Groundwater Geochemistry in Mineral Exploration

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Outline

- Introduction
- Methods
- Case Study - Porphyry Copper
- Case Study - VMS
- Other Examples
- Future Directions
- Summary

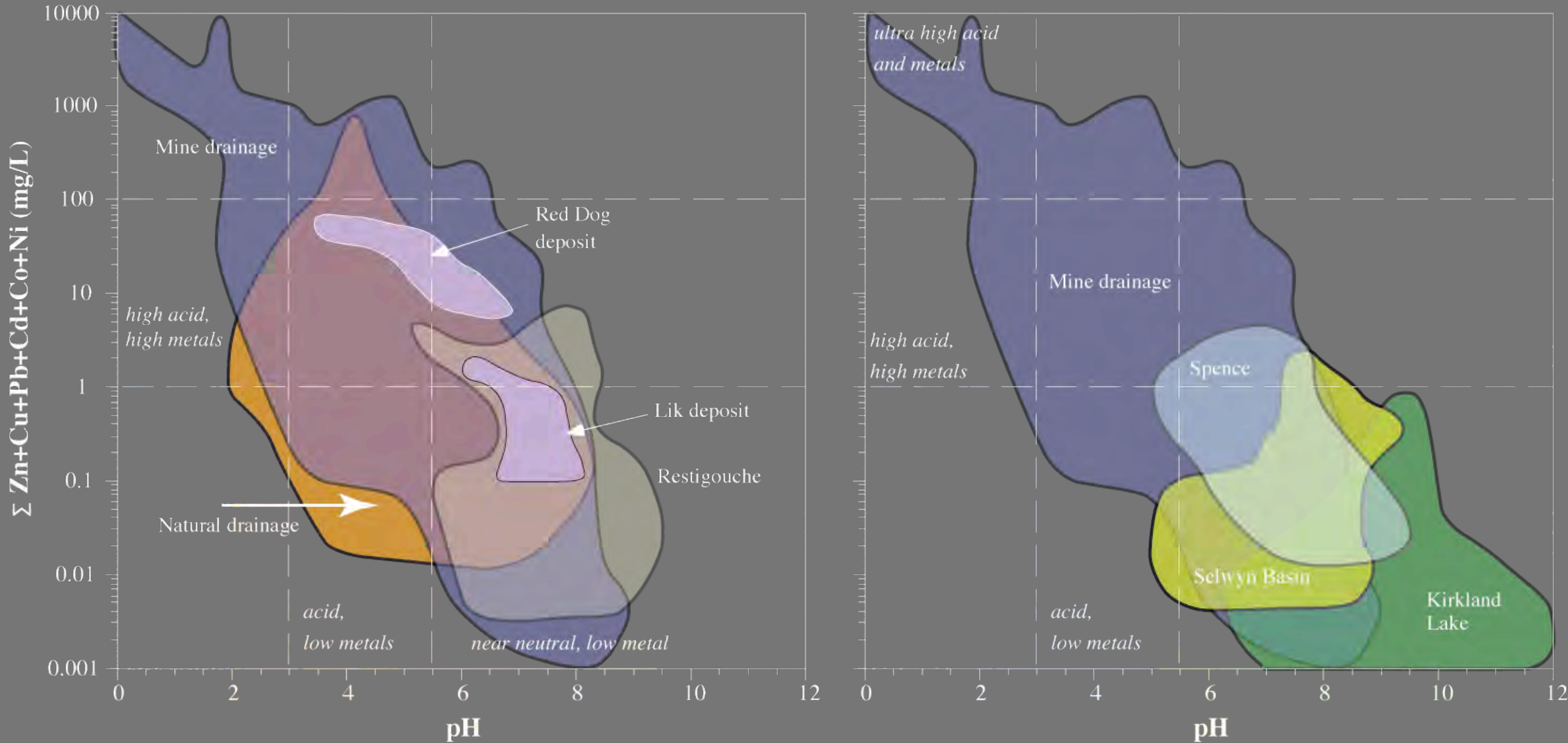
Why groundwater geochemistry?

- **Aqueous geochemistry (in the broadest sense this includes ground and surface water and stream sediments) has been successfully used in mineral exploration for some time.**
- **Significant challenge for mineral exploration is to find new and deeper deposits, particularly in areas where either thick cover exists**
- **Where past exploration has already discovered shallow mineralization and exploration must extend to greater depth**

Utility of groundwater geochemistry

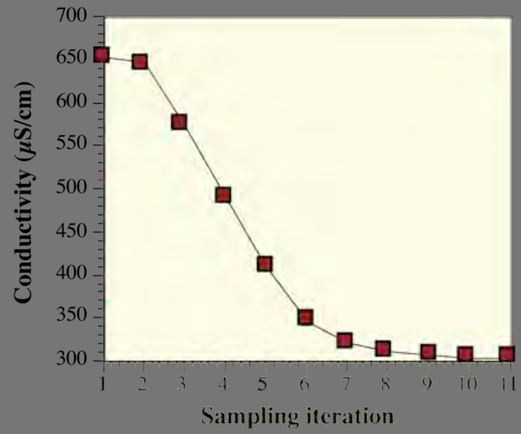
- Groundwater recharges to depth, resulting in greater likelihood of interacting with buried mineralization compared to surface geochemical methods, and thus providing a three dimensional perspective.
- Advances in understanding of ore formation processes, water-rock interaction and metal transport/attenuation in the secondary environment are enhancing the efficacy of groundwater geochemical exploration.
- New analytical technologies are resulting in lower detection limits, cheaper and more rapid analytical costs and permitting routine analysis of previously unavailable isotopes

