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

Understanding the physics

Stewart M. Hamilton

AAG Distinguished Lecturer Series

Ontario Geological Survey

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

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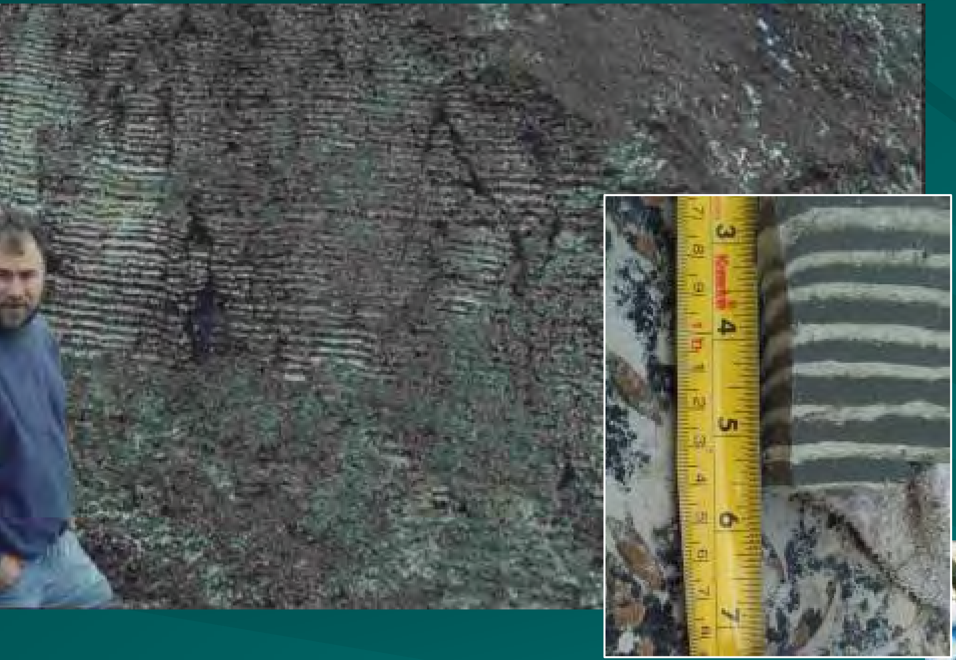
Clay Cover in Canada



- 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)

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

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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

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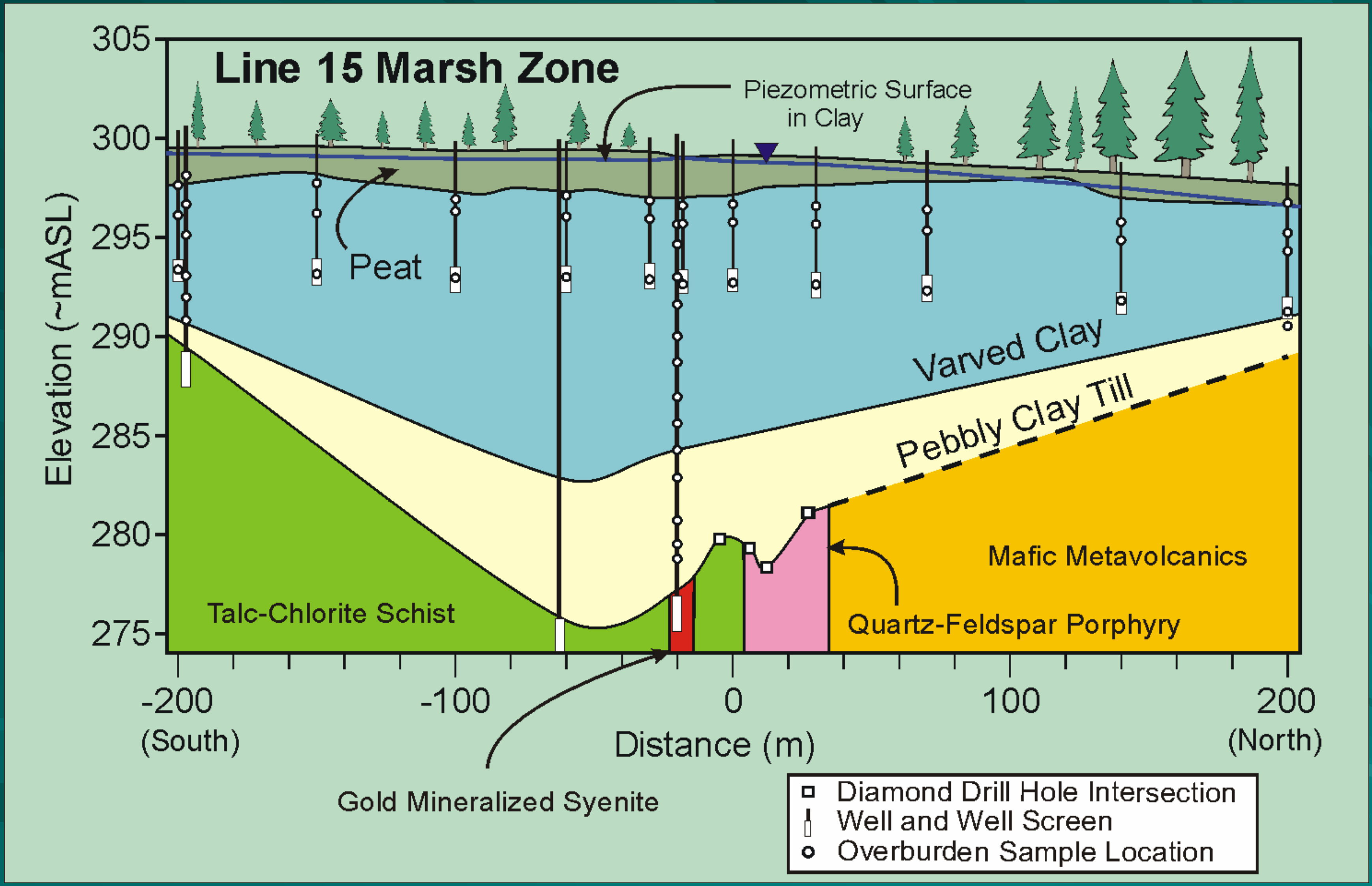
Reduced Chimneys

- "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



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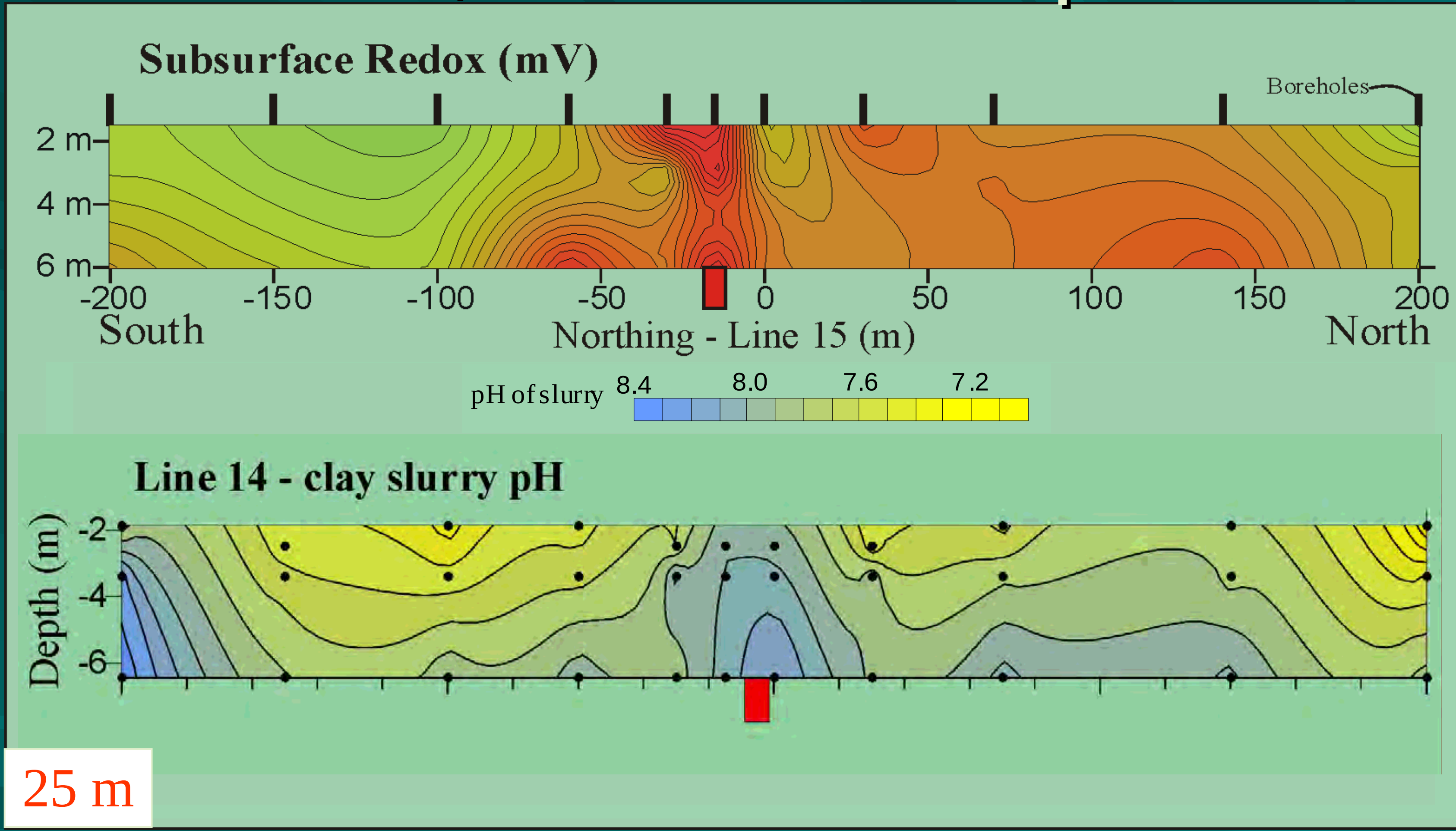
Marsh Zone, Line 15 - 3D pH & Redox



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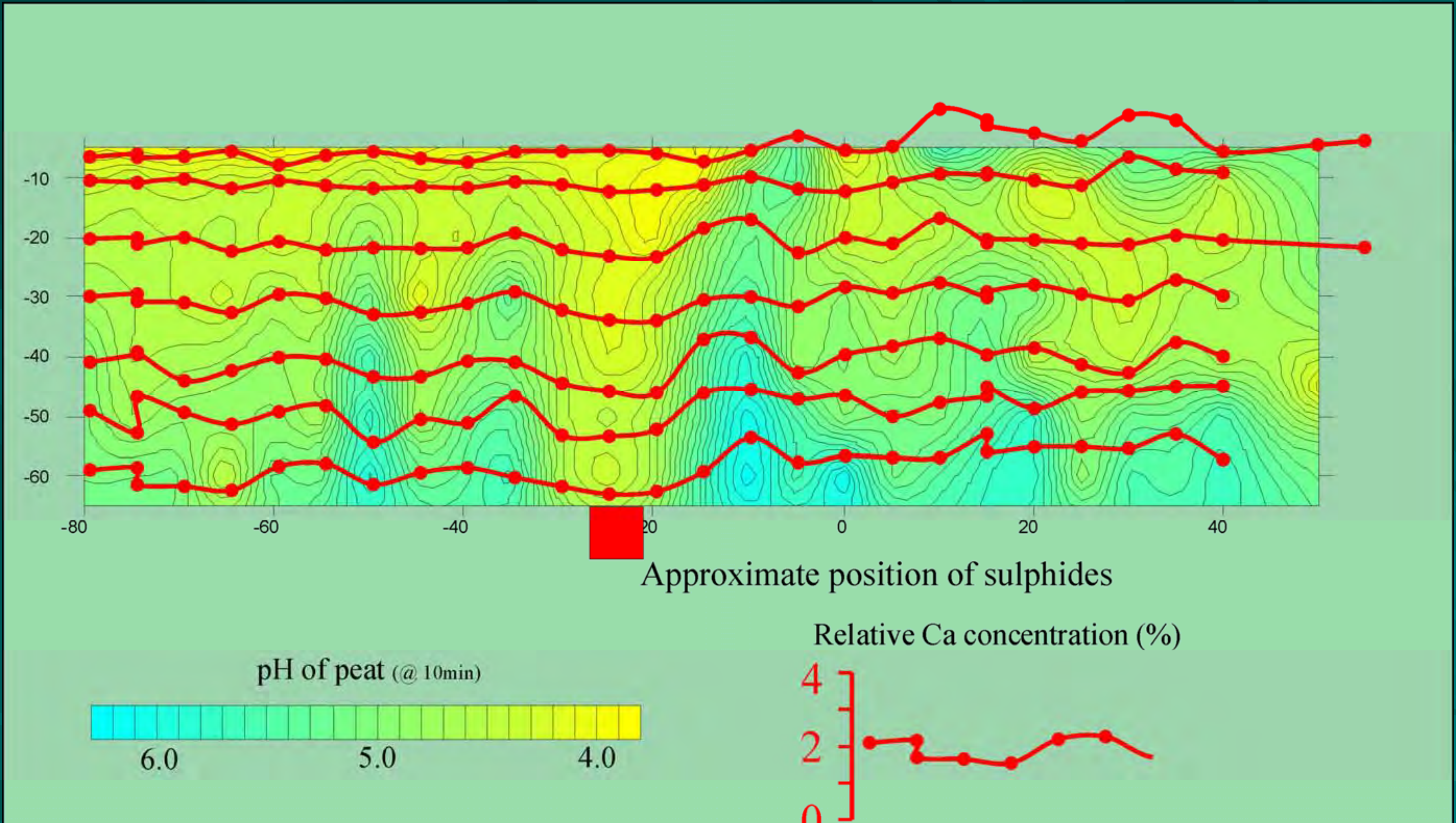
Calcium concentration in peat plotted against pH
Marsh Zone Profile Data



Note: the typical background Ca concentration increases gradually with depth from about 0.5% @ 5 cm to 2.5% @ 60 cm.

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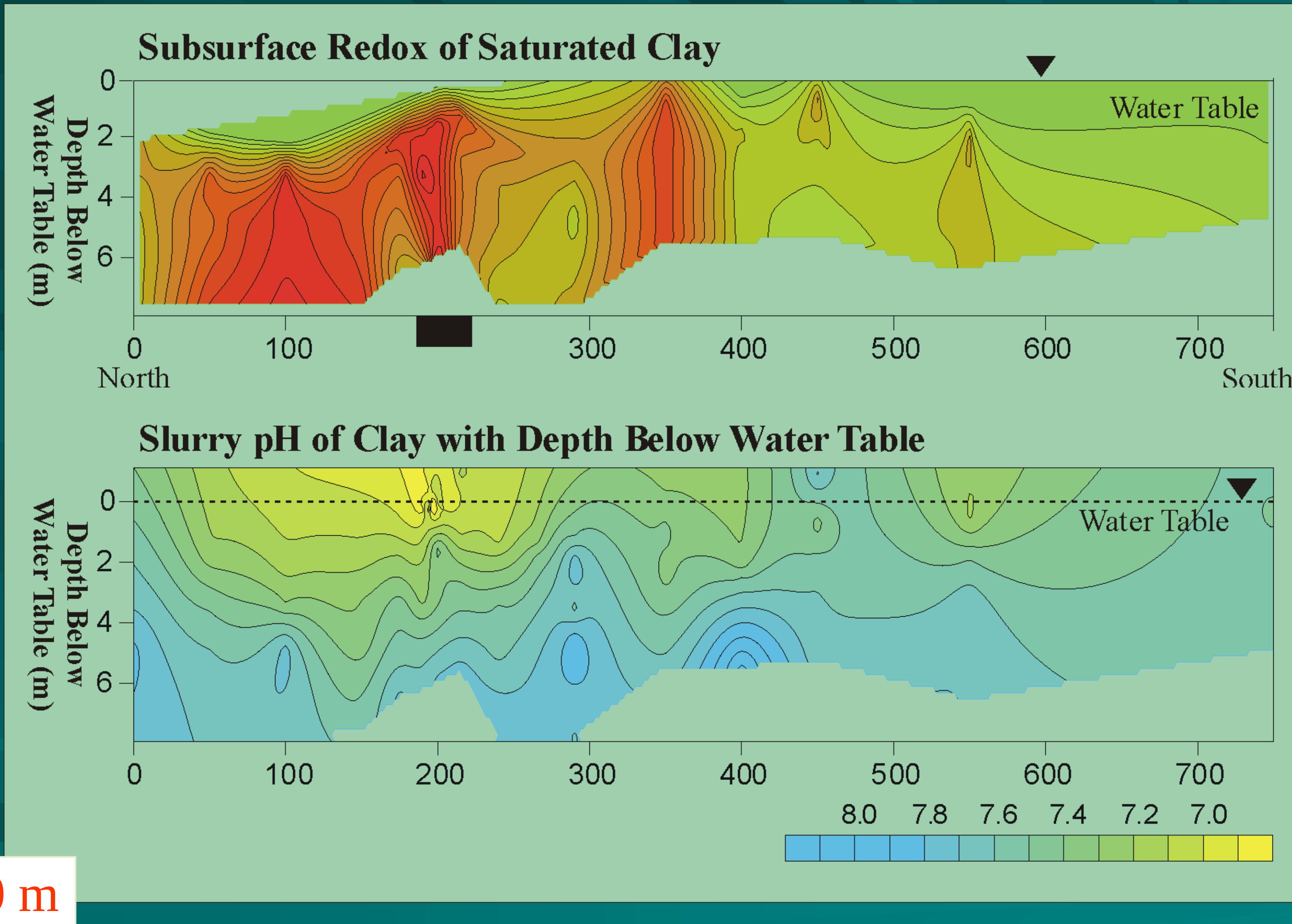
Cross Lake, Line 6 - 3D Redox & pH



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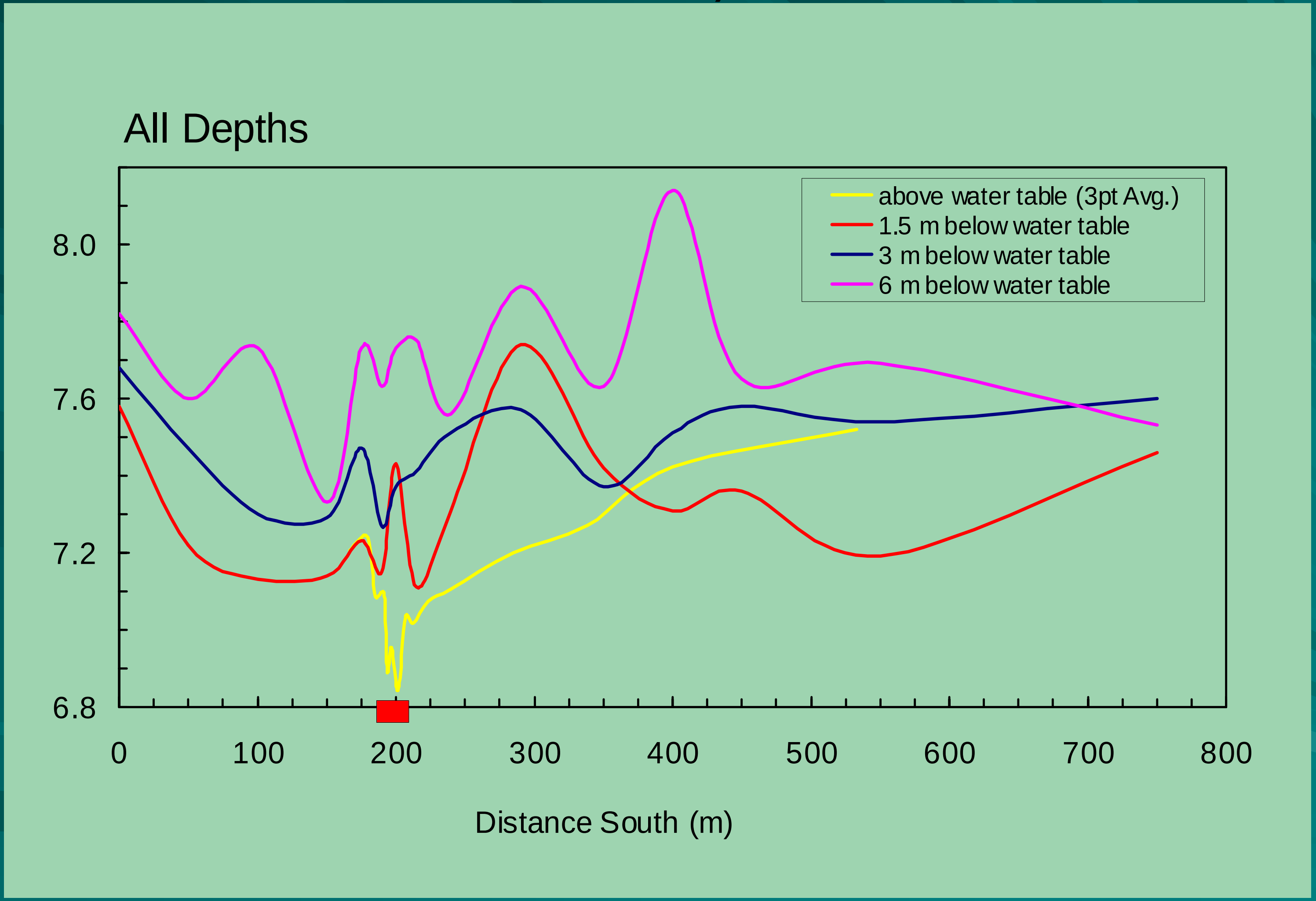
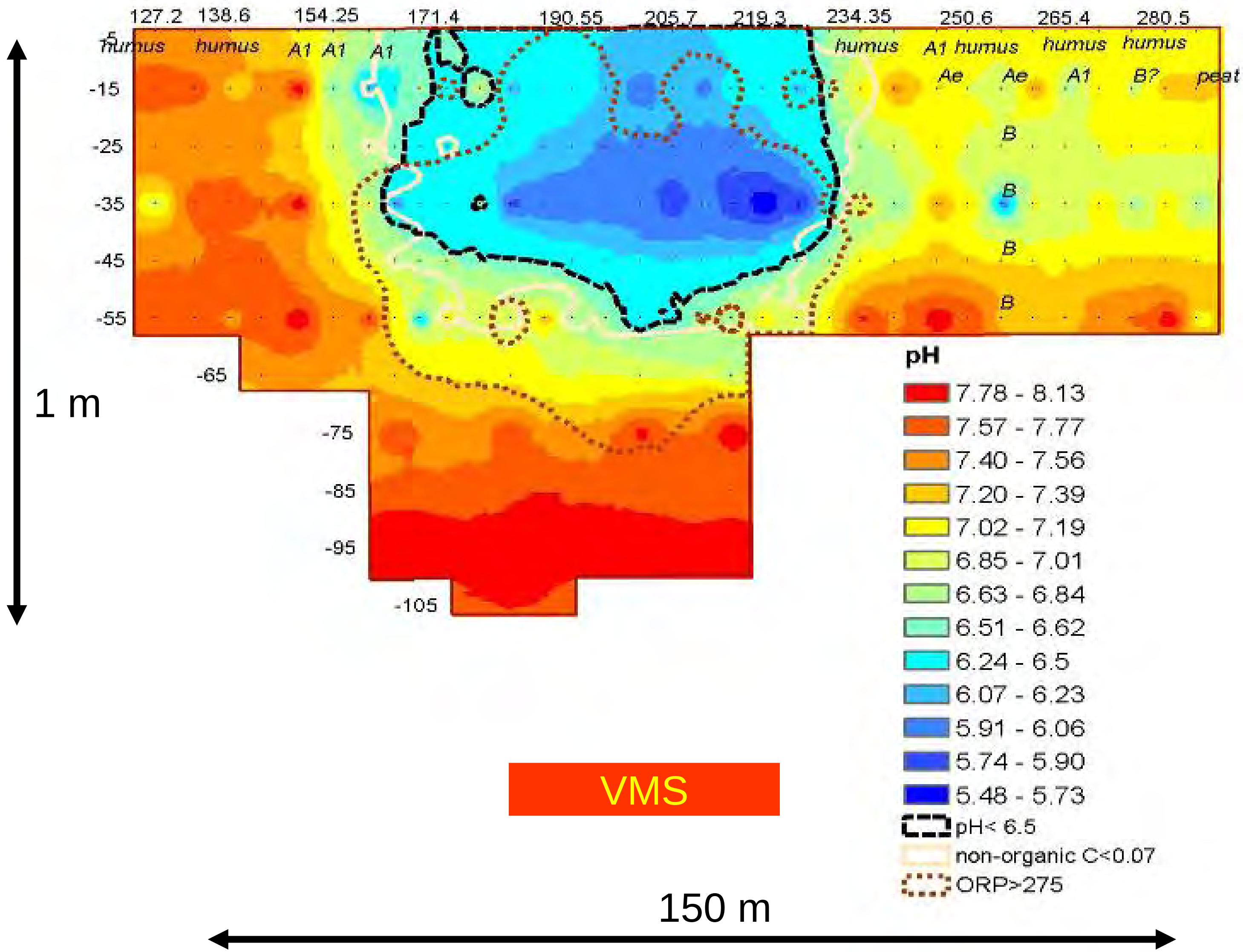
Soil Slurry pH 6 m Below Water Table, Cross Lake, Line 6



