Reduced chimneys and electrochemical transport over oxidizable geological features

AAG Distinguished Lecturer Series

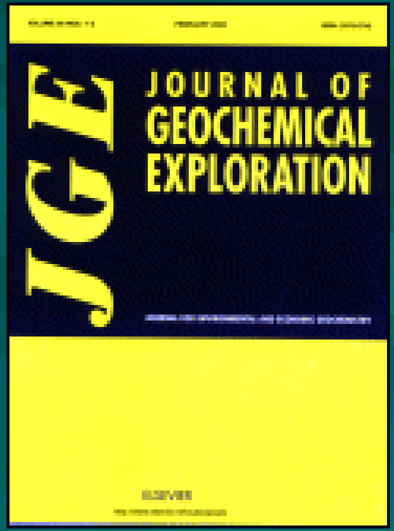
Stewart M. Hamilton

Ontario Geological Survey

THE ASSOCIATION OF APPLIED GEOCHEMISTS

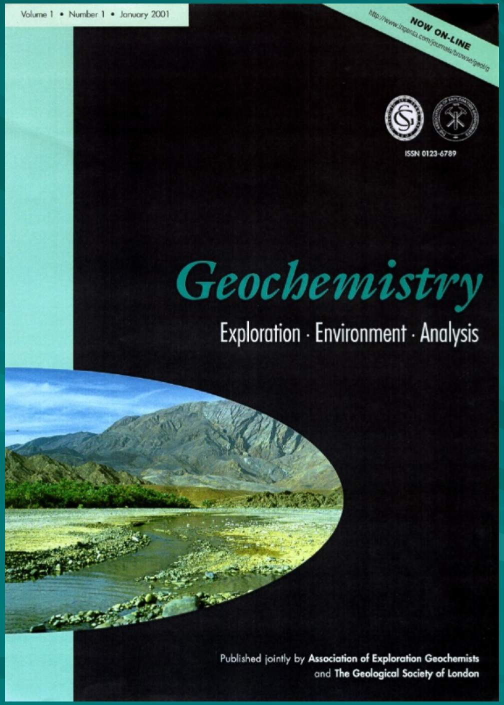
The Association's Journal

Elsevier



1972-1999

Geological Society of London



2001-present

Ontario Geological Survey

Collaboration

- Gwendy Hall, Beth McClenaghan: Geological Survey of Canada
- Eion Cameron: Eion Cameron Geochemical Inc.

- Canadian Association of Mining Industry Research Organizations (CAMIRO)
- Ontario Mineral Exploration Technologies Program (OMET)

Outline

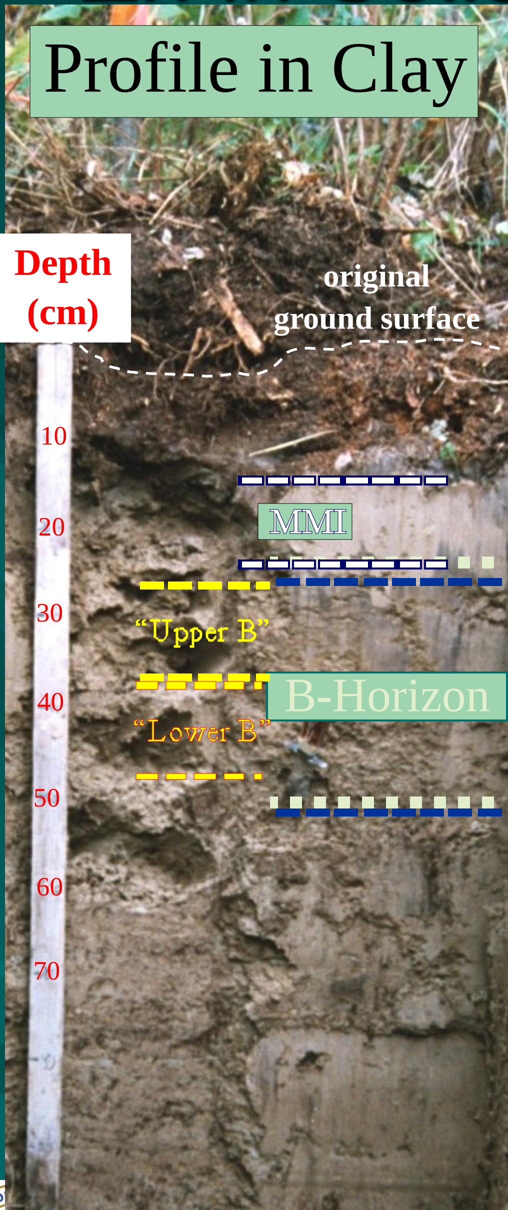
- Part 1 – Evidence supporting reduced chimneys and related phenomena
  - reduced chimneys & “acidic caps”
  - the role of bacteria & hydrocarbons in soil gas
- Part 2 – The theory of reduced chimney development
  - Problems with existing theories
  - A possible resolution: Redox-induced spontaneous polarization

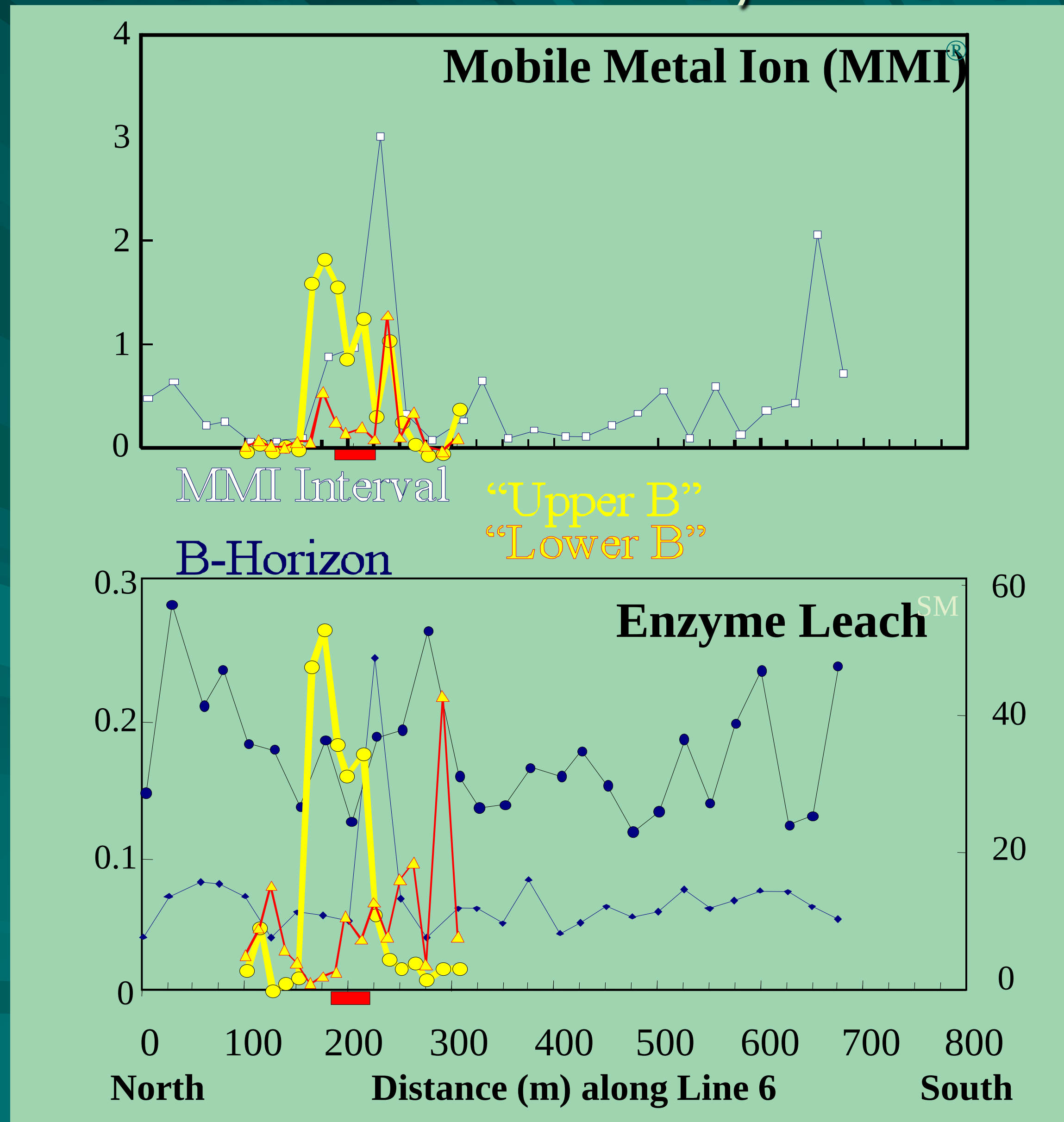
Clay Cover in Canada

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

- Very low permeability ($K_{vertical} > 10^{-10}$ m/s)
- Highly stratified (promotes horizontal dispersion)