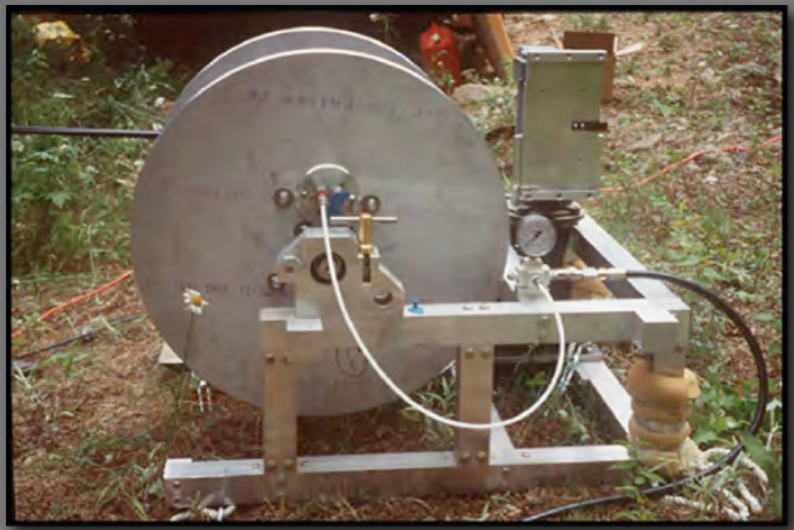
Natural waters vs AMD

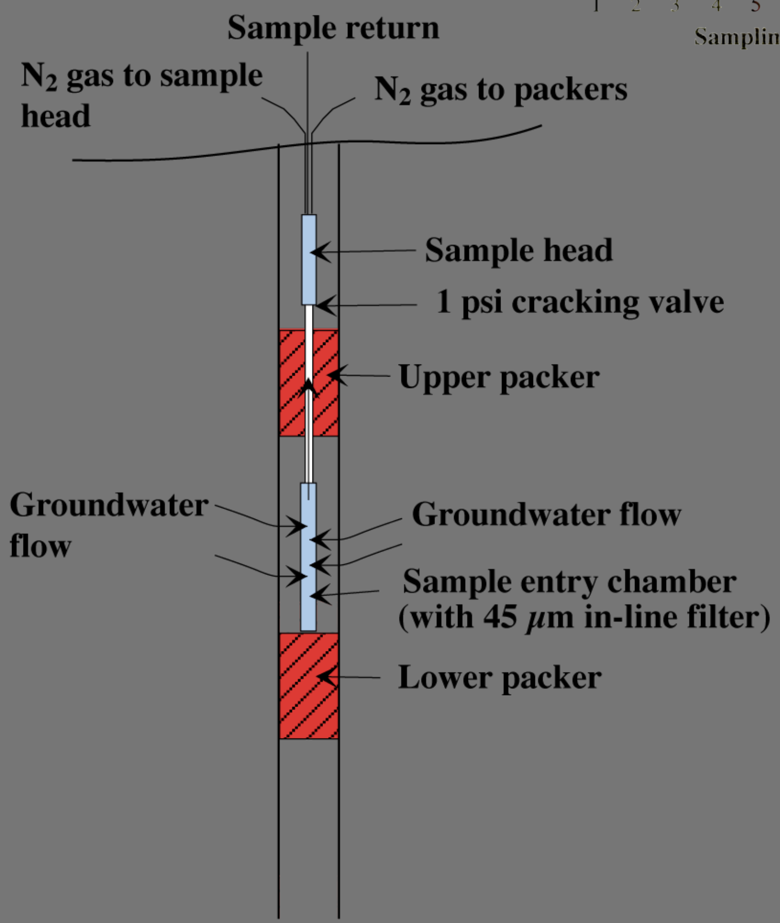


After Plumlee et al (1999), Leybourne (1998), Cameron and Leybourne (2005), Leybourne and Cameron (2006), Goodfellow (1993), Jonasson et al (1987), Kelley and Taylor (1997) and Sader et al (2007)

