Electrochemical transport of metals due to redox gradients

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

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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

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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

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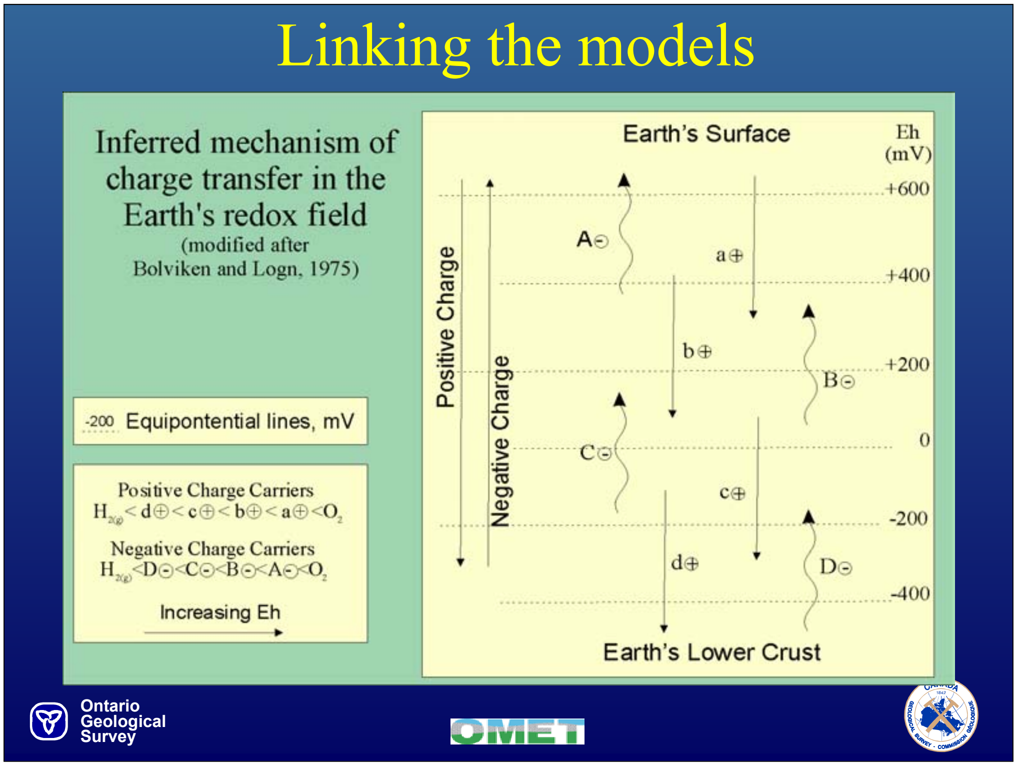
Linking the models
Inferred mechanism of charge transfer in the Earth's redox field
(modified after Bolviken and Logn, 1975)
-200 Equipontential lines, mV
Positive Charge Carriers
H2(g) < d⊕ < c⊕ < b⊕ < a⊕ < O2
Negative Charge Carriers
H2(g) < D⊝ < C⊝ < B⊝ < A⊝ < O2
Increasing Eh
Earth's Surface
Eh (mV)
+600
+400
+200
0
-200
-400
Positive Charge
Negative Charge
A⊝
a⊕
b⊕
B⊝
C⊝
c⊕
d⊕
D⊝
Earth's Lower Crust
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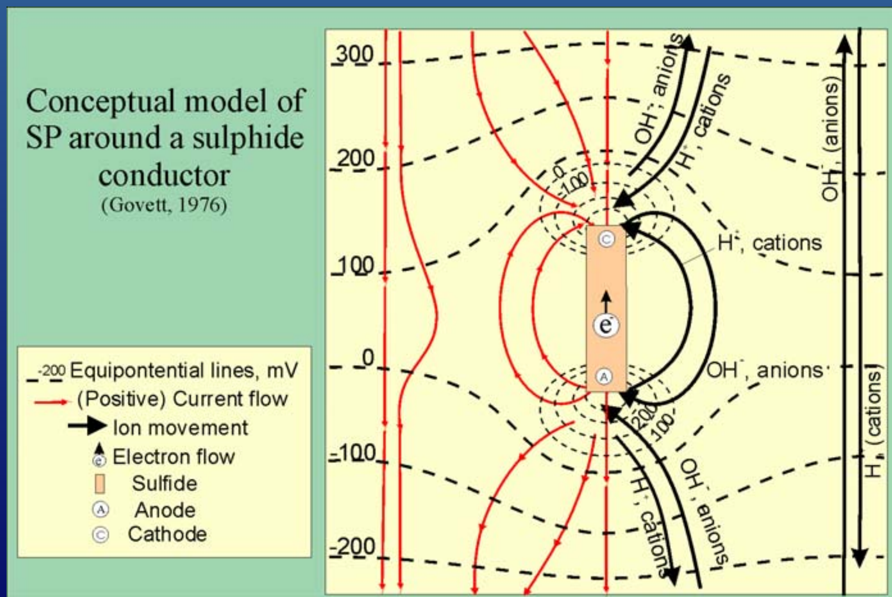
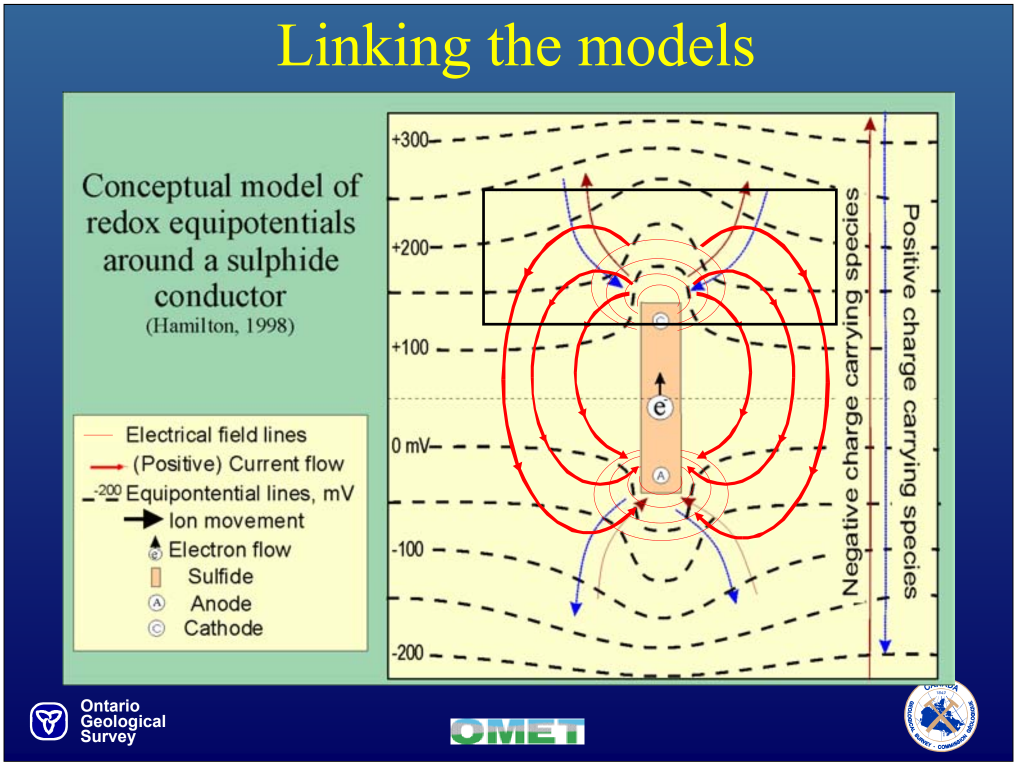
Linking the models




