zn-Pb-Cu field,
proposing a change in the base-metal content with depth. However, high Cu/(Cu+Zn) values, referred to as Cu-centres, are found over the whole vertical extent (Minz, 2013).

The massive sulphides show variable textures in drill core. Banding is due to the variation in grain size of pyrite or in the abundance of sphalerite in the groundmass surrounding the pyrite grains (Fig. 7). Locally, irregular chalcopyrite patches (referred to as chalcopyrite flame texture, Fig. 7) or abundant host rock clasts are observed in the massive sulphides.

In figure 7a, a continuous massive sulphide intersection is shown with a gradual change in Cu/(Cu+Zn) ratio from the altered volcanic host rock into the massive sulphides. The gradual change of this ratio is partly mimicked by the Ag content. Arsenic is found in relatively high concentrations in the semi-massive sulphides (Fig. 7a). The stratigraphic upper contact of the massive sulphide intersection with the sedimentary host rock is sharp (Fig. 7a). At this contact, the sedimentary host rock reveals a high content of Sb and the rock is fractured by quartz veins.

Most other massive sulphide intersections are disrupted by host rock intervals, dominantly mafic dykes but also altered volcanic intervals. Two of the disrupted massive sulphide profiles are shown in figure 7b and 7c. In both profiles there are no apparent systematic changes in the Cu/(Cu+Zn) ratio of the massive sulphides. Differences between the profiles include depth, geological setting, and the dominance of textural features. Massive sulphides revealing chalcopyrite flame textures are more common in profiles with a generally high Cu content (compare Fig. 7a and Fig. 7b with Fig. 7c). Some of the interrupted massive sulphide intersections show high Ag (> 100 ppm) and Sb (> 1000 ppm) contents over parts or entire massive sulphide intersections. Relatively narrow (max.
(2m wide) massive sulphide intervals with abundant host rock clasts are occasionally found (Fig. 7b) and these intervals are typically dominated by pyrrhotite.

In reference to optical microscopy, the massive sulphides are grouped by their dominating Fe, Cu and Zn opaque minerals, i.e. pyrite (Py), pyrrhotite (Po), magnetite (Mgt), chalcopyrite (CcP) and sphalerite (Sp) (Fig. 6b). Some textures of the massive sulphide samples are shown in figure 8. It should be noted that samples can show transitional features of different groups and there are no strict borders.

In the Po-Sp and Po-Ccp groups, pyrrhotite is the main Fe-sulphide mineral. Locally, isolated grains of pyrite (up to 500 μm diameter) are preserved in samples of these groups (Fig. 8a). Distinctively high grades of more than 1000 ppm Sn are measured in clast-rich, isolated (max. 2m width), massive sulphide intersections (Fig. 7b). The Sn-bearing phases comprise cassiterite (SnO2) and stannite (Cu2FeSnS4). The silicate clasts form so-called augen textures in thin section (Fig. 8b; cf. Petrük, 2000). The mineralogy of these clasts comprises mainly quartz, biotite and other phyllosilicate minerals such as chlorite group minerals, minor epidote group minerals, and feldspars. Beside silicate minerals, carbonate minerals form a main non-sulphide phases in samples of this group (Table 2). Zoning of dolomite group minerals is observed (SEM/BSE imaging and EDS analysis), comprising Fe-rich cores surrounded by Fe-poor margins which in turn might be rimmed by calcite. Magnetite is rarely found in samples of this group.

Massive sulphide samples of the Py group show banding related to the clustering of pyrite grains and a variation in grain size of pyrite grains (mostly ranging from 50 to 500 μm). The packing of pyrite grains locally reaches such density that grain boundaries become difficult to discern with classical reflected light microscopy (Fig. 8c). The combined Cu and Zn content of this group is generally below 6 wt% (Table 1, cf. Fig. 6b). Samples with Cu values ≥ 2 wt% are characterised by irregular-shaped chalcopyrite(-pyrrhotite) flames, imposing a deformation texture on these samples (Fig. 8d). Magnetite grains are mostly rounded to subangular and mostly range from 100 to 200 μm in diameter (Fig. 8d). Occasionally, they contain mineral inclusions, mostly pyrite.