Field methods

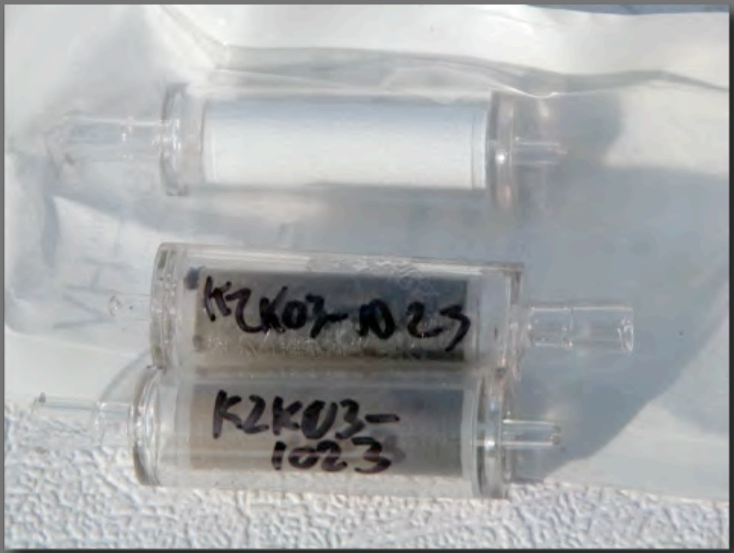


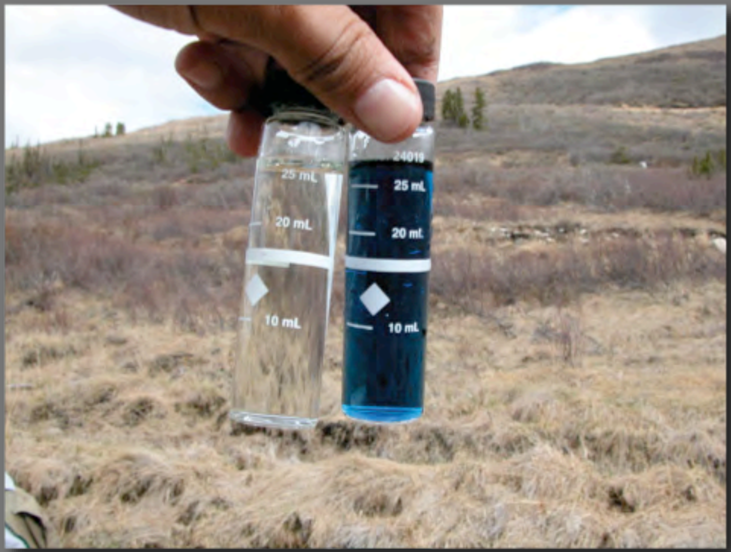




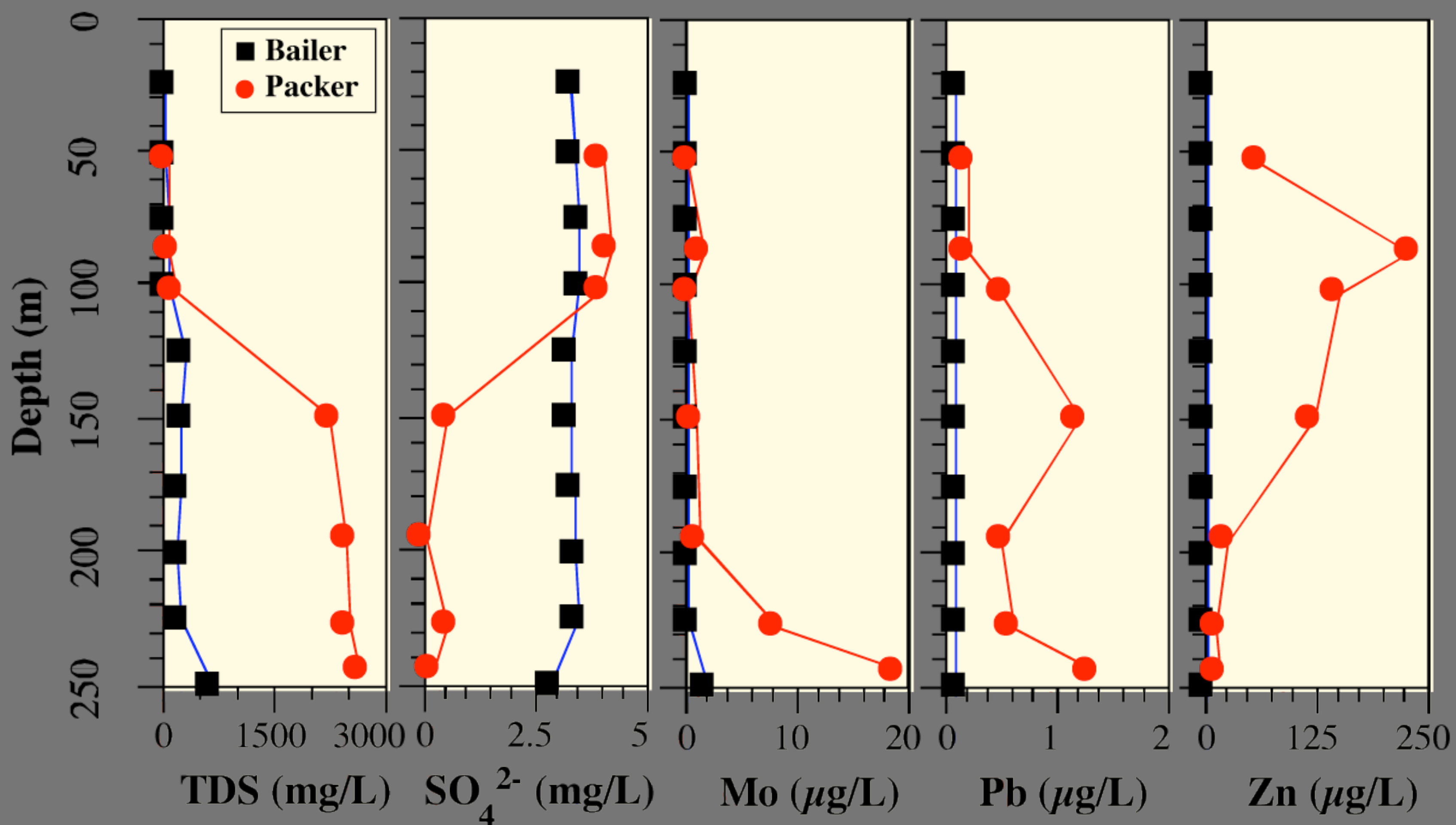
Field methods