Linking the models
Conceptual model of redox equipotentials around a sulphide conductor
(Hamilton, 1998)
Electrical field lines
(Positive) Current flow
-200 Equipontential lines, mV
Ion movement
Electron flow
Sulfide
Anode
Cathode
+300
+200
+100
0 mV
-100
-200
e
Negative charge carrying species
Positive charge carrying species
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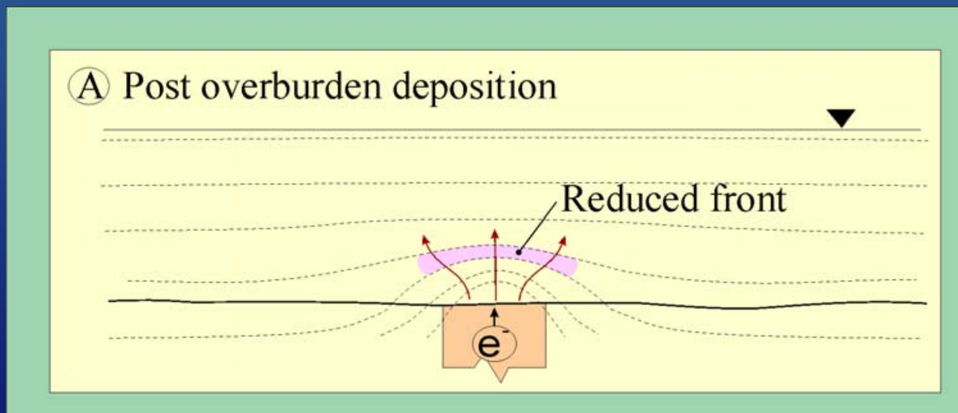
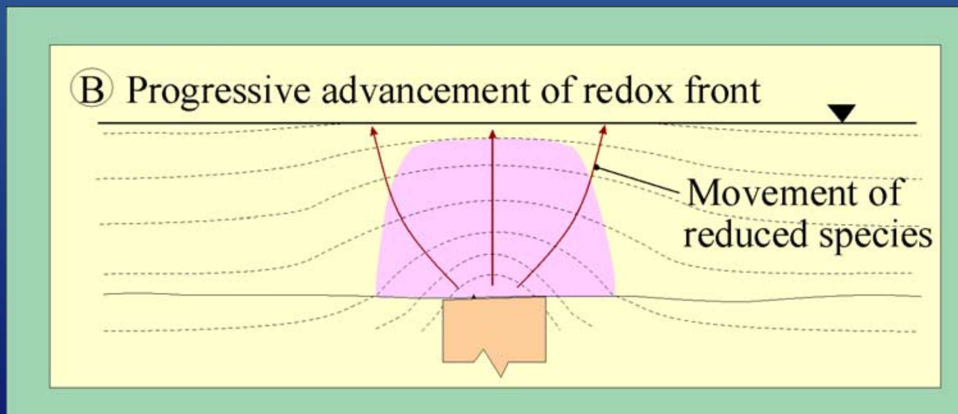
Linking the models



Linking the models



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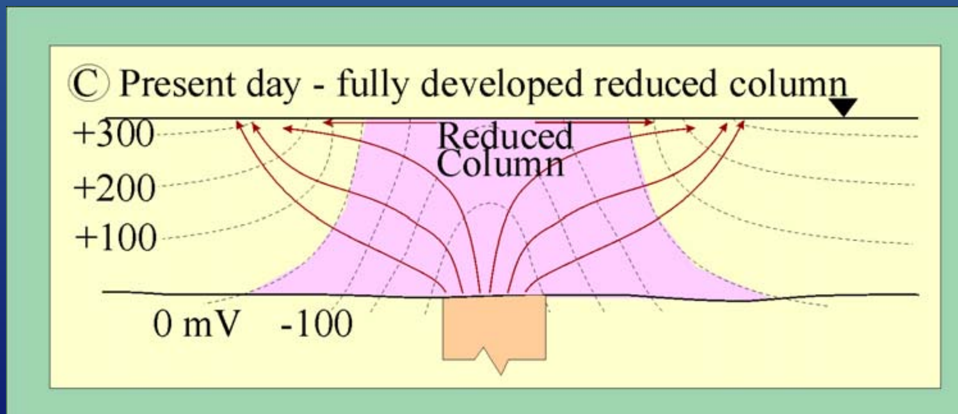
Linking the models