pH, Line 6, Cross Lake



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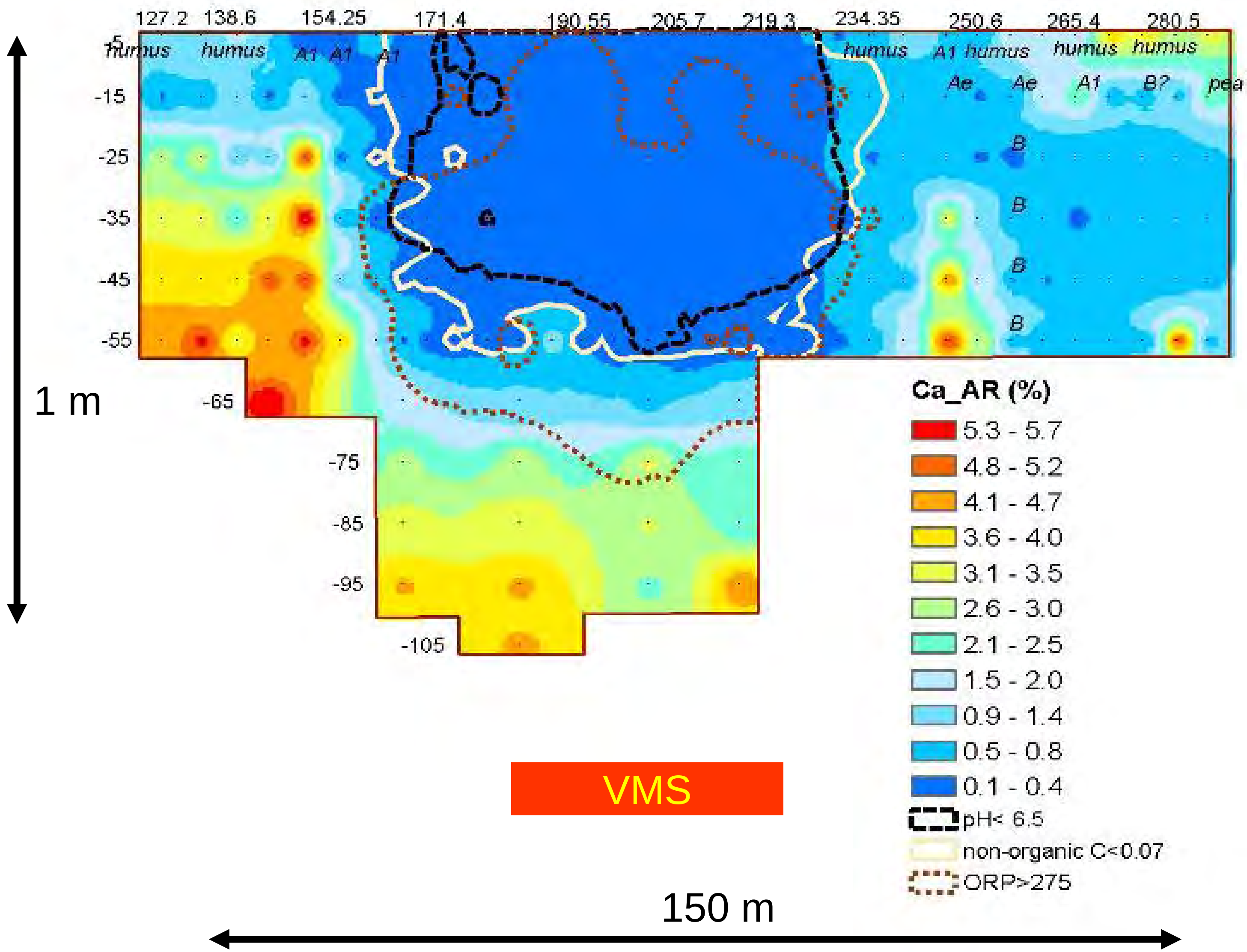
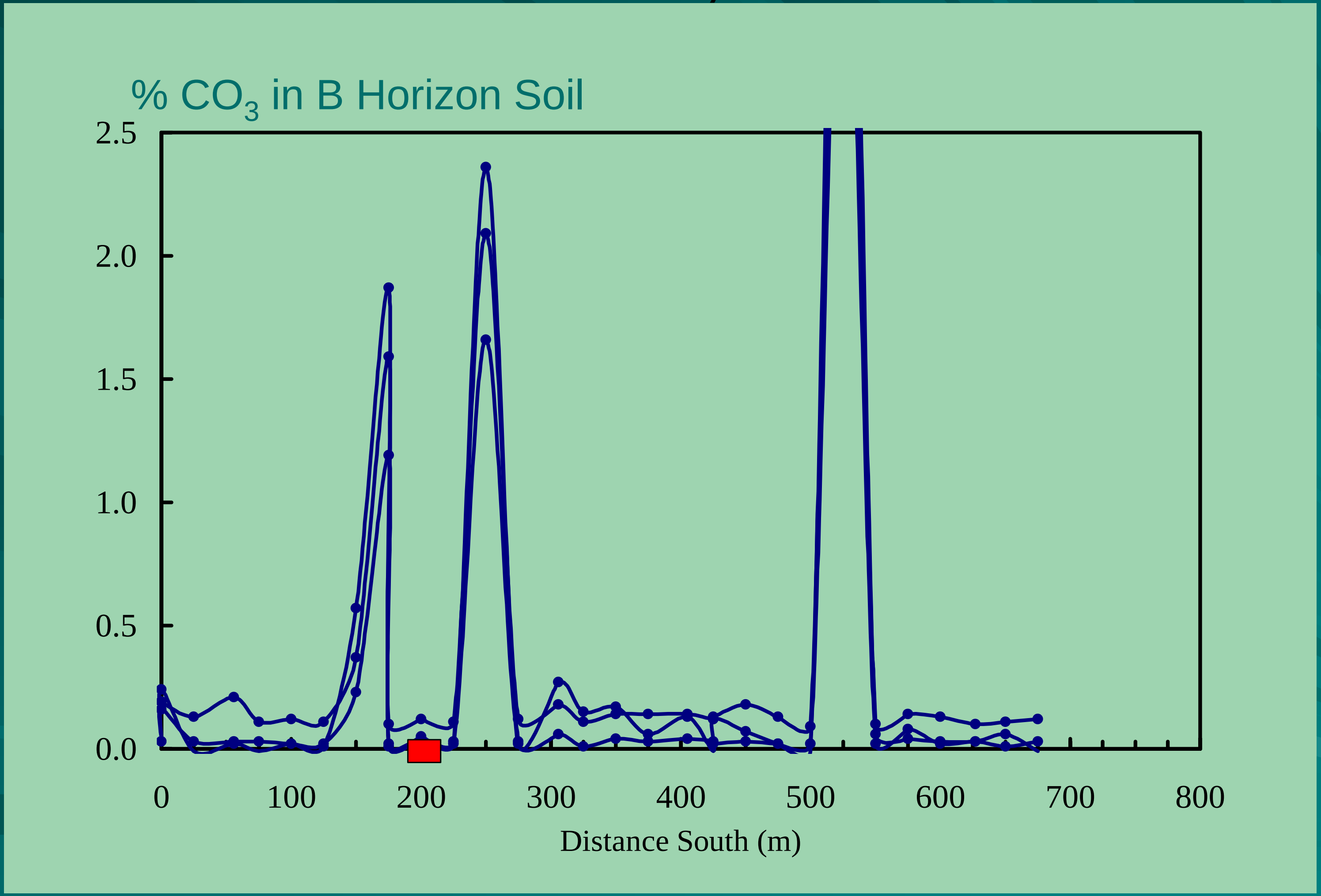
Calcium – Line 6, Cross Lake



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



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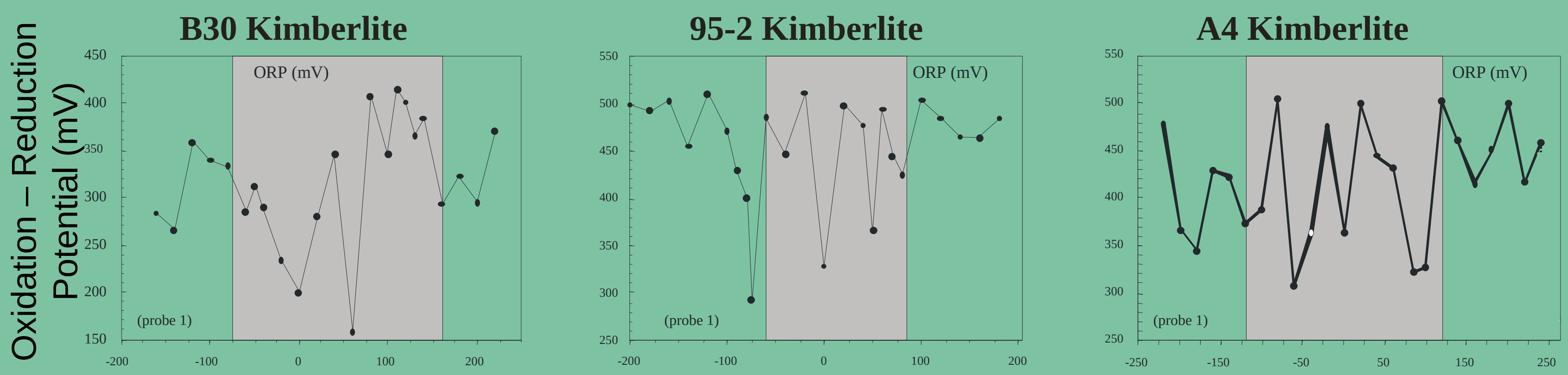
SP & Redox over Kimberlites



Forest rings as evidence of reduced chimneys

100 m

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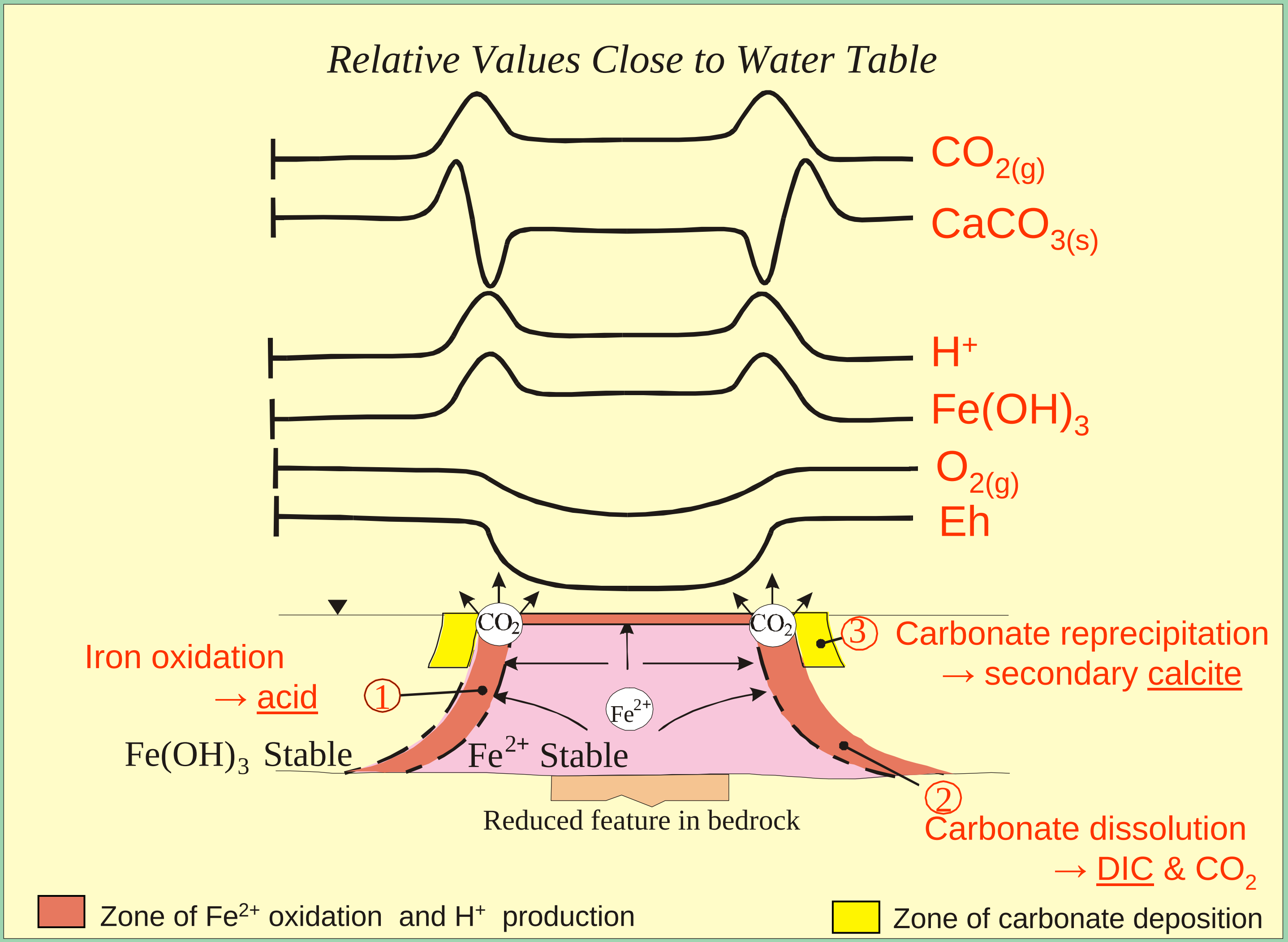
Major-Element Geochemical Response to a Wide Reduced Chimney



Hamilton, 1999; 2000

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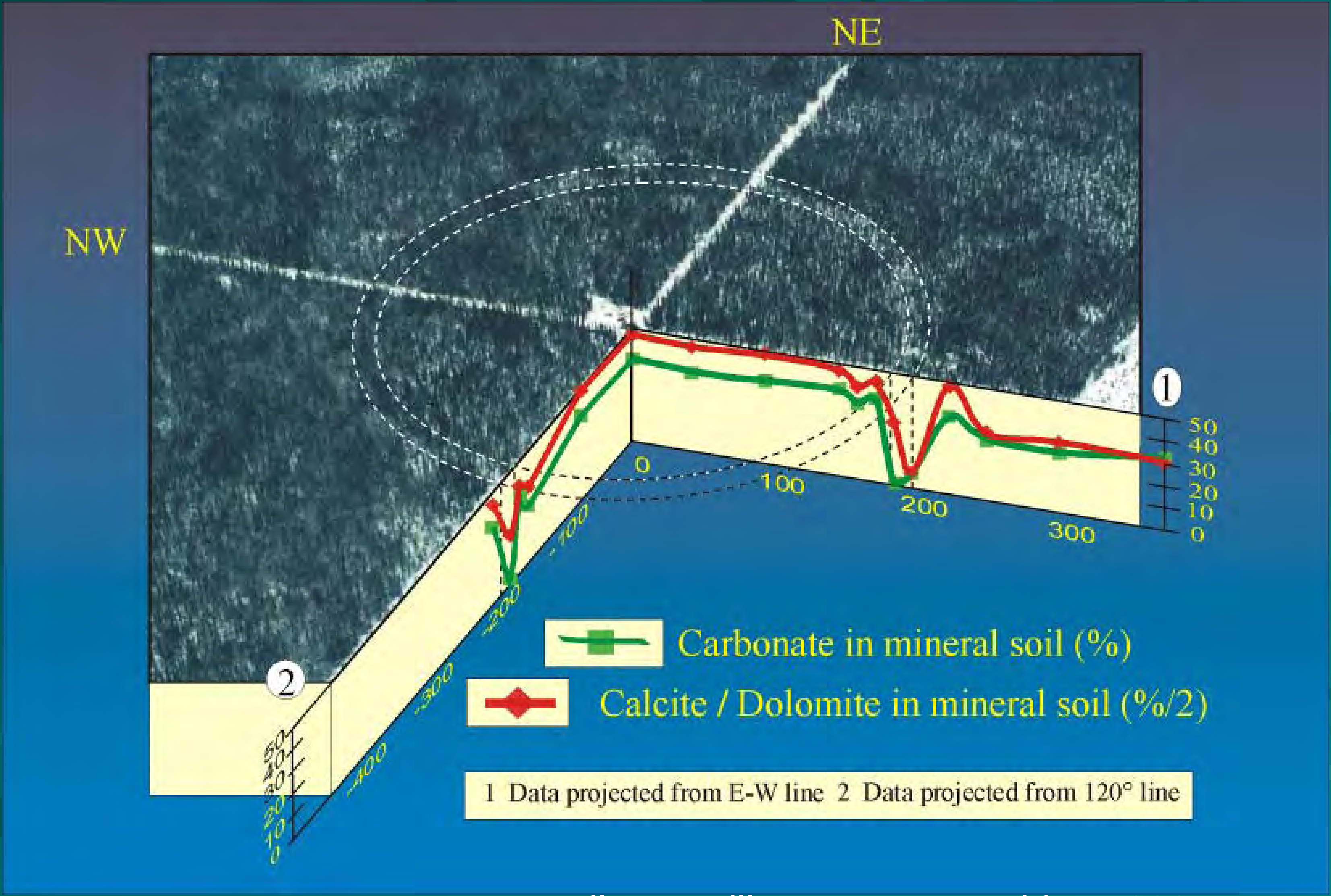
Forest Rings - “Bean” Ring



Hamilton, Veillette & Komarechka, 1999

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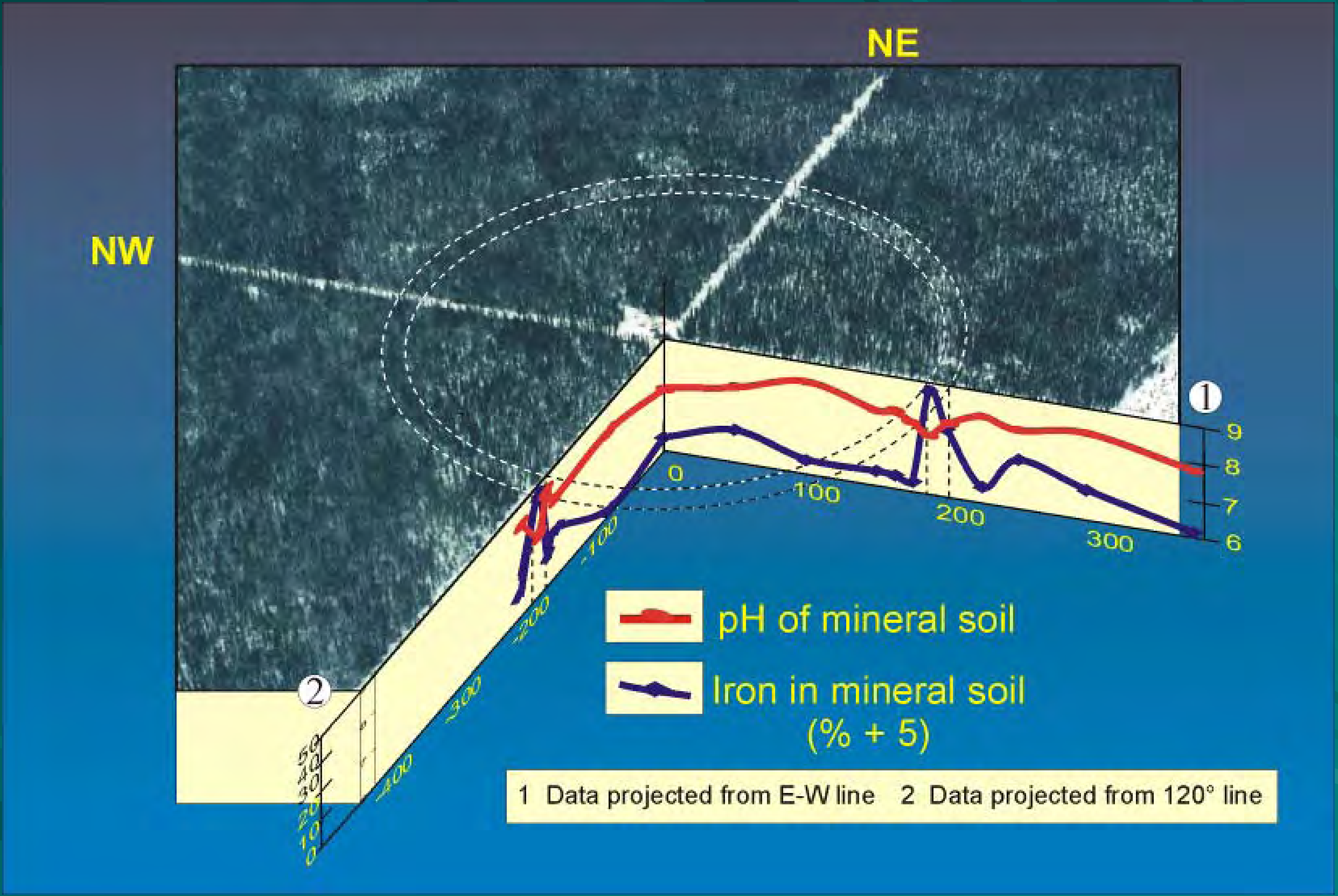
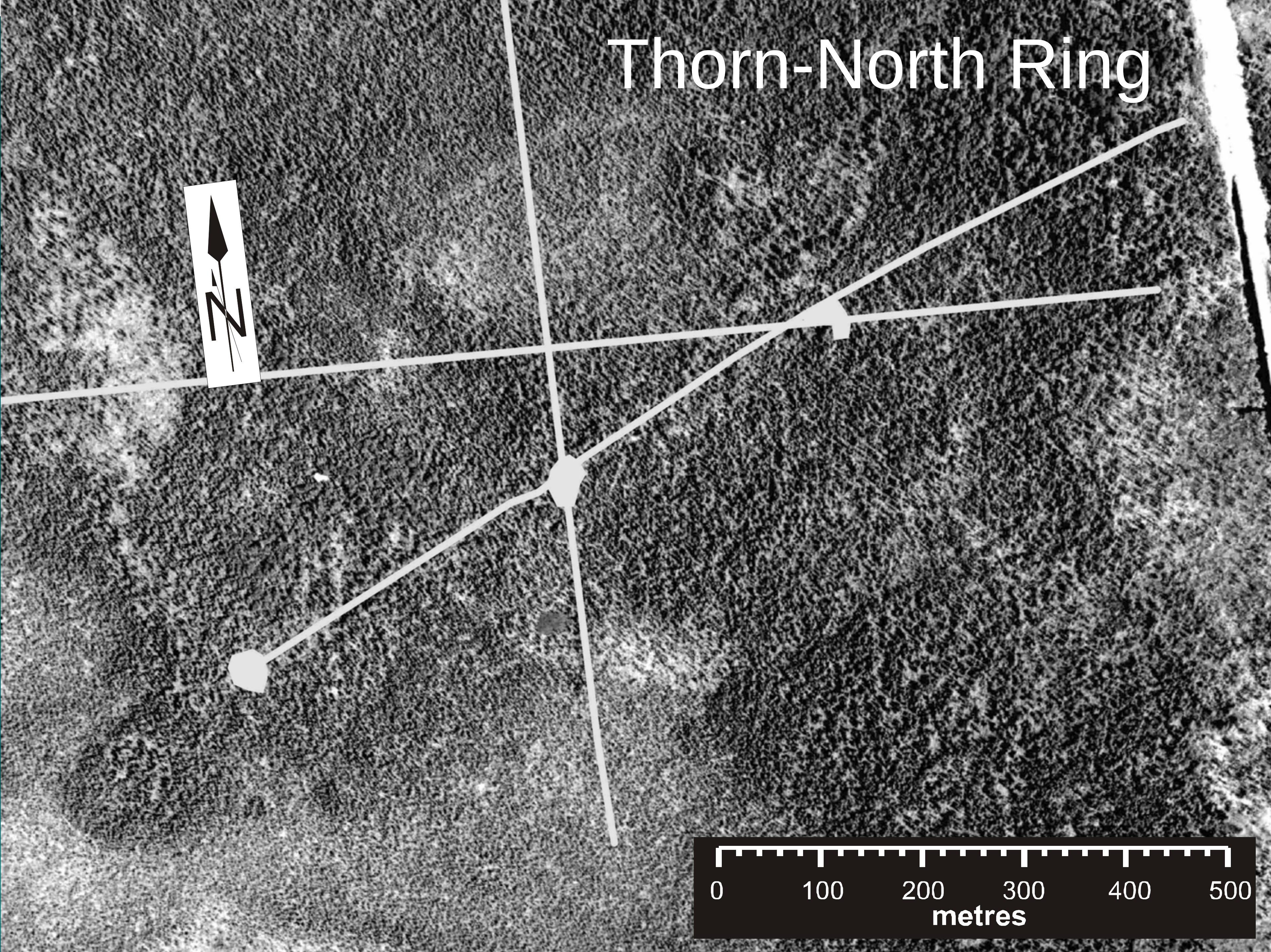
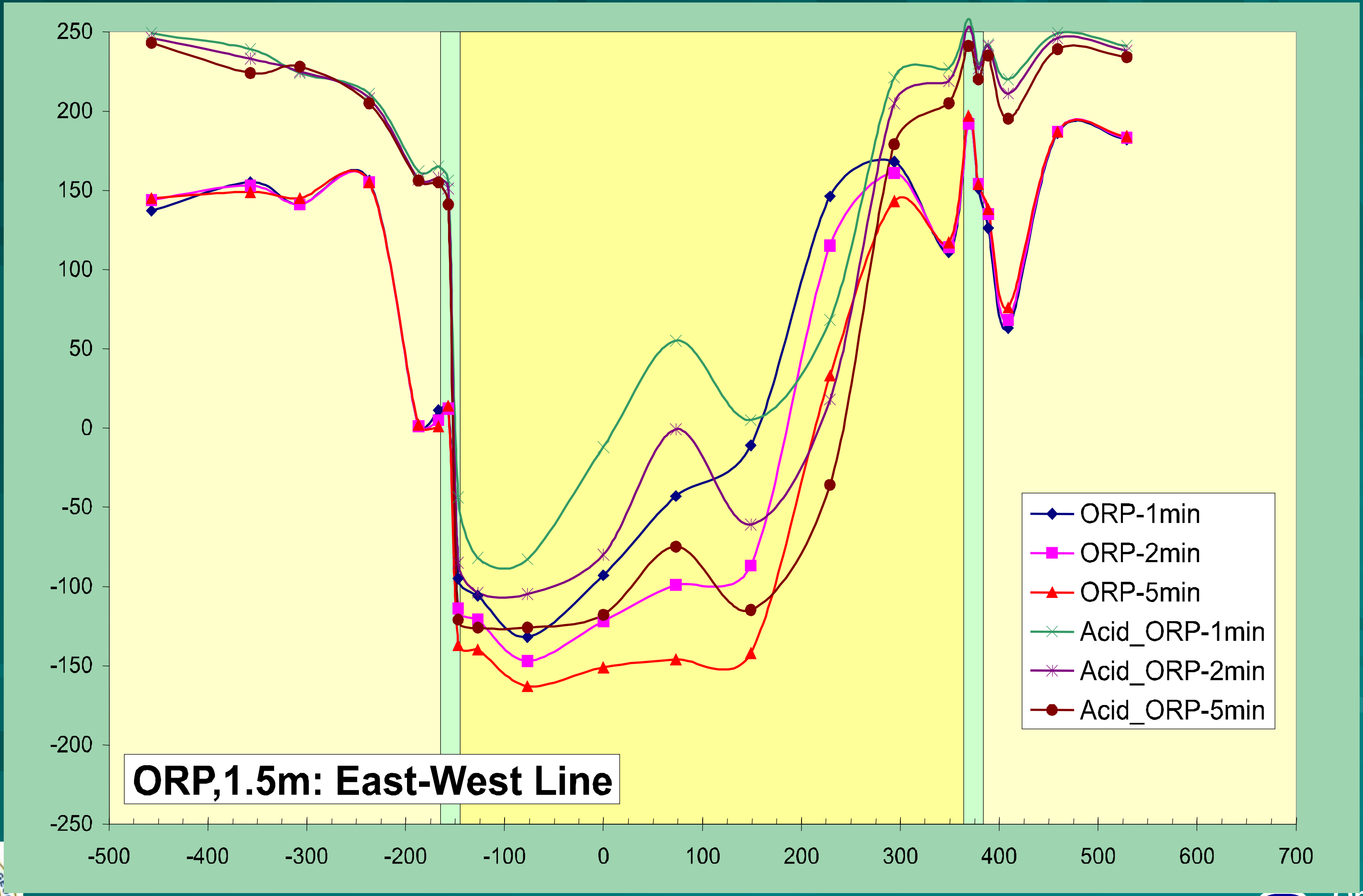
Forest Rings - "Bean" Ring



