Electrochemical transport of metals due to redox gradients

Highly predictive and somewhat problematic
...but whose problem is it?

Stew Hamilton   Gwenda Hall   Beth McClenaghan
Eion Cameron    Keiko Hattori
Outline

1. Electrochemical transport in geological literature
2. Linking the models
3. Evidence supporting redox-gradient transport from 3 classes of reduced geological bodies
4. The problem raised by redox transport
# Electrochemical transport in geological literature

## Electrical Field Transport
(Dipole around a conductor)
- Sato and Mooney
- Tilsley
- Thornbur
- Smee

## Redox Transport
(mass transport along redox gradients)
- Bolviken
- Govett
- Pirson
- Tomkins
- Veder
- Hamilton
Linking the models

Inferred mechanism of charge transfer in the Earth’s redox field
(modified after Bolviken and Logan, 1975)

-200 Equipotential lines, mV

Positive Charge Carriers: $H^+_a < d^- < c^- < b^- < a^- < O_2$
Negative Charge Carriers: $H^+_b < D^- < C^- < B^- < A^- < O_2$

Increasing Eh

Earth's Surface

Eh (mV)

-1600

-1200

-400

0

+400

+1600

Positive Charge

Negative Charge

Earth's Lower Crust

Ontario Geological Survey

OMEX
Linking the models

Conceptual model of SP around a sulphide conductor
(Govett, 1976)
Linking the models

Conceptual model of redox equipotentials around a sulphide conductor
(Hamilton, 1998)

- Electrical field lines
- (Positive) Current flow
- Equipotential lines, mV
- Ion movement
  - Electron flow
  - Sulfide
  - Anode
  - Cathode

Positive charge carrying species
Negative charge carrying species
Linking the models

A) Post overburden deposition

Reduced front
Linking the models

B) Progressive advancement of redox front

Movement of reduced species
Linking the models

Present day - fully developed reduced column
+300
+200
+100

Reduced Column

0 mV -100
Model to account for increased moisture at redox boundary in clays
(Derived from Veder, 1971)

- Reduced species (e.g., Fe²⁺, HS⁻, Mn³⁺)
- Oxidized species (e.g., SO₄²⁻, O²⁻(aq))
- Water molecules moving with transported redox-active ions
Evidence for reduced chimneys

Reduced sources investigated:
1. Mineral deposits: VMS & sulphide Au
2. Kimberlites
3. “Forest Rings”

Measurement techniques:
1. Direct ORP measurement of sediments & groundwater
2. Measurement of related parameters: pH & metals
3. Moisture content & piezometric evidence
Proposed model of Reduced Column Formation by Electrochemical Processes

1. Iron Oxidation
   \[ \text{Fe}^2+ + \frac{1}{2}\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{\text{III}}(\text{OH})_3 + \text{H}^+ \]

2. Carbonate dissolution
   \[ 2\text{H}^+ + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \]

3. Carbonate precipitation
   \[ \text{H}_2\text{CO}_3 + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]
Marsh Zone, Line 15 - 3D pH & Redox

Subsurface Redox (mV)

pH of slurry

Line 14 - clay slurry pH

Ontario Geological Survey
1. H$^+$ anomaly occurs over the reduced column
   • most intense above the water table
   • disappears below the water table

2. Intensity of pH response correlates with strength of redox negativity

Conclusion:
   Acid is produced by oxidation of reduced metals
Acid Production - Implications…2

pH anomaly is:

1. Highly localized
   • yet H⁺ is the most mobile aqueous species

2. Apparently permanent
   • yet H⁺ is one of the most reactive of aqueous species

Conclusion:

Acid production is an ongoing process
• Acid production by metal oxidation requires precipitation of insoluble metal hydroxides
• Since oxidation must continue, there must be:

1. Continuous upward movement of metals
2. Deposition of metals in the shallow subsurface
## Summary of Sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Deposit Type</th>
<th>Partial Leach Response?</th>
<th>pH Response?</th>
<th>Reduced Column?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Lake, Line 6</td>
<td>VMS (Zn, Cu, Pb)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Cross Lake, Line 40</td>
<td>VMS (Zn, Cu, Pb)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Marsh Zone, Line 15</td>
<td>Au (+ Sulphides)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Marsh Zone, Line 14</td>
<td>Au (+ Sulphides)</td>
<td>?</td>
<td>?</td>
<td>Yes</td>
</tr>
<tr>
<td>Half Moon Lake, Line 5400</td>
<td>VMS (Zn, Cu)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes*</td>
</tr>
<tr>
<td>Half Moon Lake, Line 5350</td>
<td>VMS (Zn, Cu)</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Victoria Creek, Line 500</td>
<td>Au (+ Sulphides + Graphite)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes*</td>
</tr>
<tr>
<td>Victoria Creek, Line 525</td>
<td>Au (+ Sulphides + Graphite)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes*</td>
</tr>
<tr>
<td>Victoria Creek, Line 200</td>
<td>Au (+ Sulphides + Graphite)</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