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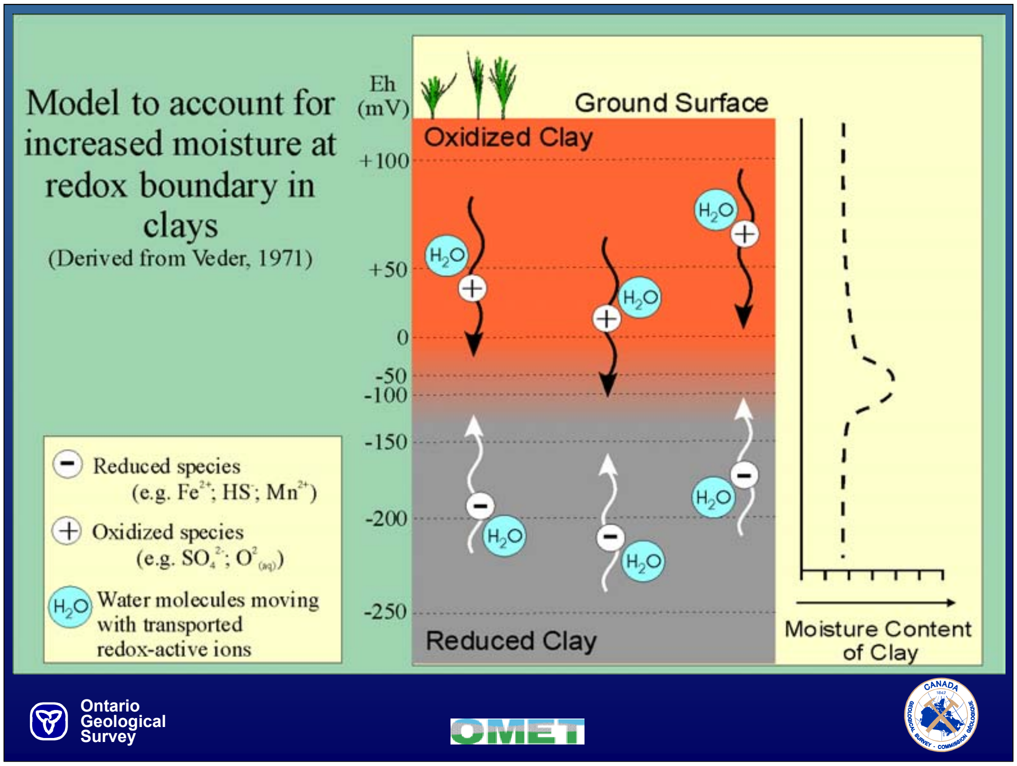
Model to account for increased moisture at redox boundary in clays
(Derived from Veder, 1971)
Eh (mV)
Ground Surface
Oxidized Clay
+100
+50
0
-50
-100
-150
-200
-250
Reduced Clay
Moisture Content of Clay
Reduced species (e.g. Fe^{2+}; HS^{-}; Mn^{2+})
Oxidized species (e.g. SO_4^{2-}; $O^{2}_{(aq)}$)
Water molecules moving with transported redox-active ions
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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

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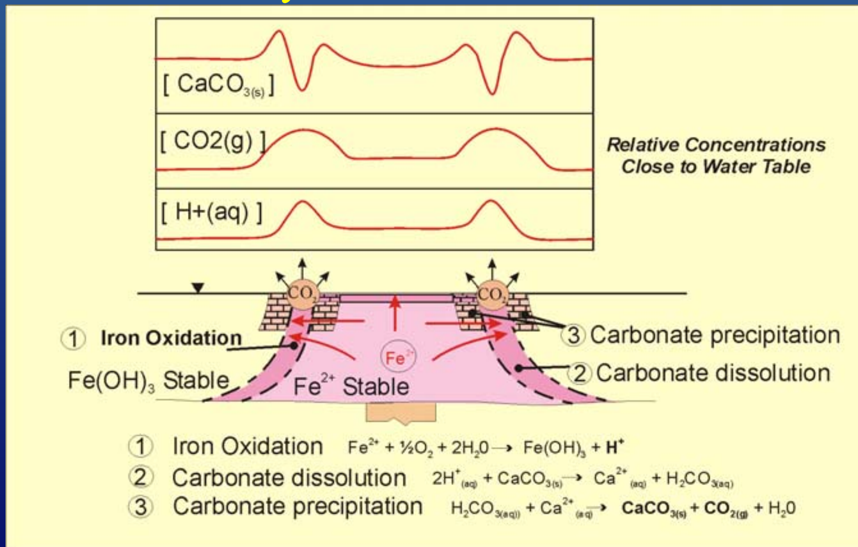
Proposed model of Reduced Column Formation by Electrochemical Processes



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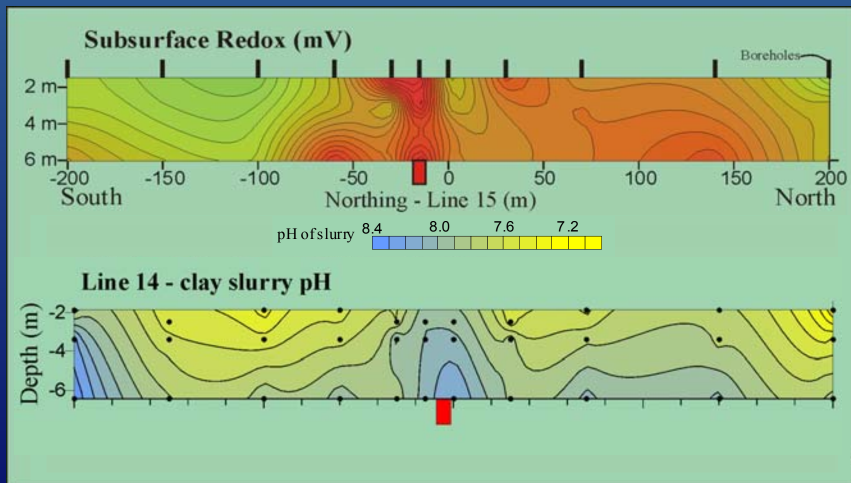
Marsh Zone, Line 15 - 3D pH & Redox



