

**EXPERIMENTAL EVALUATION OF SUBAQUEOUS DISPOSAL OF ACID
GENERATING SULPHIDE MINERALS IN THE MEGUMA SUPERGROUP,
SOUTHERN NOVA SCOTIA**

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Submitted in partial fulfillment of the
requirements for the degree of Bachelor of Science, Honours

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ABSTRACT

Development and construction projects that require the disturbance and excavation of sulphide rich bedrock in Halifax and southern Nova Scotia produce large quantities of waste rock material. This material poses a high risk potential for acid rock drainage (ARD). Acid drainage develops due to the oxidization of iron sulphides found in the Cambro/Ordovician Meguma Supergroup, southern Nova Scotia. Variations of sulphide mineral type, texture, the presence or absence of acidophilic bacteria (*Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*) and the availability of oxygen and water determine the reactivity and consequently the rate of acid generation. Subaqueous disposal is a current potential method for waste management of excavated sulphide-bearing waste rock in Nova Scotia. The concept is based on the premise that acid generation is chemically suppressed in low oxygen conditions at depth in submerged sites. This method has yet to be evaluated with regards to the Meguma Supergroup and in particular, to disposal in marine environments. Furthermore, policies and regulations for disposal of sulphide-bearing waste rock in Nova Scotia is aimed at conventional terrestrial methods, and does not adequately address disposal in a marine or freshwater environment.

This project investigates in a laboratory experiment, subaqueous disposal of sulphide bearing rock from the Meguma Supergroup in seawater compared to fresh water. Polished thin sections were prepared from a drill core sample near the Halifax International Airport. The primary sulphide minerals present were pyrrhotite, marcasite, pyrite, and chalcopyrite. The experiment was conducted using distilled water, seawater and lakewater from natural environments. One thin section was submerged in 500ml of each of the three water samples at a depth of 32 cm in graduated cylinders exposed to atmospheric conditions at room temperature (21°C). One was maintained in air as a control. Dissolved oxygen and pH measurements of the water samples were obtained at initial and final stages. Measurements indicated a slight decrease in pH and dissolved oxygen from start to finish in all water samples. Observations of surface features under reflected light were recorded and digitally imaged at 6, 15, and 40 days. Surface coatings (precipitate), color (tarnish), and topography of sulphide minerals were used as an indication of reaction. Most sulphide minerals experienced some degree of tarnish, residue, or slight color change and therefore suggested reaction. Reaction appeared to initiate at grain boundaries and radiate outward to cover the sulphide mineral surface. Results indicate that in general, the rate of sulphide reactivity is higher in seawater compared to freshwater. The overall relative degree of reactivity of sulphides in a submerged environment was marcasite > galena (inclusions) > pyrrhotite > pyrite > chalcopyrite.

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Chapter 1: INTRODUCTION

1.1 Thesis Statement and Significance

Industrial development and municipal construction projects in Halifax and southern Nova Scotia often involve excavating large quantities of sulphide-rich bedrock of the Meguma Supergroup. The conventional practice of terrestrial disposal for sulphide-rich waste material causes acid rock drainage (ARD) due to oxidation of sulphide minerals. In Nova Scotia, ARD is known to contaminate surface and ground water reservoirs and cause damage to plants, wild life, and fish. In addition, ARD often requires expensive remediation and long term monitoring and management plans. In consideration of future regional, large-scale developments in Nova Scotia, (e.g. pipeline construction for the Sable Offshore Energy Project), an effective technique to prevent or minimize the environmental and economic impact of ARD is required.

At present, sulphide-waste disposal in freshwater lakes or marine coastal waters is considered a promising control for ARD. This is based on the premise that acid-generating oxidation reactions of sulphide minerals are delayed and occur at a highly reduced rate underwater. This method is commonly employed by the Canadian mining industry as a management practice for mine tailings.

Subaqueous disposal of sulphidic-waste material in marine and freshwater systems has not been evaluated in detail in Nova Scotia to date. This study intends to investigate and compare the reactivity of sulphide minerals from the Meguma Supergroup under marine and freshwater cover in the laboratory to determine which setting is more applicable to the practice of subaqueous disposal. Secondly, it considers the pertinent policies and regulations for sulphide-waste disposal in the province of Nova Scotia with respect to subaqueous disposal.

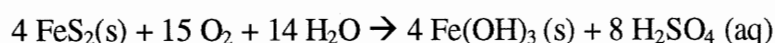
Past studies have concluded and documented ARD impact in Nova Scotia, successfully examined problematic minerals and processes of acid generation in detail, and determined techniques for locating high-risk regions. This study differs by focussing on a potential solution for the control and management of ARD at a localized, site-specific level.

1.2 Background Information

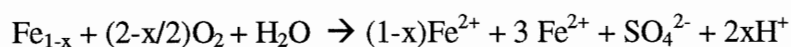
1.2.1 Acid Rock Drainage

Acid rock drainage (ARD) is a natural biogeochemical effect that develops as sulphide-bearing minerals oxidize when exposed to weathering at the earth's surface (Strumm and Morgan, 1970). Pyrite and pyrrhotite are the most important contributors to ARD in the Meguma Supergroup and to a lesser extent, sphalerite, galena, arsenopyrite, and chalcopyrite (Zentilli and Fox, 1997; Fox et al., 1996). The overall process in the development of ARD can be represented by the following simplified reactions for the oxidation of pyrite and pyrrhotite (Nicholson, 1994; Fox et al., 1997).

Pyrite:



Pyrrhotite:



The x in pyrrhotite can vary from 0 to 0.2 depending on its particular polymorph, a contributing factor to the rate of acid production. One mole of pyrite produces 2 moles of sulphuric acid compared to 1 mole of H₂SO₄ per mole of pyrrhotite, but pyrrhotite is suggested to oxidize substantially faster (Fox et al., 1997; MacInnis et al., 1994; Nicholson, 1994). It is important to note that in both cases the process consumes oxygen, and the net result is a Fe-rich, dilute

sulphuric acid solution (pH between 2 and 4 (Zentilli and Fox, 1997)), and a release of metallic trace elements. The relative rate of reactivity for individual sulphide minerals is controlled by factors such as mineral chemistry, texture, access to weathering agents, and the presence or absence of bacteria. Host rocks and surface and subsurface waters normally contain some degree of acid neutralizing capacity. Therefore, whether solutions emerge as acidic drainage also depends on the rates of acid production versus alkaline buffering. If the buffer capacity is low, or becomes depleted in the receiving environment, drainage conditions progressively become acidic.

1.2.2 Bacterially Assisted ARD

Atmospheric oxidation may be further complicated by acidophilic bacteria, *Thiobacillus ferrooxidans* (iron-oxidizing) and *Thiobacillus thiooxidans* (sulphur-oxidizing) that act as catalysts and consequently accelerate the ARD process (in optimal conditions) increasing the rate of oxidation by up to 10^2 - 10^4 times (Nicholson, 1994; Kelly, 1989). The bacteria are autotrophic and completely depend on sulphur and atmospheric conditions (N, O₂, CO₂, H₂O) for their nutritional needs (using CO₂ as a sole source of carbon), and require an optimal acidic (pH 2-3) environment (Hutchinson et al., 1966). Studies show that the rate of bacterial activity varies directly with temperature (optimal 28°C) (MEND, 1989). Bacteria may be found in both aerobic and anaerobic environments where molecular oxygen is dissolved in water if appropriate acidic conditions prevail (Kelly, 1989).

1.2.3 ARD Precipitate

The orange ferric precipitate associated with ARD is often documented as iron III hydroxide (Fe(OH)₃) and a number of iron III hydroxysulphate complexes Fe(OH)(SO₄) (Kelly, 1989). In reality the precipitate is more complex and usually contains a number of iron III oxyhydroxide

hydrates, various partially hydrolyzed forms, phosphates, aluminum oxides and occasionally other salts. At low pH values metal ions are soluble. Some precipitates form when the pH begins to rise as acidic drainage is neutralized. The critical pH value for the precipitation of iron III oxyhydroxides is $</>4.3$ (Kelly, 1989). Acidic drainage is usually more acidic than these values and dissolved iron III does not precipitate out of solution until neutralization occurs.

1.3 ARD in Nova Scotia

Acid rock drainage is a well known geoenvironmental issue in Nova Scotia. It is not restricted to the mining industry, but is generated regularly at construction sites, digging of foundations, trenches for municipal service, pipelines, quarry operations, and common waste rock piles within municipal and rural regions (Hennigar and Gibb, 1987). Table 1.1 is a summary of previous work to exemplify ARD-related environmental problems in Nova Scotia primarily due to the underlying bedrock of the Meguma Supergroup.

1.3.1 The Meguma Supergroup with respect to ARD

Acid drainage is associated with the metallic sulphide mineralization in the Cambrian-Ordovician Meguma Supergroup, which underlies $\sim 200\,000\text{km}^2$ of southern Nova Scotia, with an estimated minimum stratigraphic thickness of 14 km (Schenk, 1995, 1970). The Meguma Supergroup is host to Au districts and a variety of mineral assemblages of quartz, carbonates, Fe sulphides, (pyrite, pyrrhotite, arsenopyrite), Fe oxides, other sulphides (chalcopyrite, galena, sphalerite), silicates, and minor Fe, Cu, Pb, Sb, W, Zn, and Ag (Zentilli and Fox, 1997). Figure 1.1 is a map of southwestern Nova Scotia showing the distribution of the Meguma Supergroup. Based on the wide distribution, and proven acidic generating capacity of the Meguma Supergroup, it is apparent that construction and development on the Meguma Supergroup is difficult to avoid (Hennigar and Gibb, 1987).

The Meguma Supergroup is composed of two units, the Goldenville Group, and the overlying Halifax Group, each estimated at 7 km thickness. The Goldenville Group consists of thickly bedded, sandy, metagreywacke with thinly interbedded metasilstone. The Halifax Group comprises a thick package of fine-grained, structurally complex, gray and black slates with thinly interbedded metasilstone and sandstone (Schenk, 1970). Both tend to contain high concentrations of sulphide minerals throughout the stratigraphy. At the contact between these two Groups is the Goldenville-Halifax transition zone (GHT), which varies in thickness from 2 - 45m (Zentilli et al., 1986, Binney et al., 1986) and is cited by Zentilli and Fox, 1997 as the common denominator for more serious impact of ARD. The zone is located in the upper levels of black carbonaceous slate and is anomalously enriched in sulfides and heavy metals including Mn, As, Pb, Zn, Cu, Cr and other toxic metals (MacInnis, 1986) that increase the toxicity of the acidic drainage. The Meguma Supergroup has undergone extensive deformation. This characteristic often contributes to the increase of areal exposure of sulphide minerals and consequently the potential for ARD. Folding is upright, NE-trending and moderately plunging with multiple cleavage planes. The primary ARD minerals such as pyrrhotite and pyrite are distributed parallel to bedding and cleavage planes. When the rock is disturbed, it tends to break along cleavage planes and readily exposes the sulphide minerals. In addition, the Meguma Supergroup ranges from low metamorphic greenschist to amphibolite facies and has been affected by contact metamorphism from granitoid intrusions.

Table 1.1. Summary of previous work related to ARD in the Meguma Supergroup, Nova Scotia as an indication of major ARD impact (modified from Fox, 1999).

Environmental Protection Service	A report on the causes of fish kills in the Shubenacadie River at Enfield, Nova Scotia.	1976
Thompson, B.D.	An investigation of Meguma bedrock leaching in the Shubenacadie - Stewiacke river basin.	1978
Pettipas, B.	Union Square, Lunenburg County: a statistical evaluation of the effect of acid leachate on water quality.	1979
Kerekes, et al.	Comparison of the characteristics of an acidic eutrophic, and an acidic oligotrophic lake near Halifax, Nova Scotia.	1984
Ogden, J.G. & Machell, J.	Ionic and mass balances in a dilute acidified brown water lake.	1985
King, M.	Acid drainage and the acidification of Nova Scotia waters.	1985
Nova Scotia Research Foundation Corporation.	Test geophysical methods to detect shallow sulphide mineralization in Cambro-Ordovician slates near Halifax International Airport.	1985
Nova Scotia Research Foundation Corporation.	The evaluation of some geophysical methods for the detection of shallow sulphide mineralization (Final Report).	1985
Lutwick, G.D.	Mineral composition and acid consuming potential of Nova Scotia shales. Nova Scotia Research Foundation Corporation.	1986
Manchester, K.	A survey of quarry pits in Halifax Formation rocks of Southwestern Nova Scotia.	1986
King, M. & Hart, W.	Contribution of acidity and heavy metals to surface and groundwater by pyritiferous slates in the vicinity of the Halifax Airport.	1987
Lund, et al.	Impact of acid drainage pollution from mineralized slate at Halifax Airport.	1987
Albright, R.	Prediction of Acid Drainage in Meguma Slates.	1987
Guilcher, M.	Acid mine drainage in reactive slates: "The Halifax Airport Case".	1987
Hennigar T.W. & Gibb, J.E.	Surface and groundwater impacts of acid mine drainage from the Meguma slates of Nova Scotia.	1987
Lund, O.P.	Acid drainage from mineralized slate at Halifax Airport.	1987
McCready, R.G.L.	A review of the physical, chemical and biological measures to prevent acid mine drainage: An application to the pyritic Halifax shales.	1987
Worgan, J.	Acid mine drainage in reactive slates: "The Halifax International Airport Case" Transport Canada perspective.	1987
Murray, et al.	Laboratory and field testing of a salt-supplemented clay cap as an impermeable seal over pyritic slates.	1988
King, M. & Hart, W.	Groundwater contribution to acid drainage from the Halifax Formation in Nova Scotia.	1990
Bechard, et al.	Microbiological treatment of acidic drainage at Halifax International Airport: An update.	1992
Silver, M.	A constructed wetland system to mitigate acidic effluents from a slate quarry in Halifax County.	1993

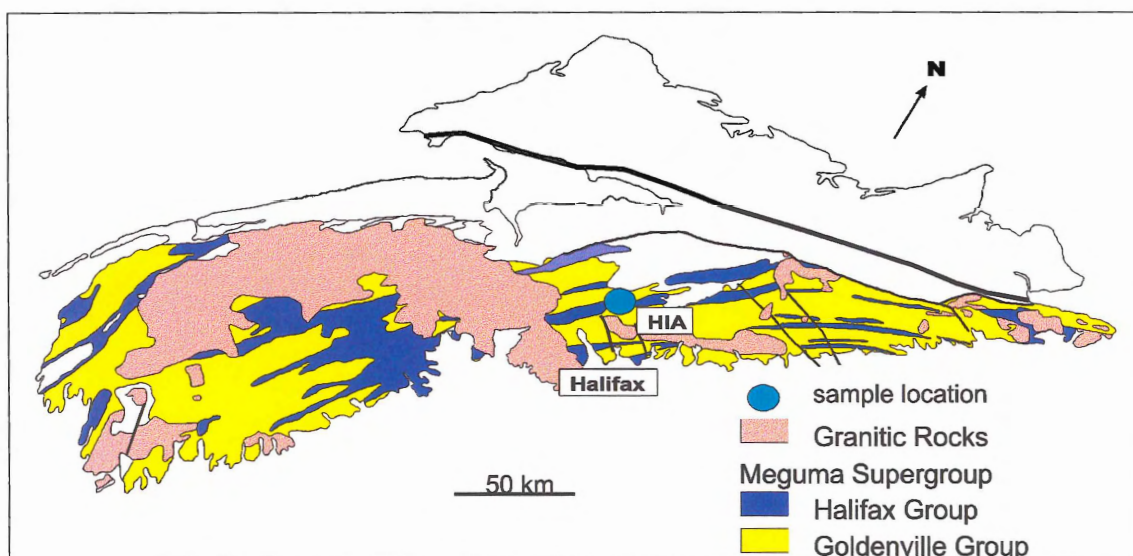


Figure 1.1. Geological map of Nova Scotia showing the distribution of potential ARD generating rocks, Halifax, and the sample site near the Halifax International Airport (HIA) (modified from the Geological Map of Nova Scotia (1979) Nova Scotia Dept. of Mines and Energy).

Metamorphism is responsible for the alteration of mineralogy and texture of sulphide minerals and in particular, the abundance of pyrrhotite over pyrite encountered in the Meguma Supergroup. Hydrothermal sulphide-rich veins formed as a result of these processes provide an additional source for potential acid drainage.

1.4 Subaqueous Disposal of Sulphidic Waste Material

Land based disposal often results in acid rock drainage and concomitant leaching of trace elements. An alternative method is the practice of depositing reactive slates underwater. In theory, acid generation is chemically inhibited by limiting oxygen availability and biological components at depth under water (EMCBC, 1998). In turn, lesser amounts of metals and non-metals are released into surrounding environments in comparison to land-based disposal site surface runoff.

Observations made in specific field studies at Buttle Lake, British Columbia and Anderson Lake, Manitoba support the technique of underwater disposal. Westmin's Myra Falls mine in B.C.'s Strathcona Provincial Park discharged a total of 5.5 million tonnes of reactive tailings into Buttle Lake (the domestic water source for the town of Campbell River) for seventeen years and these tailings are presently disposed of on land (BC research cited in Pederson, 1983). Pederson and Losher (1984), and Pederson (1983) report that the oxidation of mine tailings on the lake bottom, ~87m depth, was reduced due to the minimized exposure and decreased quantity of dissolved oxygen at the lake bottom. A similar outcome is documented at the shallow, eutrophic Anderson Lake, which has received 0.75 million tonnes of primarily pyrrhotite and pyrite gangue mineral tailings annually for the last decade from the Hudson Bay Mining and Smelting's Snow Lake mill. Water quality monitoring every three years has revealed that metal concentrations and pH are contained within the federal effluent guidelines.

The past decade has seen considerable research in regard to the significance and causes of ARD in Nova Scotia. However, there is to date no strong assurance that subaqueous disposal is an effective technique in all cases within a lacustrine or submarine environment in Nova Scotia. Additional factors such as natural chemistry of the receiving environment, physicochemical conditions, hydrochemical conditions, and in lake settings, the morphology, hydrology, physical and chemical limnology, biological characteristics, lake turnover, residence time, and circulation and mixing features remain largely unaddressed. Overall, subaqueous disposal appears to be site specific and requires extensive assessment and regulation before implementation.

1.5 Policies and Regulations for Marine and Freshwater Disposal

Canada strives for a progressive attitude towards achieving a balance between development and environmental protection. Policies concerning subaqueous disposal can be traced back to the *Constitution Act*, 1867. This Act designates the provinces as “owners” of respective watersheds and delegates the responsibility of handling hazardous material to the provincial government under respective policies and regulations.

At the federal level, water is considered a natural resource and the *Canada Water Act* (1970) and the *Federal Water Policy* (1987) provide the framework for provincial actions.

Regulations for marine disposal fall under the jurisdiction of the *Ocean Dumping Regulations* (1988) under the *Canadian Environmental Protection Act* (1988, 1996). Marine disposal is generally restricted on all accounts. Exceptions to these regulations are granted if an application and fee are delivered to the minister who must approve the proposed disposal method and site. Applications are to be filed in advance and require detailed descriptions of waste material, disposal localities and alternate options available.

