Reaction Modeling of Drainage Quality in the Duluth Complex, Northern Minnesota, USA

Robert Seal[1], Kim Lapakko[2], Nadine Piatak[1] and Laurel Woodruff[1]

1. *U.S. Geological Survey*
2. *Minnesota Department of Natural Resources (retired), USA*

ABSTRACT

Reaction modeling can be a valuable tool in predicting the long-term behavior of waste material if representative rate constants can be derived from long-term leaching tests or other approaches. Reaction modeling using the REACT program of the Geochemist's Workbench was conducted to evaluate long-term drainage quality affected by disseminated Cu-Ni-(Co-)-PGM sulfide mineralization in the basal zone of the Duluth Complex where significant resources have been identified. Disseminated sulfide minerals, mostly pyrrhotite and Cu-Fe sulfides, are hosted by clinopyroxene-bearing troctolites. Carbonate minerals are scarce to non-existent. Long-term simulations of up to 20 years of weathering of tailings used two different sets of rate constants: one based on published laboratory single-mineral dissolution experiments, and one based on leaching experiments using bulk material from the Duluth Complex conducted by the Minnesota Department of Natural Resources (MNDNR). The simulations included only plagioclase, olivine, clinopyroxene, pyrrhotite, and water as starting phases. Dissolved oxygen concentrations were assumed to be in equilibrium with atmospheric oxygen. The simulations based on the published single-mineral rate constants predicted that pyrrhotite would be effectively exhausted in less than two years and pH would rise accordingly. In contrast, only 20 percent of the pyrrhotite was depleted after two years using the MNDNR rate constants. Predicted pyrrhotite depletion by the simulation based on the MNDNR rate constant matched well with published results of laboratory tests on tailings. Modeling long-term weathering of mine wastes also can provide important insights into secondary reactions that may influence the permeability of tailings and thereby affect weathering behavior. Both models predicted the precipitation of a variety of secondary phases including goethite, gibbsite, and clay (nontronite).

INTRODUCTION

Predicting long-term weathering behavior of mine waste, though a formidable challenge, holds great importance for the mining industry. Traditional static tests, such as acid-base accounting, provide information about maximum potential acidity, but offer no insight about how that acidity may evolve over time. Results from static tests have great value as screening tools, which form the basis for more costly and labor-intensive studies, such as kinetic tests. Kinetic tests, such as humidity-cell experiments, provide empirical information about the time-dependent weathering of mine waste, but are generally limited by the experimental duration. The longest duration leaching experiments are probably those conducted by the Minnesota Department of Natural Resources (MNDNR), which have been ongoing for more than 24 years, on waste rock from the Duluth Complex, northern Minnesota (Kellogg et al., 2014). The MNDNR also has weathering test results from ongoing 10-year experiments on tailings derived from pilot metallurgical tests on Duluth Complex low-sulfide ores hosted by troctolitic rocks (Lapakko, Olson & Antonson, 2013a). For permitting purposes, time scales of these lengths are challenging as is scaling laboratory tests up to a mine scale. Barrel tests and instrumented tests on waste-rock and tailings piles are being used once mine development has begun to help address this challenge (Smith et al., 2013; Lindsay et al., 2009).

Uncertainty about the long-term behavior of mine waste clouds the decision-making process for many mine-permit applications. Extrapolating laboratory results significantly into the future has significant uncertainty, particularly for experiments in which the acid-generating potential has not been exhausted. This report explores the possibility of using geochemical reaction modeling to predict the long-term weathering behavior of mill tailings from low-sulfide Duluth Complex Cu-Ni-(Co)-PGM ores (Fig. 1). Acid-generating potential is the initial focus of this ongoing study. Major and trace element behavior will be a future emphasis.

The Duluth Complex of northern Minnesota has high potential for future mining of large tonnage, low grade Cu-Ni-(Co)-PGM resources (Ripley, 2014). Collectively, estimated reserves exceed 4.4 billion tons with approximately 0.66 percent Cu, 0.2 percent Ni, and total PGMs ranging between 0.3 and 0.6 mg/kg (Pd > Pt) (Listerud and Meineke (1977). The ores are found in troctolites and gabbros in the lower 100 to 300 m of the Partridge River and South Kawishiwi intrusions (Fig. 1) (Ripley, 2014). The host rocks comprise plagioclase, clinopyroxene, and olivine, with minor amounts of orthopyroxene, biotite, potassium feldspar, and ilmenite; the rocks are essentially devoid of carbonate minerals (Lapakko, Olson & Antonson, 2013a; Ripley, 2014). The principal sulfide minerals are pyrrhotite, chalcopyrite, cubanite, and pentlandite.

