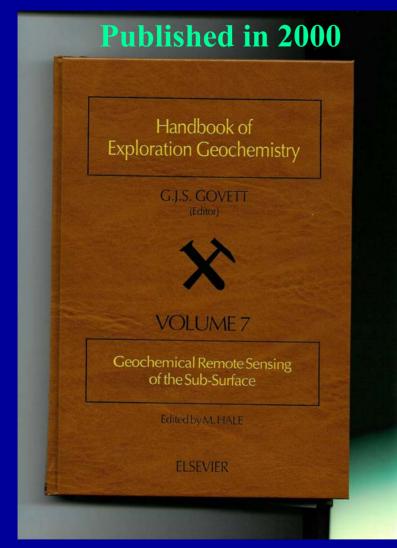
Punctuated equilibria in the 30-year evolution of geochemical exploration under cover

Gwendy E.M. Hall Geological Survey of Canada, Ottawa





Authors include Hale, Hinkle, Lovell Butt, Gole, Dyck, Carr, Jonasson, Hamilton, Putikov and various Chinese scientists expert in gas and electrogeochemical methods.

GEEAA, 2004, Part 1 Cameron et al. "Finding deeply buried deposits..."

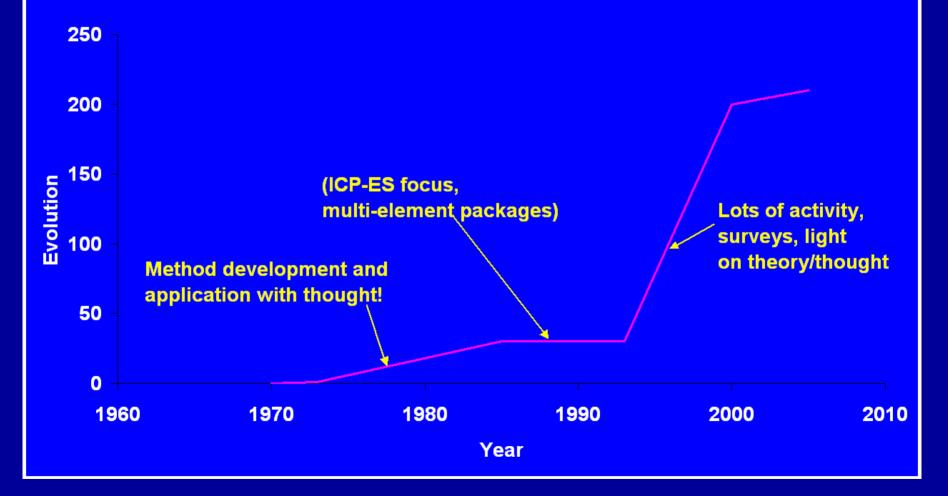


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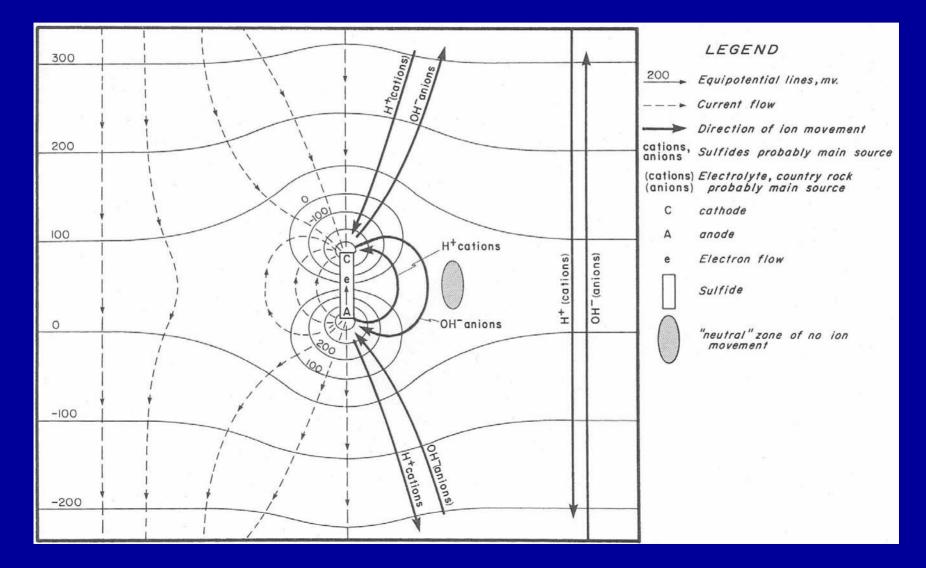




Bradshaw et al., 1974-5, JGE *Conceptual Models in Exploration Geochemistry*

- Models of geochemical anomalies in different types of terrain. Focuses on 'conventional' migration mechanisms from a deposit: mechanical (HClO₄) and hydromorphic dispersion (EDTA);
- Advocates use of both weak and strong attacks on soils/sediments to understand the anomaly, as well as sampling at different depths;
- *"Overburden sampling indicates that 5-10 ft of varved clay would normally serve to inhibit surface soil response"*

Electrochemical models in the '70s: Govett et al. and Bolviken & Logn



Gerry Govett et al. in the 1970s

Paper, presented in a 1972 IGES, demonstrated a surface response (B-hor) in the sulphide's elements and in conductivity through glacial overburden over Ni-Cu-Co min. in NB and in post-min. cover over pyritic deposits in Cyprus and in lab experiments:

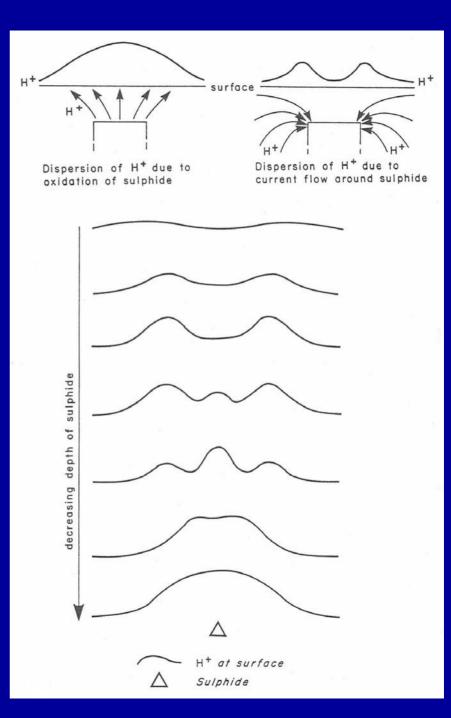
Accented that differences in electrode potential of different sulphides lead to different dissolution rates;

Electrochemical processes may control amount and kinds of ions released from a sulphide and play a major role in their dispersion;

Suggested <u>different extraction techniques</u> may highlight the small differences in [element] in soils.

From Govett in '76

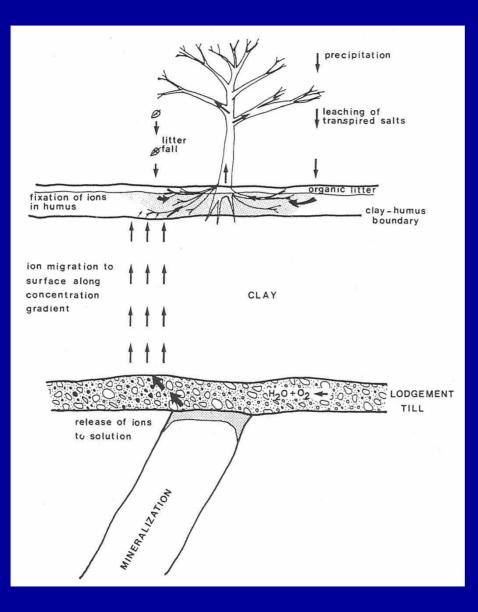
Shape of anomaly (apical vs rabbit-ears) was dictated by the distance to the deposit: apical from chemical dispersion of H⁺ and rabbit-ears from electrochemical dispersion from depth



Gerry Govett et al. in the 1970s

- It is the <u>shape</u> rather than the magnitude of the response that's important.
- Sampling interval of 10-25' is minimum.
- <u>H+ and conductivity</u> are excellent indicators and should be measured on all samples.
- A-horizon slightly superior to B-horizon.
- Water-soluble Zn, Cu etc showed the same shaped response as HNO₃-soluble, just lower amounts.