Hamilton, Veillette & Komarechka, 1999


Thorn-North Ring
N
0
100
200
300
400
500
metres

ORP of Sediments, 2 m Depth Thorn-North Ring



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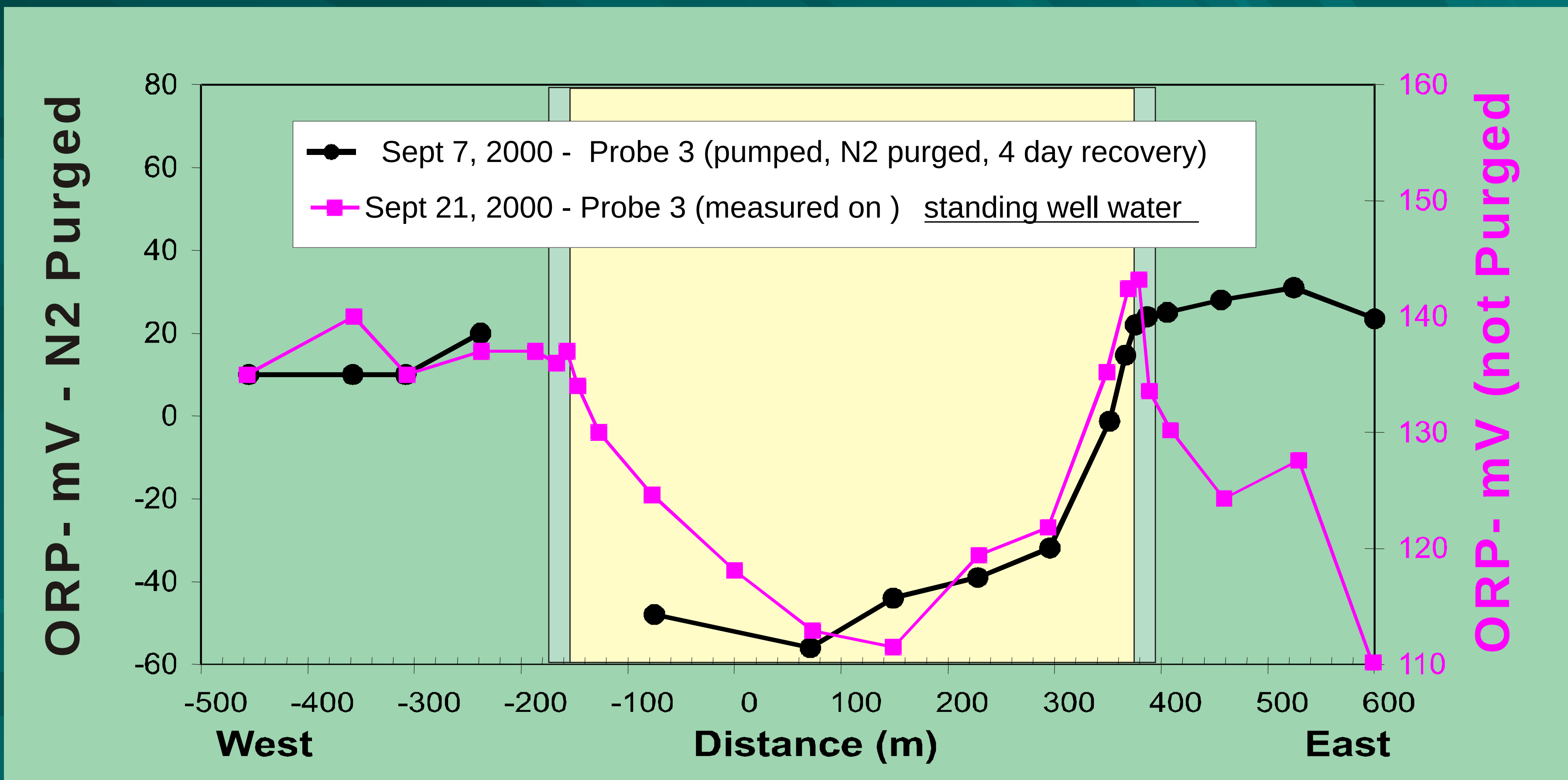
ORP of Groundwater, 8 m Depth Thorn-North Ring



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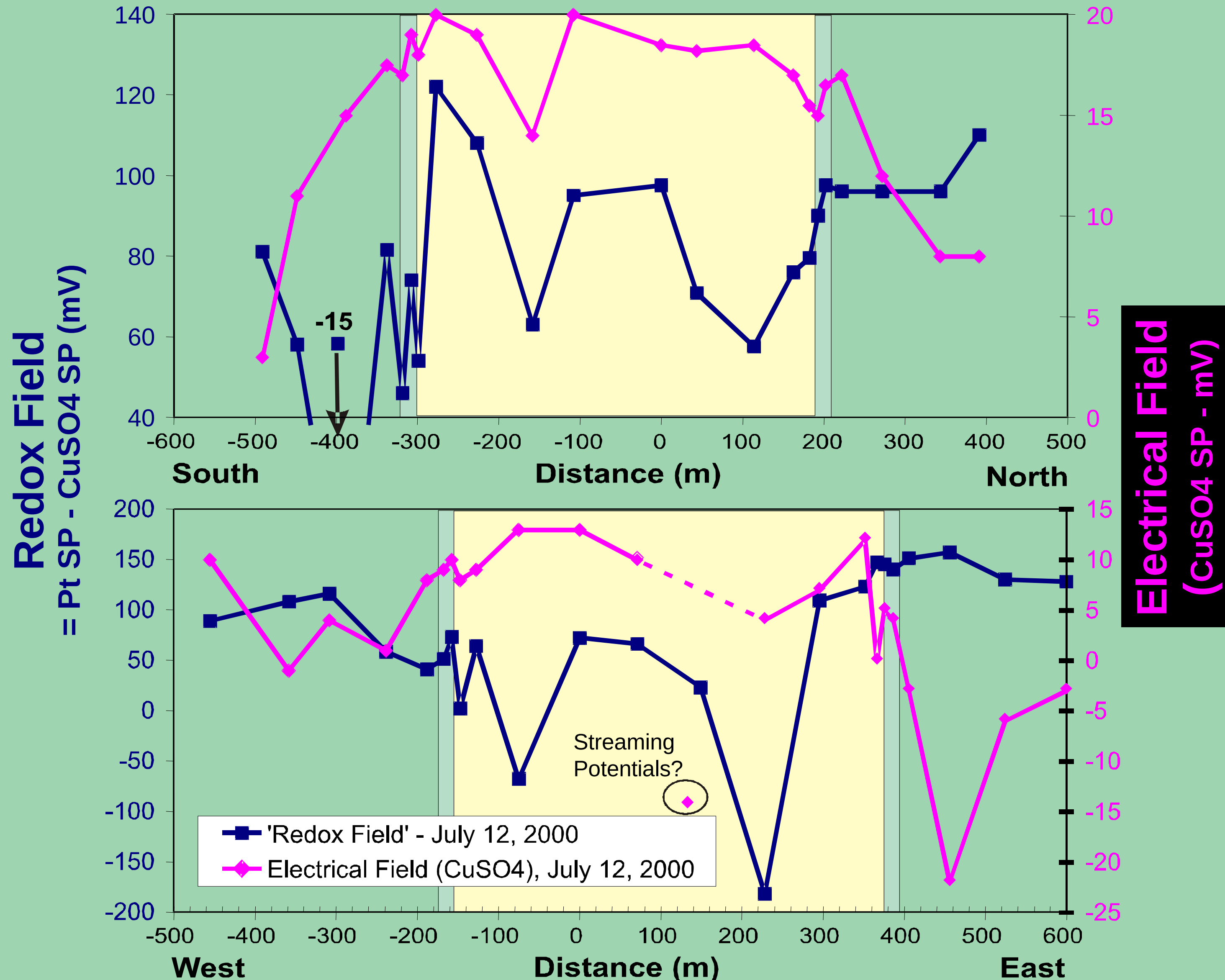
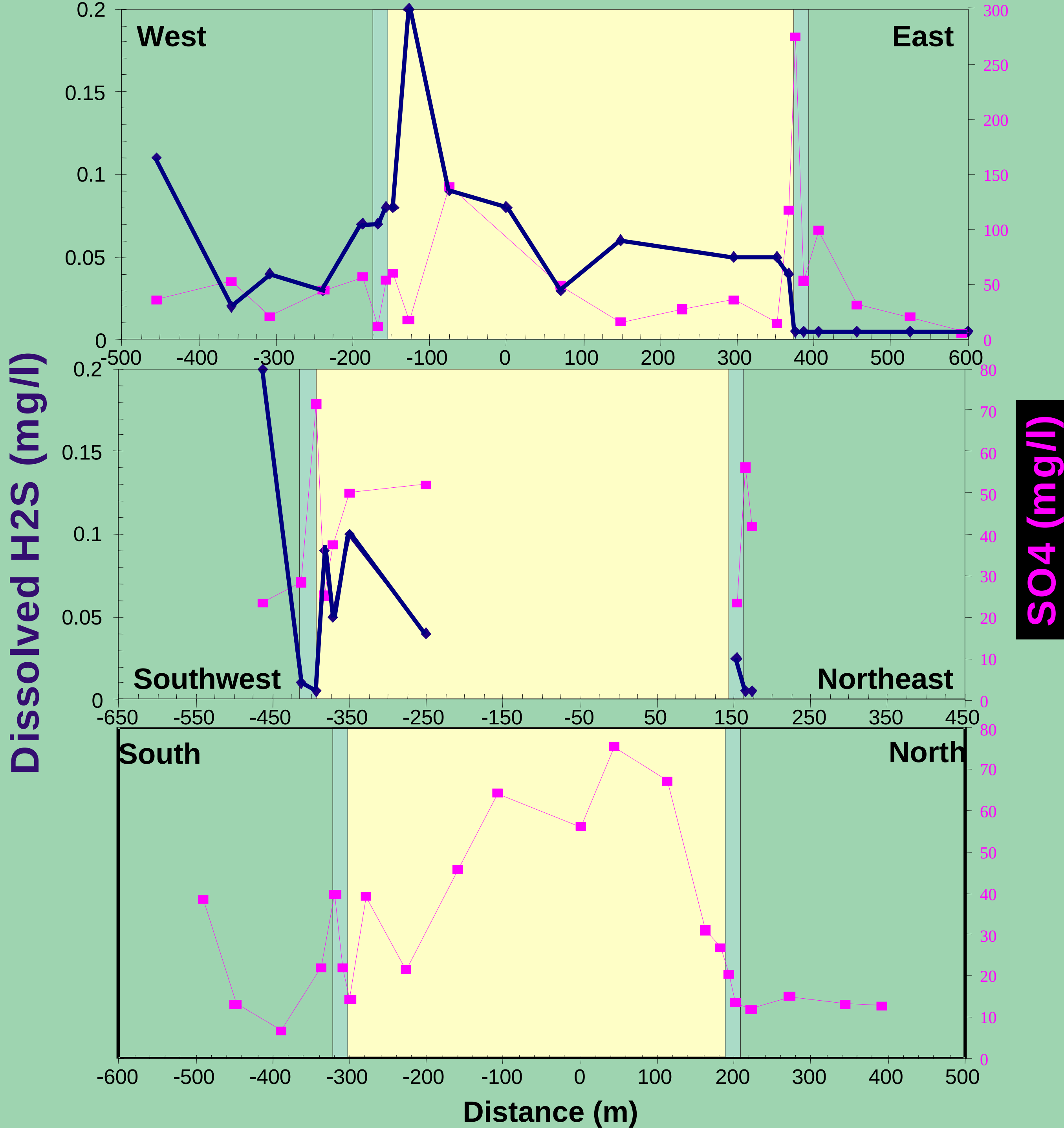
Down-Hole SP Redox Field

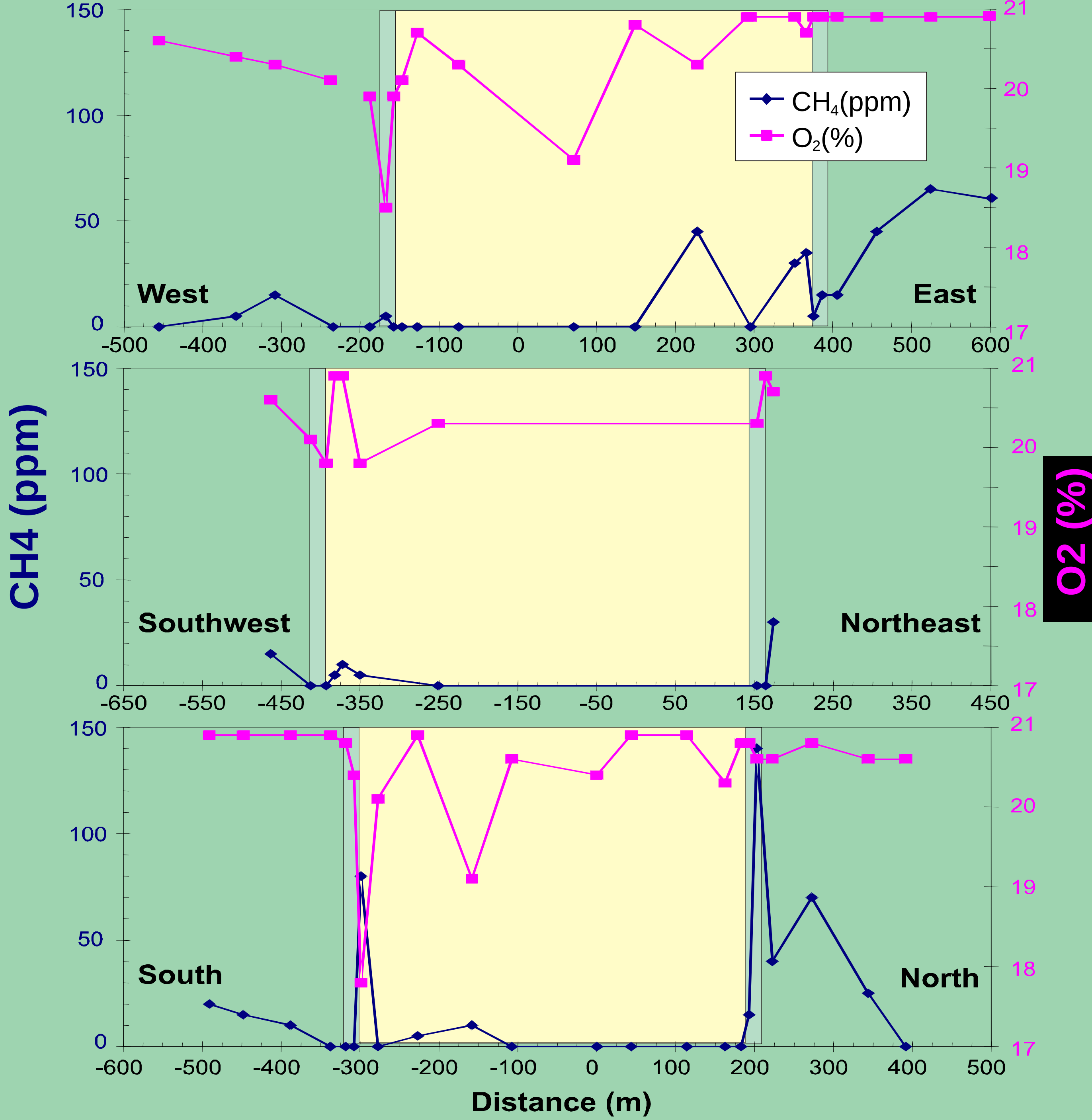
Electrical Field



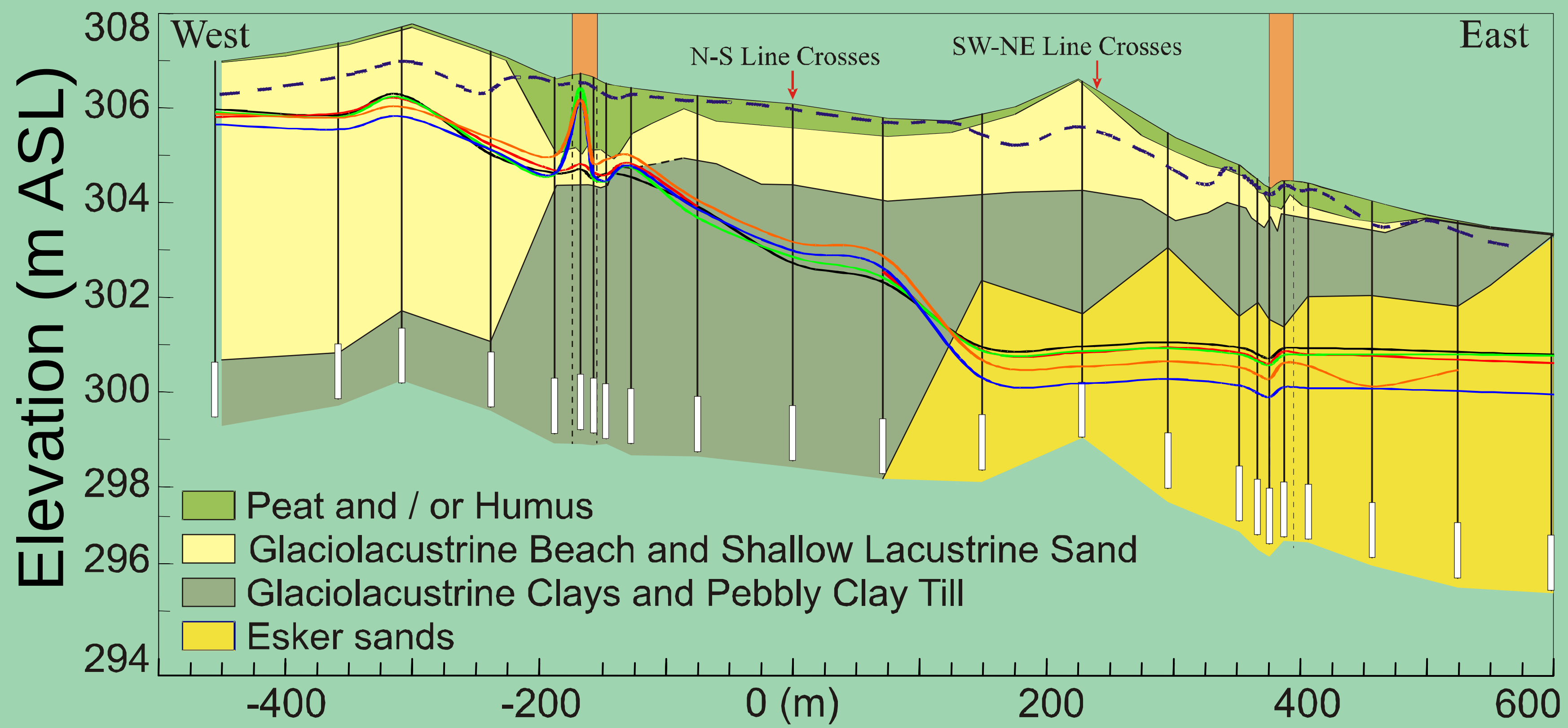
H_2S & SO_4^{2-} in Groundwater



Methane and Oxygen in Well Headspace



Water Table and Pieziometric Surface – Thorn North Ring



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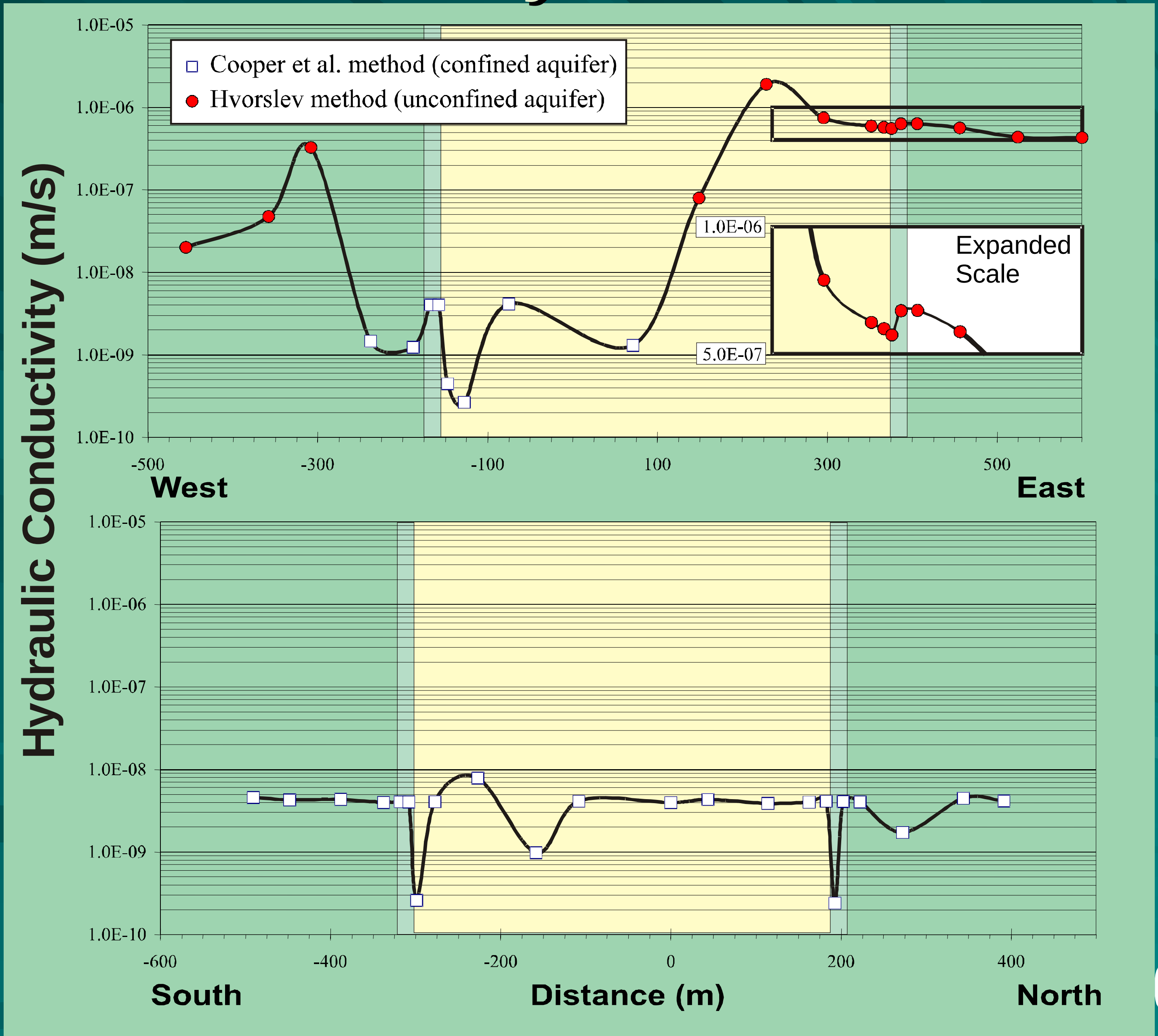
Permeability of Sediments



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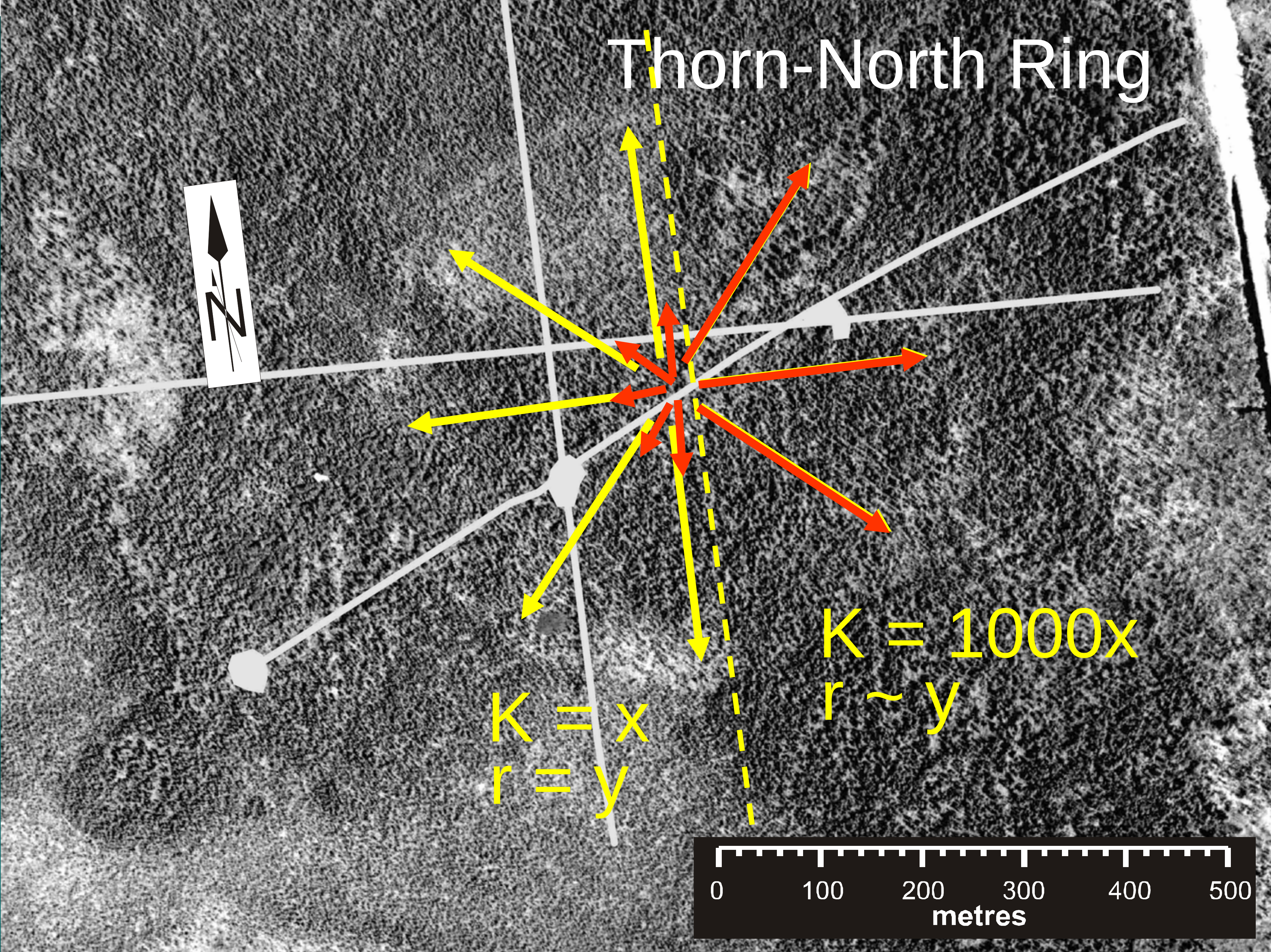
Thorn-North Ring
N
K = 1000x
r ~ y
K = x
r = y
0
100
200
300
400
500
metres