METHODOLOGY

Conceptual framework

The goal of this study is to explore the feasibility of using geochemical reaction computer software to model the long-term weathering behavior of tailings generated from the disseminated, low-sulfide ores at the base of the Duluth Complex for time periods spanning decades. The 10-year weathering test results for pilot-test tailings from the Duluth Complex low-sulfide ores are used as a basis to validate various simulation parameters (Lapakko et al., 2013a). The disseminated sulfide ores at the base of the complex are characterized by a low sulfide content (generally < 1 wt. % S)

and virtually no carbonate minerals (Lapakko and Antonson, 2012; Lapakko, Olson & Antonson, 2013a; Ripley, 2014). Thus, the acid-neutralizing potential of the mine waste is supplied by silicate minerals such as plagioclase, olivine, and pyroxene.
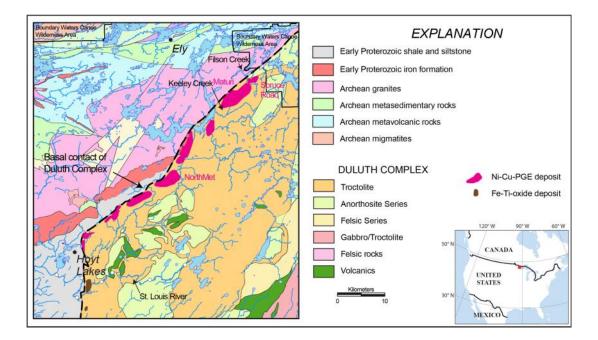

Figure 1 Geologic map of the Duluth Complex and older rocks in the vicinity of the disseminated Cu-Ni-(Co)-PGM deposits.

Software

The software package used in this study is the suite of programs included in the Geochemist's Workbench, primarily the program REACT (Bethke, 2008; Bethke and Yeakel, 2014). REACT simulates the reaction of a specified mass of solid with 1 kg of solution. Equilibrium modeling titrates increments of the solid into the solution, following a specified number of steps, allowing reaction progress to be followed. Kinetic modeling, using user-defined rate constants for solids, reacts a specified amount of solids with 1 kg of solution for a specified amount of time.

Thermodynamic and Kinetic Data

This study used the Lawrence Livermore National Laboratory (LLNL) thermodynamic database supplied with the Geochemist's Workbench for these simulations, because it contained data applicable to the silicate, sulfide, and sulfate phases included in the study. Two sets of kinetic data were used. The first set is the compilation of published single-mineral rate constants from Palandri & Kharaka (2004). The second set, from Kellogg et al. (2014), is based on normative-style calculations from weathering tests on waste rock from the Duluth Complex.

The initial system

The model system used in this study is based on the 10-year laboratory weathering tests by Lapakko, Olson & Antonson (2013a) performed in small reactors on mill tailings derived from metallurgical testing. The sample comprised plagioclase (An$_{57}$; 57 %), clinopyroxene (X$_{Mg}$ 0.77; 11 %), olivine (X$_{Mg}$ 0.55; 9.8 %), quartz (9.8 %, assumed to be contamination of the sample from the country rock), and biotite (X$_{Mg}$ 0.65; 5.7 %) with trace amounts of ilmenite, potassium feldspar, and orthopyroxene. The sample contained 0.2 wt. % sulfur, assumed for the purposes of modeling to be present as pyrrhotite, which is known to be the most common sulfide mineral in the Duluth Complex (Ripley, 2014). Lapakko, Olson & Antonson (2013a) were only able to identify chalcopyrite in their mineralogical characterization of their tailings sample, but they assumed the presence of both pyrrhotite and pentlandite.

For this exercise, the mineralogy of the starting model system was simplified to consist of plagioclase, clinopyroxene, olivine, and pyrrhotite. To account for solid-solution effects, the two end members of binary solid-solution series were included in proportion to the average composition for these minerals as described by Lapakko, Olson & Antonson (2013a). Thus, the simulations included plagioclase as both albite and anorthite, clinopyroxene as diopside and hedenbergite, and olivine as forsterite and fayalite. Pyrrhotite was assumed to be stoichiometric troilite (FeS). The masses of these phases, normalized to 100 percent, are presented in Table 1.

Table 1 Mineralogical composition of model system and dissolution rate constants.