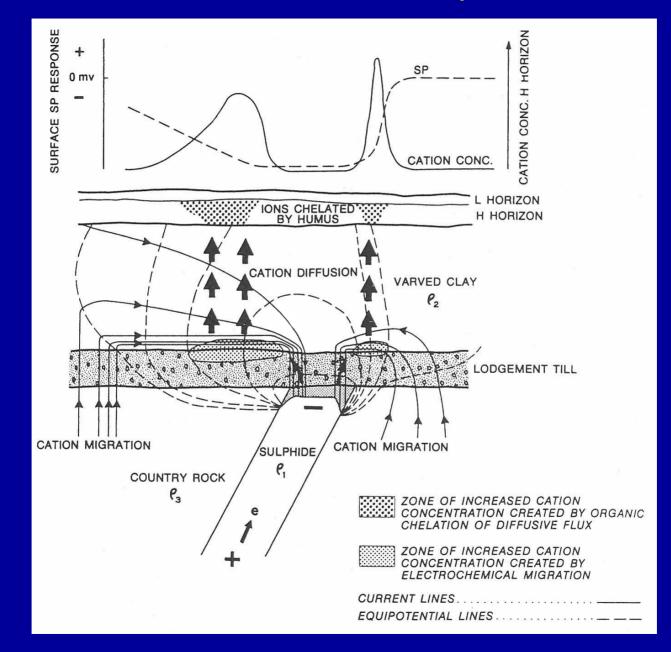
Barry Smee's model in 1979



Diffusion through 5 m of clay would take ~250 y for H+ and ~5000 y for ¹/₂ Zn²⁺

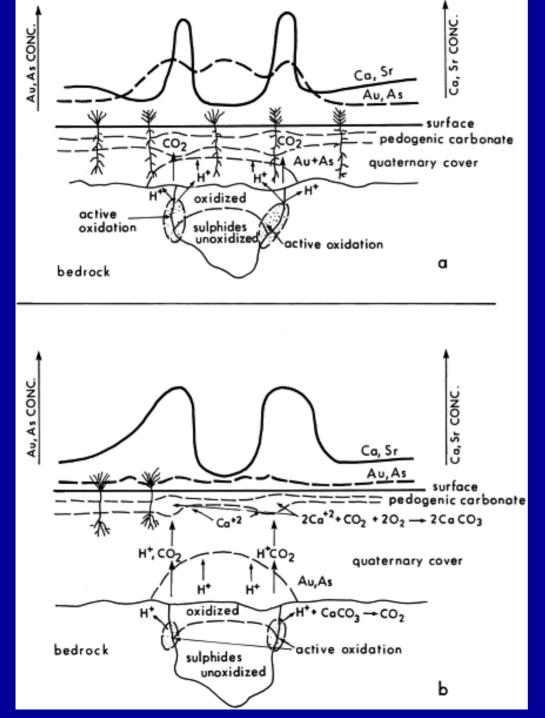
Provides access
 to O₂-rich GW
 to promote
 dissolution of
 sulphide

Smee and Govett in the early-mid 1980s



Smee and Govett in the early-mid 1980s

- Smee showed in lab experiments, by doping with ⁶⁵Zn, rabbit-ear peaks at 'surface' of clay above sides of a cathodic electrode at base of clay and data obtained showed that only H⁺ could penetrate ~20 m of clay in 8000 yrs.
- In various case studies, he demonstrated the best indicators were pH and conductivity (B-hor) but also showed indirect responses of pH-sensitive elements such as Ca and Mg. Introduced ratioing of partial leach/total [element] to highlight redistribution (Ca, Mg, Fe).
- Govett et al. demonstrated similar H⁺ and conductivity anomalies over 3 Australian deposits (especially Elura where there was no conventional response) & later over exotic cover at Thalanga.
- Both 'groups' and others noticed lower [Org C] in humus over mineralisation, attributed to changes in pH (fulvates in solution) and bacterial activity degrading organic matter.

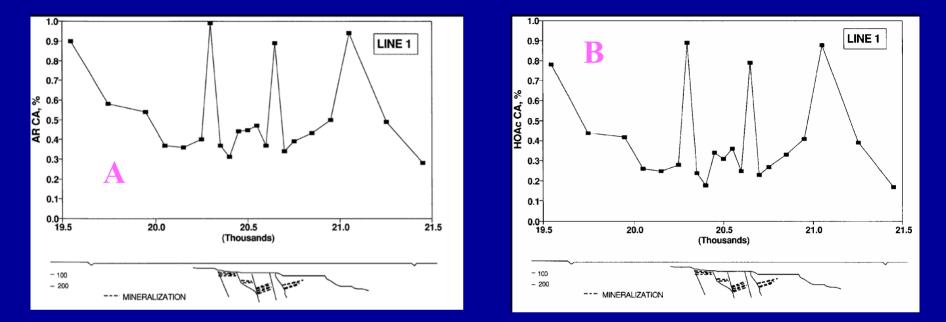


Conceptual model for desert soils (a) shallow (b) deep overburden

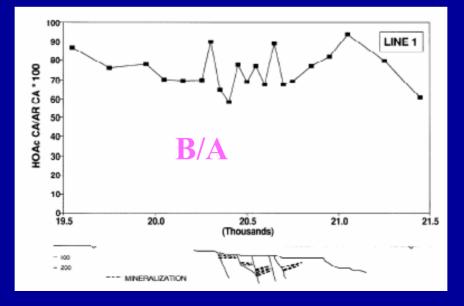
Smee, JGE, 1998

Marigold epithermal Au

Smee, late '90s to present: Ca as indicator, Marigold



Ratio of partial to strong leach response



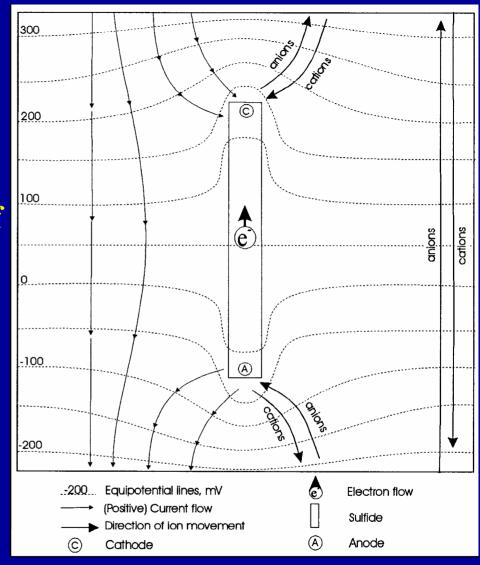
Smee, late '90s to present

- Dialogue in Explore, reinforcing the contention that "target ions do not make it to surface", only H⁺, and therefore a simple pH meter in the field is almost all you need (as long as there is some sulphide in the deposit).
- All other responses said to be indirect as a result of shift in pH, after 25 yrs of experience globally.
- Plea for an ion migration specialist!

Stew Hamilton, 1998 to present

Focussed on an explanation for geochemical soil anomalies observed through thick saturated exotic overburden, such as those reported for the Abitibi greenstone belt. Challenged models of Govett, Bolviken in that they are *electrolytic* rather than *voltaic* cells: counter-ion movement between the cathode and anode would not occur. Ion movement at top and bottom of this voltaic cell would be similar to that of Govett but charge transfer in the electrolyte and the maintenance of charge balance are facilitated *only* by the migration (mass transfer) of ions toward or away from their respective electrodes.

Effect of sulphide conductor on the background redox equipotential field in bedrock; groundwater near upper end of conductor becomes reduced but not as reduced as that at lower end

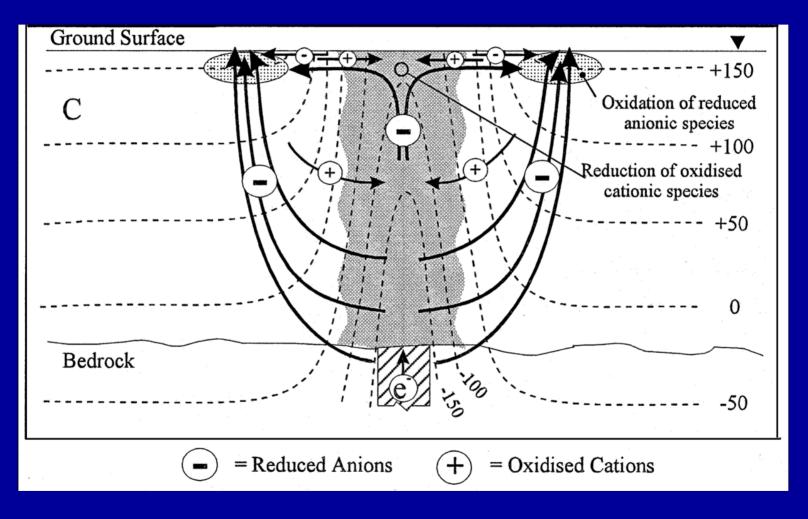


From Hamilton, 1998, JGE

Stew Hamilton, 1998 to present

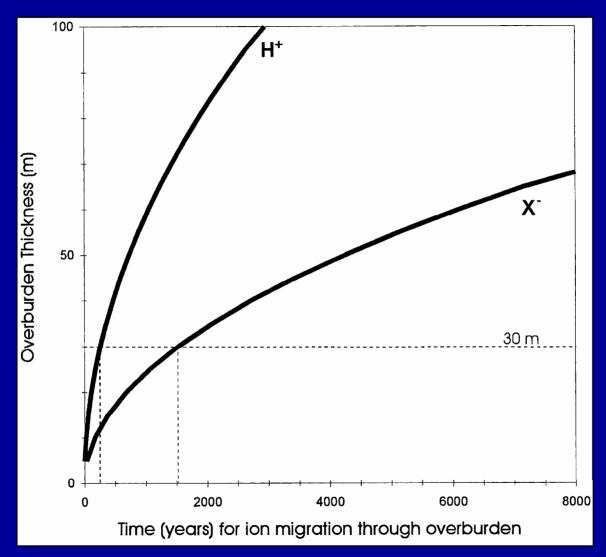
- As electrons move up the conductor, oxidising agents in overlying overburden are consumed and a negative redox anomaly develops above the conductor relative to the surrounding overburden. High redox gradients in this area induce rapid migration of reduced anions (later 'species') away from the top of the conductor. This redox front moves upward (much faster than chemical diffusion) until it reaches a continuous source of oxidising agents. Thus, a reduced column is formed between the bedrock mineralisation and surface.
- Rabbit-ear anomalies at surface could result from both upward movement of reduced anions to the flanks of the column and inward movement of oxidised cations.
 Depletions of Fe and Mn in the centre of the column might be due to their higher mobility in reduced environments.