Due to Nova Scotia's unique ARD issues there exists the *Sulphide Bearing Material Disposal Regulations* (1991) contained in the *Nova Scotia Environment Act* (1994, 1995). Under these regulations, any significant disturbance to sulphide-bearing material legally requires prediction of ARD potential, monitoring, and proper remediation of sites and/or correct handling of waste material.

Mining and related activities are regulated by the Nova Scotia Department of Natural Resources and require permission and reporting of activities to this department. Such activities may be subject to the *Sulphide Bearing Materials Regulations* (1991).

1.6 Significance of this work

Studies have concluded that ARD is a problem for biological ecosystems and in particular to southern Nova Scotia and the Halifax region. In turn, many reviews and recent theses have been aimed at the understanding of primary ARD minerals, processes, and reviewing the effectiveness of precautionary measures outlined by sulphide-bearing disposal regulations specific to Nova Scotia (Table 1.2).

The focal point of this thesis work was to evaluate by relative comparison, in laboratory experiments, the mineral reactivity specific to the Meguma Supergroup, Nova Scotia in the context of subaqueous disposal in freshwater versus marine environments. In addition, an attempt was made to evaluate potential barriers to the implementation of subaqueous disposal in terms of current regulations and policies in Canada.

Table 1.2. List of recent theses related to ARD in the Meguma Supergroup.

Student	Degree	General Topic
Jones, R.A. – 1997	BSc - Dalhousie University	Relative sulphide oxidation rates
Brown, J.C.S. - 1997	Master of Environmental Studies - Dalhousie University	Precautionary principle as applied to acid rock drainage regulations
Robinson, C. - 1996	BSc - Dalhousie University	Mineralogy and acid base accounting
Knee, K. - 1995	BSc - Dalhousie University	Mineralogy and magnetic susceptibility
Bottaro, C.S. - 1994	BSc - St. Mary's University	Inhibiting sulphide oxidation
Samostie, A. – 1994	Master of Environmental Studies - Dalhousie University	GIS for predicting ARD risk
Bechard, G.M. - 1993	PhD - Carleton University	ARD treatment using microbiological processes
King, M. W. G. – 1987	Master of Applied Science - Technical University of Nova Scotia	Acidity and heavy metals in surface and groundwater near HIA
Roberts, J.D. – 1986	Master of Environmental Studies - Dalhousie University	Use of peat for ARD treatment

1.7 Organization

The overall study is organized to address three main topics associated with ARD. The first section reviews present knowledge relevant to ARD (Chapter 1), the problem in Nova Scotia, and the topic of subaqueous disposal (Chapter 2). It includes a discussion of Canadian regulations and policies to identify the legal aspects in relation to the concept of subaqueous disposal of sulphide bearing waste rock (Chapter 3). The second section is the set-up and results of an experiment that simulates three separate subaqueous environments (Chapter 4). The final section is a summary of results (Chapter 5), discussion, conclusions, and recommendations for future study (Chapter 6).

Chapter 2: SUBAQUEOUS DISPOSAL

2.1 Introduction to Subaqueous Disposal

Background theory and case studies pertaining to subaqueous disposal are presented in this chapter. Kinetic data suggest that the oxidation of pyrite in aqueous systems is strongly dependent on the availability of oxygen and ferric iron (Nordstrom, 1982; Singer and Strumm, 1970). The rate of reactivity is also dependent on the temperature, pH, surface area, and the presence or absence of bacteria. Many other secondary soluble and insoluble iron minerals result from this process and depend on the degree of oxidation, solution composition, and activity of water.

Both the oxygen concentration and oxygen diffusion rate within freshwater and marine waters is significantly less than that in atmospheric terrestrial environments. Oxygen concentrations are further decreased in anoxic environments found in stagnant, eutrophic water bodies. This is especially the case with increasing depths. These factors may play an important role to create ideal conditions for subaqueous disposal of potentially reactive sulphidic waste material.

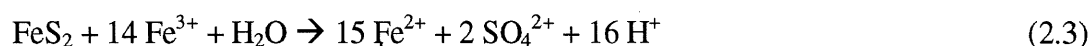
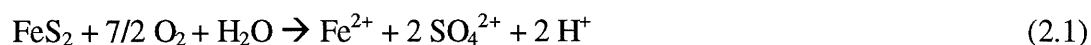
A primary concern in the subaqueous disposal of reactive sulphidic waste is the release of metals into the overlying water column. Dissolved oxygen in bottom waters diffuses into subsurface sediments (or in the case of subaqueous disposal, into waste rock) at a rate calculated by 'Ficks First Law of Diffusion'. Marine and freshwater environments differ, but it is found that sediments can act either as a sink or a source for metals.

Subaqueous disposal has gained support from several field studies conducted at Anderson Lake, Manitoba, Buttle Lake, BC (Pederson, 1983, 1985; Pederson and Losher, 1988; Pederson et

al., 1991), and in a seawater environment at the Island copper mine on Vancouver Island (BHP Minerals Ltd. Impact Report, 1994, cited in Ellis et. al, 1995).

2.2 ARD Reactions and the Importance of Oxygen

The simplified chemical reactions for the breakdown of pyrrhotite and pyrite cited in section 1.2.1 need to be examined in greater detail in order to assess how ARD may be prevented in a subaqueous environment. For example, the oxidation of pyrite can be described by a multistage series of three chemical reactions listed below.



propagation cycle

Reaction (2.1) describes the oxidation of sulfide and consequent dissolution of pyrite (FeS_2). In this reaction, oxygen is the electron acceptor and the reduced oxygen combines with the oxidized sulfur to yield sulphate, H^+ , and ferrous iron (Fe^{2+}) in solution. Reaction (2.2) describes the oxidation of dissolved ferrous iron (iron II) to ferric iron (iron III) in solution. Reaction (2.3) is a propagation cycle in which pyrite is oxidized by ferric iron (Fe^{3+}) instead of oxygen, as in step (2.1) again contributing to increased acidity in solution. It is considered a propagation cycle because the products have the potential to reenter the reaction cycle at (2.2). Therefore, the amount of acid released into an environment is dependent on the oxygen present, in addition to the rate of generation of ferrous iron (Fe^{2+}) in solution.

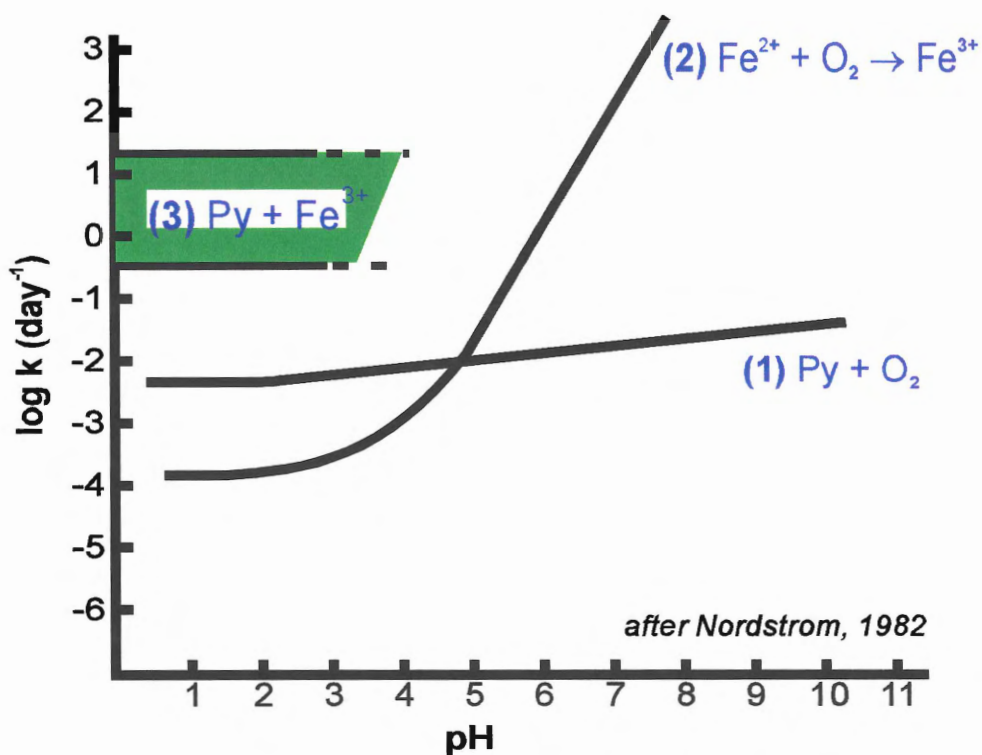
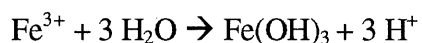


Figure 2.1.A. An abiotic comparison of rate constants as a function of pH for step (1) the initial oxidation of pyrite (Py) by oxygen (O_2); step (2) the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}); and step (3) the oxidation of pyrite (FeS_2) by ferric iron (Fe^{3+}). The rate of reaction for step (1) is very slow with only a slight increase at pH values > 3.5 . The rate of reaction for step (2) is low at low pH values but increases steadily at pH values > 3.5 . The rate of reaction for step (3) is very high, but is restricted to pH values < 4 , and requires the product of step (2) to commence.

The quality of Fe-sulphides and rate of Fe^{3+} in solution determine the net acid generated. In turn, the rate of reaction in abiotic conditions is determined primarily by pH as illustrated by Figure 2.1(a). At low pH values, ferric iron (Fe^{3+}) oxidizes pyrite more rapidly than oxygen and more rapidly than dissolved ferrous iron (Fe^{2+}) can be oxidized by oxygen (Nordstrom, 1982). Acidic solutions are generated and the pH decreases. This is why Singer and Strumm (1970) and Nordstrom (1982) note reaction (2) as the rate-limiting step that produces the Fe^{3+} . This reaction (2) occurs very slowly at pH values < 3.0 and rapidly at neutral to alkaline pH values.

Figure 2.1(b) is the same pH vs. rate of reaction diagram representing the intervention of microbacterial activity. With the addition of bacteria, the rate of step (2) increases substantially thereby keeping the supply of Fe^{3+} high. This rate is estimated to increase by 2 – 4 orders of magnitude in the presence of bacteria (Nicholson, 1994). Figure 2.2A shows the cycle mediated by bacteria. If the bacteria did not exist, the production of ARD would occur at an extremely slow rate.

At higher pH values, ferric iron produced in step (2) subsequently hydrolyzes to form insoluble precipitates of ferric hydroxide ($\text{Fe}(\text{OH})_3$) and generates more acid.



This reaction contributes to increased acidity as Fe^{3+} becomes soluble, takes over as the oxidizing agent and in turn, limits the reactivity of step (3) to low pH values. This step maintains optimal conditions for bacterial activity and promotes continuous cyclic reactions. However, this reaction will not take place unless the initial oxidation of iron occurs.

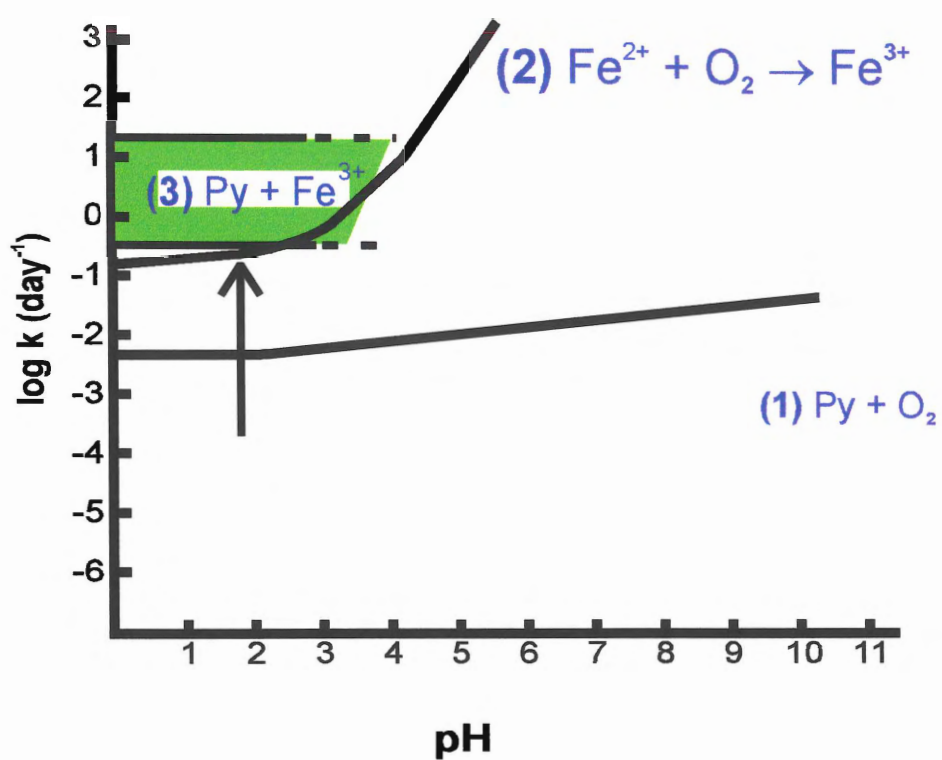


Figure 2.1.B. Schematic model of steps (1) - (3) with the addition of bacterial activity. The rate of reaction for step (2) has increased fueling step (3) with ferric iron (Fe^{3+}).

Fig.2.2A

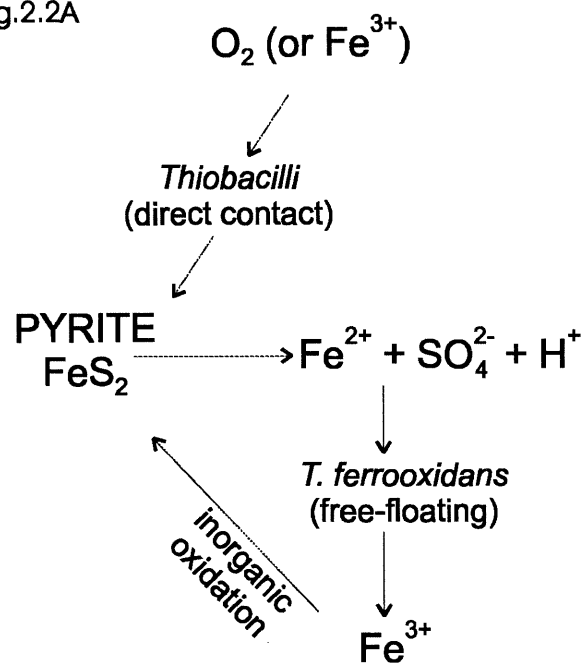


Figure 2.2.A. Illustrated representation of the oxidation of pyrite (steps 1, 2, and 3) (after Nordstrom, 1982).

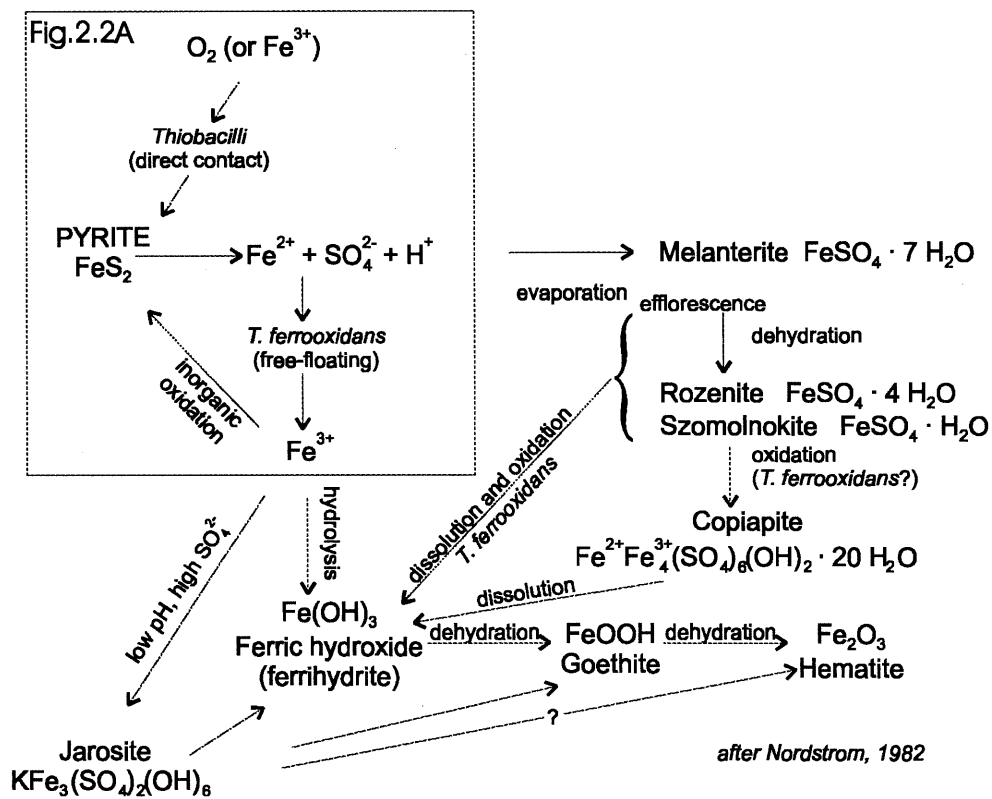


Figure 2.2.B. Multistage oxidation of pyrite and relationships between oxidizing agents, secondary minerals and catalysts (after Nordstrom, 1982).