Zn in Soils - Cross Lake VMS, Line 6





30 m

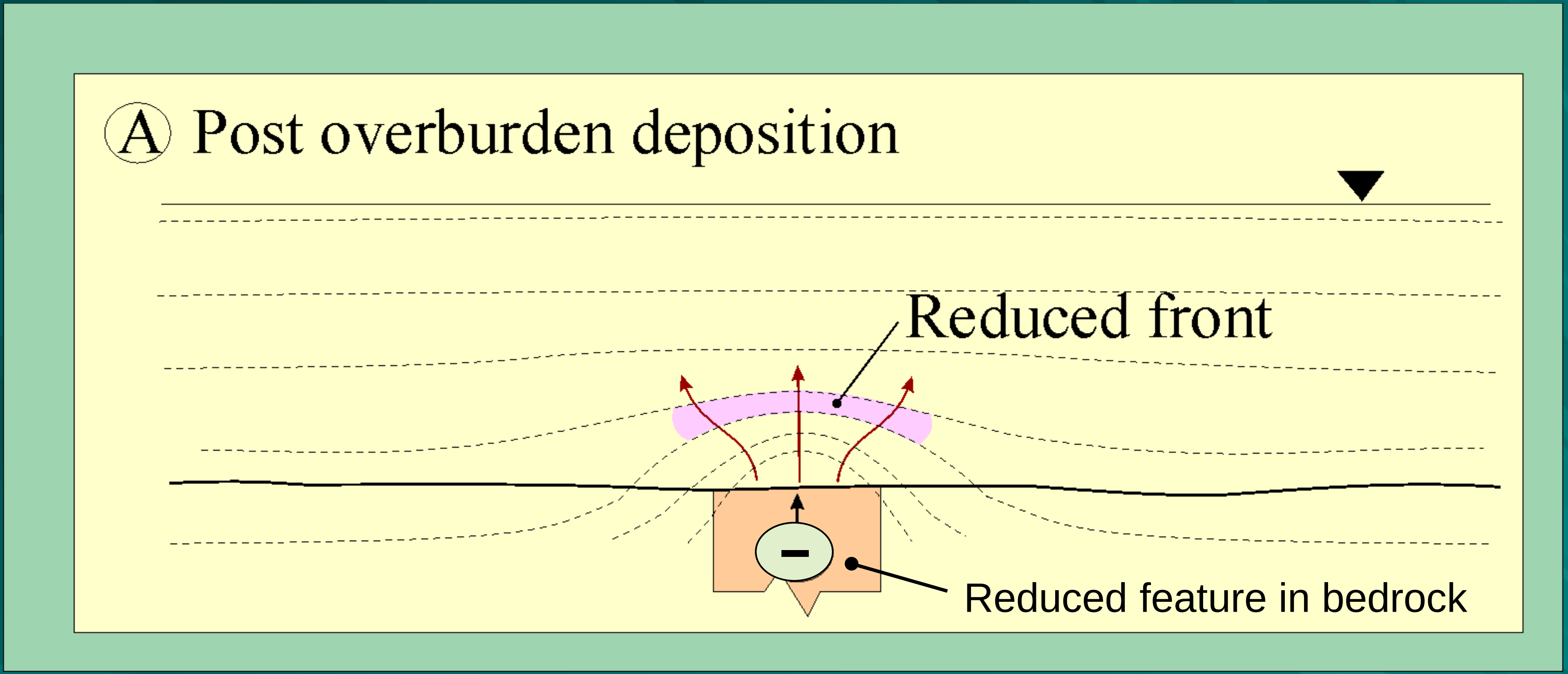
Ontario Geological Survey

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

Ontario Geological Survey

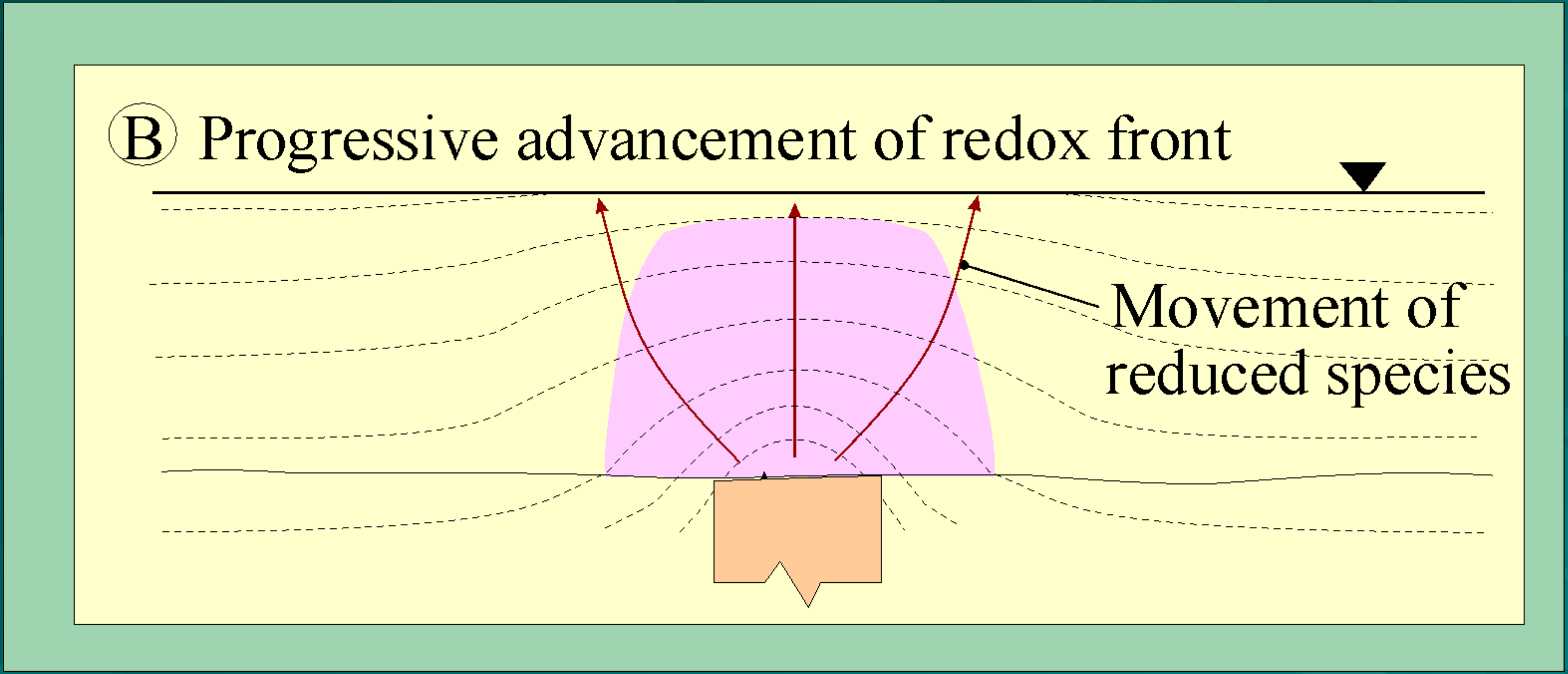
Reduced Chimney Development



Hamilton, 1998

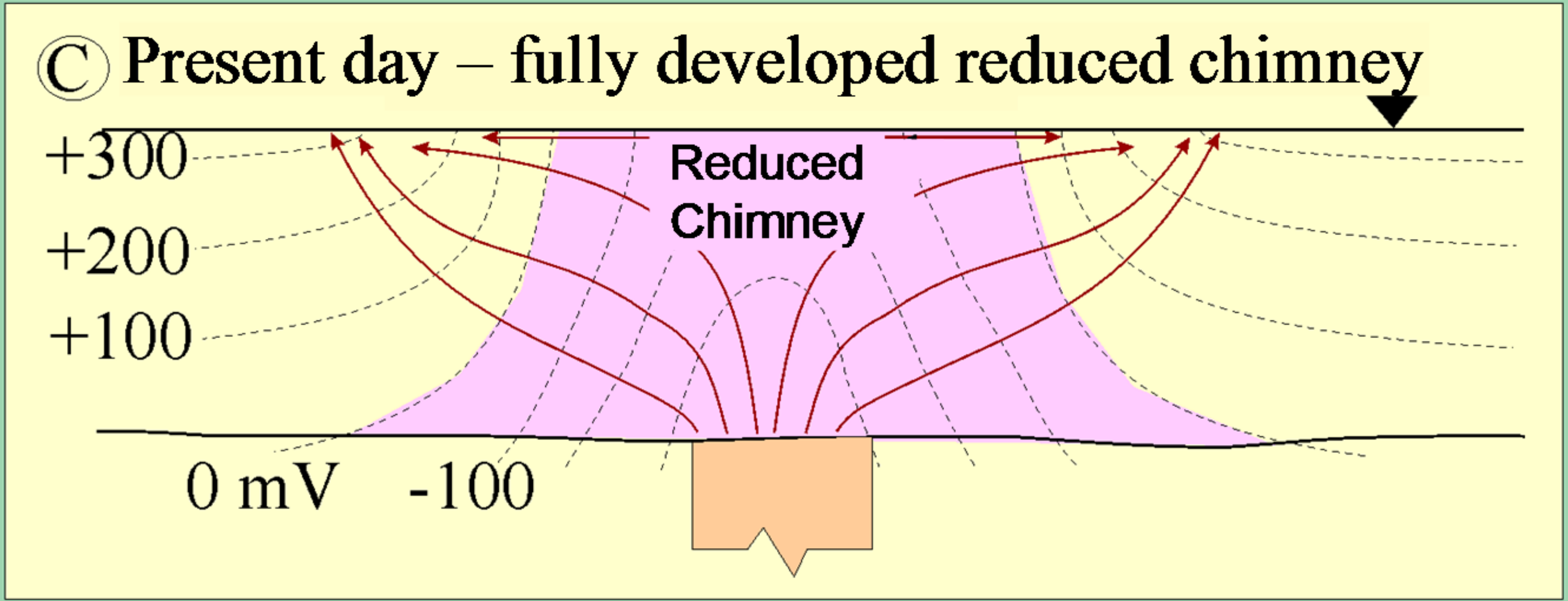
Ontario Geological Survey

Reduced Chimney Development



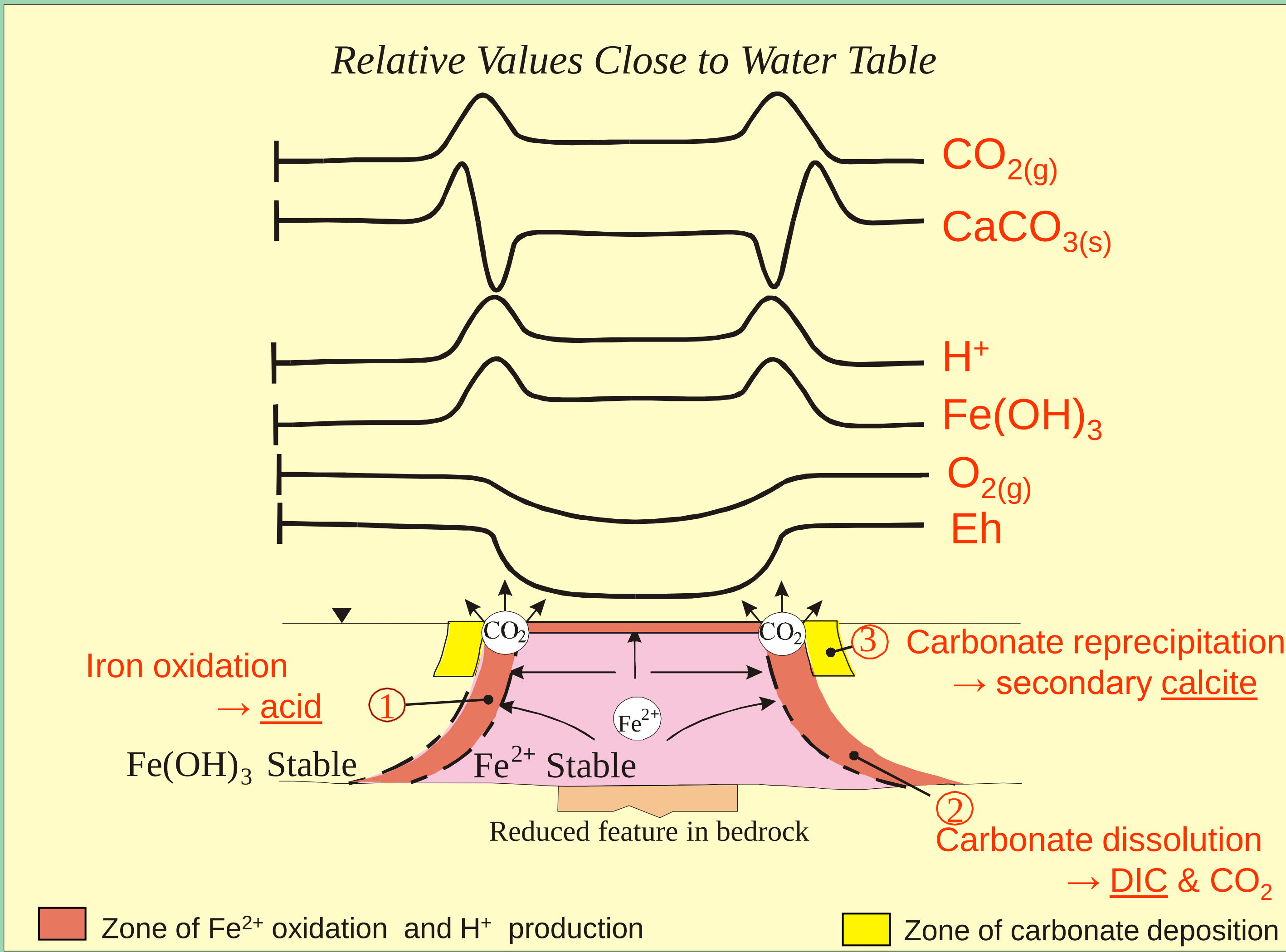
Hamilton, 1998

Reduced Chimney Development



Hamilton, 1998

Major-Element Geochemical Response to a Wide Reduced Chimney

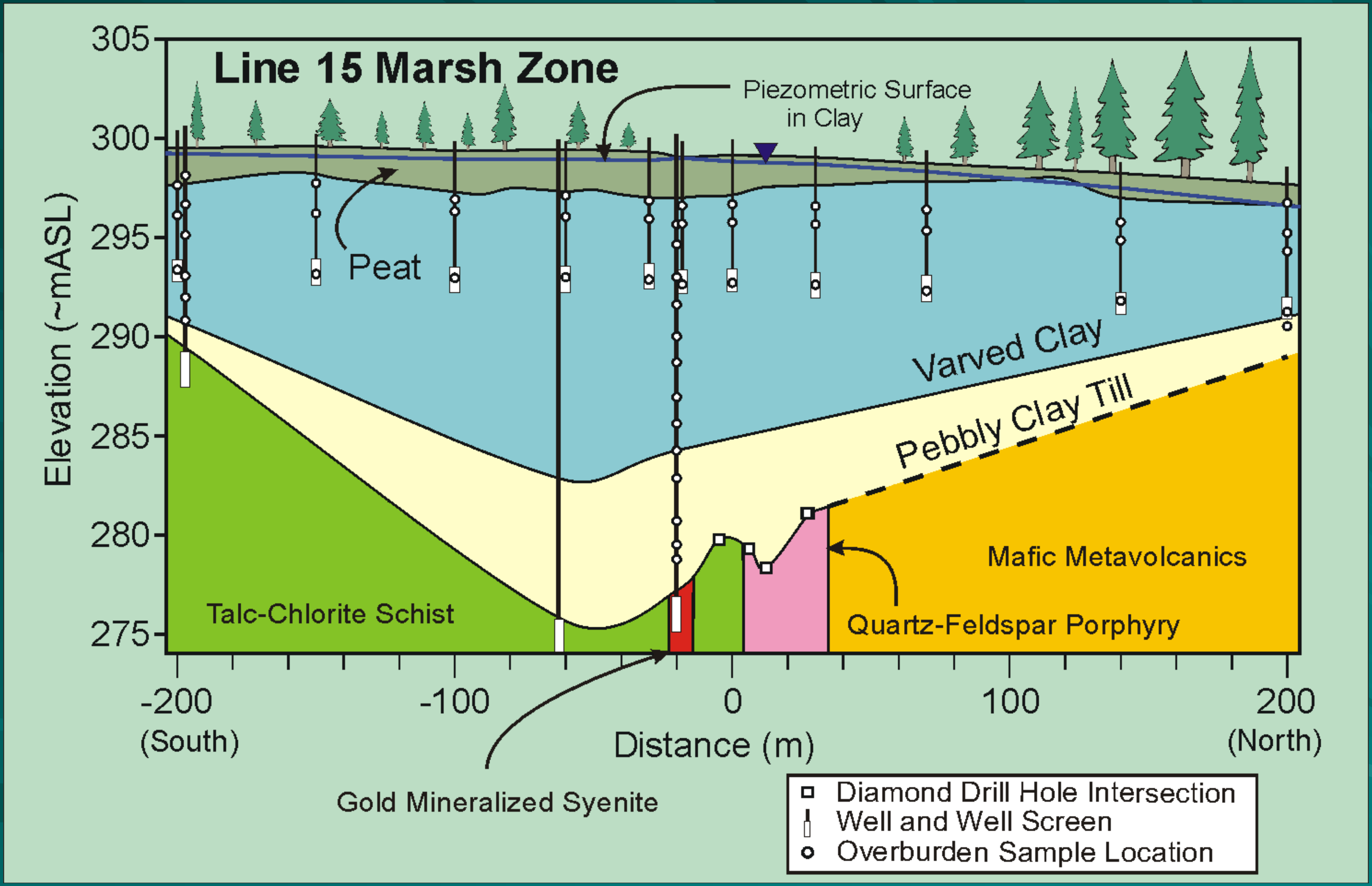


Hamilton, 1999; 2000

Ontario Geological Survey


Marsh Zone

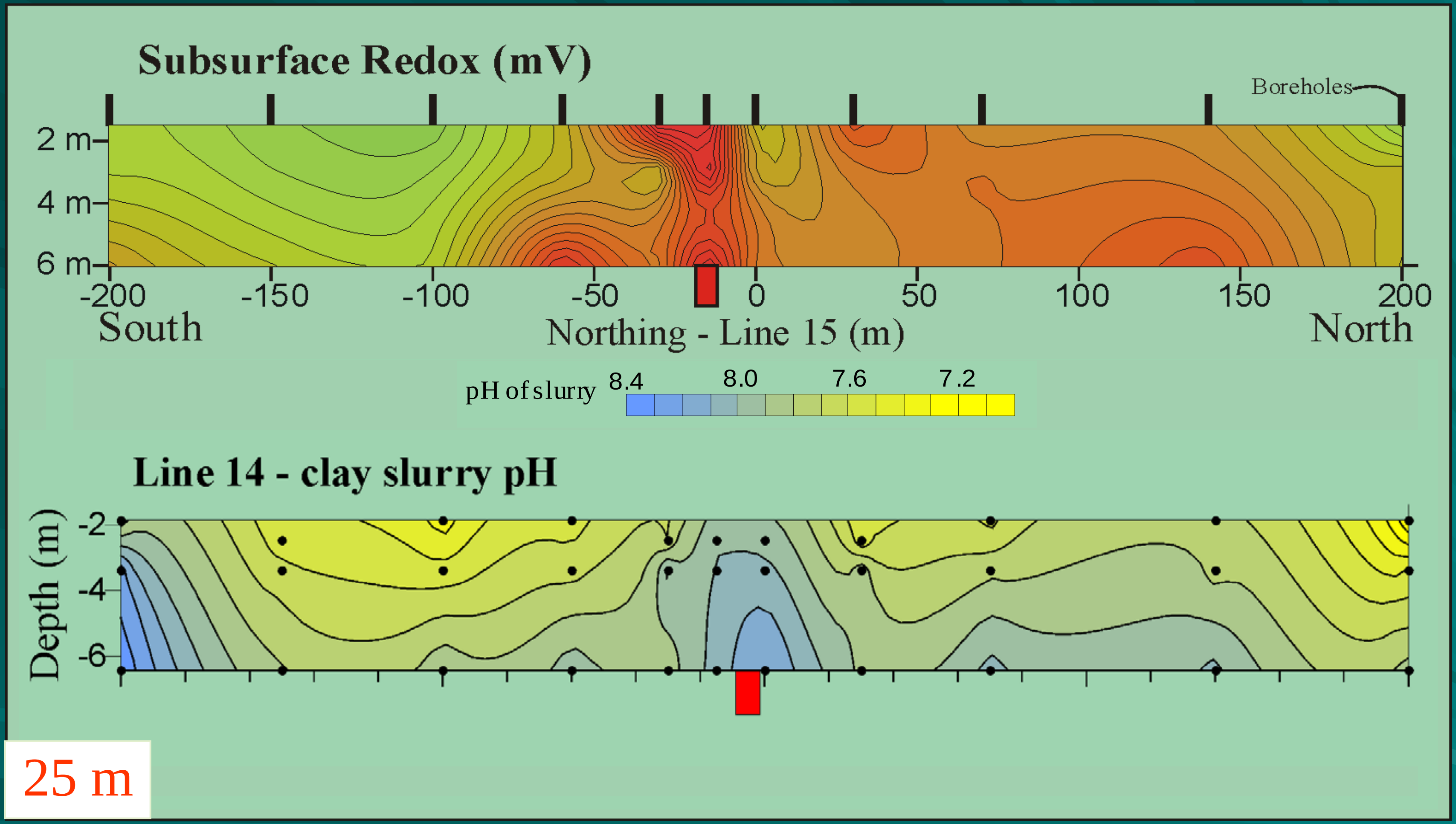
Marsh Zone Overburden Stratigraphy



THE ASSOCIATION OF APPLIED GEOCHEMISTS 1970

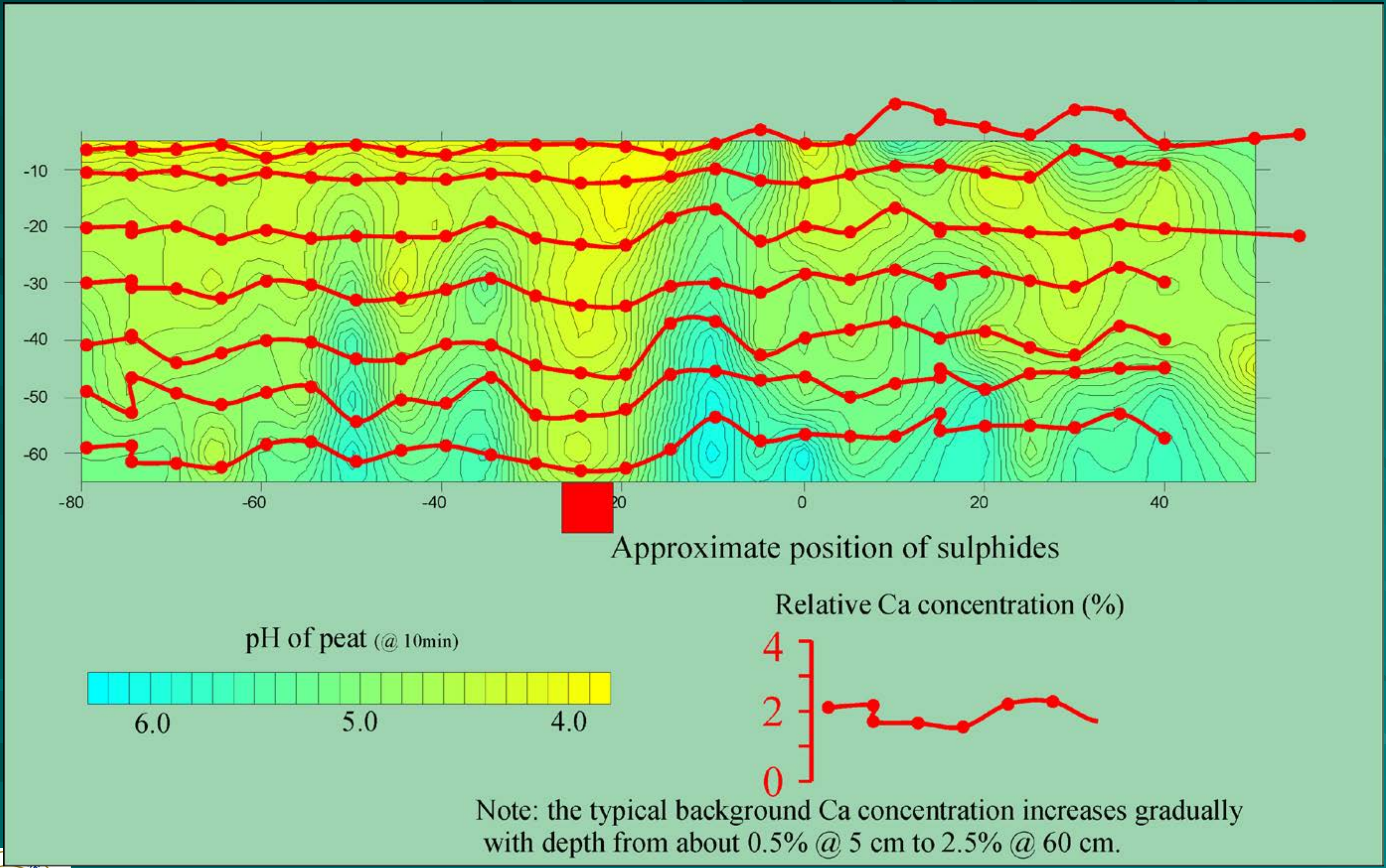
Ontario Geological Survey

Marsh Zone, pH & Redox in Clay

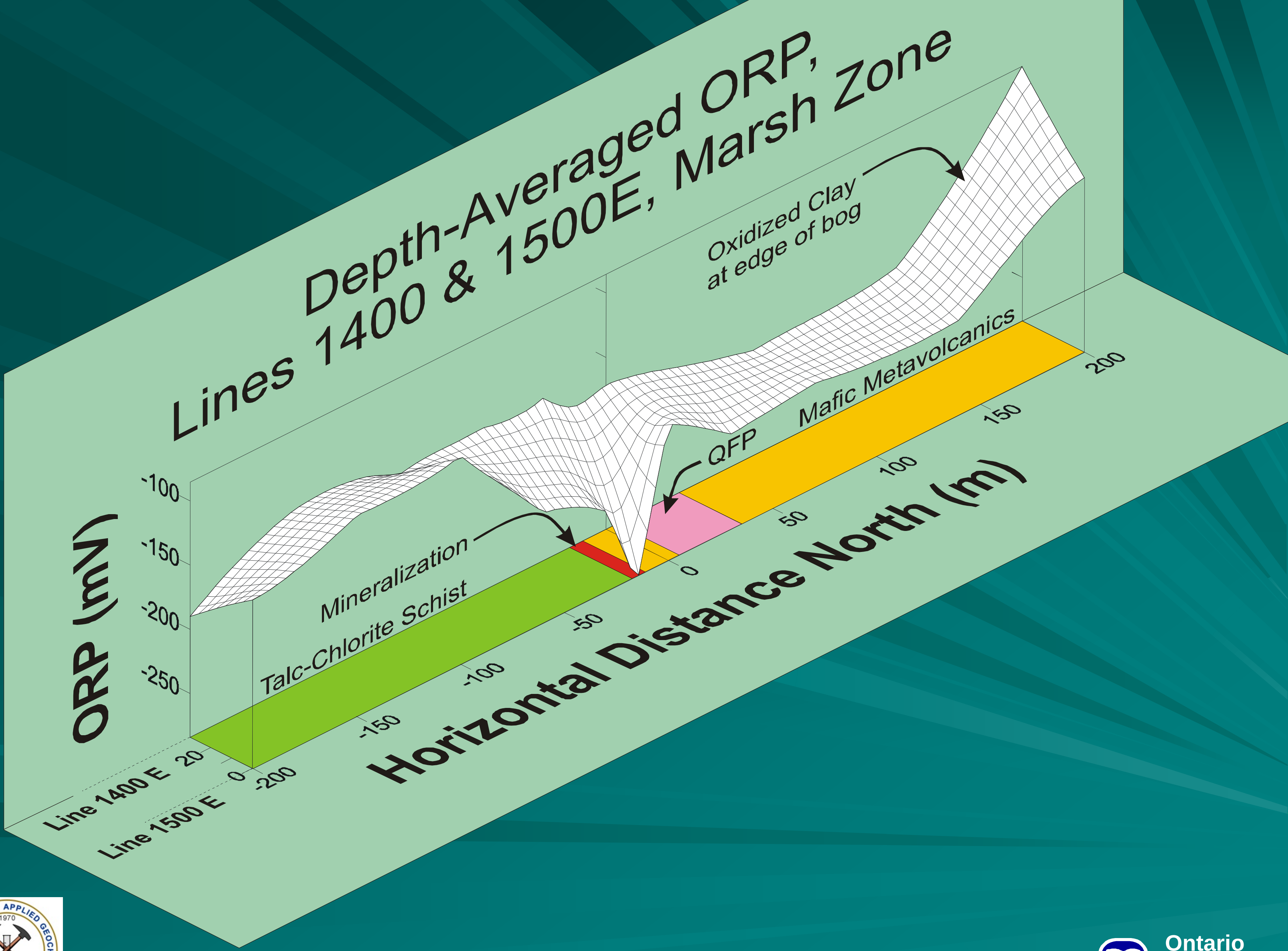


Ontario Geological Survey

Ca and pH in peat , Marsh Zone



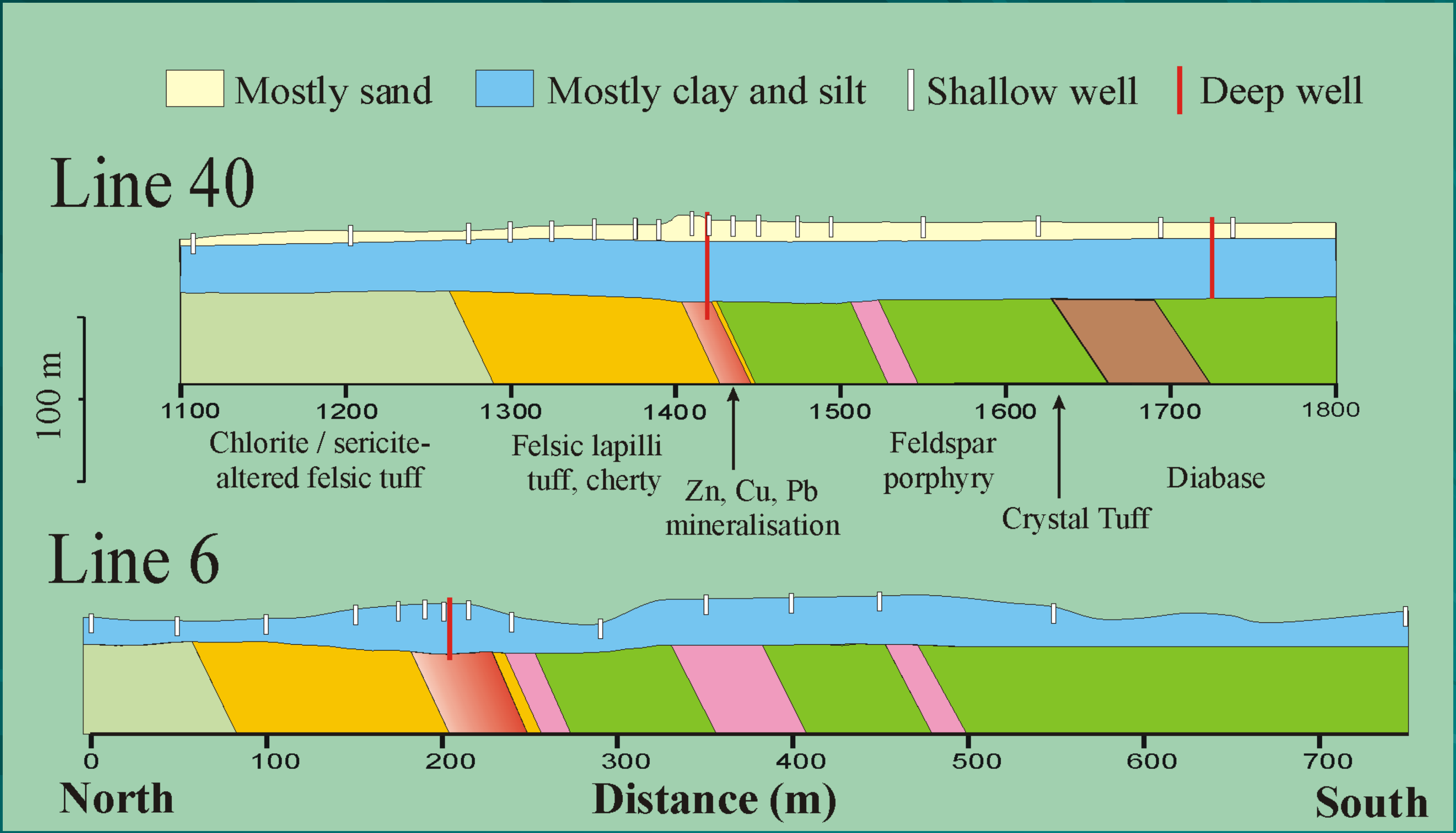
Ontario Geological Survey



Ontario Geological Survey

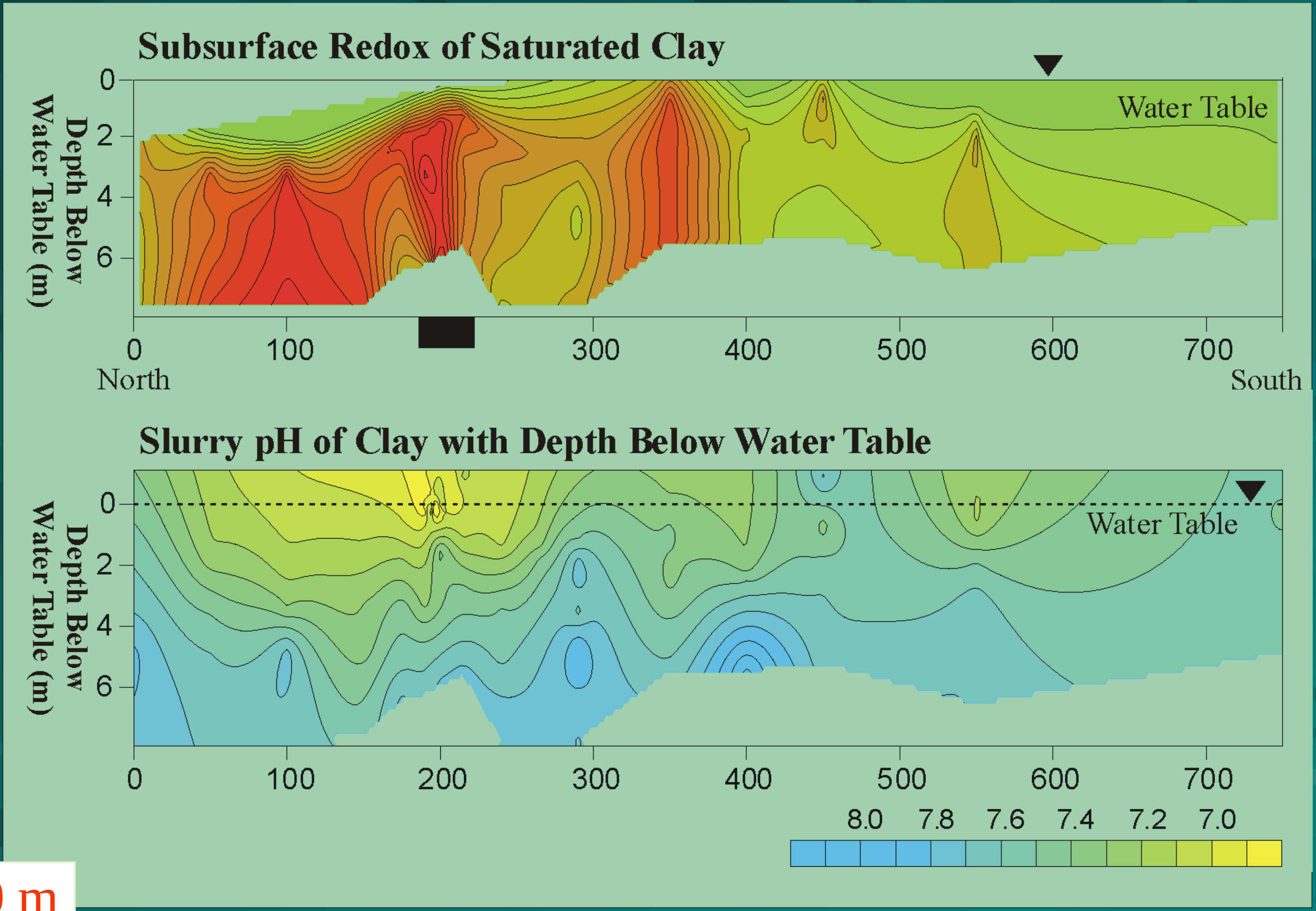

Cross Lake VMS

Cross Lake Stratigraphy



Ontario Geological Survey

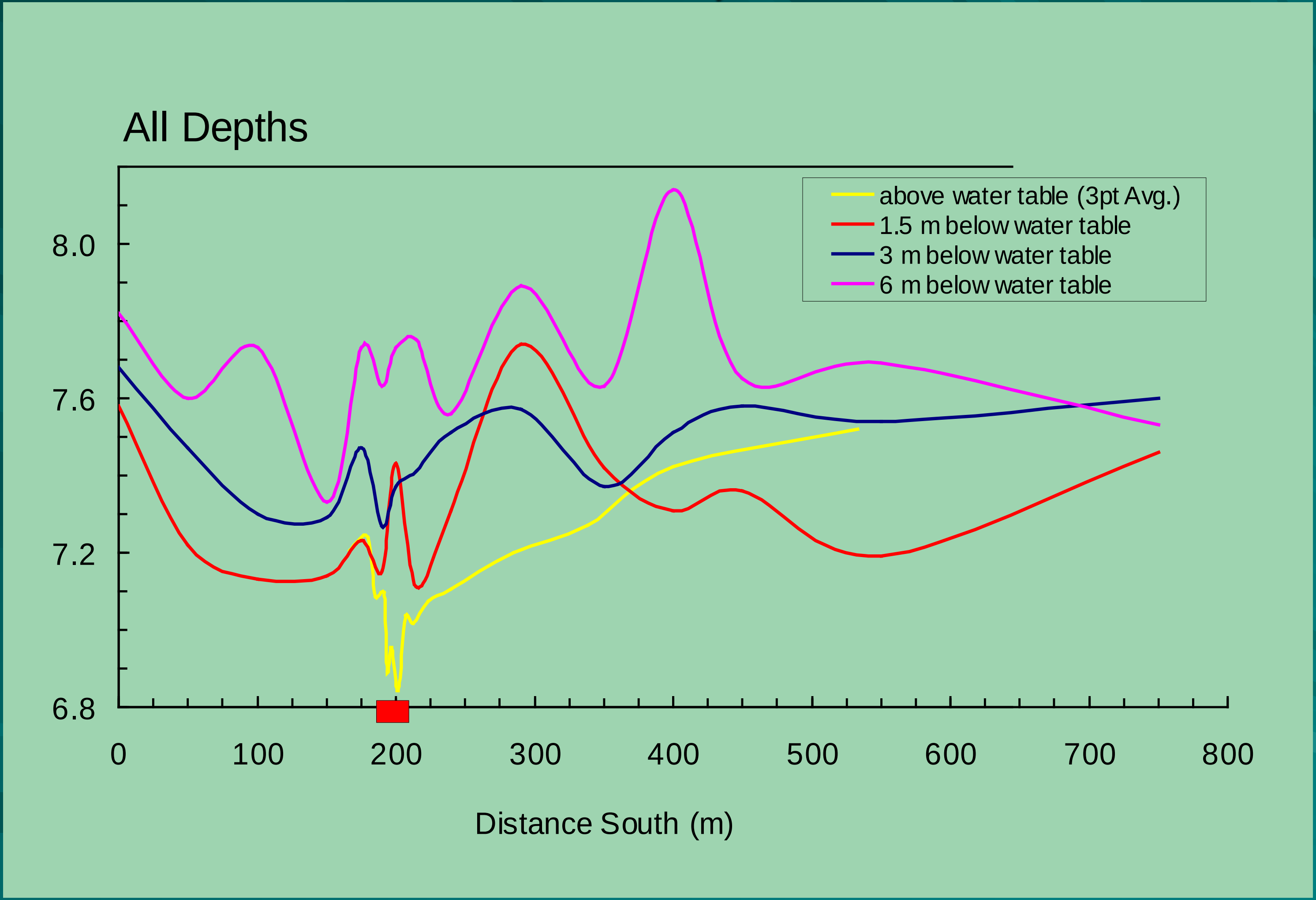
Cross Lake, Line 6 - 3D Redox & pH



30 m

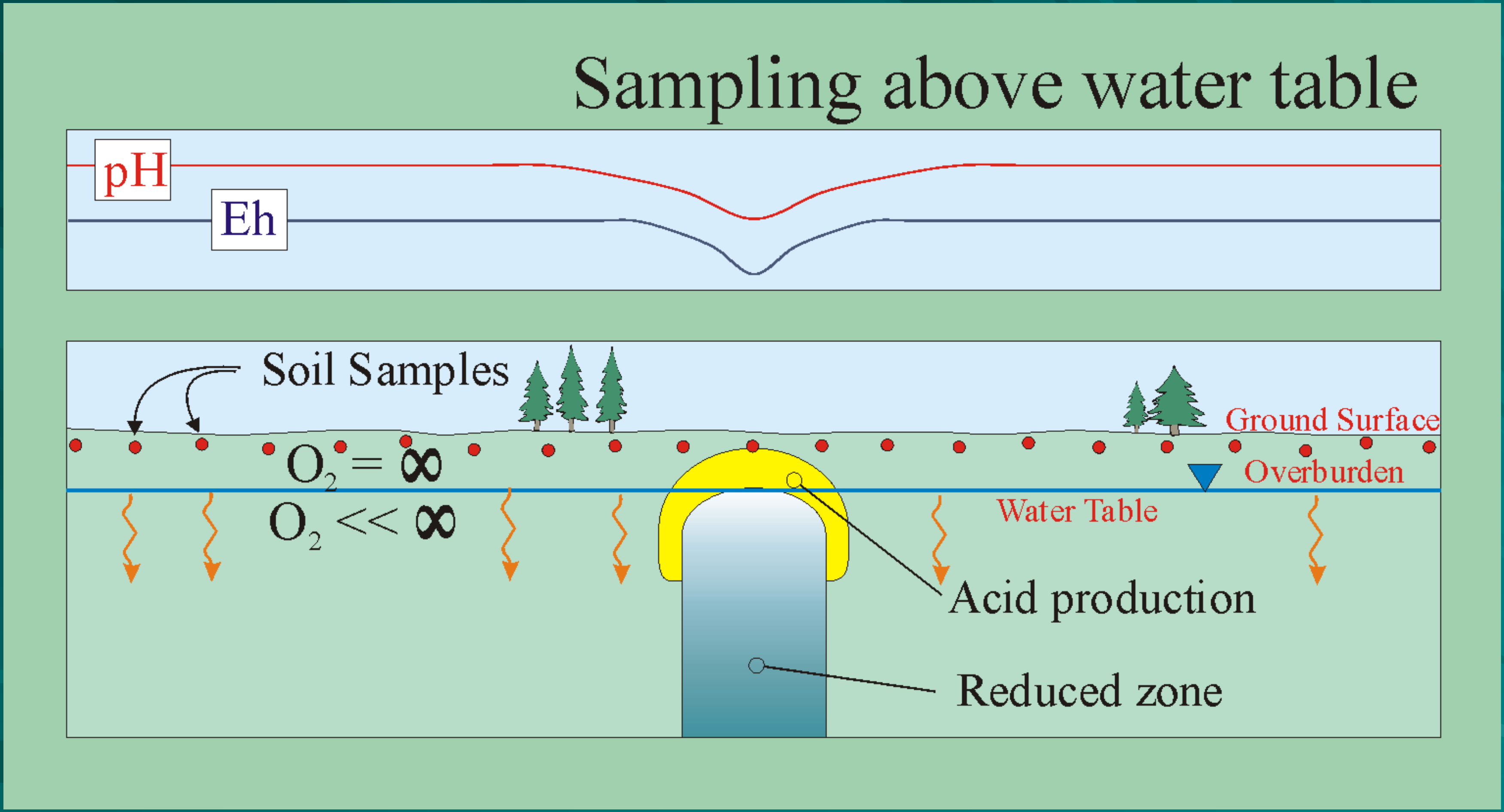
Ontario Geological Survey

Soil Slurry pH 6 m Below Water Table, Cross Lake, Line 6



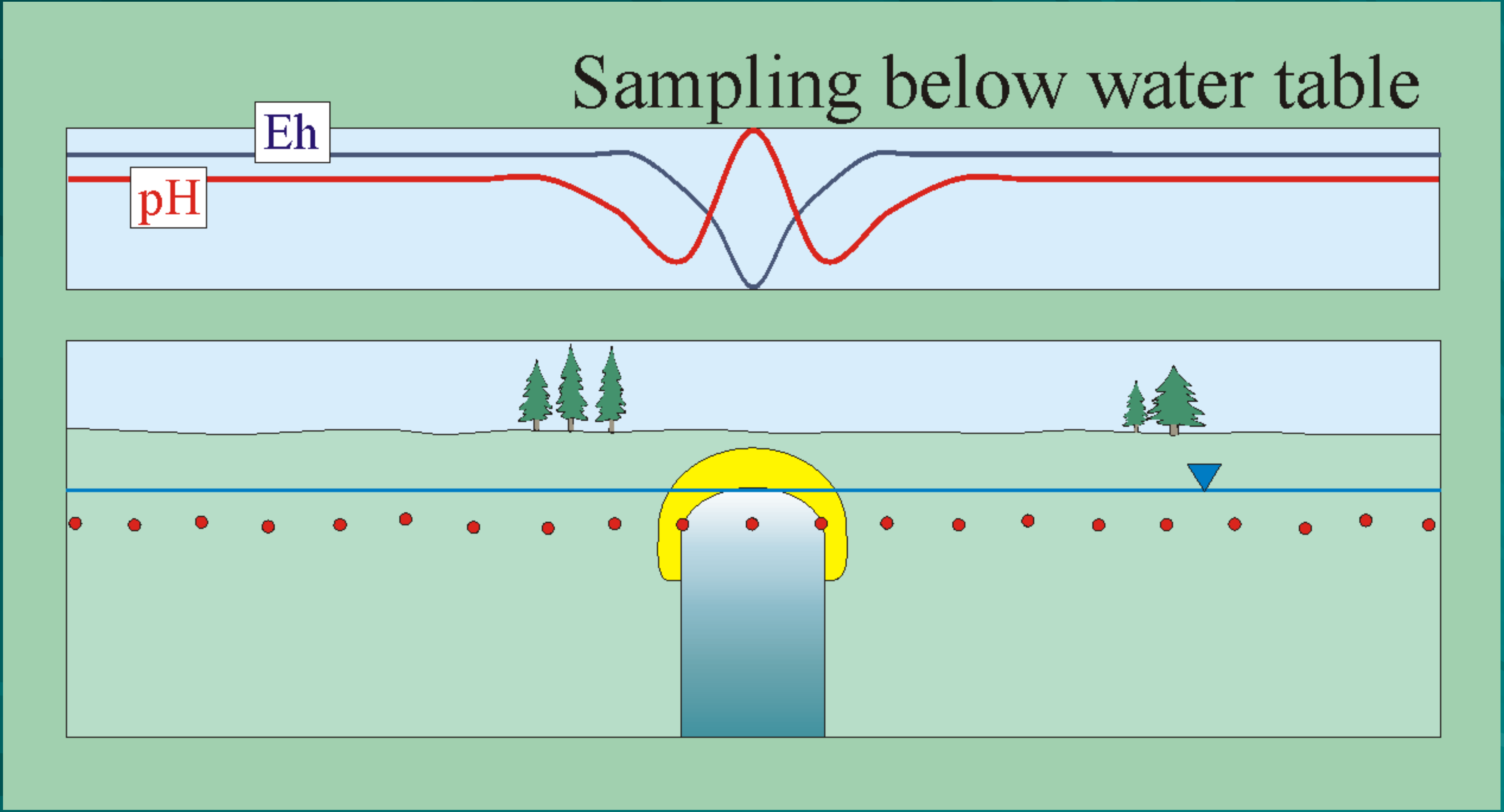
Ontario Geological Survey