Modification of redox-equipotential lines in glacial overburden overlying sulphide conductor



From Hamilton, 1998, JGE, flow of redox-active species

Ion migration time as a function of overburden thickness, potential difference of 300 mV

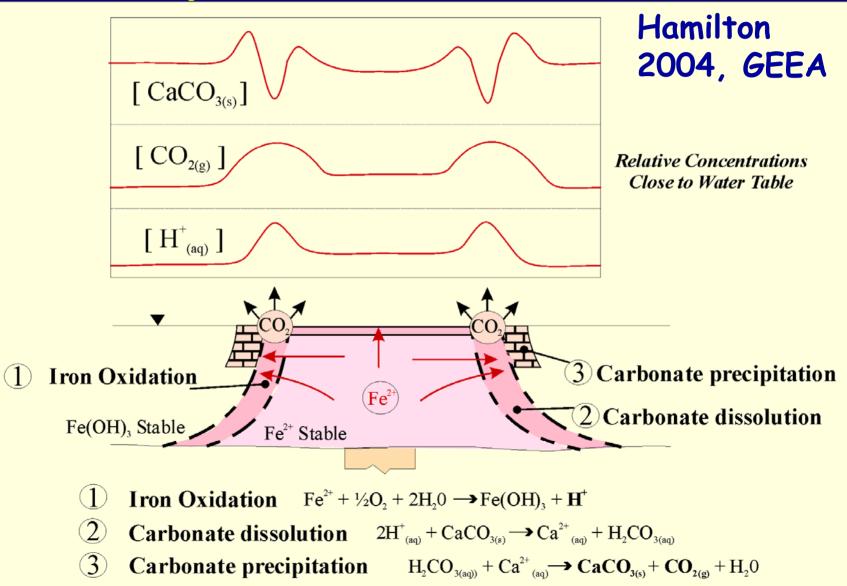


From Hamilton, 1998, JGE



Inward movement and attenuation of oxidised species

Outward movement and attenuation of reduced species



1990s: Rudgeophysika comes to Canada, thanks to Scintrex (Harry Seigel), later to Australia

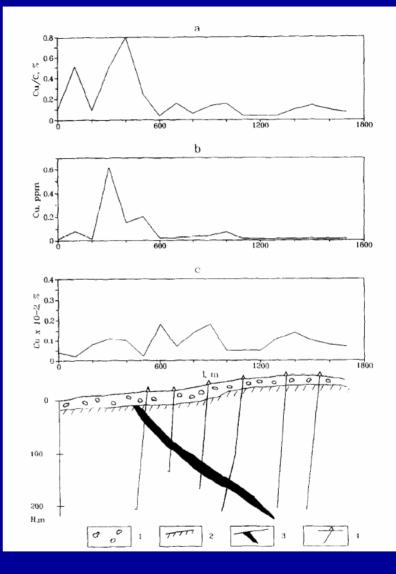
- Ryss, Goldberg, Antropova demonstrate methods developed in '70s and '80s:-
- MPF pyrophosphate extraction
- TMGM non-crystalline Feox
- **CHIM** electromobile elements (as cations)
- MDE/MDI like CHIM but no DC current applied
- Anomalies typically located directly over mineralisation; perhaps 3-fold wider; within same landscape, intensity independent of depth, 'fast migration' of ions



MPF: M-humates, fulvates

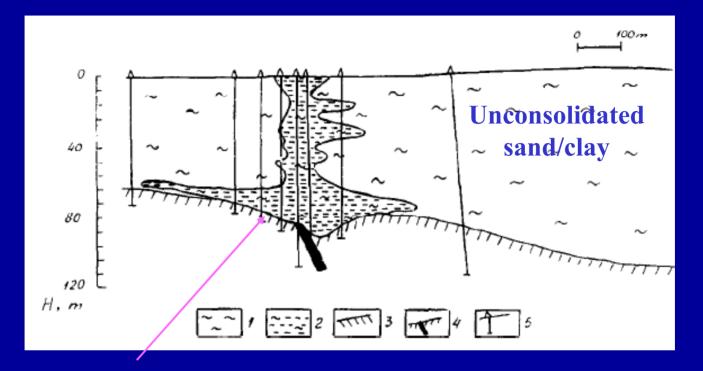
CHIM: in-situ electromobile M

Aqua regia



From Alekseev et al., JGE, 1996

From Alekseev et al., JGE, 1996



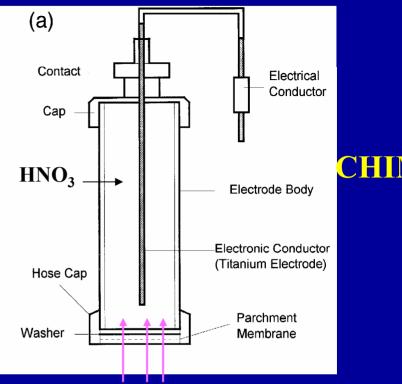
"Dispersion halo of mobile Cu forms"

"Haloes of metals in mobile forms are jet-shaped (1-10 m in diameter), stretching from the mineralised rock to the surface, and appear as vertical columns"

Leinz et al., JGE 1998

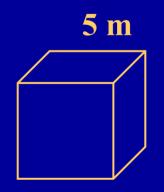
USGS (Smith, Leinz, Hoover, '93 to ~'98) developed their own "NEOCHIM"

- USGS design inhibits diffusion of acid into the soil and allows collection of both cations and anions and flexibility to change receiver solution.
- Tested over disseminated Au deposits
- in Nevada and found constricted but



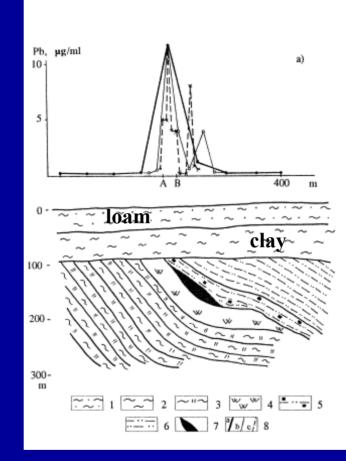
Cations from soil

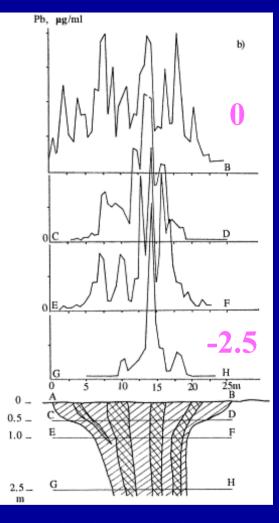
intense anomalies correlated with faulting that some of the partial extractions also picked up (not always, NEOCHIM superior here). However, no indication of the Mike deposit, probably cos of 150 m of impermeable cover. Better than partials as sampled orders of magnitude more sample and surface contamination not a real issue but expensive! Russian literature does not seem to refer to rabbit-ear or apical shapes, just 'heterogeneous'. Furthermore, only deposit elements are reported as anomalies



Loam experiment







50, 20, 5-m spacing

0, 0.5, 1, 2.5 m depth sampling

Goldberg, JGE, 1998

Barringer's "Airtrace": in the '70s!



-To collect and analyse atmospheric particulate matter (> 10 μm), specifically volatile exudates from vegetation which carry metals taken up in biogeochemical cycling;
-Verified principle via radioactive tracer

doping of vegetation;

-Capture particulates on tape and analyse by laser-ICP-ES in lab;

-5' resolution in chopper (25' above treetops), 200' in fixed-wing.