Field methods



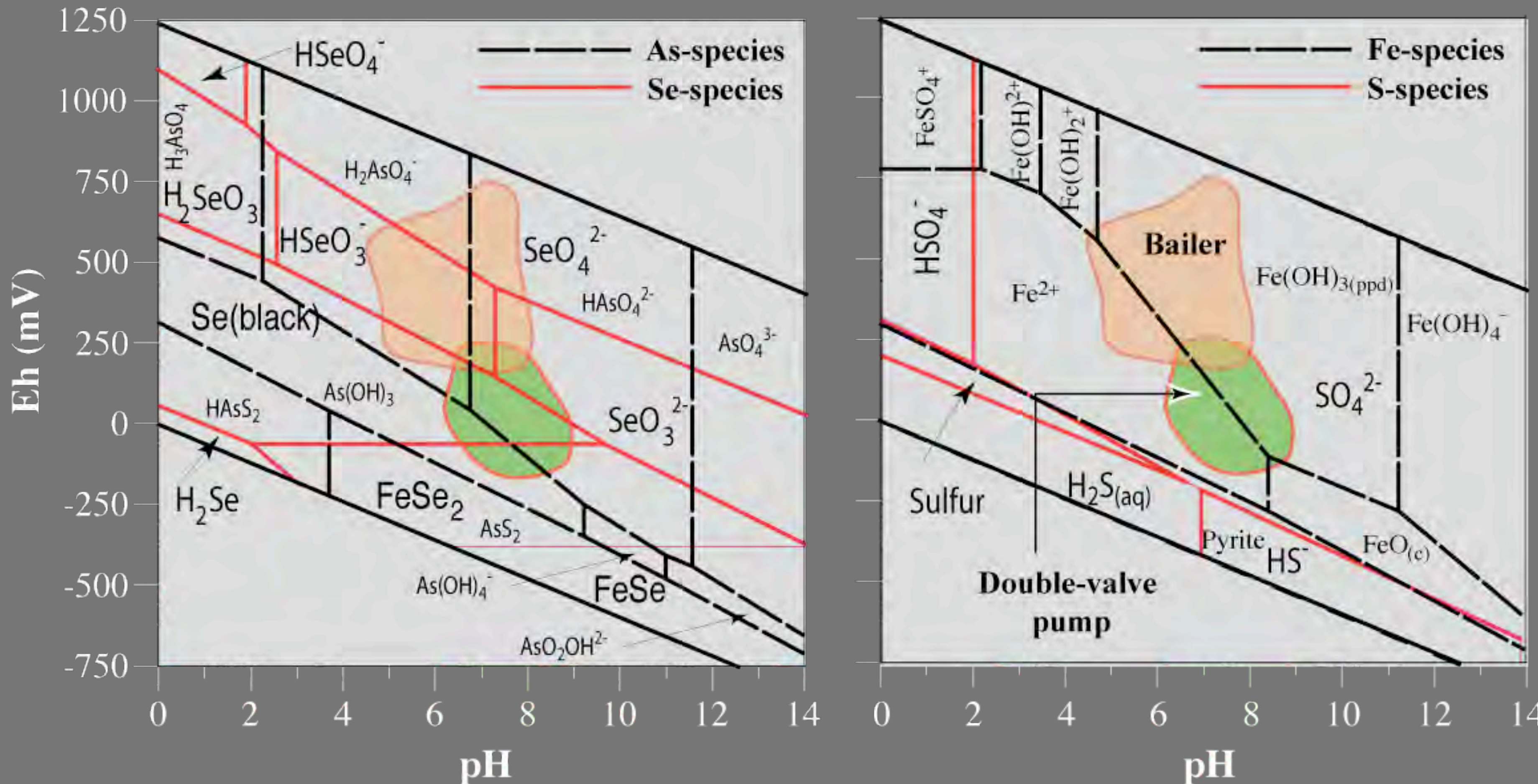


Packer versus bailer



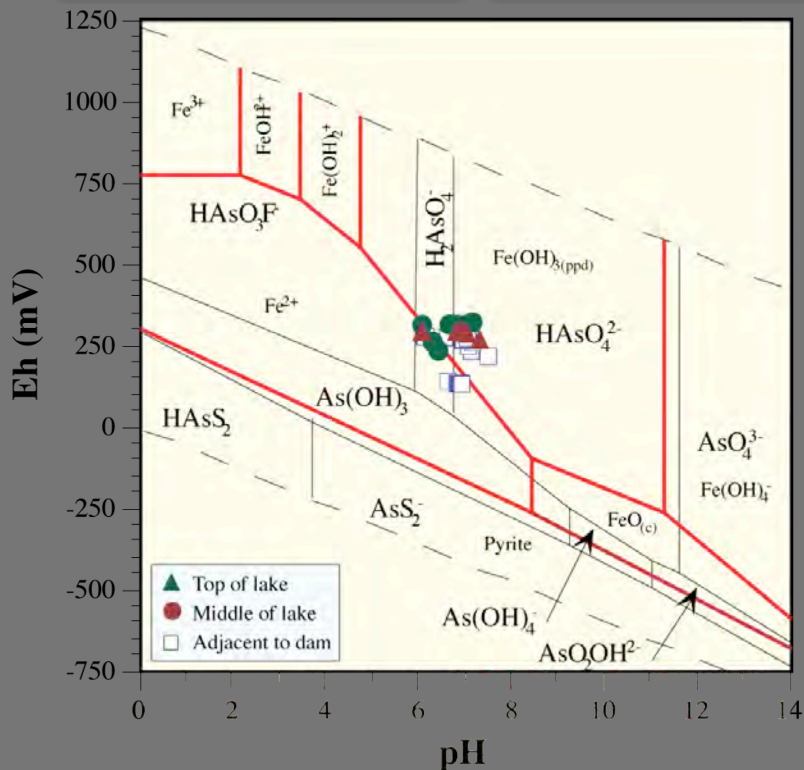
The best way to sample groundwater!