Development of pH Anomaly Above A Reduced Area in Overburden



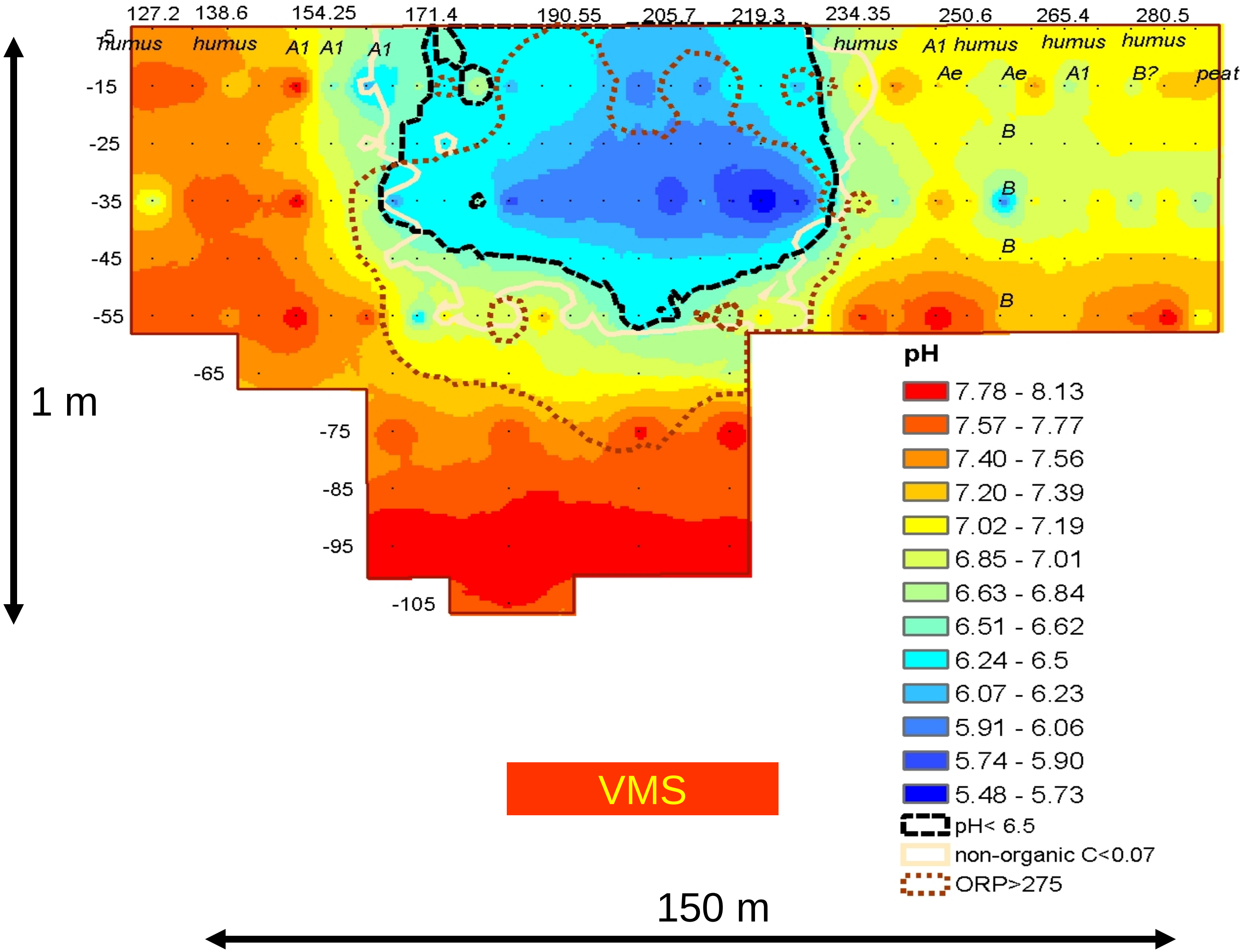
Ontario Geological Survey

Development of pH Anomaly Above A Reduced Area in Overburden



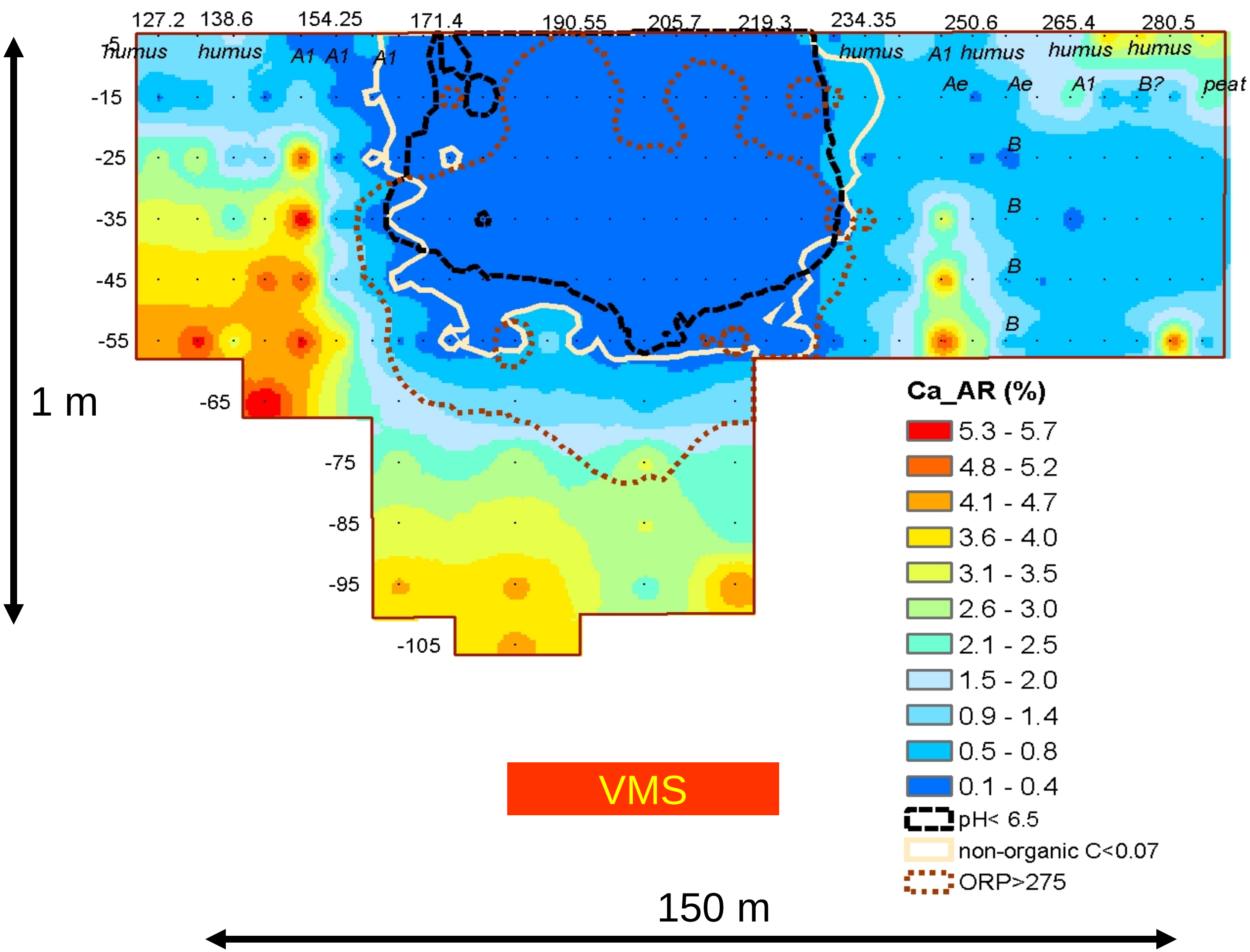
Ontario Geological Survey

pH, Line 6, Cross Lake



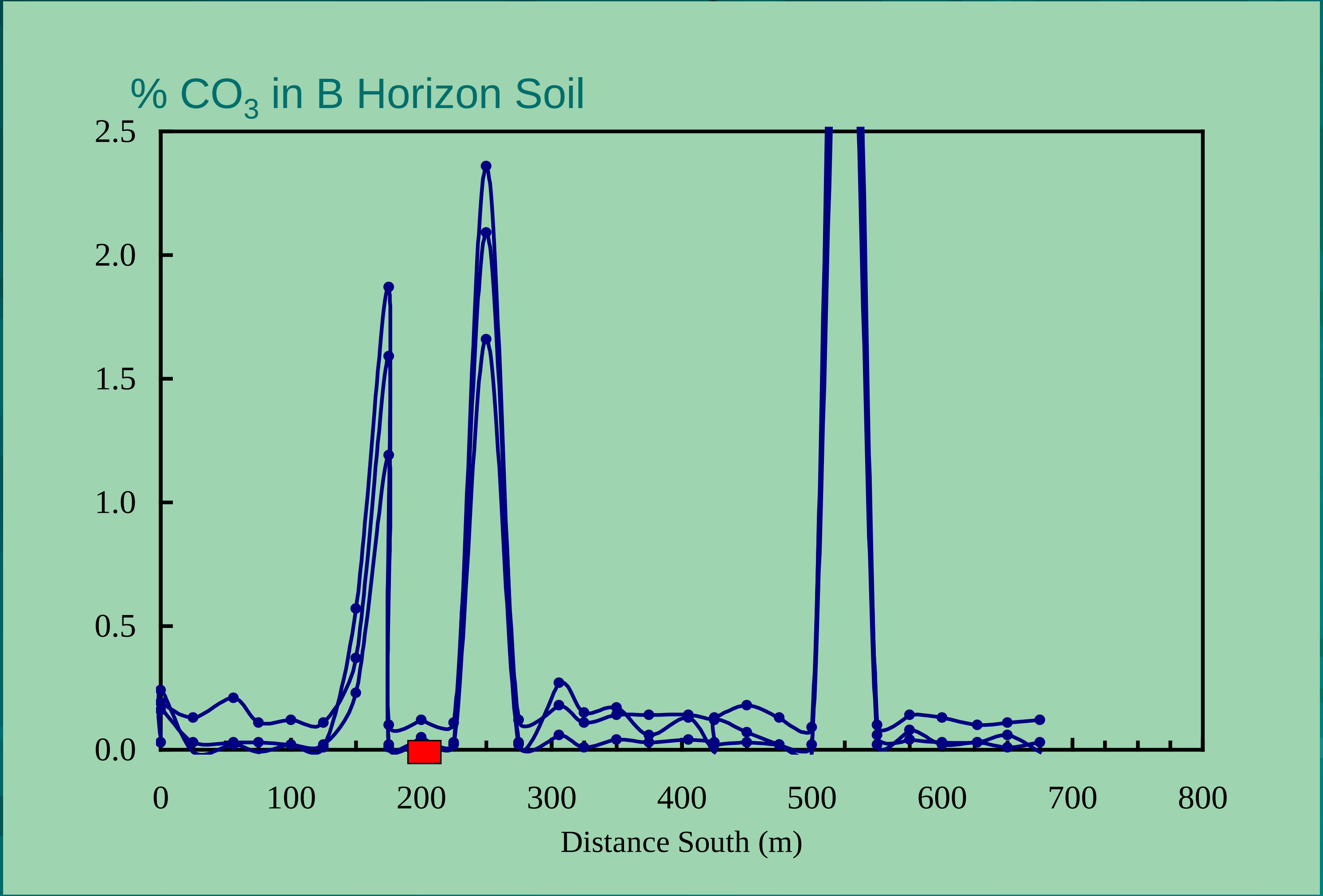
Ontario Geological Survey

Calcium – Line 6, Cross Lake



Ontario Geological Survey

% CO_3 in B-Horizon Soil
Cross Lake, Line 6



Ontario Geological Survey

Acid Production - Implications…1

1. H^+ anomaly occurs over the reduced chimney
   - 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

Ontario Geological Survey

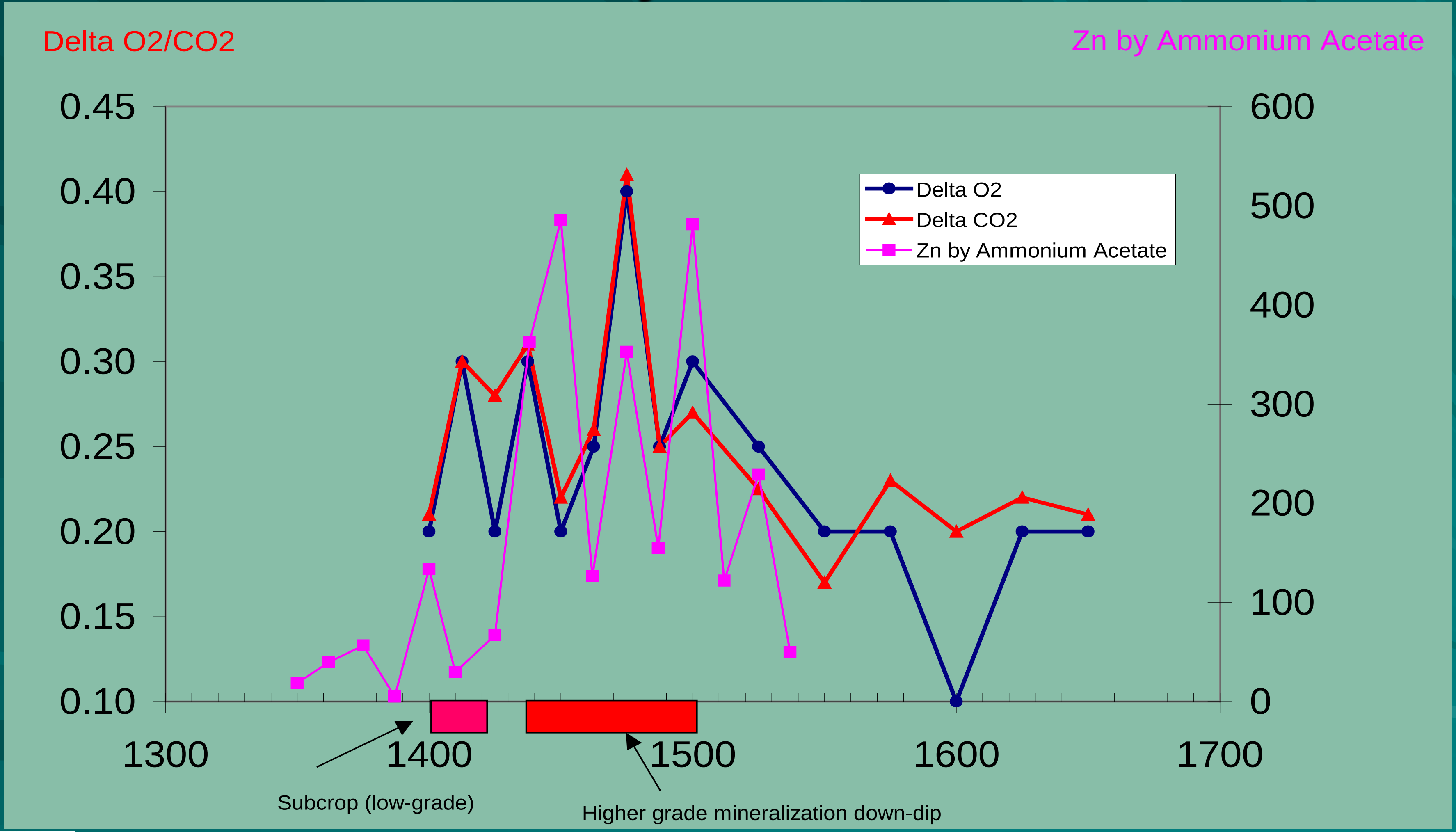
Acid Production - Implications…3

- Acid production by metal oxidation requires *precipitation* of insoluble metal hydroxides
- Since oxidation must continue, there must be:

1. <u>Continuous upward movement of metals</u>
2. <u>Deposition of metals in the shallow subsurface</u>

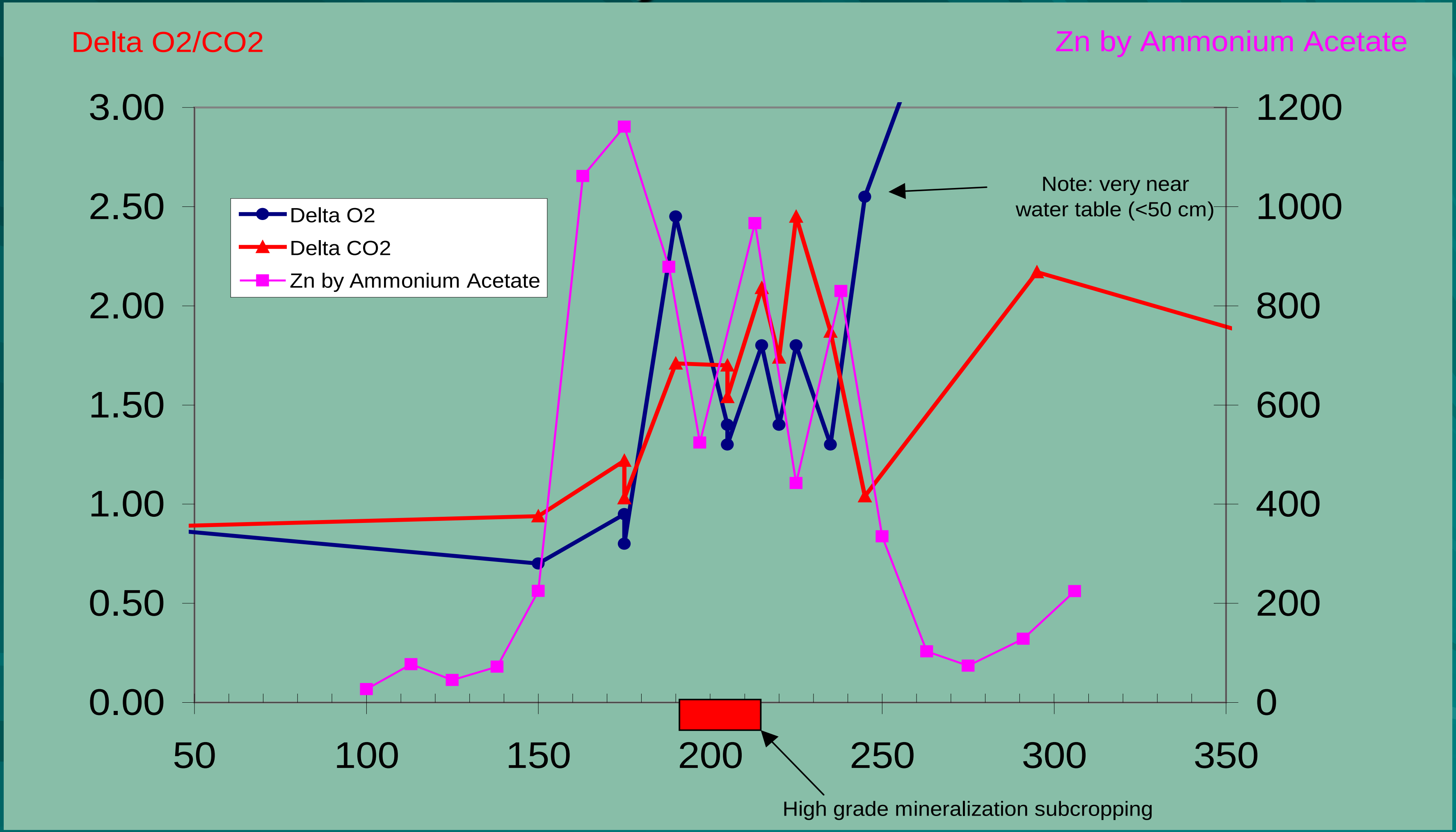
Cross Lake, Line 40

Soil Gas vs. Zn by Ammonium Acetate



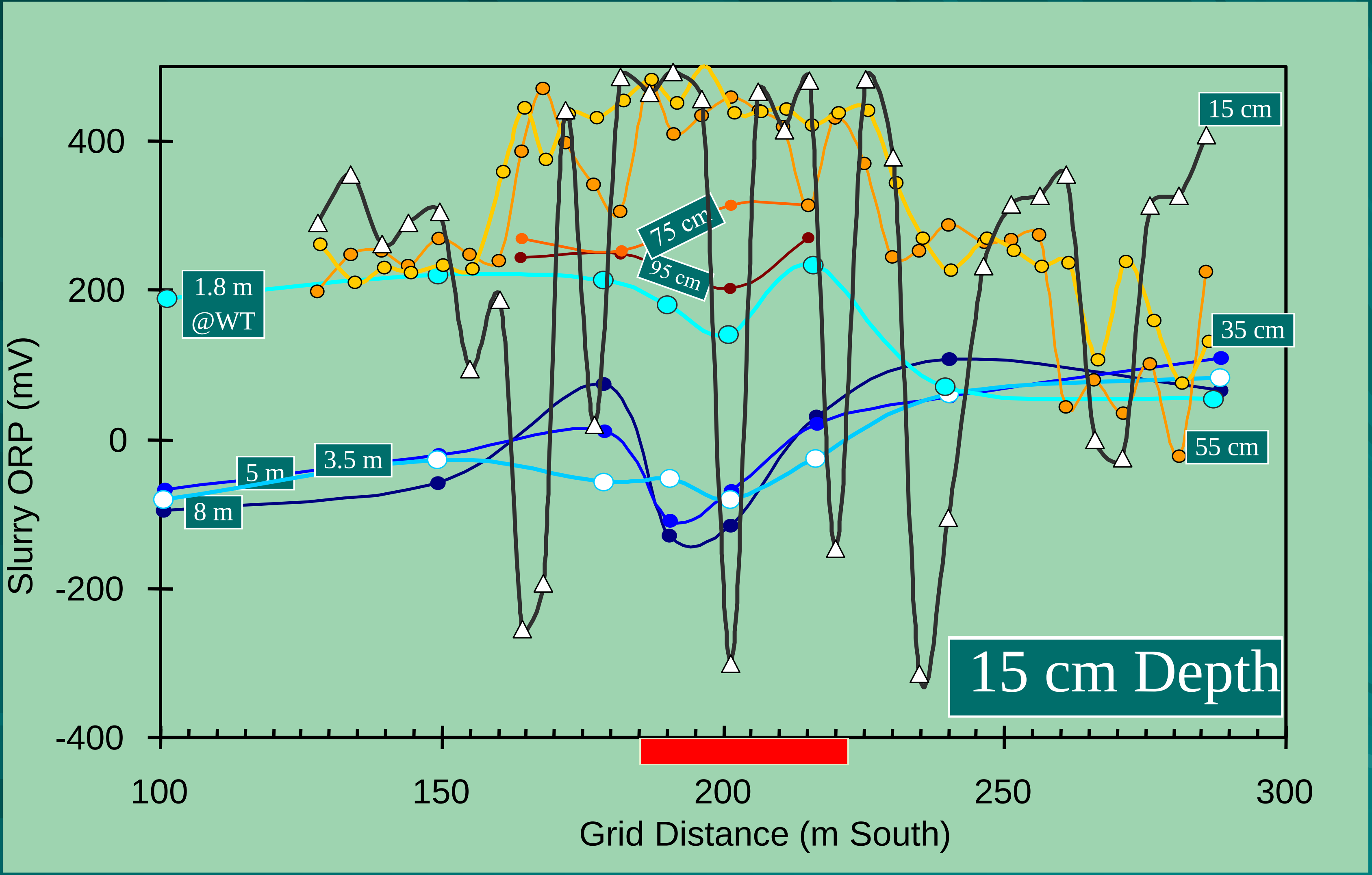
Ontario Geological Survey

Cross Lake, Line 6
Soil Gas vs. Zn by Ammonium Acetate



Ontario Geological Survey

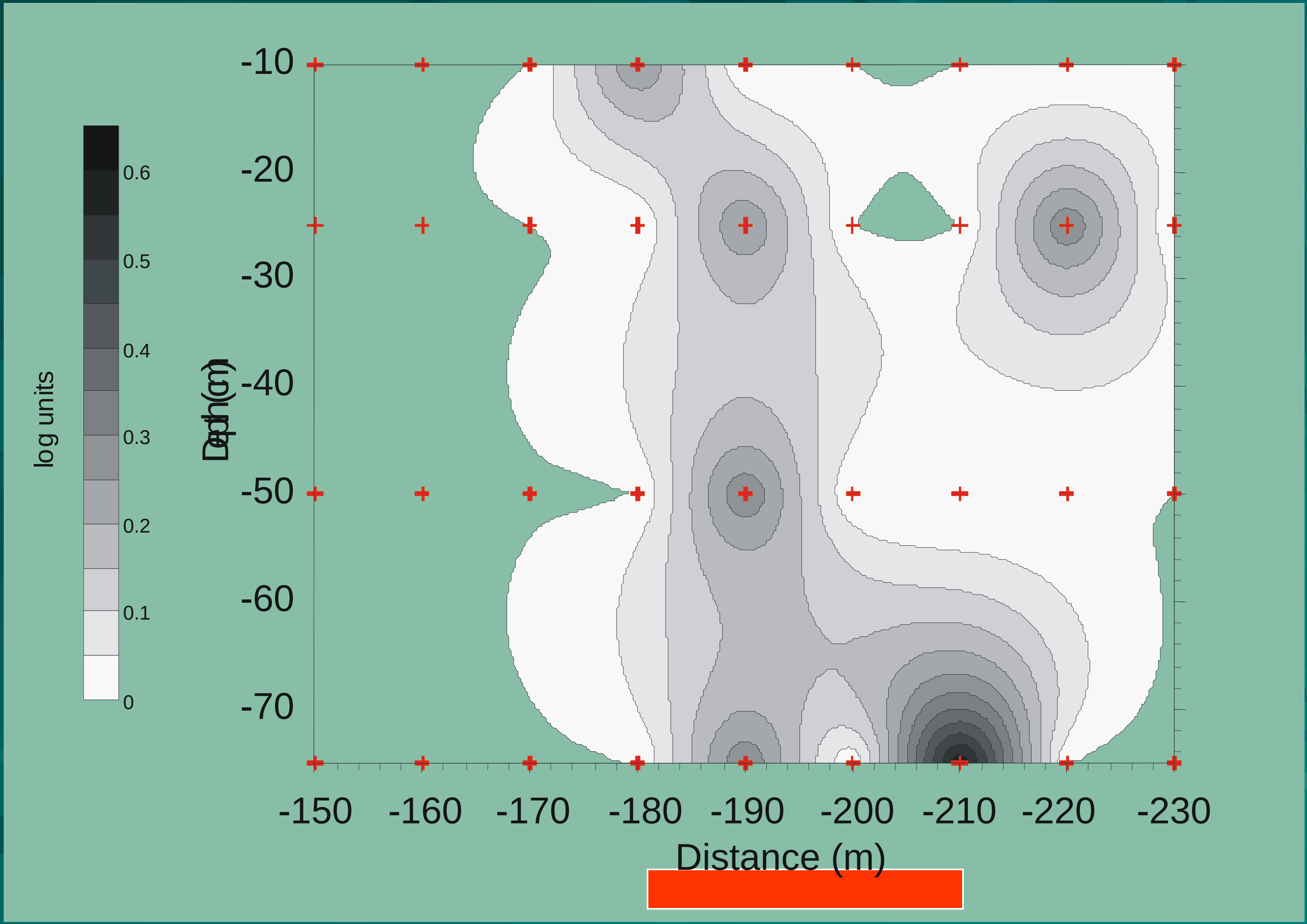
Line 6 ORP Data - All Depths



(Probe No.1 for all depths except 1.8m & 15cm which show P3&P6 data respectively transformed using the linear relationship of each with P1; 5 minutes equilibration for well samples; 10 minutes for trench samples)