Soil gas exploration under cover

- "We search for the veins by observing the hoarfrosts, which whiten all herbage except that growing over the veins, because the veins emit a warm and dry exhalation...." Agricola, 1556
- Excellent sources of info are Klusman's 1993 book (*Soil Gas and Related Methods for Natural Resource Exploration*) & Kesler's 1990 special issue of the JGE.
- Gases exist in rock in following states: free in pores; adsorbed on minerals/organic; in solid solution; in micro or fluid inclusions.

Challenges with gases

- Often measuring perturbations on a very high background (e.g. CO₂, CH₄, He);
- Variability in the near-surface environment can be extremely high due to such conditions as P, T, moisture, meteorological events, season, geomorphology, vegetation;
- Desorption from soil, rather than real-time sampling, to reduce above is also prone to error due to soil characteristics ([Org C, clay, Feox]); so collectors (activated C) sometimes deployed

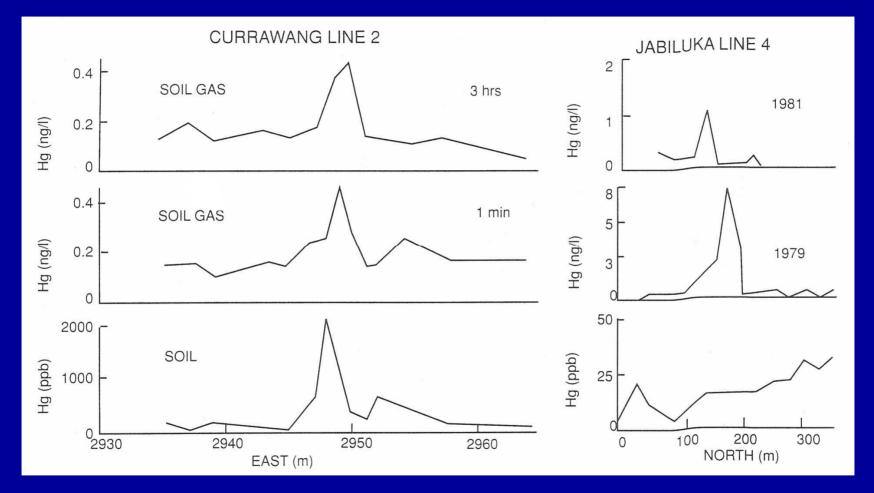
'Conventional' gases used in exploration under cover

- Stable gases such as Hg, Rn, He;
- Lots of activity in the '70s (NURE, URP), early '80s;
- Led to development of 'Track-Etch' technique (cup) for Rn and Ag/Au wires in inverted cups for Hg, Scintrex Hg Zeeman spectrometer;
- Rn successful in Canada (Dyck, Gingrich..);
- Butt & Gole ('85, '86) concluded He of little use as background variation was so high (overburden-dominated), structure-controlled. Reimer at USGS published many He surveys.

'Conventional' gases used in exploration under cover: <u>Hg</u>

- McCarthy was a pioneer in use of Hg: early '70s used Au chips for 2-h collection, truck-mounted spectrometer, good success in Nevada under ~ 30 m alluvial cover. Affected by P&T, precipitation, time (and structure), though.
- Fursov in former USSR reported many successful Hg soil gas surveys under cover, e.g. Cu deposit in the Urals under 350 m (sandstone, clay, limestone) was found this way. Numerous reports where soil itself was ineffective. Intensity of anomaly not indicative of depth, size or grade.

Carr et al. (1986): Hg in soil gas, 40 deposits



Outcropping Zn-Cu-Pb, wet climate Transported sandy cover, Au-U dry climate

Mercury in air/soil gas instruments today

Tekran 2537 Au/AFS 0.1 ng/m³



Jerome Au film/resistance 3000 ng/m³



Lumex RA 915+ Zeeman AAS 2 ng/m³ (2 models)

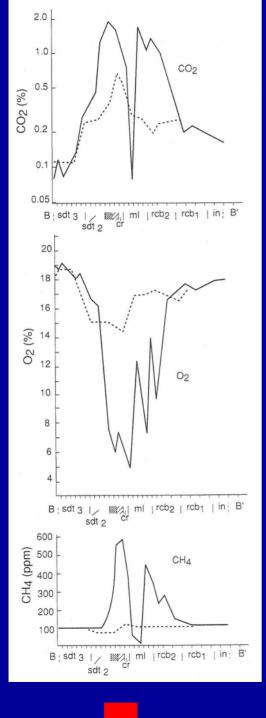


'Conventional' gases used in exploration under cover: CO₂ and O₂

- CO₂ formed by oxidation of sulphide and dissolution of carbonate in host by acid so formed; CO₂ can also originate from outgassing via major fracture systems
- Sulphide must be oxidising: by infiltration of air, oxygenated GW, or electron-acceptor other than O₂; oxidation enhanced enormously bacteria, by 10⁶ (e.g. Thiobacillus ferrooxidans)
- However in the near-surface soil by far the most important/active contributor to CO_2 and uptake of O_2 is microbial activity (Lovell, Vol 7), then plant respiration etc ; the former activity depends on such parameters as moisture content (>/>), redox, pH, T. Microbial production of CO_2 favours light isotopic signature (v. negative $\delta^{13}C$)

'Conventional' gases used in exploration under cover: CO₂ and O₂

- Case histories (USSR, Lovell, McCarthy, Ball) report successes mostly in arid and semi-arid climates;
- Given the (high) solubility of CO₂, it may not be reasonable to assume that in wet terrains the source of a CO₂ anomaly is at depth, near oxidising mineralisation, as in the challenge of McCarthy's interpretation (in '80, published in '86) by Alpers (in '86, published in '90) of the CO₂ anomalies at the Crandon deposit.

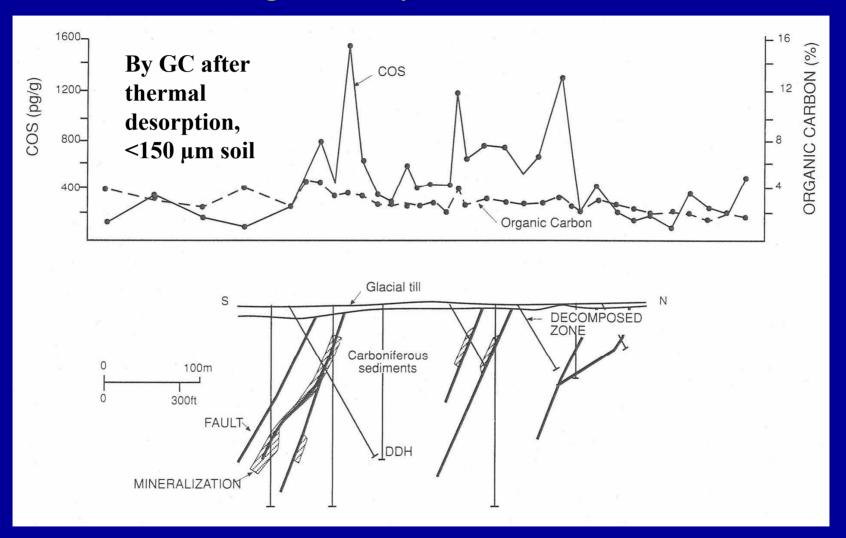


-From McCarthy et al., '86: **Crandon VMS deposit.** Covered by 25-65 m of glacial till, water table depth is 15-36 m. -Dotted response is after a rain event, but not 'washed out' on all lines surveyed. -Where water table was deeper, CO₂ and O₂ anomalies were greater. Data indicated microenvironments of oxidation and reduction (methanogenesis) $-\delta^{13}$ C by Alpers was not different from bgd, should have been much lighter from the limestone of the country rock. Klusman was critical of Alpers' sampling, too much air drawn in.

'Less conventional' gases: S+

Various S gases should be formed during weathering, of these COS would be the most stable, CS_2 next, whereas SO_2 and methylated S species are highly soluble and their rates of generation lower (see Oakes & Hale, '87, most applications are in arid/semi terrain with shallow mineralisation)

From Oakes & Hale, '87: soil gas over Pb-Zn deposit (Keel), 2-7 m of glacial clay-rich till, wet climate



Thorough work over numerous deposit types, found COS successful mostly in arid terrain, to depths of 90 m

'Less conventional' gases: S+, in the '90s

- Hinkle et al. carried out simulated weathering on drill cores from Santa Cruz porphyry Cu deposit and found anomalous concentrations of CO₂, COS, CS₂ and SO₂ (pyrite was main S mineral); O₂ (air) was essential;
- Kesler et al. found anomalous concs. of COS, CS₂ and CH₄, with low CH₄/CH₄ + C₂H_{40r6}) in soils over sediment-hosted micron-Au deposits (Alligator Ridge & Yankee); also compared desorption of gases vs Carbotrap collectors, different depths. Couldn't distinguish signals over mineralisation vs faults. Advocated more R&D for deeply buried deposits.