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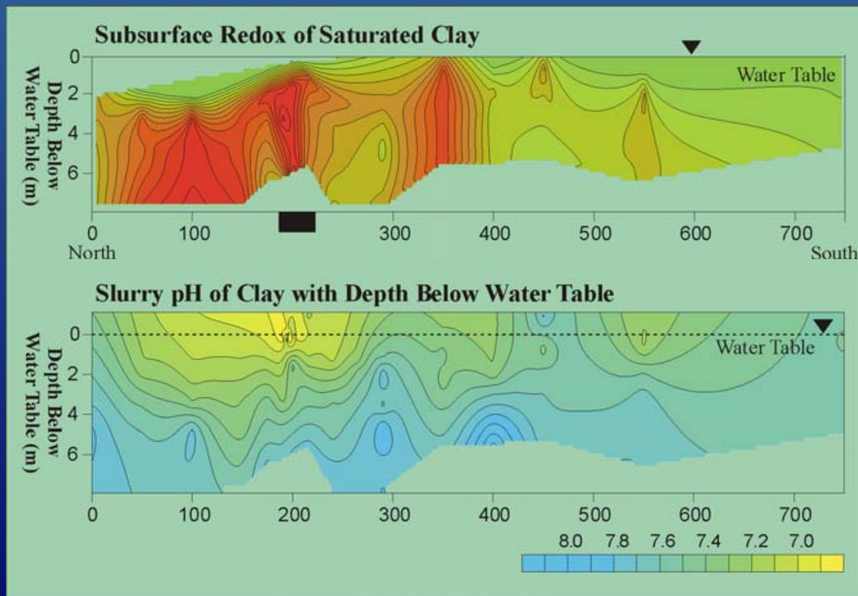
Cross Lake, Line 6 - 3D Redox & pH



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Acid Production - Implications…1

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

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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

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Acid Production - Implications…3

- 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

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Summary of Sites

Site	Deposit Type	Partial Leach Response?	pH Response?	Reduced Column?
Cross Lake, Line 6	VMS (Zn, Cu, Pb)	Yes	Yes	Yes
Cross Lake, Line 40	VMS (Zn, Cu, Pb)	Yes	Yes	Yes
Marsh Zone, Line 15	Au (+Sulphides)	Yes	Yes	Yes
Marsh Zone, Line 14	Au (+Sulphides)	?	?	Yes
Half Moon Lake, Line 5400	VMS (Zn, Cu)	Yes	Yes	Yes*
Half Moon Lake, Line 5350	VMS (Zn, Cu)	No	No	No*
Victoria Creek, Line 500	Au (+Sulphides +Graphite)	Yes	Yes	Yes*
Victoria Creek, Line 325	Au (+Sulphides +Graphite)	Yes	Yes	Yes*
Victoria Creek, Line 200	Au (+Sulphides +Graphite)	No	No	No*

* Inferred from SP

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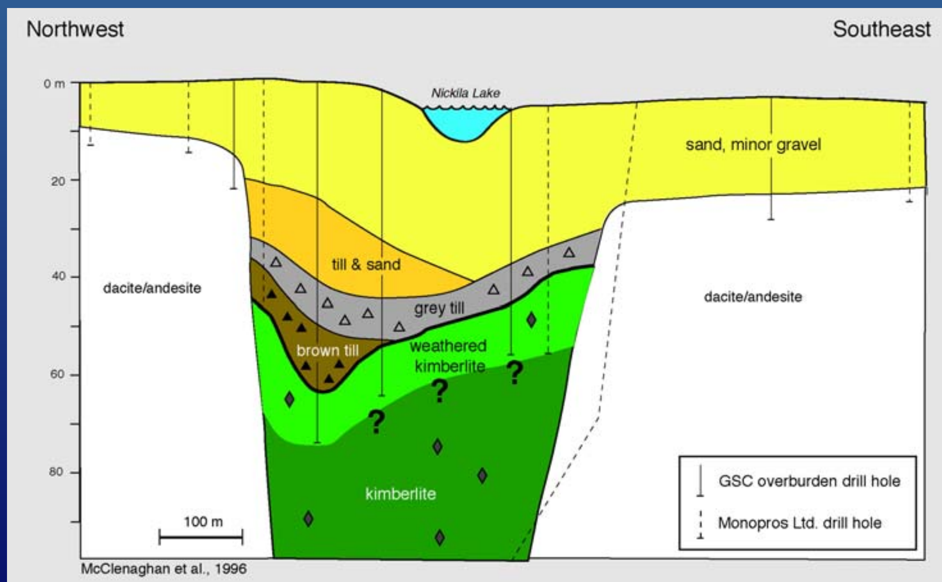
B30 kimberlite (GSC-TGI)

Other sites: A4, 95-2 kimberlites



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B-30 Kimberlite

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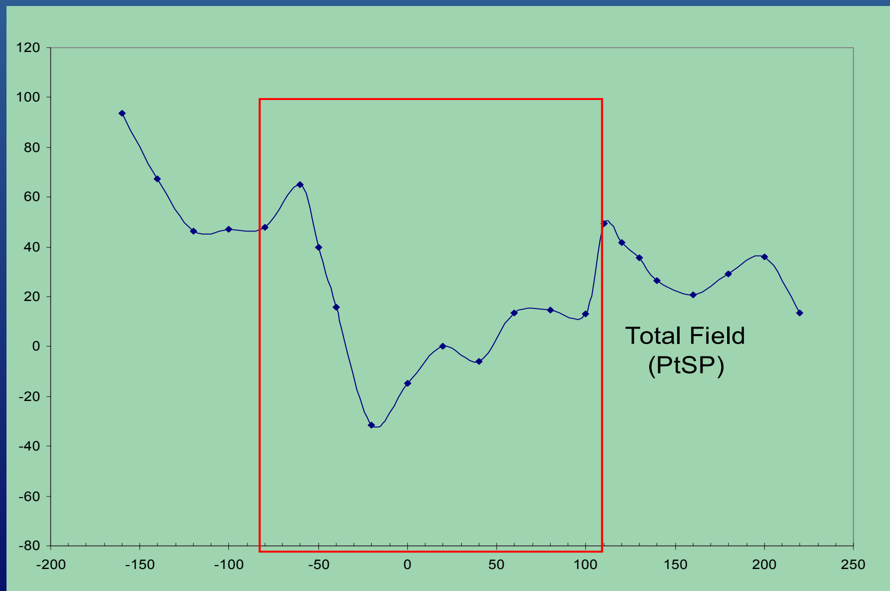
B-30 Kimberlite