* Inferred from SP
B30 kimberlite (GSC-TGI) Other sites: A4, 95-2 kimberlites

McClenaghan et al., 1995
B-30 Kimberlite

Total Field (PtSP)
Forest Rings
Forest Rings - “Bean” Ring
Forest Rings - “Bean” Ring

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

1. Data projected from E-W line
2. Data projected from 120° line
Redox - Bean Ring

- Down-hole SP (mV)
- Soil ORP (mV)
- Groundwater ORP (mV)

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Redox in Soils @ 5m depth - Thorn-N Ring

ORP, 1.5m: East-West Line

-250 -200 -150 -100 -50 0 50 100 150 200 250
-560 -460 -360 -260 -160 0 160 260 360 460 560

- ORP-1min
- ORP-2min
- ORP-5min
- Acid_ORP-1min
- Acid_ORP-2min
- Acid_ORP-5min
This is the bulge on line 40. This is particularly interesting because the well screens on this line are completed mostly in sand. A bulge such as this, consistently maintained is virtually impossible to explain by normal hydrogeological processes (differential recharge would last only hours to days; upwelling of groundwater is precluded by strong downward gradients).

One speculative explanation is electro-osmosis, which is an increase in hydraulic pressure due to an electrochemical gradient across a porous medium. Whatever the cause, it is statistically near-certain that it is related to the boundary between reduced and oxidized overburden and therefore the bulges are more than just an interesting sideline. To maintain a permanent bulge of this magnitude in clean sand requires a large and constant source of energy and this indicates the geochemical mechanism that causes the reduced conditions in the first place is releasing a huge amount of energy.
A groundwater “bulge” occurs over mineralization on all sites investigated. It involves a sudden and significant increase in the water level of the well or wells that penetrate the reduced column on each line. On line 6 (shown here) the bulge occurs in wells 29 or 30 depending on the dataset.

The bulges are permanent and have been seen on both Lines 6 and 40 and at the Marsh Zone. Related groundwater phenomena occur on all 8 of the lines drilled on two of the forest ring sites investigated. Considering the number of wells on each line and the probability of them occurring in these locations by chance is less than 1 in one million.
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Water Levels - Rings

Thorn-N Water Levels, West-East

Inside Ring

Ground Surface
Moisture Content in Shallow Sand Over a VMS (?) Conductor (Cross Lake, south grid)

- Depth to capillary water in vadose zone
- Moisture Content @ 10 - 20 cm
- VMS (?) Conductor

Distance north along Tie-Line 13 (m)

Depth to capillary water (m)

% Moisture Content in sand (by vol.)
\[ J_j = \frac{-zF}{RT} D_j C_j \frac{\delta \phi}{\delta x} + D_j \frac{\delta C}{\delta x} + C_j \frac{\delta H}{\delta x} \frac{K}{n} \]

**Electromigration term**

**Diffusive term**

**Velocity (advection) term**

- \( J_j \): flux of species “j” in the x direction
- \( \delta \): Voltage (electrical field)
- \( D \): Diffusion coefficient
- \( C \): Concentration
- \( z \): valence (of j)
- \( F \): Faraday’s constant
- \( R \): ideal gas constant
- \( T \): temperature
- \( K \): hydraulic conductivity
- \( H \): hydraulic pressure
- \( n \): porosity (of porous medium)

**Species “j”**
Summary

• geologists, for many years have observed “reduced chimneys” and macroscopic redox gradients - phenomena which are virtually unknown to electrochemists
• many geologists have independently (and sometimes inadvertently) postulated that mass transport along redox gradients could account for this
• since the “general mass transfer equation” cannot account for the presence of reduced chimneys or groundwater bulges, the equation is clearly missing a term
• it is proposed that redox gradient transport is the missing term and that ...
• geologists stop trying to use electrochemical equations to account for these phenomena but rather to recognize that they lie outside the explanation of current physics theory