'Less conventional' gases: hydrocarbon-based

- Carter's thesis in the '80s: hydrocarbon gases from ~ 3000 samples from Irish deposits. Found broad CH₄ haloes with enrichment of heavier C₂-C₅ alkanes/alkenes over mineralisation. Inferred that hydrocarbons were released during ore formation, most mobile CH₄ would travel the furthest. Suggested this as regional technique.
- Disnar ('90) measured free and sorbed hydrocarbon signatures (C_1 to C_4 alkanes/alkenes) persistent in host rock (limestone, bearing Ba-Zn-Pb min.), indicative of hydrothermal alteration during ore genesis.
- Klusman ('93) briefly discussed volatile methylated/ethylated forms of As, Sb, Se, S, Te, Pb....(stability is an issue to be addressed). Only touched on hydrocarbons for Min Ex where a sedimentary host rock was present, no case histories.

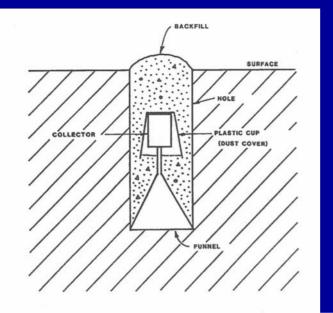
Into 21st Century with SDP and SGH

SDP	SGH
Sample high in B (10-15 cm below LFH), clear of organic-rich horizon. Integrate over 1 m ² . Create template over known min. Can sieve in field to <80-mesh. Gravity separation to 0.2-2 μm.	Sample in B where highest conc. of clays, amorphous Fe/Mn oxides.
Pyrolysis at 450C, MS analysis, 44 cpds. Aliphatic and aromatic hydrocarbons; halogens, halogenated hydrocarbons; organic sulphur gases; carbonyl sulphides; He and Ar; SO ₂ , H ₂ S, CO ₂	C5-C17 range of hydrocarbons, 162 cpds. Extraction and GC-MS.
Report SDP 'Sum' and 'Count' and principal cpds that feature in template. Proprietary algorithm uses cpd ratios to reduce noise, effects of lithology, soil type, faults	All 162 cpd responses reported but also use FA, PCA, neural net etc to define multiple coincident responses.

Migration pathways of gases

- Short half-life of ²²²Rn (3.8 days) showed that mechanism of migration cannot only be by diffusion (slow) but by advection through fracture & fault zones, seismic pumping – good discussion by Dyck & Jonasson (2000, Vol 7) – as in hydrocarbon anomalies above oil/gas reservoirs.
- Led Kristiansson & Malmqvist ('82, '84) to propose concept of 'streaming' by a carrier gas ('geogas') which is acceptable for movement of trace gases but particulate matter and ions? However, they reported success in numerous case histories for deeply buried min. (e.g. ~ 100 m) in Scandinavia by deployment of polystyrene film collectors in soil and even in snow (As).

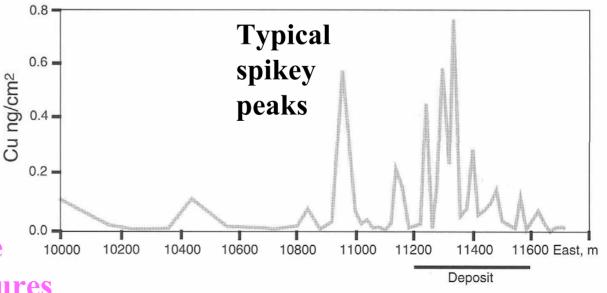
Migration pathways of gases: the PSIROGAS project



Johnson, Griffin, Rutherford, Giblin et al. Collected gas on polystyrene film, ~ 30 days, analysis by PIXE

<u>Cu</u> at Osborne Cu-Au deposit in Proterozoic rocks covered by 30-60 m fractured sedimentary rock (Mesozoic)

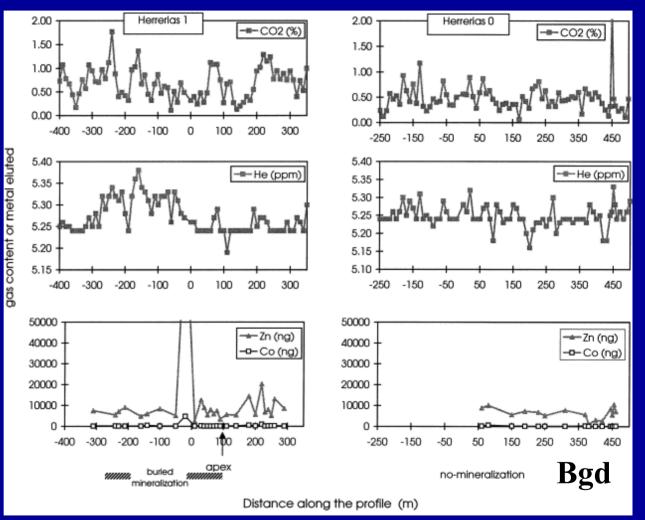
SEM indicated 0.6 evaporation of salts from water droplets Concluded signals are from evaporating GW brought to surfac by aerosols along fractures



Migration of gases contd: Pauwels et al., '99

 Supports K&M theory of movement of particulate matter in gas stream (CO₂) through fractures (5-20 cm h⁻¹);

 Deployed activated charcoal collectors for ~ 100 days



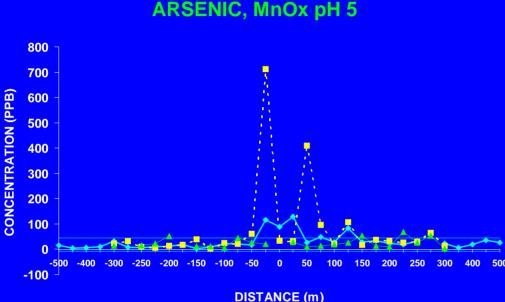
Herrerias VMS in Iberian Pyrite Belt, depth of 50-240 m hosted in black shales, GW at -4 to -35 m

Gas migration to surface at underground nuclear test sites

<u>Carrigan et al.</u>, Nature, 1996, 382: 528-531, Trace gas emissions on geological faults as indicators of UN testing. (SF₆>>He to reach surface)

"Trace gases are transported to the surface within periods of a week to a year, by flow along faults and fractures driven by barometric pressure variations...models of gas transport in a fractured porous medium subject to barometric surface pressure variations indicate that the speed of transport along fractures over a vertical scale of hundreds of metres is orders of magnitude greater than the diffusion rate".

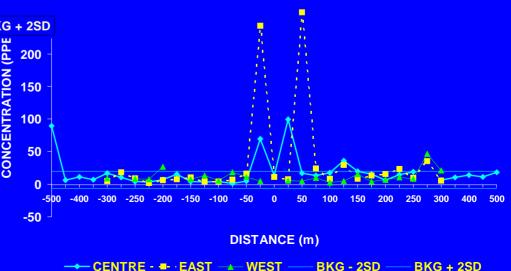
Soil sampling for detection of nuclear events: NTS, Nevada Mineral Quarry, DOB 385 m in 1990, above water table



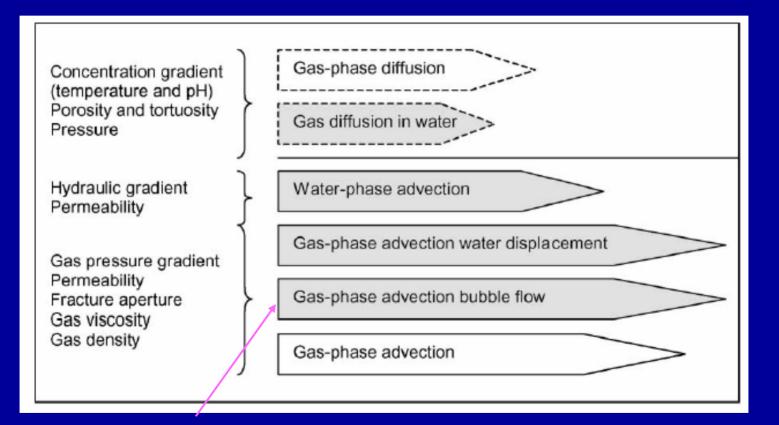
Some elements (e.g. As, Sb, S) could have volatilised from the blast but their anomalies by 'total' are subtle compared to 'partial' signatures

LANTHANUM, MnOx pH 5

CENTRE - CEAST - WEST BKG-2SD BKG+2SD Others (e.g. REEs) show a redistribution to much more mobile forms



Etiope & Martinelli, 2002: *Migration of carrier and trace gases in the geosphere: an overview*, Physics of the Earth and Planetary Interiors



Four mechanisms of transport: floatation within bubble, surface-active binding on G-W interface, aerosol, volatiles

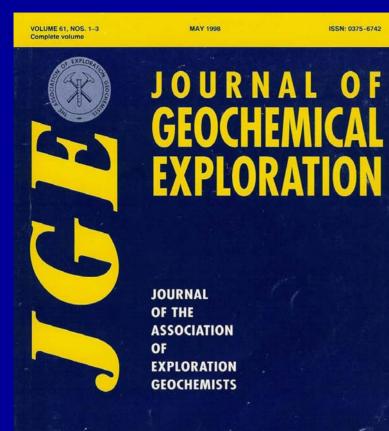
Partial/selective leaches: early 1990s, ICP-MS is established gradually

- Clark transfers enzyme leach (targeting am. MnO₂ phase) from USGS to Hoffman's Actlabs, with numerous case histories of success subsequently described; theories proffered for rabbit-ear/halo ('oxidation suite', with vapour transport of WClO₄, ZrCl₄?) and apical anomalies.
- Mann creates MMI series of ligand-based weak leaches, targeting weakly bound elements rather than 'phases' and uses response ratios instead of absolute concentrations.

