The Assessment of the ARD potential for a ‘Climax’ type porphyry molybdenum deposit in a high Arctic environment

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Abstract. The Malmbjerg (a porphyry granitic ridge) in eastern Greenland hosts a significant world class molybdenum deposit of the ‘Climax’ (high-F low base metals) type. The detailed characterisation of the potential of the Malmbjerg deposits to release Acid Rock Drainage (ARD) and Potentially Problematic Elements (PPE) was undertaken as part of the feasibility study. To do this a comprehensive assessment has been undertaken of the deposit’s potential waste-rock and low grade ore environmental geochemistry using static (acid base accounting, whole rock assays, modified EPA 1312 contact test) and kinetic (humidity cell) testwork. The pyritic mineralisation of the Malmbjerg occurs as a shell around the molybdenite zone. However, in general, sulfide content of the rocks is low, being less than 0.03 wt% in much of the intrusive complex, the mafic and trachyte dykes and in the unmineralized sandstone unit. The majority of rocks that are likely to be acid generating are the greisen zones, the pyritized sandstone, the pyritized granite and the mineralized porphyry units. Although sulfide content does not exceed 2wt%, inorganic carbon or carbonate minerals are not abundant and are dominated by siderite which has a low capacity for acid buffering. Consequently the actual potential to neutralize acid is low in the system so any acid generation is noticeable. The majority of lithologies in the Malmbjerg deposit show low levels of reactivity and as such it is difficult by static testing to confirm the potential for acid generation. However, humidity cell testwork (run for up to 95 weeks) has demonstrated that leachate pH has in many samples demonstrated a gradual decrease in pH conditions over an extended period of time but at release rates significantly less than indicated by static testing alone.

Additional Key Words: ARD molybdenum

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INTRODUCTION

The Malmbejrg intrusion hosts a porphyry molybdenite deposit of the Climax (high-F, low base metal) type. Examples of similar deposits worldwide include Climax, Henderson, Mount Emmons and Silver Cliff (Colorado, USA), Pine Grove (Utah, USA), Questa (New Mexico, USA), Mount Hope (Nevada, USA) and Nordli (Norway). Deposits of this type typically contain several hundreds of millions of tons of ore at grades of 0.1 to 0.3% MoS\(_2\). Malmbejrg represents a significant world class deposit of this type ranking third in size after Climax and Henderson (White et al., 1981). The general genetic model is magmatic hydrothermal involving:
• Large volumes of magmatic, highly saline aqueous fluids that mobilize Mo and other metals from genetically related source magmas.

• Multiple stages of brecciation due to very high fluid pressures and explosive pressure release that in combination with the cooling of the intruded rock is causing the deposition of ore along fractures and other weakness zones.

• Opposite moving, sometimes pulsing pressure and temperature gradients often causing several mineralizing events.

The hydrothermal mineralizing event is followed by a period with incursion of meteoric water due to high temperature gradients causing post-mineralization argillic alteration of the host rocks and resulting in partial oxidation of molybdenite to secondary molybdenum minerals including ferrimolybdate, bamfordite and ilsemannite. Alteration of host and surrounding country rocks leads to the emplacement of large quantities of pyrite on the outermost hemispherical alteration shell. Low molybdenite contents of this zone result in a significant proportion of the waste rock being of Potential Acid Forming (PAF) material. This paper presents the methods and results of testwork undertaken to determine the potential for Acid Rock Drainage (ARD) and Elemental Leaching (EL) from the Malmbjerg project and qualitatively compares these to hydrogeochemical data from surface run-off.

GEOLGY AND PETROLOGY OVERVIEW

The Malmbjerg molybdenum deposit is located about 35km south of Mestersvig airfield on the east coast of Greenland at 72 northern latitude and 24 western longitude. The area is part of the southeast boundary of the Werner Bjerge Tertiary intrusive province related to North Atlantic seafloor spreading and magma production bordering the north eastern part of the Jameson land sedimentary basin.