Mineral	Component	Abundance	Surface Area	Rate Constant (k)	Rate Constant (k)
Units		mass %	cm^2 g^{-1}	mol cm^{-2} sec^{-1}	mol cm^{-2} sec^{-1}
Source		Lapakko, Olson & Antonson (2013a)	Estimated This Study	Palandri & Kharaka (2004)	Kellogg et al. (2014)
Plagioclase	Albite	31.1	330.0	2.75E-17	6.2E-17
	Anorthite	41.2	330.0	1.6E-15	6.2E-17
Clinopyroxene	Diopside	10.7	330.0	1.1E-16	8.8E-16
	Hedenbergite	3.2	330.0	1.1E-16	8.8E-16
Olivine	Forsterite	7.1	330.0	1.0E-14	1.4E-16
	Fayalite	5.7	330.0	2.0E-15	1.4E-16
Pyrrhotite	Pyrrhotite	1.0	330.0	2.0E-12	2.2E-14

The grain size and surface area of reacting phases were estimated on the basis of the particle-size distribution data of Lapakko, Olson & Antonson (2013a). All minerals were assumed to have the same particle size (Table 1).

A dilute surface-water solution was chosen from Filson Creek, upstream of the mineralized basal zone of the Duluth Complex (Piatak et al., 2015; Table 2). At an active mine, waters percolating through tailings piles will likely be a combination of process water and local precipitation. The solution was assumed to be saturated with respect to atmospheric oxygen and buffered by the atmosphere.

Table 2 Starting solution composition for modeling simulations

Parameter	Units	Concentration
pH	S.U.	6.7
Na	mg L^{-1}	1.3
K	mg L^{-1}	0.2
Ca	mg L^{-1}	3.7
Mg	mg L^{-1}	2.8
Al	mg L^{-1}	0.1
Fe	mg L^{-1}	0.1
SiO$_2$	mg L^{-1}	1.0
SO$_4^{2-}$	mg L^{-1}	1.6
HCO$_3^-$	mg L^{-1} as CaCO$_3$	12.2
Cl	mg L^{-1}	1.0

Modeling Approach

This modeling exercise attempts to reproduce the laboratory weathering results of Lapakko, Olson & Antonson (2013a), focusing on acid generation and neutralization, and sulfur geochemistry. The tailings examined by Lapakko, Olson & Antonson (2013a) had an acid-generating potential (AP) of 6.2 kg CaCO$_3$/t and an acid-neutralizing potential (NP) of 19 kg CaCO$_3$/t, which results in a neutralizing potential ratio (NPR) of 3.1, and a classification of "not potentially acidic drainage generating". Their study was designed to investigate mineral dissolution rates under air saturated conditions rather than to simulate field conditions. Additional information that is useful for validation purposes can be found in Lapakko, Olson & Antonson (2013b), Lapakko et al. (2013), and Wenz et al. (2013). For the weathering tests on tailings (Lapakko, Olson & Antonson, 2013a), pH dropped from a starting value of approximately 7.5 to a minimum value of approximately 6.4 over the course of the 10-year experiment. The pH drop was most rapid in the first year of the experiments, and showed generally gradual decreases for the remainder of the experiments. Sulfate was released at the greatest rates in the first two years of the experiment and then leveled off. At the end of 10 years, the amount of remaining sulfur in the solids was between 45 and 49 percent of the starting concentration (0.2 wt. %). In contrast, Kellogg et al. (2014) conducted similar tests on waste rock (75 g; particle size 50 – 150 μm diameter) of varying starting sulfide sulfur contents ranging from 0.18 to 1.64 wt. %. In these experiments, pH started at near-neutral values (7 – 8), but reached minimum values of approximately 3 in the most sulfur-rich samples. The pH profiles were more complex with the high sulfur samples exhibiting increased pH values after reaching their minima. Sulfate release was similarly complex, with significant release early and a decrease over time, followed by maxima that correlated with pH minima in the high sulfur samples. In these experiments, the amount of sulfur remaining in the solids ranged between 0 and 55 percent of the starting concentration.

Using the starting conditions described above, the interaction of the solution with tailings was simulated by allowing fixed amounts of solids to react with 1 kg of solution for either 10 or 20 years. Under these scenarios, the sensitivity of the simulations was evaluated by using the different sets of rate constants described above, by varying the water/rock ratio, changing the starting concentration of sulfide-sulfur, and by changing the pyrrhotite dissolution rate constant relative to silicate rate constants. The pH of the model simulations is the primary screening tool to assess the success of the modeling at this stage, followed by the sulfur geochemistry.