Partial/selective leaches: through the '90s

- Huge amount of application in exploration, other leaches are created or resurrected from early '80s and modified ('Hydroxs', pyrophosphate, HCl, acetates, RegoleachTM, followed later by TerraleachesTM...);
- Skepticism grows as some leaches are not properly designed, ICP-MS corrections not made, sample collection is improperly carried out, survey site is not well understood (topography, lithology and soil type change etc), element migration mechanisms remain undefined.

Special Issue on Selective Extractions, 1998



Special Issue
SELECTIVE EXTRACTIONS
G.E.M. Hall and G.F. Bonham-Carter (Editors)

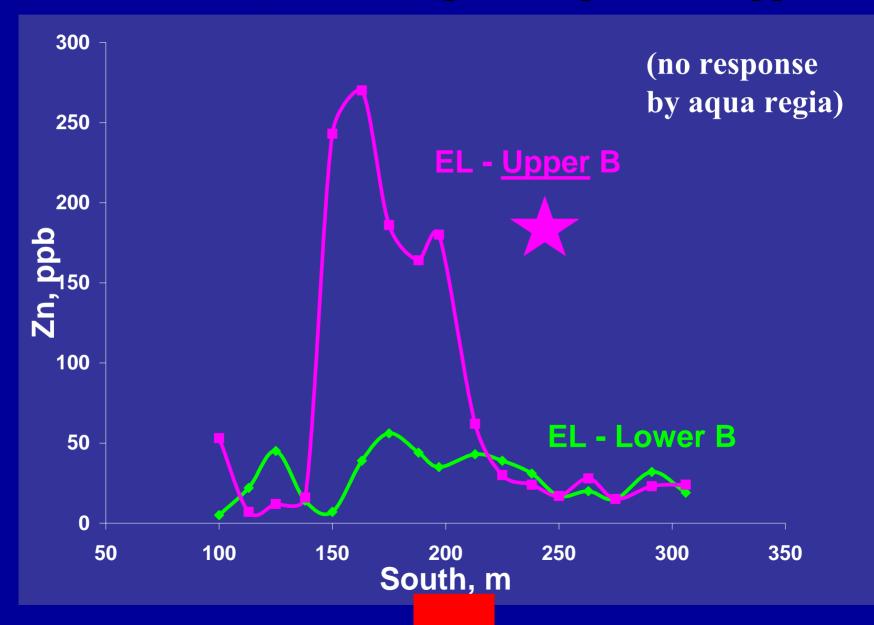
ELSEVIER http://www.elsevier.nl/locate/jgeoexp Mixture of successful case histories and critiques: e.g. Bajc's observation of anomalies associated with geological features, grain size; other papers on resorption during leaching, false anomalies due to pH shift in leaches caused by change in sample type.

CAMIRO and OMET projects in Canada, late '90s into 2004

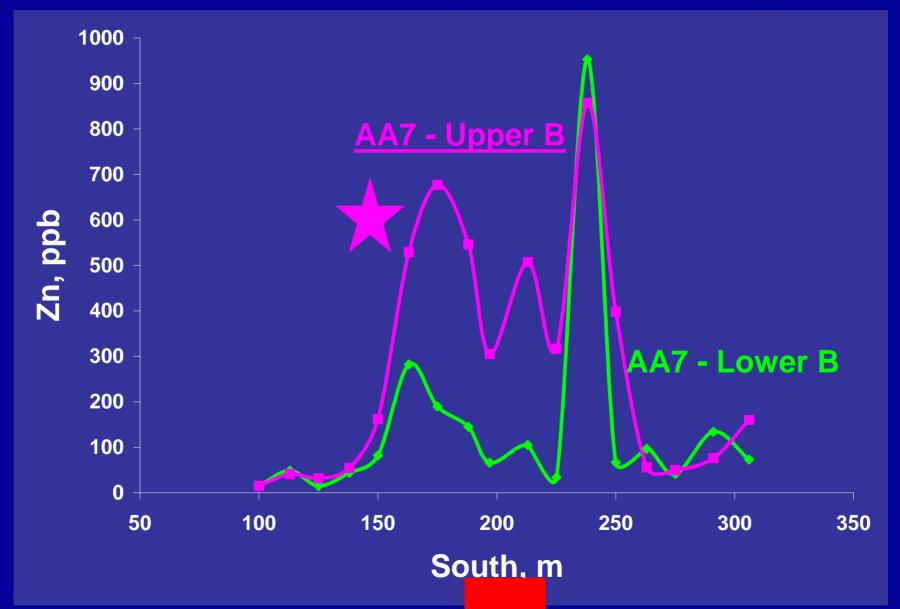
- CAMIRO project was led by Eion Cameron, with Hall, Hamilton, McClenaghan, Leybourne <u>"Deep</u> <u>Penetrating Geochemistry"</u> to better understand dispersion of elements from deposits, in Canada (VMS, Cross Lake), USA (Au, Mike), Chile (porphyry Cu, Spence);
- OMET project same team (-Leybourne), coordinated by Hall, main focus on Cross Lake (30-50 m of cover, glacial sediments), what have we learned?

• Depth of sampling is absolutely critical: top of mineral soil (podsol or luvisol soils), no mixing of horizons.

Line 6, 2000, Enzyme Leach on Upper (0-10 cm) and Lower B (10-20 cm): great response on upper B

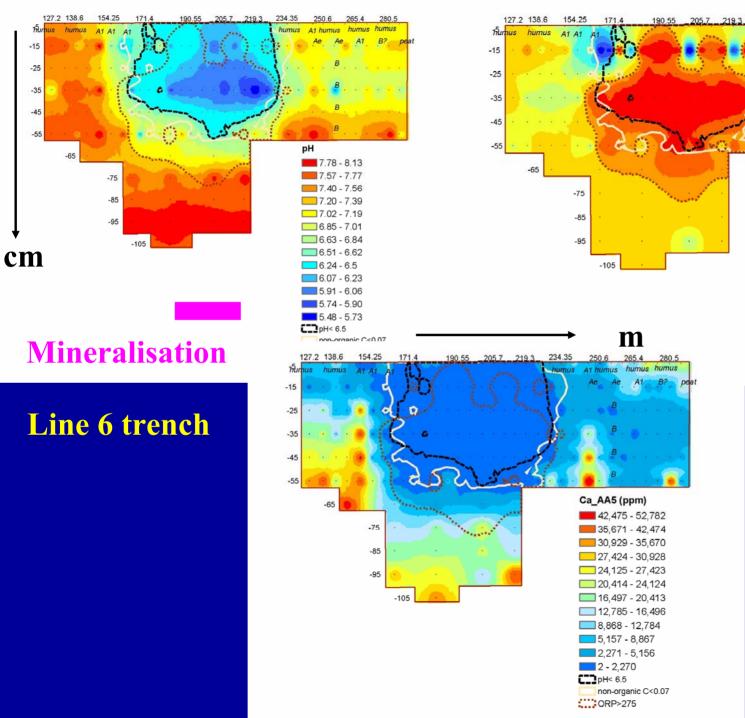


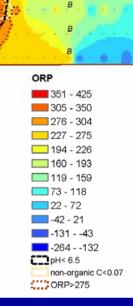
Line 6, 2000, AA7 leach on Upper (0-10 cm) and Lower B (10-20 cm): great response on upper B



- Depth of sampling is absolutely critical: top of mineral soil (podsol or luvisol soils), no mixing of horizons
- Measured a reduced chimney above mineralisation from water table to at least 8 m

- Depth of sampling is absolutely critical: top of mineral soil (podsol or luvisol soils), no mixing of horizons
- Measured a reduced chimney above mineralisation from water table to at least 8 m
- The huge H⁺ anomaly (~80 m wide), or 'acid cap', outlined by trenching the top metre, has an enormous effect on (endogenic) element distribution, to create anomalies of comparable size: not indicative of elements from depth.