The Py-Sp-Ccp and Py-Ccp-Sp groups can be subdivided by their Zn content (Py-Sp-Ccp with Zn > 5 wt%, Py-Ccp-Sp with Zn < 5 wt%, cf. Fig. 6b). The Cu content is generally above 2 wt% (Table 1, cf. Fig. 6b). Samples with high chalcopyrite content tend to also have relatively high pyrrhotite content. They often lack distinct banding textures, but deformation textures such as flame-like chalcopyrite are documented (Fig. 8d-f, Fig. 7). A tight intergrowth of arsenopyrite with chalcopyrite and pyrrhotite is locally observed in samples of this group (Fig. 8f). Some samples of the Py-Ccp-Sp group contain both abundant magnetite and pyrrhotite. Thus, they are allocated to a separate group, termed Py+Po+Mgt-Ccp-Sp group (Fig. 6b). However, they do not form a separate cluster in the Py-Ccp-Sp ternary plot (Fig. 6b).

1 rounded non-sulphide spots in the massive sulphides. Please note that the term is not used a strict sedimentary sense.
Fig. 7. Massive sulphide intersections in drill core: a) undisrupted, b) disrupted (massive sulphide package enclosed by sedimentary rocks), c) disrupted (massive sulphide intersections in contact with brecciated altered volcanic host rock at ca. 172 m and sedimentary rocks below 245 m).
**Fig. 8.** Massive sulphides (reflected light microscopy): a) large fractured pyrite grain in a pyrrhotite-chalcopyrite-sphalerite groundmass and intergrowths of galena and bournonite, b) augen texture of silicate minerals hosting gudmundite, c) dense packing of pyrite grains, d) pyrite-magnetite dominated sample with chalcopyrite flames, e) orientated texture of pyrrhotite and partly also chalcopyrite, f) fine intergrowths of chalcopyrite, pyrrhotite and arsenopyrite, g) pyrite showing atoll texture and sphalerite-pyrrhotite diablastic intergrowth, h) pyrite fractured by pyrrhotite, galena and native antimony. Mineral abbreviation: Ant – native antimony, Apy – arsenopyrite, Ccp – chalcopyrite, Gd – gudmundite, Gn – galena, Mgt – magnetite, Po – pyrrhotite, Py – pyrite, Sp – sphalerite.

The Py-Sp group has relatively low Cu content (generally below 2 wt%), while the Zn content is relatively high (ranging from 7 to 15 wt%, Table 1, cf. Fig. 6b). Pyrite grains often show embayments, especially when they are totally surrounded by sphalerite (atoll texture, Fig. 8g). They range in size mainly from 200 to 500 μm (up to 1000 μm diameter) and can host inclusions of sphalerite and occasionally galena or tetrahedrite (Fig. 8h). Despite sphalerite forming the dominant mineral embedding pyrite grains, pyrrhotite is locally present and in this case imposes a banded texture on the ore. Locally, pyrrhotite is found as fractures within pyrite grains or in diablastic intergrowth in the sphalerite groundmass (Fig. 8e and h). The abundance of magnetite appears to be variable and ranges from absent to common in samples of this group.

So far, no systematic differences are noticed in the Sb mineralogy of different base-metal groups of the massive sulphides (Table 2). Based on optical microscopy it is observed that tetrahedrite, bournonite, meneghinite and boulangerite are associated with sphalerite and galena, as well as pyrrhotite and arsenopyrite, whereas gudmundite is often found associated with chalcopyrite, pyrrhotite, silicate minerals and calcite. These observations are only qualitative and, so far; are neither quantified nor linked to a 3D geological model of the Rockliden mineralisation.