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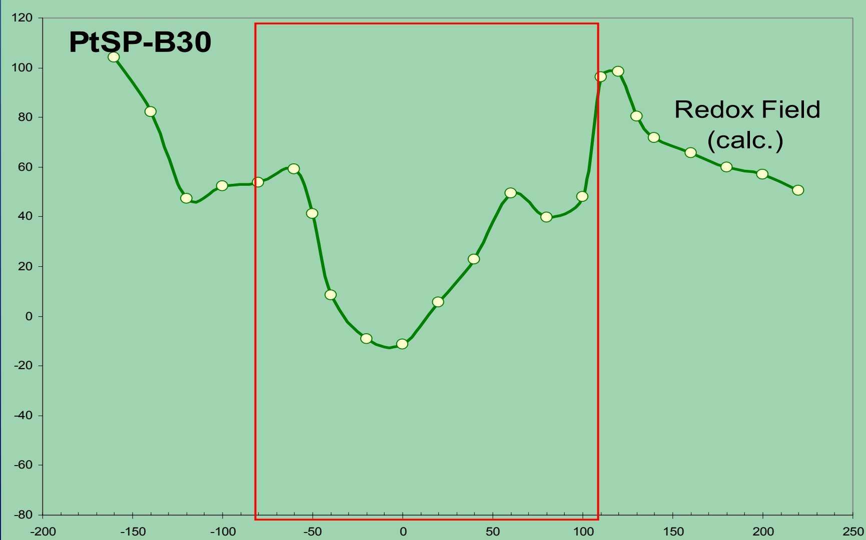
B-30 Kimberlite



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Forest Rings

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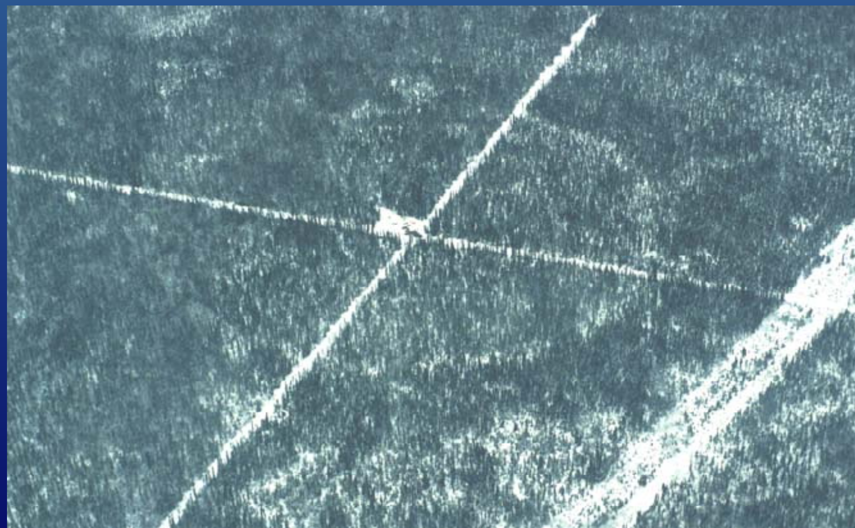
Forest Rings - “Bean” Ring



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Forest Rings - “Bean” Ring
NE
NW
1
2
0
100
200
300
-100
-200
-300
-400
50
40
30
20
10
0
Carbonate in mineral soil (%)
Calcite / Dolomite in mineral soil (%/2)
1 Data projected from E-W line 2 Data projected from 120° line
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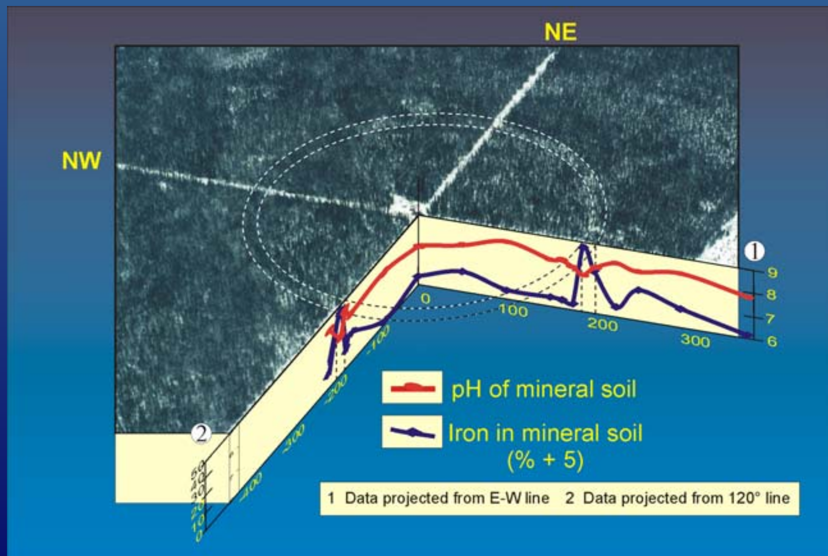
Forest Rings - "Bean" Ring



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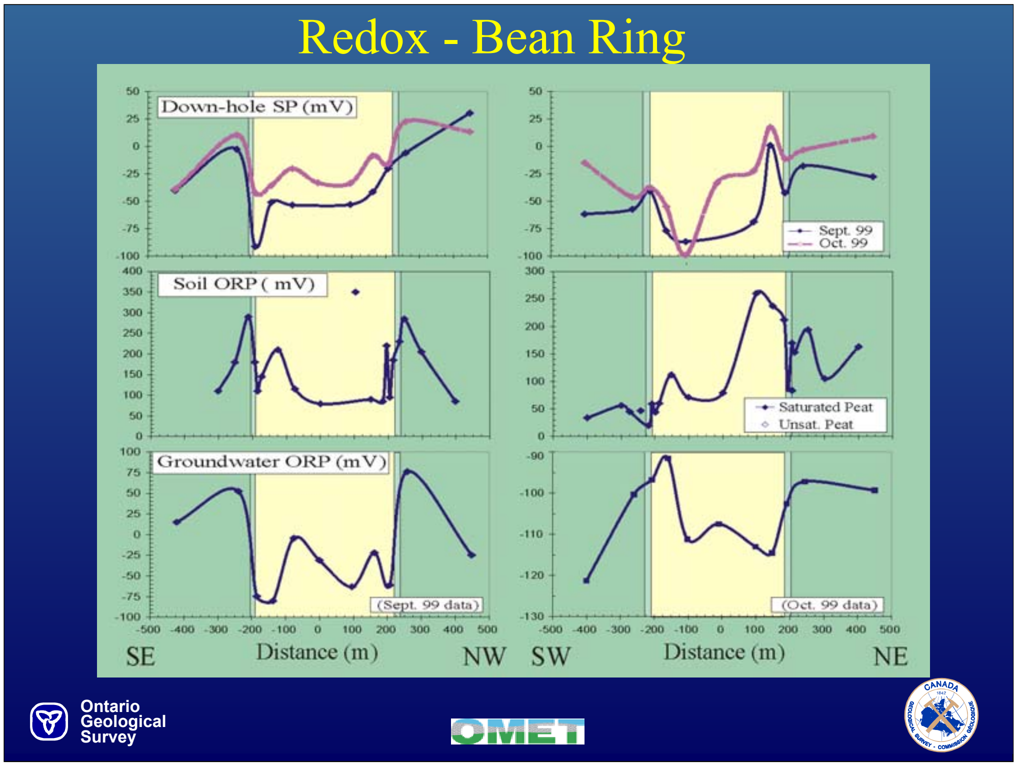