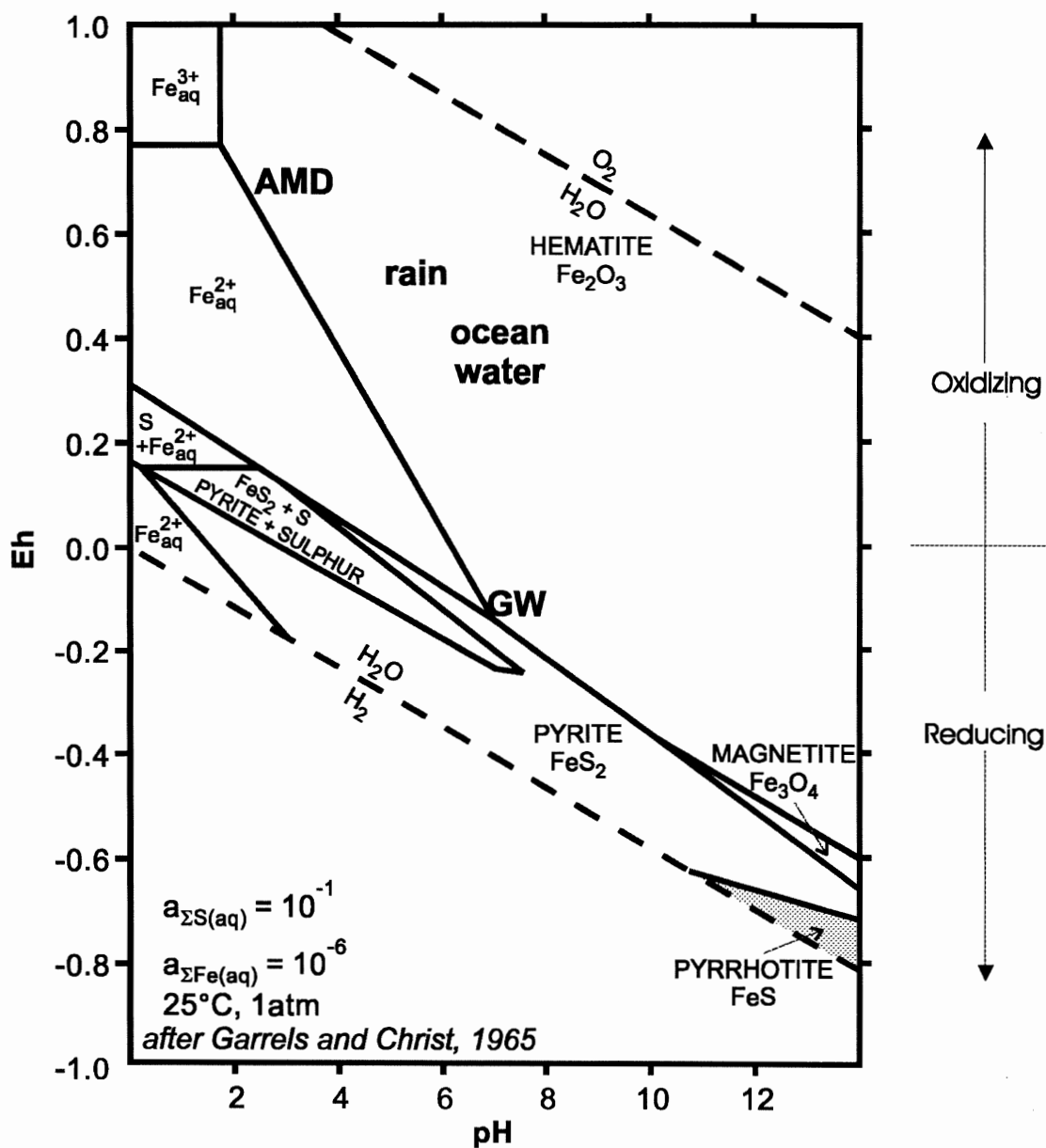


Figure 2.3. Eh vs. pH diagram for the Fe-S-H₂O system at 25°C and 1 atmosphere total pressure. Total dissolved sulfur species equals 10^{-1} , total activity of iron species equals 10^{-6} (adapted from Garrels and Christ, 1965). Illustrates the relative placement of typical oxidizing waters, acid mine drainage (AMD), rain, ocean water, and ground water (GW).

An overall schematic model showing pyrite oxidation is illustrated in Figure 2.2A. Figure 2.2B (after Nordstrom, 1982) illustrates the same schematic model in addition to its relationship between oxidizing agents, secondary minerals and catalysts. The resultant range of side products depends on water content, degree of oxidation and time include iron sulfate, iron oxide, and iron hydroxide minerals.

The thermodynamic stability domains of primary ARD sulphides in the Fe-S-H₂O system are illustrated in a Eh versus pH diagram in Figure 2.3. This diagram is depicted at a temperature of 25°C and a pressure of 1 atmosphere for a total activity of 10⁻⁶ for dissolved iron species and the total activity of dissolved sulphur species of 10⁻¹. Nearly every reaction in the Fe-S-H₂O system involves electron transfer. Problematic minerals of the Meguma Supergroup, pyrite and pyrrhotite are thermodynamically stable in reducing aqueous environments. At higher Eh conditions, such as rainwater, ferric iron (Fe³⁺), and ferrous iron (Fe²⁺) are stable. Therefore, high Eh conditions lead to the oxidation of pyrite and pyrrhotite to yield the Fe²⁺ or Fe³⁺ species. This is especially important in the initiation of ARD generation. Also, according to the diagram, under these conditions pyrrhotite will be less stable than pyrite.

2.3 Importance of Available Surface Area

The rate of acid formation is found to be directly proportional to the total surface area of sulfide minerals (Nicholson, 1994). Therefore, one kilogram of very small particles will generate acid more quickly than one kilogram of large particles. In addition, if sulphide particles become coated with layers of ferric hydroxide (as described in section 2.1), diffusion of oxygen to the unoxidized substrate will be restricted (Nicholson, 1994).

This is important to consider in the context of subaqueous disposal. The disposal of coarse grained particles into a freshwater or marine environment may be impeded by low specific surface

area. The sulphide minerals contained in coarse grained rock fragments might be shielded from reaction, depending on fracture, cleavage, and texture.

2.4 Interstitial Oxygen

The low oxygen levels found in natural lacustrine and marine waters originate by diffusion across the water / atmosphere boundary. The concentration of dissolved oxygen in water can reach a maximum of 8.6 ppm at 1 atmosphere (Kelly, 1989). This value is far below the concentration of oxygen in air (23.14 wt.% O₂, Houghten, 1977). Diffusion progresses slowly downwards from the water-atmosphere interface. The diffusion constant for oxygen in water is $\sim 2 \times 10^{-6}$ cm²/sec. This value is nearly five orders of magnitude less than the diffusion constant for oxygen in air, ~ 0.178 cm²/sec (MEND, 1989). Figure 2.4 depicts the results of this process and schematically demonstrates the decrease in dissolved oxygen concentration in a natural water column with depth. Dissolved oxygen may be further lowered in the presence of respiring bacterial communities (Pederson et al. 1991). If the rate of oxygen consumption by the bacterial degradation of organic matter in a natural lacustrine or marine system dominates over the rate of supply of O₂ (via diffusion and advection), then an effective environment for subaqueous disposal is created.

2.5 Ficks Law of Diffusion

As discussed above, oxygen is the primary initial oxidant and therefore governs the diagenetic release of metals contained in sulphidic slate waste at the sediment-water interface in aqueous systems. Dissolved oxygen in bottom waters will diffuse into sediments along a gradient of decreasing concentration established by consumption at or below the sediment – water interface. Estimation of the concentration gradient is complicated by the ‘diffusive boundary layer’ that lies directly above the sediment-water interface and poses a problem where concentration gradients are very steep (in anoxic conditions). The quantity of oxygen that can diffuse to a given sediment

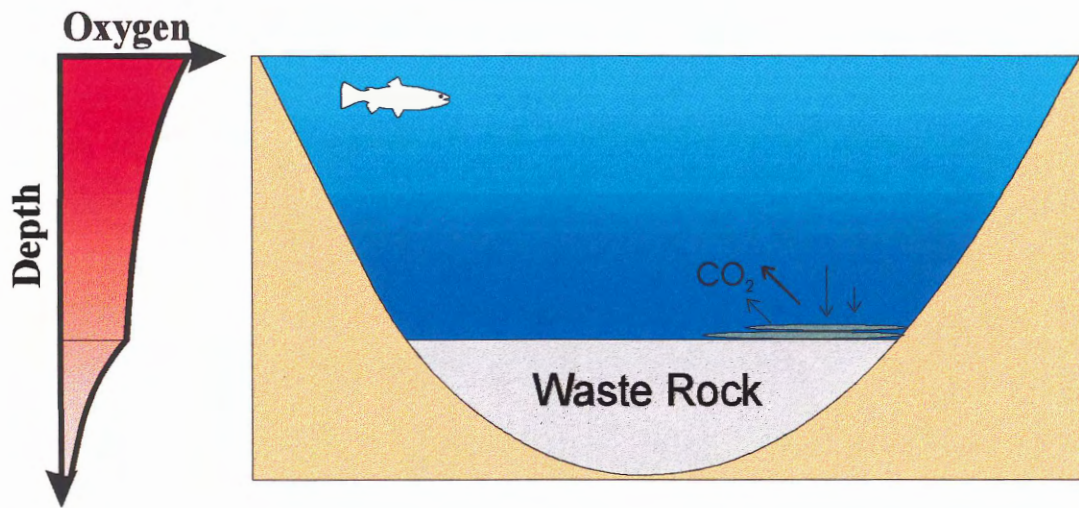


Figure 2.4. A simplified schematic representation of subaqueous disposal in ideal anoxic conditions demonstrating the gradient in oxygen concentration with depth.

depth is determined by the steepness of the concentration gradient across the sediment-water interface, sediment porosity, and tortuosity. Tortuosity is the path of a diffusing molecule described by the formation factor F and diffusion coefficient that varies as a function of temperature and pressure (MEND, 1989). 'Fick's First Law of Diffusion' describes this process.

$$J_z = -\phi \left(\frac{D_{j(T,P)}^0}{F} \right) \frac{dC}{dZ} \quad (1)$$

J_z = the quantity of O_2 that can diffuse per unit time to a given depth below the interface
($\mu\text{mol}/\text{cm}^{-2} \text{sec}^{-1}$)

dC/dZ = the steepness of the concentration gradient ($\mu\text{mol cm}^{-4}$)

ϕ = sediment porosity

$D_{j(T,P)}^0 / F$ = tortuosity

Fick's First Law also describes the process by which dissolved metals diffuse into lacustrine sediments. A downward flux is created in anoxic conditions and at shallow sediment depths. This process is reversed in unpolluted marine waters that lack anoxic layers (MEND, 1989). The concentration of metals in pore waters of marine sediments is usually greater than that in the overlying bottom water. In this case, sediments act as a source rather than a sink and release metals into the water column (Pederson, 1985). In summary, 'Ficks First Law of Diffusion' allows for a quantitative assessment of the available oxygen concentration to submerged waste rock. Sulphidic waste deposited in well-oxygenated waters (allowing for sulphide reactivity) will release metals into the overlying water column (an indication of sulphide reactivity). In poorly

oxygenated waters (low sulphide reactivity), sediments may potentially digest metals contained in the overlying water column may move into the bottom sediments via diffusion.

2.6 Microbiological Communities in the Subaqueous Environment

Bacteria occupy an ecological niche that is easy to create and maintain in a terrestrial environment. Organisms attach to an exposed, moist sulphide surface, obtain its nutritional requirements and proceed to act as a catalyst for oxidation reactions in that micro environment. The resultant acid generated in turn will maintain desired conditions for growth and expansion.

In a subaqueous environment these conditions may be more difficult to maintain. Under water, oxygen availability is limited by the solubility of oxygen, water depth, and by other CO₂-respiring bacterial communities. In addition, a lake bottom, or sea bed is prone to periodic dilution by surrounding water due to active currents. In the absence of current the diffusion of acid out of the micro environment would be more rapid than the diffusion of oxygen supply into the micro environment (MEND, 1989). Therefore, conditions required for sulphur and iron oxidizing bacteria may be difficult to maintain.

Bacterial activity is deterred in seawater due to the chloride ion toxicity (BC research, 1991, cited in MEND, 1989). Laboratory studies (MEND, 1989) show that reduced bacterial leaching from metals occurred at 25% seawater and / or salinity that exceeds 13 ppt. Adaptable strains of marine thiobacilli exist (Tilton et al., 1967) that are distinctly different from terrestrial types, yet to the best of our knowledge, these have not been directly studied with reference to ARD and subaqueous disposal in marine settings.

2.7 Case Studies

Subaqueous disposal has gained support from several field studies conducted at Anderson Lake, Manitoba, Buttle Lake, British Columbia (Pederson, 1983, 1985; Pederson and Losher, 1988;

Pederson et al., 1991), and in a seawater environment at the Island copper mine on Vancouver Island (BHP Ltd. Minerals Impact Report in Ellis, 1994). Table 2.1 summarizes the conditions for the case studies and the following sections describe an overview of results derived from studies cited above. Tailings in both lakes, although they differ substantially in bathymetry and sediment input, produce only a fractional amount of diffusive metals into the overlying pore waters (acidic leachate) compared to metal levels found commonly in terrestrial based acid mine drainage. It is suggested by Pederson (1991) that the tailings are in most cases acting as sinks for metals rather than sources to overlying lake waters. Both freshwater systems report an overall negligible negative impact on the water quality, biota, and surrounding environments. These studies concluded that submerged reactive waste material covered with natural sediments does not appear to degrade the quality of overlying lake water, and as a result, works to suppress the problem of ARD (Pederson, 1991; Brouwer, 1991; MEND, 1989). This is applied to both deep and shallow water columns (Pederson, 1991). The following brief descriptions summarize representative examples of subaqueous disposal in eutrophic and oligotrophic freshwater lakes, and seawater settings.

2.7.1 Anderson Lake, Manitoba

Anderson lake, Manitoba, is shallow, polluted, and anoxic at sub-bottom depths (mesotrophic to eutrophic). It is located on the Precambrian shield; an area of low buffering capacity (Rescan Environmental Services, 1990). To present, the lake has received 8×10^6 tonnes of tailings in addition to acidic drainage from an old mining road built of tailings. Metals were found to diffuse into the tailings from overlying pore water, and are being precipitated as authigenic sulphide minerals.

2.7.2 Buttle Lake, British Columbia

Buttle Lake, British Columbia, is an oligotrophic, deep (87m), well-oxygenated freshwater system. This lake received reactive tailings from the nearby Westmin massive sulphide mine until 1984. Studies show that it has experienced only a small 0.5 nmol/L efflux of Zn into the overlying waters (MEND, 1991). Island Copper Mine, Vancouver Island

The Island Copper Mine operated by BHP Minerals Canada Ltd, was situated on the northern tip of Vancouver Island, British Columbia. As of June 1993, three years before official closure, 347 million tonnes of tailings were discharged into the saltwater fiord of Rupert Inlet since production began in 1971. Primary ore minerals within the tailings included chalcopyrite, molybdenite, pyrite, sphalerite, bornite, and galena. Tailings were mixed with twice the volume of seawater, and released at 40 meters depth. Environmental considerations for the outfall consisted of resuspension and upwelling of the silt size particles due to wave action or storm activity causing subsequent ARD production and trace metal release. In contrast, the chemical behaviour of tailings following deposition did not contaminate the overlying water column with trace metals due to the suppressed ARD generation (BHP Minerals Impact report, 1994; Ellis et al., 1995). Benthic communities proximal to discharge points suffered lowered population density and diversity but regional populations of Pacific salmon and Dungeness crabs were not affected. At closure, the open pit was flooded with water from Rupert Inlet and topped with freshwater. It was concluded that submarine tailings disposal was an effective management technique with lower acid rock drainage potential compared to terrestrial waste piles.

Table 2.1. Summary of case studies for subaqueous disposal.

Location	Minerals Mined	Quantity of waste (tonnes)	Tailings composition	Tailings Discharged	Trophic Status
Anderson Lake, Manitoba	Cu, Pb, Zn	7,300,000	Pyrite, pyrrhotite, chalcopyrite, sphalerite, arsenopyrite	1979 - present	Meso-eutrophic
Buttle Lake, British Columbia	Cu, Pb, Zn	5,000,000	Pyrite, chalcopyrite, galena, sphalerite	1966 - 1984	Oligotrophic
Island Copper Mine, British Columbia	Cu	347 million	Chalcopyrite, molybdenite, pyrite, sphalerite, bornite, galena	1996-present remediation	Fiord, seawater environment

2.8 Environmental Concerns

Although field studies have provided preliminary confirmation to the theory of sub-aqueous disposal, natural water systems are rarely consistent and difficult to control. Many considerations beyond the scope of this thesis for the disposal of reactive waste rock in a marine or lake setting apply. These may include any interacting or single features such as benthic organic matter, input and output to the water body, bathymetry, trophic status, initial quality of the site, aquatic life, lake uses, residence time, sedimentation rates, general water chemistry, and hydrology.

Chapter 3: POLICY AND REGULATION FOR DISPOSAL OF SULPHIDIC SLATES

3.1 Introduction to Policies and Regulations

The prevention and management of acid rock drainage (ARD) in Nova Scotia is captured in a range of policies and regulations enforceable at both federal and provincial levels. Legislation is more advanced in Nova Scotia in comparison to all other provinces in Canada for the disposal of sulphidic-waste rock. This regulatory framework is attributed to the problematic Meguma Supergroup slates. Legislation in regards to disposal of solid waste products in freshwater and marine environments exists primarily at the federal level, but applies as a framework for provincial action.

It is imperative to provide industry, the public, and scientific researchers with an overview of the existing Canadian regulatory framework relevant to the issue of ARD. In turn, this assists regulatory agencies, and researchers, to assess the performance of mitigating ARD by compliance, and development of appropriate waste management methods.

The following chart (Figure 3.1) maps those policies and regulations that apply to the disposal of sulphide bearing materials in a subaqueous environment in the Province of Nova Scotia. The flow chart is a simplified version of this legislation. In actuality, the system is interlinked at various levels of government and often influenced by private sector interests. There is a great degree of duplication and overlap in jurisdiction that makes it difficult to interpret and even more difficult for industry to comply with. Worse yet, gaps in regulations (e.g. coastal zones) complicate policies and regulations further. International regulations and agreements also affect environmental legislation, but are omitted from the chart because they are beyond the scope of this study.

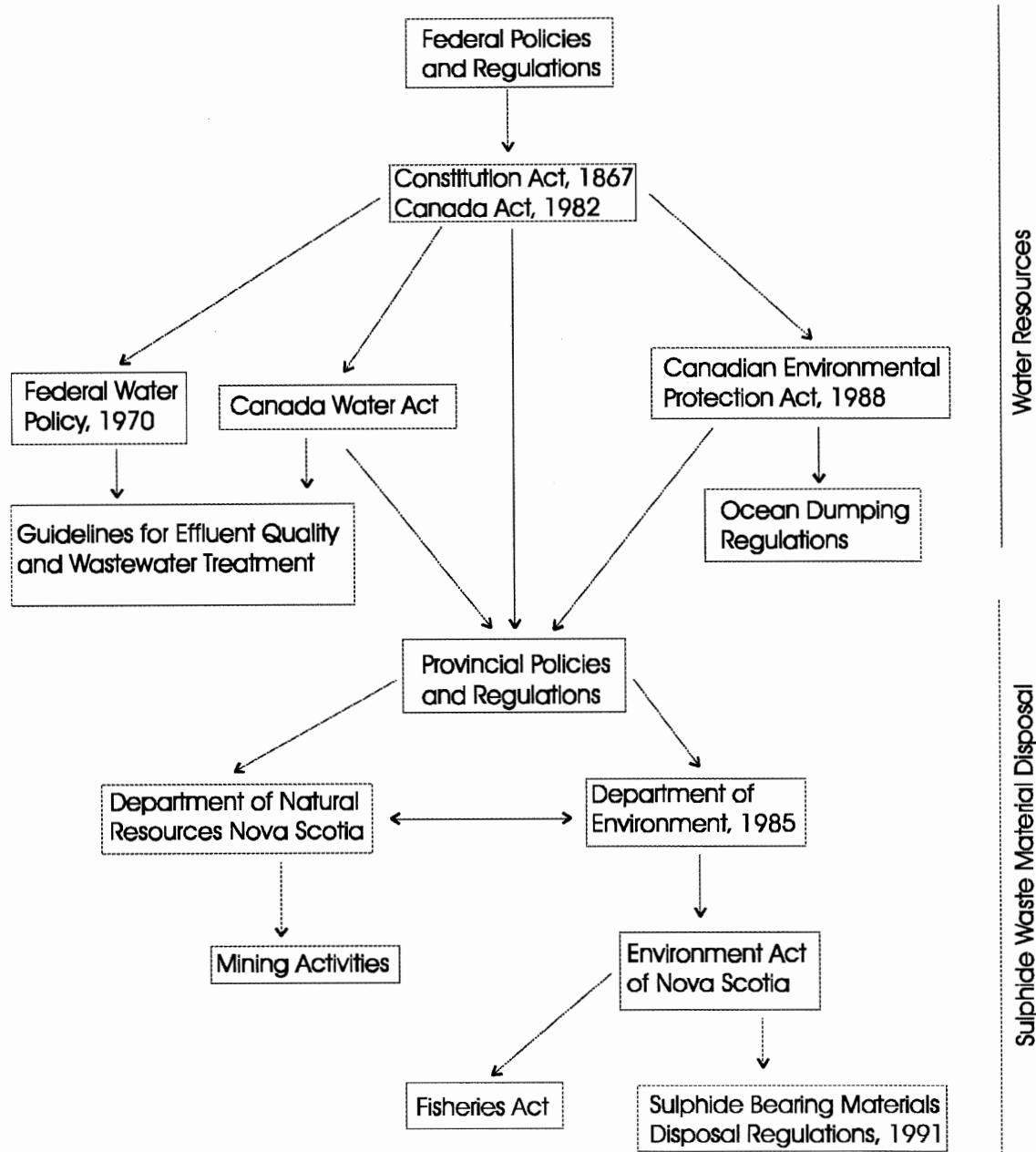


Figure 3.1. Simplified flow chart of policies and regulations concerning subaqueous disposal of sulphide bearing waste material in Nova Scotia.