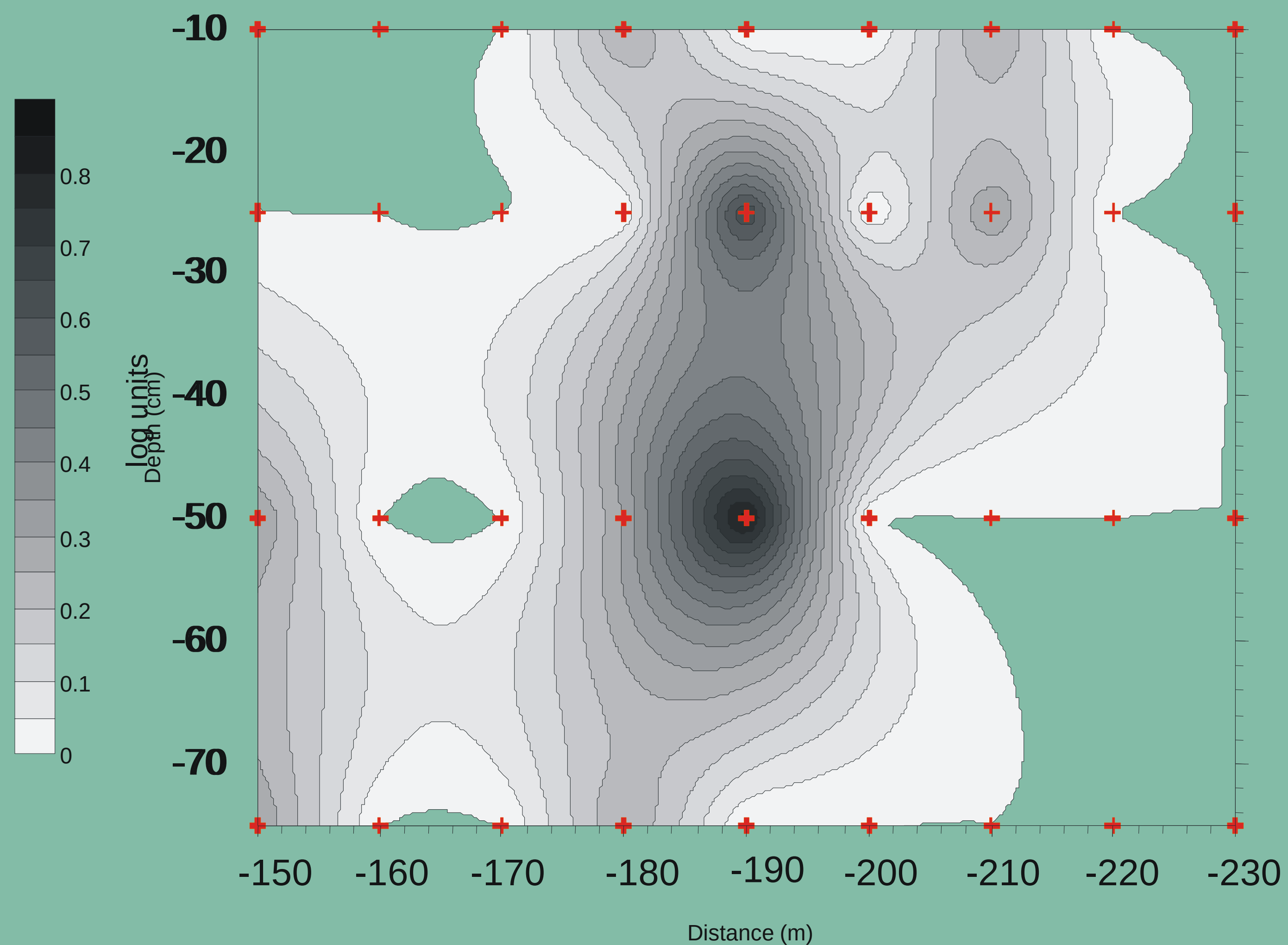
Ontario Geological Survey

SRBs - Cross Lake - 14 m from line



Slide courtesy of Gordon Southam

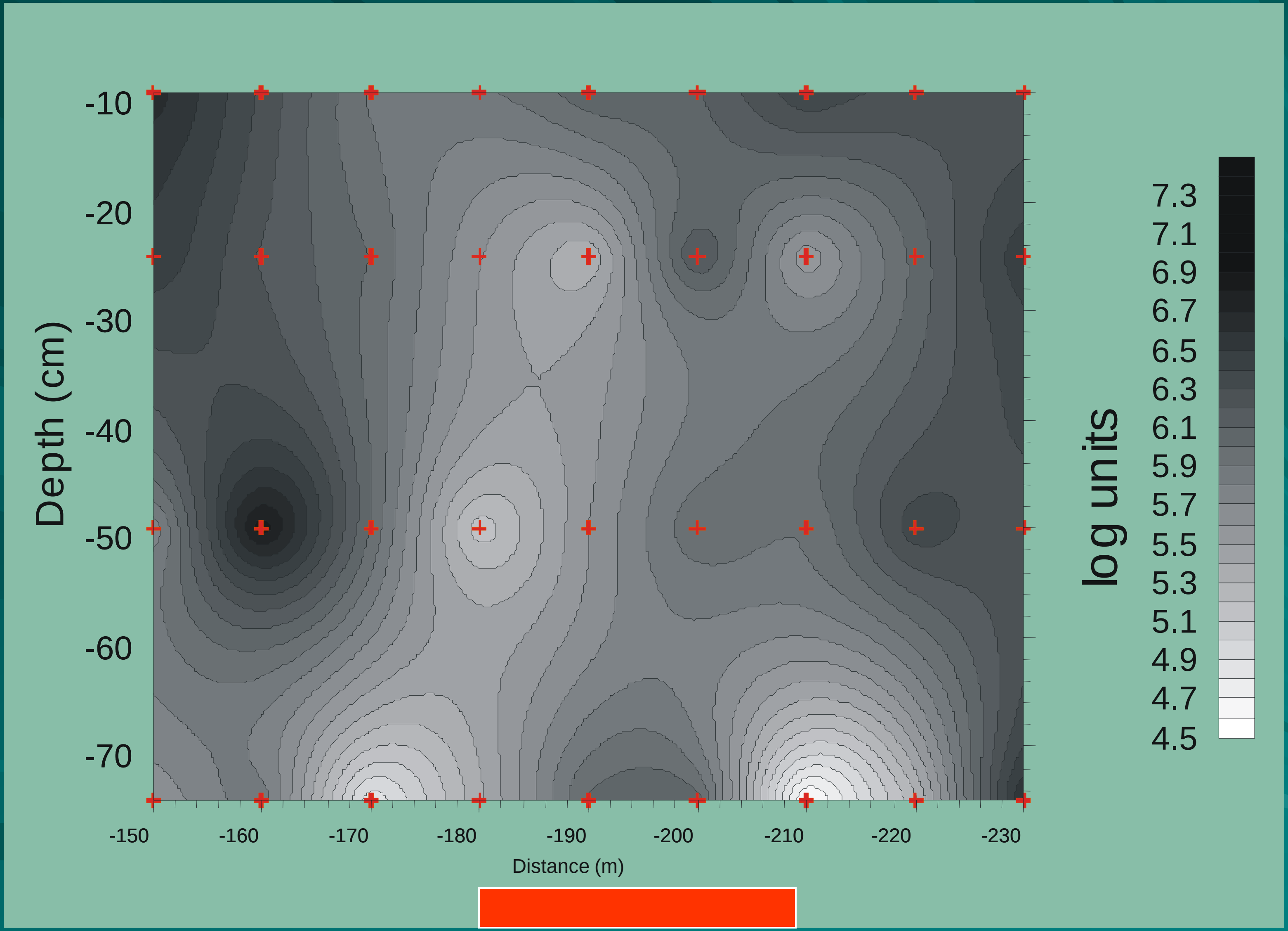
SRBs - Cross Lake - 12 m from line



Slide courtesy of Gordon Southam

Ontario Geological Survey

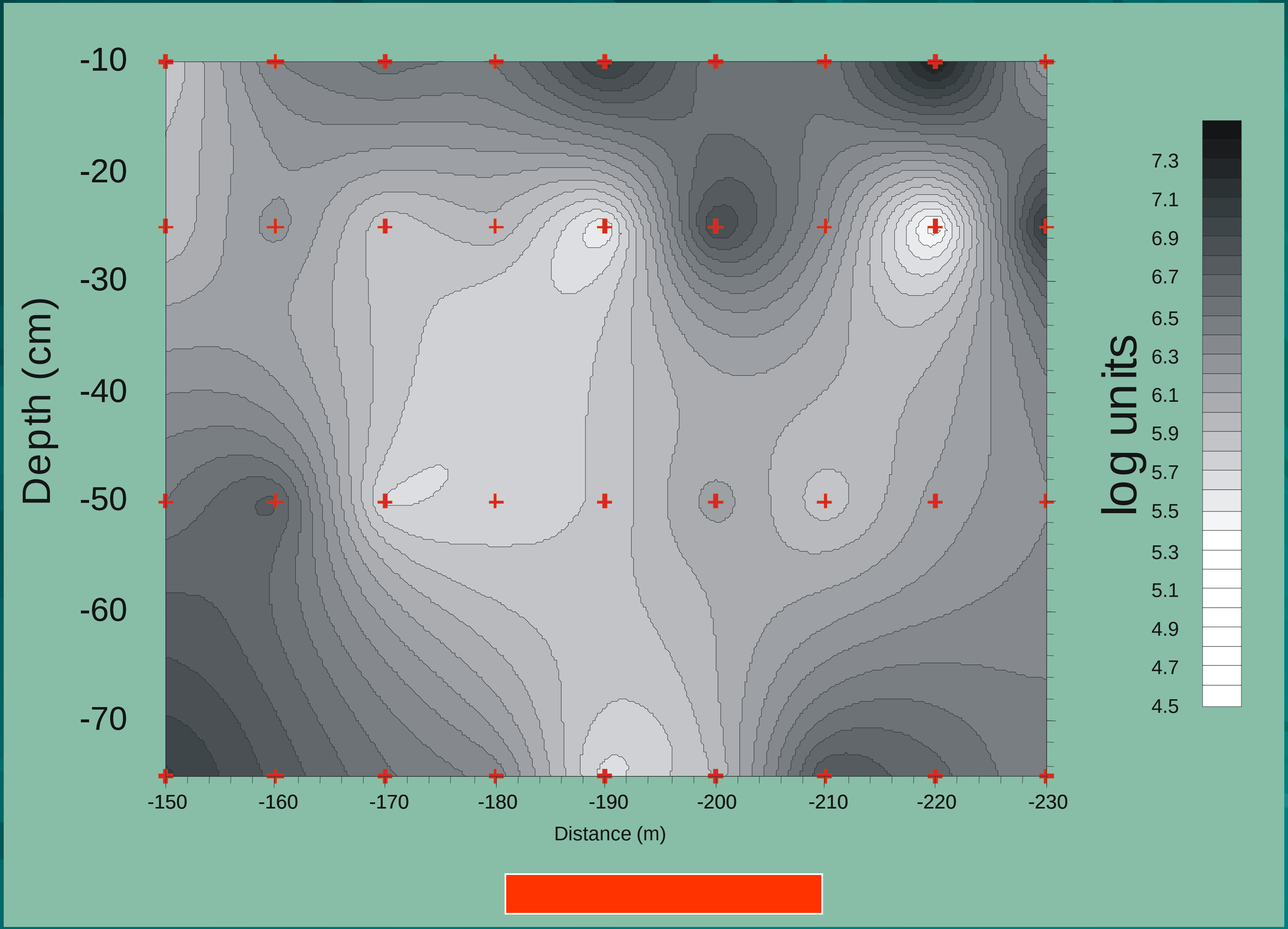
Aerobic Heterotrophs - Cross Lake - 12 m from line



Slide courtesy of Gordon Southam

Ontario Geological Survey

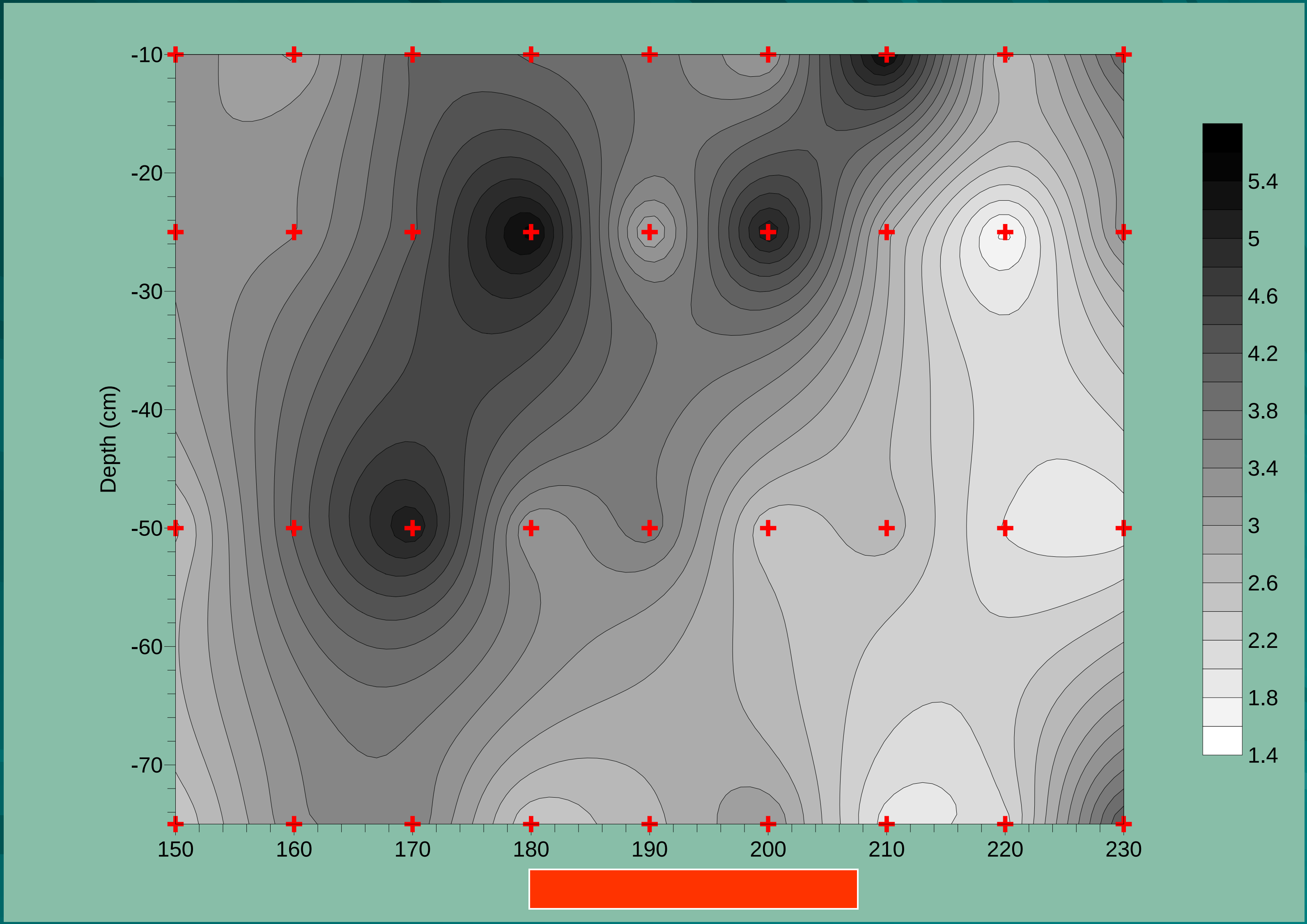
Aerobic Heterotrophs - Cross Lake - 12 m from line