Redox - Bean Ring
Down-hole SP (mV)
Sept. 99
Oct. 99
Soil ORP (mV)
Saturated Peat
Unsat. Peat
Groundwater ORP (mV)
(Sept. 99 data)
(Oct. 99 data)
SE
Distance (m)
NW
SW
Distance (m)
NE
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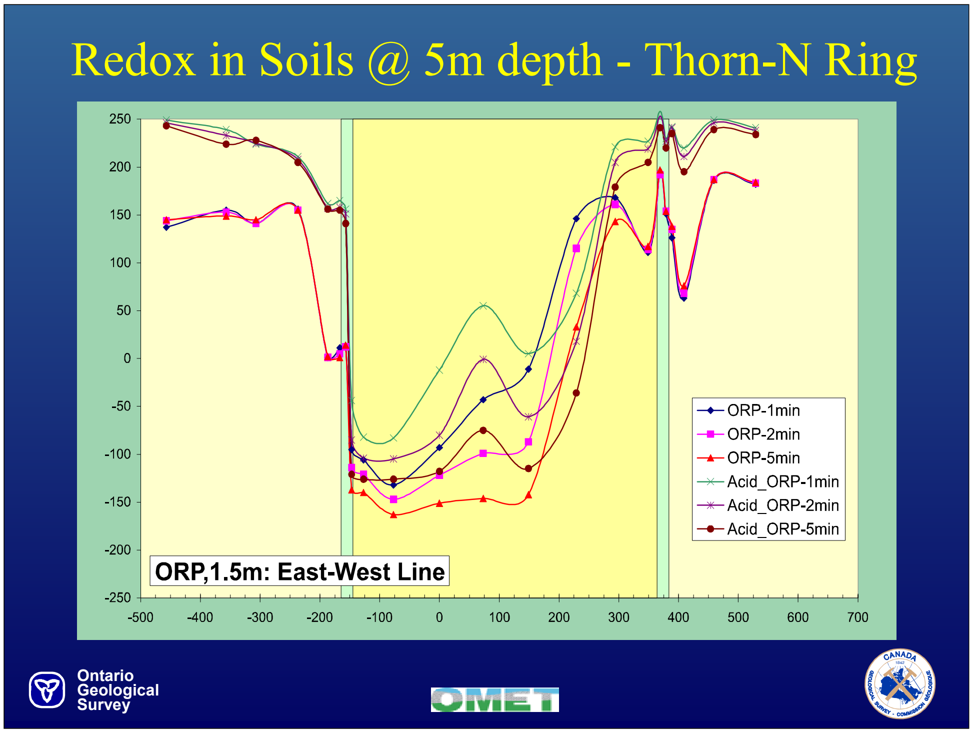
Redox in Soils @ 5m depth - Thorn-N Ring
ORP,1.5m: East-West Line
ORP-1min
ORP-2min
ORP-5min
Acid_ORP-1min
Acid_ORP-2min
Acid_ORP-5min
250
200
150
100
50
0
-50
-100
-150
-200
-250
-500
-400
-300
-200
-100
0
100
200
300
400
500
600
700
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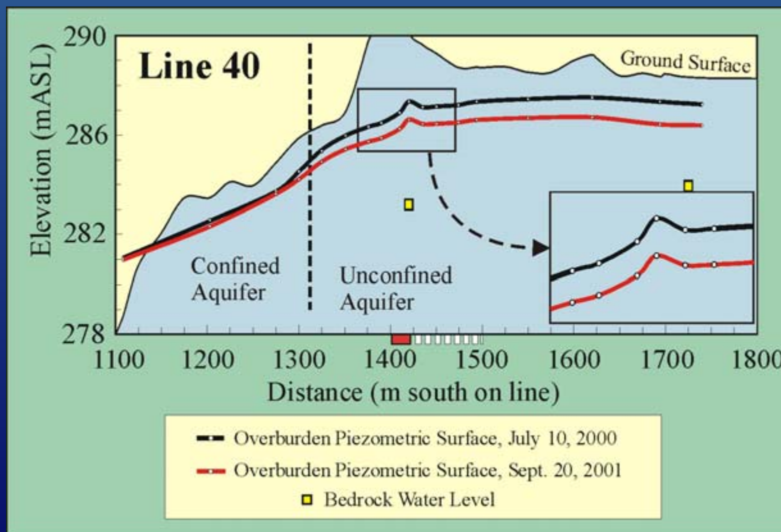
Groundwater Bulge in Sand
Cross Lake, Line 40