Soil Gas Hydrocarbons

- 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

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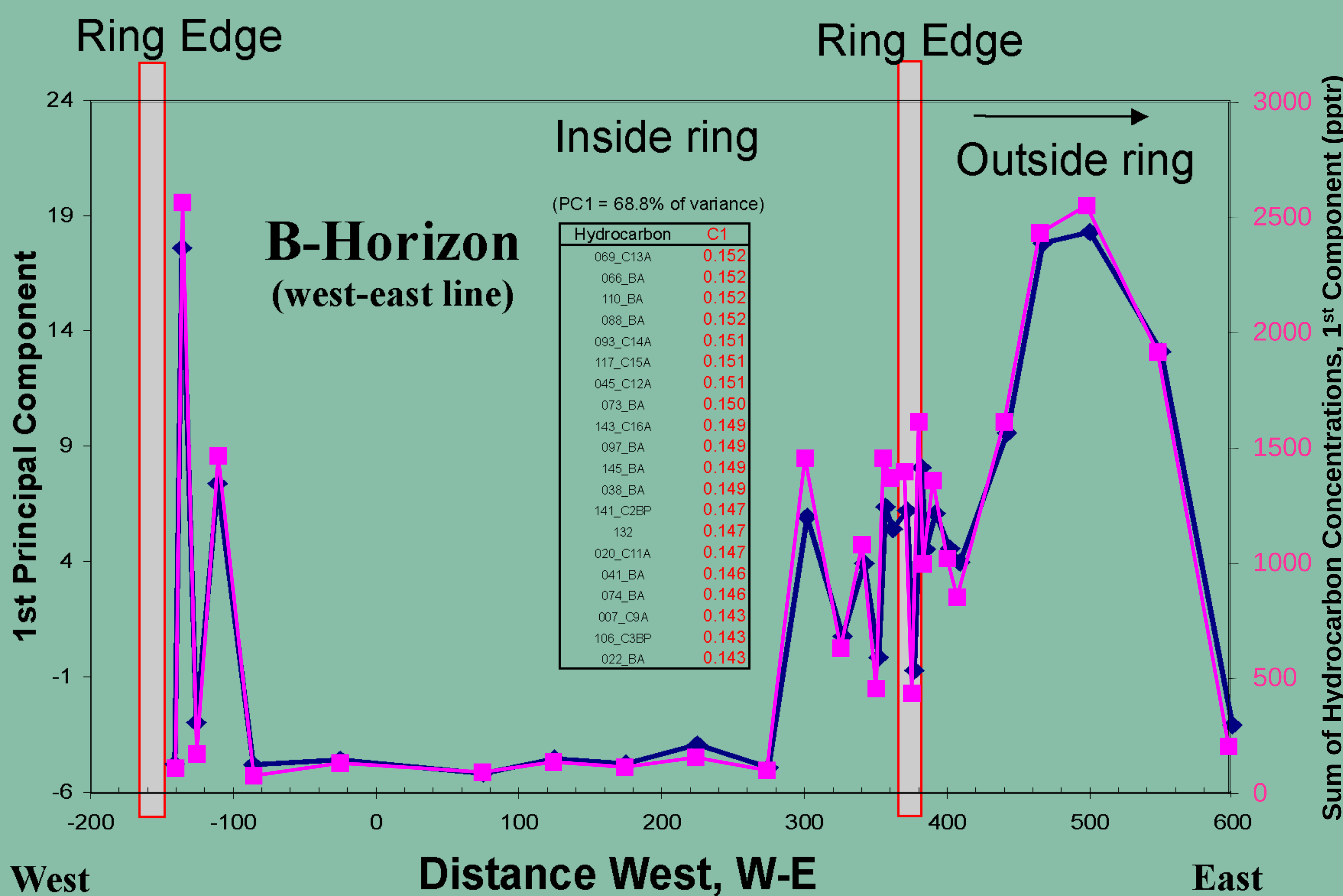
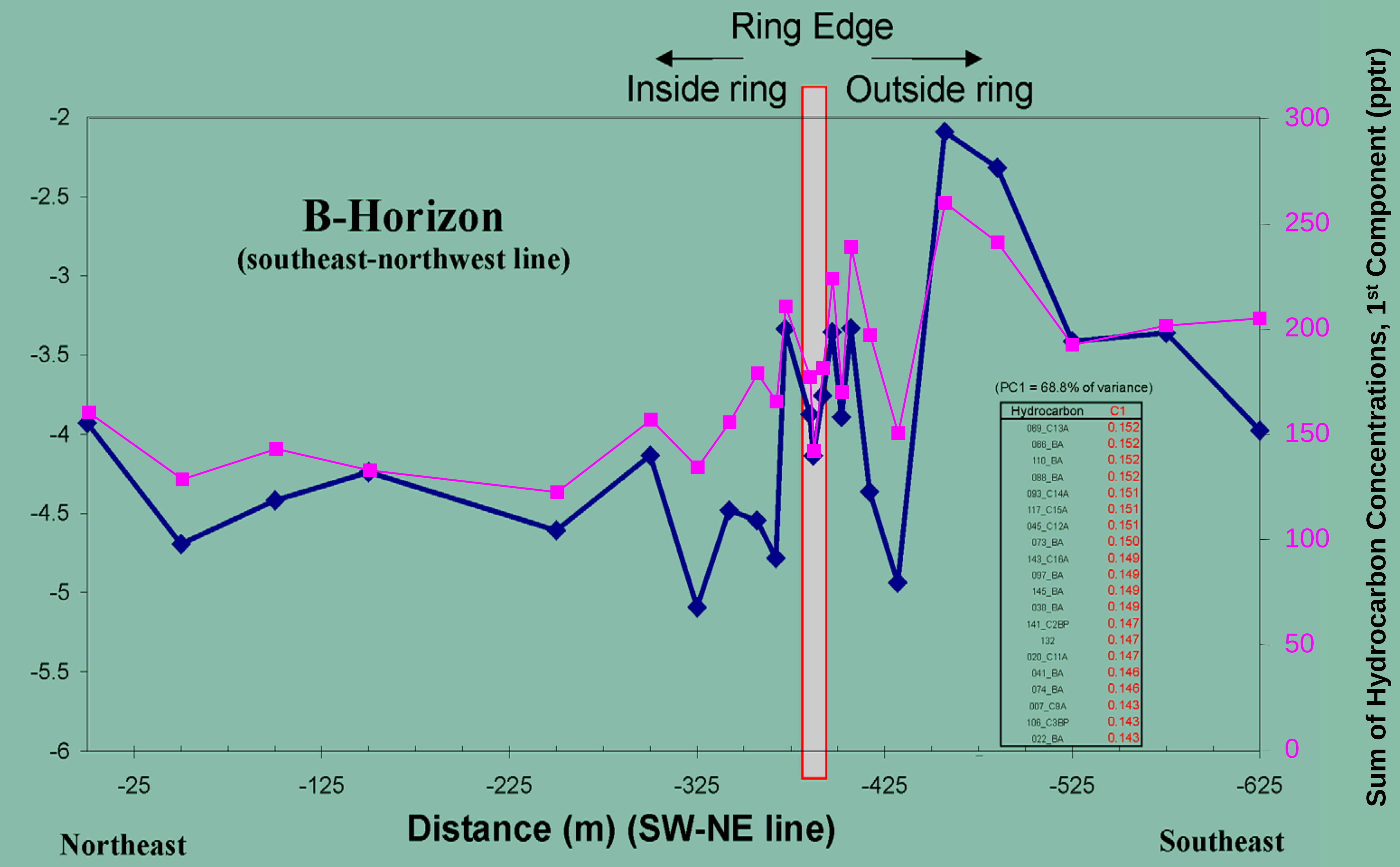
Soil Gas Hydrocarbon – Thorn N.



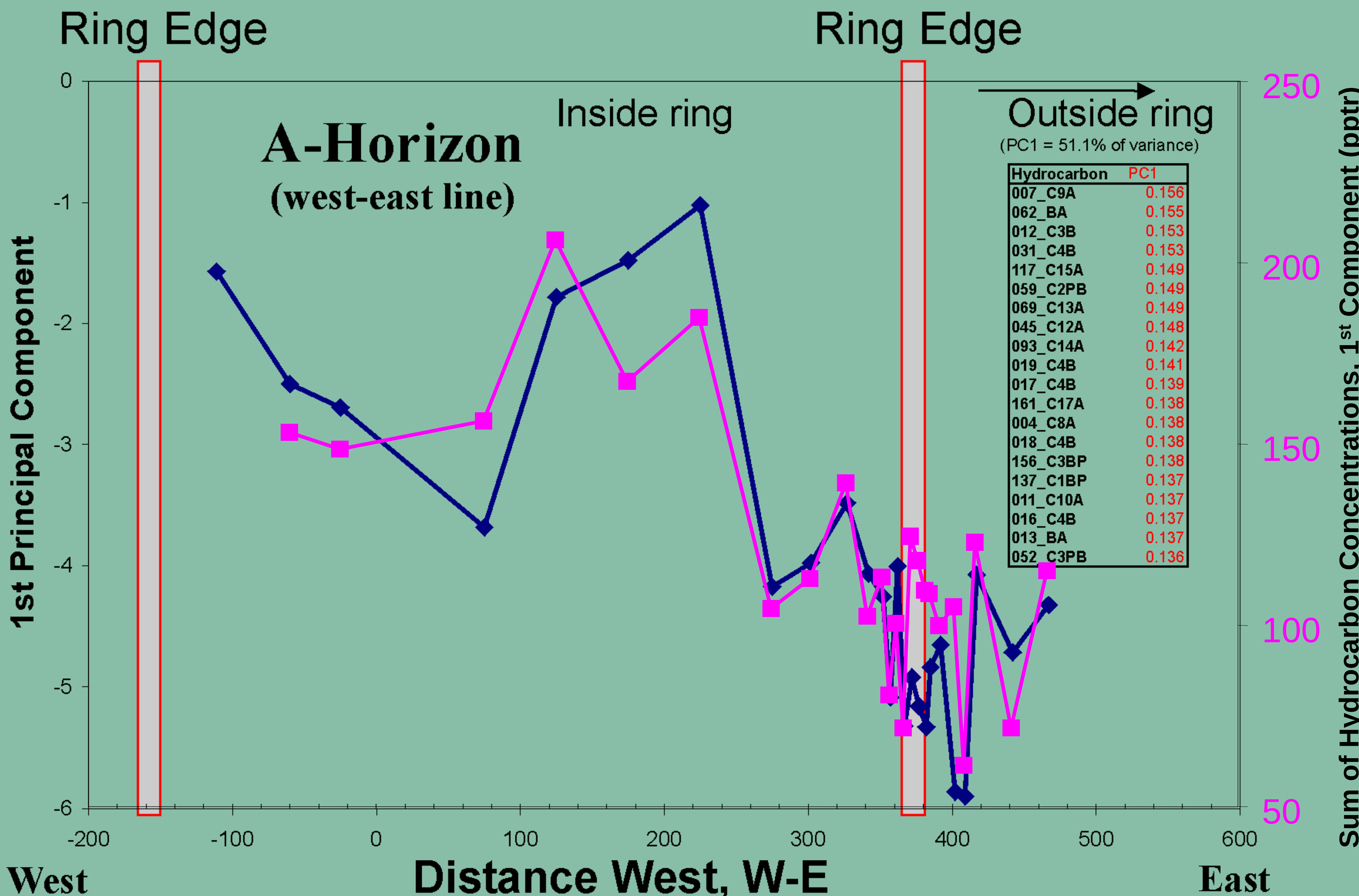
Hydrocarbon	C1
069_C13A	0.152
066_BA	0.152
110_BA	0.152
088_BA	0.152
093_C14A	0.151
117_C15A	0.151
045_C12A	0.151
073_BA	0.150
143_C16A	0.149
097_BA	0.149
145_BA	0.149
038_BA	0.149
141_C2BP	0.147
132	0.147
020_C11A	0.147
041_BA	0.146
074_BA	0.146
007_C9A	0.143
106_C3BP	0.143
022_BA	0.143

Soil Gas Hydrocarbon – Thorn N.

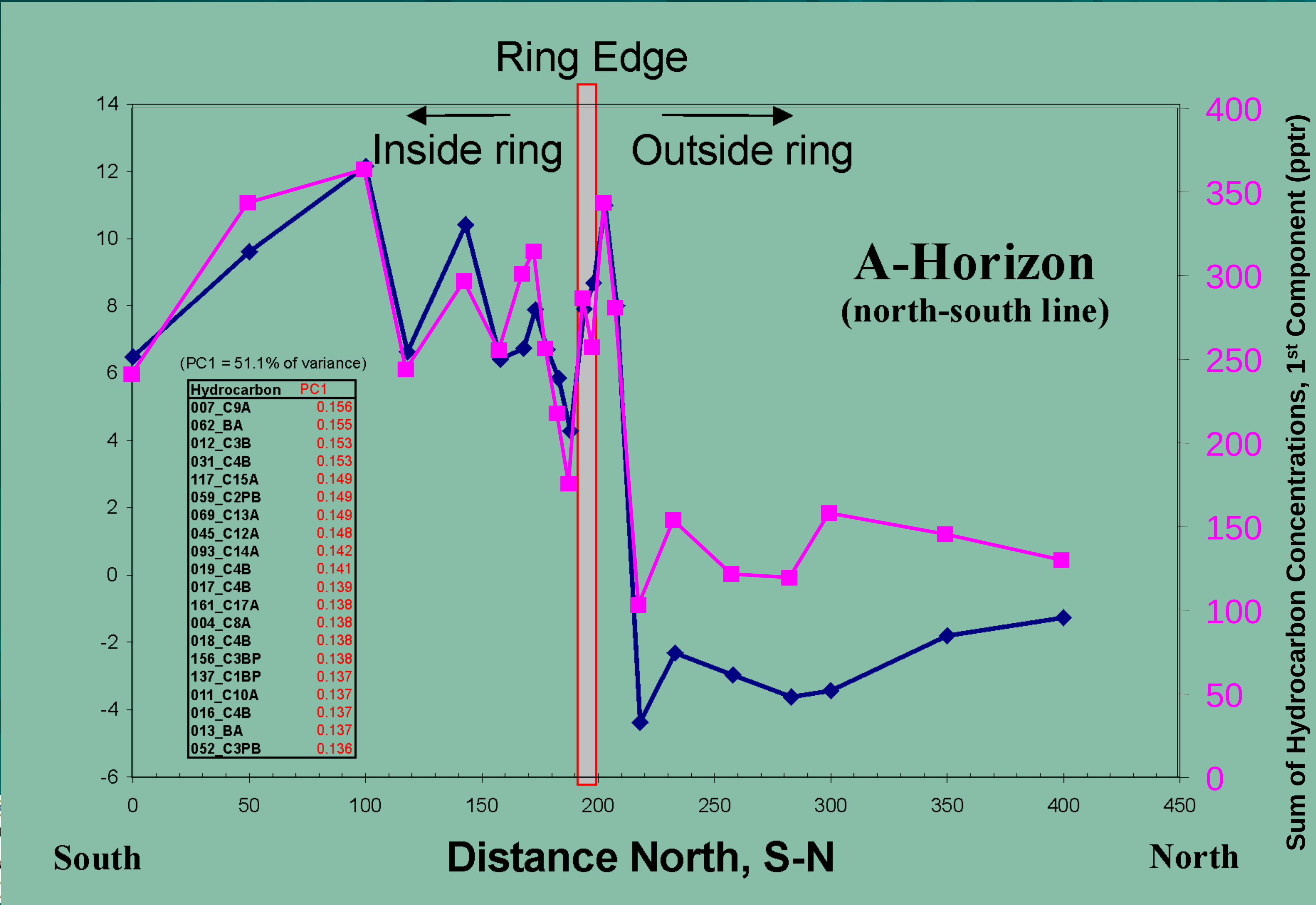


Hydrocarbon	C1
069_C13A	0.152
066_BA	0.152
110_BA	0.152
088_BA	0.152
093_C14A	0.151
117_C15A	0.151
045_C12A	0.151
073_BA	0.150
143_C16A	0.149
097_BA	0.149
145_BA	0.149
038_BA	0.149
141_C2BP	0.147
132	0.147
020_C11A	0.147
041_BA	0.146
074_BA	0.146
007_C9A	0.143
106_C3BP	0.143
022_BA	0.143

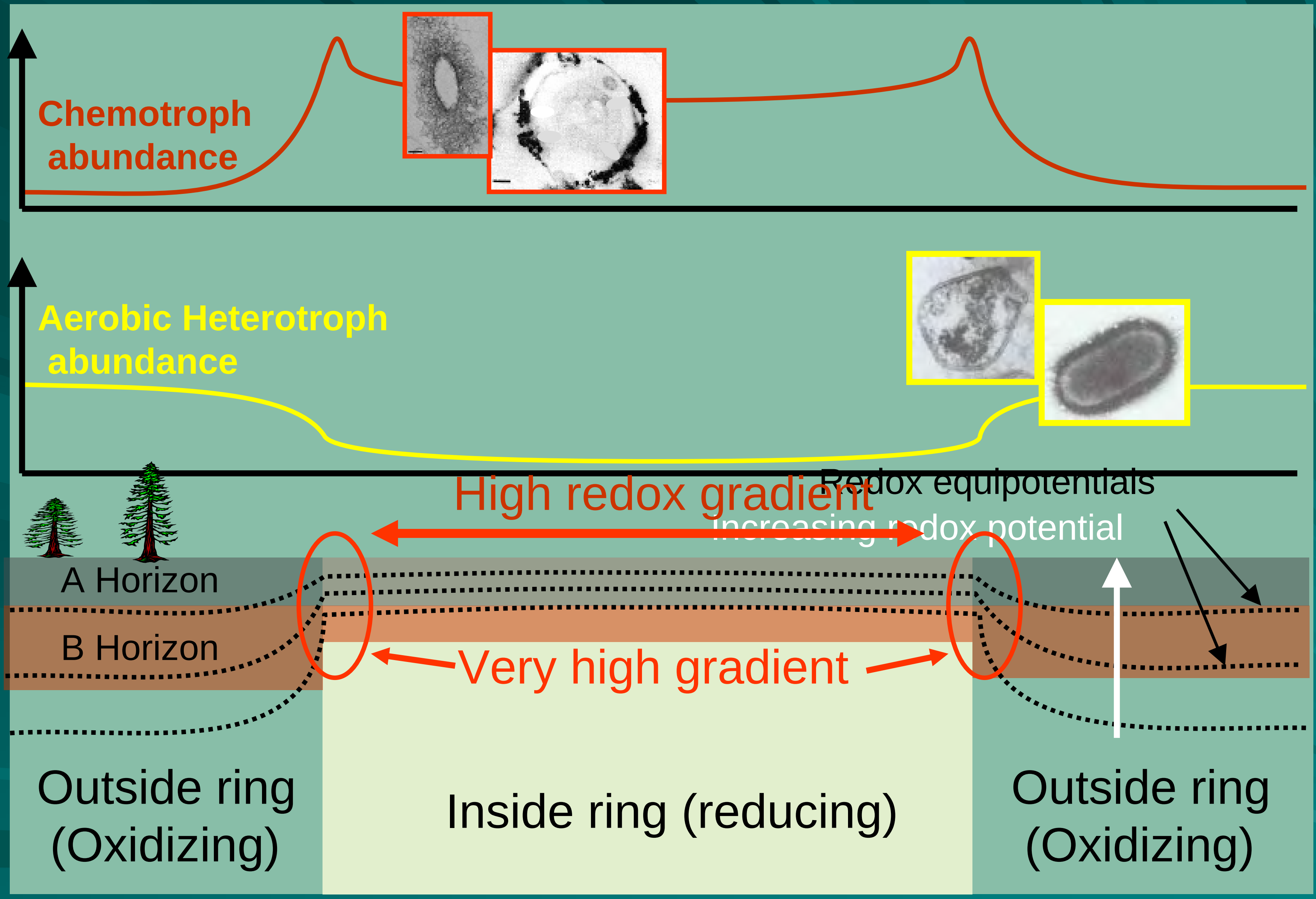
Soil Gas Hydrocarbon – Thorn N.



Soil Gas Hydrocarbon – Thorn N.



Hydrocarbon	PC1
007_C9A	0.156
062_BA	0.155
012_C3B	0.153
031_C4B	0.153
117_C15A	0.149
059_C2PB	0.149
069_C13A	0.149
045_C12A	0.148
093_C14A	0.142
019_C4B	0.141
017_C4B	0.139
161_C17A	0.138
004_C8A	0.138
018_C4B	0.138
156_C3BP	0.138
137_C1BP	0.137
011_C10A	0.137
016_C4B	0.137
013_BA	0.137
052_C3PB	0.136



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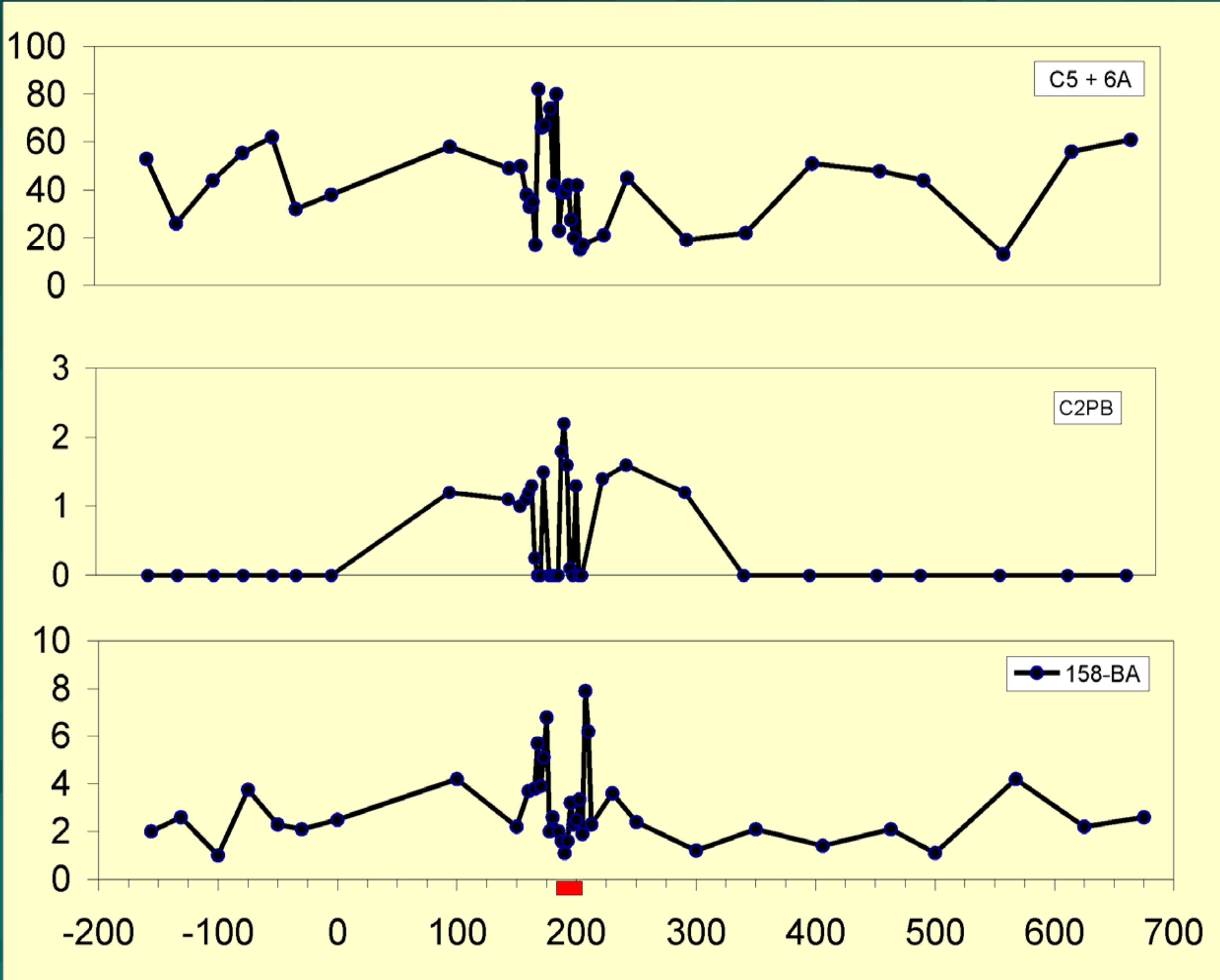
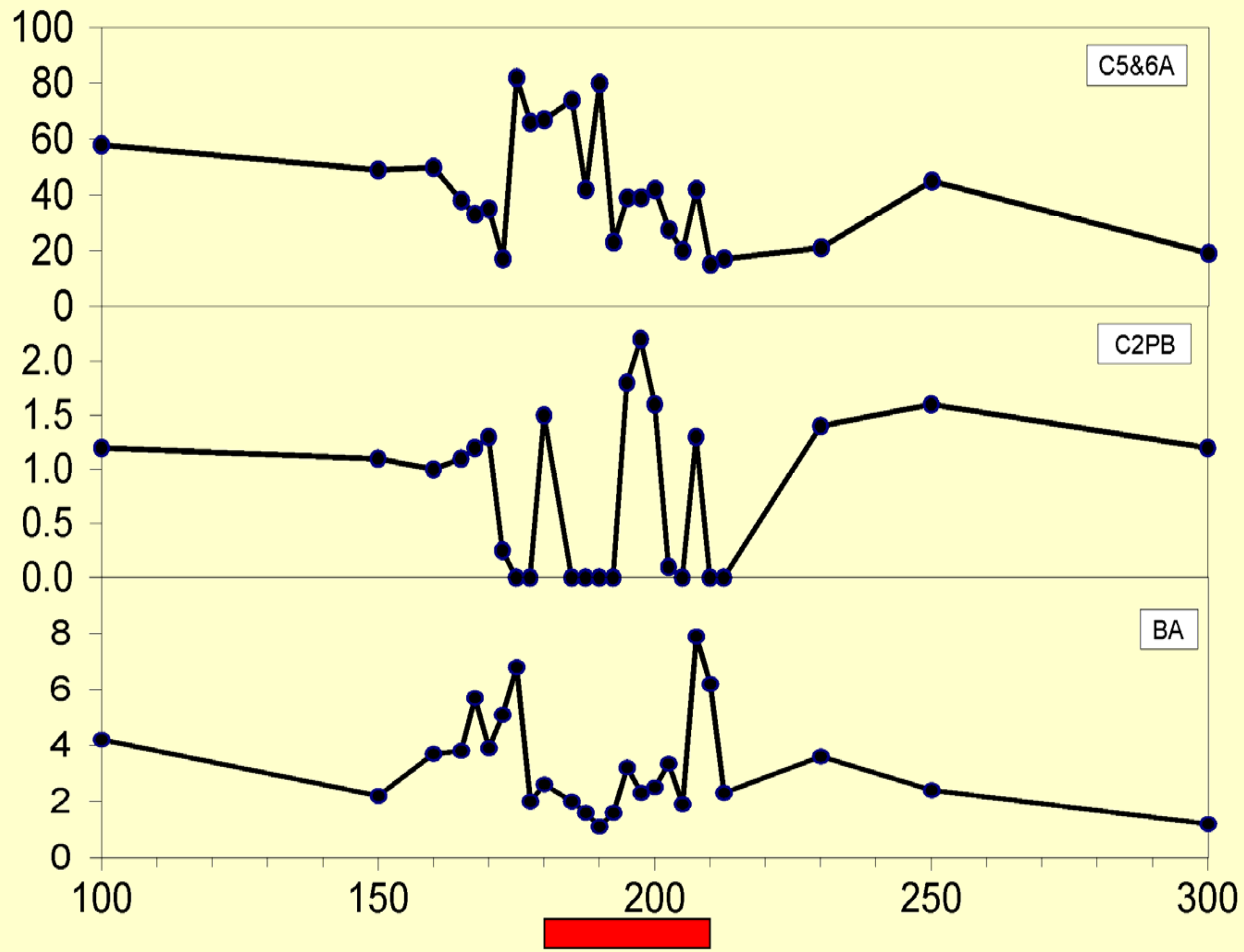
Soil Gas Hydrocarbons

