Electrochemical transport, reduced chimneys and “forest rings” over oxidizable geological features

Understanding the physics

Stewart M. Hamilton
Outline

1. Background:
   - vertical element transport; reduced chimneys

2. Evidence for reduced chimneys
   - Over sulphides, kimberlites & “forest rings”

3. How reduced chimneys form

4. Implications
   - To: geochemistry; geophysics; hydrogeology; microbiology
Clay Cover in Canada

- Very young: 8-12 kA
- Thick: 25 to > 50 m
- Plastic / fully saturated
- Extensive: >10^5 km^2

- Very low permeability
  \( (K_{\text{vertical}} > 10^{-10} \text{ m/s}) \)

- Highly stratified (promotes horizontal dispersion)
Problems With Vertical Element
Mobility Through Clay

- Too slow: not enough time to develop anomalies on surface since deposition
- Why vertical? Horizontal stratification would promote lateral dispersion
Vertical Element Transport

It is now clear that metals from buried mineralization are making their way to surface through young glacial clays.

- pH anomalies are coincident with metal anomalies
- Carbonate mobilization / deposition is related to the pH responses
- Vertical redox anomalies or “reduced chimneys” occur in the surfical materials covering buried features
- The very strong spatial coincidence suggests the phenomena are all genetically related to the same process
Reduced Chimneys

“Reduced chimneys” are vertical zones in overburden or groundwater that have lower redox than surrounding areas.

They were first postulated to occur (Hamilton, 1998) as a product of “redox-gradient” transport of elements from buried mineralization to surface.

The chimneys were first observed in 1999 over “Forest Rings” and then in 2000 over mineral deposits.
Marsh Zone Stratigraphy

Line 15 Marsh Zone

- Piezometric Surface in Clay
- Peat
- Varved Clay
- Pebby Clay Till
- Mafic Metavolcanics
- Quartz-Feldspar Porphyry

Elevation (~mASL)

Talc-Chlorite Schist

Gold Mineralized Syenite

Diamond Drill Hole Intersection
Well and Well Screen
Overburden Sample Location
Marsh Zone, Line 15 - 3D pH & Redox

Subsurface Redox (mV)

Northing - Line 15 (m)

-200 -150 -100 -50 0 50 100 150 200

-200 0 200

South North

pH of slurry

8.4 8.0 7.6 7.2

Line 14 - clay slurry pH

Depth (m)

-2 -4 -6

25 m
Calcium concentration in peat plotted against pH
Marsh Zone Profile Data

Approximate position of sulphides

pH of peat (@ 10min)

Relative Ca concentration (%)

Note: the typical background Ca concentration increases gradually with depth from about 0.5% @ 5 cm to 2.5% @ 60 cm.
Soil Slurry pH 6 m Below Water Table, Cross Lake, Line 6

All Depths

Distance South (m)
pH, Line 6, Cross Lake

150 m

1 m

VMS

Ontario Geological Survey
Calcium – Line 6, Cross Lake Lake

[Map showing calcium levels with legend and contour lines]

Ca_AR (%)
- 5.3 - 5.7
- 4.8 - 5.2
- 4.1 - 4.7
- 3.6 - 4.0
- 3.1 - 3.5
- 2.6 - 3.0
- 2.1 - 2.5
- 1.5 - 2.0
- 0.9 - 1.4
- 0.5 - 0.8
- 0.1 - 0.4

pH < 6.5
non-organic C < 0.07
ORP > 275
% $\text{CO}_3$ in B-Horizon Soil
Cross Lake, Line 6
SP & Redox over Kimberlites

B30 Kimberlite

95-2 Kimberlite

A4 Kimberlite

Oxidation – Reduction Potential (mV)

(probe 1)

ORP (mV)

(probe 1)
Forest rings as evidence of reduced chimneys
Major-Element Geochemical Response to a Wide Reduced Chimney

Relative Values Close to Water Table

- $\text{CO}_2(g)$
- $\text{CaCO}_3(s)$
- $\text{H}^+$
- $\text{Fe(OH)}_3$
- $\text{O}_2(g)$
- $\text{Eh}$

Iron oxidation $\rightarrow$ acid
$\text{Fe(OH)}_3$ Stable
$\text{Fe}^{2+}$ Stable
Reduced feature in bedrock