The deposit is hosted in a stock of alkalic I-type leuco-granites and rhyolitic porphyries of mid-Tertiary age intruded into Lower Permian Rode Group clastic sediments constituting the bulk of the Malmbjerg Mountain at the south tip of the Høstakken Mountain (1197m). The Permian clastic sedimentary Rode Group form the host rocks to the Malmbjerg stock and were deposited in a terrestrial clastic basin on the eastern edge of the North America-Greenland (Laurentia) continent (Kofoed, 2006). The sub-aerial exposure of the Malmbjerg stock on the side of the ridge is shown in Figure 1 along with the generalised field relationships of the Malmbjerg complex and country rocks. A general description of the Malmbjerg lithotypes is included in Table 1.
Figure 1. View of the Malmbjerg ridge and generalised field relationships of Malmbjerg complex and country rocks (from SRK, 2008)

Table 1. Summary descriptions of the main Malmbjerg rock types

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granites</td>
<td>Fine to medium grained leucogranites subdivided into perthite and porphyritic (transitional between perthite granite and Arcturus porphyry) units</td>
</tr>
<tr>
<td>Greisen</td>
<td>Exist throughout the stock and in some parts of the sediments. Quartz-tourmaline-wolframite-sulphide assemblages with interstitial fluorite gangue, and topaz</td>
</tr>
<tr>
<td>Porphyry</td>
<td>Two porphyry units can be identified. The Arcturus porphyry has a similar composition to the granites and forms the contact phase of the intrusives. The Schuchert porphyry is the latest intrusive phase of the pre/syn mineralisation units.</td>
</tr>
<tr>
<td>Aplites</td>
<td>Emplaced within the granite intrusion possibly in several phases*. Contain veins of quartz with irregular pyrite grains and central zones of these veins consist of fluorite.</td>
</tr>
<tr>
<td>Pyritic sandstone</td>
<td>The Rhode group sediments consist of arkose sandstones and conglomerates and siltstone / mudstone units which typically contain lithic clasts and visible pyrite scattered throughout rocks in contact with porphyries. These rocks have been subdivided in this study to pyritic sandstones and non-pyritic sandstones based on sulfide sulfur content of greater than or less than 0.5%</td>
</tr>
<tr>
<td>Sandstones</td>
<td></td>
</tr>
<tr>
<td>Dykes</td>
<td>Minor intrusions of mafic, trachyte and lamprophyre dykes and intrusive sheets were emplaced after the close of hydrothermal mineralization in late Tertiary. These do not contain significant sulfide mineralisation.</td>
</tr>
</tbody>
</table>

*Kofoed, 2006

ENVIRONMENTAL GEOCHEMISTRY ASSESSMENT

Total Metal Chemistry
Total metal chemistry enables the determination of Potentially Problematic Elements (PPE) within rock samples. This is generally done in accordance with Price (1997) in which the total concentrations are compared to average crustal concentrations and, in accordance with Price (1997), any constituent at greater than three times crustal abundance is classed as a PPE and warrants further examination. The four acid digest method was used for determination of total metals chemistry in which a pulverised sub-samples is digested in a mixture of hydrofluoric, perchloric, nitric and hydrochloric acids and heated to dryness. The final solution is generated in dilute Aqua Regia and analysed using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). This method gives near total digestion for many elements but with some volatilization losses of arsenic, chromium, antimony, and mercury. Some resistant elements e.g. zircon are only partial dissolved and boron is excluded.

Acid Generation Assessment
For the acid generation assessment of the samples, a modified Sobek method was employed where the acid potential (AP) and neutralisation potential (NP) are determined as kg CaCO₃. Analysis of both sulfur and carbon was undertaken with a Leco S/C144 DR analyser at the School of Engineering, Cardiff University. Sulfide sulfur and organic carbon was determined after a weak acid (2M HCl) leach of a pulverised sample whilst total carbon and sulfur was determined from un-leached sample. The difference between total and
leached fractions is taken to be sulfate sulfur and inorganic carbon. These portions are then used to determine AP and NP respectively.