234.35

humus

250.6

A1 humus

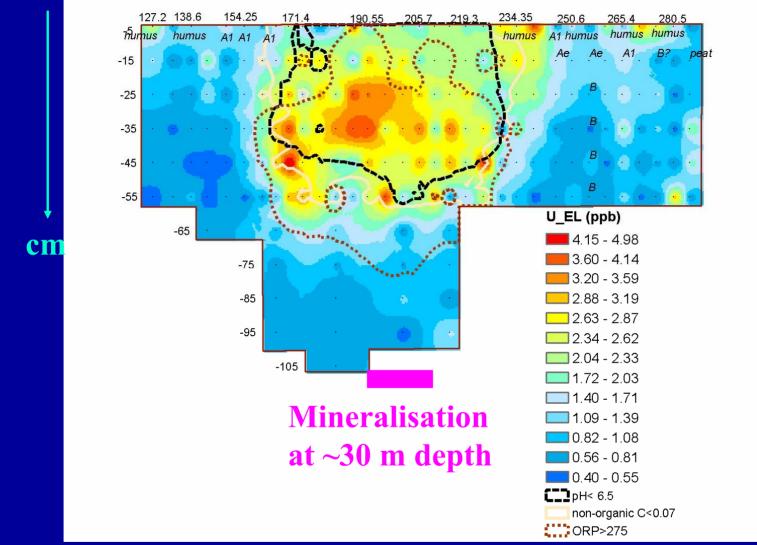
В

265.4

humus humus

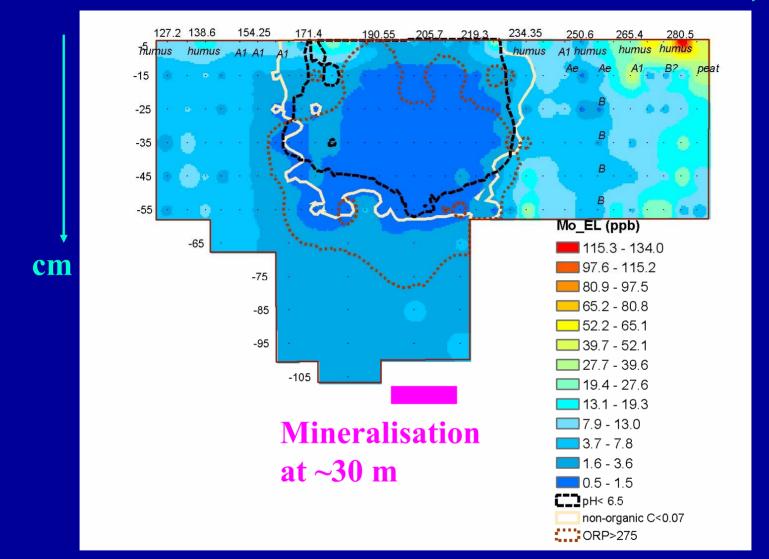
280.5

82



m

U (+Th, REEs) show apparent enrichment by EZ (and by weak HCl and AA7) Probably due to greater availability or solubility in EZ Produces positive/apical anomaly

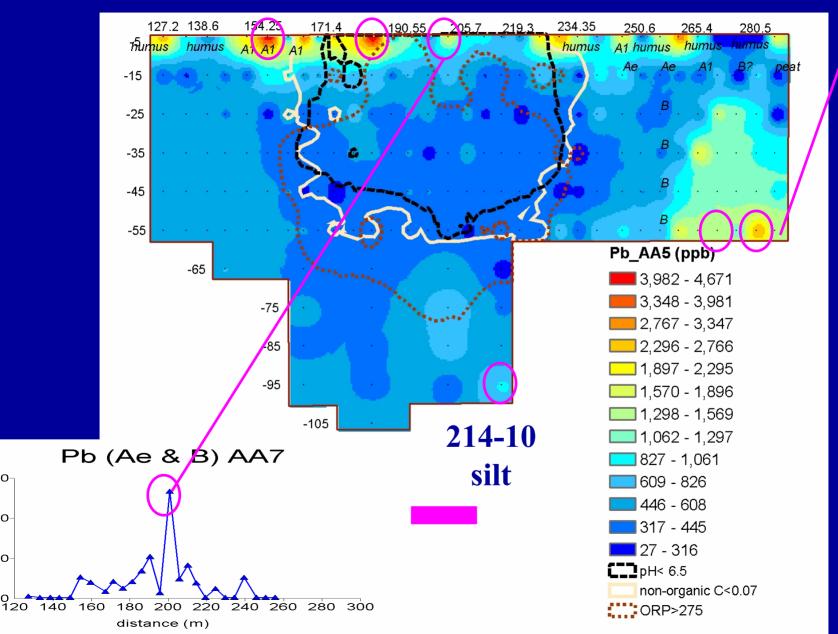


Anions Mo, V, As, Sb, I = PC3 for the Enzyme Leach data and appear 'depleted' in the acid cap probably because they are in a form which is less stable/soluble in the EL Produces apparent 'rabbit-ear' anomalies

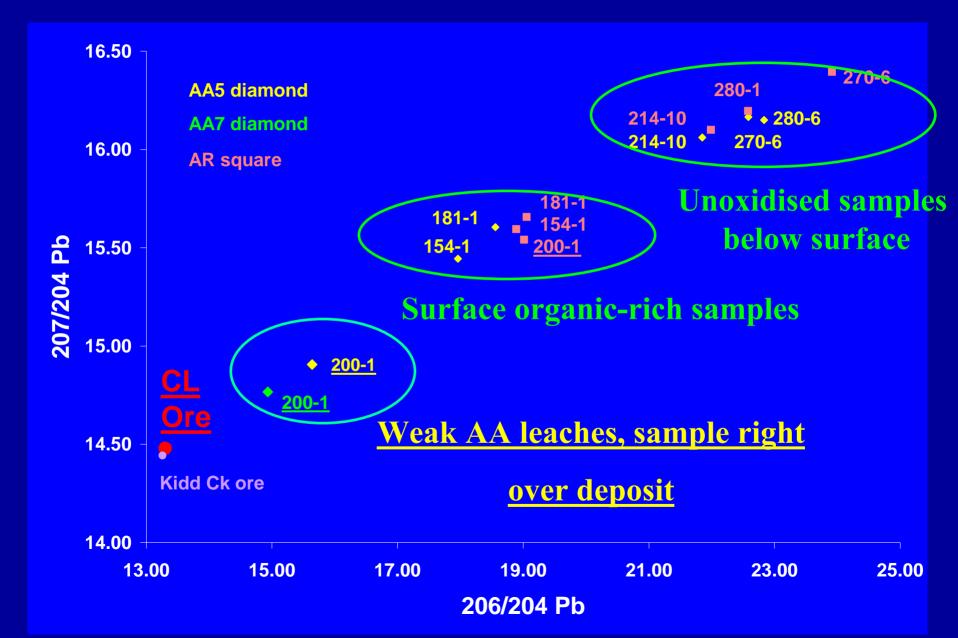
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 Proof of element migration from the deposit at depth through glacial overburden to the surface, by Pb isotopes and partial leach