**5 Discussion**

Based on the content of sulphide minerals, massive (> 50 wt%), semi-massive and disseminated (< 15 wt%) mineralisation types can be distinguished in the Rockliden deposit. The latter is dominated by silicate minerals and forms the host rock to the mineralisation. Several rock types can be distinguished in geochemical classification diagrams and the following lithologies: felsic volcanic rocks, sedimentary and mafic rocks, are discussed below together with the mineralogy of the massive sulphides and its implications on mineral processing.

**5.1 Lithology and Petrography**

Several mafic rock types have been described from the Rockliden area, including gabbro intrusions, greenstones, dolerite dykes and basalt (Depauw, 2009; Mattsson and Heeroma, 1985; Raat and Årebäck, 2009). So far only one mafic rock type, referred to as mafic dykes, is
distinguished in this study (Fig. 3f) and studied in more detail. Although they represent a volumetrically minor host rock, it is suggested that more detailed geochemical and petrological studies on the mafic rocks should be conducted since those situated close to the mineralisation are expected to influence the content of critical metals (e.g. Sb and Ag) in the deposit. Also, their relative timing in relation to the massive sulphide mineralisation and the potential overprinting effect on the mineralisation should be studied in more detail. Other mafic rocks such as gabbro intrusions and dolerite dykes have been suggested to post-date the formation of the massive sulphides at Rockliden (Depauw, 2009; Kousa and Lundqvist, 2000; Söderlund et al., 2006).

It is shown that the sedimentary and felsic volcanic rocks can be largely distinguished by their Yb and La content (Fig. 3e). However, their trace element chemistry is partly overlapping (Fig. 3b and c) and it was suggested in earlier studies by Mattsson and Herroma (1985) that the sedimentary rocks may represent distal tuffitic rocks to the Rockliden felsic volcanic rocks. On a regional scale other rocks have been proposed as potential source rocks for the infill of the Boholian Basin (Claesson et al., 1993; Depauw, 2009; Patchett et al., 1987). It is, however, beyond the scope of this study to draw any conclusions on the provenance of these rocks.

Given the combination of felsic volcanic and sedimentary host rocks, and the base-metal content of Rockliden (Fig. 6a, cf. Barrie et al (1999)), the mineralisation is suggested to represent a bimodal (cf. Fig. 3c) felsic VHMS deposit, which is in accordance with earlier studies by Depauw (2009) and Raat and Årebäck (2009). Mattsson and Heeroma (1985) sketched an idealised pre-deformational mineral zoning pattern in a first report on the Rockliden deposit, showing an overall mineralogical zoning of the main sulphide phases which is known for massive sulphide deposits associated with felsic volcanic rocks (Galley et al., 2007).

5.2 Mineralogical Indications of Deformation

The metamorphic grade of the host rocks is suggested to be relative low, generally greenschist facies (Depauw, 2009). However, the geometry of the ore body is complex due to deformation and most massive sulphide intersections are disrupted by thin, partly brecciated host rock intervals. Within the massive sulphides, textural features interpreted to be related to metamorphism are observed:

(1) Banding may have been enhanced during deformation since galena, sphalerite, pyrrhotite and chalcopyrite are suggested to be relatively mobile compared to pyrite at the Rockliden metamorphic conditions (Clark and Kelly, 1973; Depauw, 2009). However, the extent of metamorphism on this texture is unknown, as banding might also be a primary feature or a recrystallization event in young (unmetamorphosed “prototype”) VHMS deposits (Eldridge et al., 1983; Mattsson and Heeroma, 1985). Corrosion of pyrite grains (by sphalerite, chalcopyrite and pyrrhotite) and recrystallisation of pyrite and related changes in grain sizes has been suggested to occur during metamorphism (Petruk, 2000). However, rounding of pyrite grains and the formation of atoll textures have also been ascribed to modification by ore forming solutions (Eldridge et al., 1983).
(2) Locally, pyrrhotite is the dominating non-base-metal-bearing sulphide mineral in thin, massive sulphide intersections (marginally to massive sulphides or enclosed by sedimentary rocks). Also, pyrrhotite is found to fill fractures in large pyrite grains (Fig. 8h). These observations are in accordance with the interpretation of pyrrhotite formation related to sulphur loss during metamorphism and deformation (Depauw, 2009; Mattsson and Heeroma, 1985). Furthermore, pyrrhotite is documented in diablastic intergrowth with sphalerite and pyrrhotite and chalcopyrite often show foliated, elongated and schistose textures. These features were ascribed to metamorphism of massive sulphides (Petruk, 2000).

