



# The Diavik Waste-Rock Project: Factors controlling sulfide oxidation at the micro and macro scale.

21th ANNUAL BRITISH COLUMBIA-MEND ML/ARD WORKSHOP

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# **Site Location**







#### Zone of continuous permafrost MAAT ~ -9°C

#### Research Goals – Sulfide Oxidation in a Permafrost Region

 Understand the geochemical, hydrological, and thermal conditions controlling the generation of acidic leachate from waste rock stockpiles in a permafrost environment

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## **Research Goals: Micro- to Macro-Scale**

- Scaling the temporal evolution of sulfide mineral weathering from laboratory to field systems
  - Improving the conceptual model
  - Developing more representative reactions rates





## **Test Piles Research Area**



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Active Zone Lysimeters

**Covered Test Pile** 

Type I Test Pile 0.035 wt.% S.

Type III Test Pile 0.053 wt.% S. 3 m Type I 1.5 m Till 13 m Type III 0.082 wt. % S

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# **Research Facilities**

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- Laboratory humidity cell experiments
  - 18 Cold room (4 °C)
  - 18 Room Temperature (22 °C)
- Instrumented full-scale waste rock dump
  - 4 x 40 m vertical drill holes
  - 1 x 80 m vertical drill hole
  - horizontal instrument string









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• We see this...

G





 and we want to envision this...









#### but what we have is this.











# Need to correlate sulfur evolution with metal products



#### Fe oxides

Fe (oxy)hydroxides (e.g., FeO(OH))

Intermediaries (other polysulfides, sulfite, thiosulfate, elemental S)

S-enriched layer (e.g., FeS<sub>2</sub>)

Unreacted pyrrhotite surface



# **Grain Scale Alteration**

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# **Element Relations**

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• Relation of Fe, Ni, and S within the grain system



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# Small Difference in Mineralogy and Changes in the Weathering Environment

 Strong differences in mineral oxidation with variations in weathering in the same climate

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# Estimates of Net Infiltration to Crest of Type III pile (Penman-Monteith)

Year	Rainfall (mm)	Estimated Net Infiltration	<b>Percent Net Infiltration</b>
		(mm)	(%)
2006	58 (applied)	51	88* (applied)
2007	153 (61mm applied	92	60* (applied and natural)
	and 92mm natural)		
2008	154	88	57
2009	74	11	15
2010	98	40	41
2011	146	84	58
2012	68	9	13
2013	91	26	29





### Type III Pile Outflow



Cumulative and Daily Outflow Volumes from the South Basal Drain





# **Stable Isotope Analysis**

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#### Goal

- Determine the contributions of snowmelt and rainfall to recharge through the batters of the type III pile
- Examine evaporation in the batters of the pile
- Background:
  - Snow and rain have unique isotopic ratios
  - The slope of the line created when plotting stable isotopes gives information about the evaporative history of the sample
- Method
  - Analyze samples of rain, snow, and effluent from the north drain







**Stable Isotope Analysis: Results** 

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- Slope of the line defined by the effluent ~ 8
- Outflow from May to July heavily influenced by snowmelt
- Good correlation between pH of outflow and the contribution of snowmelt to the outflow



# Stable Isotope Analysis: Key Conclusions

- The circum-neutral outflow observed each spring is a result of snowmelt travelling through preferential pathways to the basal liner
- 40% of the outflow collected by the north drain was derived from the infiltration of snowmelt (2011-2013)
- There is minimal evaporation following the infiltration of water into the north batter of the pile

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#### Pile Wet-up and First Flush of Matrix Pore Water





#### **Observations of Progressive Weathering**



#### **Establishing Internal Geochemical Stability**



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#### **Geochemical Evolution:**

 Wetting front reached the base of the core in 2008 (TDR sensors) confirmed with applied tracers Cl<sup>-</sup> and Br<sup>-</sup>, as well as blasting residuals NO<sub>3</sub><sup>-</sup>, NH<sub>3</sub>, and Cl<sup>-</sup>

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- Declining pH
- Stepwise progression through acidneutralizing phases
- Increases in SO<sub>4</sub>, major cations and trace metals
- Ni is the best indicator of sulfide (pyrrhotite) oxidation – no secondary mineral controls, limited sorption at low pH's in pile



### Core Basal Drainage vs. Total Basal Drainage



Continuous flow weighted results - for days without geochemical samples mean values estimated using flow data and bracketing geochemical data



# **Explaining Core Drainage Trends**

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4000 -

2000 -

#### Dec 2012 0 **Caused by:** -2 -2 -4 -14 -6 1. Residence time / outflow day Elevation (m) -8 -10 182022 -14 -10 -6 -12 relationship -10 -14 -12 -16 -8 -18 2. Sustained winter oxidation, 12 -20 -10 -22 100 -14 -10 -24 emphasised near the pile -26 -26 -12 -8 -16 -6 base -14 -30 -20 -10 20 30 10 0 Distance (m) 8000 (mg L<sup>-1</sup>) 80 6000 -

80

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2012

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- Determine relationships between intrinsic rates, temperature and mineral surface area
- Quantify reactions mechanisms



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### **Conceptual Model**



Sulfide oxidation simulated using shrinking core model.



#### Geochemistry

Equilibrium:

- pO<sub>2</sub>: 0.21
- pCO<sub>2</sub>: 0.000317

Kinetic:

- Pyrrhotite, pentlandite, chalcopyrite, sphalerite, calcite, biotite, muscovite, k-feldspar, albite, and quartz dissolution
- Jarosite, ferrihydrite, gibbsite, and amorphous silica precipitation
- Fe<sup>2+</sup> and S<sup>0</sup> oxidation

#### Hydrology

Steady flow:

 Constant flow DI water totaling 500 mL wk<sup>-1</sup>





## **Conceptual Model**

polysulfide mechanism of sulfide mineral oxidation

Af, Lf

 $Fe^{2+} + 0.25O_{2(aq)} + H^+ \rightarrow Fe^{3+} + 0.5H_2O$ 

Pyrrhotite

 $\begin{array}{l} Fe_{0.852}Ni_{0.004}Co_{0.001}S + 1.714Fe^{3+} \rightarrow \\ 2.566Fe^{2+} + 0.004Ni^{2+} + 0.001Co^{2+} + S^{0} \end{array}$ 

Chalcopyrite

 $CuFeS_2 + 4Fe^{3+} \rightarrow 5Fe^{2+} + Cu^{2+} + 2S^0$ 

Sphalerite

 $ZnS + 2Fe^{3+} \rightarrow 2Fe^{2+} + Zn^{2+} + S^0$ 

Pentlandite

 $(Fe, Ni, Co)_9S_8 + 18Fe^{3+} \rightarrow$ 22.5Fe<sup>2+</sup> + 3.6Ni<sup>2+</sup> + 0.9Co<sup>2+</sup> + 8S<sup>0</sup>

 $S^0 + 1.5O_{2(aq)} + H_2O \rightarrow SO_4^{2-} + 2H^+$ 





### **Preliminary Geochemical Solution**



2004 Type III, 22 °C



### **Preliminary Geochemical Solution**





# **Journal Publications**

- Amos, R.T., Blowes, D.W., Bailey, B.L., Sego, D.C., Smith, L., Ritchie, A.I.M. (In press) Waste-rock hydrogeology and geochemistry. Applied Geochemistry.
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  - Smith, L.J.D., Bailey, B.L., Blowes, D.W., Jambor, J.L., Smith, L., Sego, D.C. (2013c) Diavik waste rock project: Initial geochemical response from a low sulfide waste rock pile. Applied Geochemistry 36, 210-221.
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# **Questions?**