1. Zone of $\text{Fe}^{2+}$ oxidation and $\text{H}^+$ production
2. Carbonate dissolution $\rightarrow$ DIC & CO$_2$
3. Carbonate reprecipitation $\rightarrow$ secondary calcite
Forest Rings - “Bean” Ring

Hamilton, Veillette & Komarechka, 1999

- pH of mineral soil
- Iron in mineral soil (% + 5)

1 Data projected from E-W line
2 Data projected from 120° line
Thorn-North Ring
ORP of Sediments, 2 m Depth
Thorn-North Ring

ORP, 1.5m: East-West Line
ORP of Groundwater, 8 m Depth
Thorn-North Ring

Sept 7, 2000 - Probe 3 (pumped, N2 purged, 4 day recovery)
Sept 21, 2000 - Probe 3 (measured on ) standing well water
Down-Hole
SP
Redox
Field

Electrical
Field

Redox Field = Pt SP - CuSO₄ SP (mV)

Electrical Field (CuSO₄ SP - mV)
H$_2$S & SO$_4^{2-}$ in Groundwater
Methane and Oxygen in Well Headspace

CH4 (ppm)

O2 (%)

Distance (m)
Ontario Geological Survey

Water Table and Pieziometric Surface – Thorn North Ring

Elevation (m ASL)

-400 -200 0 200 400 600

West

East

N-S Line Crosses

SW-NE Line Crosses

Peat and / or Humus

Glaciolacustrine Beach and Shallow Lacustrine Sand

Glaciolacustrine Clays and Pebbly Clay Till

Esker sands
Permeability of Sediments

Hydraulic Conductivity (m/s)

- Cooper et al. method (confined aquifer)
- Hvorslev method (unconfined aquifer)

Expanded Scale

West

East

South

Distance (m)

North
Ontario Geological Survey

Thorn-North Ring

$K = x$

$K = 1000x$

$r = y$

$r \sim y$
It has been discovered recently that measurable responses exist in hydrocarbon compounds in soils above mineral deposits.

Somewhat similar suites of hydrocarbons in the pulped rock of the same deposits suggested they might be originating from the deposits.

Another potential source of hydrocarbons is bacterial exhalation and biomass from increased microbial activity over the deposit.
Soil Gas Hydrocarbon – Thorn N.

B-Horizon
(west-east line)

(PC1 = 68.8% of variance)

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>C1</th>
</tr>
</thead>
<tbody>
<tr>
<td>069_C13A</td>
<td>0.152</td>
</tr>
<tr>
<td>066_BA</td>
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<td>088_BA</td>
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<td>073_BA</td>
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<td>145_BA</td>
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<td>038_BA</td>
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<td>141_C3EP</td>
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<td>022_BA</td>
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</tbody>
</table>
Soil Gas Hydrocarbon – Thorn N.

A-Horizon
(west-east line)

Sum of Hydrocarbon Concentrations, 1st Component (pptr)

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>PC1</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>062_BA</td>
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<tr>
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<td>093_C14A</td>
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<td>019_C4B</td>
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<tr>
<td>017_C4B</td>
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<tr>
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<td>004_C8A</td>
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<tr>
<td>052_C3PB</td>
<td>0.136</td>
</tr>
</tbody>
</table>
Ontario Geological Survey

A Horizon

B Horizon

Inside ring (reducing)

Outside ring (Oxidizing)

Chemotroph abundance

Aerobic Heterotroph abundance

High redox gradient

Very high gradient

Redox equipotentials

Increasing redox potential

Chemotroph abundance

Aerobic Heterotroph abundance
Soil Gas Hydrocarbons

Cross Lake
Line 6

- C5 + 6A
- C2PB
- 158-BA
Soil Gas Hydrocarbons

Cross Lake Line 6 (expanded)
SRBs - Cross Lake - 14 m from line

Slide courtesy of Gordon Southam
SRBs - Cross Lake - 12 m from line

Distance (m)

Depth (cm)

log units

Slide courtesy of Gordon Southam
Aerobic Heterotrophs - Cross Lake - 12 m from line

Slide courtesy of Gordon Southam
Aerobic Heterotrophs - Cross Lake - 12 m from line

Depth (cm)

Distance (m)

log units

Slide courtesy of Gordon Southam
Anaerobes - Cross Lake - 12 m from line

Slide courtesy of Gordon Southam
Anaerobes - Cross Lake - 14 m from line

Slide courtesy of Gordon Southam
ORP at Bean Ring - 1999

Soil ORP (Sept - mV)