Cross Lake
Line 6

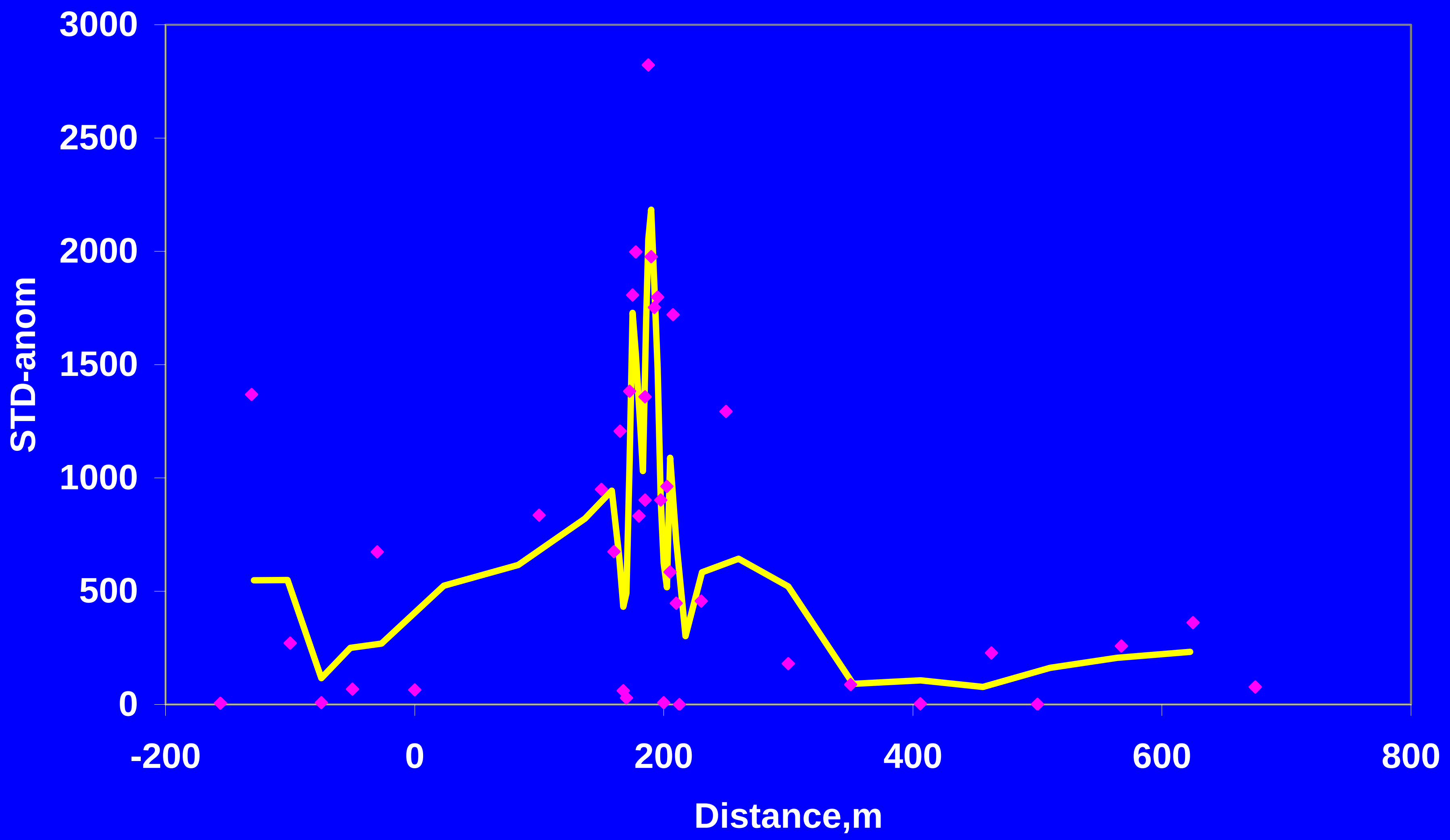


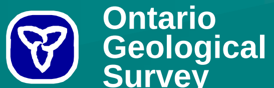
Soil Gas Hydrocarbons

Cross Lake
Line 6
(expanded)

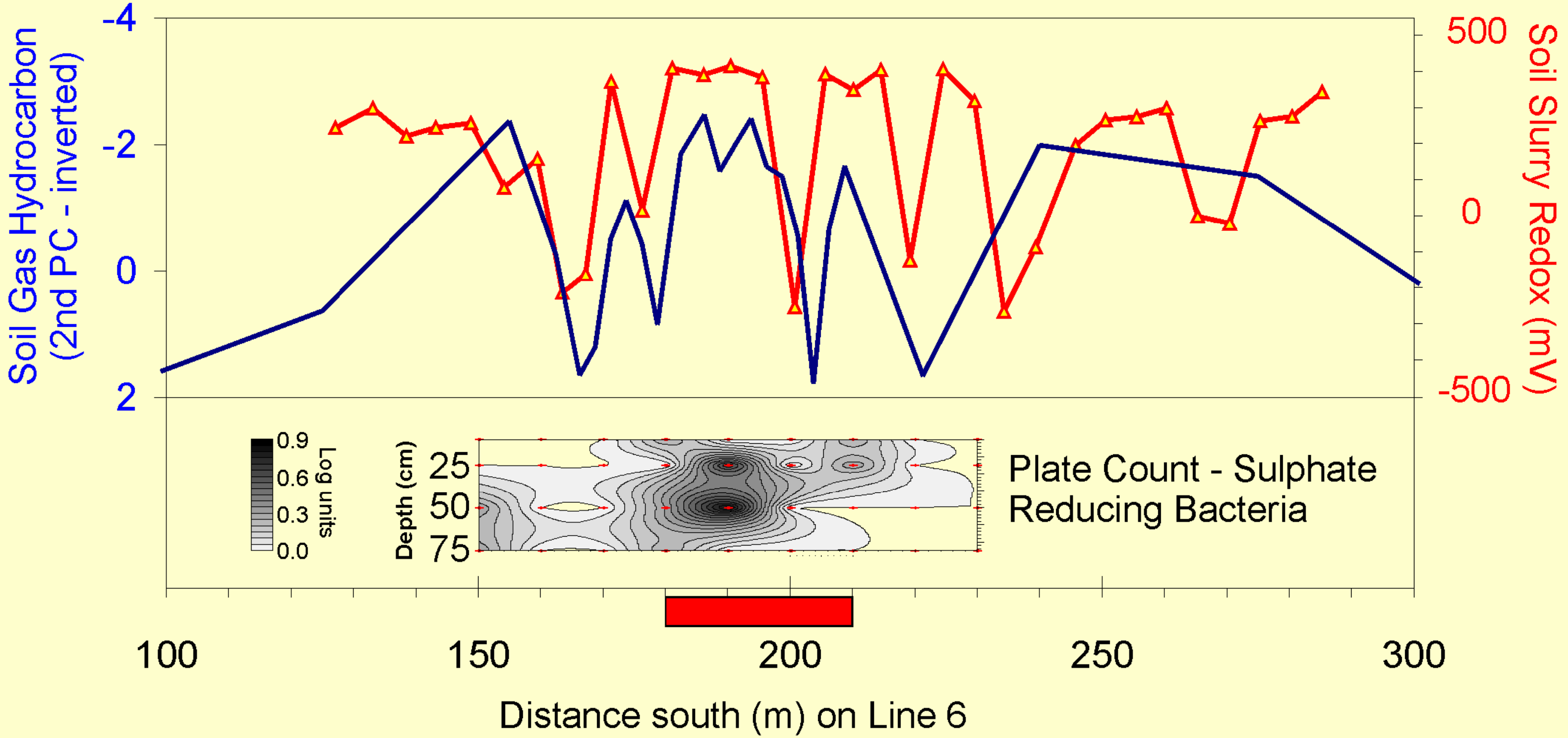


SDP, Line 6, anom



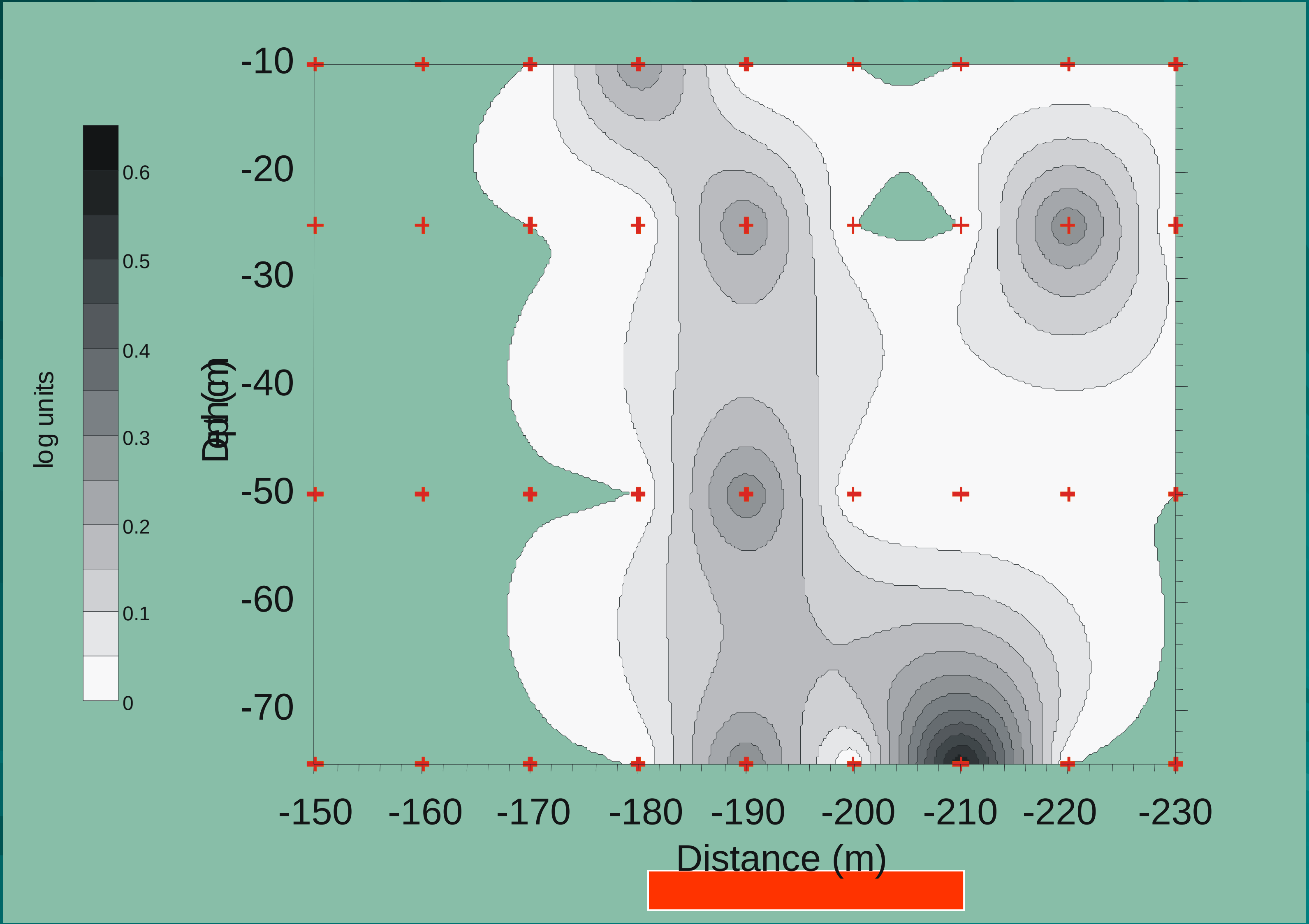


SGH & Redox



Soil Gas Hydrocarbon
(2nd PC - inverted)
-4
-2
0
2
500
0
-500
Soil Slurry Redox (mV)
0.9
0.6
0.3
0.0
Log units
Depth (cm)
25
50
75
Plate Count - Sulphate
Reducing Bacteria
100
150
200
250
300
Distance south (m) on Line 6

SRBs - Cross Lake - 14 m from line



Slide courtesy of Gordon Southam

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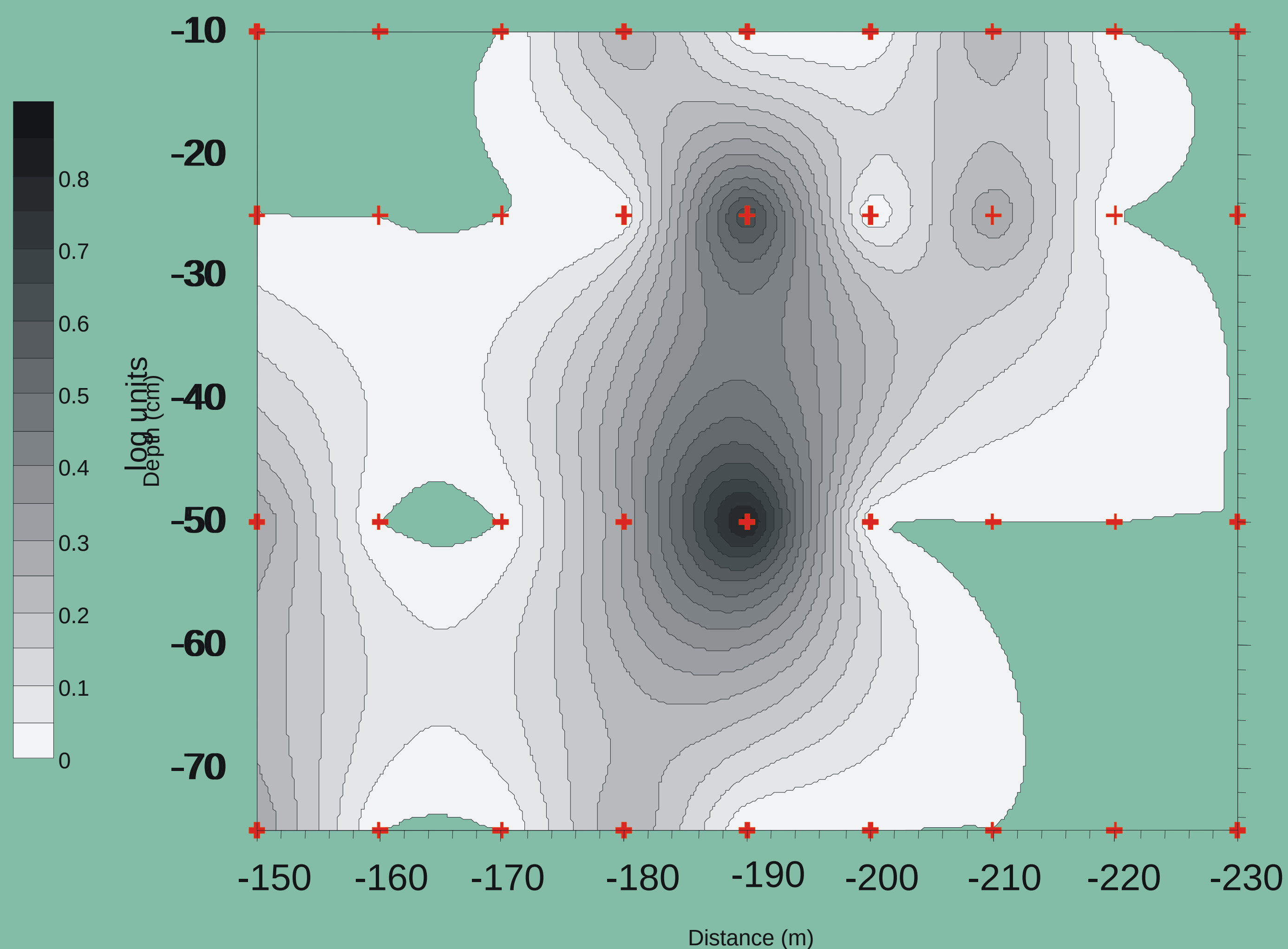
SRBs - Cross Lake - 12 m from line



Slide courtesy of Gordon Southam

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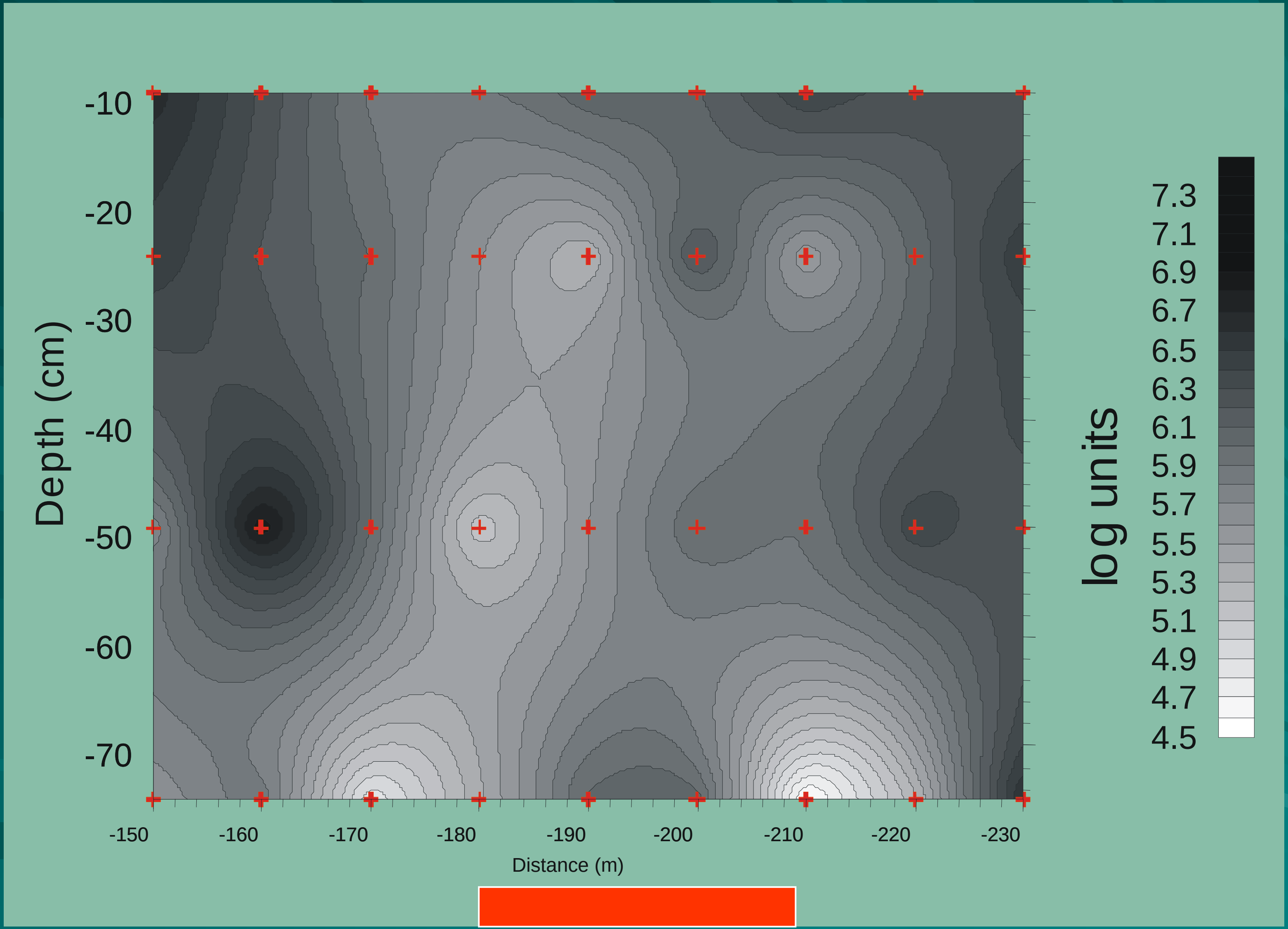
Aerobic Heterotrophs - Cross Lake - 12 m from line



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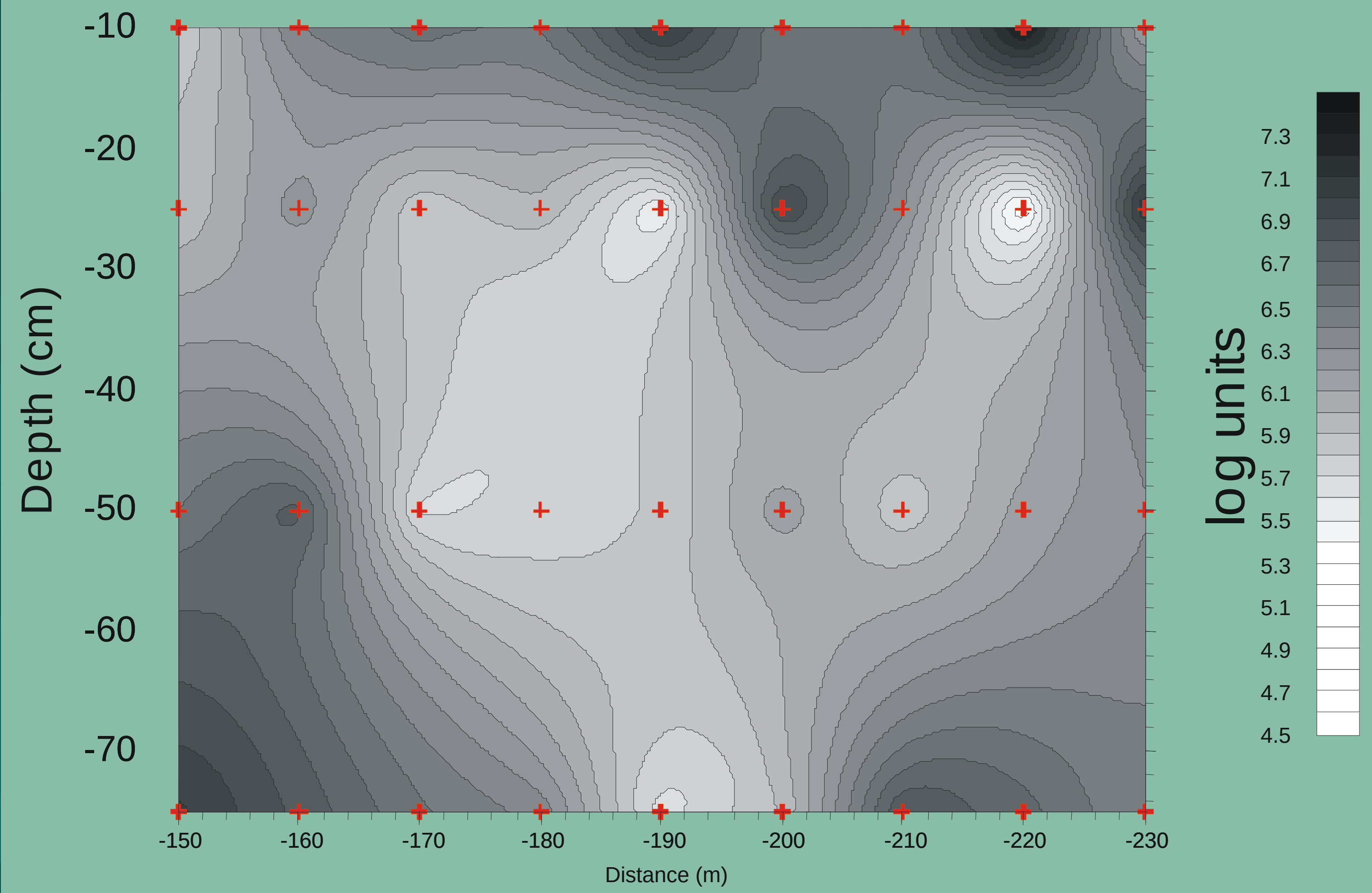
Aerobic Heterotrophs - Cross Lake - 12 m from line