RESULTS AND DISCUSSION

Rate Constants

Two sets of rate constants for the dissolution of silicate minerals and pyrrhotite were used in this study (Table 1): (1) Those based on single-mineral laboratory experiments compiled from the literature (Palandri & Kharaka, 2004); and (2) Those based on weathering tests on waste rock from the Duluth Complex (Kellogg et al., 2014). The variation of pH over the course of a 10-year simulation shows distinct differences between the two sets of rate constants (Fig. 2a). The simulations based on the MNDNR (Kellogg et al., 2013) values show a steady decrease from the starting value (6.7) to a value of 6.3 at 10 years, which is similar to pH evolution observed in the weathering tests of Lapakko, Olson & Antonson (2013a). In contrast, the rate constants based on single-mineral laboratory experiments have a distinctly different pattern. This simulation has a more rapid drop in pH, reaching a mínimum of approximately 5.8 between Years 1 and 2, followed by an increase in pH to approximately 8.4 in Year 9. Therefore, the rate constants based on single-mineral experiments predict the exhaustion of acid-generating potential from pyrrhotite and acid-neutralization by silicates that are significantly faster than the empirical observations in the tailings weathering tests (Lapakko, Olson & Antonson, 2013a). However, the rate constants based on the weathering tests on Duluth Complex waste rocks provide a better description of the pH evolution in the tailings weathering tests. Kellogg et al. (2014) summarized their pyrrhotite dissolution rate constants in terms of minimum, maximum, and average values. A comparison of these values, and that of Palandri & Kharaka (2004) relative to the MNDNR silicate rate constants shows that the MNDNR maximum value best describes the tailings weathering test (Fig. 2b). The MNDNR silicate rates were used for the remainder of the simulations. Because of the limited pH range shown by the experiments of Lapakko, Olson & Antonson (2013a), the silicate dissolution rates were assumed to be constant.

Water/Rock Ratio

The water/rock ratio of the experiment has a profound effect on the resulting pH of the simulation. Weathering tests using 1 kg of solid, which is leached with 0.5 kg of water on a weekly basis, would be exposed to a water/rock ratio of 26/1 per year or 260/1 over the course of 10 years. Simulations were made using water/rock ratios of 1/1, 10/1, 100/1, 260/1, and 1000/1 (Fig. 3). Based on these results, the water-dominated simulations appear to describe the tailings weathering experiments better than that the rock-dominated simulations. The water/rock ratio corresponding to 10 years of weathering tests (260/1) results is a lower pH than observed, which suggests that: (1) the effective reactive (i.e., exposed) mass of pyrrhotite may be significantly less than the total present; (2) the pyrrhotite dissolution rate constant used is too fast; (3) that the silicate dissolution rate constants are too slow; or (4) a combination of these factors.
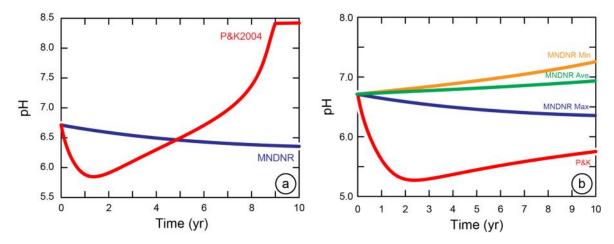
Figure 2 Comparison of rate constants for the dissolution of minerals in tailings. a. Comparison of single-mineral constants (P&K2004, Palandri & Kharaka, 2004) and empirical constants (MNDNR, Kellogg et al., 2014); b. Comparison of pyrrhotite dissolution constants from Kellogg et al. (2014) for their maximum (MNDNR Max) average (MNDNR Ave) and minimum (MNDNR Min) observed rates and from Palandri & Kharaka (2004; P&K).

Effect of Sulfide Content

The sulfide content of mine waste determines its acid-generating potential. To assess the sensitivity of the model simulations to sulfide content, simulations were run at various sulfide contents that span the range that has been observed in the ores in the basal zone of the Duluth Complex: 0.2, 0.5, 1.0, and 2.0 wt. % S (Kellogg et al., 2014; Lapakko, Olson & Antonson, 2013a, b; Fig. 4a). The simulations show the influence of sulfide content on pH. The simulations with the highest sulfide content produced the lowest pH values, reaching a low of 3 in the simulation with 2 wt. % S. These relationships of sulfide content to pH variations are similar to those observed by Kellogg et al. (2014) for weathering tests on waste rock from the Duluth Complex. They divided their samples into three groups on the basis of sulfide content and origin of sample material. Their Group I (0.18 – 0.22 wt. % S) produced pH values above 6, Group II (0.4 – 0.58 wt. % S) reached a low of approximately pH 3.5, and Group III (0.71 – 1.64 wt. % S) reached a low of pH 3.