pH and Eh

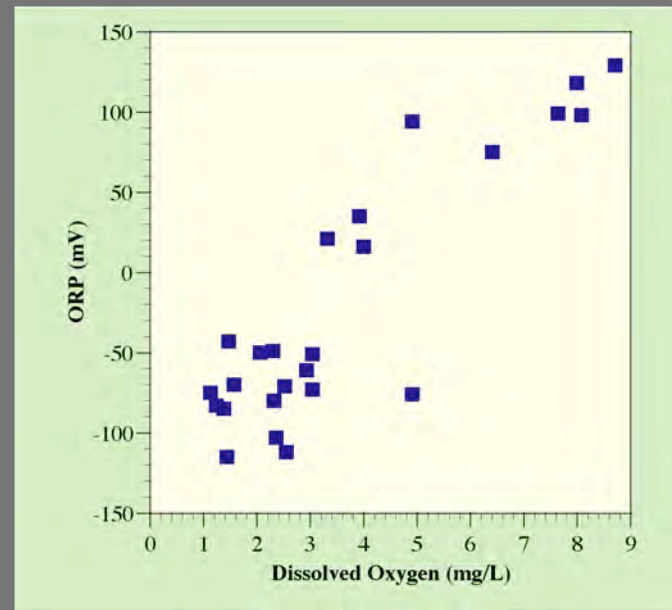


As-species
Se-species
Fe-species
S-species
Eh (mV)
pH
HSeO4-
H3AsO4
H2SeO3
HSeO3-
H2AsO4-
SeO4 2-
HAsO4 2-
AsO4 3-
Se(black)
As(OH)3
HAsS2
SeO3 2-
H2Se
FeSe2
AsS2
As(OH)4-
FeSe
AsO2OH2-
FeSO4+
Fe(OH)2+
Fe(OH)2+
HSO4-
Fe2+
Bailer
Fe(OH)3(ppd)
Fe(OH)4-
SO4 2-
Sulfur
H2S(aq)
Pyrite
HS-
FeO(c)
Double-valve pump

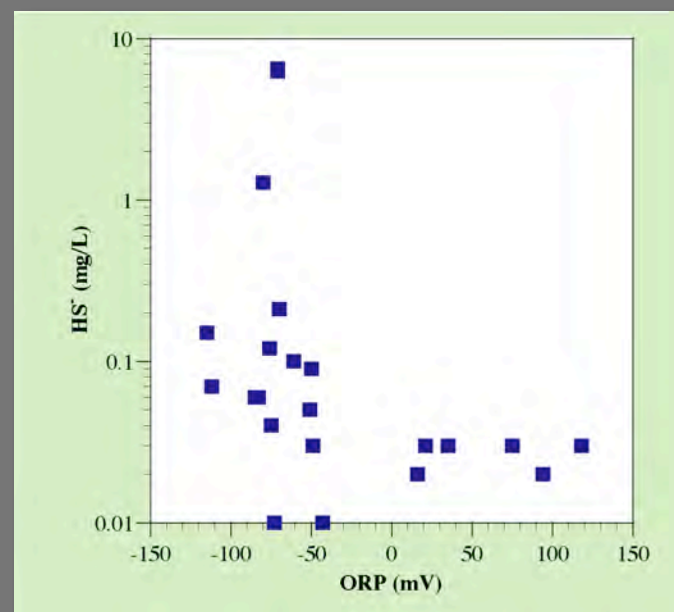
Redox



Eh (mV)
pH
Fe^{3+}
$FeOH^{2+}$
$Fe(OH)_2^+$
$HAsO_3F^-$
$H_2AsO_4^-$
$Fe(OH)_{3(ppd)}$
Fe^{2+}
$HAsO_4^{2-}$
$As(OH)_3$
$HAsS_2$
AsO_4^{3-}
$Fe(OH)_4^-$
AsS_2^-
$FeO_{(c)}$
Pyrite
$As(OH)_4^-$
AsO_2OH^{2-}
Top of lake
Middle of lake
Adjacent to dam