- (1) Environment Act of Nova Scotia -Sulphide Bearing Material Disposal Regulations
- (2) Canadian Environmental Protection Act, 1988- Ocean Dumping Regulations (1988, SOR/89-500)
- (3) Canada Water Act (RSC 1985, c.C-11) - Guidelines for Effluent Quality and Wastewater Treatment at Federal Establishments
- (4) The mining industry and effluent limitations falls under the jurisdiction of NSDNR.
- (5) Fisheries Act (specific to mining operations, CRC 1978c819 Subsection 36(3))

3.2 Legislation for Water Resources - Constitution Act (1867)

The *Constitution Act*, 1867 designates the provinces as owners of both surface and groundwater. This denotes the responsibility for flow regulation, authorization of water use development and the authority to legislate areas of water supply, pollution, thermal and hydroelectric power. The federal government regulates areas that may have an economic impact on a national level such as navigation, fisheries, and water that falls on federal lands, territories, and reserves of Canada's aboriginal peoples. A shared responsibility is designated in terms of inter-provincial water use, agriculture, significant national issues, and health matters.

3.1.1 Federal Water policy, 1987

The federal water policy is a statement of the federal government's philosophy and goals concerning freshwater use by the provinces. This is a mandate that does not involve legislation but only sets forth projected goals and a framework for producing legislation. It establishes strategies for water pricing, science leadership, integrated planning, legislation, and public awareness.

3.2.1 Canada Water Act

The federal government passed the *Canada Water Act* in 1970 to provide regulations that allow an increased focus of water resource management to fall under the jurisdiction of each province.

The Canada Water Act is, "*An Act to provide for the management of the water resources of Canada, including research and the planning and implementation of programs relating to the conservation, development and utilization of water resources*" (Canada Water Act, R.S., c. 5(1st Supp.), s. 1.)

Part II – *Water Quality Management* (subs. 9) of the *Canada Water Act* (1970) strictly prohibits pollution of waters by disposal of waste of solid, liquid, gas, or waste that may result from waste material, “except in quantities and under conditions prescribed with respect to waste disposal in the water quality management area in question, including the payment of any effluent discharge fee prescribed therefore...” Therefore the permission to dispose of waste in a natural water body is subject to Her Majesty in right of Canada or a province [subs. (3)] and the Governor in Council may make regulations prescribing the quantities, effluent discharge fees, pre-treatment, analysis, and water quality studies [*Regulations* -subs. (18.2)].

Those guilty of an offence are liable under Offences and Punishment [subs. (30.1)]. A conviction for violation requires the offender to pay a fine that cannot exceed \$5,000 Canadian. Each offense is recorded and after the end of each fiscal year is contained within a report on operations under the *Canada Water Act*, 1970, that is laid before Parliament.

3.3 Canada Environment Protection Act, 1988, 1996

The Canada Environment Protection Act provides a statutory framework emphasizing a precautionary and preventive approach to environmental issues in Canada. It is established as “cradle to grave” management mandate.

3.1.2 Ocean Dumping Regulations, 1988

Subaqueous disposal in a marine environment must be granted approval under both the *Sulphide Bearing Materials Disposal Regulations*, 1991, and the *Ocean Dumping Regulations*, 1988, which is defined under the jurisdiction of the *Canada Environment Protection Act*, 1988, 1996.

These regulations apply to any quantity of waste product that exceeds a regulated amount set for disposal. The procedure for disposal is to acquire a permit by means of application to the minister. The application cost is \$2,500 Canadian.

Reports are filed under subsection [68 (4)] of the Act and require information regarding the locality, name / address of company and/or owner, particulars concerning the method, quantity, and capacity of the container that it is released. In addition, the report must include the geographic coordinates of the dump site, logs, and description of the activity. Thirdly, a detailed description of the substance dumped is recorded and Part C of the application including information on alternate methods of disposal. Lastly, Part D is concerned with the historical methods by which dumping took place, and why ocean disposal is chosen.

3.4 The Environment Act of Nova Scotia, 1991-

3.4.1 Sulphide-Bearing Material Disposal Regulations

The *Sulphide-Bearing Material Disposal Regulations*, 1991, has been developed in response to the specific problem associated with ARD in Nova Scotia. The disruption of Halifax slates and disposal of the resultant waste rock is managed under the authority of the *Nova Scotia Environment Act*, (1994-95). Defined within this act are the *Sulphide-bearing Material Disposal Regulations* (1991). The act guides the design and use of disposal sites for problematic waste rock and furthermore controls and monitors the disposal of sulphide bearing materials. This act is divided into three compartments. The first requirement is for any large-scale excavation and disposal of sulphide bearing slate to undergo predictive testing to determine the acidic potential of rock units at a proposed site. Secondly, an approval for appropriate disposal prior to commencement of the activity must be obtained. Finally, a monitoring program at any development located on the Meguma Supergroup must be deployed. This act applies to construction and municipal

development activities and in certain cases, mining activities (which fall under the jurisdiction of the Nova Scotia Department of Natural Resources).

Sections (6) to (9) define the proper screening, sampling, analysis and evaluation for development. Developments are considered under this section if the excavated volume is over regulated limits and if the sulphur content in the material is equal to or greater than 0.4 % (12.51 kg H₂SO₄/tonne) [subs.2(6)]. All data concerning this section are to be forwarded to the Administrator before commencing work at the site.

Sections (9) to (11) generally outline the proper conditions of disposal and disposal sites. No particular type of disposal method is specified for management of ARD, yet in all cases, terrestrial disposal is implied, and requires a rehabilitation plan to be employed. Section (9) regards the basic requirements for minimizing the extent and amount of time that the material is exposed to oxidizing conditions. Section 10 states that the disposal of this material must be at an approved disposal site. Site requirements indicate that disposal sites are specifically at least 60m from a watercourse.

There is the option to bypass the regulations whenever it is *"to be established by the minister and the minister believes on reasonable and probable grounds that the requirement set will not prevent an adverse effect"* [subs 11(c)].

In conclusion, this is only a brief version of those policies and regulations that have a direct influence on the disposal of sulphide-bearing material in a subaqueous environment. The reader is referred to references cited within the text for specific details of regulatory legislation. Overall, there exist no guidelines specific to the technique of subaqueous disposal that outline and regulate the procedure.

Chapter 4: EXPERIMENTAL SETUP AND ANALYTICAL METHODS

4.1 Background

The reactivity of sulphide minerals underwater is governed by complex interactions between the geochemical characteristics of individual sulphide minerals and the physical, chemical, and biological attributes of the receiving waterbody. Therefore it is difficult to evaluate of subaqueous disposal in laboratory experiments accurately. The experiment was specifically designed study primary problematic sulphide minerals of the Meguma Supergroup and water samples representing actual waterbodies in the region. The aim of the experiment was to compare the relative reactivity of sulphides in freshwater and seawater.

4.2 Sample Descriptions

4.2.1 Core Sample

Core sample BH-20-2 was collected from the Halifax Group in the Meguma Supergroup near the Halifax International airport (Figure 4.1). This core was selected to represent primary potential ARD sulphide minerals inherent to the Meguma Supergroup and problematic for municipal and regional construction and development.

The sample is composed of black metasiltstone with large (1mm – 1.5cm), elongate lenses of pyrrhotite and marcasite primarily concentrated parallel to cleavage planes and cross-cutting the bedding surface. The pyrrhotite is bronze-colored with some tarnished surfaces and in several cases marcasite has been completely or partially plucked out and a hole remains.

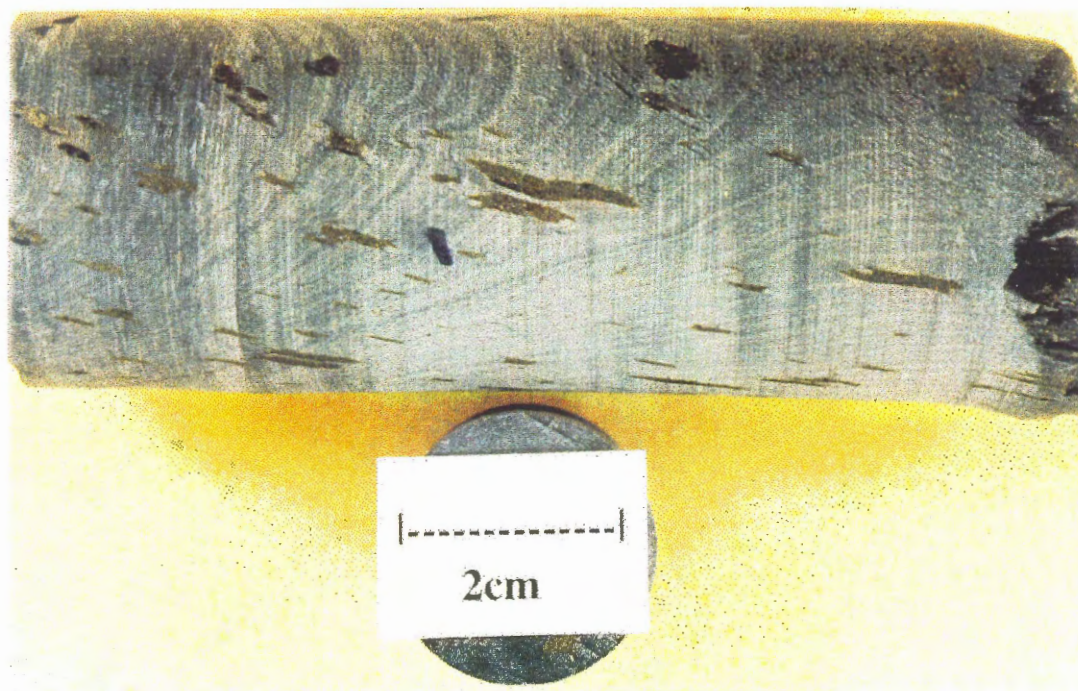


Figure 4.1. Core sample BH-20-2, Meguma Supergroup, composed of black metasilstone and elongate grains of pyrrhotite. Collected near the Halifax International Airport (Refer to Figure 1.1.).

Five parallel slabs were cut from the core in order to sample similar mineralogy. Polished thin sections were prepared from the slabs and labeled #BH-20-II, A-E. Three of the five thin sections were submerged in water samples, one thin section was used as a control, and one used for microprobe analysis.

4.2.2 Polished Thin Section Description

The thin sections were examined under reflected light on a Zeiss Axioplan ore microscope. Three distinct areas were chosen on each thin section to represent adequately the overall mineralogy and textures found. Those chosen were as follows: 1) pyrite, 2) pyrrhotite / marcasite, and 3) pyrrhotite associated with chalcopyrite. Each location was individually sketched and described as a reference region for experimentation.

All thin sections contain elongate (1mm – 1.5cm) pyrrhotite lenses aligned parallel to cleavage planes. Pyrrhotite and marcasite grains are anhedral and subgrains are visible under cross polars. Minor sulphide inclusions exist within the pyrrhotite. Titanium oxides, rutile or anatase (identified by microprobe analysis (appendix A)), commonly outline the boundary of the pyrrhotite lenses. Chalcopyrite is commonly found bordering the perimeter of pyrrhotite grains. Small (0.1-0.3mm), skeletal pyrite grains and arsenopyrite are randomly scattered throughout the matrix.

4.2.3 Microprobe

The JEOL 733 electron microprobe aided in sulphide mineral identification and documentation of mineral chemistry. Results are given in Appendix B. Each analysis was acquired with 40 seconds counting time with an accelerating voltage of 15 KV and a beam current of 15 – 16 nA. The size of the probe spot was approximately 1 micron. The raw data were corrected by the Links ZAF matrix correction program. Calibration (done by R. Mackay,

Dalhousie University) used cobalt metal. Precision for ten analyses on cobalt metal was $\pm 0.5\%$ at one standard deviation. Accuracy for major elements was ± 1.5 to 2.0% relative.

4.2.4 Water Samples

Water samples were collected and stored in 1 litre Nalgene plastic bottles that were rinsed several times with sample water before collection. Two liters of seawater were collected from the Northwest Arm in Halifax on January 12, 1999 and two liters of freshwater from Lake Banook in Dartmouth on January 10, 1999. These samples were chosen to represent typical candidate waterbodies for subaqueous disposal within the region although possible pollutants contained within the water were not evaluated. A two liter sample of distilled water was obtained from the Fission Track Lab at Dalhousie University.

Initial and final pH and temperature measurements were obtained using pH meter ATI Orion model 290A pH meter calibrated with pH buffers 4 and 7. Dissolved oxygen was recorded using a YSI model 51B meter upon conclusion of the experiment.

4.3 Experimental Set up

4.3.1 Microscope

The three mapped thin section locations were observed under a Zeiss Axioplan reflected light microscope with an automated x-y stage at zero, six, fifteen, and forty days at different magnifications, and x-polars.

4.3.2 Digital Imaging

The Zeiss Axioplan microscope was fitted with a JVC CCD camera connected to an Intel image grabber in an IBM-compatible PC. This produced a digital image at magnifications 5X, 10X, and 20X for all five thin sections using the software Digital Video Producer. Filenames were systematically organized according to slide identification letter, location. On the slide a code

identifying the use of polarizers: np-no polarizer, p-polarizer, xp-cross polars were recorded. All attributes for the image grabber software, colour (c), tint (t), saturation (s), and brightness (b) were held constant in all images throughout all time intervals with a few exceptions. Exceptions were made to match the actual color observed under reflected light and are recorded in Appendix B.

4.4 Procedure

The reactivity tests were conducted in 500mL graduated cylinders. Each cylinder was washed with detergent, rinsed with HCl, and then with distilled water (six times), followed by 200 ml of the respective sample water before use. All three thin sections were held in identical upright positions by a plastic mount. These mounts were attached to a glass rod for easy removal without contamination of the water sample during the experiment. One thin section was submerged in 500 ml of each of the three water samples at a depth of 32 cm. The solutions were exposed to the atmosphere at room temperature (18-23°C). One thin section (E) was maintained in air as a control and thin section (D) was carbon coated and used for microprobe analysis.

The thin sections remained submerged for 6 days after which they were removed individually, rinsed with methanol, digitally photographed, rinsed again with methanol and returned to their respective water samples all within the same time period. This procedure was repeated at 15 days and 40 days.

It is necessary to note that although preparation procedures may affect the area of interest, all thin sections used in the experiment were treated identically and therefore the resulting differences in reactivity among the minerals are assumed to be due only to each respective water sample.

Chapter 5: RESULTS

5.1 Electron Microprobe Results

Microprobe analysis (Appendix A) of thin section (D) was used to verify sulphide mineral identification in the BH-20-II core sample. Thin section (D) represented all thin sections (A, B, C, and E). BH-20-II contains pyrrhotite, pyrite, marcasite, chalcopyrite, arsenopyrite, and rutile. Figure 5.1 is a scatter plot of hexagonal pyrrhotite compositions determined using microprobe analysis compared with five ideal polymorphs of Fe_{1-x} plot of atomic % S versus Fe.

5.2 Reactivity of Sulphidic Slates by Digital Image Analysis

Sulphide reactivity rate was judged by analysis of surface features, the degree of tarnish, and /or color changes of specific locations on the thin section. Under reflected light, orange-brown, blue, and grey-black colors, precipitate residue, and surface etchings were considered evidence for reactivity. Thin section (E) was maintained in air as a control for comparison (Figure 5.0), no apparent surface changes were observed. Each thin section (A - E) was imaged at each time interval. The following results are systematically organized in three parts. First, a brief introduction is provided to explain the terminology used to describe the observations. Secondly, a time series of changes from 0 - 40 days in each thin section under water is illustrated in digital images according to respective location sites chosen. Lastly, the specific surface change observed in the variation of mineral reactivity, recorded at each time interval throughout the duration of the experiment is presented in chart format.

5.3 Description of Digital Images

An overall reactivity rating of low, moderate or high was assigned to each of the three thin sections based on the comparison of surface features. A general time frame in which the majority of reaction occurred is documented based on the comparison with the immediately

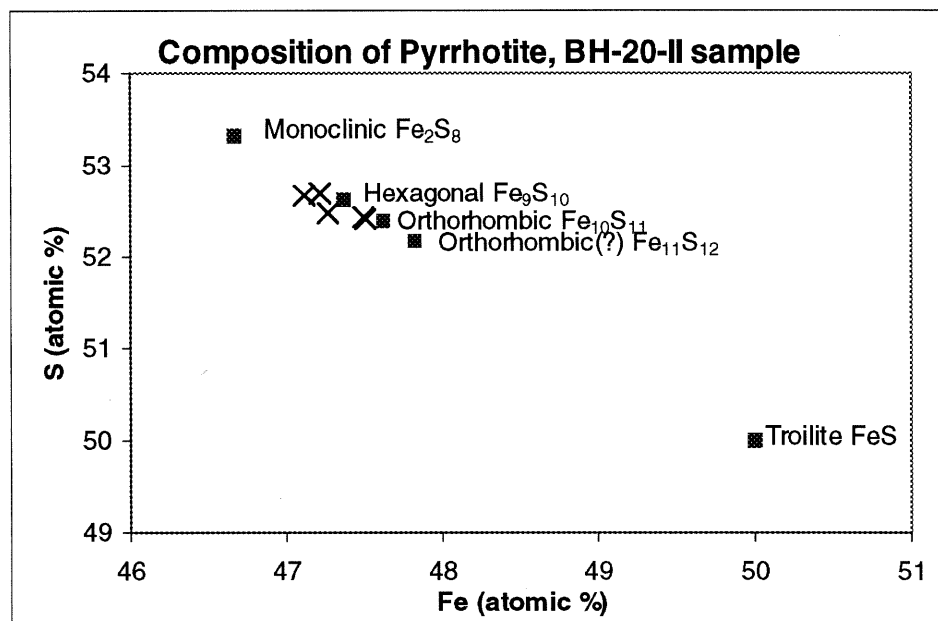


Figure 5.1. Scatter plot of S versus Fe (atomic %) for pyrrhotite compositions from sample BH-20-II, thin section (D), illustrated as crosses in comparison to five ideal forms of pyrrhotite, illustrated as solid squares (after Craig and Scott, 1974).