Slide courtesy of Gordon Southam

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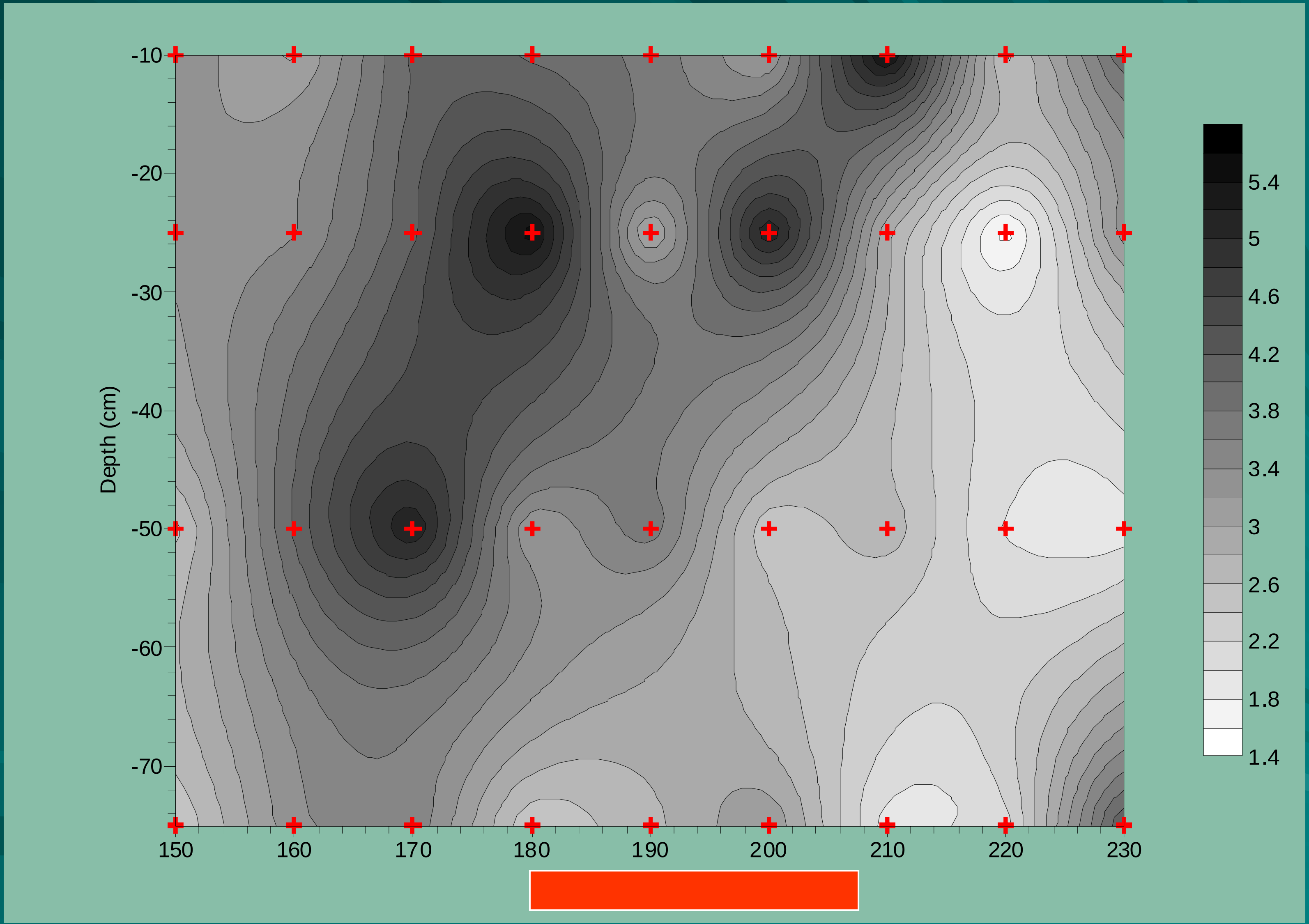
Anaerobes - Cross Lake - 12 m from line



Slide courtesy of Gordon Southam

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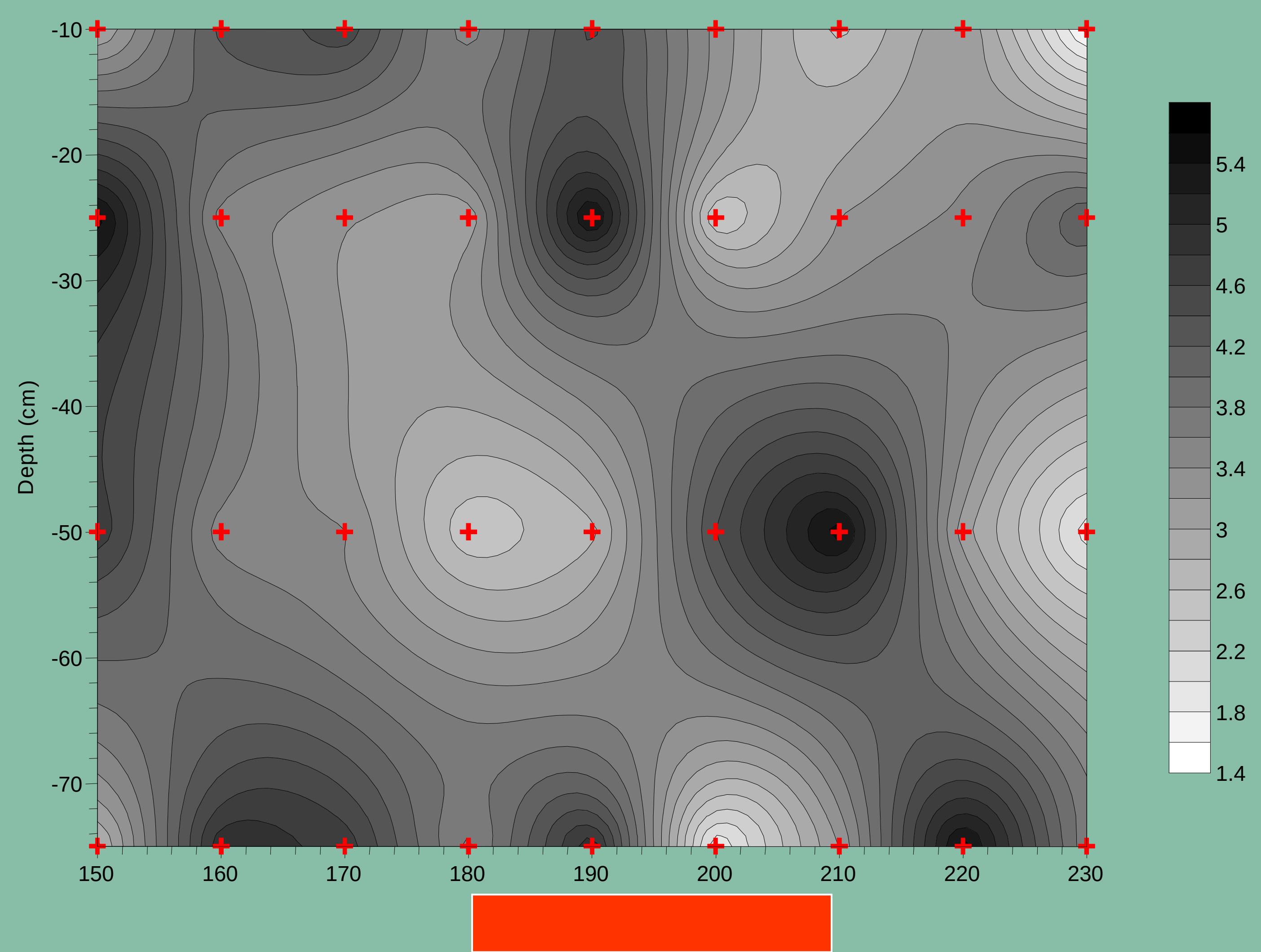
Anaerobes - Cross Lake - 14 m from line



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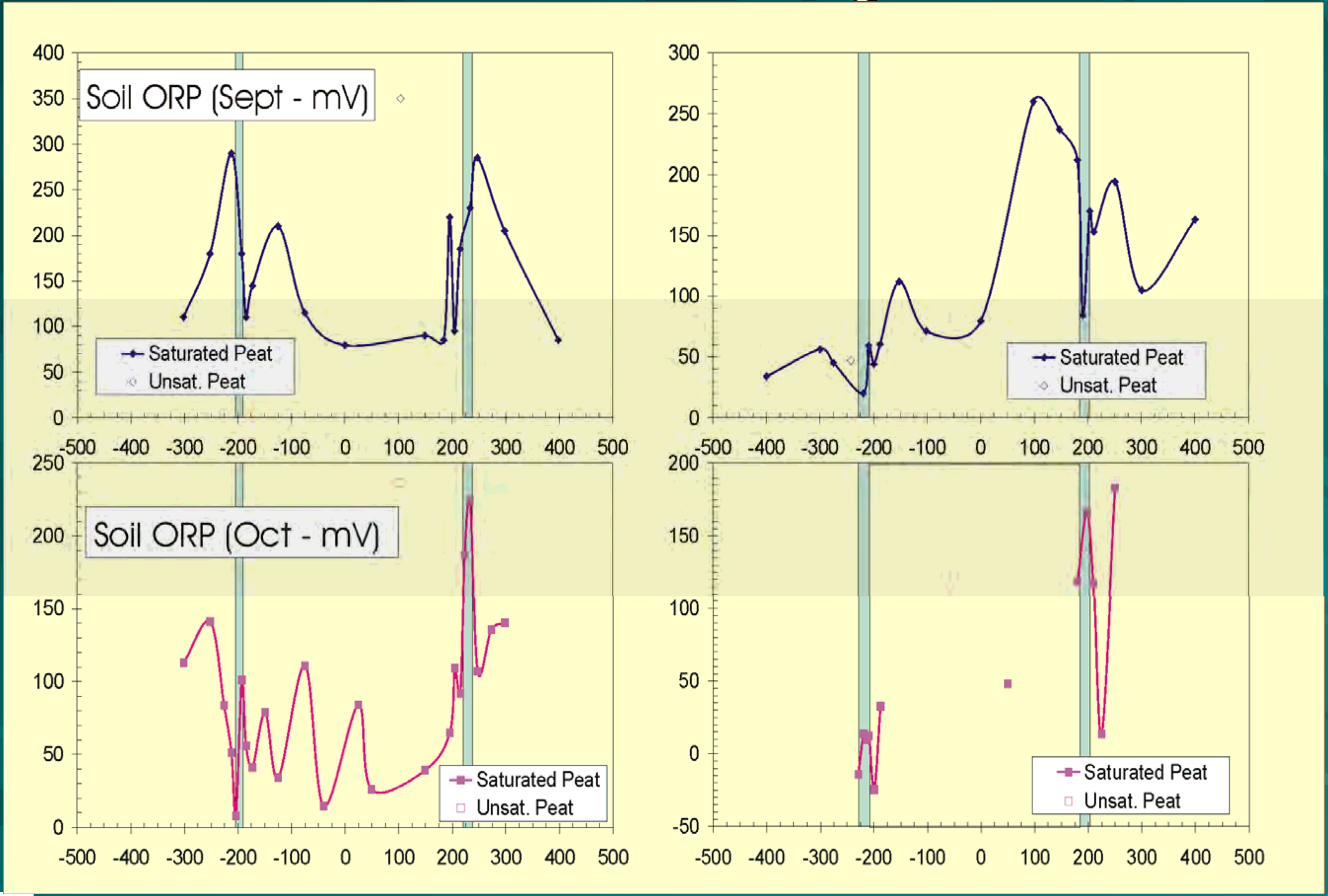
ORP at Bean Ring - 1999



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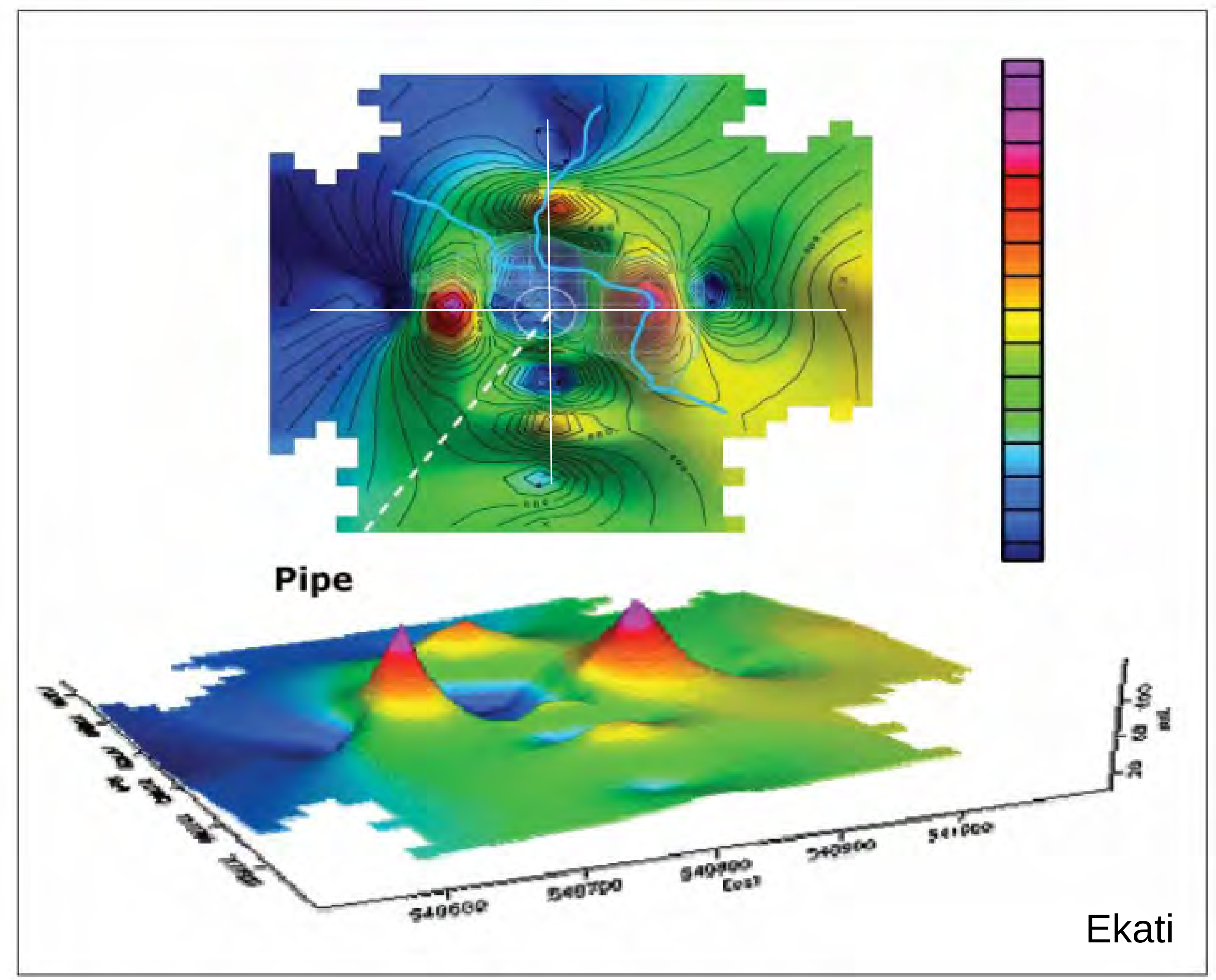
Soil Gas Hydrocarbons over Kimberlites



Source: Actlabs

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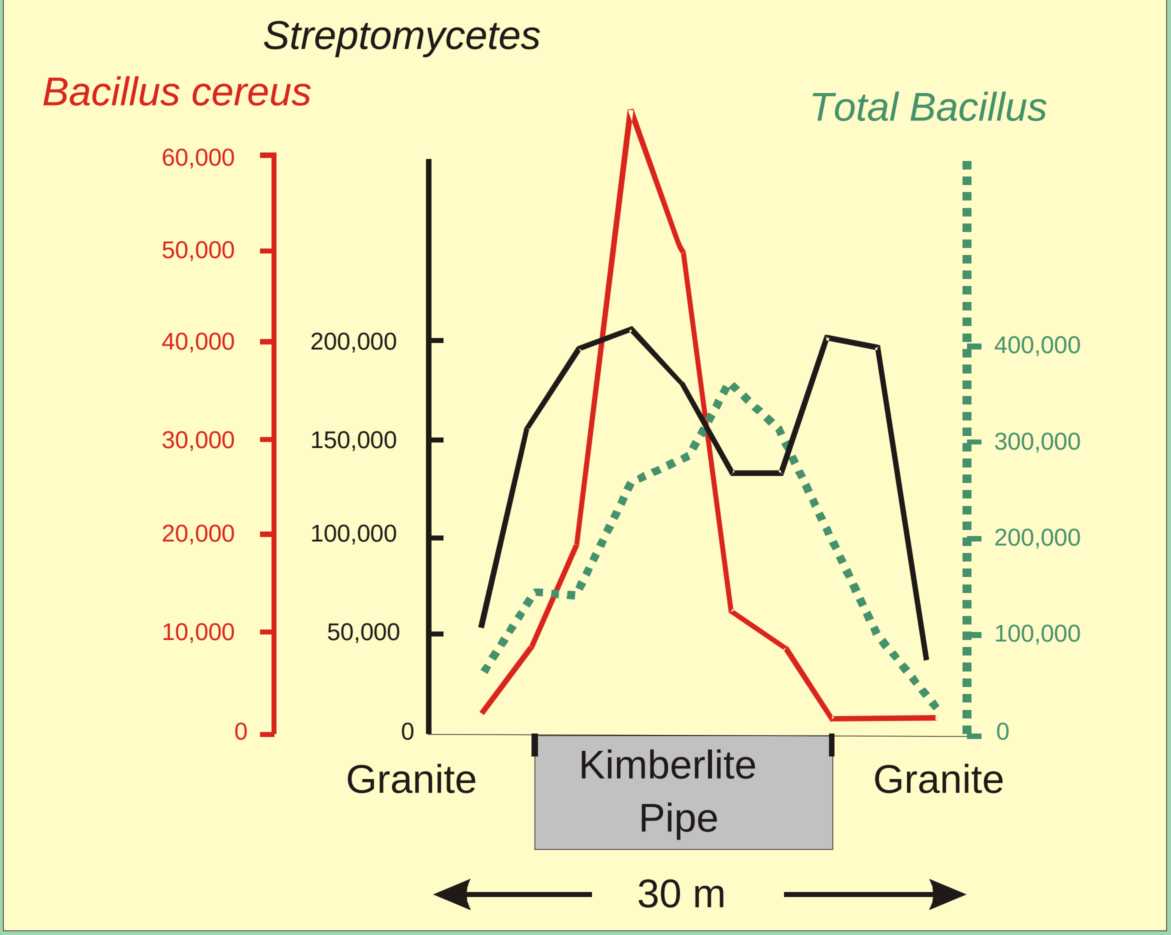
Bacterial Plate Counts

Green Mountain Kimberlite, Colorado



From Alexander, 1986

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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

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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)

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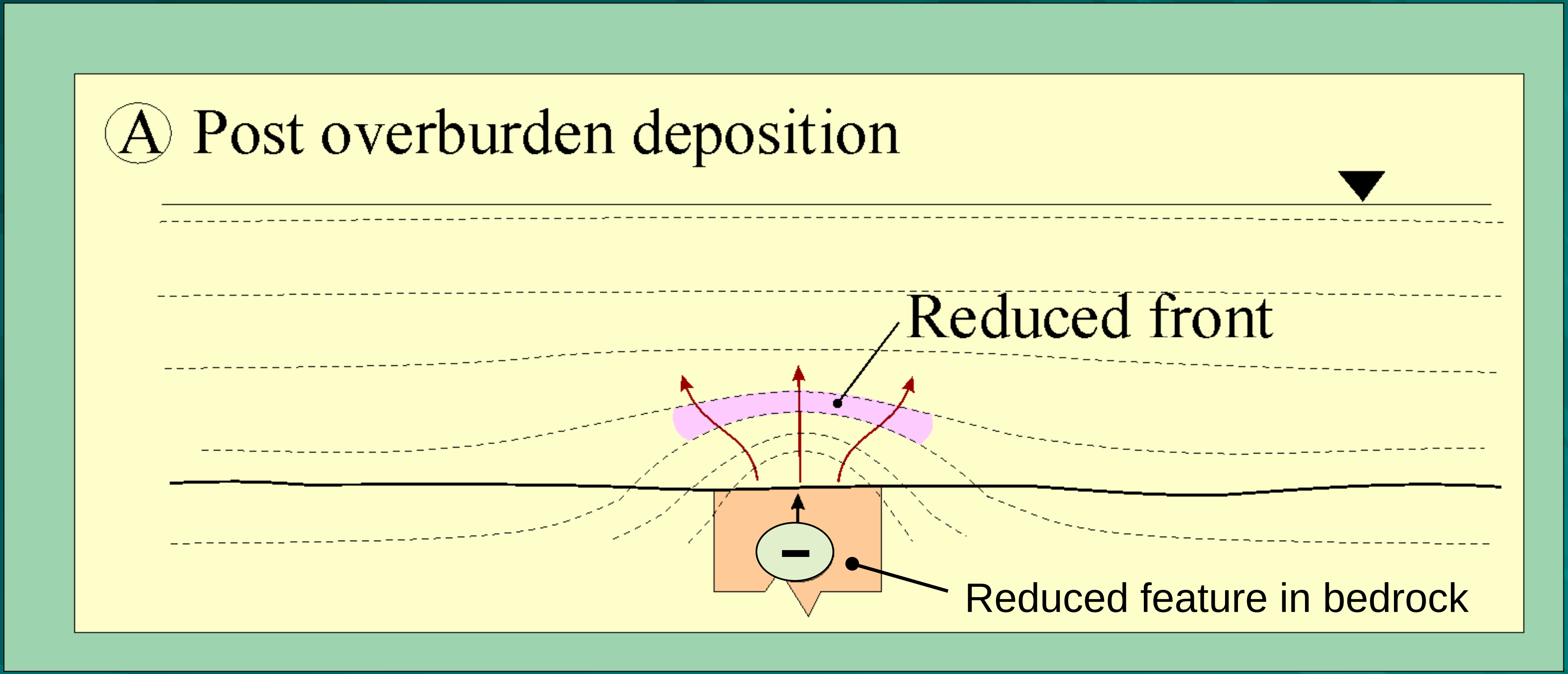
Reduced Chimney Development



Hamilton, 1998

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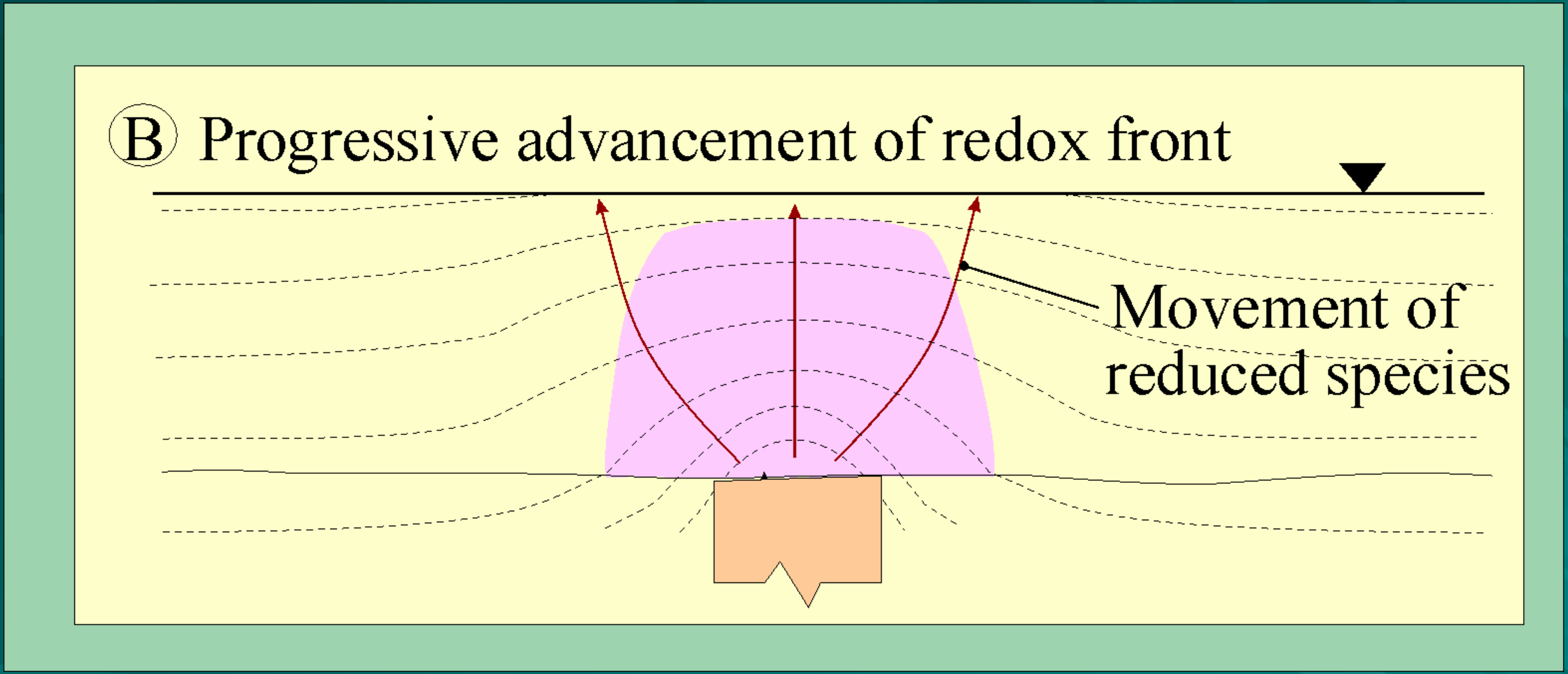
Reduced Chimney Development