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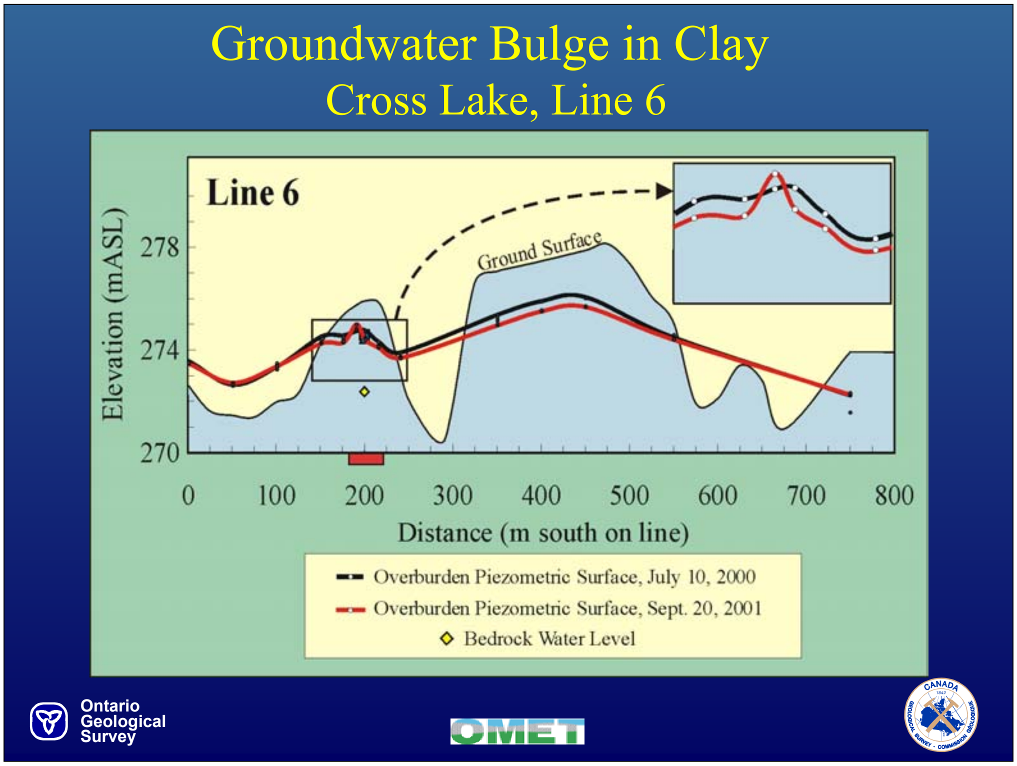
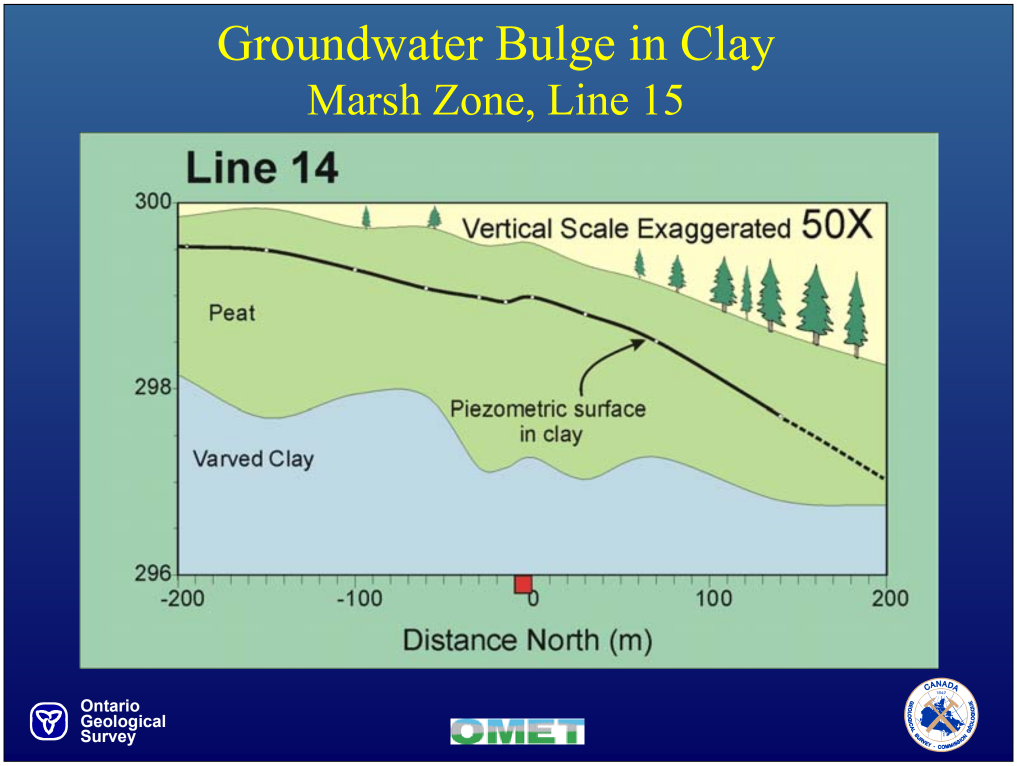
This is the bulge on line 40. This is particularly interesting because the well screens on this line are completed mostly in sand. A bulge such as this, consistently maintained is virtually impossible to explain by normal hydrogeological processes (differential recharge would last only hours to days; 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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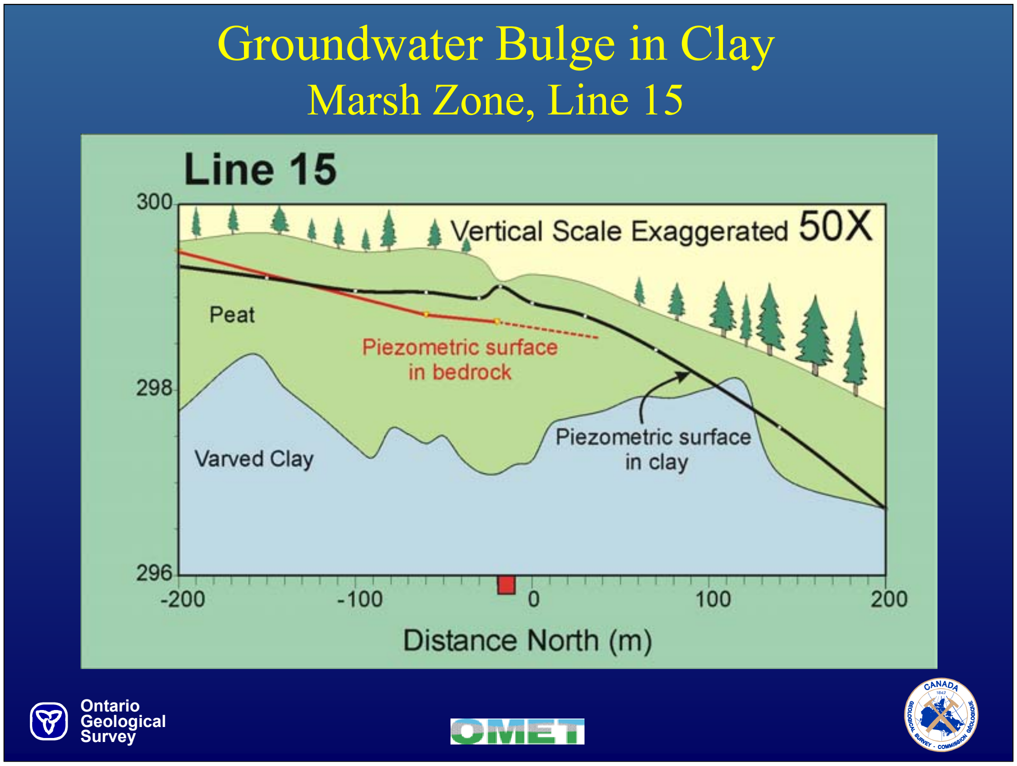