Control (E) Start - Final

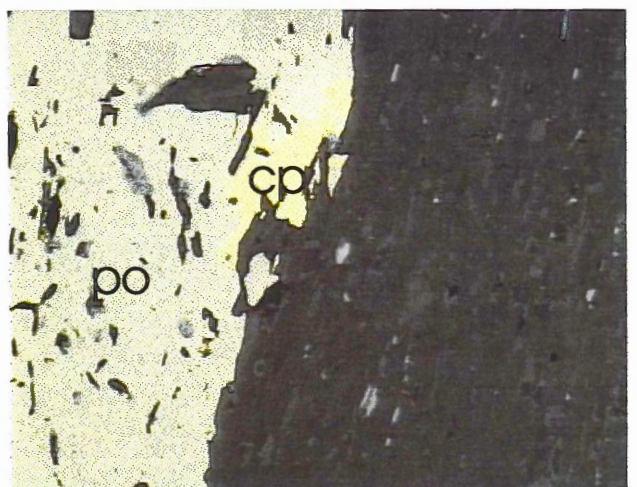
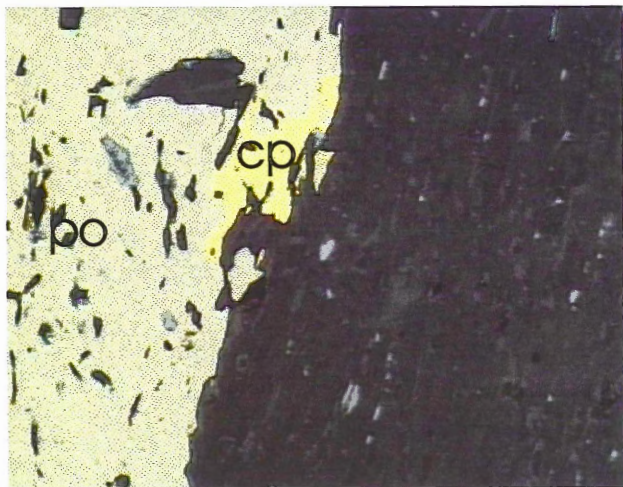
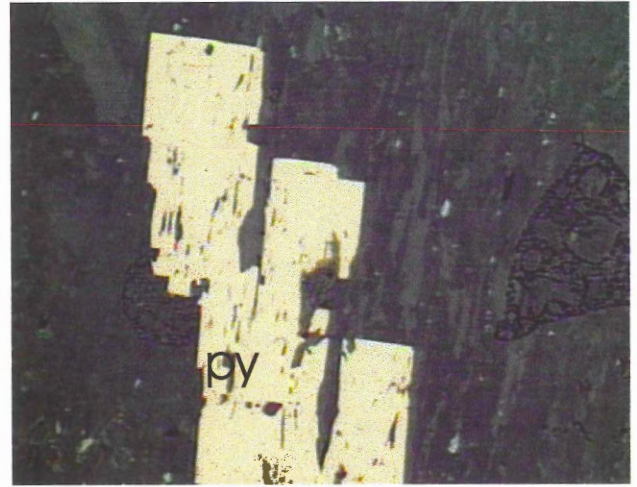
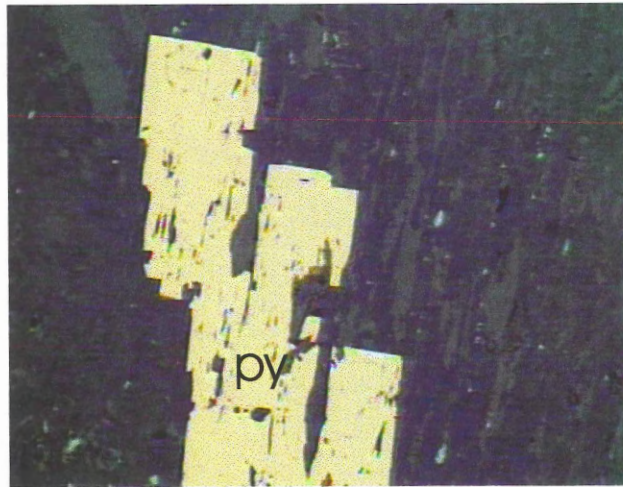


Figure 5.0. Time series of the control at zero and 40 days.

previous time imaged for each mineral location. All additional surficial changes, including color, precipitate and additional differences are recorded directly as observed.

5.3.1 Distilled Water (Thin Section A)

Overall reaction of sulphide minerals under distilled water cover in comparison to freshwater and seawater was rated at moderate (Figures 5.3A-C and Table 5.1). Surficial change was negligible in pyrite. A significant amount of surface change occurred primarily between 6 and 40 days initiated at outer edges of the pyrrhotite adjacent to chalcopyrite and along the perimeter of chalcopyrite. Inclusions judged by the change from grey to dark brown appeared completely reacted. A slight amount of surface tarnish appeared on the marcasite or pyrrhotite.

5.3.2 Lakewater (Thin Section B)

Overall reaction of sulphide minerals under freshwater water cover in comparison to distilled and seawater was rated at low (Figures 5.3A-C and Table 5.2). Surficial change was negligible in pyrite from 0 to 40 days. Moderate reaction occurred primarily between 0 and 15 days in pyrrhotite or marcasite and chalcopyrite. Slight amounts of surface tarnish were detected along grain perimeters. Reaction occurred primarily at small inclusions (Figure 5.3D), in holes and in the chalcopyrite. A moderate amount of reaction occurred from 0 to 40 days in pyrrhotite / marcasite.

5.3.3 Seawater (Thin Section C)

Overall reaction of sulphide minerals under seawater cover in comparison to distilled and freshwater was rated at high (Figures 5.3A-C and Table 5.3). Surficial change in pyrite and pyrrhotite or marcasite associated with chalcopyrite was consistent from 0 to 40 days. At 40 days, all sulphide minerals appeared to be covered in brown to black tarnish in addition to blue reflectance. Reaction appeared to begin at outer boundaries, holes, and inclusions and increased from 0 to 40 days. Observed surface topography changes and precipitate was apparent at all sample

from 0 to 40 days. Observed surface topography changes and precipitate was apparent at all sample locations. A high amount of reaction was detected within the first 6 days in pyrrhotite or marcasite.

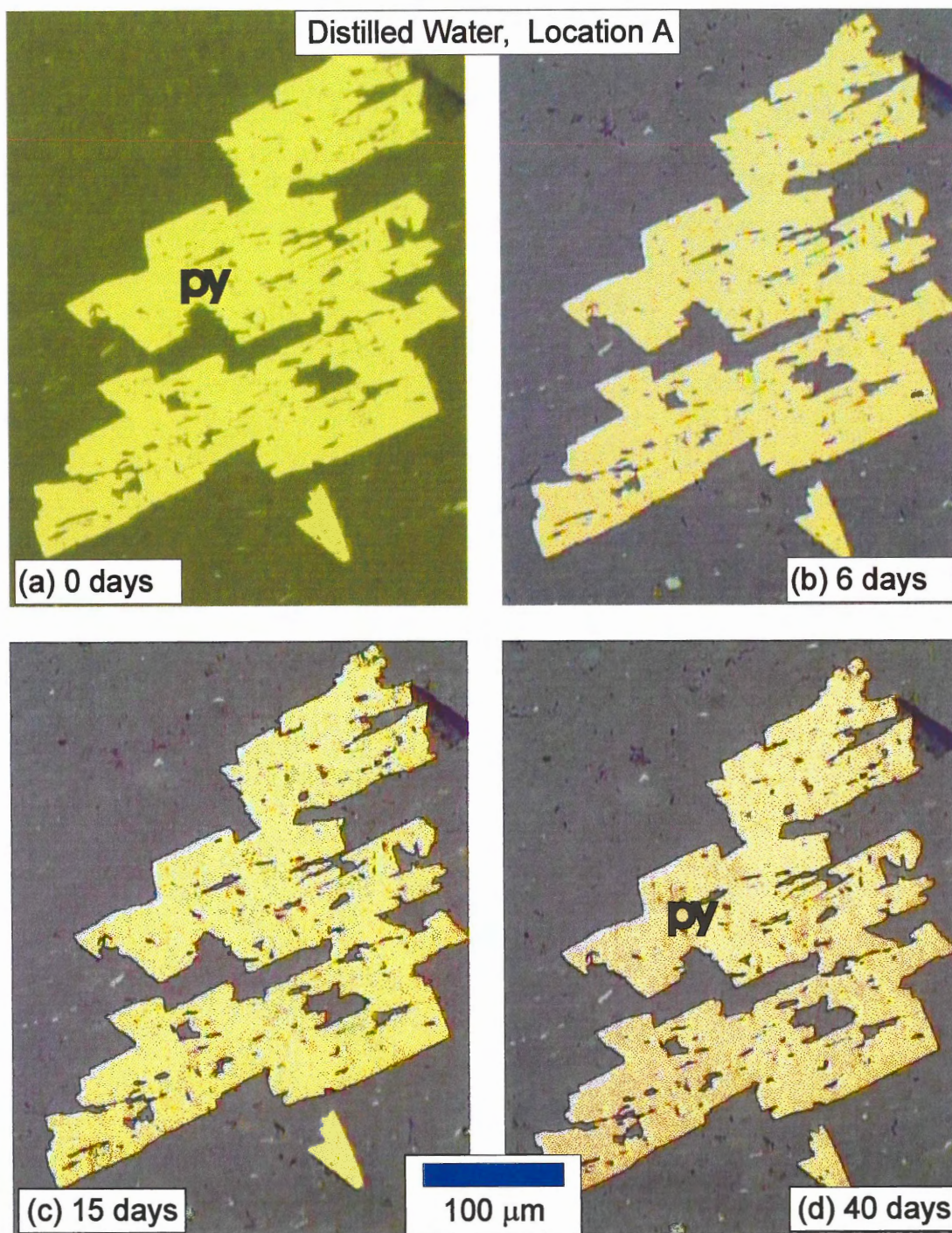


Figure 5.1.A Pyrite (py) location A at magnification 20X under distilled water cover (32 cm depth) at 0, 6, 15, and 40 days. Note the green and red tint is a product of software attribute values (does not indicate reaction).

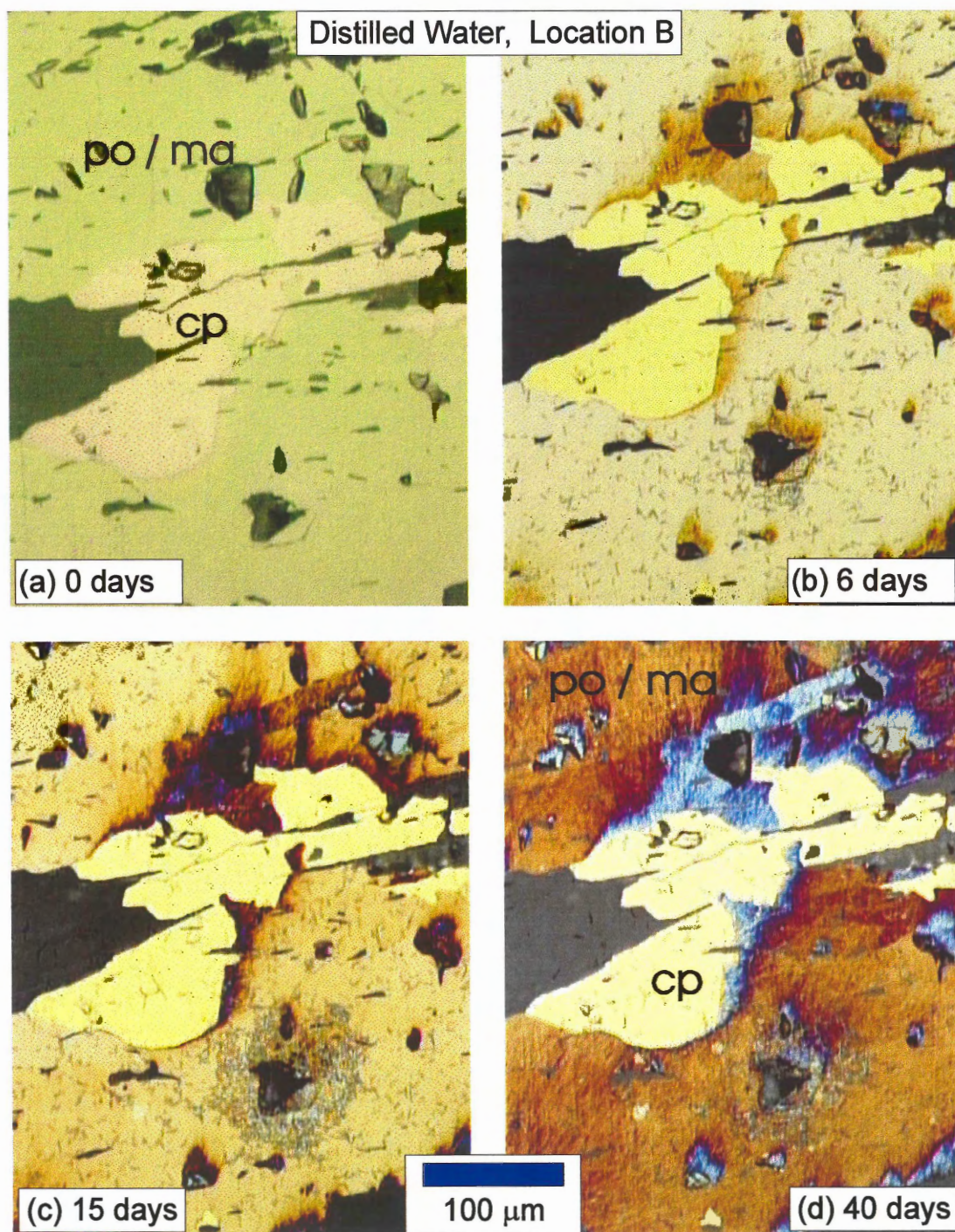


Figure 5.1.B Pyrrhotite (po) / marcasite (ma) and chalcopyrite (cp) location B at magnification 20X under distilled water cover (32 cm depth) at 0, 6, 15, 40 days.

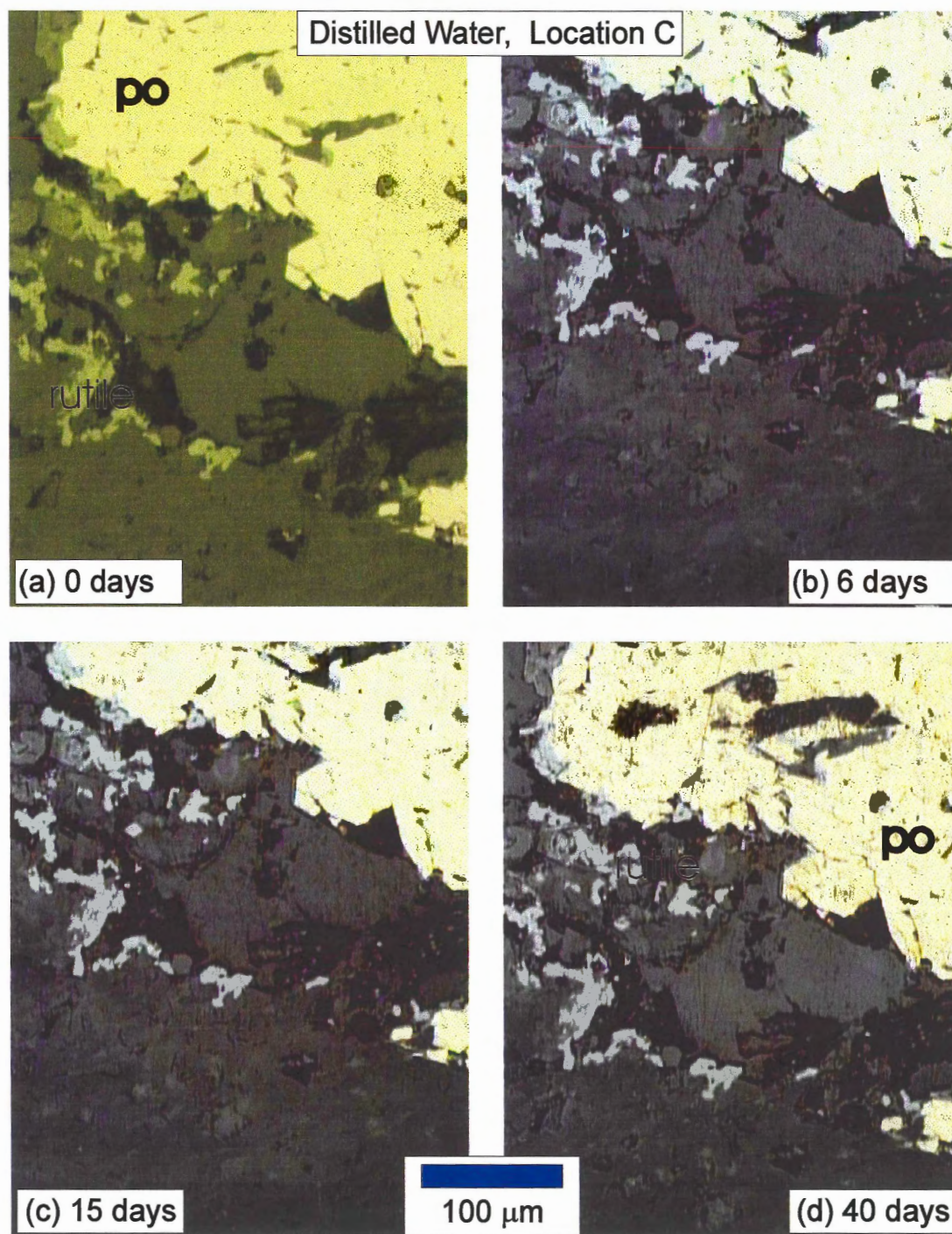


Figure 5.1.C Pyrrhotite (po) / marcasite (ma) and rutile location C at magnification 20X under distilled water cover (32 cm depth) at 0, 6, 15, 40 days.

Table 5.1. Summary of recorded reactivity of sulphidic minerals at three chosen locations under distilled water cover (32 cm depth), thin section A.