Hamilton, 1998

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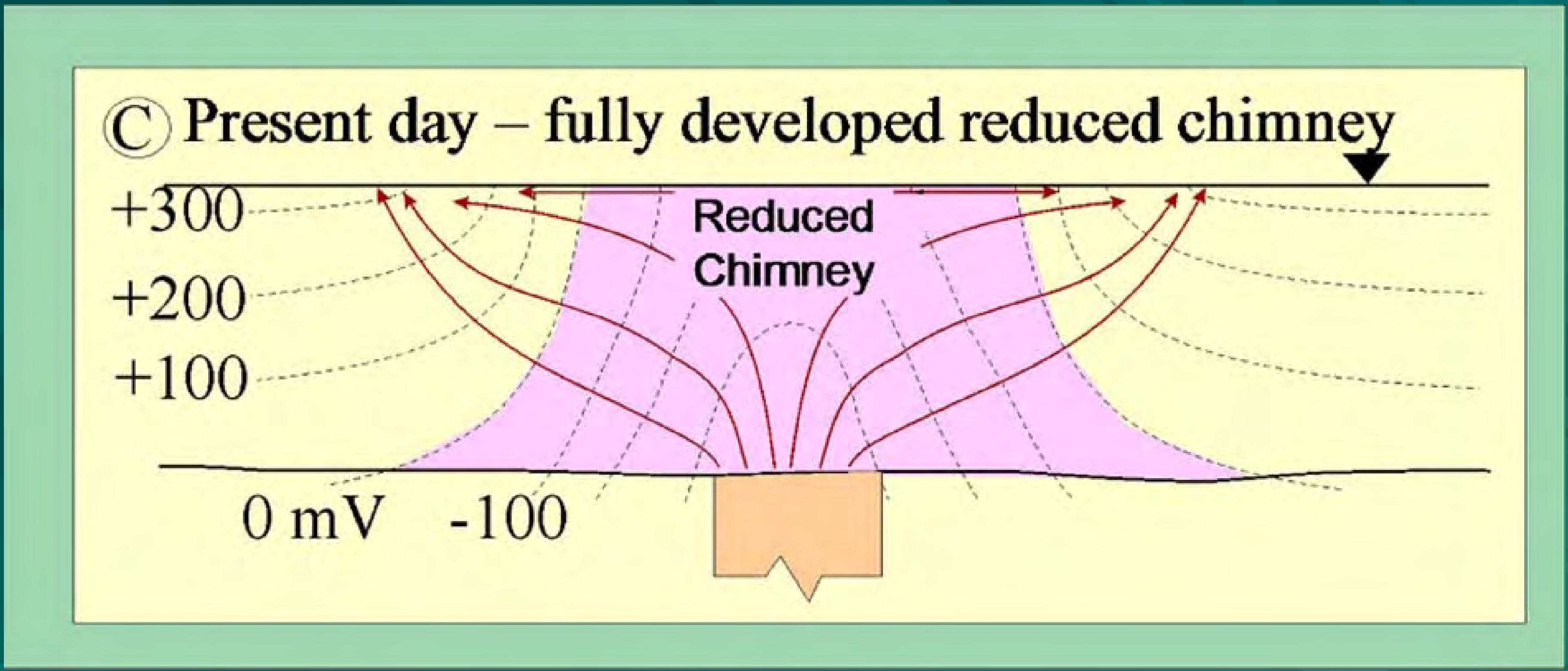
Reduced Chimney Development



Hamilton, 1998

Charge & Mass Transport

$J_j =$

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

ϕ = 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

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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

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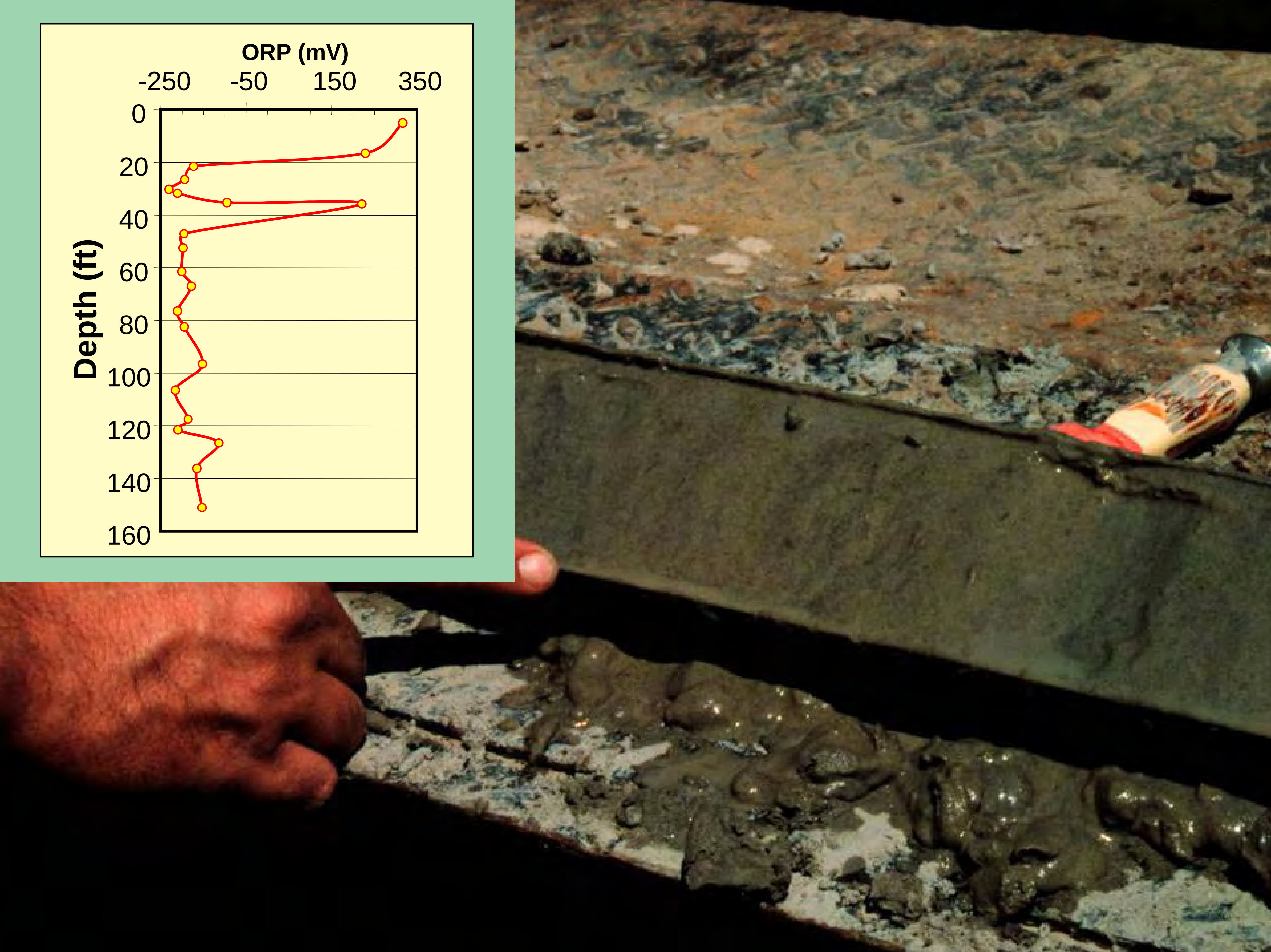
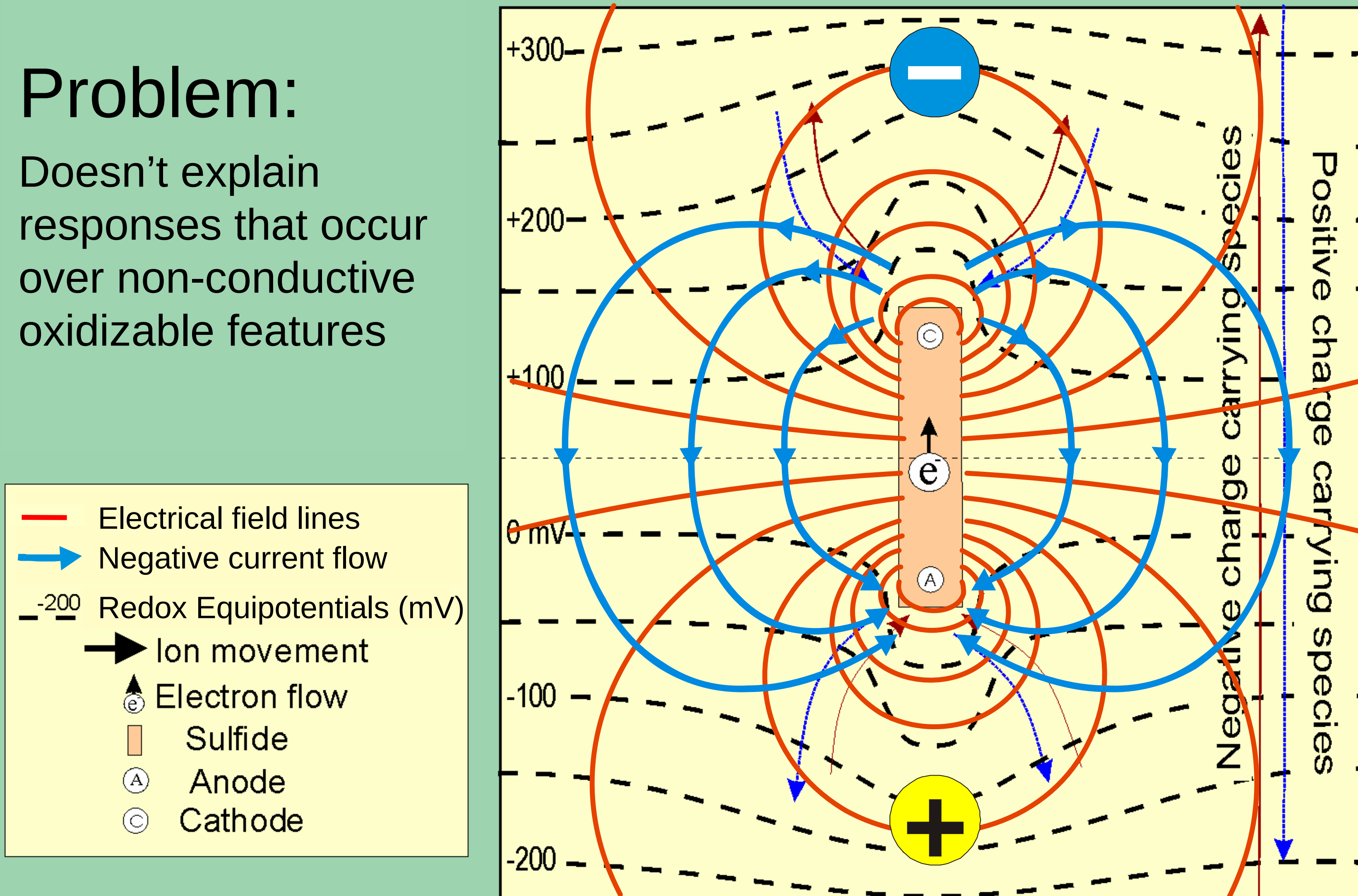

ORP (mV)
-250
-50
150
350
Depth (ft)
0
20
40
60
80
100
120
140
160

Sulphide Dipole (Hamilton, 1998 after Govett)

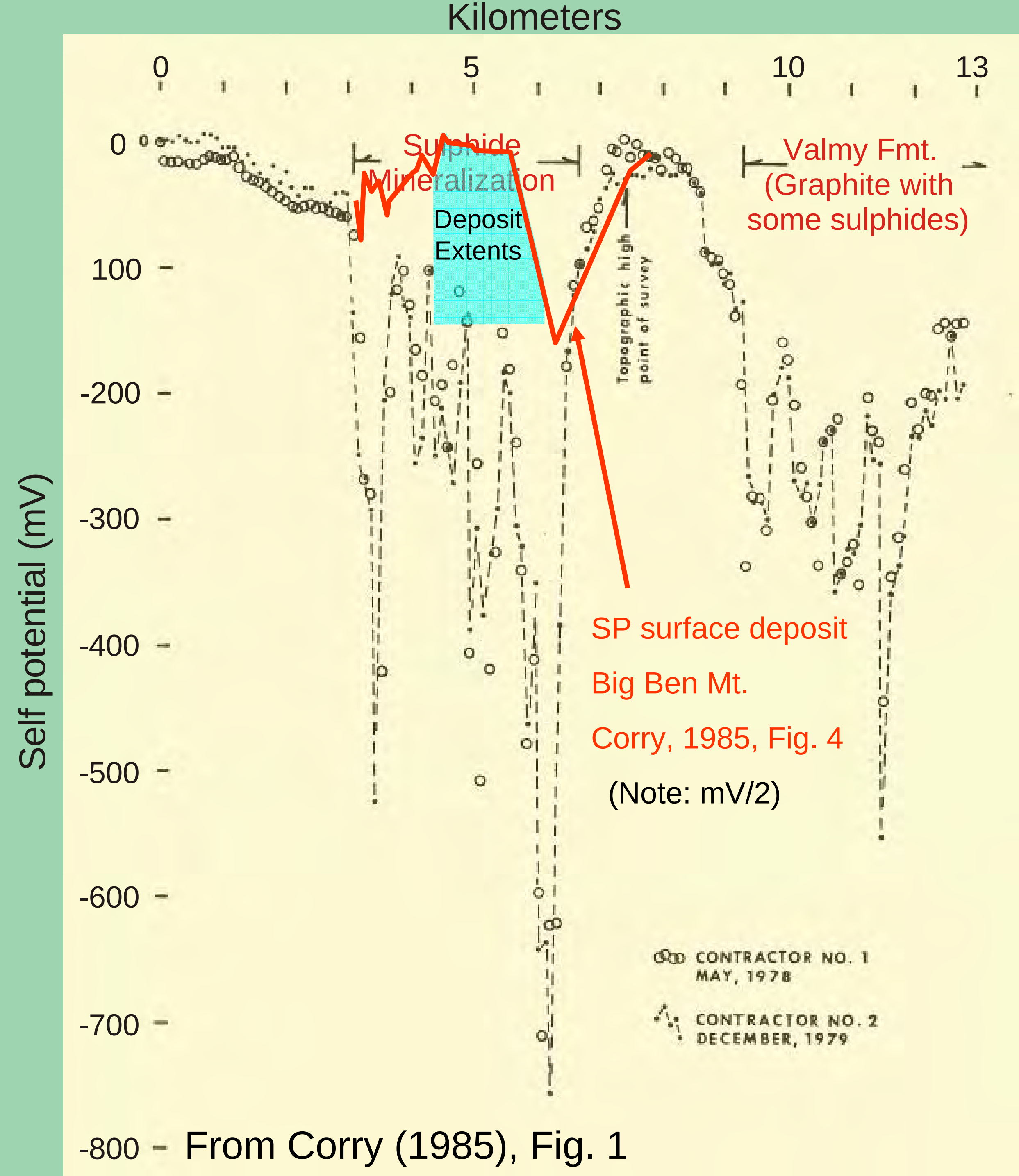
Problem:

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



SP Surveys over Porphyry Sulphides

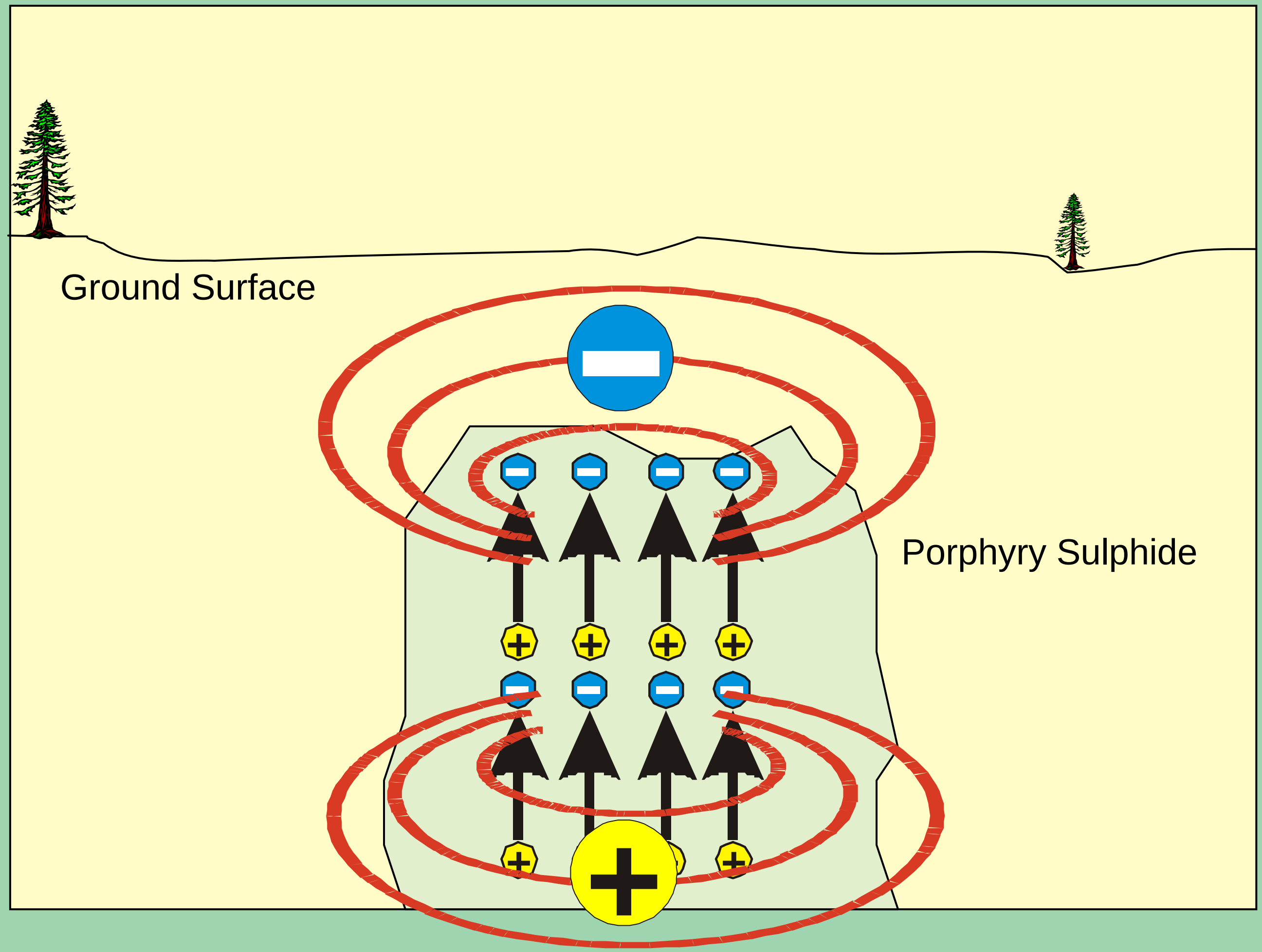
Little Cottonwood Canyon, Battle Mountain Nevada



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)

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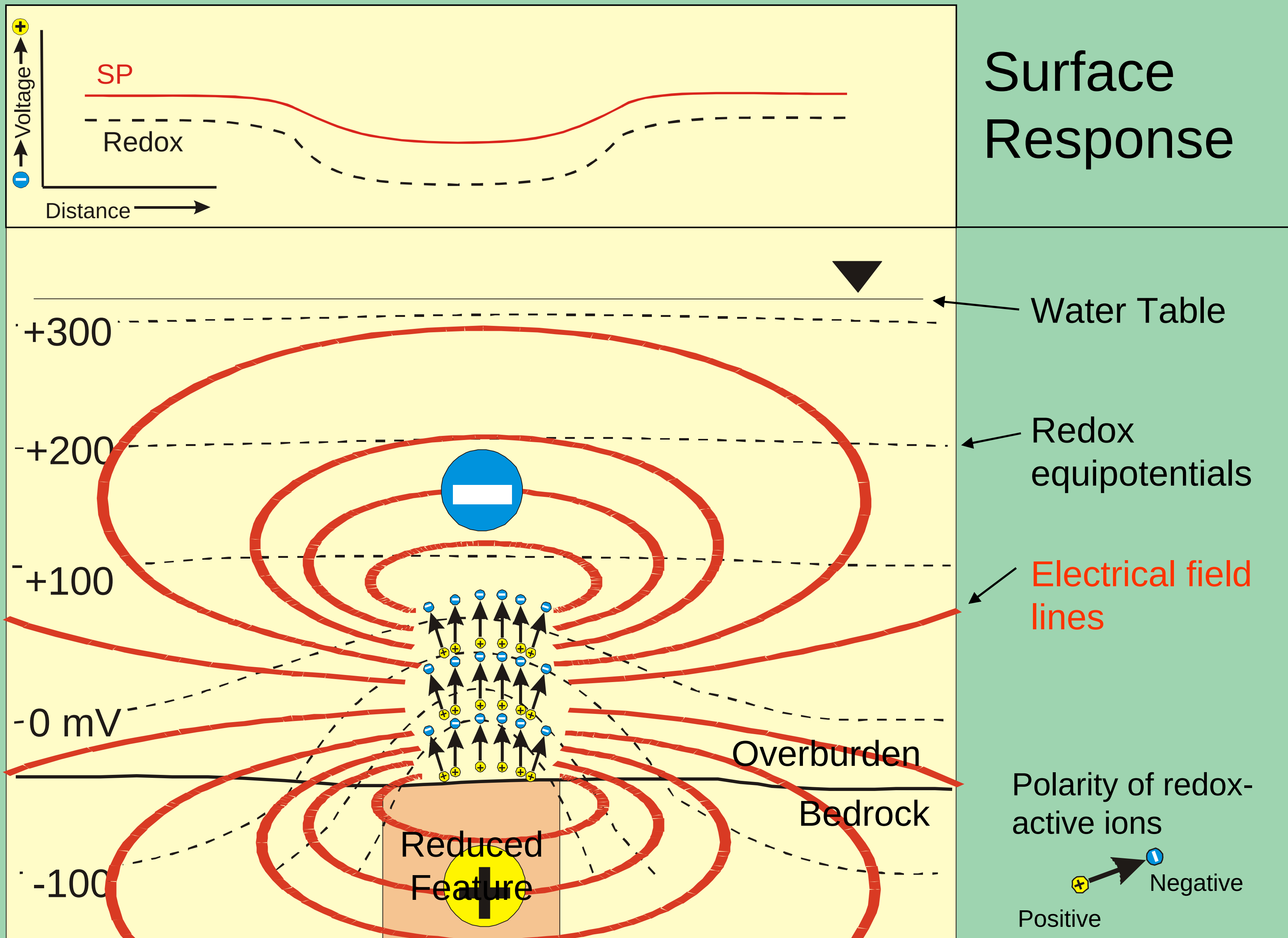
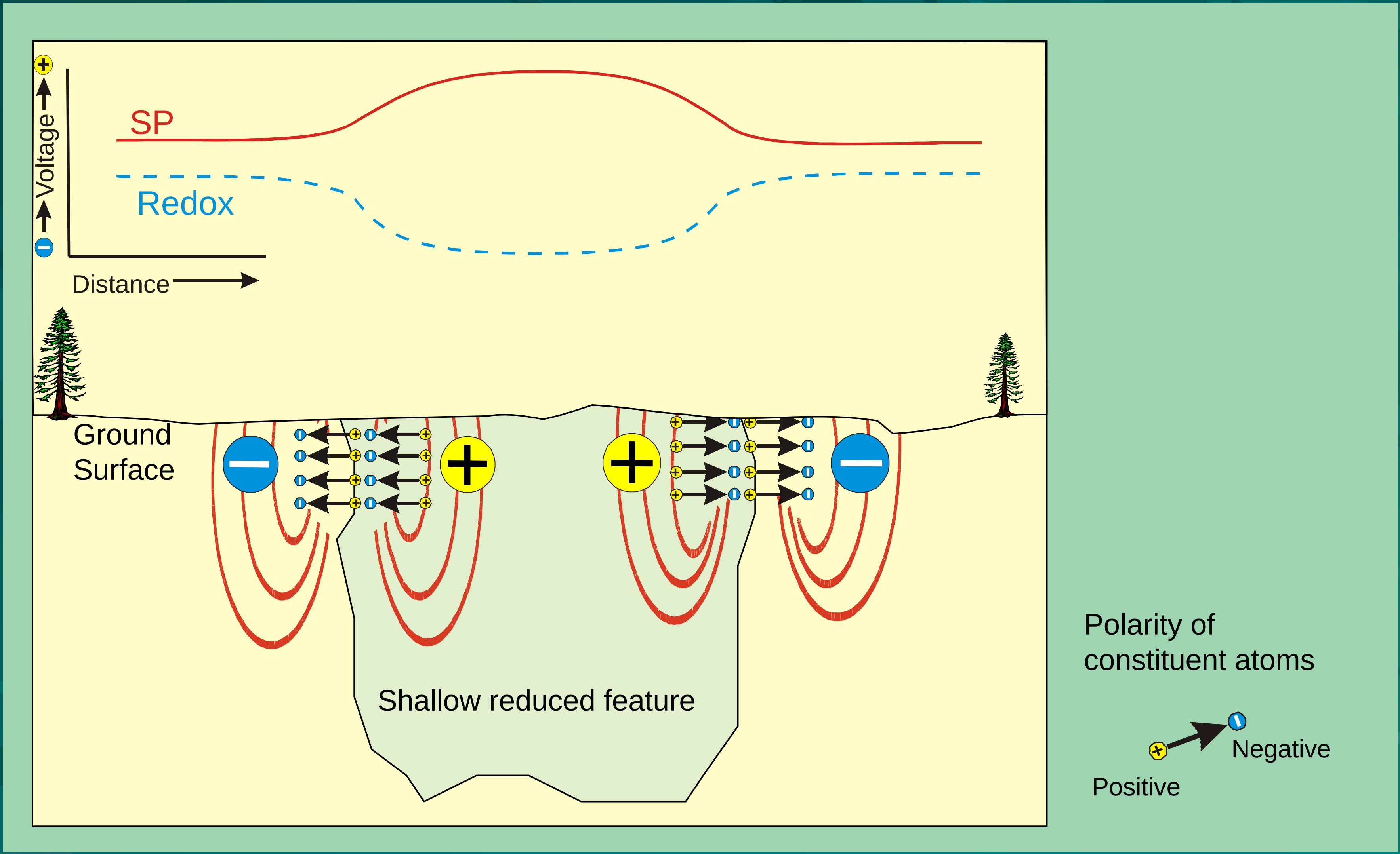
Redox-Induced Spontaneous Polarization



Spontaneous Polarization over a 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 <u>landfill leachate</u> and the containment of <u>nuclear waste</u>, 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.