The effectiveness of this modeling approach can also be evaluated by comparing the predicted depletion of sulfide-sulfur in the tailings with observed depletion in the weathering tests (Lapakko, Olson & Antonson, 2013a). Figure 4b shows both the measured depletion of pyrrhotite (red dots) and the predicted depletion of pyrrhotite (blue line) with time. The measured depletion reflects a greater initial loss of pyrrhotite in the first year, perhaps due to oxidation of very fine sulfide grains, but the rate slows in subsequent years compared to the predicted loss of pyrrhotite. However, the general agreement between the observed and predicted depletion of pyrrhotite indicates that the model provides a reasonable description of pyrrhotite weathering.
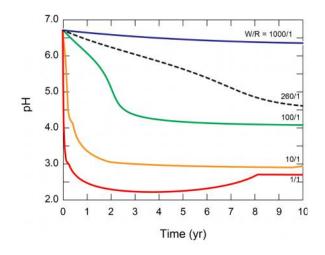
Figure 3 The effect of water rock ratio on the pH variation of 10-year model simulations.
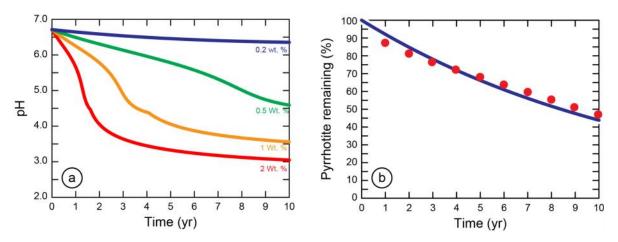

Figure 4 Influence of sulfur geochemistry. a. The effects of different total sulfide contents on pH. b. Comparison of predicted (blue line) with observed depletion of sulfide-sulfur (red dots).

Long-Term Implications

The effectiveness of REACT to describe the general aspects of tailings weathering for the low-sulfide ores of the Duluth Complex suggests that useful insights can be gained from reaction modeling. The pH reaches a minimum around Year 13 (Fig. 5a), indicating that the amount of pyrrhotite has been exhausted to the point where the rate of acid neutralization exceeds the rate of acid generation. The pyrrhotite content at the end of year 20 is predicted to be 20 percent of the starting concentration.
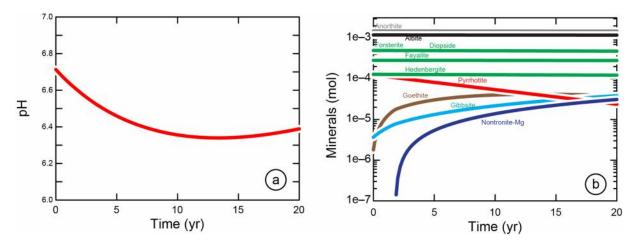
8

Figure 5 Twenty-year simulation of the weathering of low-sulfide tailings from the Duluth Complex. a. Variation of pH with time. b. Variation of primary and secondary minerals

The simulation indicates that pyrrhotite dissolution occurs at a much greater rate than plagioclase, olivine, and clinopyroxene dissolution (Fig. 5b). The simulation predicts the secondary phases, including aluminum and ferric hydroxides, and clay (nontronite), should form (Fig. 5b). In a tailings pile, these secondary phases could decrease permeability and limit weathering rates. The sulfate salts gypsum and epsomite are predicted to be significantly undersaturated throughout at the simulation at high water/rock ratios. However, at low water/rock ratios, gypsum becomes saturated. Thus, gypsum may be an important secondary phase that could limit the infiltration of water in the vadose zone of tailings storage facilities.

CONCLUSION

In concert with established methods, computer-based reaction modeling represents another promising tool to assess the long-term behavior of tailings. One of the greatest limitations for applying this approach is the lack of appropriate rate constants for mineral dissolution. Rate constants derived from single-mineral laboratory experiments appear to be unrealistically fast to describe weathering tests. Rate constants based on weathering tests are more realistic, but their derivation is more problematic because multiple minerals are dissolving simultaneously in these experiments. Long-term simulations can identify potential secondary phases that can influence the permeability of tailings and affect their weathering behavior, and thus permit a more insightful interpretation of other types of mine-waste weathering data.