(3) Mattsson and Heeroma (1985) suggested that the formation of magnetite is related to secondary (ore-modifying) events as they observed magnetite bands cross-cutting the banding in the massive sulphides. Similar observations were made in this study. Moreover, magnetite locally contains abundant inclusions of pyrite and pyrrhotite (Fig. 3.5e; Minz, 2013), akin to magnetite porphyroblasts which were interpreted as metamorphic feature in VHMS deposits studied by Petruk (2000).

5.3 Mineralogical Parameters in Context of Mineral Processing

Based on the qualitative mineralogical results of this study, it is proposed that the content of base-metal-bearing sulphide minerals can be calculated reliably from Cu and Zn assays as sphalerite and chalcopyrite are the main carriers of these elements in the massive sulphides. Exceptions are only Fe-rich gahnite and Zn-rich chromite for Zn and tetrahedrite, bournonite and meneghinite for Cu. In most cases, these minerals are not expected to influence the Zn and Cu content significantly as they are found as trace minerals in the host rocks and massive sulphides. However, the modal mineralogy does not directly reveal textural features. Some textural features potentially affect the processing of the massive sulphides. For example pyrite-sphalerite banding will cause anisotropic mineralogical hardness contrast and micro-textures will control grain and related liberation size (cf. Butcher, 2010).

From the overlap of Fe-Ccp-Sp and Py-Ccp-Sp massive sulphide groups in the ternary Py-Ccp-Sp plot (Fig. 6b), it is clear that not the entire mineralogy can be calculated by the element-to-mineral conversion based on the limited number of elements commonly assayed in drill core. Furthermore, the direct calculation of pyrite from simple Fe assays is not possible since other Fe-bearing minerals such as magnetite occur beside pyrite and pyrrhotite in the massive sulphides. The importance of quantitative information on Fe-bearing minerals in massive sulphides was illustrated for the magnetite content in ore from the Black Mountain polymetallic base metal mine, South Africa (Williams and Holtzhausen, 2001). The magnetite content was shown to influence the comminution performance by increasing the hardness of the ore, and the flotation performance by lowering the grade of valuable minerals (Williams and Holtzhausen, 2001). In this study, no systematic variations in the magnetite content have been documented at Rockliden. In studies by Mattsson and Heeroma (1985), it was found that magnetite is more abundant in massive sulphides from the north-western part of the deposit. The overall magnetite content in the Rockliden ore is
expected to be low compared to the Black Mountain ore and might not affect the processing of the Rockliden massive sulphides significantly (Bolin, pers. comm., 2013-02-04). However, the pyrite content and the silicate mineralogy might have a significant impact on the processing, e.g. by regulating throughput and hardness of the ore material.

A relation of the Sb mineralogy to rock types of Rockliden was proposed by Minz et al. (2013). Mafic dykes contain mostly bournonite, meneghinite or tetrahedrite; altered felsic volcanic rocks contain locally gudmundite and various Sb-bearing sulphosalts; and massive sulphides contain tetrahedrite, bournonite or gudmundite as main Sb-bearing trace minerals (Minz et al., 2013). Indications were also found that the Sb mineralogy of the massive sulphides might change with depth (Minz et al., 2013) and towards the north-west of the Rockliden deposit (Mattsson and Heeroma, 1985).