Slide courtesy of Gordon Southam

Ontario Geological Survey

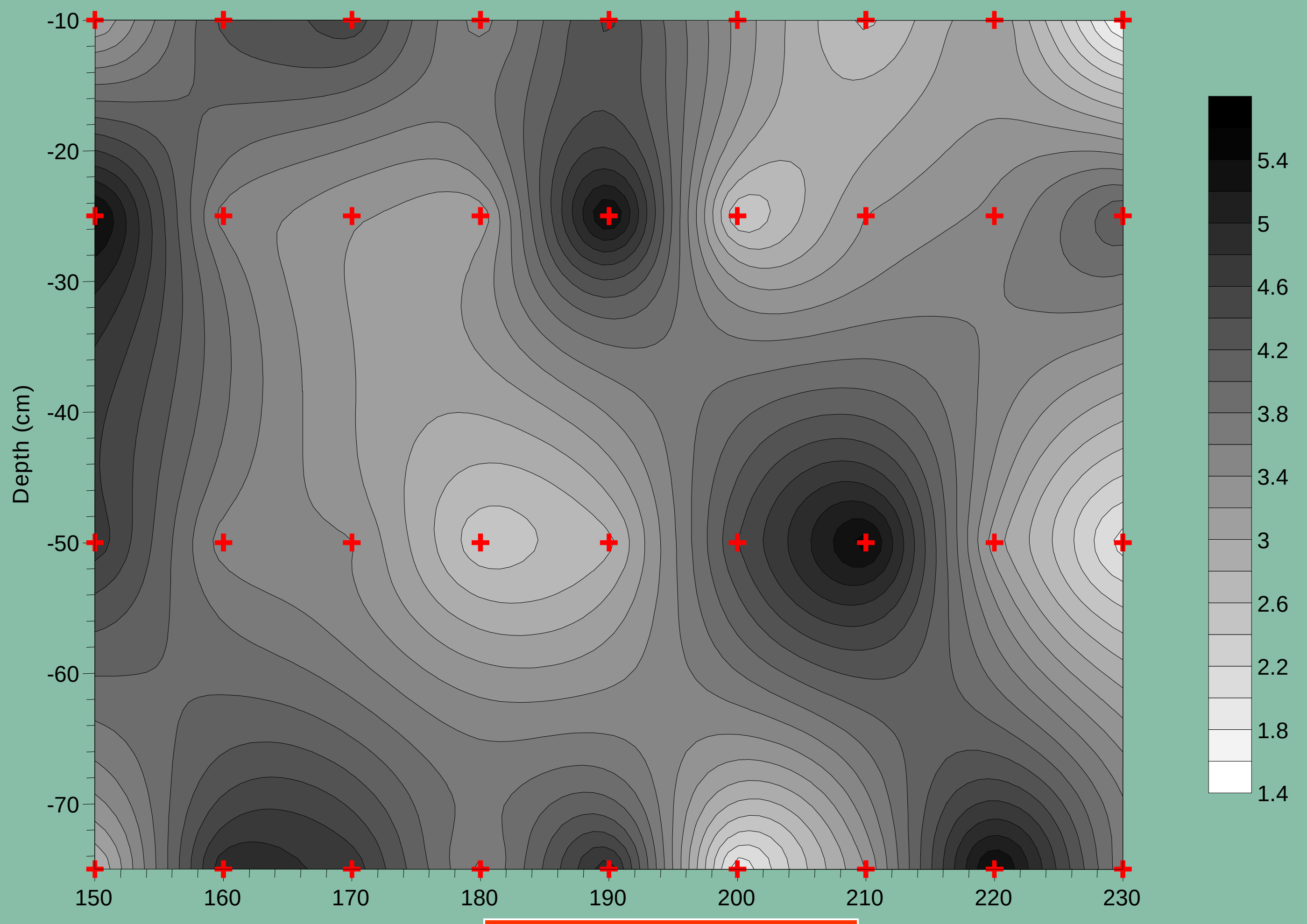
Anaerobes - Cross Lake - 12 m from line



Slide courtesy of Gordon Southam

Ontario Geological Survey

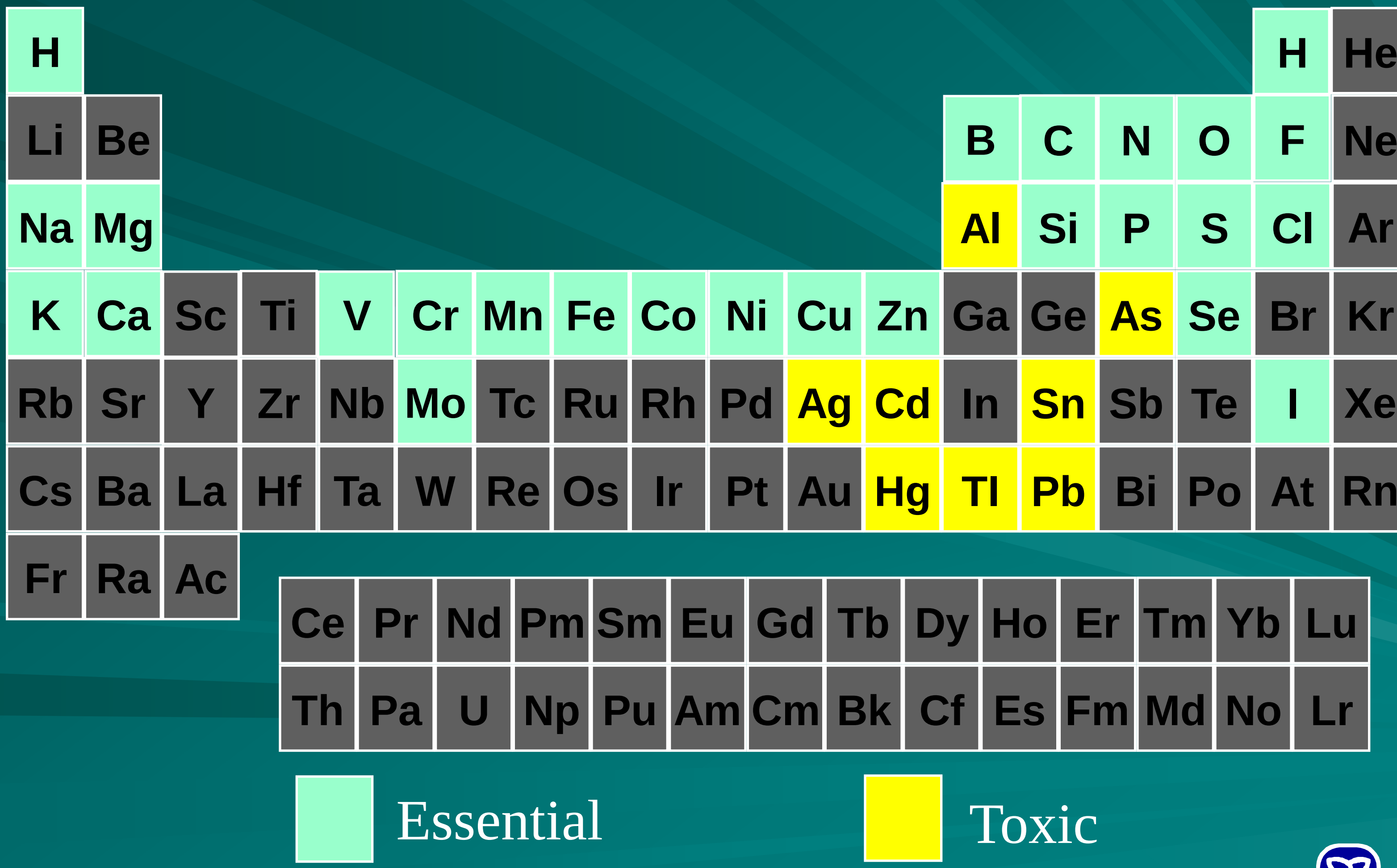
Anaerobes - Cross Lake - 14 m from line



Slide courtesy of Gordon Southam

Ontario Geological Survey

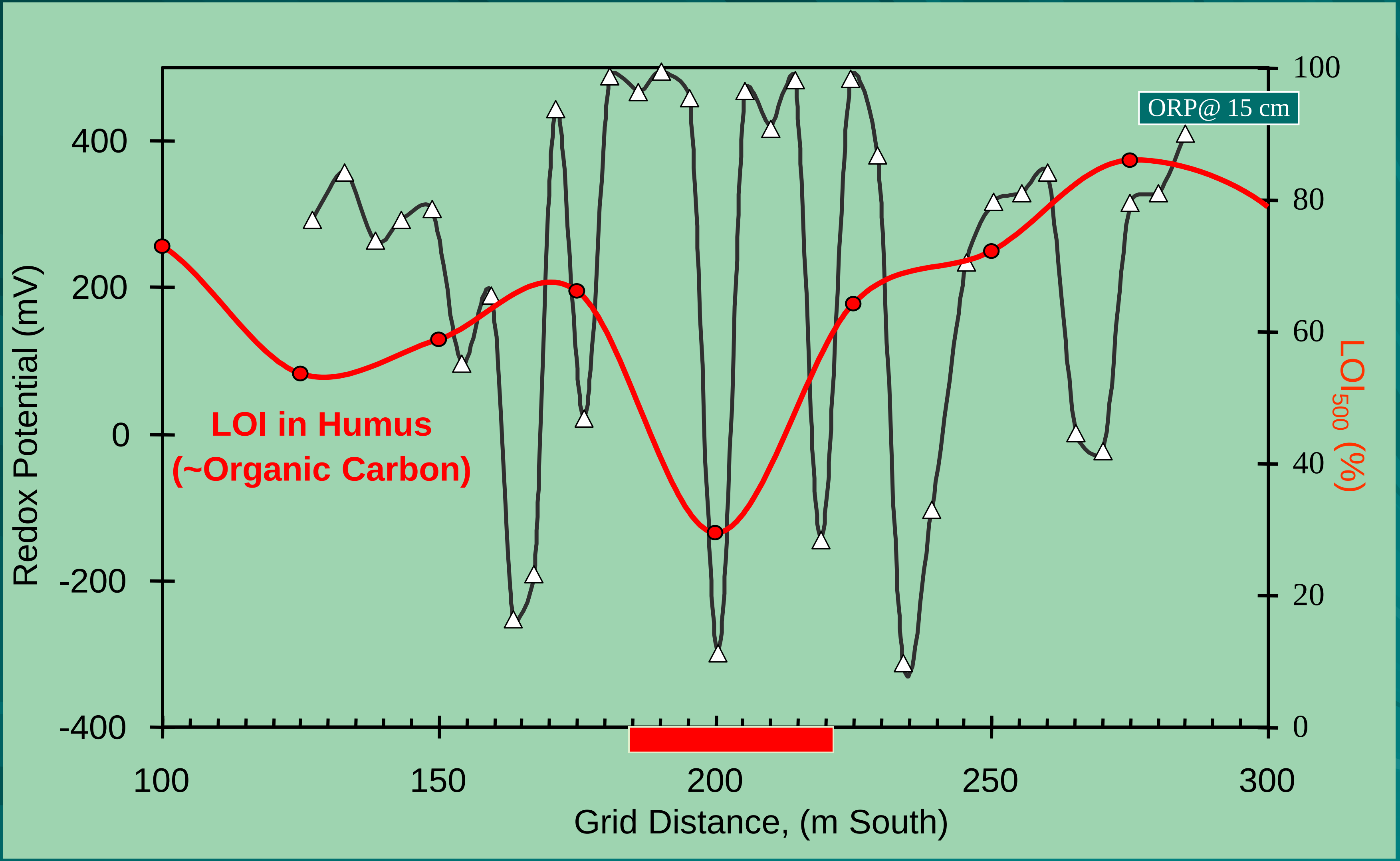
Essential Elements in Biology



Slide courtesy of D. Kelley, WMC

Ontario Geological Survey

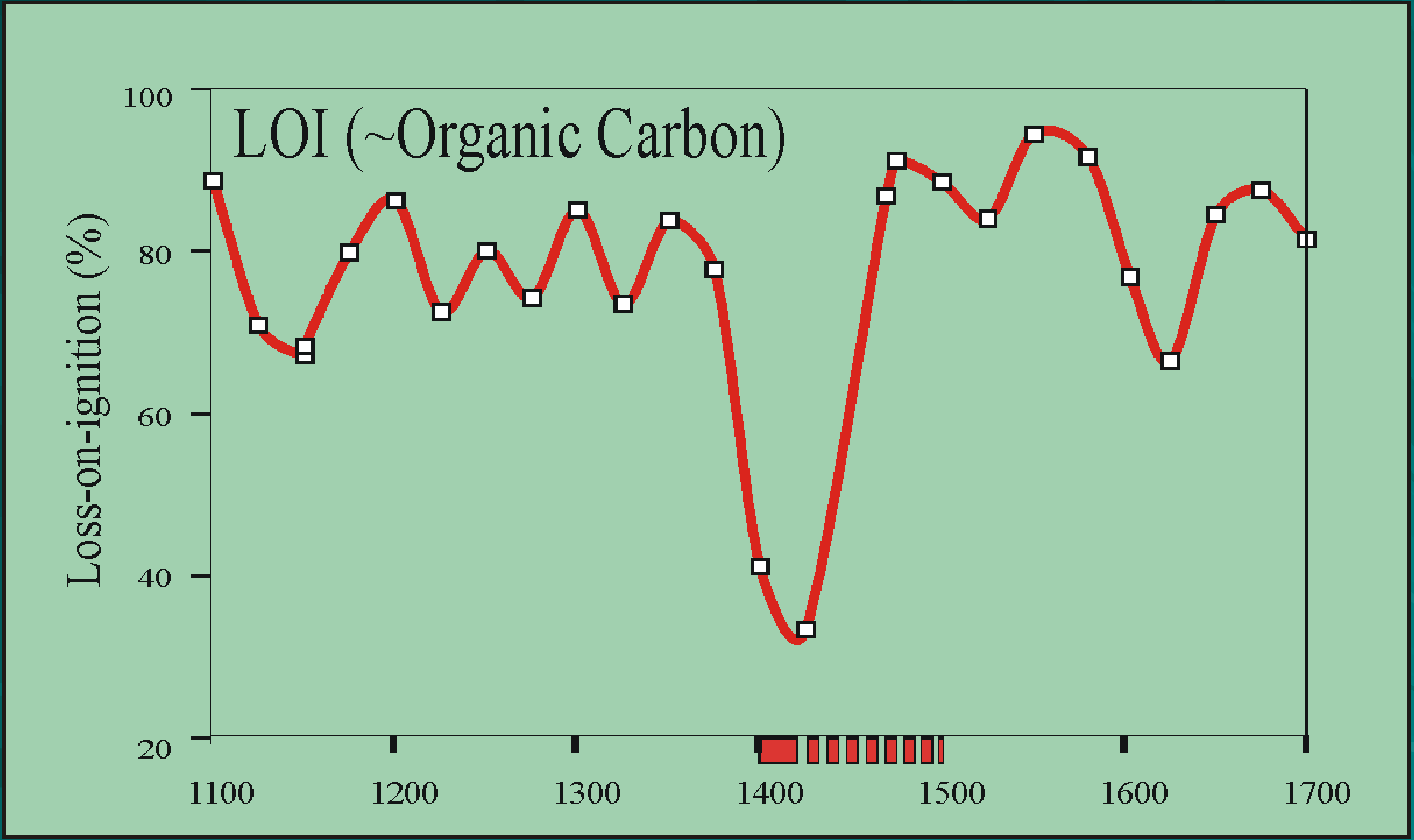
ORP @ 15cm vs. LOI_{500} in Humus



(Transformed P6 ORP data after 10 minutes of equilibration; LOI_{500} from 1999 humus samples)

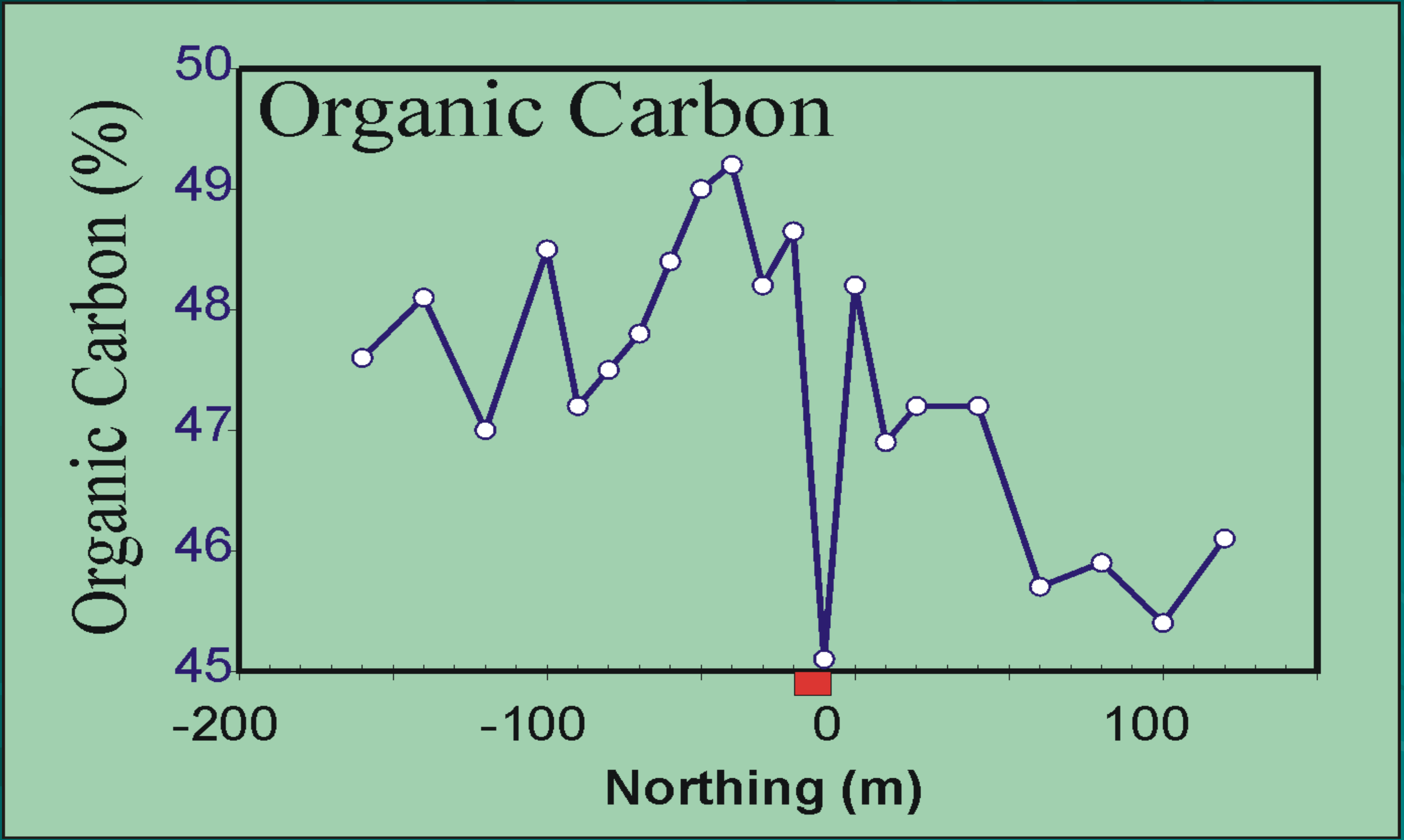
Ontario Geological Survey

Cross Lake Line 40



Ontario Geological Survey

Marsh Zone, Line 15



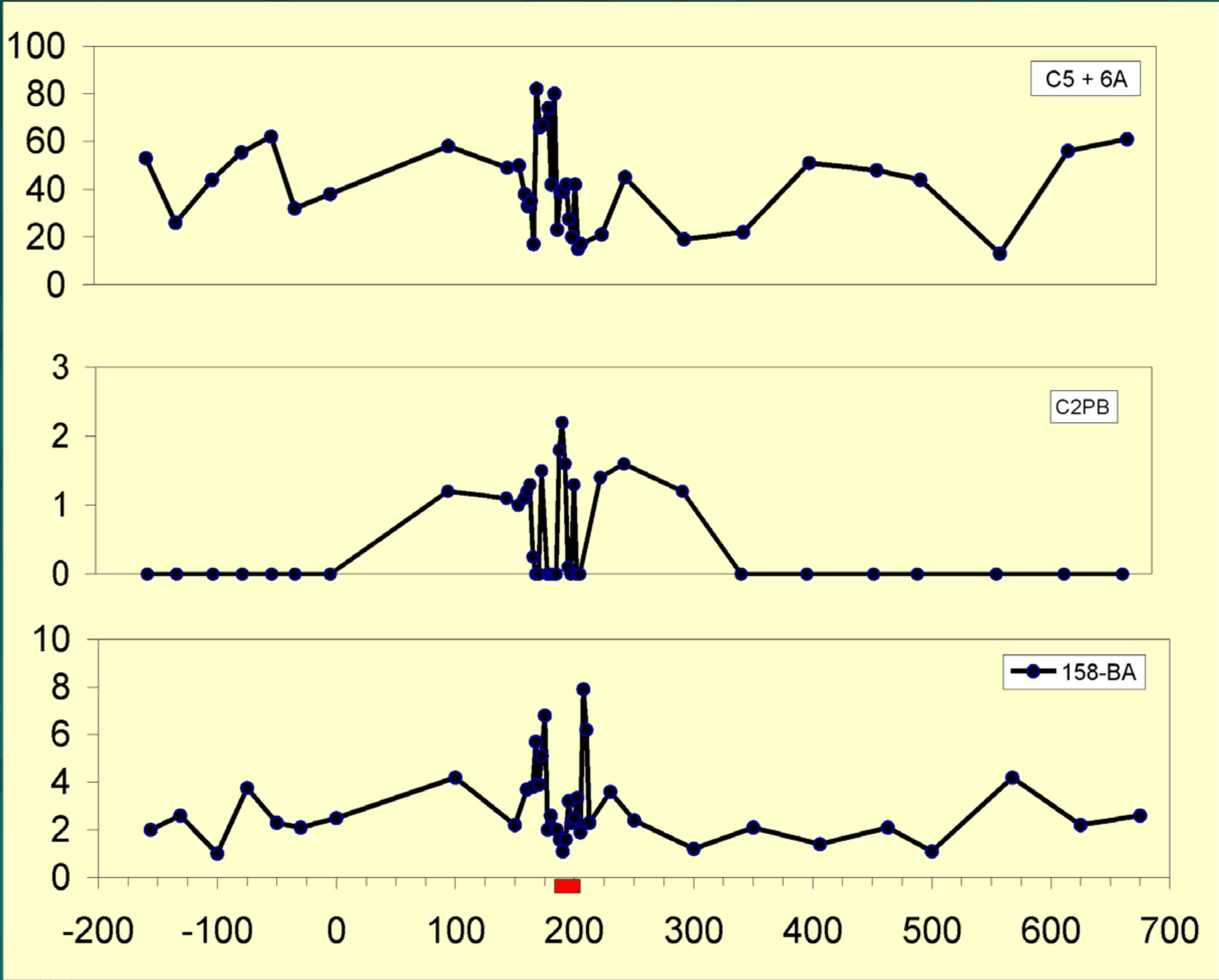
Soil Gas Hydrocarbons

- It has been discovered recently that measurable anomalies 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
- <u>Problem:</u> thick, young clays would restrict movement of large, sticky hydrocarbon molecules to surface

Ontario Geological Survey

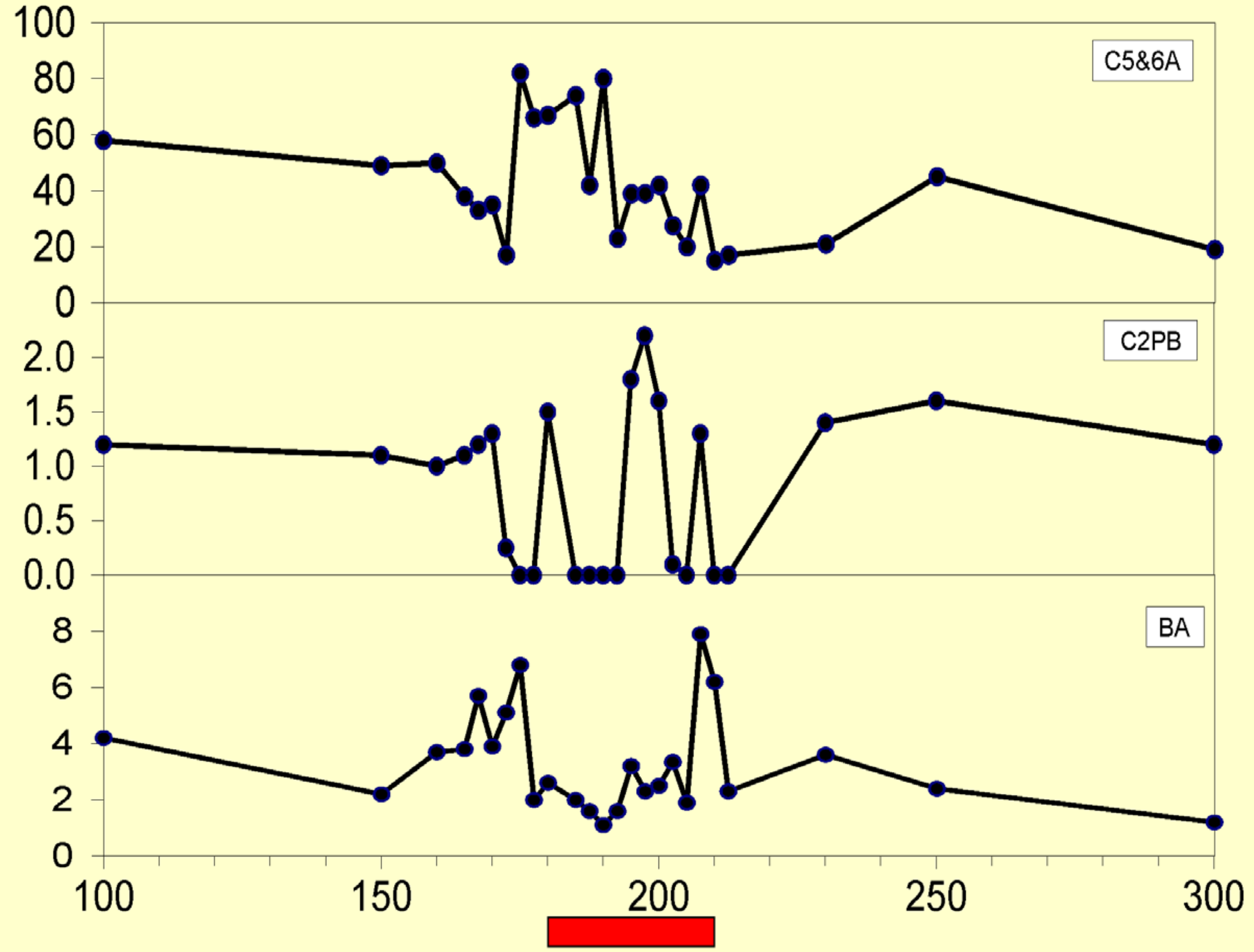
Soil Gas Hydrocarbons

Cross Lake
Line 6

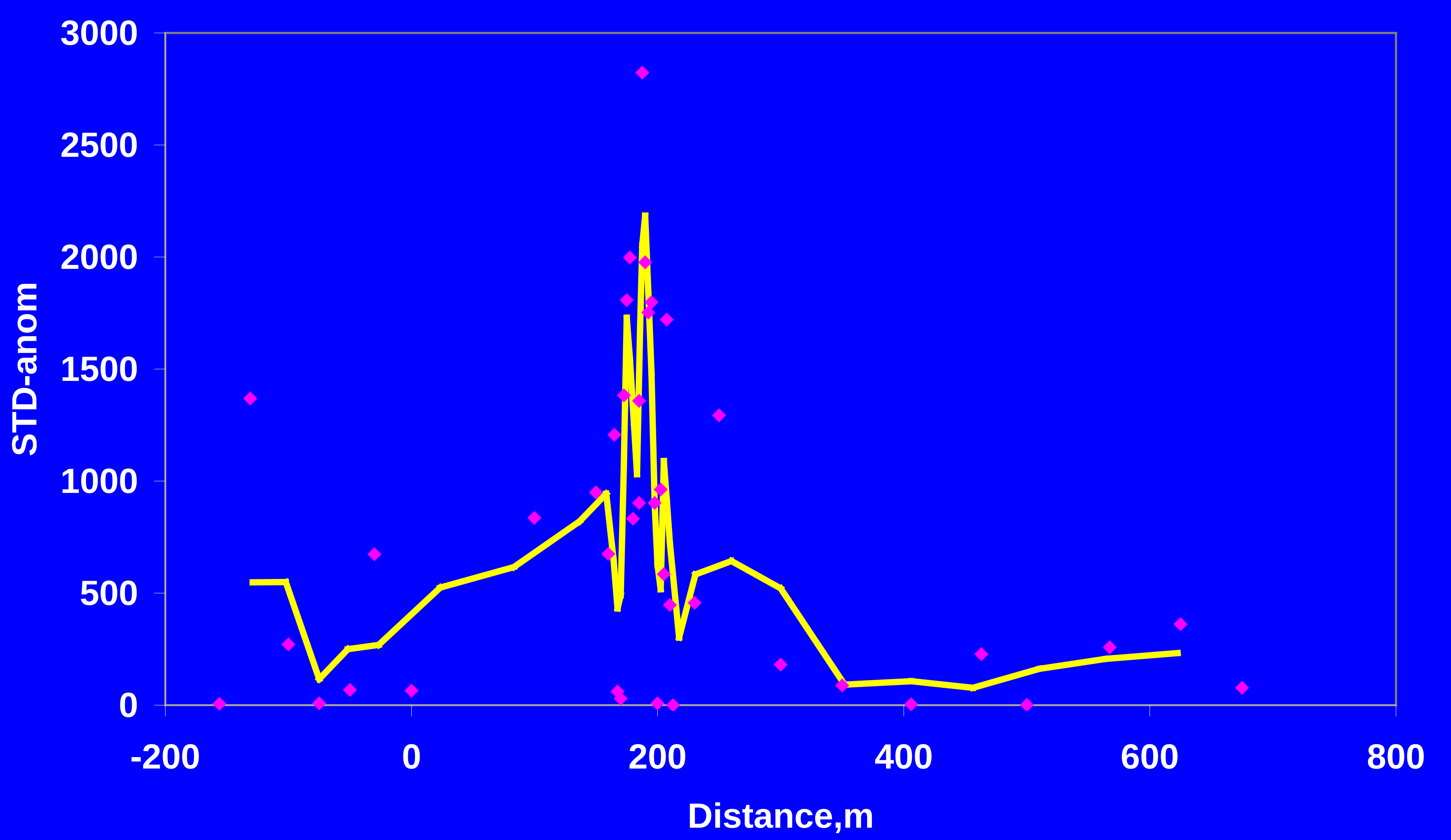


Soil Gas Hydrocarbons

Cross Lake
Line 6
(expanded)

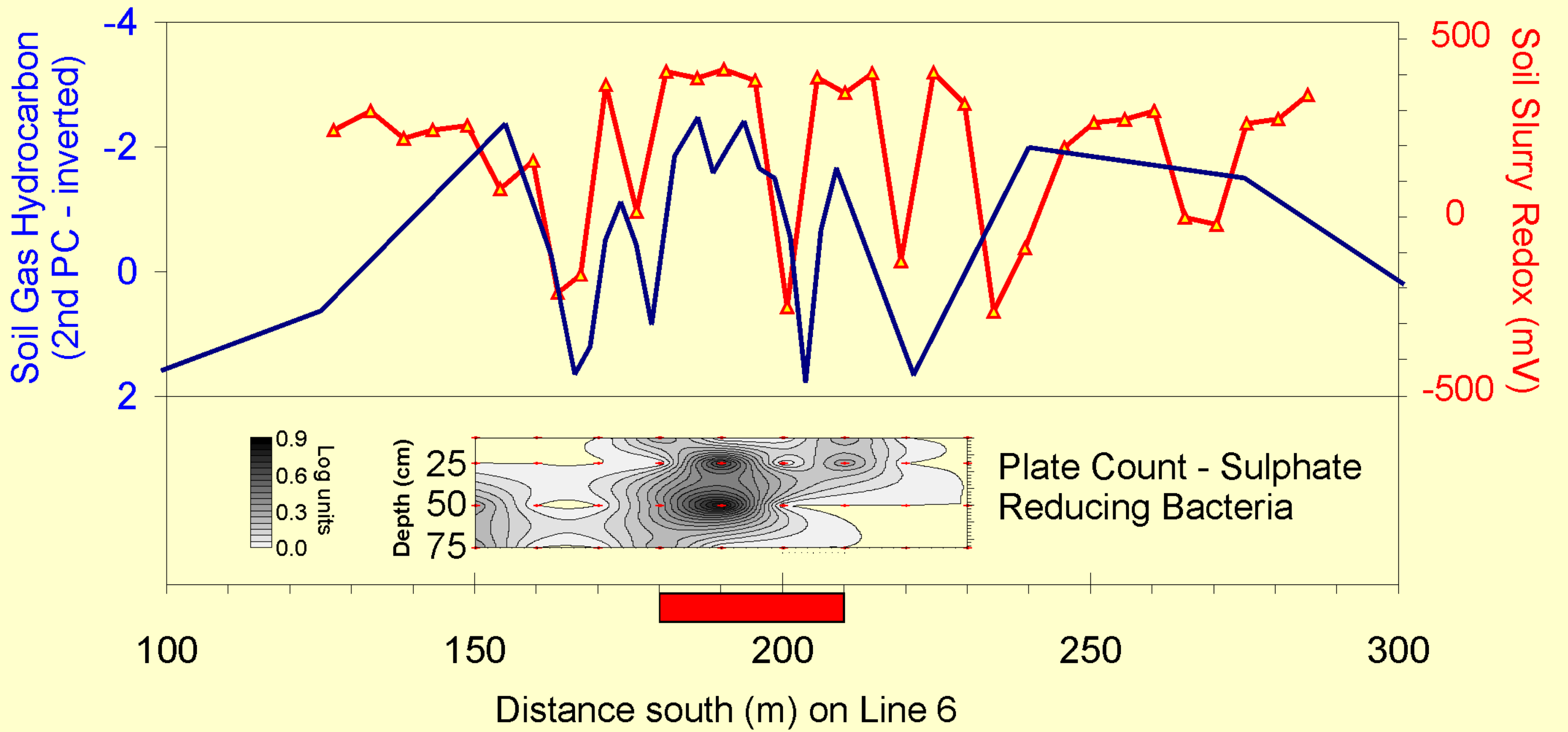


SDP, Line 6, anom



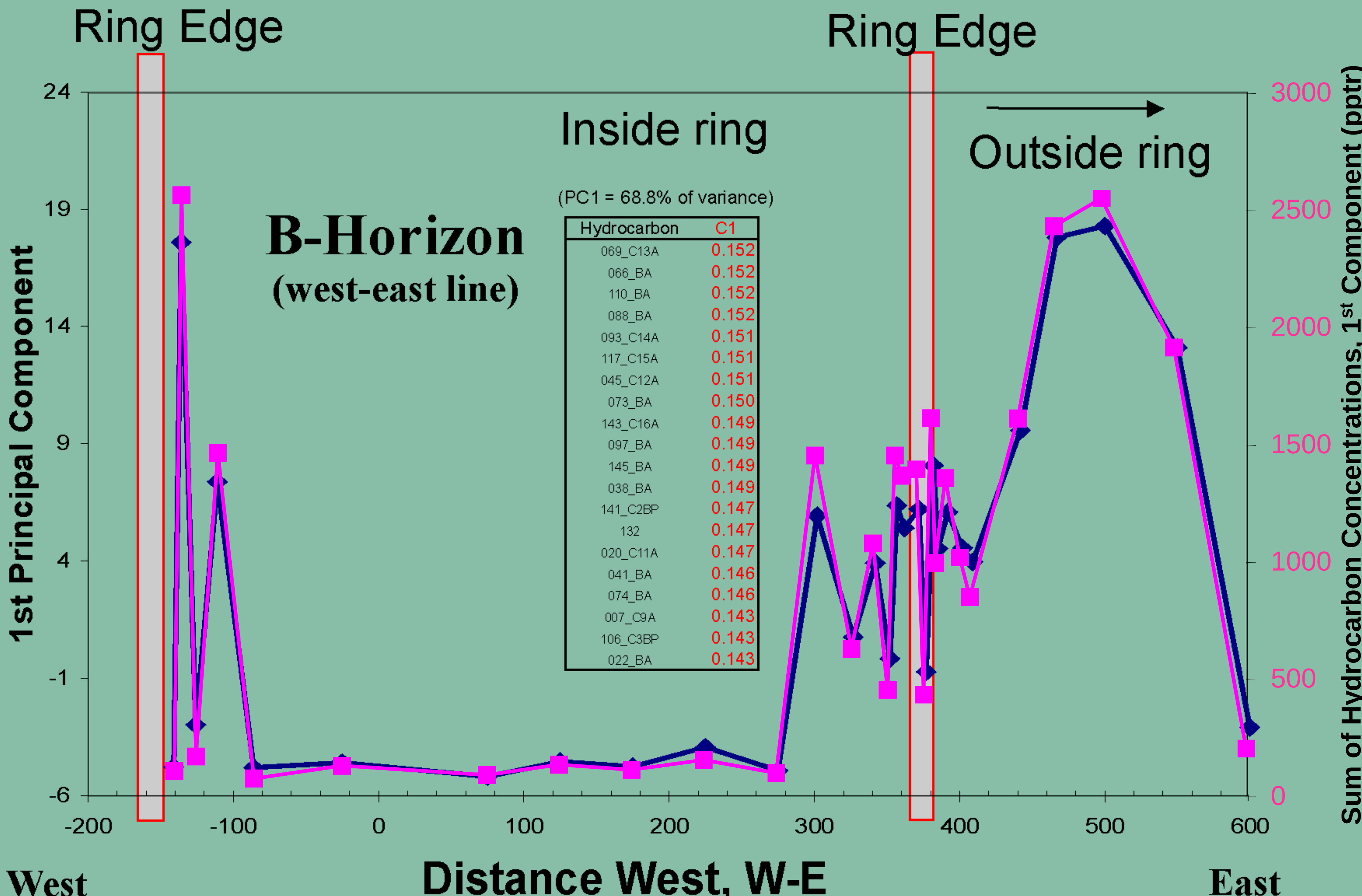
Ontario Geological Survey

SGH & Redox



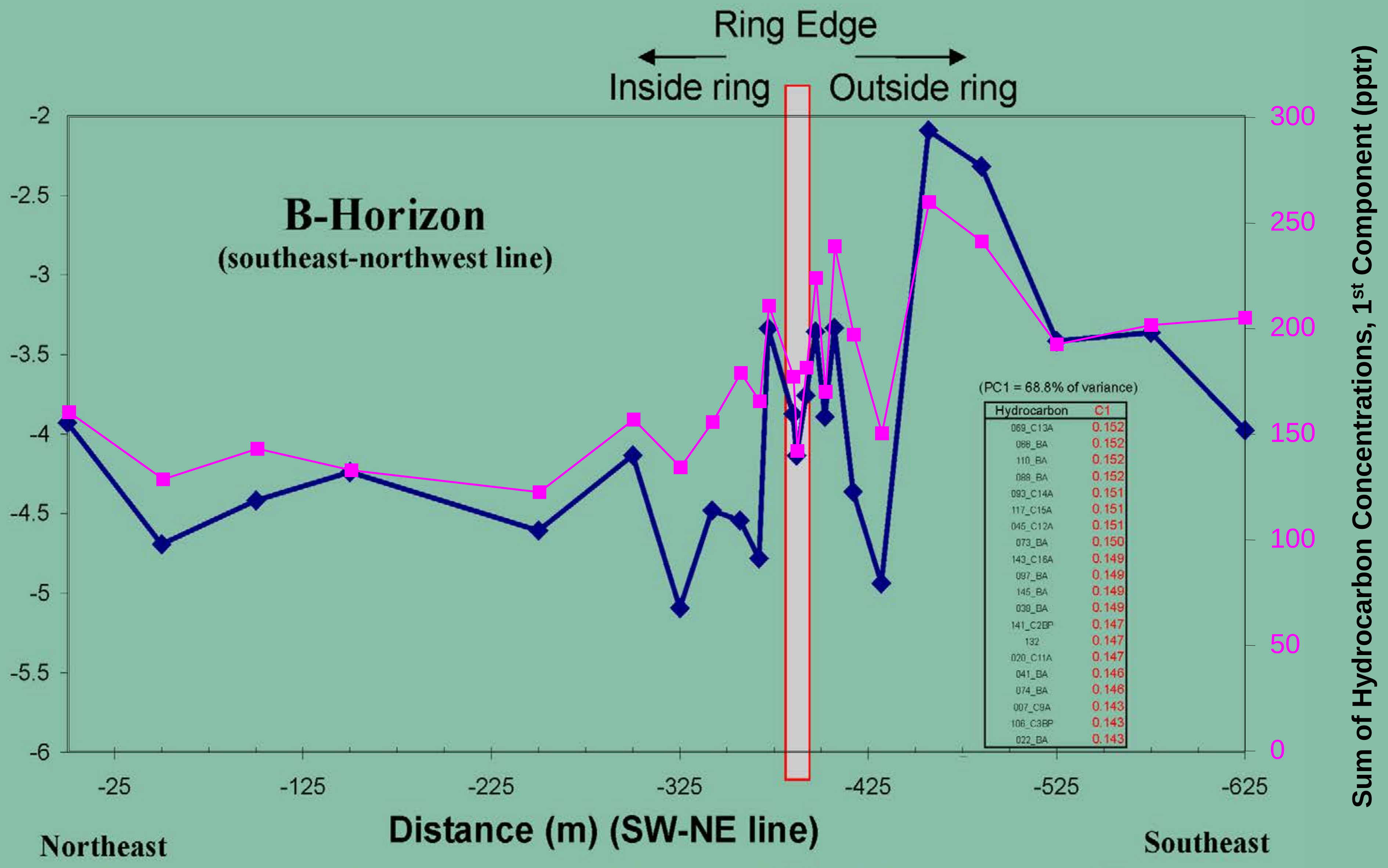
Ontario Geological Survey

Soil Gas Hydrocarbon – Thorn N.