**Assessment of Leachable Metals (US EPA 1312)**

To assess the levels of leachable components a simple 24 hour contact test is undertaken in the form of a modified US EPA 1312 (ASTM, 1992). In the test 100 g of material is agitated for 23 hours with 300 mL of deionised water. The well mixed leachate is then left to stand for an hour before the supernatant is decanted off and filtered. The filtrate is then analysed for pH, conductivity and alkalinity, in addition to a suite of anions and cations.

**Kinetic Testing**

Kinetic testing was undertaken on a sub-selection of samples in order to determine the long term acid generating and elemental leaching properties of these samples. A modified version of the ASTM 5744 (ASTM, 2001) Humidity Cell Test (HCT) was utilised (Bowell et al., 2006). A weekly cycle was run consisting of three days dry, three days humid air circulation followed by a deionised water flush on day seven. The HCT testing was undertaken in two phases with the phase 1 HCT running for up to 95 weeks.

**ENVIRONMENTAL GEOCHEMISTRY RESULTS**

**Total Metal Chemistry**

A number of elements were found to be elevated with respect to average crustal abundance within the Malmbjerg deposit. Figure 2 shows the percentage of samples which contain elements at greater than 3x crustal abundance for the analysed elements. Of these elements greater than 50% of sampled waste rock has greater than 3x crustal abundance of Te, Mo, W, Ba, S, Li and Bi. Selenium and silver are included but, due to detection limits being greater than 3x crustal abundance, an assessment cannot be made. In addition to these, Sn, Th, Cd, Li, Cr, Pb, As, and Zn also exceed 3x crustal abundance of 10 to 50% of samples.

![Figure 2. Percentage of Malmbjerg whole rock samples where analyte concentrations are greater than 3x crustal abundance](image)
The term PPE indicates only that an element exists at elevated concentrations and does not give an indication of the element’s mobility and potential for release in to the environment upon atmospheric exposure and leaching. Factors which determine this include mineral solubility, pH of the leachate waters and the redox conditions under which waste rock is stored. In general, exposure to oxidising conditions will promote sulfide oxidation and associated release of acidity, sulfate and dissolved metals. The production of acidity may also mobilise certain elements whose dissolved concentration is governed by the solubility of metal oxides (for instance Fe, Al and Mn) which are common elements in rock-forming minerals.

Acid Generation Assessment

Although sulfide content does not exceed 1.5wt%, inorganic carbon or carbonate minerals are not abundant. In general these are dominated by siderite which has a low capacity for acid buffering, as the dissolution of this mineral (Fe$^{2+}$CO$_3$) generates as much acid (from the oxidation of ferrous to ferric iron) as it generates buffering capacity. Consequently the actual potential to neutralize acid is low in the system so any acid generation is noticeable. Figure 3 plots the values of Neutralising Potential Ratio (NPR=NP/AP) against the Net Neutralising Potential (NP-AP) for the Malmbjerg rock types. Zones are indicated for Not Acid Forming (NPR> 3 and NNP >20) and Potentially Acid Forming (NPR<1 and NNP <-20). The zone between these points is also included in which acid generation is uncertain. In general the greisenized and the majority of the pyritized sandstones samples plot within the PAF zone and are likely to produce acid leachates during atmospheric exposure. The post mineralisation dyke samples are the only rock type that plot predominantly within the NAF zone whilst the majority of the granites, sandstones, aplites and porphyry units plot within the uncertain zone.