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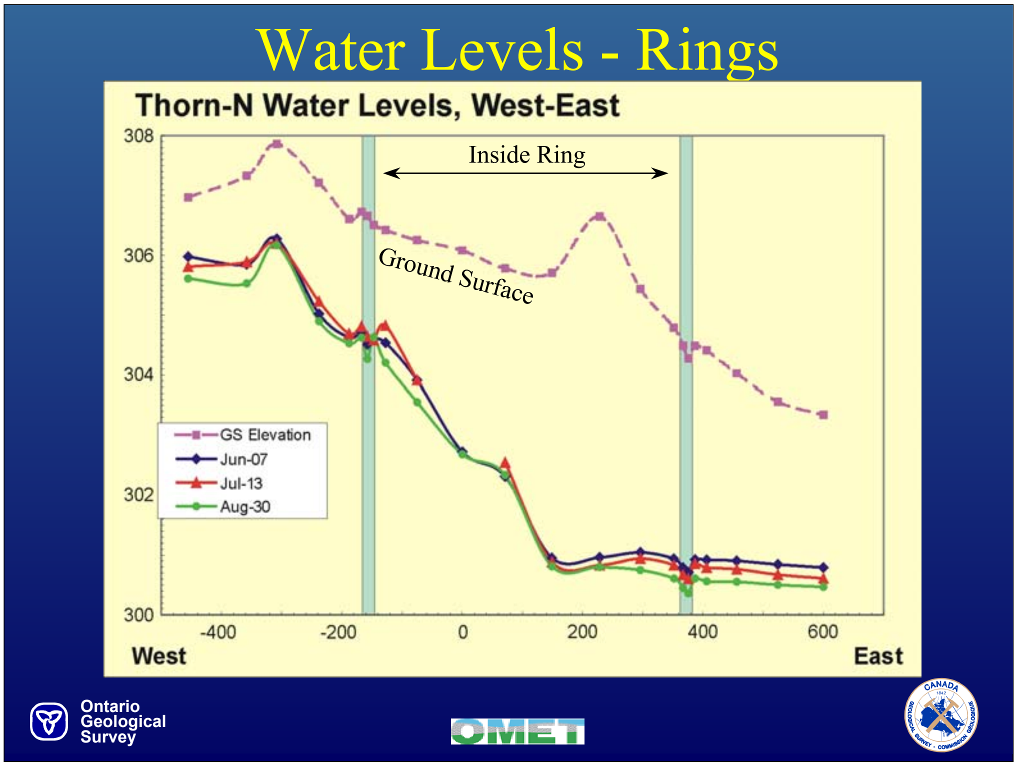
Water Levels - Rings
Thorn-N Water Levels, West-East
Inside Ring
Ground Surface
GS Elevation
Jun-07
Jul-13
Aug-30
308
306
304
302
300
-400
-200
0
200
400
600
West
East
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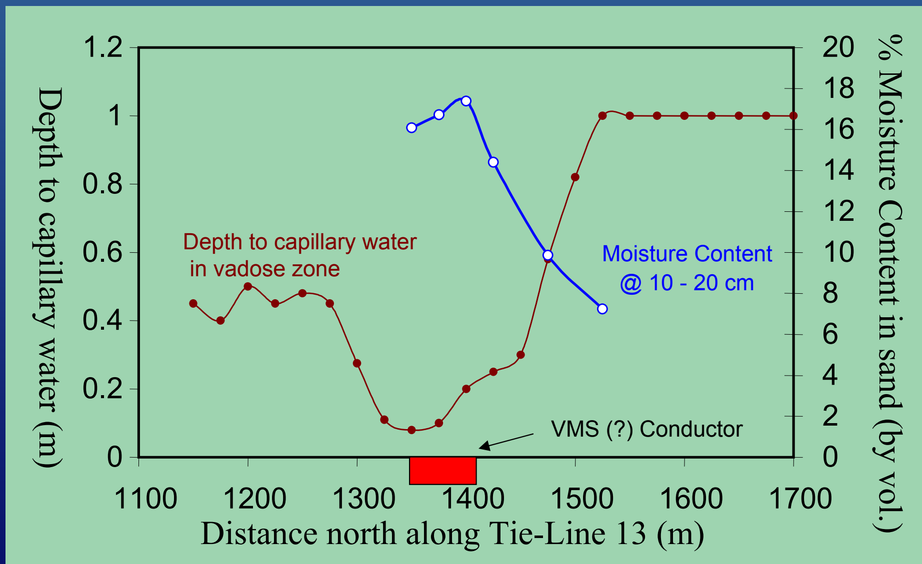
Moisture Content in Shallow Sand Over a VMS (?) Conductor (Cross Lake, south grid)



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Nernst-Planck Equation

$$J_j = \underbrace{- \frac{-zF}{RT} D_j C_j \frac{\delta\phi}{\delta x}}_{\text{Electromigration term}} \underbrace{- D_j \frac{\delta C}{\delta x}}_{\text{Diffusive term}} \underbrace{+ C_j \frac{\delta H}{\delta x} \frac{K}{n}}_{\text{Velocity (advection) term}}$$

j = species "j"	δ = Voltage (electrical field)
D = Diffusion coefficient	K = hydraulic conductivity
C = Concentration	H = hydraulic pressure
z = valence (of j)	n = porosity (of porous medium)
F = Faraday's constant	J_j = flux of species "j" in the x direction
R = ideal gas constant	
T = temperature	

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Summary

- geologists, for may 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

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