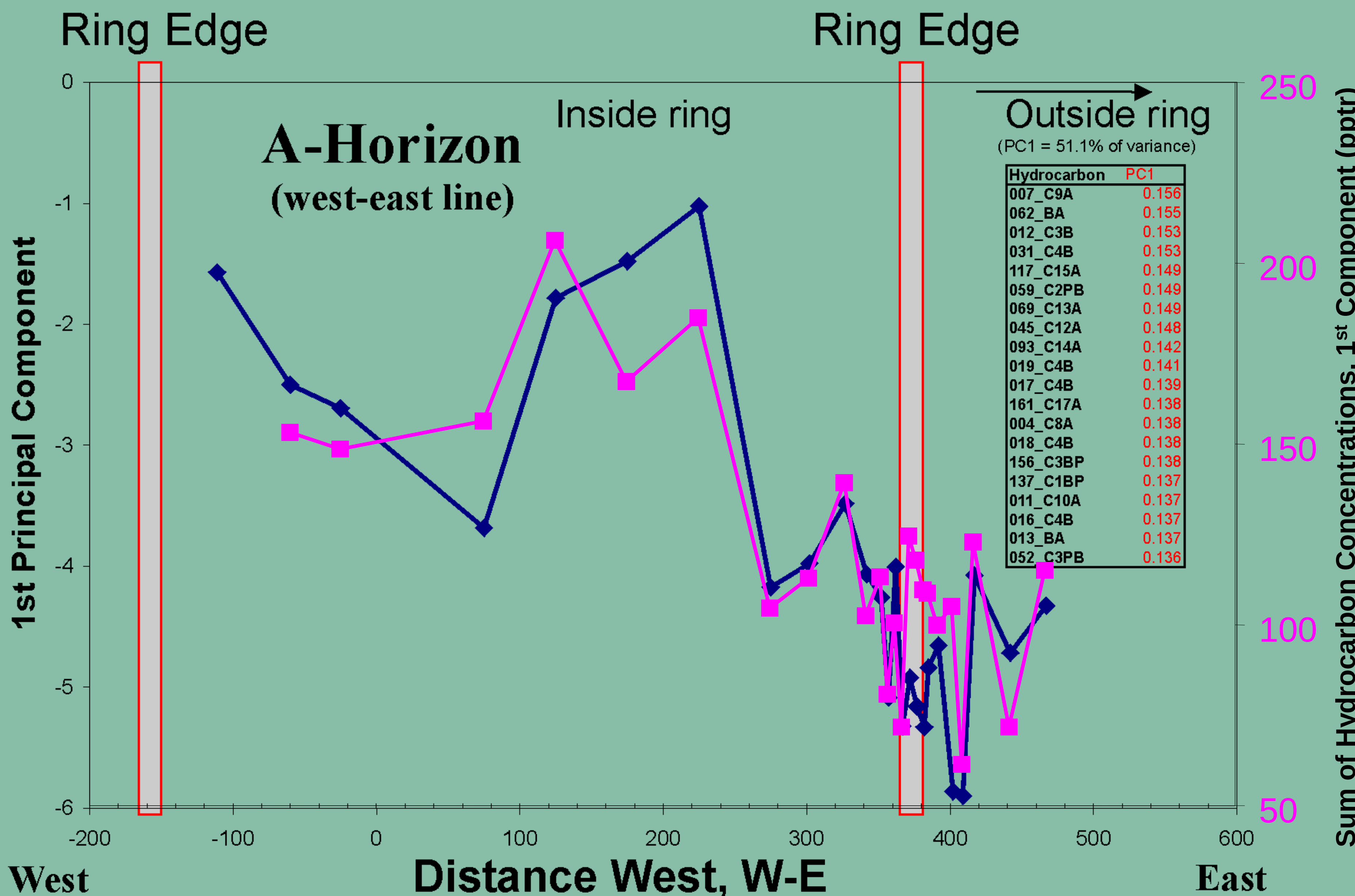
Hydrocarbon	C1
069_C13A	0.152
066_BA	0.152
110_BA	0.152
088_BA	0.152
093_C14A	0.151
117_C15A	0.151
045_C12A	0.151
073_BA	0.150
143_C16A	0.149
097_BA	0.149
145_BA	0.149
038_BA	0.149
141_C2BP	0.147
132	0.147
020_C11A	0.147
041_BA	0.146
074_BA	0.146
007_C9A	0.143
106_C3BP	0.143
022_BA	0.143

Soil Gas Hydrocarbon – Thorn N.

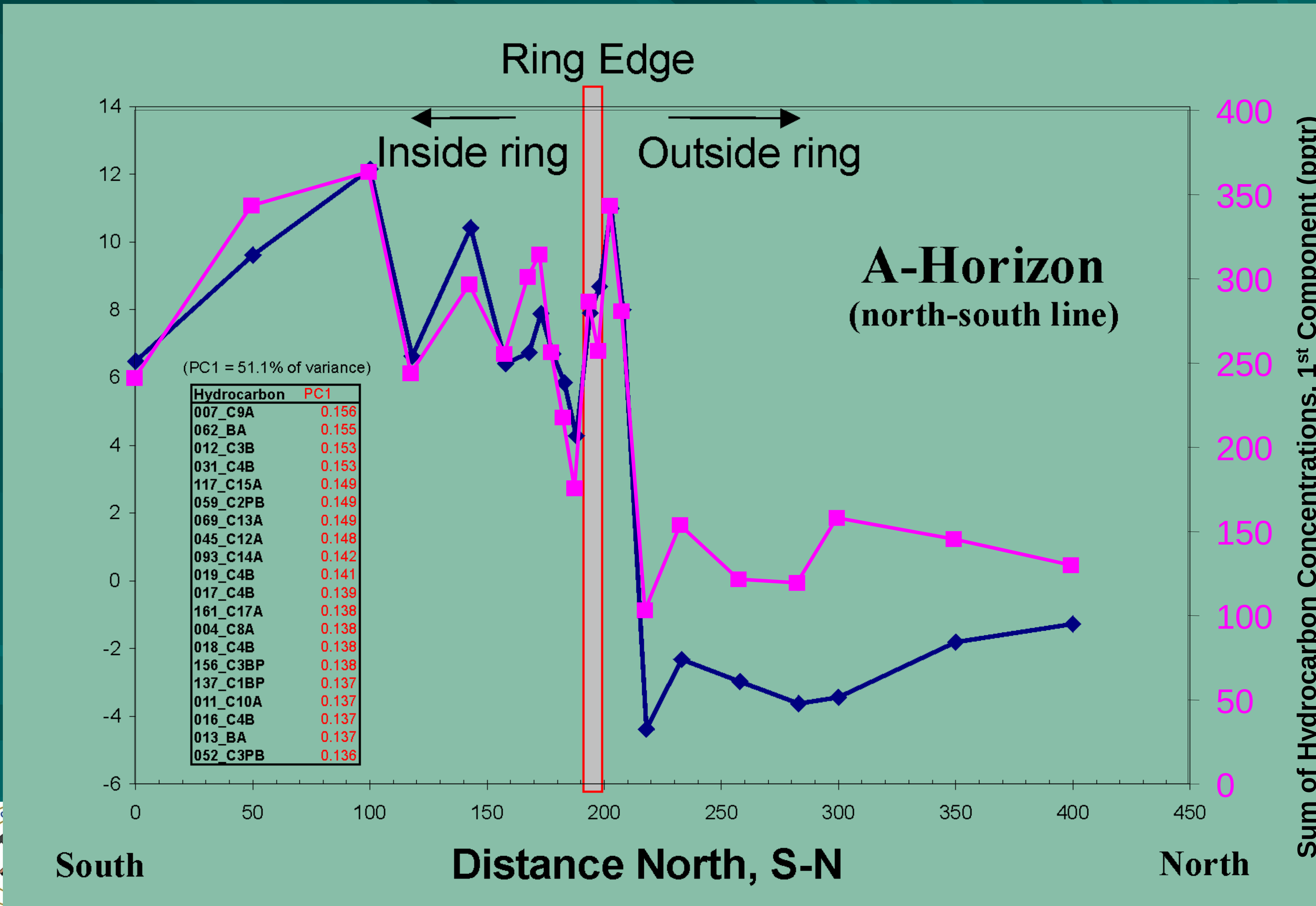


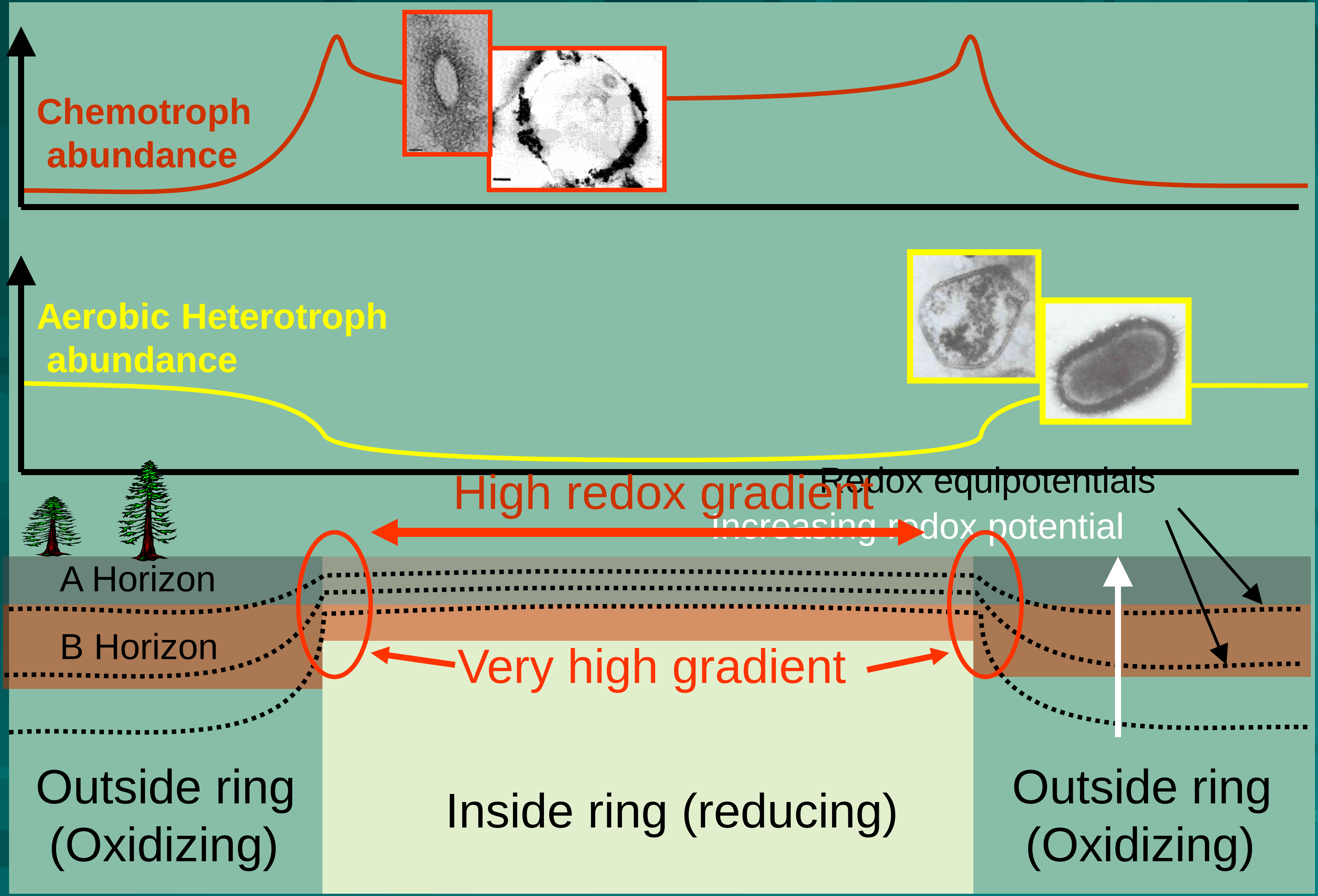
Hydrocarbon	C1
069_C13A	0.152
066_BA	0.152
110_BA	0.152
088_BA	0.152
093_C14A	0.151
117_C15A	0.151
045_C12A	0.151
073_BA	0.150
143_C16A	0.149
097_BA	0.149
145_BA	0.149
038_BA	0.149
141_C2BP	0.147
132	0.147
020_C11A	0.147
041_BA	0.146
074_BA	0.146
007_C9A	0.143
106_C3BP	0.143
022_BA	0.143

Soil Gas Hydrocarbon – Thorn N.



Soil Gas Hydrocarbon – Thorn N.





Chemotroph
abundance
Aerobic Heterotroph
abundance
High redox gradient
Redox equipotentials
Increasing redox potential
A Horizon
B Horizon
Very high gradient
Outside ring
(Oxidizing)
Inside ring (reducing)
Outside ring
(Oxidizing)

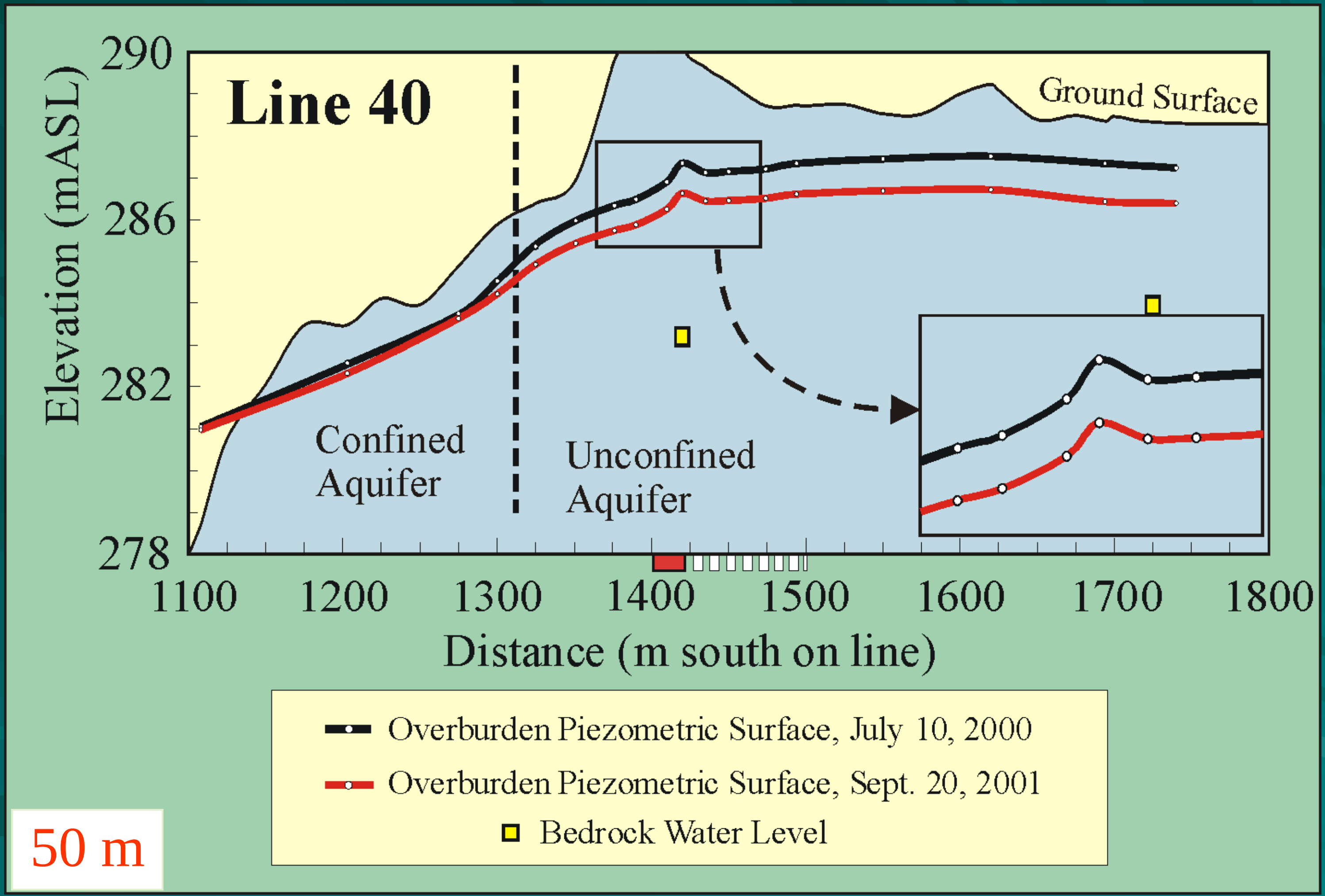
The source of hydrocarbons

- Hydrocarbon anomalies correlate with:
  - Mineralization (spatially)
  - Reduced chimneys (spatially)
  - Redox variation
  - pH anomalies in soil
  - O_2 depletions / CO_2 enrichments in soil gas
  - Organic carbon depletions
  - Metal enrichments
  - Increased bacterial populations

The source of hydrocarbons

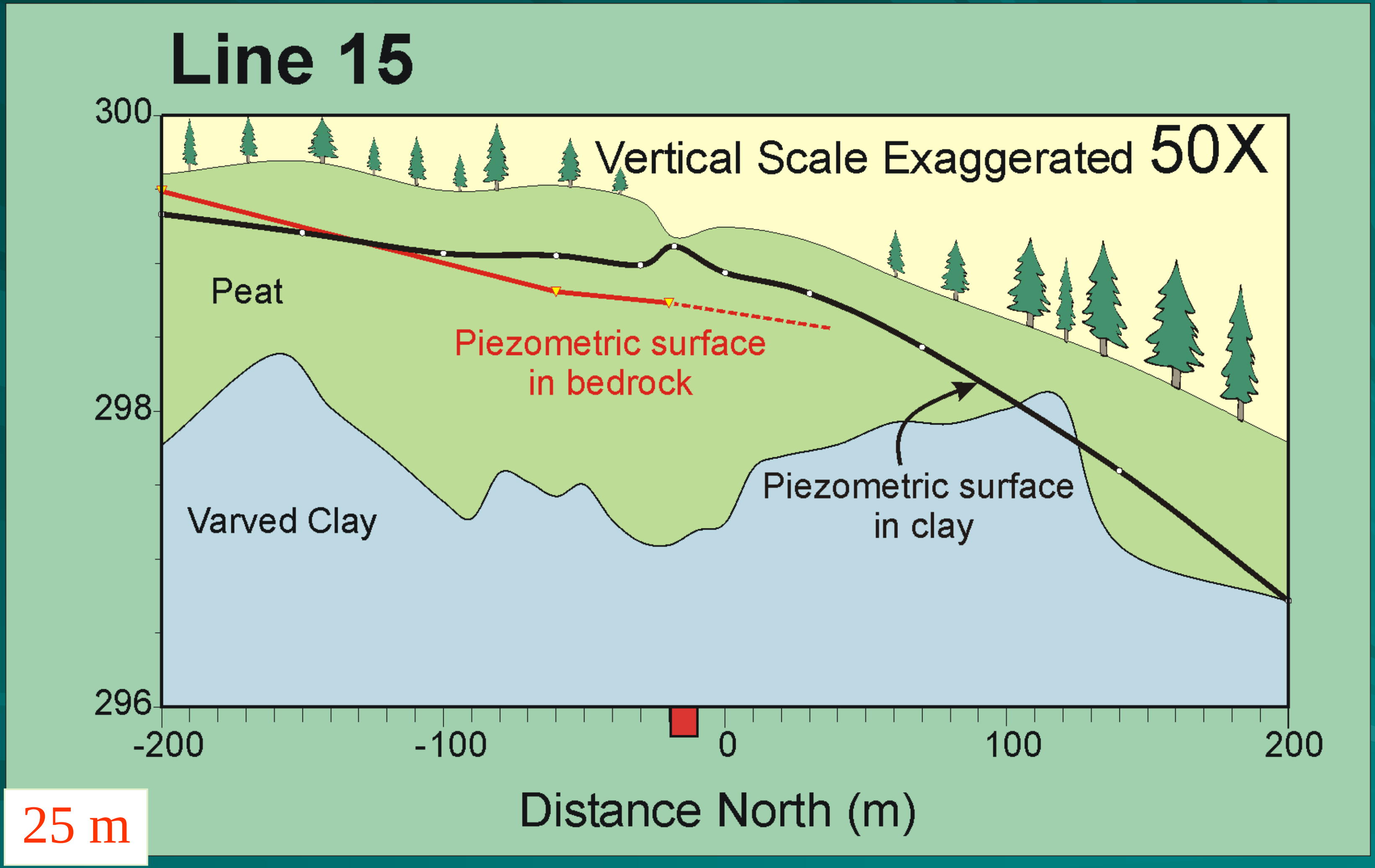
- Conclusions:
  1. Source of hydrocarbons is bacterial biomass and microbial exhalation above the reduced chimney
  2. Increased hydrocarbons result from increased microbial activity
  3. Increased microbial activity results from enhanced redox gradients and a greater availability of essential nutrients over the chimney

Groundwater Bulge in Sand
Cross Lake, Line 40



Ontario Geological Survey

Groundwater Bulge in Clay
Marsh Zone, Line 15



Ontario Geological Survey

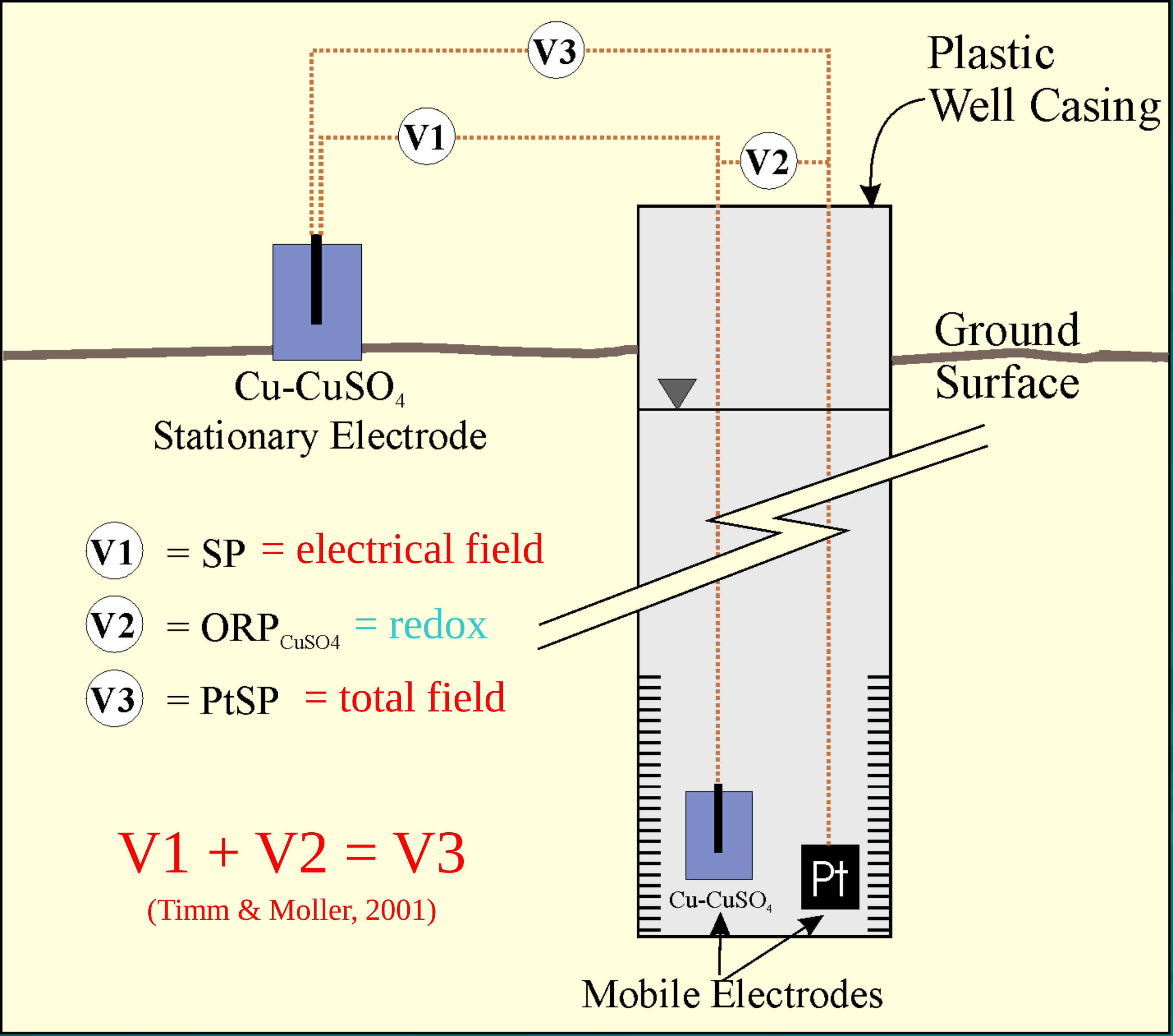
Spontaneous Potential Over Reduced Non-Conductors