**Recorded Reactivity of Sulphidic Minerals
in Distilled Water**

Mineral	6 days	15 days	40 days
Pyrite Figure 5.1.A	no significant change detected	no change	no change
Comments:	greenish tint at time zero, and reddish tint at 40 days is not an indication of reactivity, this is due to variation of software attributes		
Pyrrhotite Adjacent to Chalcopyrite Figure 5.1.B	brown tarnish along the boundary of chalcopyrite and holes; outer edges of inclusions display blue colors; scratches/etching on pyrrhotite; no reaction noted for chalcopyrite	increase in brown tarnish at outer boundary, holes, and inner regions of pyrrhotite; scratches/etching consistent with previous observations; inclusions appear completely reacted; chalcopyrite remains unchanged	initial brown-orange tarnish areas completely reacted, additional blue colors; increase of scratch/etching; chalcopyrite slightly reacted at outer boundaries
Comments:	a significant amount of reaction detected consistently between 6 - 40 days		
Pyrrhotite / Marcasite Figure 5.1.C	orange-brown tarnish; minor scratch/etching; no indication of reaction of rutile detected	slight increase of orange-brown tarnish; no increase of scratching/etching; no change in rutile detected	slight increase of orange brown tarnish; no change of etching/scratching; no change in rutile detected
Comments:	low reactivity; changes occurred primarily within the first 6 days		

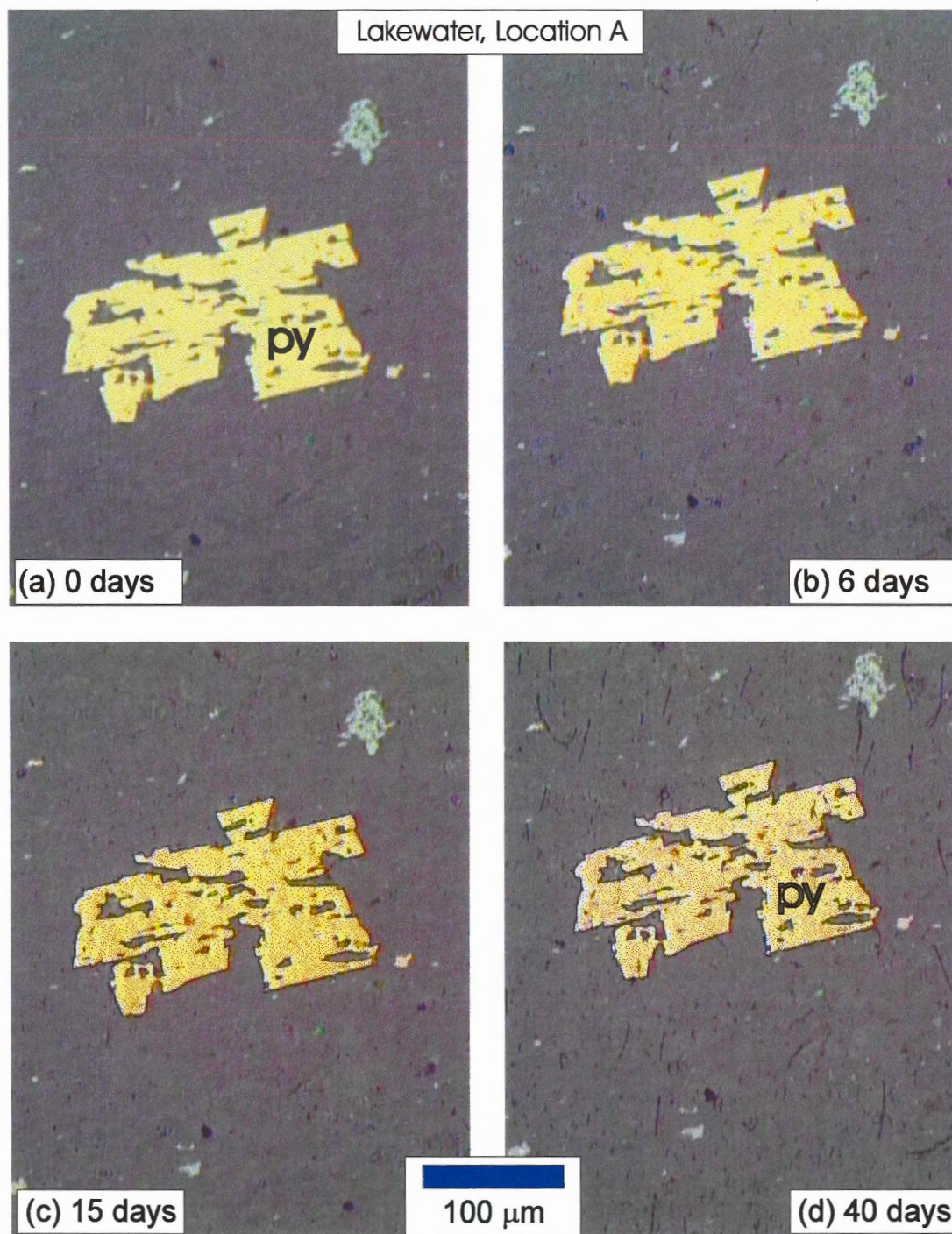


Figure 5.2.A Pyrite (py) location A at magnification 20X under freshwater cover (32 cm depth) at 0, 6, 15, and 40 days.

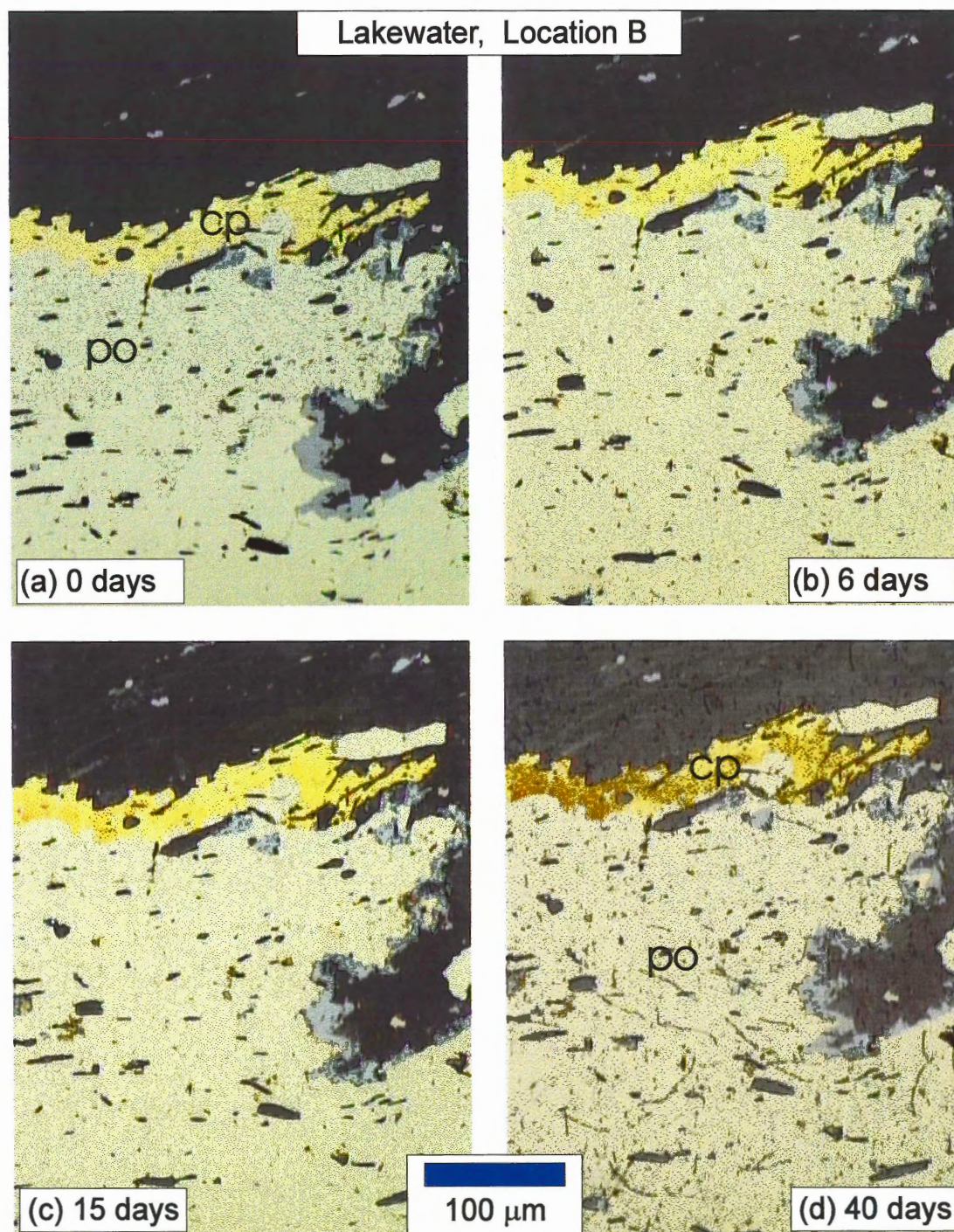


Figure 5.2.B Pyrrhotite (po) / marcasite (ma), chalcopyrite (cp) rimmed by rutile, location B at magnification 20X under freshwater cover (32 cm depth) at 0, 6, 15, and 40 days.

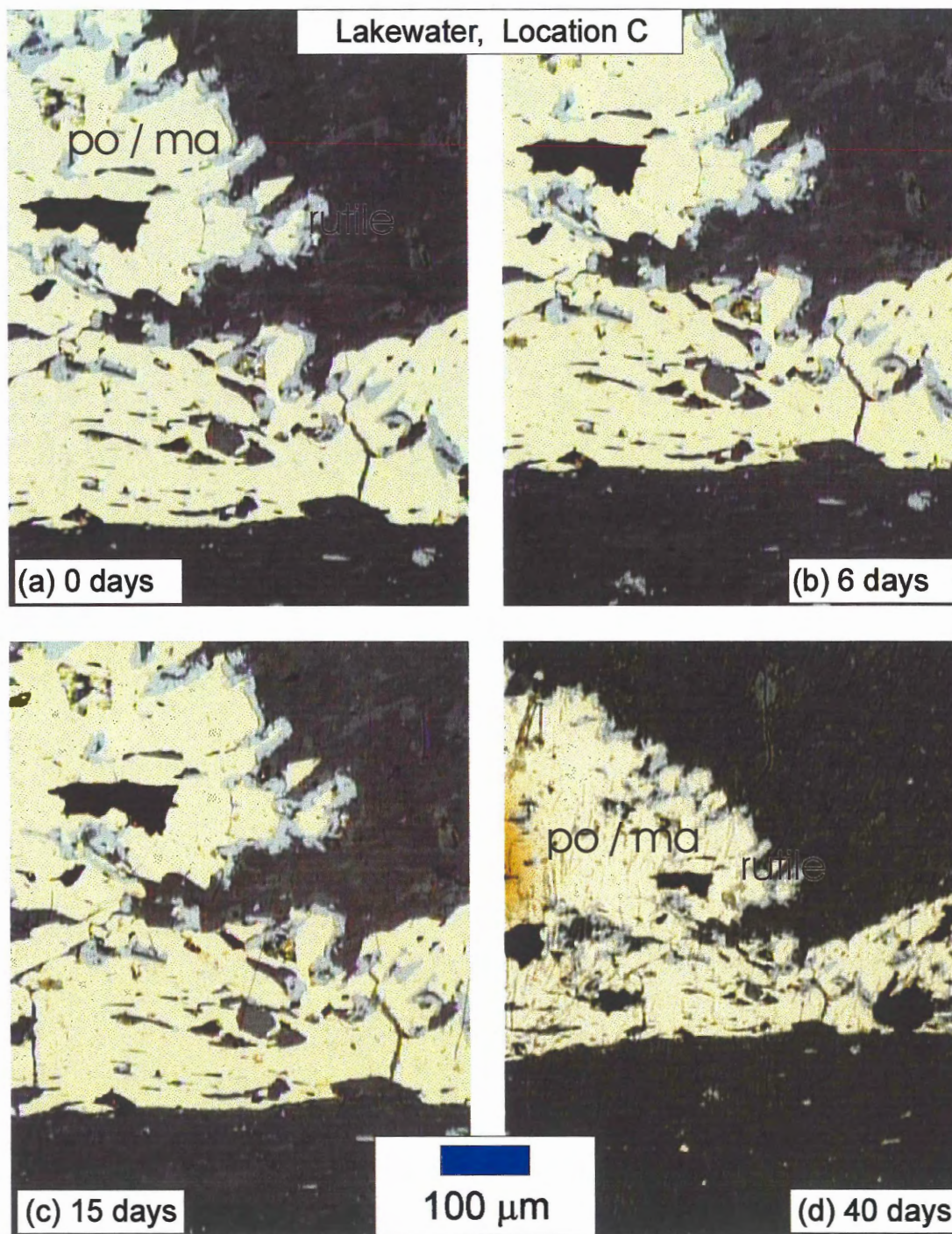
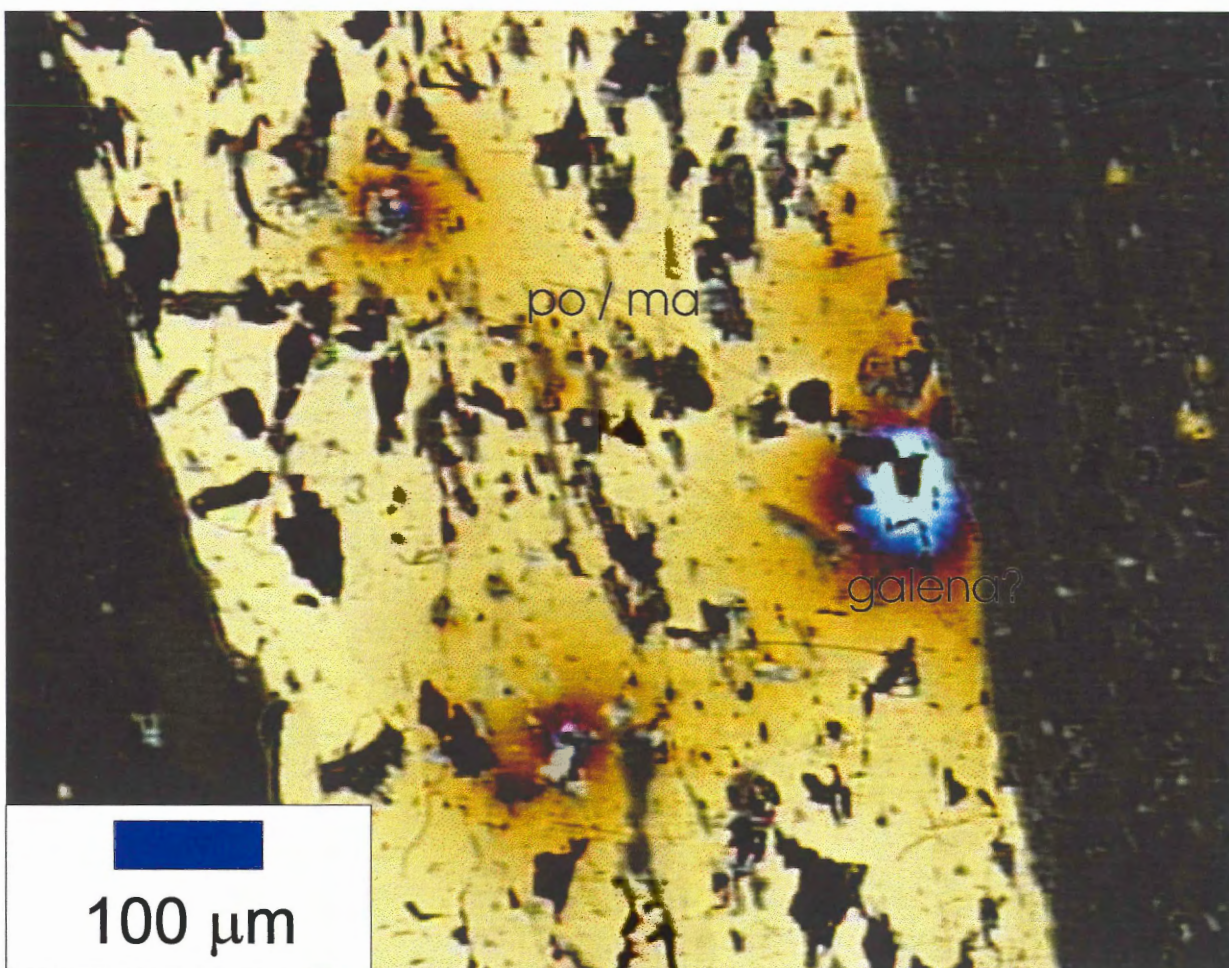


Figure 5.2.C Pyrrhotite (po) / marcasite (ma) rimmed by rutile, location C at magnification 20X, 40 days at magnification 10X, under freshwater cover (32 cm depth) at 0, 6, 15, and 40 days.



15 days

Figure 5.2.D. An example of a reaction observed at inclusions in pyrrhotite (po) under freshwater cover.

Table 5.2. Summary of recorded reactivity of sulphidic minerals at three chosen locations under lake water cover (32 cm depth), thin section B.

**Recorded Reactivity of Sulphidic Minerals
in Lake Water**

Mineral	6 days	15 days	40 days
Pyrite 5.2.A	no change detected	no change	no change
Comments:	greenish tint at time zero, and reddish tint at 40 days is not an indication of reaction, this is due to variation of software attributes		
Pyrrhotite Adjacent to Chalcopyrite 5.2.B	orange-brown tarnish at inclusion boundaries within the pyrrhotite; minor etching/scratches noted; no change in rutile	slight change from 6 days; orange brown tarnish detected within the chalcopyrite; no change in the rutile	noticeable increase in etching/scratching; no increase of tarnish since 15 days
Comments:	moderate reaction; most changes occurred within the first 15 days		
Pyrrhotite / Marcasite 5.2.C	orange-brown tarnish at the outer edges of holes; no change in rutile	slight increase of orange-brown tarnish; no change in rutile	increase of orange-brown tarnish at holes and randomly within the grain (possibly at small inclusions)
Comments:	moderate reaction; consistent from zero to 40 days		

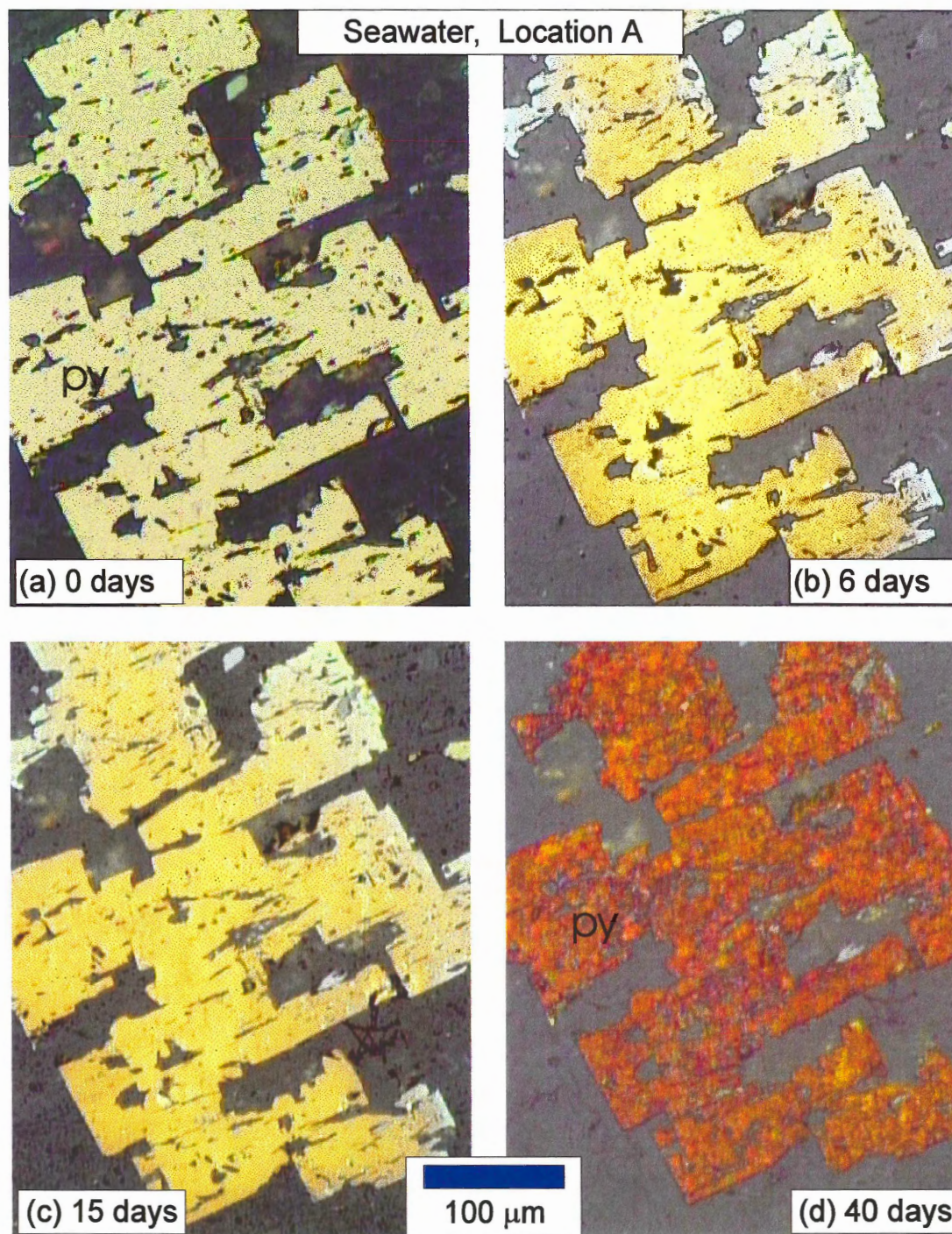


Figure 5.3A Pyrite (py) location A at magnification 20X under seawater cover (32 cm depth) at 0, 6, 15, and 40 days.