![Figure 3. Plot of Neutralising Potential Ratio against Net Neutralising Potential](image)

Assessment of Leachable Metals

Figure 3 shows the concentration of Mn against pH in the EPA 1312 test (see above) showing an increasing concentration with decreasing pH. Similar behaviour is also observed with Fe and Al. In general, the greisen, mineralised granites and pyritized sandstones
samples produce the most acidic leachates and release the highest concentrations of Al, Mn and Fe; the porphyries and dyke units generally do not produce acid leachates whilst the sandstones form a smooth transition between acid forming and not acid forming.

Figure 4. Plot of manganese concentration against pH in the contact test leachates. Inset plot shows dry rock mass sulfate sulfur concentration (%) against EPA 1312 pH

In the synthetic leach EPA 1312 test it is clear that acidic high sulfate leachates can develop by weathering of the granite, pyritized sandstone and greisen zone units. Fluoride, sulfate, Al, Zn, Cd, Cu, As, Mn, Mo, Fe, Cr, Ni may present issues in leachates from the most reactive rock units. In addition beryllium from the mineralized granite may also be an issue. In addition pH (EPA 1312) is roughly dependant on the dry mass sulfate sulfur concentration of the sample as determined in the ABA testwork. The majority of the granite, porphyry and sandstone units produce circum-neutral leachates in the short term EPA test, however, these samples plot largely within the uncertain acid-forming category (Figure 3) and therefore further classification was required to determine the long term ARD/ML potential of these samples.

**Kinetic Testing**

Humidity cell leachates are elevated in a similar suite of elements as the EPA1312 leachates. This includes; fluoride, sulfate, Al, Zn, Cu, As, Mn, Mo, Fe, Cr and Ni. However it is observed that these elemental releases subside to a steady state after this time period. Figure 5 shows the leachate pH of 11 granite and sandstone samples over a 90 week period. Samples R07, 05, 06, 03 and 04 all have NPR < 0.5 and NNP < -5 and generally produce acid pH (~pH 3) in less than 10 weeks. The granite sample 26910 has a NNP < -24.55 and almost no NP. This would be expected to produce acidity rapidly, however the leachate pH decreases from circumneutral to pH 3.5 over 60 weeks. The three granite samples 28952, 28951 and 26905 initially produce alkaline pH leachates which decrease gradually over the duration of the testwork. Pyrite within the granite (and sandstone units) largely consists of massive cubic crystals within quartz and fluorite veins and disseminated pyrite is rare to absent. The relatively low surface area of the pyrite (as compared to microscopic
disseminated forms) results in slow reaction rates and minimal acid release. Therefore, pyrite oxidation is likely to be of a low intensity but it is possible that samples that initially produce alkaline pH may become acid over a long time scale. The sandstone samples 26935 and R1 have NNP values greater than -5 and sulfide sulfur contents less than 0.5%, and these are not expected to release acidity.

Figure 5. Plot of humidity cell pH against time

**Hydrogeochemistry**

Surface water in the vicinity of the Malmbjerg deposit is predominantly of the Ca-HCO₃ type and consists largely of glacial meltwaters. The average temperatures in the project area are sub zero (centigrade), therefore reduced sulfide reaction rates should be expected in natural ARD. However dominant anions in waters draining the Malmbjerg deposit are sulfate with elevated fluoride and moderately acidic pH (as low as pH 3.1 reported). Due to the low pH, Al can occur as a major secondary cation. Elevation of these parameters is typical of water catchments in most sulfide mineralised zones. However, the high fluoride contents found in waters proximal to the Malmbjerg deposit are indicative of fluorine rich porphyry Mo systems and associated fluorite and fluoride rich biotite mineral dissolution. Elevated concentrations of the elements Cd, Cu, Ni and U are also evident in proximal waters.

**Hydrogeochemistry and Test work comparison**

Glacial erosion has exposed a significant portion of the Malmbjerg mineralised zone to sub-aerial weathering. This has given a significant opportunity to qualitatively compare leachates produced during natural weathering (under field conditions) with leachates produced under laboratory conditions.