Soil ORP (Oct - mV)
Soil Gas Hydrocarbons over Kimberlites

Source: Actlabs
Bacterial Plate Counts
Green Mountain Kimberlite, Colorado

From Alexander, 1986
The source of hydrocarbons

Hydrocarbon anomalies correlate with:

- Mineralization (spatially)
- Reduced chimneys (spatially)
- Redox variation
- pH anomalies in soil
- \((O_2\text{ depletions} / CO_2\text{ enrichments in soil gas})\)
- (Organic carbon depletions)
- (Metal enrichments)
- Increased bacterial populations
The source of hydrocarbons

Conclusions:

1. Source of hydrocarbons is bacterial biomass and microbial exhalation above the reduced chimney
2. Increased hydrocarbons result from increased microbial activity
3. Increased microbial activity results from enhanced redox gradients and a greater availability of essential nutrients over the chimney
The Formation of Reduced Chimneys by Electrochemical Transport

Reduced chimneys could conceivably form by:

- Gaseous dispersion
- Fluid movement
- Diffusion
- Electrical field transport
- (Redox gradient transport)
Reduced Chimney Development

A Post overburden deposition

Reduced front

Reduced feature in bedrock

Hamilton, 1998
Reduced Chimney Development

B Progressive advancement of redox front

Movement of reduced species

Hamilton, 1998
Reduced Chimney Development

© Present day – fully developed reduced chimney

+300
+200
+100

0 mV -100

Hamilton, 1998
\[ J_j = \delta \phi - zFRT D_j C_j - \delta C \delta x + C_j K_n \]

- \( J_j \): flux of species “j” in the x direction
- \( \phi \): Voltage (electrical field)
- \( K \): hydraulic conductivity
- \( H \): hydraulic pressure
- \( n \): porosity (of porous medium)
- \( J_j \): flux of species “j” in the x direction

Terms:
- Electromigration term
- Diffusive term
- Velocity (advection) term

Symbols:
- \( j \): species “j”
- \( D \): Diffusion coefficient
- \( C \): Concentration
- \( z \): valence (of j)
- \( F \): Faraday’s constant
- \( R \): ideal gas constant
- \( T \): temperature

Nernst-Planck (i.e. general mass transfer) Equation
Problems with Redox Transport
(and models of Veder, Bolviken, Govett, Pirson, Tomkins, and Hamilton)

- Movement of charge and mass due to a redox gradient is not supported by physics
- Intervening oxidized strata should short-circuit the charge transfer process
Problem:
Doesn’t explain responses that occur over non-conductive oxidizable features

- Redox Equipotentials (mV)
  - Ion movement
  - Electron flow
    - Sulfide
    - Anode
    - Cathode

- Electrical field lines
- Negative current flow
- Positive charge carrying species

Sulphide Dipole (Hamilton, 1998 after Govett)
SP Surveys over Porphyry Sulphides

Little Cottonwood Canyon, Battle Mountain Nevada

Valmy Fmt. (Graphite with some sulphides)

SP surface deposit
Big Ben Mt.
Corry, 1985, Fig. 4
(Note: mV/2)

-800 – From Corry (1985), Fig. 1
Spontaneous Polarization of Sulphide Deposits (Corry, 1985)

Problem:
- Permanent polarity means folded or overturned deposits should exhibit positive poles on surface (which never happens)
- Can’t account for non-metallic targets
- Cannot allow for mass or charge movement – system is static

Simplification of model of Corry (1985)
Redox-Induced Spontaneous Polarization

Surface Response

Water Table
Redox equipotentials
Electrical field lines
Polarity of redox-active ions
Positive
Negative

Distance
Voltage

+300
+200
+100
0 mV
-100
Reduced Feature
Overburden
Bedrock

Surface Response

Redox
SP

Ontario Geological Survey
Spontaneous Polarization over a Shallow Reduced Feature

Polarity of constituent atoms

Positive

Negative

Ground Surface

Shallow reduced feature
Implications to Geophysics (electrical)