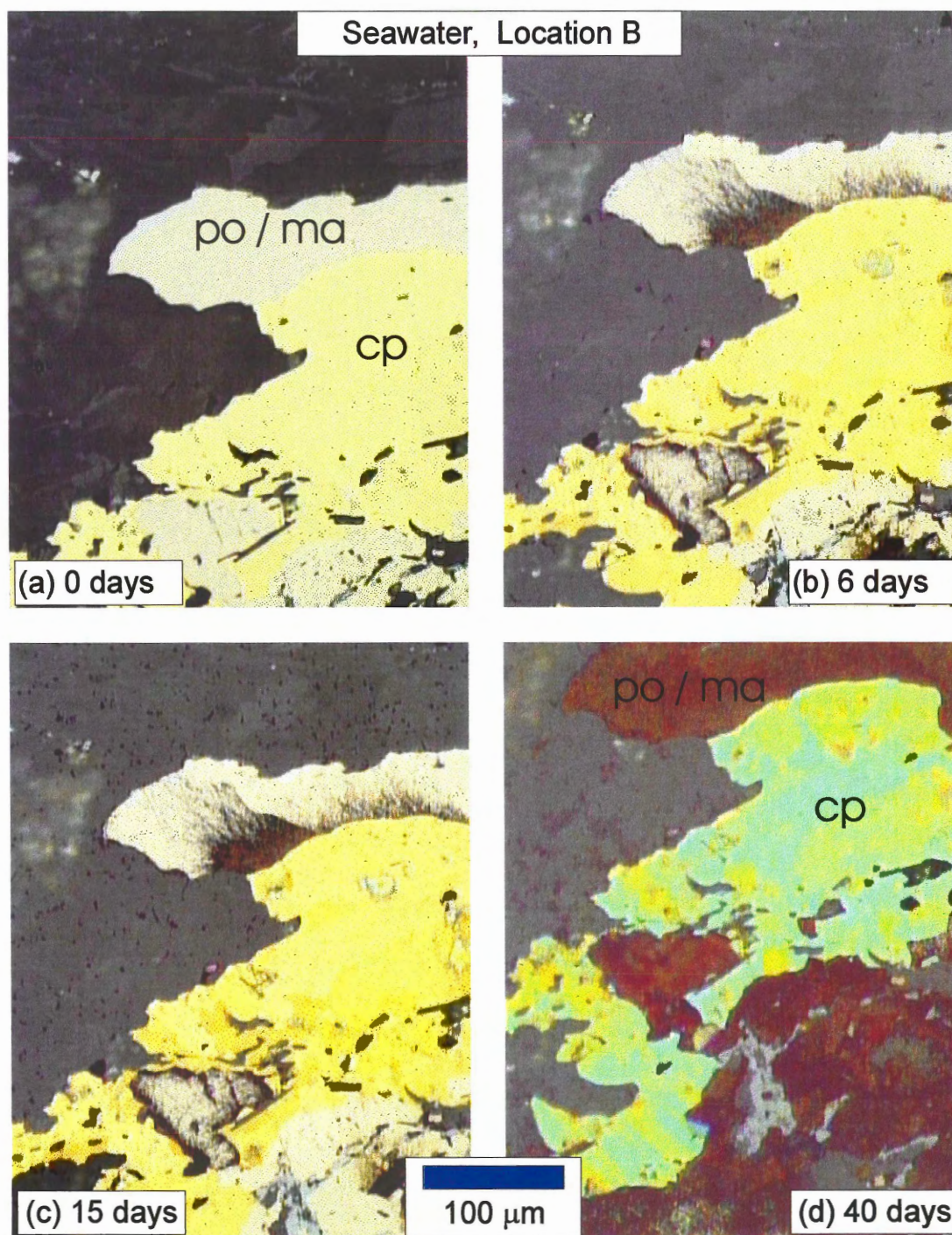


Figure 5.3B Pyrrhotite (po) / marcasite (ma), chalcopyrite (cp) location B at magnification 20X under seawater cover (32 cm depth) at 0, 6, 15, and 40 days.

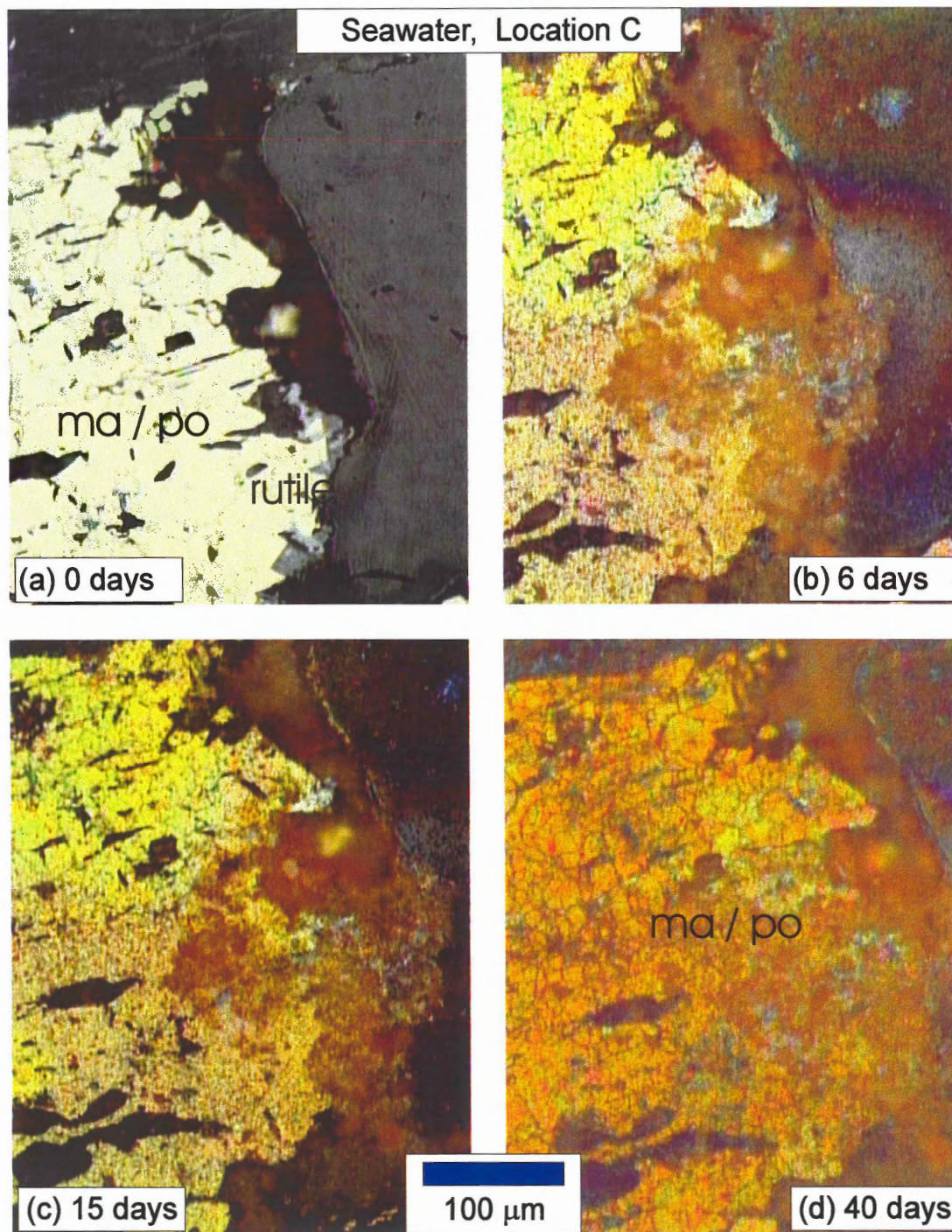


Figure 5.3.C Pyrrhotite (po) / marcasite (ma) outlined by rutile location C at magnification 20X under seawater cover (32 cm depth) at 0, 6, 15, and 40 days.

Table 5.3. Summary of recorded reactivity of sulphide minerals at three chosen locations under seawater cover (32 cm depth), thin section C.

**Recorded Reactivity of Sulphidic Minerals
in Sea Water**

Mineral	6 days	15 days	40 days
Pyrite 5.3.A	Orange-brown tarnish, blue color at edges	increase of orange brown tarnish, blue color within the inner regions	completely covered with orange-brown tarnish
Comments:	High reaction detected consistently from time zero to 40 days		
Pyrrhotite Adjacent to Chalcopyrite 5.3.B	Black tarnish on pyrrhotite at boundary with chalcopyrite and at holes; slight variation of yellow within chalcopyrite	increase of black tarnished regions; distinct variation of yellow tones in chalcopyrite	completely covered with black and orange-brown tarnish; blue BF colors detected within chalcopyrite
Comments:	High reaction detected consistently from time zero to 40 days		
Pyrrhotite / Marcasite 5.3.C	Blue/black/orange-brown colors throughout the grain increasing in intensity towards outer edges	consistent with day 6	Consistent with day 6, 15
Comments:	High reaction detected within the first 6 days		

5.4 Water Sample Results

5.4.1 pH values

At standard temperature (21°C), the initial pH values of all water samples are shown in Table 5.4.A. Distilled and lakewater samples entering the experiment are near neutral; seawater is only slightly more alkaline. The pH values at 40 days, the complete duration for the experiment, are displayed in Table 5.4.B. The pH values measured at similar standard temperatures appear to have no significant change for all water samples containing the sulphide bearing thin sections. Seawater has decreased by only 0.2 pH measurements and lakewater has increased by 0.8 pH units.

5.4.2 Dissolved Oxygen measurements

Dissolved oxygen measurements (Table 5.5) in Part A (Probe Suspended in Water Column) show variable values at the top of the water column, with a slight decrease gradient at depth. Part B, Table 5.5 (Measure of Water Sample Extracted from Cylinder) documents increased values in comparison to those measured within the cylinder. This is the case for all water samples utilized in the experiment at time 40 days.

Table 5.4. Temperature and pH measurements at A) day zero and B) day 40**A) TEMPERATURE AND pH AT ZERO DAYS**

Sample	pH measurement	Temperature °C
Distilled	6.68	21.1
Lake Banook #1	6.78	21.1
Lake Banook #2	6.9	21.0
Seawater #1	7.89	18.3
Seawater #2	7.88	18.9
pH 7 buffer check	7.01 / 6.99	21.0
pH 4 buffer check	4.03	21.0

B) TEMPERATURE AND pH AT 40 DAYS

Sample	pH measurement	Temperature (°C)
Distilled	6.68	19
Lake Water	7.73	19.2
Seawater	7.62	19.2

Table 5.5. Dissolved oxygen measurements.

DISTILLED WATER- THIN SECTION A**Part A: Measured Probe Suspended in Water Column**

Sample	Depth (ml)	Temperature (°C)	Dissolved Oxygen (mg/l)	Comments
Top	450	21.5	5.14 - 6	Fluctuating
Middle	250	21.5	4.6	Stable
Bottom	50	21.5	3.86	Stable

Part B: Measured Water Extracted from Cylinder

Sample	Depth (ml)	Temperature (°C)	Dissolved Oxygen (mg/l)	Comments
Pipette off 150ml	-150	21	7.14	Stable
	-300	20.9	7.08	Stable
	-450	20.9	7.06	Stable

FRESHWATER - THIN SECTION B**Part A: Measured Probe Suspended in Water Column**

Sample	Depth (ml)	Temperature (°C)	Dissolved Oxygen (mg/l)	Comments
Top	450	20.8	6.2 - 7.8	Unstirred, fluctuating
Middle	250	20.8	6.1	Stable
Bottom	50	20.8	5.77	Stable

Part B: Measured Water Extracted from Cylinder

Sample	Depth (ml)	Temperature (°C)	Dissolved Oxygen (mg/l)	Comments
Pipette off 150ml	-150	19.7	8.47	new membrane, calibration
	-300	20.7	8.4	
	-450	20.9	8.38	

SEAWATER- THIN SECTION C**Part A: Measured Probe Suspended in Water Column**

Sample	Depth (ml)	Temperature (°C)	Dissolved Oxygen (mg/l)	Comments
Top	450	21.4	4.92 - 6.1	Fluctuating
Middle	250	21.4	4.29	Stable
Bottom	50	21.5	3.34	Stable

Part B: Measured Water Extracted from Cylinder

Sample	Depth (ml)	Temperature (°C)	Dissolved Oxygen (mg/l)	Comments
Pipette off 150ml	-150	20.9	6.32	
	-300	20.3	6.49	Poor pipette –extra air
	-450	21	6.33	

Chapter 6: DISCUSSION AND CONCLUSION

6.1 Introduction

Digital images show that sulphide minerals in thin section submerged under distilled water, freshwater, and seawater all exhibit some degree of change (with the exception of pyrite in distilled). This suggests an overall potential for reactivity of sulphide minerals in a submerged setting. The observed changes which represent reactivity are collectively discussed in terms of image surface analysis and differences in water quality from start to finish. Reactivity is implied directly from observations and supported by past studies and the background information provided in Chapters 1 and 2. The question of whether there is direct evidence of oxidation will be addressed in detail below.

6.2 Sulphide Mineralogy

The microprobe analysis confirmed that the BH-20-II core sample contained pyrrhotite, marcasite, pyrite, chalcopyrite, arsenopyrite and rutile. All of the sulphide minerals and notably pyrrhotite and marcasite are reported in Section 1.3.1 as problematic minerals for ARD in Nova Scotia.

The pyrrhotite in the BH-20-II sample has a Fe/S ratio comparable to the hexagonal and orthorhombic polymorph (Figure 5.1). The stability field for pyrrhotite as demonstrated in the Eh - pH diagram (Figure 2.3), lies farthest away from oxidizing surface waters (refer to Table 5.5). The sample waters in this study carry relatively high dissolved oxygen content and therefore resemble surface waters. It is inferred that sulphide minerals present in the core sample of this study all possess a high potential for reaction in their respective sample water.

6.3 Surface Tarnish as an Indicator of Oxidation

Tarnish was detected in this study by analysis of digital images. The sulphide minerals under each water cover exhibit differing degrees of brown-tarnish and blue-purple reflectance color. In the case of seawater, a deep orange-brown color and obvious changes in mineral topography were evident. In addition, the amount of blue-purple, and orange-brown tarnish increased at later stages between day 15 and day 40 of the experiment. On a larger scale, the orange-brown precipitate found in outcrops and streambeds is a common indicator associated with acid rock drainage. As shown in Figure 2.2, the orange-brown precipitate is probably the reaction product of the hydrolysis of ferric iron to ferric hydroxide. To arrive at this stage, oxidation reactions producing ferrous and ferric iron generate acidity. Therefore, the observation of surface tarnish suggests oxidation of sulphide minerals and ultimately the production of acid.

The interpretation of surface coatings to indicate oxidation reactions of sulphide minerals is supported by the work of Steger (1982) who observed the oxidation of pyrrhotite within a temperature – humidity chamber. This series of quantitative experiments using a spectrophotometer found a correlation between the colors of the surface tarnish and migrating reaction zones of differing thickness corresponding to the extent of oxidation. The cycle of reflectance spectra in Steger's study proceeds from black-brown tarnish → blue-purple → orange-brown corresponding to variable degrees of water-insoluble reaction products, FeSO_4 , $\text{Fe}(\text{OH})(\text{SO}_4)\cdot\text{H}_2\text{O}$, $\text{Fe}(\text{OH})_3$ and S. Steger also states that the formation of Fe oxides and Fe sulphates is an essential factor in the observed reflectance spectra and that oxidation is necessary for the formation of the reaction products.

The Steger (1982) study provides a useful background for the interpretation of oxidation from surface tarnish. However, all reaction products in Steger's study were identified within a

humidity cell, whereas the experiments in this study maintain a high water to rock ratio. Therefore, oxidation products of sulphide minerals immersed in water may be more troublesome to define (refer to Section 6.6).

6.4 Distribution of Tarnish

The distribution of tarnish was not uniform over the surface of individual mineral grains. Surface coatings appeared to initiate along the perimeter of sulphide minerals, particularly adjacent to sulphide inclusions, and eventually covered the surface uniformly. Sulphide minerals in distilled water and seawater developed a similar uniform surface coating after 40 days whereas minerals in freshwater samples experienced reaction only at isolated locations within the pyrrhotite (refer to Figure 5.3D).

It is reasonable to infer that boundaries between minerals are areas of high energy and therefore exist as initial targets for reaction. In addition, minerals often exhibit differences in topography as an artifact of polishing and this may have provided an added opportunity for access to mineral surfaces. Yet this does not explain why the interface between subgrains identified in pyrrhotite did not show enhanced reactivity. It is concluded that the difference in polishing surface topography would be less pronounced among subgrains of the same mineral compared to boundaries between different minerals.

Galvanic effects are another important factor for explaining the localized reaction at an interface between sulphide minerals. Galvanic reactions may affect the amount of sulphide oxidation and can be used to explain which sulphide minerals react first. Different sulphides in close proximity can act like a battery, with one sulphide behaving like the cathode, and the other as the anode (Kwong, 1995). This effect is compatible with observations of enhanced surface tarnish in pyrrhotite adjacent to chalcopyrite both in distilled water (Figure 5.3.1B) and seawater (5.3.3B).