Table 2 compares Potentially Problematic Elements that occur at elevated concentrations in leachates produced during field weathering; contact test and kinetic test leachates in whole rock analysis are also shown for comparison. In each case all Potentially Problematic Elements found at elevated concentrations in any sample leachate are highlighted as it is
assumed that the field hydrogeochemical data represents an average of all exposed mineralised rock units.

Comparison of the data shows that the laboratory leaching data (at least qualitatively) predicts the release of some of the PPE determined to be present in the mineralised zone run-off waters. However, some analytes (such as As) are not present at elevated concentrations in the field data but are present in contact test and HCT leachates. This could be due to increased attenuation of As on ferric hydroxides in the field and therefore decreased mobility. This may also account for the relatively low Mo and W concentrations observed in the leachates which all occur as oxyanions with reduced mobility under acid conditions.

Table 2. Potentially Problematic Elements based on field and laboratory data

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Whole rock</th>
<th>Contact test</th>
<th>HCT</th>
<th>Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cations</td>
<td>As, Mo, Cd, Cu, Cr, W, Sn, Zn</td>
<td>Al, Fe, Mn, Zn, Cd, Cu, As, Mo, Cr, Ni</td>
<td>Al, Fe, Mn, Zn, Cd, Pb, Cu, Cr, As, U, Ni</td>
<td>Al, Cd, Co, Cu, U, Ni, Zn</td>
</tr>
<tr>
<td>Anions</td>
<td>(F, S²⁻)</td>
<td>F, SO₄</td>
<td>F, SO₄</td>
<td>F, SO₄</td>
</tr>
</tbody>
</table>

CONCLUSIONS
Mineralization in the Malmbjerg porphyry molybdenum deposit is largely comprised of quartz stockworks and veins that host molybdenite with accessory wolframite, scheelite, fluorite as well as uranium and thorium oxides. Chalcopyrite, sphalerite and galena are also present in peripheral vein mineralization. Pyrite occurs as a shell around the molybdenite zone. Sulfide content throughout the deposit is low, never being observed above 2 percent sulfide. The majority of rocks that are likely to be acid generating are the pyritized sandstone, the pyritized granite and the mineralized porphyry units. Although sulfide content does not exceed 1.5wt%, inorganic carbon or carbonate minerals are not abundant in the units either and in general are dominated by siderite that has negligible potential for acid buffering. Consequently the actual potential to neutralize acid is low in the system so any acid generation is noticeable. The low reactivity exhibited in the acid generation potential is also observed in EPA 1312 leaching tests. Consequently it is likely that any acid generation or metal leaching that does occur will occur over a long period of time for the majority of lithologies. The exception to this appears to be the partially oxidized pyritized sandstones that are highly reactive and generate acidic metal-sulfate rich leachate and show potential for acid generation in Acid Base Accounting testwork.

The low levels of reactivity in the tested host rocks make it difficult to confirm the potential for acid generation by static testing. However, acid generation is predicted to be most likely from the pyritized sandstone, pyrite-bearing granite and porphyry units that are immediately adjacent to the ore shell. The majority of waste rock to be extracted (approximately 79 percent) does not appear to have potential for acid generation and is classed as being “non-acid-generating” in this study, although it must be recognized the material also has little potential for acid neutralization and is essentially chemically inert. The kinetic testing demonstrates the potential for acid generation and metal leaching from the rock units that will be exposed in the Malmbjerg molybdenum deposit during mining. In addition assessment of hydrogeochemical data indicate acid conditions with pH as low as 3.1. It has been shown that the most reactive rock units producing the most acidic sulfate rich water are the pyritized sandstone and pyrite-bearing granite and greisen zone units and it has been qualitatively demonstrated that laboratory testwork can predict the Potentially Problematic Elements that may occur during field leaching. This is despite the laboratory
conditions greatly favouring chemical and biochemical leaching as compared to arctic field conditions. Currently, further research is underway to determine the effect of temperature on leaching rates.

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REFERENCES