Generally, the Sb-bearing minerals are associated with base-metal minerals. This mineral association is suggested to be reflected in the composition of particles after comminution of the ore and this is expected to influence the distribution of Sb-bearing minerals during flotation (Minz et al., 2013). Similar to Rockliden, the association with sulphide minerals is known also for polymetallic sulphide ore deposits. For example, bournonite is commonly observed adjacent to galena and tetrahedrite or meneghinite (e.g. Anderson, 1940; Wagner and Cook, 1997; Wen et al., 1991). Additionally, Sb-bearing minerals are found intergrown with pyrrhotite at Rockliden (Fig. 8h). It is expected from S²-temperature diagrams that sulphosalts such as meneghinite and bournonite are stable in the pyrrhotite field at higher temperatures, i.e. > ca. 200 °C (Mookherjee and Mishra, 1984). Given these considerations on the ore formation, a hydrothermal ore modification event cannot be excluded at Rockliden. It was suggested in earlier studies that remobilisation of Sb occurred during the intrusion of dolerite dykes related increase in temperature (Depauw, 2009).

Understanding the variation in Sb mineralogy in relation to lithological units and structural features (potentially favouring hydrothermal modification) will help predicting the Sb-mineralogy of feed material to the mineral processing stage at Rockliden. Such information has to be based on a geological model. A 3D geological model for Rockliden is currently under construction at the Boliden Exploration Department.

6 Conclusion

Based on the total sulphide content of whole rock samples, it is possible to distinguish between disseminated to semi-massive and massive sulphides at the Rockliden deposit. Among the disseminated to semi-massive sulphide samples, felsic volcanic, sedimentary and mafic rocks can be distinguished on their geochemical and petrographic characteristics. Felsic volcanic and sedimentary rocks form the main host to the massive sulphides. The felsic volcanic rocks show spatially extensive alteration zones and are dominated by sericite and quartz with minor carbonate and chlorite group minerals. The altered felsic volcanic rocks show locally elevated concentrations in Sb, often connected to quartz veining in the host rock. Among the mafic rock types, one unit referred to as mafic dykes, is found in relatively narrow drill core intersections, partly located
within the massive sulphides. These mafic dykes are dominated by amphiboles, plagioclase and biotite, and contain traces of Zn-rich chromite and Cr-V-rich magnetite. They show elevated concentrations in Sb and, although they are found in relatively narrow intervals, they are concluded as important in the Sb balance of the Rockliden ore material.

Massive sulphide samples are classified based on their chalcopyrite (Ccp), sphalerite (Sp), pyrite (Py), pyrrhotite (Po) and magnetite (Mgt) content. The following groups were distinguished: Po-Sp, Po-Ccp, Py, Py+Po+Mgt-Ccp-Sp, Py-Ccp-Sp, Py-Sp-Ccp and Py-Sp. The content of pyrite, pyrrhotite and magnetite is expected to be relevant to processing of the ore material, however, need to be quantified with methods different from element-to-mineral conversion. The chalcopyrite and sphalerite content is expected to be approximated by element-to-mineral conversion using chemical assays. Different ore textures potentially relevant to the processing of the ore, such as banding and complex intergrowths, are suggested to be evaluated using (automated) microscopic tools. SEM-based methods (automated mineralogy) should lead to the quantification of trace minerals, e.g. Sb-bearing minerals, which may be critical to metallurgical processing steps of the Cu-Pb concentrate. Differences in the Sb mineralogy are recognised between the mafic and felsic volcanic host rocks and also between host rocks and massive sulphides.

The subject of ongoing research is to verify and quantify process-relevant rock-intrinsic parameters (cf. Walters and Kojovic, 2006), as well as rock-related and deposit-scale variations in the mineralogy. This data is expected to lead to refinement of the proposed qualitative classification of the mineralisation. Furthermore, such data is aimed to form the basis of the Rockliden 3D geometallurgical model.

Acknowledgements

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References