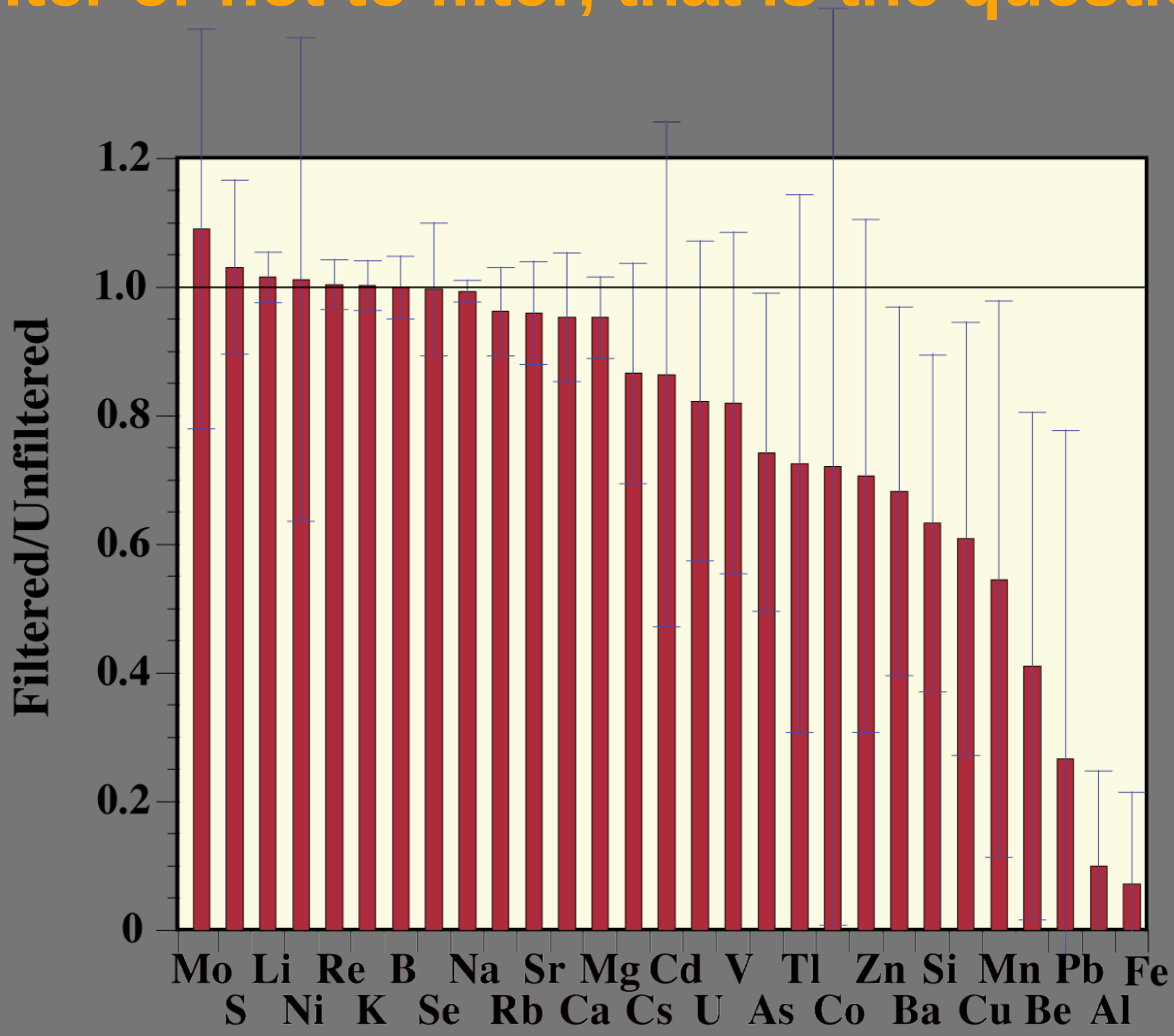


ORP (mV)
Dissolved Oxygen (mg/L)



HS^- (mg/L)
ORP (mV)

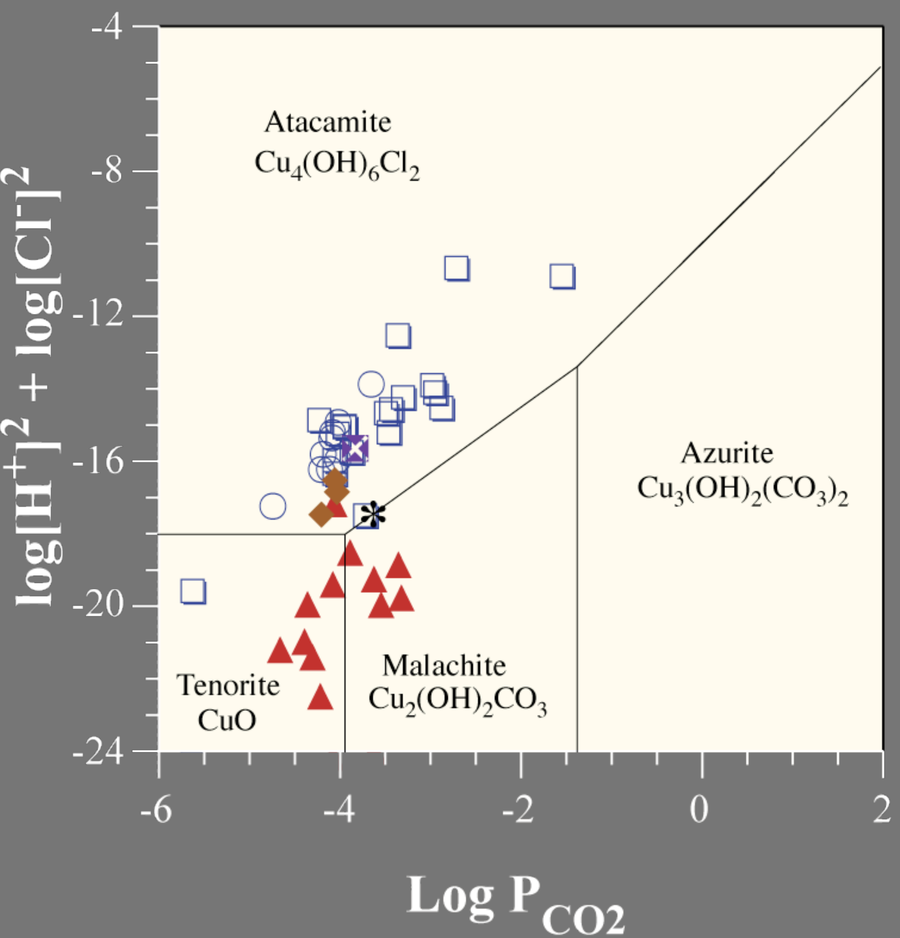
To filter or not to filter, that is the question