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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

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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

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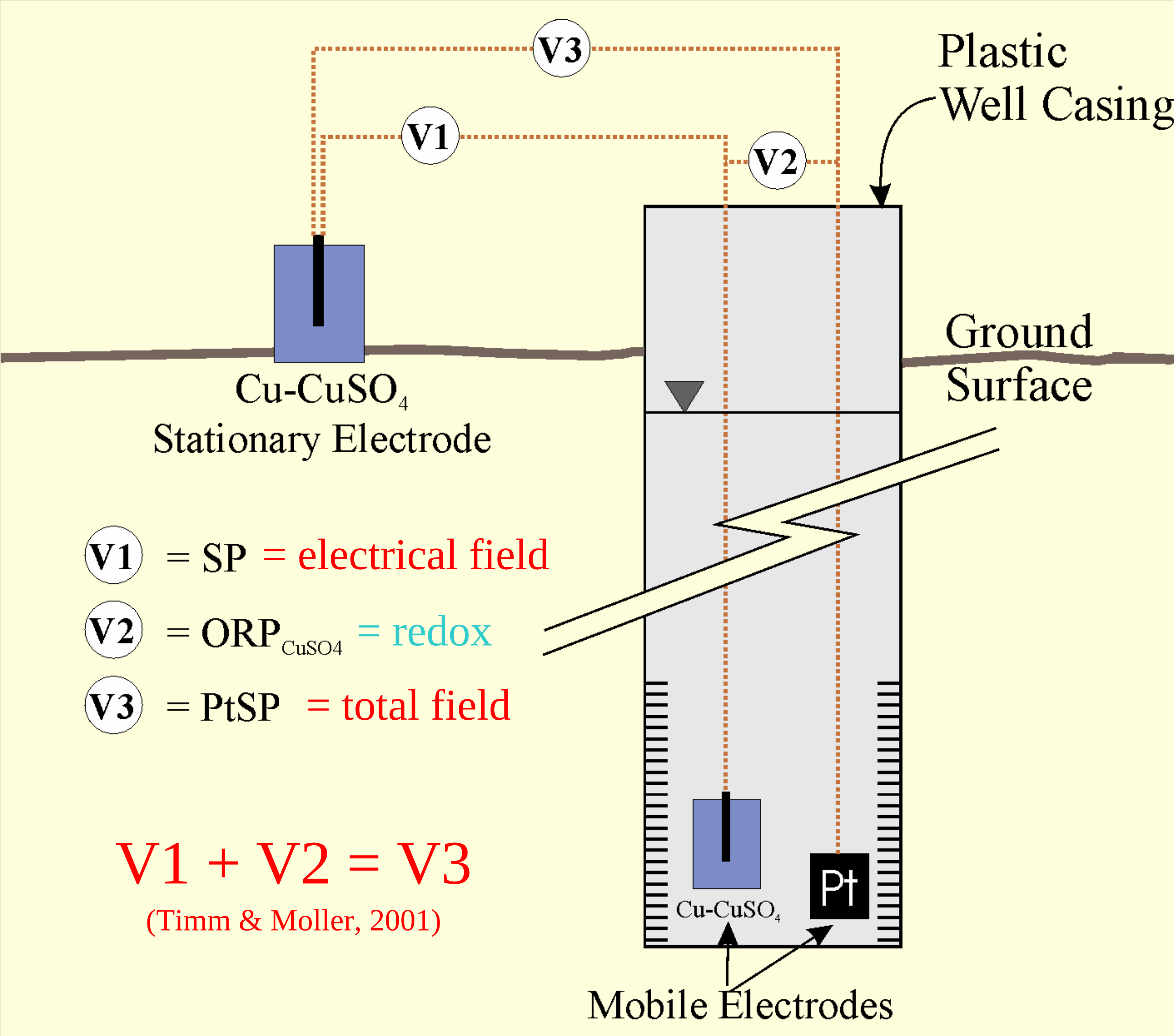
Platinum Spontaneous Potential (PtSP)



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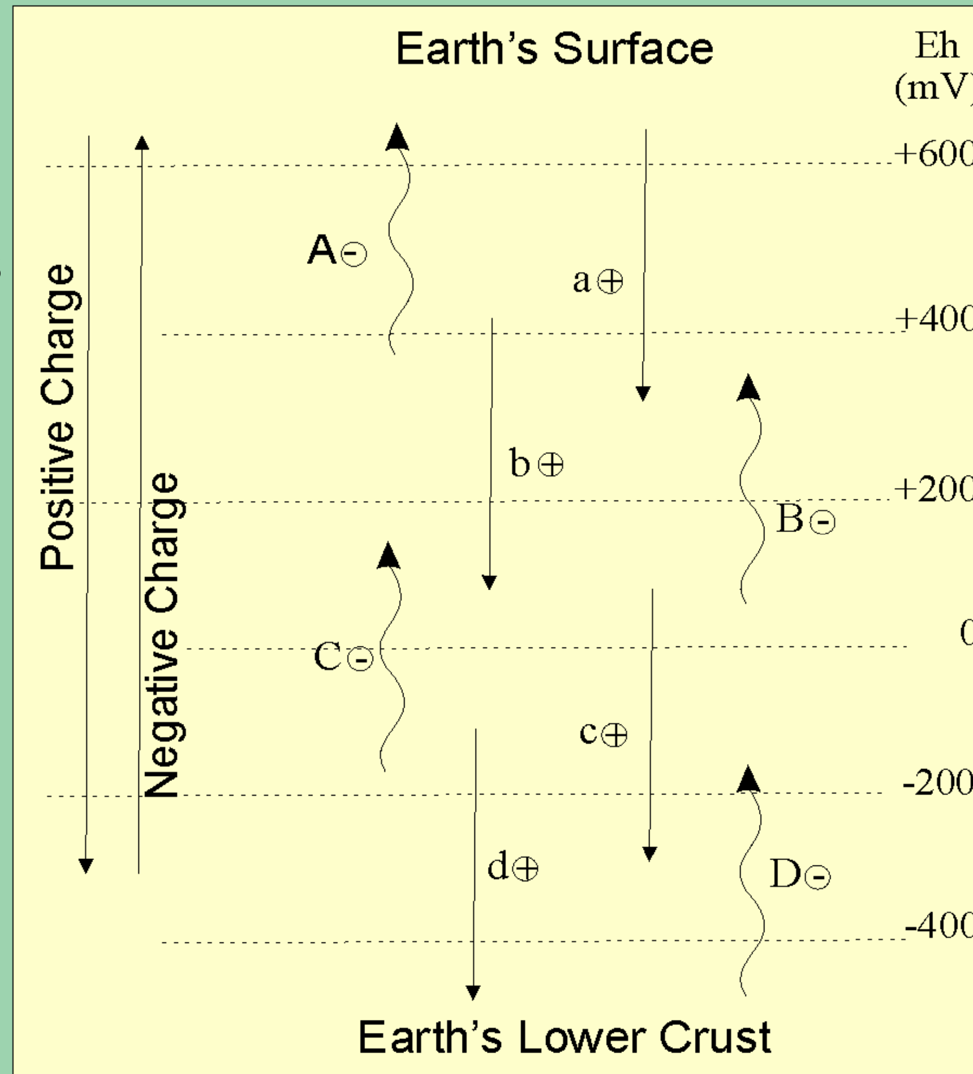
Redox Gradient-Induced Flux (Bolviken)

Problem:

Movement of charge and mass in a redox gradient is not supported by physics



-200 Equipontential lines, mV

Positive Charge Carriers

$H_{2(g)} < d\oplus < c\oplus < b\oplus < a\oplus < O_2$

Negative Charge Carriers

$H_{2(g)} < D\ominus < C\ominus < B\ominus < A\ominus < O_2$

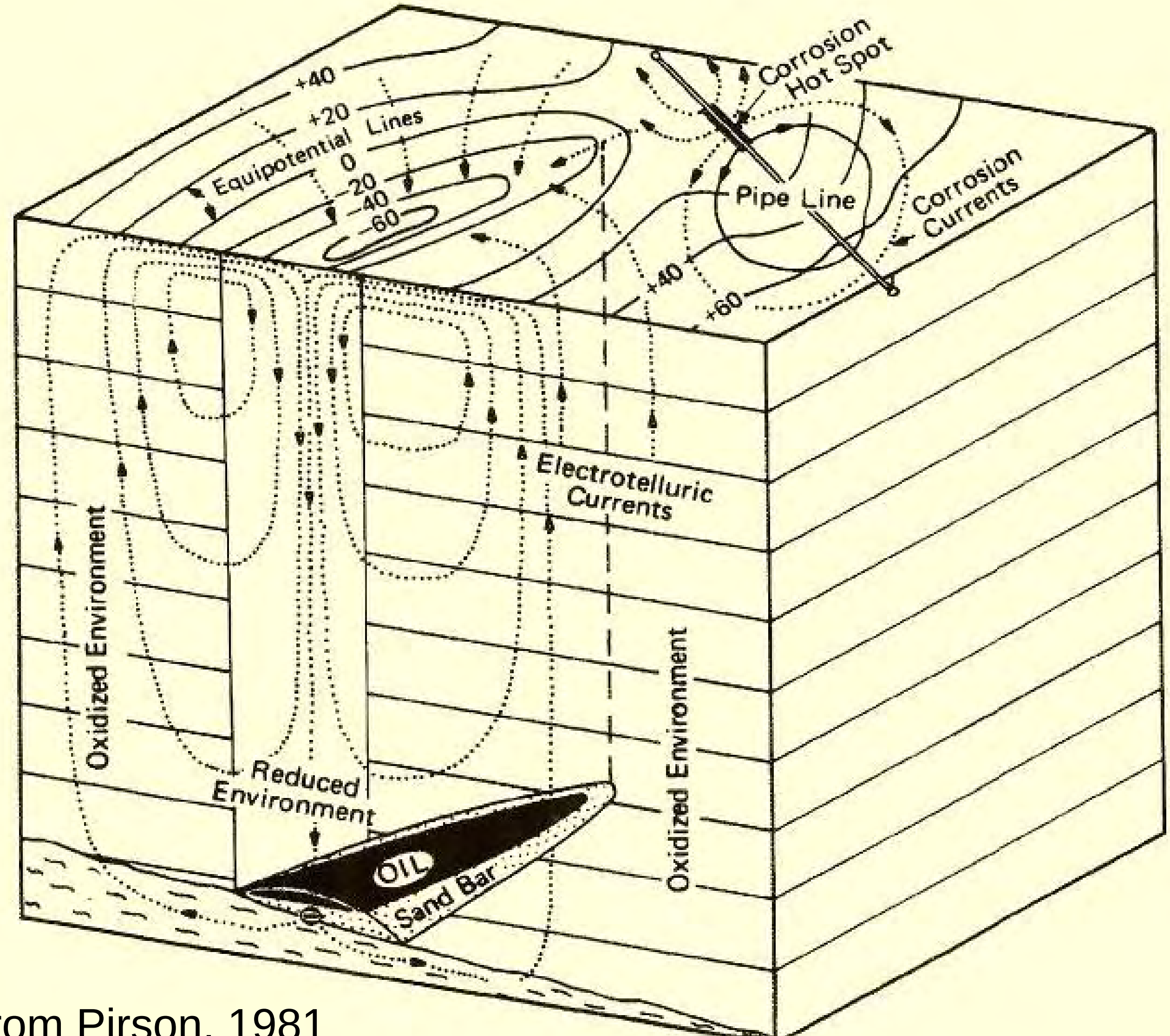
Increasing Eh →

Bolviken & Logn, 1975

Theory of Electrotelleric Currents Over an Oil Reservoir

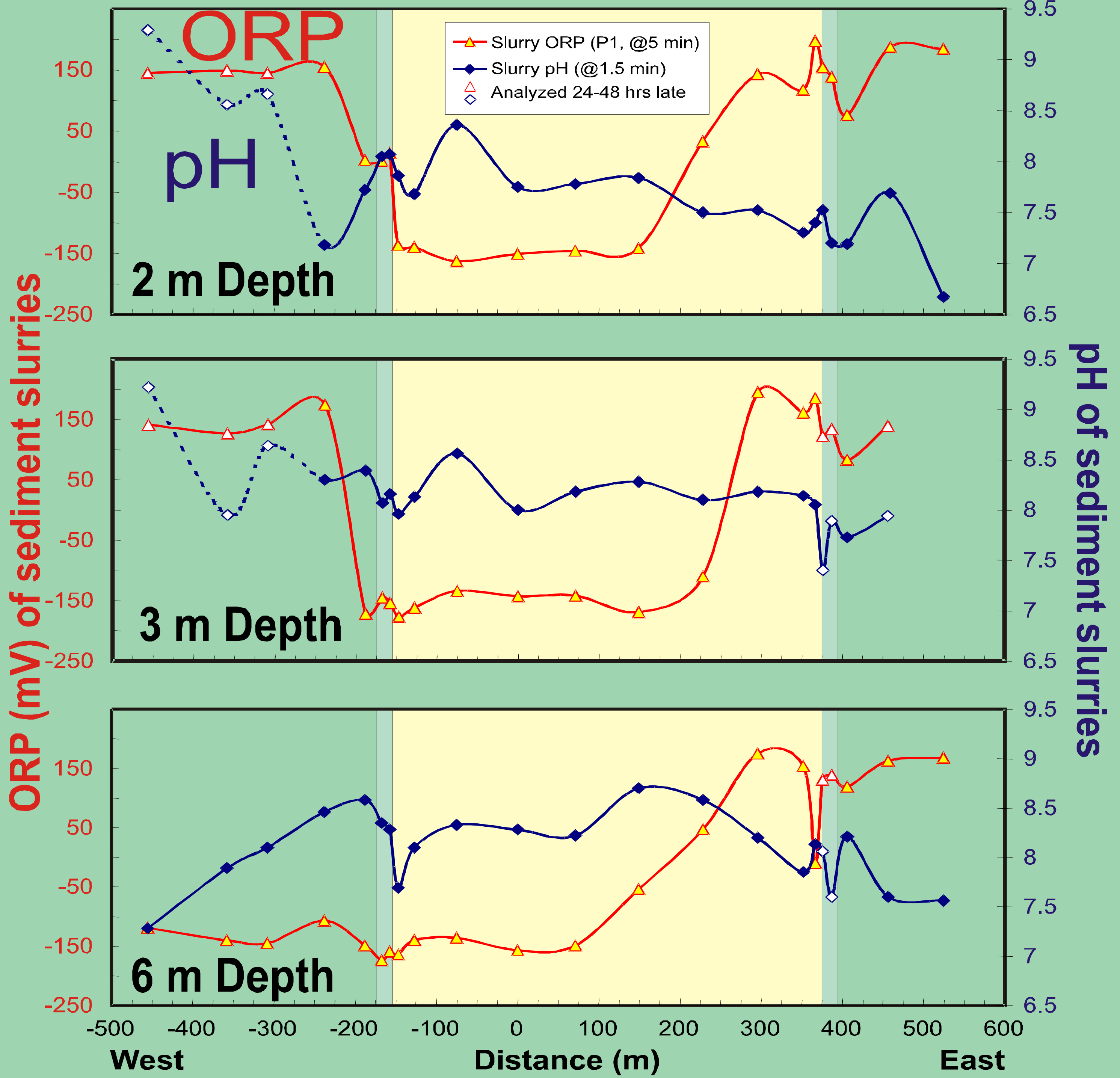
Problem:

- 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)

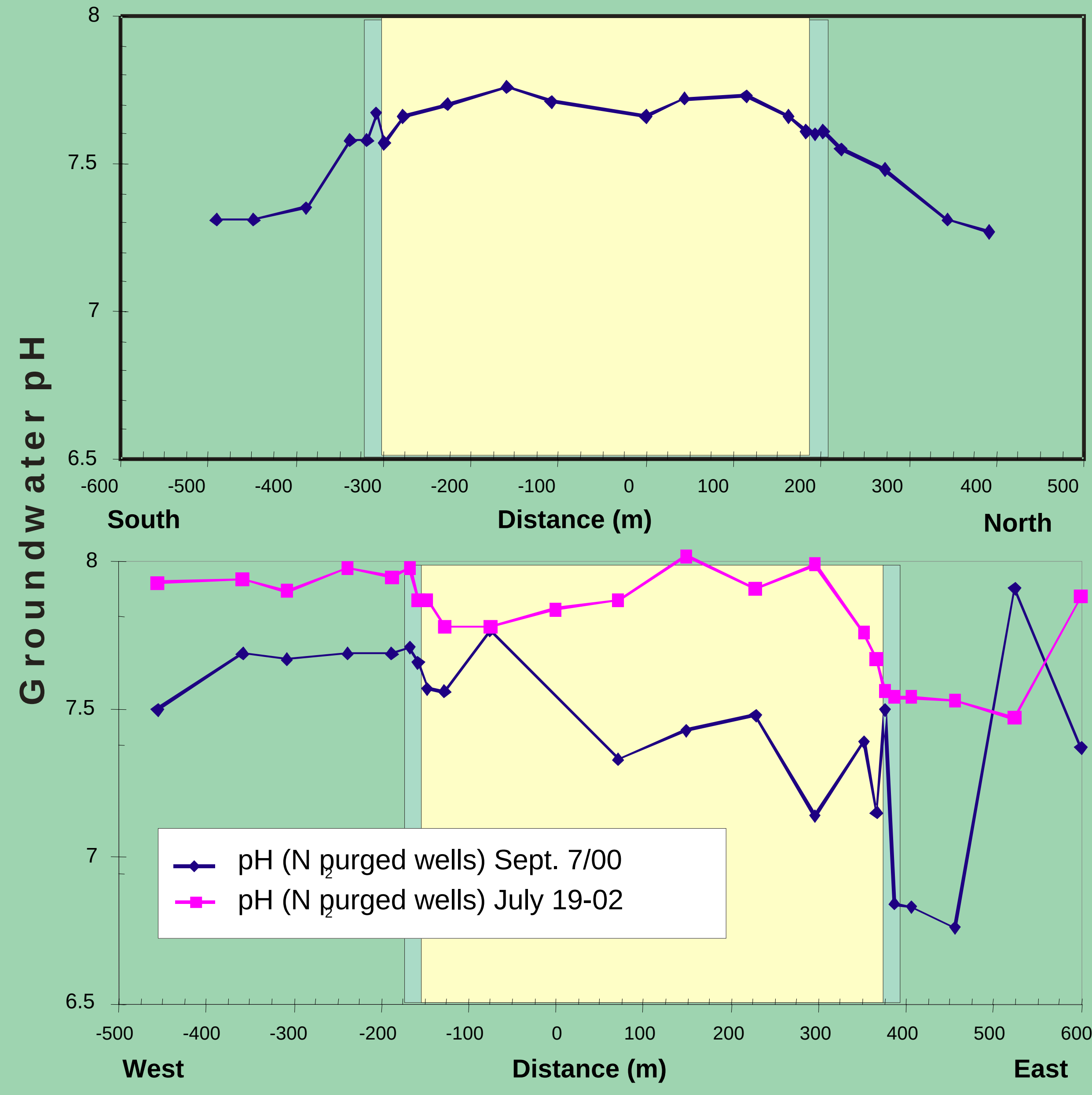


From Pirson, 1981

ORP & pH of Sediments



pH of Groundwater



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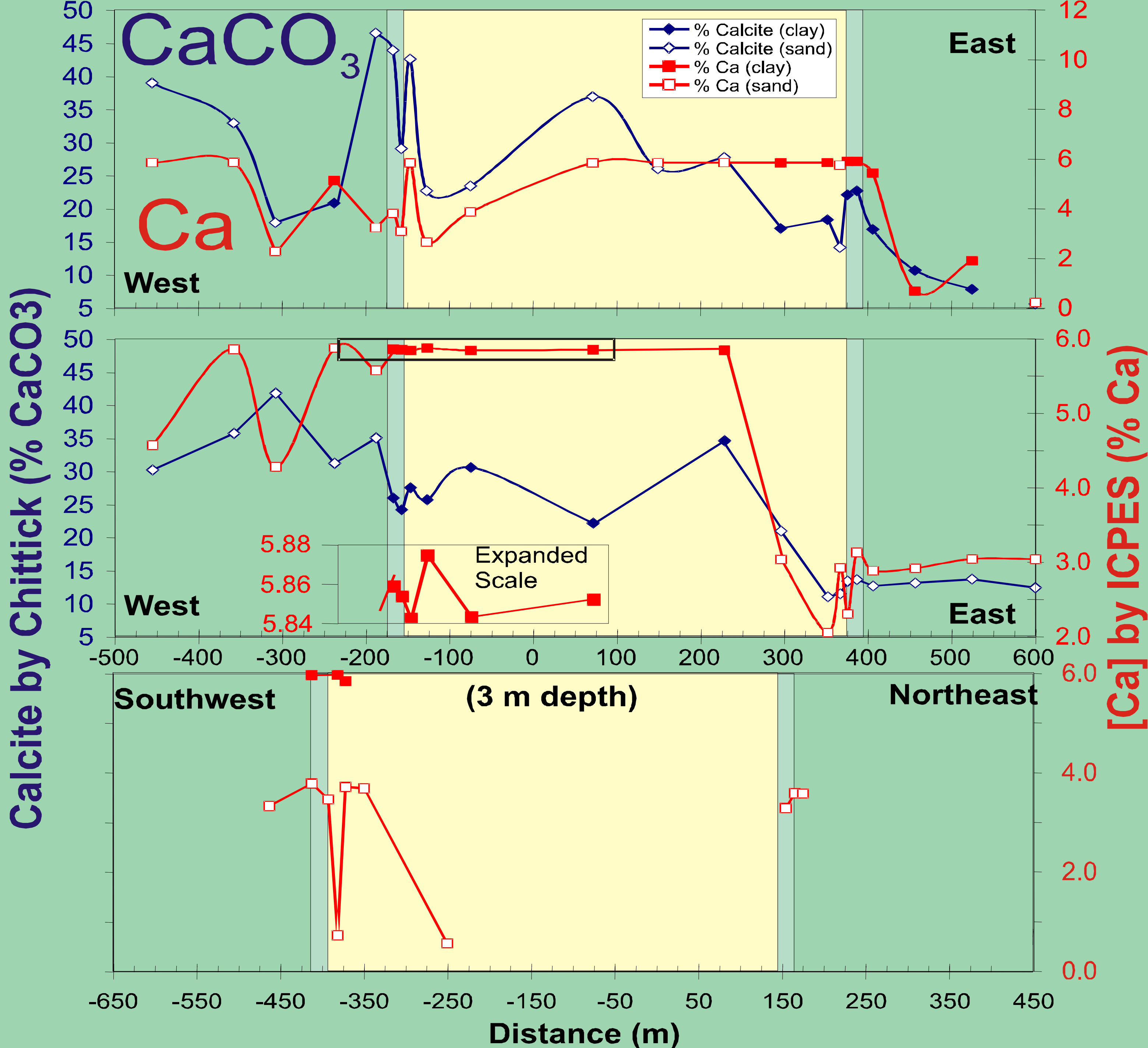
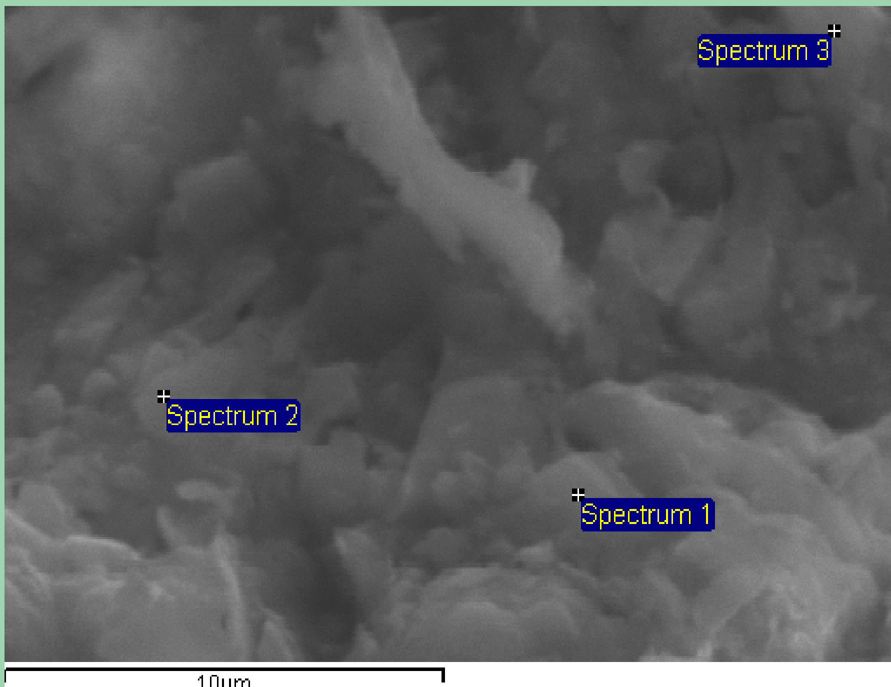
Carbonate in Sediment

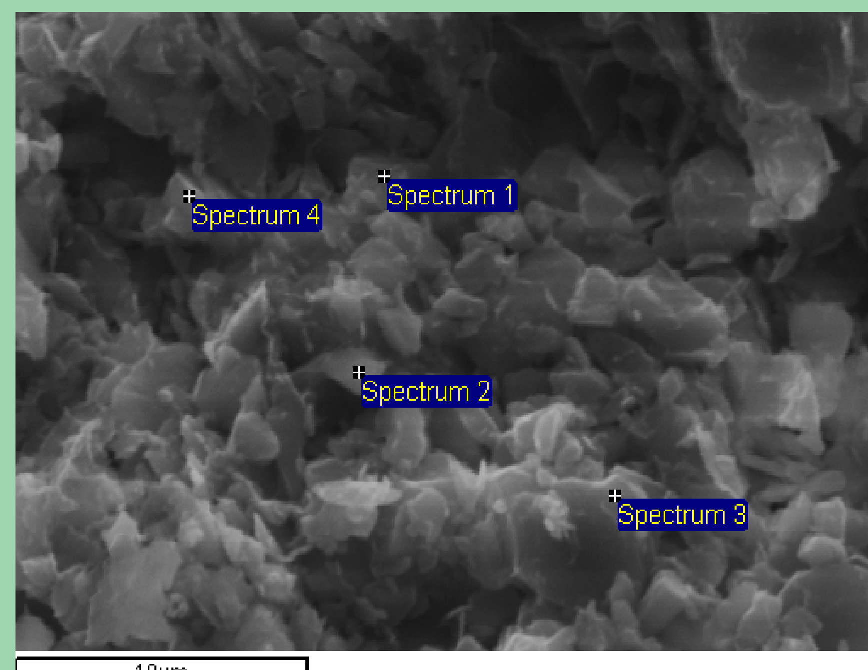


Carbonate Mobility (Cheecka Ring)



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 SO_4^{2-} and drop in H_2S & $O_{2(g)}$
    - 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 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

THE ASSOCIATION OF APPLIED GEOCHEMISTS 1970

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