1. Kimberlites
2. "Forest Rings"

THE ASSOCIATION OF APPLIED GEOCHEMISTS 1970

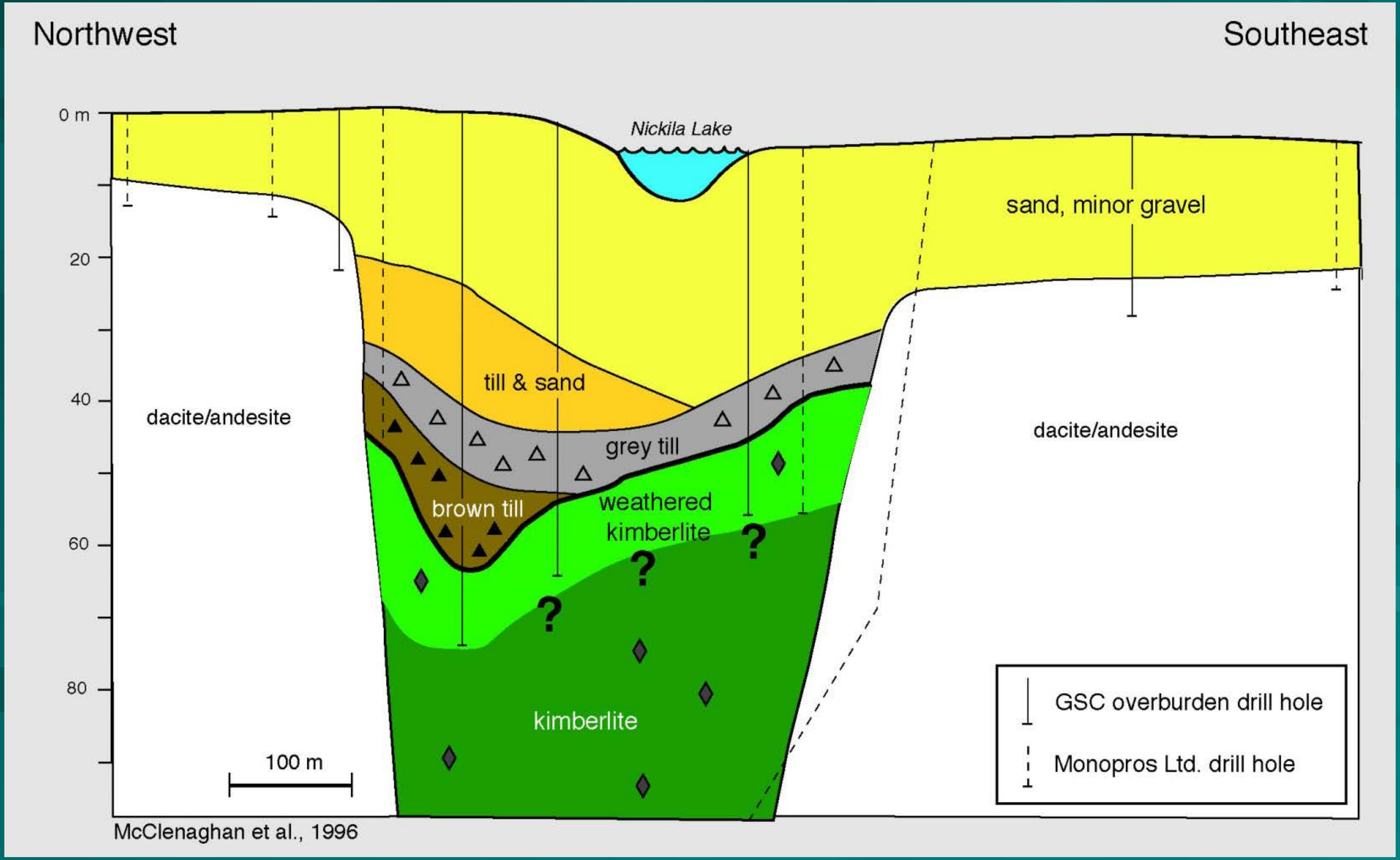
Ontario Geological Survey

Platinum Spontaneous Potential (PtSP)



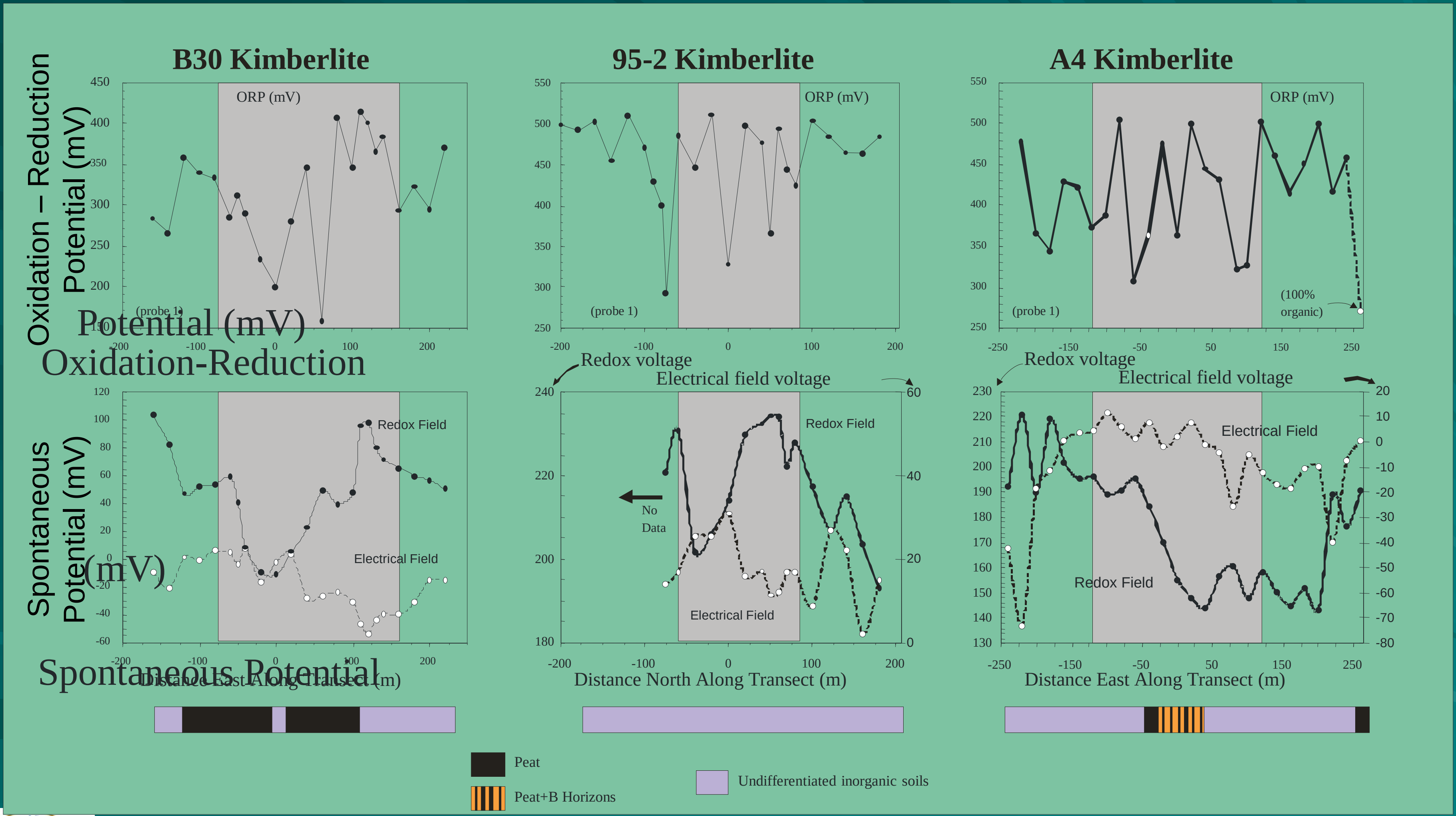
Case studies - kimberlites

B-30 kimberlite (other sites = A4, 95-2)



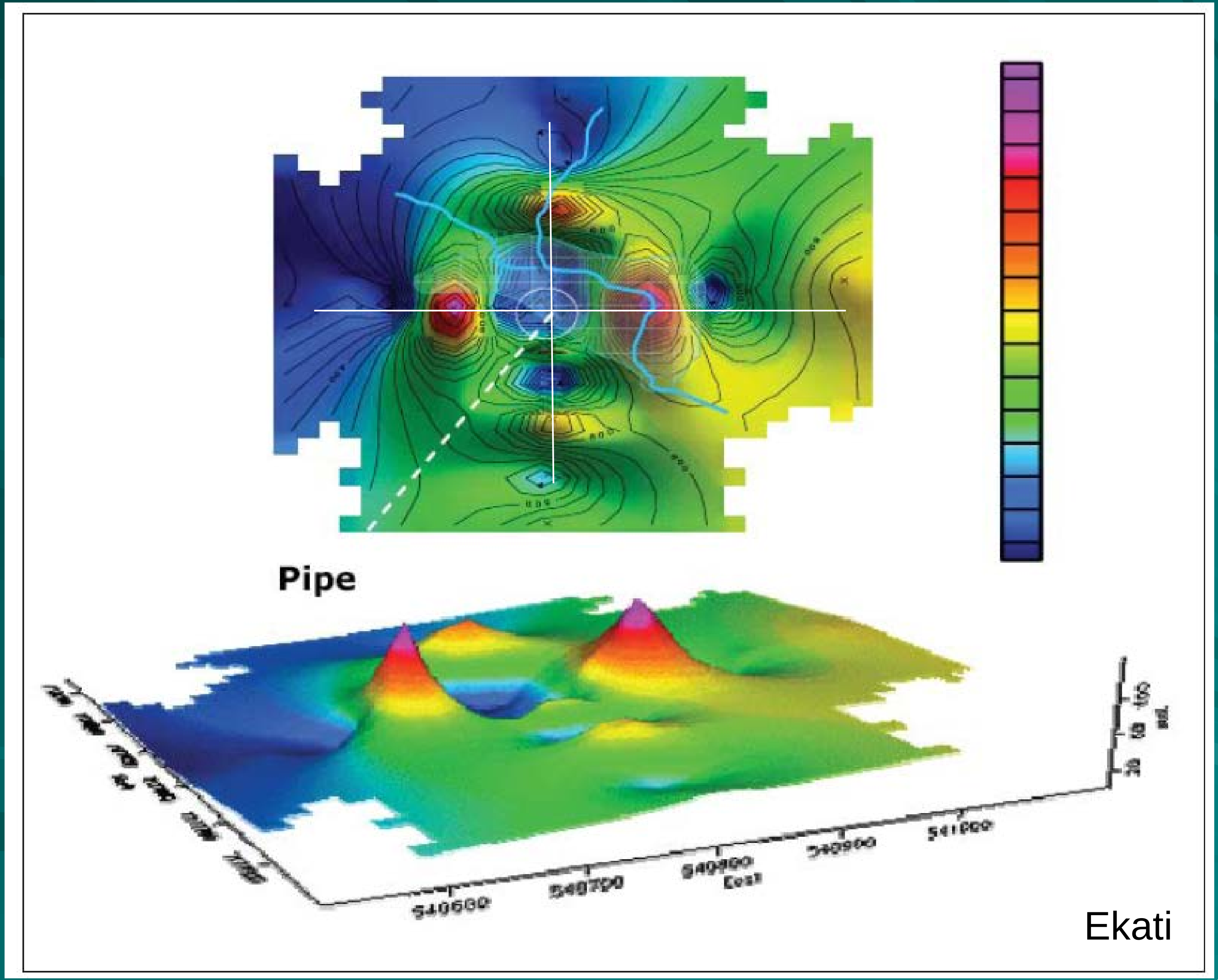
Ontario Geological Survey

SP & Redox over Kimberlites



Ontario Geological Survey

Soil Gas Hydrocarbons over Kimberlites

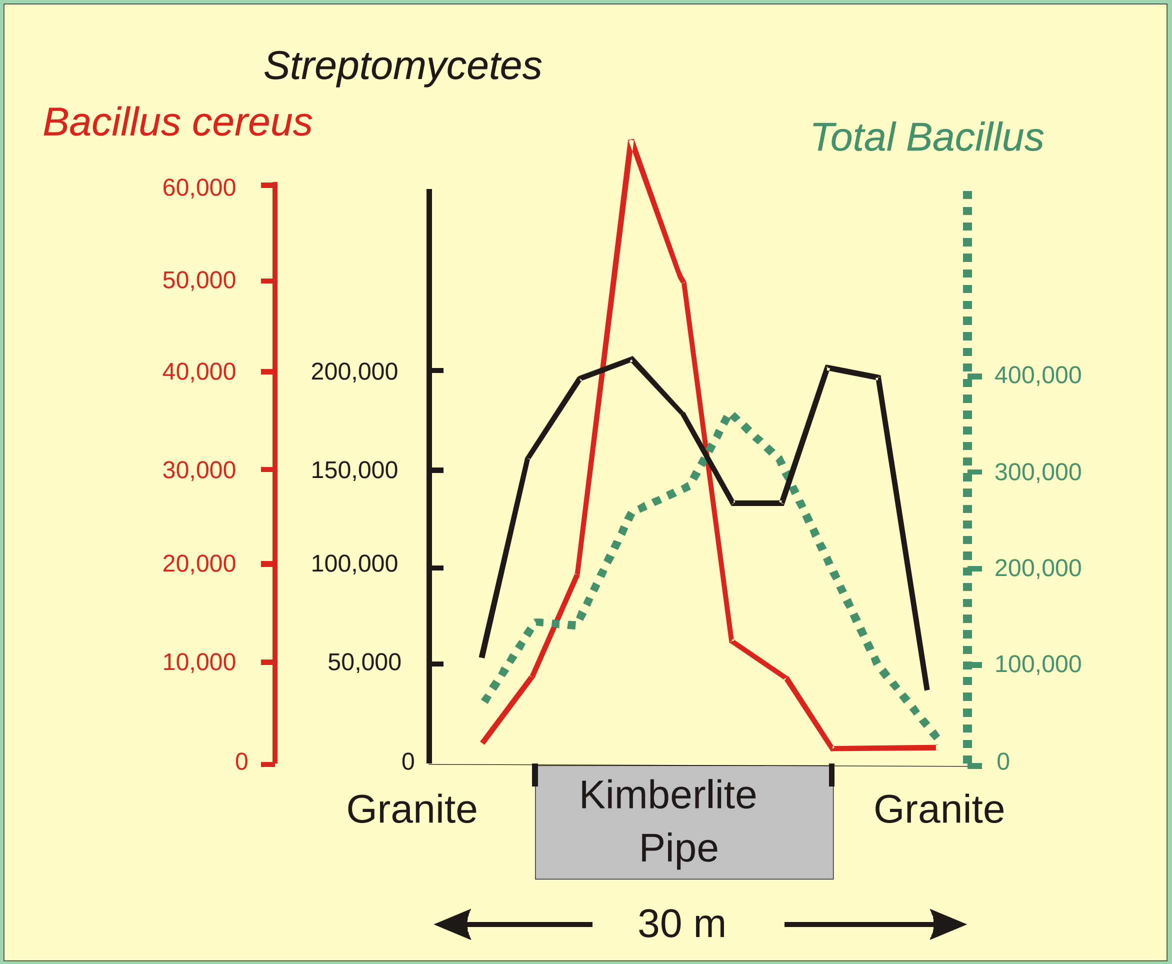


Source: Actlabs

Ontario Geological Survey

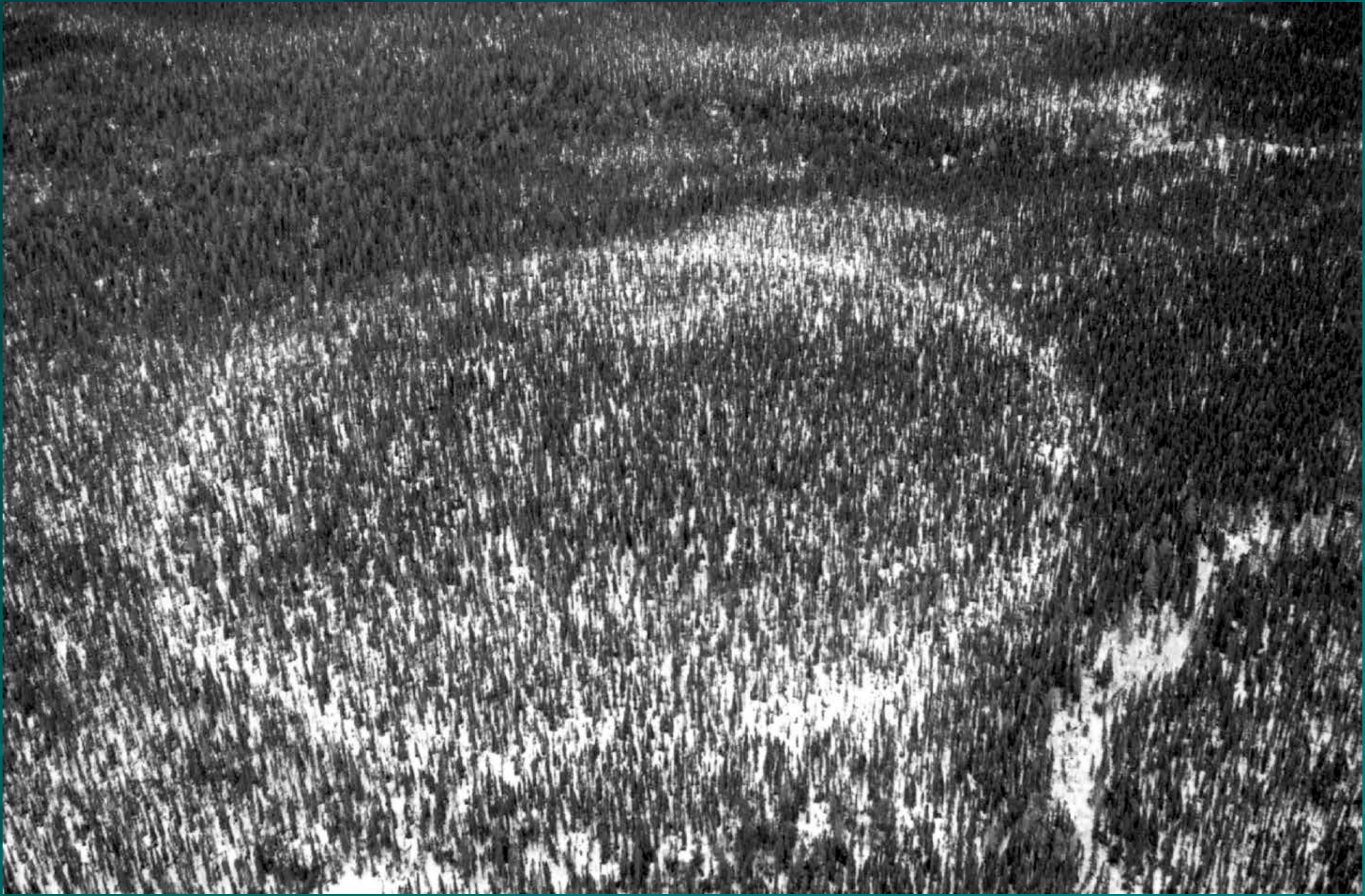
Bacterial Plate Counts

Green Mountain Kimberlite, Colorado



From Alexander, 1986

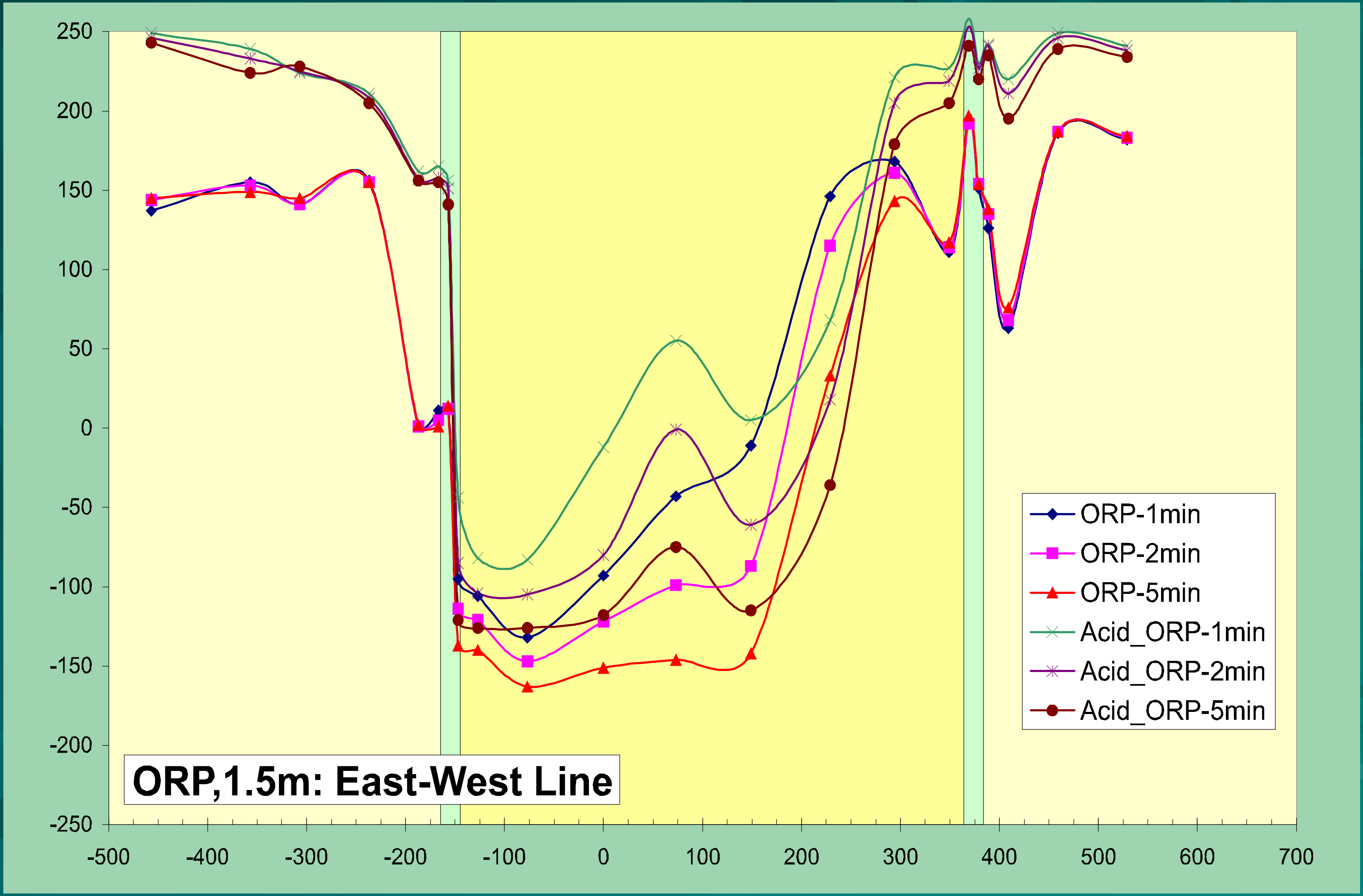
Ontario Geological Survey



THE ASSOCIATION OF APPLIED GEOCHEMISTS 1970

Ontario Geological Survey

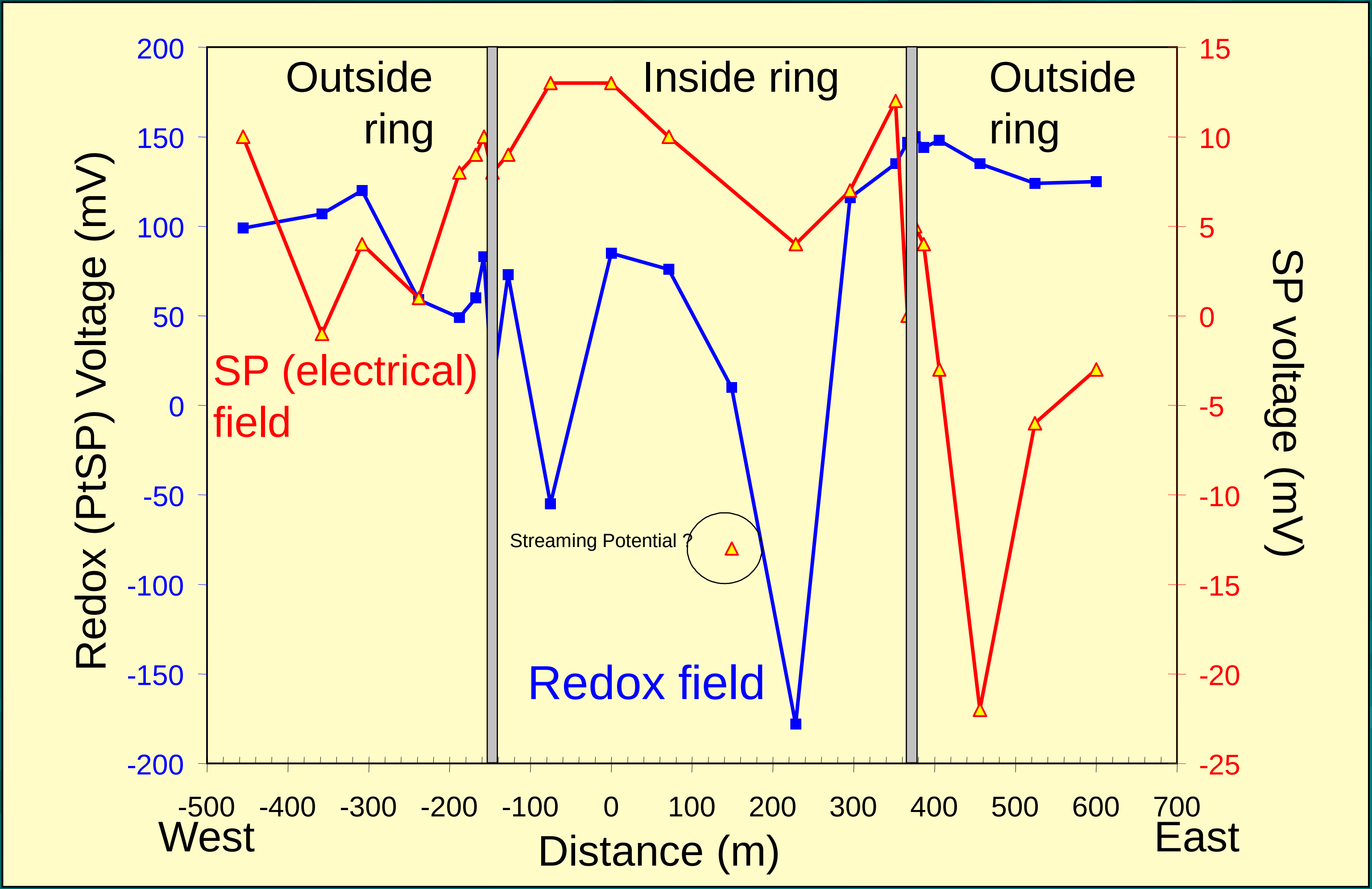
Redox in Soils @ 1.5m depth - Thorn-N Ring