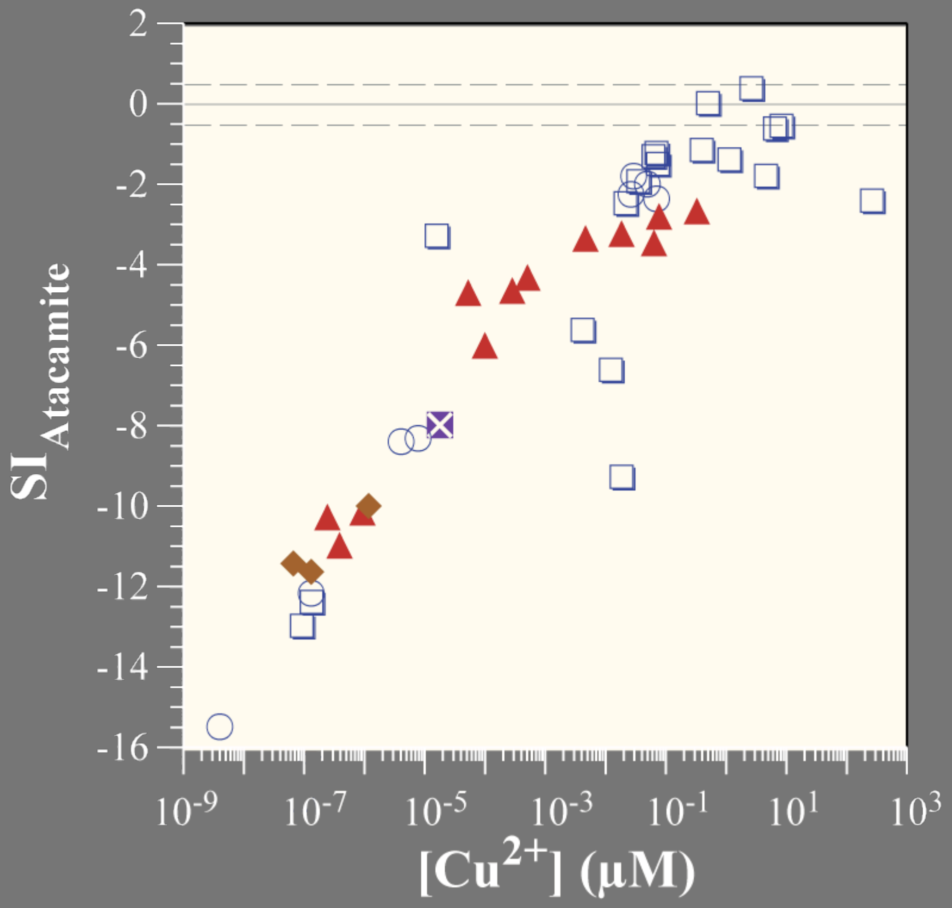


Lab methods

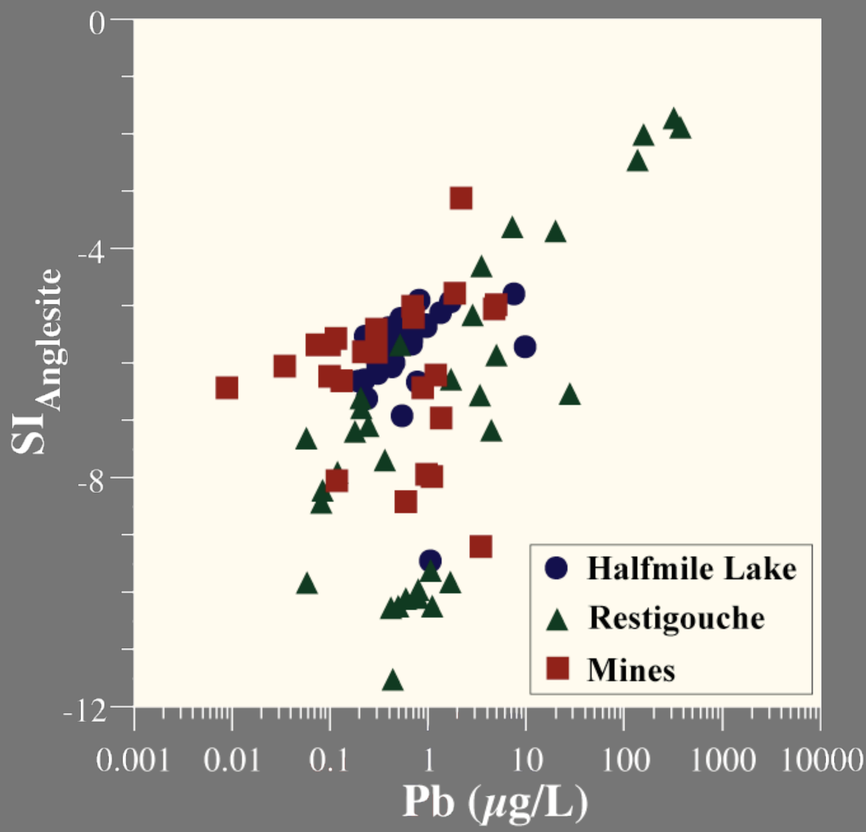
- Variety of methods used, depending on the nature of the study
- Major cations by ICP-OES
- Trace metals/metalloids by ICP-MS
- Anions by chromatography, but S can also be done by ICP
- Alkalinity by titration
- Isotopes by various forms of MS (TIMS, IRMS, MC-ICP-MS etc)