ACKNOWLEDGEMENTS

REFERENCES

Bethke, C.M. (2008) *Geochemical and Biogeochemical Modeling*, Cambridge University Press, Cambridge, UK, 2nd Edition, 543 p.

Bethke, C.M., and Yeakel, S. (2014) *Reaction Modeling Guide, The Geochemist's Workbench, Release 10.0*. Aqueous Solutions LLC, Champaign, Illinois, 98 p.

Kellogg, C., Lapakko, K., Olson, M., Jenzen, E., and Antonson, D. (2014) Laboratory dissolution of blast hole samples of Duluth Complex rock from the South Kawishiwi Intrusion: Twenty-four year laboratory experiment, Minnesota Department of Natural Resources Report, 314 p. Accessed 16 Sept. 2014 at http://files.dnr.state.mn.us/lands_minerals/reclamation/mndnr_blast_hole_expt_2014.pdf

Lapakko, K.A., and Antonson, D.A. (2012) Duluth complex rock dissolution and mitigation techniques: A summary of 35 years of DNR research 51 p. Accessed 16 Sept. 2014 at http://files.dnr.state.mn.us/lands_minerals/reclamation/mndnr_research_summary_2012.pdf

Lapakko, K.A., Olson, M.C., and Antonson, D.A. (2013a) Duluth Complex tailings dissolution: Ten-year laboratory experiment, Minnesota Department of Natural Resources Report, 54 p. Accessed 16 Sept. 2014 at http://files.dnr.state.mn.us/lands_minerals/reclamation/mndnr_dc_tailings_2013.pdf

Lapakko, K.A., Olson, M.C., and Antonson, D.A. (2013b) Dissolution of Duluth Complex Rock from the Babbitt and Dunka Road Prospects: Eight-year laboratory experiment, Minnesota Department of Natural Resources Report, 88 p. Accessed 16 Sept. 2014 at http://files.dnr.state.mn.us/lands_minerals/reclamation/mndnr_dc_wasterock_2013.pdf

Lapakko, K., Leopold, L., Mehleis, E., Theriault, S., Jagunich, A., and Antonson, D.,(2013) Subaqueous Disposal of Sulfidic Waste Rock: Seven-year laboratory column experiment, Minnesota Department of Natural Resources Report, 62 p. Accessed 16 Sept. 2014 at http://files.dnr.state.mn.us/lands_minerals/reclamation/mndnr_subaqueous_columns_2013.pdf

Lindsay, M. B., Condon, P. D., Jambor, J. L., Lear, K. G., Blowes, D. W., and Ptacek, C. J. (2009) Mineralogical, geochemical, and microbial investigation of a sulfide-rich tailings deposit characterized by neutral drainage. Applied Geochemistry, v. 24, p. 2212-2221.

Listerud, W.H., and Meineke, D.G. (1977) Mineral resources of a portion of the Duluth Complex and adjacent rocks in St. Louis and Lake counties, northeastern Minnesota. Minnesota Department of Natural Resources, Division of Minerals, Report 93, 74 p.

Palandri, J.L., and Kharaka, Y.K. (2004) A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. U.S. Geological Survey Open-File Report 2004-1068, 64 p.

Piatak, N.M., Seal, R.R., II, Jones, P.M., and Woodruff, L.G. (2015) Copper toxicity and organic matter: Resiliency of watersheds in the Duluth Complex, Minnesota, USA. Proceedings, ICARD-IMWA2015, 10 p.

Ripley, E.M. (2014) Ni-Cu-PGE Mineralization in the Partridge River, South Kawishiwi, and Eagle Intrusions: A Review of Contrasting Styles of Sulfide-Rich Occurrences in the Midcontinent Rift System. Economic Geology, v. 109, p. 309-324.

Smith, L. J., Moncur, M. C., Neuner, M., Gupton, M., Blowes, D. W., Smith, L., and Sego, D. C. (2013) The Diavik Waste Rock Project: Design, construction, and instrumentation of field-scale experimental waste-rock piles. Applied Geochemistry, v. 6, p. 187-199.

Wenz, Z., Lapakko, K., and Antonson, D. (2013) Rock composition, leachate quality and solute release as a function of particle size for three waste rock types: An 18-year laboratory experiment, Minnesota Department of Natural Resources Report, 117 p. Accessed 16 Sept. 2014 at http://files.dnr.state.mn.us/lands_minerals/reclamation/the_particle_size_experiment_report_2013.pdf