In this case, preferential oxidative dissolution occurs at the anode (pyrrhotite), while protecting the cathode (chalcopyrite) in agreement with studies by Kwong, (1995).

6.5 Water Quality

Acid generated in the oxidation process is considered a reaction product and is also absorbed into the surrounding aqueous medium. The aqueous environment acts as the buffering solution to low amounts of acid released. The resulting overall affect on pH is minimal and therefore it is reasonable to expect water quality results to show no significant change, as found in this study (Table 5.4.B).

The *in situ* measurements of dissolved oxygen obtained by suspending the DO probe directly within the cylinder (Table 5.4.A) are considered more reliable than those obtained by the extraction method (Table 5.4.B). This is attributed to contamination by atmospheric oxygen during removal. In addition, the water column for each sample in this study appeared to have a slightly decreasing oxygen concentration with depth and values between water samples differ only slightly (within 1mg/l). The variable “top” measurements obtained in all water samples using this method are attributed to the constant exchange of atmospheric oxygen at the surface. The “bottom” measurements are approximately 1-2 mg/l less than “top” measurements, yet overall these values are comparable to those found within typical surface waters in Nova Scotia lakes (Freedman, 1989). The ambient oxygen concentration will decrease with an increase in depth in a water column, resulting in decreased oxidation at depth (Figure 2.4, Chapter 2). This implies a process that consumes oxygen at the bottom of a natural water body. As mentioned above, the water samples of this experiment are considered oxidizing and unstable for sulphide minerals. Therefore, the rate of reaction observed in this experiment is likely accelerated compared to an anoxic environment. However, the enhanced rate was needed in order to complete the study in a

reasonable time frame. The enhanced rates do not negate the ability to compare relative reactivity of the different sulphides in the different water types and may be likened to conditions encountered in a well-oxygenated lake such as that of Buttle Lake, BC.

6.6 Relative Differences in Mineral Reactivity under each Water Cover

Natural waters contain a variety of dissolved components. Seawater is an aqueous solution of various salts, and distilled water is a relatively pure water form that still contains fractional amounts of dissolved components, and lakewater contains varying levels of gases, and elementary substances. The very low concentration of dissolved components in distilled water represents a useful end member in this study. The seawater falls at the opposite extreme with typically 35 parts per thousand dissolved solids and high concentrations of Na^+ , Cl^- , and SO_4^{2-} . The lakewater occupies a state in between.

6.6.1 Distilled Water

The reactivity of sulphide minerals in distilled water is moderate compared with seawater (high) and lakewater (low). Only pyrrhotite was reactive, while chalcopyrite and pyrite were unreactive. This result agrees with the relative reactivity observed in other studies, and with the galvanic effects. The initial pH of the distilled water was near neutral (6.7), and dissolved oxygen measurements indicate oxidizing conditions. The greater reactivity of pyrrhotite versus pyrite in slightly oxidizing waters agrees with the Eh / pH diagram (Figure 2.3). As stated above, distilled water is relatively pure, and would therefore have no buffering capacity and small amounts of acid production would be expected to decrease the pH. It was not the case for this experiment, therefore the amount of oxidation must be small and this is reflected in the observations of tarnish.

6.6.2 Lakewater

The reactivity of sulphide minerals in thin section B immersed in freshwater from Lake Banook indicates a low relative rate of reaction over 40 days. Little change was observed following the initial slight reaction of pyrrhotite as inclusions in the first 15 days (Figure 5.3D). In fact, comparison revealed that samples in freshwater reacted less rapidly than those in distilled water even though the pH and dissolved oxygen concentration of the lakewater are very similar to the distilled water values.

There are several possible explanations for the observed reactivity at inclusions in pyrrhotite. The first is that bacterial activity has been initiated in a microenvironment. If this is the case, oxidation must have occurred to initiate the optimal conditions required for survival. Previous studies on the sulphide minerals of the Meguma Supergroup found that galena oxidized much faster than hexagonal pyrrhotite. Therefore, the bright tarnish on the pyrrhotite might result from rapid dissolution of galena inclusions producing a local microenvironment with a lower pH. The nature of the inclusion is speculative as these inclusions were not observed at a studied location and so there are no images from time zero available for comparison.

6.6.3 Seawater

The results of this study indicate the rate of reaction of sulfide minerals under seawater is increased compared to freshwater and distilled water. This reaction took place progressively over 40 days. As the pH level was not acidic prior to or after the experiment, reactions must have been initiated in an alkaline setting.

Several possibilities for the increased reactivity of seawater are proposed. The first concerns the high concentration of dissolved salts (including sodium chloride and sulfate) contained in

seawater. This situation is analogous to the common situation known to create rust on metal surfaces that contain iron. Corrosion occurs by an electrochemical oxidation mechanism that requires a water solution through which ions can move. This process is intensified in seawater, due to the dissolved salts in seawater which supply the ions necessary for the conduction of current. With an adequate amount of dissolved oxygen, provides a recipe for a highly corrosive situation for iron sulfide minerals present in the thin section.

A second possibility is that the reaction rate of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ is accelerated in the set of reactions described in Section 2.1. This can be supported by reference to Singer and Stumm (1970), who found that solutions containing Cl^- (chloride) and SO_4^{2-} (sulfate), as in the case of seawater, accelerate the reaction of ferrous iron to ferric iron at near neutral pH values. Considering that this is the rate limiting step involved in the further oxidative dissolution of sulphide minerals (pyrite), a faster rate would increase the supply of Fe^{3+} and thus feed the propagation cycle, therefore increasing the rate of reaction of sulphide minerals in seawater.

The existence of sulphate in seawater could lead to an earlier appearance of tarnish. According to Le Chatelier's Principle, if a chemical system is disturbed at equilibrium by adding a species (reactant or product), the reaction will proceed to consume part of the added species. Conversely, if the species is removed, the system shifts to store part of that species. Therefore, the higher concentration of sulfate found in seawater may shift the equilibrium towards the precipitate and promote the formation of sulfate coatings on the mineral surfaces, thereby exhibiting an apparent increased rate of reaction. However, the amount of tarnish on the pyrite (Figure 5.3.3C), as evidence from surface topography, suggests an oxidative dissolution of significant depth (possibly several microns). If the same degree of reaction was taking place in all water types,

significant depressions relative to surrounding silicate minerals would be observed, and this was not the case.

6.7 Conclusions and Implications for Subaqueous Disposal

Within the framework of this experimental evaluation, two primary conclusions are apparent. The first is that the reaction rate of pyrrhotite, marcasite, pyrite, and chalcopyrite found in the Meguma Supergroup is higher in seawater compared to freshwater. Secondly, policies and regulations specific to sulphide waste disposal in Nova Scotia focus on terrestrial methods. Furthermore, the legislation for marine or freshwater disposal is prohibited unless granted special permission and regulations (if any) for coastal zones remain ambiguous.

It would not be wise to advocate the subaqueous disposal of sulphidic waste rock into freshwater systems based on a lower reactivity, for several reasons. Each freshwater system is unique and contains a abundant biological and hydrological features. Based on these features, the method of subaqueous disposal is site-specific. In addition, sulphide waste material contained in any natural system is subject to the changes of that natural system. Storage in natural systems could therefore be perceived as a storage site for future generation of ARD. The majority of freshwater systems in southern Nova Scotia lie directly on the Meguma Supergroup. Considering the importance of pH in controlling the rate of reaction for sulphide minerals, an initial lower buffering capacity would not be adequate to neutralize even small amounts of acid produced from oxidizing waste rock and may in fact promote oxidization. Therefore, the implementation of subaqueous disposal in southern Nova Scotia must incorporate additional field studies, empirical data and well defined and enforceable regulatory procedures.

6.8 Recommendations and Future Studies

Future studies would benefit from the use of an ore microscope with a rotating stage to map thin sections prior to experimentation. The automated x / y stage was a useful tool in order to keep samples in the same orientation and to relocate specific regions quickly. In contrast, it was difficult to distinguish specific characteristics of the sulphide minerals in this study because the stage could not be rotated. Another advantage would be to use the computer control option for the stage to image the entire thin section. This would allow for quick data acquisition and an increased number of study sites on the thin section. As a result, it would be possible to capture a larger representative sample of results, thereby increasing precision.

Digital imaging produced clear images that were easy to assess. However, the consistency of color and intensity values of the software over the duration of the experiment must be improved. It would be useful to have an effective calibration surface material for the camera system. Such calibration material must remain stable over long time periods. In addition, the CCD camera was approximately ten years old and an updated version might have produced better images.

Small dark lines were observed as an additional surficial feature. These linear features are considered to result from delamination of the thin section from the microscope slide. The surface “etch” marks noted in each thin section correspond to the recorded appearance of cracks and after the first six days. Regions less affected by delamination also displayed fewer linear features. For future experimentation, a thin section cement with greater water resistance should be used.

Future studies regarding subaqueous disposal would benefit from the investigation of other specific components. For instance, this study did not examine water chemistry in detail; therefore, it would provide greater insight to measure the water chemistry prior to and throughout the experiment. This would enable the identification and control of dissolved components that control

reactivity. Primarily, this could allow for correlation of changes with the concentration of dissolved oxygen. A low pH for the initial solution state could simulate a lower water-rock ratio. It may also prove advantageous to evaluate the influence of surface area of the sulphide-bearing material and the effects of pre-oxidized waste rock in a submerged setting. In addition, this study considered primarily abiotic, relative reaction rates under water, and therefore, it is imperative to assess the role of bacteria present in freshwater or marine environments. Finally, considering the site-specific nature of subaqueous disposal, experiments in natural settings would be beneficial prior to subaqueous disposal of sulphide-bearing waste rock.

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APPENDIX A: Microprobe Data

Mineral	Spot #	Cu	Fe	As	S	Ni	Zn	Ti	Total	Comment
pyrrhotite	1	0.00%	50.04%	0.14%	49.11%	0.71%	0.00%	0.00%	100.1%	
pyrrhotite	2	0.00%	47.11%	0.14%	52.68%	0.08%	0.00%	0.00%	99.67%	
inclusion	3	0.00%	7.09%	0.00%	50.35%	0.00%	42.56%	0.00%	96.41%	
inclusion	4	0.00%	3.77%	0.00%	49.88%	0.00%	45.99%	0.00%	65.31%	out of focus
pyrrhotite	5	0.00%	47.22%	0.00%	52.69%	0.09%	0.00%	0.00%	100.5%	perimeter
pyrrhotite	6	0.00%	47.27%	0.18%	52.47%	0.09%	0.00%	0.00%	101.2%	
chalcopyrite	7	24.22%	26.40%	0.00%	49.39%	0.00%	0.00%	0.00%	99.41%	
pyrite	8	0.00%	34.44%	0.00%	65.51%	0.05%	0.00%	0.00%	100.0%	
pyrite	9	0.00%	34.80%	0.00%	65.13%	0.07%	0.00%	0.00%	97.92%	
pyrite	10	0.00%	33.80%	0.00%	66.01%	0.18%	0.00%	0.00%	101.1%	
pyrite	11	0.00%	34.11%	0.13%	65.77%	0.00%	0.00%	0.00%	101.9%	
marcasite	12	0.00%	33.88%	0.14%	65.98%	0.00%	0.00%	0.00%	102.2%	irregular grain
marcasite	13	0.00%	33.85%	0.00%	66.15%	0.00%	0.00%	0.00%	102.1%	error
marcasite	14	0.00%	34.27%	0.00%	65.73%	0.00%	0.00%	0.00%	102.3%	Irregular grain
pyrrhotite	15	0.00%	47.49%	0.00%	52.45%	0.07%	0.00%	0.00%	100.4%	
pyrrhotite	16	0.00%	47.50%	0.00%	52.42%	0.08%	0.00%	0.00%	101.0%	
pyrrhotite	17	0.00%	47.63%	0.00%	52.65%	0.09%	0.00%	0.00%	101.3%	
rutile	18	0.00%	1.15%	0.00%	0.00%	0.00%	0.00%	92.0%	50.49%	not calibrated

APPENDIX B: Digital Image Catalogue

List of digital images

FILES CREATED

January 7th, 8th, 1999

Set-up

-microscope-

- blue filter out
- light source 5.5 volts
- files saved under C:\dvp\work\xpt\start.bmp
- filename: slide letter, location, magnification, np- no polarizer, p, polarizer, xp- cross polars

Thin Section Description

Elongate, pyrrhotite lenses aligned parallel to cleavage planes. Thin sections labelled # BH- 20-II, A- E. A-D have been observed, mapped, described, and digitally photographed. Sample location is HIA

Table

The following table records all filenames and attributes of the frames produced at 0 days. An attempt was made to be consistent with colour (c), tint (t), saturation (s), and brightness (b). Three main locations were chosen on each thin section, a pyrite grain, a pyrrhotite with chalcopyrite, and pyrrhotite.

Table of Digital Photographs

Filename	c	t	s	b	Comments / Description
a1-20np	70	200	63	150	pyrite, arsenopyrite (?)
a1-10np	70	200	63	134	
a1-5np	70	200	62	118	unfocussed, not a useful picture
a2-20np	70	208	63	158	section of a pyrrhotite grain, with smaller inclusions
a2-10p	70	208	63	150	
a2-5p	70	208	63	134	
a3-20p	70	200	63	158	Pyrrhotite grain with chalcopyrite (reference point- grid A-J across the pyrrhotite)
a3-10p					
a3-10xp	80	128	63	134	A-in, sequence of frames saved to average together, show subgrains
a3-10np	80	128	63	102	*** good
A3-5np	64	128	63	102	
A3-5p	64	128	63	142	Too dark
B1-20np	88	128	63	62	Pyrrhotite grain rimmed with chalcopyrite, and light grey material (?)
B1-20xp	79	128	63	146	Trying for subgrains but its too dark
B1-10np	80	128	63	102	Fine fractures but the 20X is better
B1-10xp	117	128	63	134	Subgrains, A-in
B1-10p	55	128	63	92	A-in, too dark, badly focussed
B1-5np	64	128	63	102	
B1-5xp	117	128	63	134	Subgrains visible

B1-5p	64	152	63	78	
B2-20np	62	160	95	94	Pyrite, pyrrhotite
B2-20p	62	160	95	94	Too dark, tint is green A-in
B2-10p	94	160	103	90	
B2-5np	62	160	95	94	
B3-20np	80	128	63	102	Standard values for video source-pyrite
B3-20p	80	128	63	102	
B3-20xp	72	128	63	142	
C1-20np	62	160	95	94	***good, pyrite
C1-10np	62	160	95	94	
C1-5np	62	160	95	94	
C2-20np	80	128	63	102	Pyrrhotite with inclusions (illmenite?)
C2-10np	80	128	63	102	
C2-5np	80	128	63	102	
C2-5xp	80	128	63	102	subgrains visible
C3-20np	80	128	63	102	Pyrrhotite with chalcopyrite
C3-20xp	80	128	63	102	Subgrains visible
C3-20p	80	128	63	102	***good
C3-10p	64	128	63	110	
C3-10xp	64	128	63	110	
C3-10np	80	128	63	102	
C3-5np	80	128	63	102	
C3-5xp	80	128	63	102	
C3-5p	64	128	63	110	
D1-20np	62	160	95	94	Pyrite

D1-10np	62	160	95	94	
D1-5np	62	160	95	94	
D2-20np	80	128	63	102	Pyrrhotite and chalcopyrite
D2-20xp	64	128	63	110	
D2-10np	80	128	63	102	
D2-10xp	64	128	63	110	
D2-5np	80	128	63	102	
D2-5xp	64	128	63	110	Not useful
D3-20np	80	128	63	102	Pyrrhotite
D3-20xp	46	128	63	134	Saved as sequence of frames, subgrains visible
D3-10np	80	128	63	102	
D3-10xp	46	128	63	134	Saved as sequence of frames, subgrains visible
D3-5np	80	128	63	102	
D3-5xp	46	128	63	134	Saved as sequence of frames, subgrains visible
E1-20np	80	128	63	134	Pyrrhotite
E1-10np	80	128	63	134	
E1-10xp	46	128	63	134	
E1-5np	80	128	63	134	
E2-20np	80	128	63	134	Chalcopyrite, pyrrhotite
E2-20xp	46	128	63	134	
E2-10np	80	128	63	134	
E3-20np	62	160	95	94	Pyrite
E3-10np	62	160	95	94	
E3-5np	62	160	95	94	Not good

Photographs- Time Zero

Monday, January 11th, 1999

Set-up

Thin section orientation- 95 044/ left / reversed. Film- kodak gold, ASA 100, 36 exp.

Light source is 11 volts. Magnification on microscope- 1,0X. Blue filter in. Photos taken at three locations on each thin section, under 0, and -1, exposure adjustment.

Under plane polarized light and x-polars (A-in) at 5X, 10X, 20X magnification.

Frame # (photo)	Thin Section Location	Exposure Time at 0 sec	Exposure Time at -1 sec	Comments / Description
1, 2	A1-20p	1.12	.56	Pyrite
3, 4	A1-10p	2.24	1.12	
5, 6	A2-10p	.89	.45	Pyrrhotite
7, 8	A2-5p	.71	1.41	
9, 10	A3-20p	.63	.31	Pyrrhotite, chalcopyrite
11,12	A3-10xp	4.49	2.24	Subgrains visible
13, 14	A3-10np	.18	.11	
14, 15	B1-20np	.18	.09	Pyrrhotite, chalcopyrite
16, 17	B1-10xp	5.04	2.52	
18, 19	B2-20np	.45	.22	Pyrite
20, 21	B2-10p	.45	.22	

22, 23	B3-20np	.25	.13	Pyrrhotite
24, 25	B3-20xp	4.49	2.24	
26, 27	C1-20np	.16	.8	Pyrite
28, 29	C1-10np	.35	.18	
30, 31	C2-20np	.28	.14	Pyrrhotite
32, 33	C3-10xp	5.66	2.83	Subgrains
34, 35	C3-10np	.25	.13	
Film #2				
1, 2	C3-10xp	4.00	2.00	
3, 4	D1-20np	.14	.07	Pyrite
5, 6	D1-10np	.18	.9	
7, 8	D2-20np	.18	.9	Pyrrhotite, chalcopyrite
9, 10	D2-10np	.22	.11	
11, 12	D2-10xp	5.04	2.52	Subgrains
13, 14	D3-20np	.2	.1	Pyrrhotite
15, 16	D3-10np	.18	.9	
17, 18	D3-10xp	4.00	2.00	Subgrains
19, 20	E1-20np	.18	.9	Pyrrhotite
21, 22	E1-10np	.2	.1	
23, 24	E1-10xp	3.77	1.59	Subgrains
25, 26	E2-20np	.22	.11	Pyrrhotite, chalcopyrite
27, 28	E2-10np	.22	.11	
29, 30	E2-20xp	4.00	2.00	Subgrains
31, 32	E3-20np	.31	.16	Pyrite
33, 34	E3-10np	.56	.28	

35				10X magnification scale
36				20X magnification scale