Ontario Geological Survey

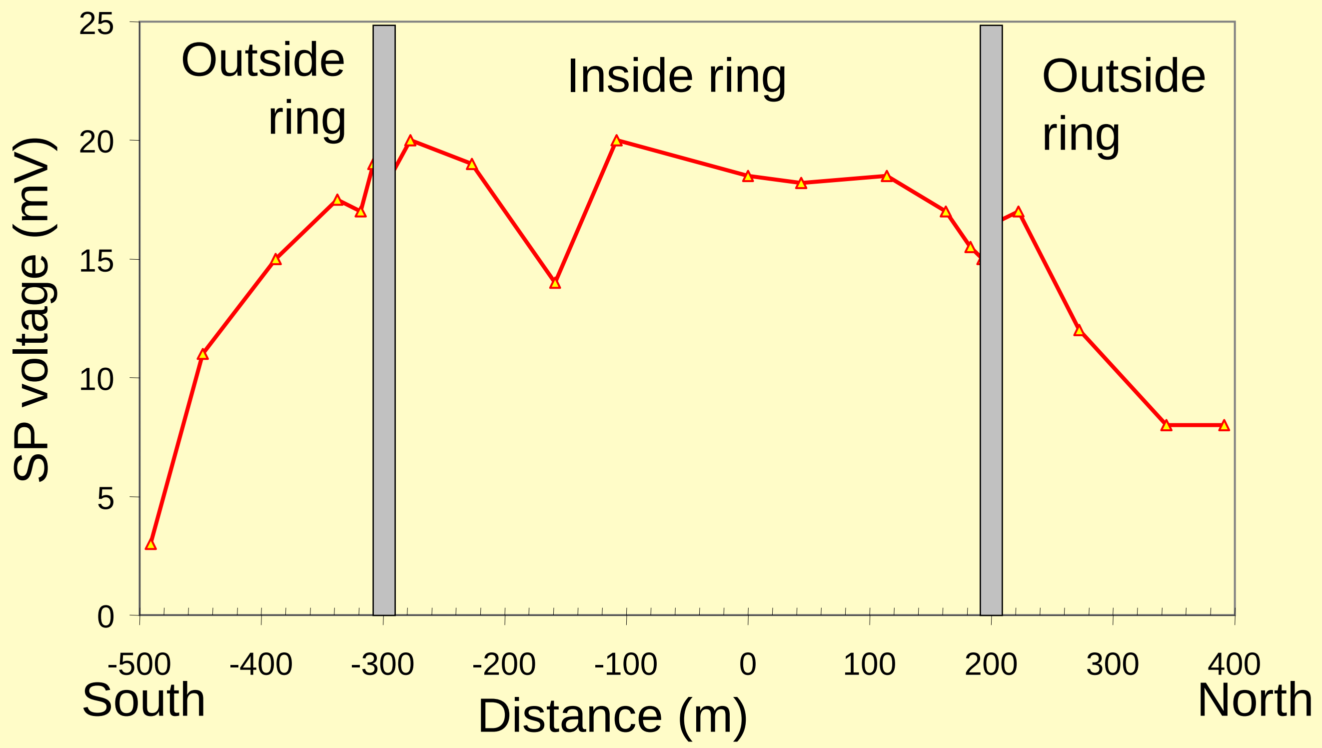
Redox and SP – “Forest Ring” Site

(Measured down-hole in plastic monitoring wells)



Thorn-North ring, east-west transect

SP – Forest Ring Site



Thorn-North ring, south-north transect

Ontario Geological Survey

Part II - Dispersion & Transport Mechanisms

- Diffusion
- Fluid movement
- Gaseous dispersion
- Electrical field transport
- Redox gradient transport

Electrochemical transport in geological literature

Electrical Field Transport
(Dipole around a conductor)

- Sato and Mooney
- Tilsley
- Thornbur
- Smee

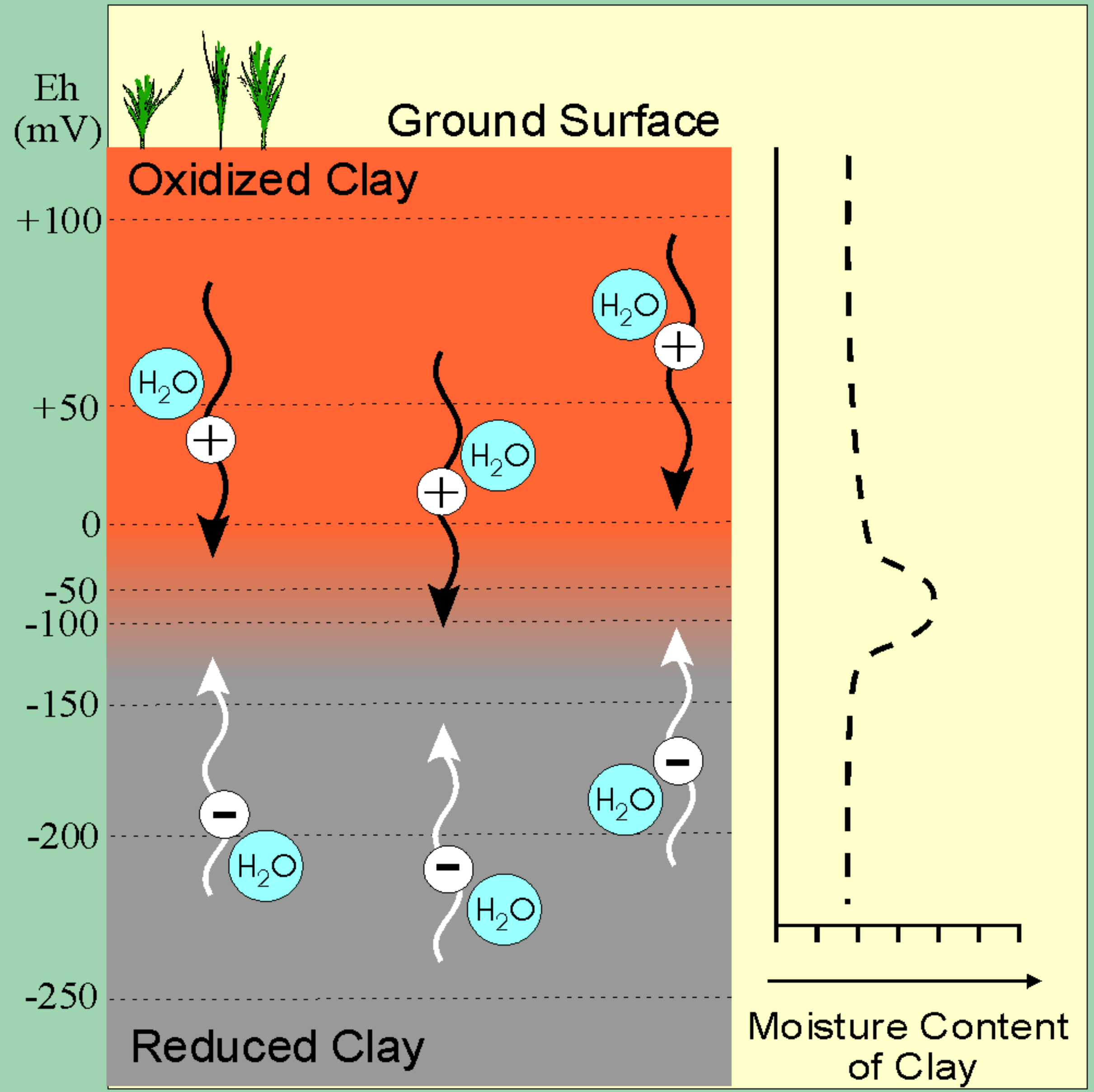
Redox Transport
(mass transport along redox gradients)

- Bolviken
- Govett
- Pirson
- Tomkins
- Veder
- Hamilton

Ontario Geological Survey

Model to account for increased moisture at redox boundary in clays

(Derived from Veder, 1971)



- Reduced species (e.g. Fe^{2+}; HS^-; Mn^{2+})
- Oxidized species (e.g. SO_4^{2-}; $O^2_{(aq)}$)
- H_2O Water molecules moving with transported redox-active ions

Ontario Geological Survey

Charge & Mass Transport

$$J_j = -\frac{-zF}{RT} D_j C_j \frac{df}{dx} - D_j \frac{dC}{dx} + C_j \frac{dH}{dx}\frac{K}{n}$$

Electromigration term

Diffusive term

Velocity (advection) term

j = species "j"

D = Diffusion coefficient

C = Concentration

z = valence (of j)

F = Faraday's constant

R = ideal gas constant

T = temperature

f = Voltage (electrical field)

K = hydraulic conductivity

H = hydraulic pressure

n = porosity (of porous medium)

J_j = flux of species "j" in the x direction

Nernst-Planck
(i.e. general mass transfer) Equation

Ontario Geological Survey

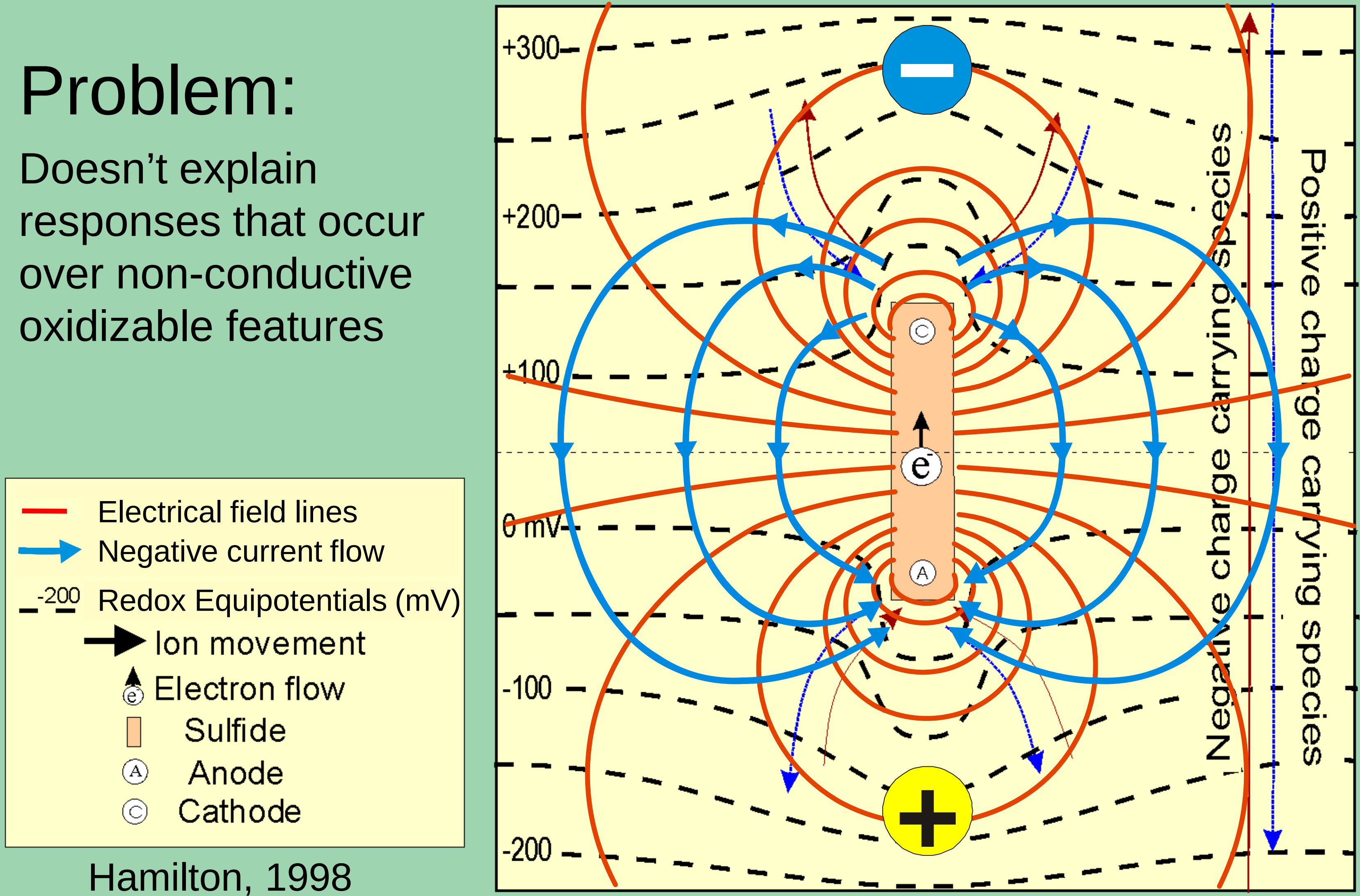
Problems with redox-gradient transport
(and Hamilton, Bolviken, Govett, Pirson, Tomkins, and Veder models)

- 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

Sulphide Dipole (Hamilton, 1998 after Govett)

Problem:

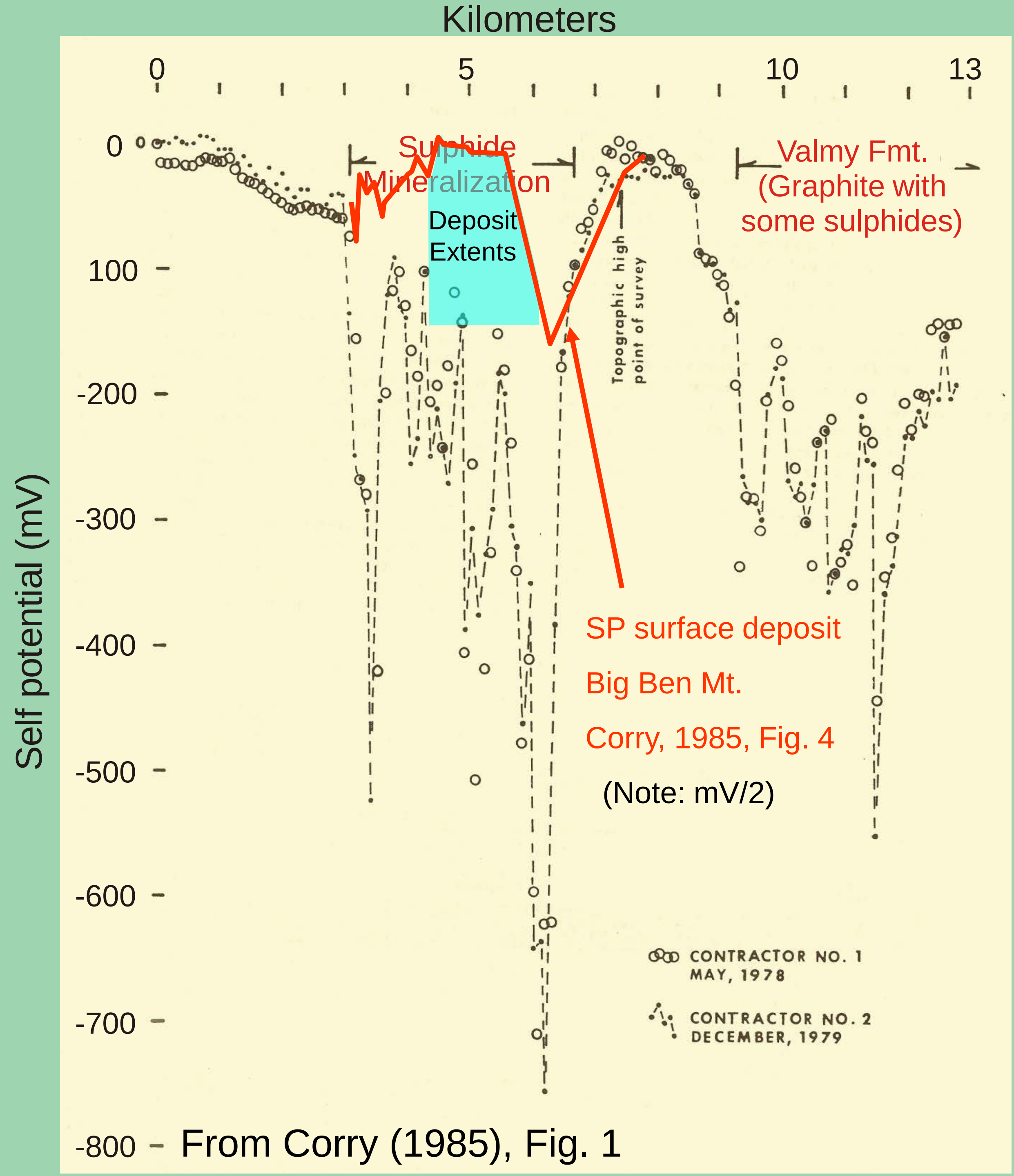
Doesn't explain responses that occur over non-conductive oxidizable features



Hamilton, 1998

SP Surveys over Porphyry Sulphides

Little Cottonwood Canyon, Battle Mountain Nevada

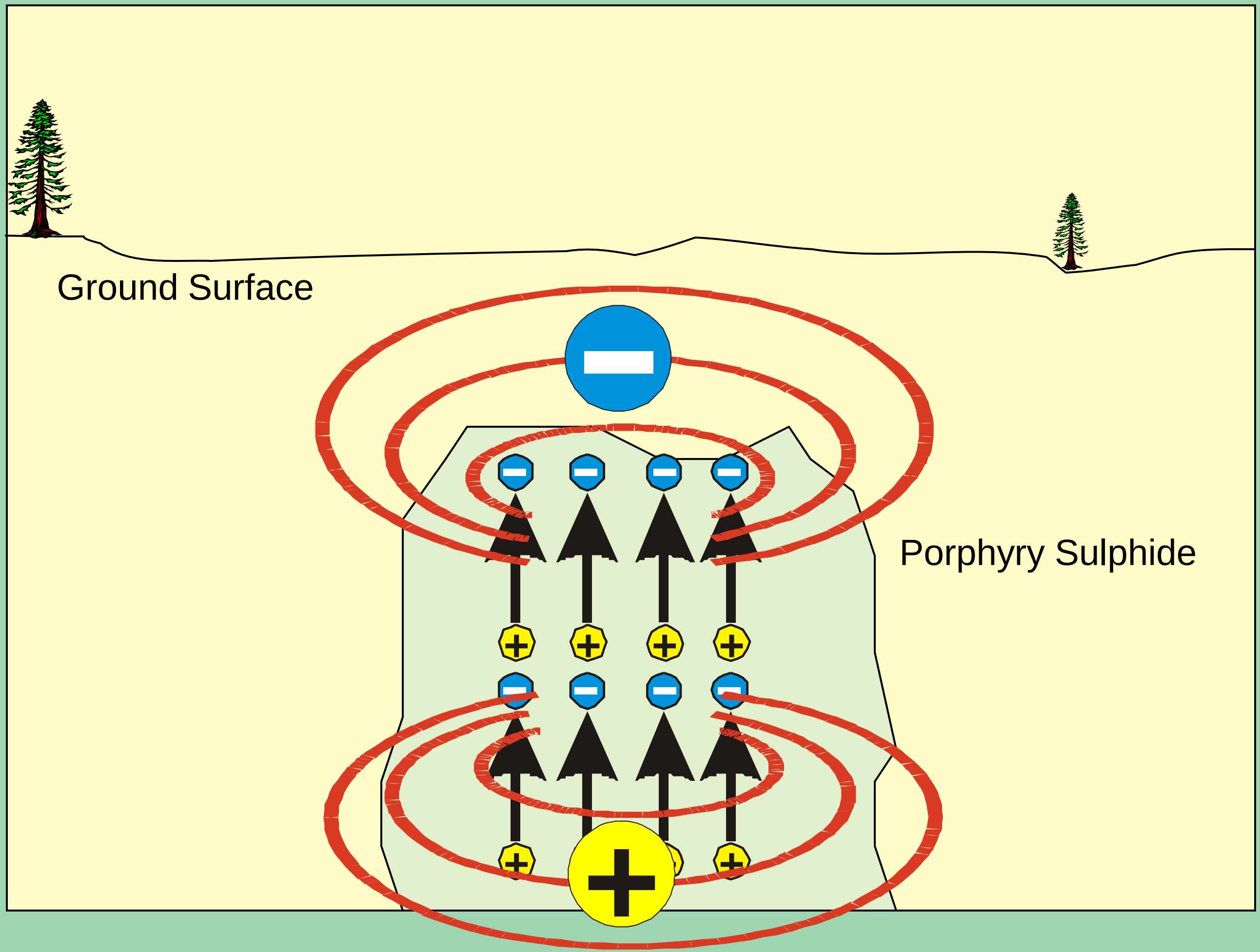


From Corry (1985), Fig. 1

Spontaneous Polarization of Sulphide Deposits (Corry, 1985)

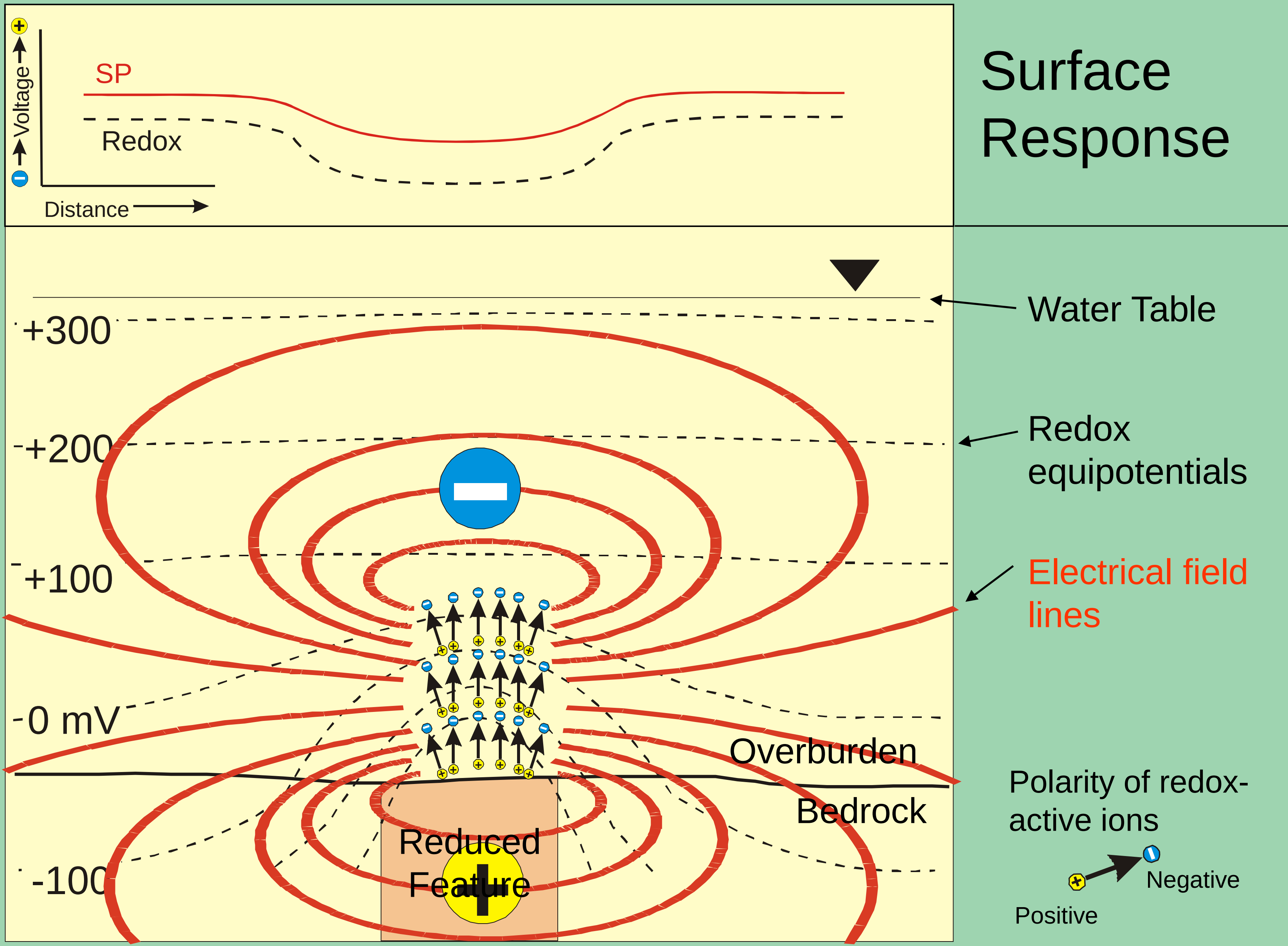
Problem:

- 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

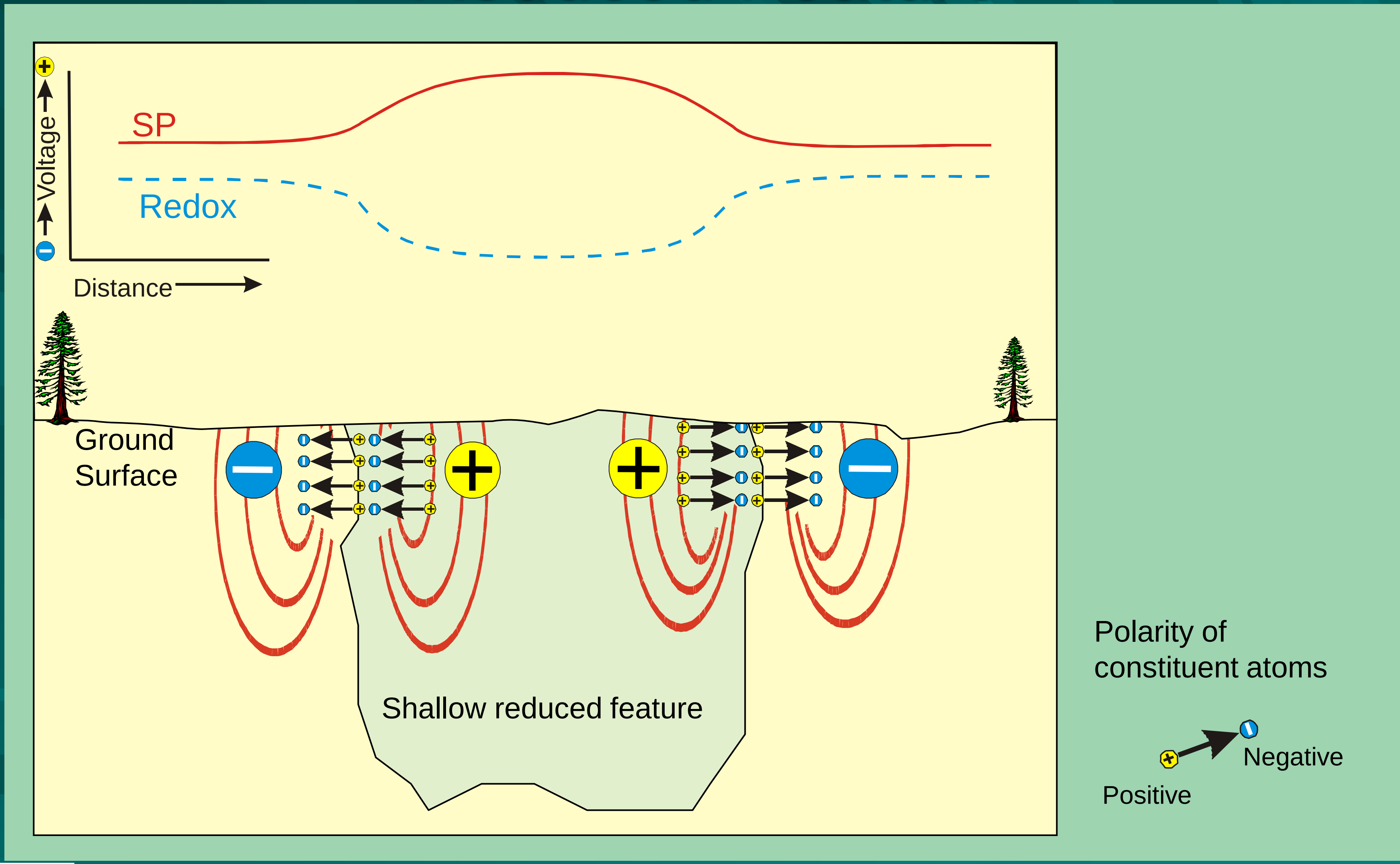


Simplification of model of Corry (1985)

Redox-Induced Spontaneous Polarization



Spontaneous Polarization over a Shallow Reduced Feature



Ontario Geological Survey

Summary…

- Abundant evidence indicates reduced chimneys occur over sulphides, kimberlites, oil and natural gas
- It is likely that they can form over any other large oxidizable geological feature in the subsurface
- It is proposed that a strong redox gradient induces spontaneous polarization, and the associated electrical field induces the movement of mass and charge above the reduced feature

Ontario Geological Survey

Summary

Implications of model:

- Mass and charge transfer can occur between mineralization and surface – accounting for soil geochemical anomalies among other things
- Consistent with physics and
- Unifies many of the existing models that otherwise appear to be in conflict