- SP occurrence over ore deposits is currently not understood, has no governing equation and therefore cannot be modelled.
- That which cannot be modelled does not exist.
- Redox-induced spontaneous polarization (RISP) could account for SP over redox-active conductive and non-conductive features.
- It is compatible with most of the previously published models – each of the earlier models are describing different parts of the same process.
- Explaining the origins of SP is the first step in development of an equation, which would allow modelling of SP; a resurgence in the use of SP as a geophysical exploration tool; and will help to focus geochemical sampling in more advantageous areas.
Implications to Hydrogeology

- By Darcy’s Law the groundwater bulges and depressions associated with the redox boundaries cannot exist.
- The piezometric and chemical data, particularly for the rings indicate large-scale mass and charge flux that is due neither to advection nor diffusion.
- Almost all advective-dispersive models that are used for contaminant transport modelling consider only advection and diffusion in solute dispersion.
- These models are most often used to model the transport of landfill leachate and the containment of nuclear waste, both of which materials are highly redox active. An additional transport mechanism based on redox gradients would obviously have important implications to the validity of these models.
Implications to Microbiology

Evidence of microbiological processes is ubiquitous over the rings, kimberlites & sulphides.

Over the sulphides and rings we see production of hydrocarbons that correlates with negative redox and elevated bacterial counts.

At the edges of various rings we see very sudden changes in geochemistry and redox that are almost certainly due to microbial action.

These appear to be the same processes that occur around deep-sea vents, brine-pools and gas hydrates but are much more accessible and less expensive to study.
Implications to Geochemistry

The data shown here uniquely demonstrate a link between microbiology, geochemistry, geophysics and hydrogeology.

Some of these links have been apparent for years but there has recently been a huge increase in our ability to quantify them, thanks in part to new analytical techniques and the discovery of redox as a critical link in the processes.

We now face a new geochemical paradigm, which we can best exploit for mineral exploration if we focus on understanding why responses happen on surface in addition to knowing where they happen.

... We also need more people.
Platinum Spontaneous Potential (PtSP)

\[ V_1 + V_2 = V_3 \]

(Timm & Moller, 2001)
Problem:
Movement of charge and mass in a redox gradient is not supported by physics

Positve Charge Carriers
$H_{2(g)} + d^+ + c^+ + b^+ + a^+ + O_2$

Negative Charge Carriers
$H_{2(g)} + D^- + C^- + B^- + A^- + O_2$

Increasing Eh

Bolviken & Logn, 1975
Problem:
- Electrons cannot move freely in an aqueous medium
- No mechanism was given for the induction of ionic current except redox differences between surface and depth (which is contrary to physics)

From Pirson, 1981
ORP & pH of Sediments

**ORP**

2 m Depth

3 m Depth

6 m Depth

**pH**
pH of Groundwater

- North-South
  - pH values range from 6.5 to 8
  - pH values increase from -500 to 0
  - pH values decrease from 0 to 500

- East-West
  - pH values range from 6.5 to 8
  - pH values increase from -500 to 0
  - pH values decrease from 0 to 500

Legend:
- Blue diamonds: pH (N purged wells) Sept. 7/00
- Pink squares: pH (N purged wells) July 19-02
Carbonate in Sediment

CaCO$_3$ vs. Distance (m)

West

East

Southwest

Northeast

Calcite by Chittick (% CaCO$_3$)

[Ca] by ICPES (% Ca)

Expanded Scale

5.88

5.86

5.84
Carbonate Mobility (Cheecka Ring)

Inside Active Rim
- Carbonate completely removed
- Only silicate clays remain
- Porosity increased

Adjacent to Active Rim
- Large amount of carbonate
- Euhedral crystals
- Porosity decreased
- Permeability decreased
Implications to Microbiology

Evidence of microbiological processes is ubiquitous over the rings, kimberlites & sulphides.

Over the sulphides and rings we see production of hydrocarbons that correlates with negative redox and elevated bacterial counts.

At the edges of various rings we see:
- very sudden rise in $\text{SO}_4^{2-}$ and drop in $\text{H}_2\text{S} & \text{O}_2(g)$
  - suggests sulphide oxidizing bacteria
- OR an increase in iron and sharp drop in pH
  - suggests iron oxidizing bacteria
- sharp increases in methane at ring edge
  - suggests $\text{CO}_2$ consuming methanogenic bacteria
- rapid reversal of redox with rise in water table
  - suggests facultative bacteria such as SRBs & Fe oxidizers

These appear to be the same processes that occur around deep-sea vents, brine-pools and gas hydrates but are much more accessible and less expensive to study.