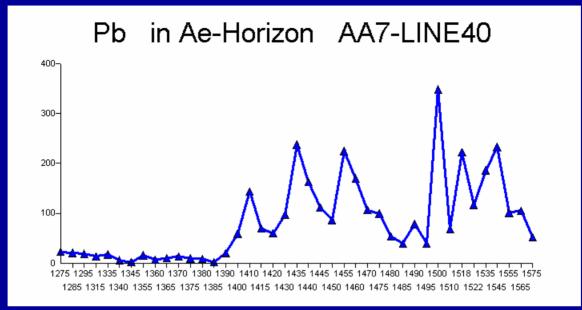


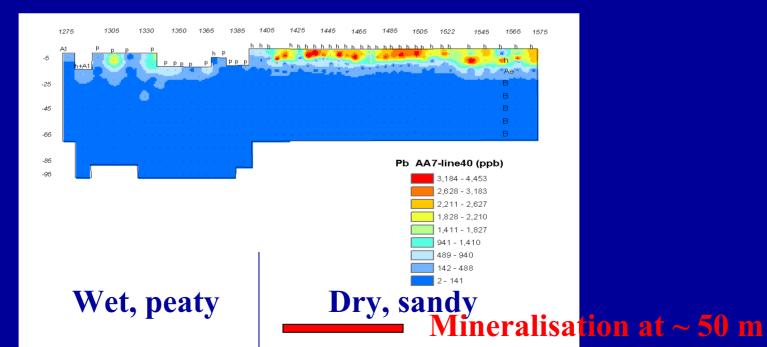
Pb isotopes, Line 6



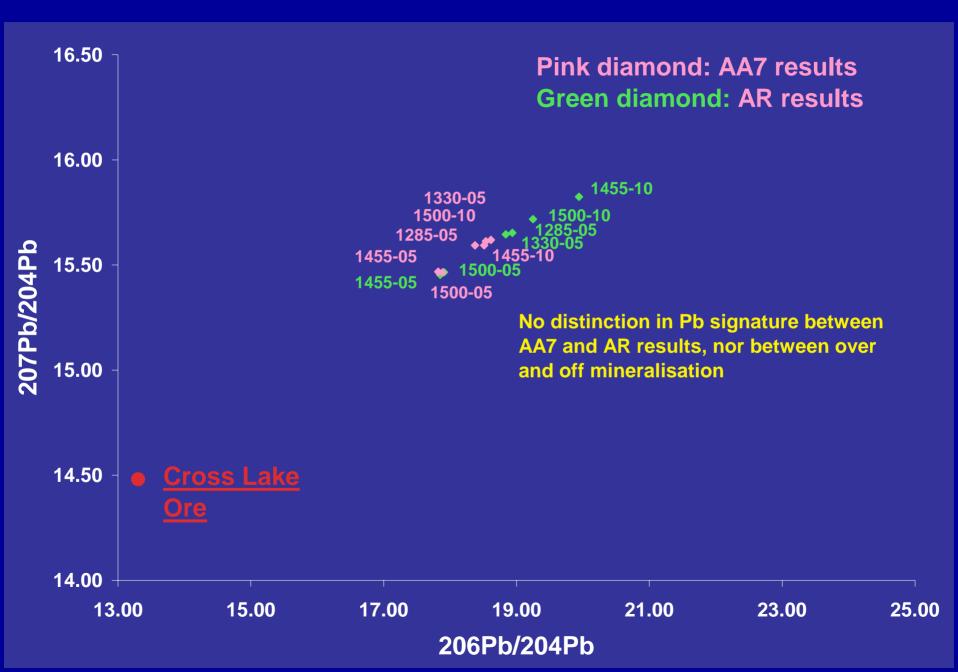
- Proof of element migration from the deposit at depth through glacial overburden to the surface, by Pb isotopes and partial leach
- Recognition of 'false' anomalies created by such situations as a terrain change, change in soil drainage and leaching down-profile

Line 40 Pb anomaly by AA7



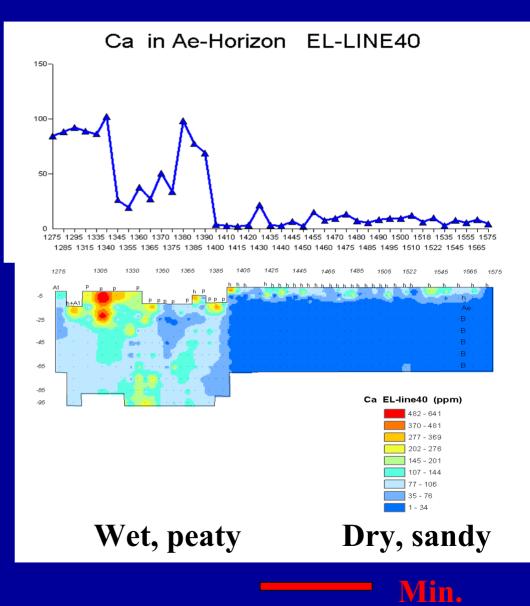


Line 40 humus and Ae samples

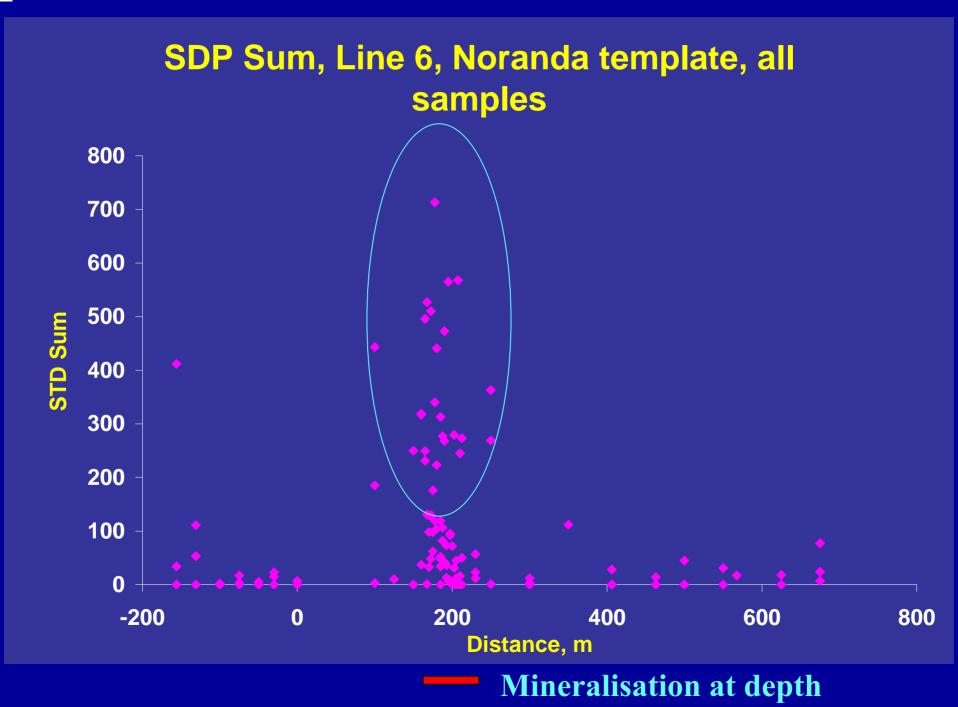


Line 40 Ca in Ae horizon by Enzyme leach

Same for other partial leaches: distinct difference in response with terrain change; Ca more concentrated in peat than in humus, leaches down to Ae to produce 'false' anomaly. If the terrain changed back into a dry sandy area, a rabbit-ear anomaly would exist!

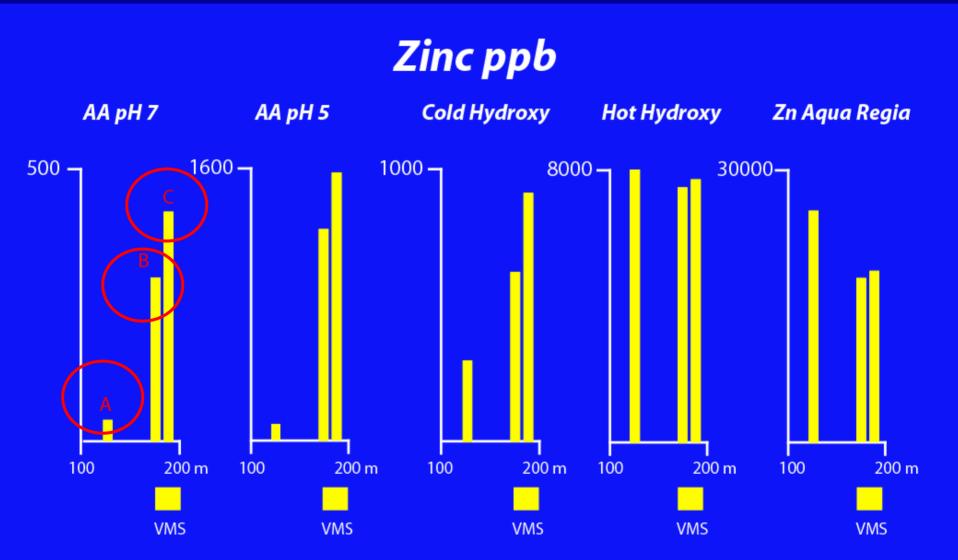


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- Optimal leach to use depends on types and duration of processes occurring, age of overburden etc....

Line 6, 2000, relative signals of samples off ('A') and over mineralisation ('B', 'C') in upper B for different leaches



Future directions

• We need a greater convergence of the disciplines, especially with microbiology, and soil science, to answer such questions as

-Is the elemental zone of interest controlled by microbes? How much of a role do they play in organic depletion, O_2 depletion, CO_2 enrichment? Are hydrocarbon-based gases coming from the deposit and/or from the near-surface?

- How does the zone of interest vary with terrain type?
- Why do some deposit elements show a response and not others (e.g. Cu at Cross Lake, appears leached away at surface). Why does Fe not give a good response?
- Further clarity required re the elements showing an indirect response.
- Much more isotopic analysis needed.
- Watch progress in nanoparticle science, relevant

Finally, some wishful thinking.....

- Enough with secrecy in our science!! How are we supposed to make progress in this exploration approach if we don't know what forms of the elements we are dissolving or gases we are measuring?.. Is there fractionation of gases in the measurement process?
- Let's publish more, the overwhelming majority of the data is in industry's vaults.
- Case histories more information needed on the survey site and let's see the aqua regia response too.
- Really delineate the background signal and let not our eyes see 'anomalies' caused simply by increased sample density over mineralisation.

Cross Lake when we finished with it!