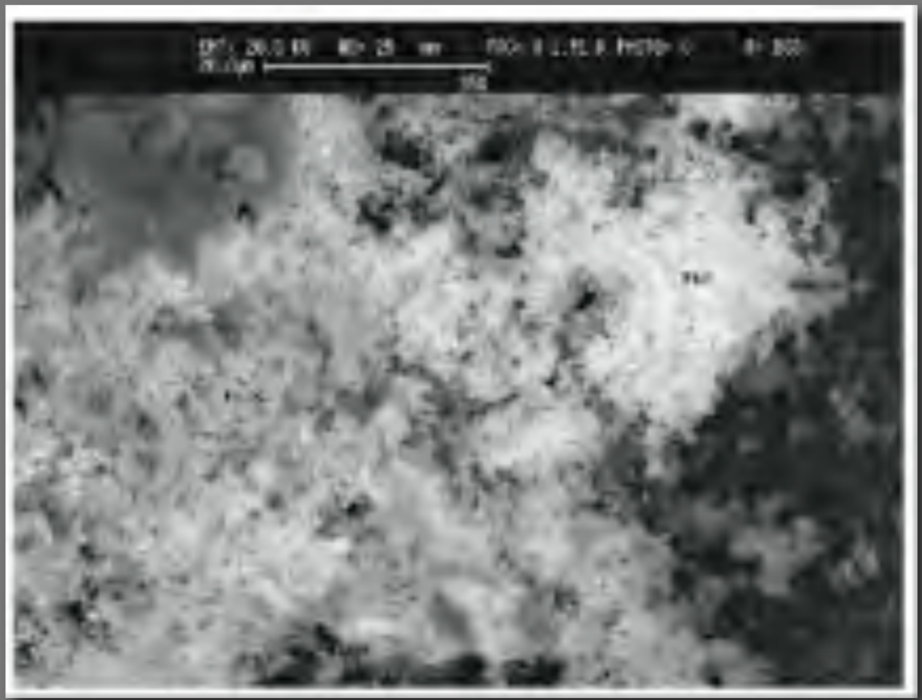
Speciation and modeling



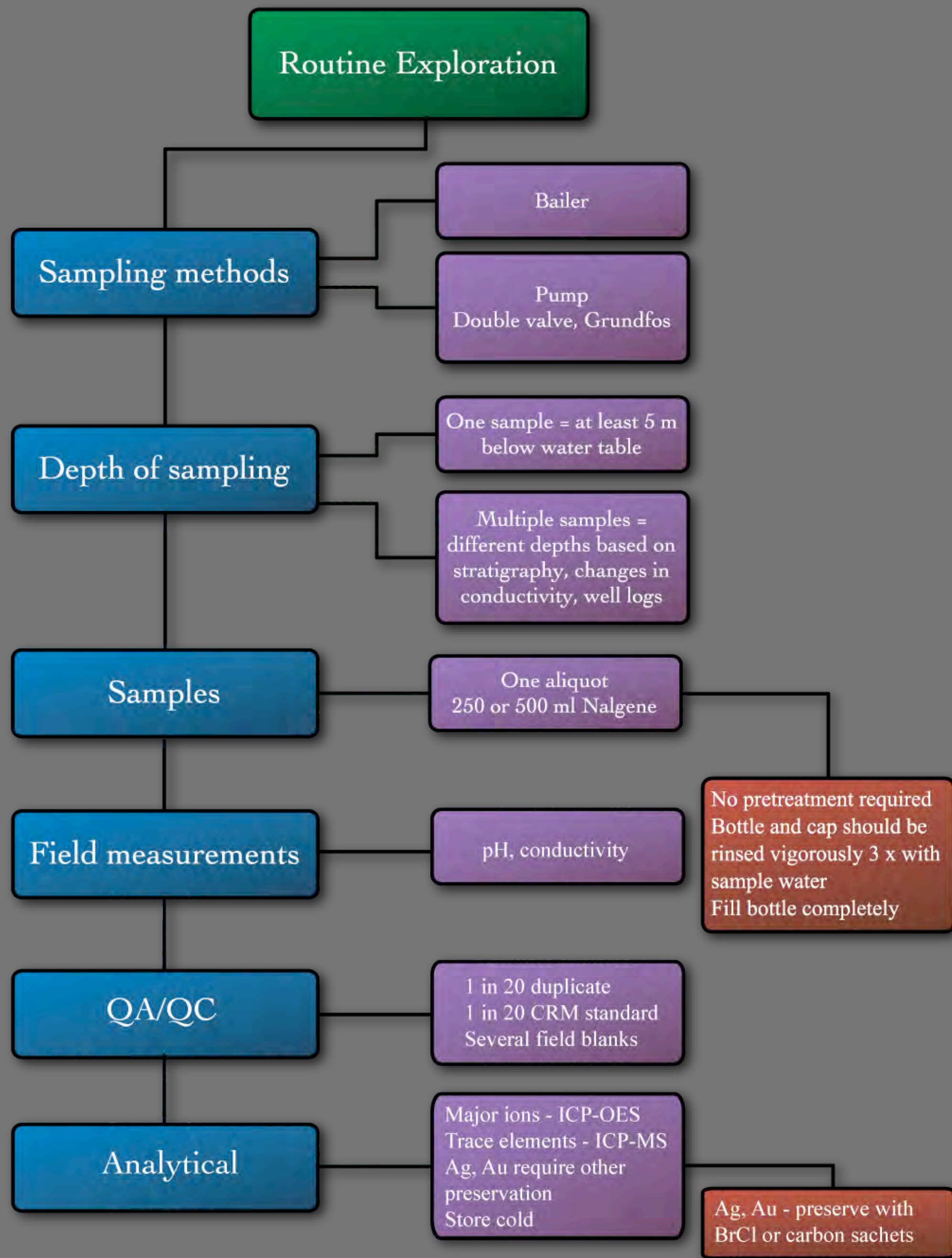


Speciation and modeling

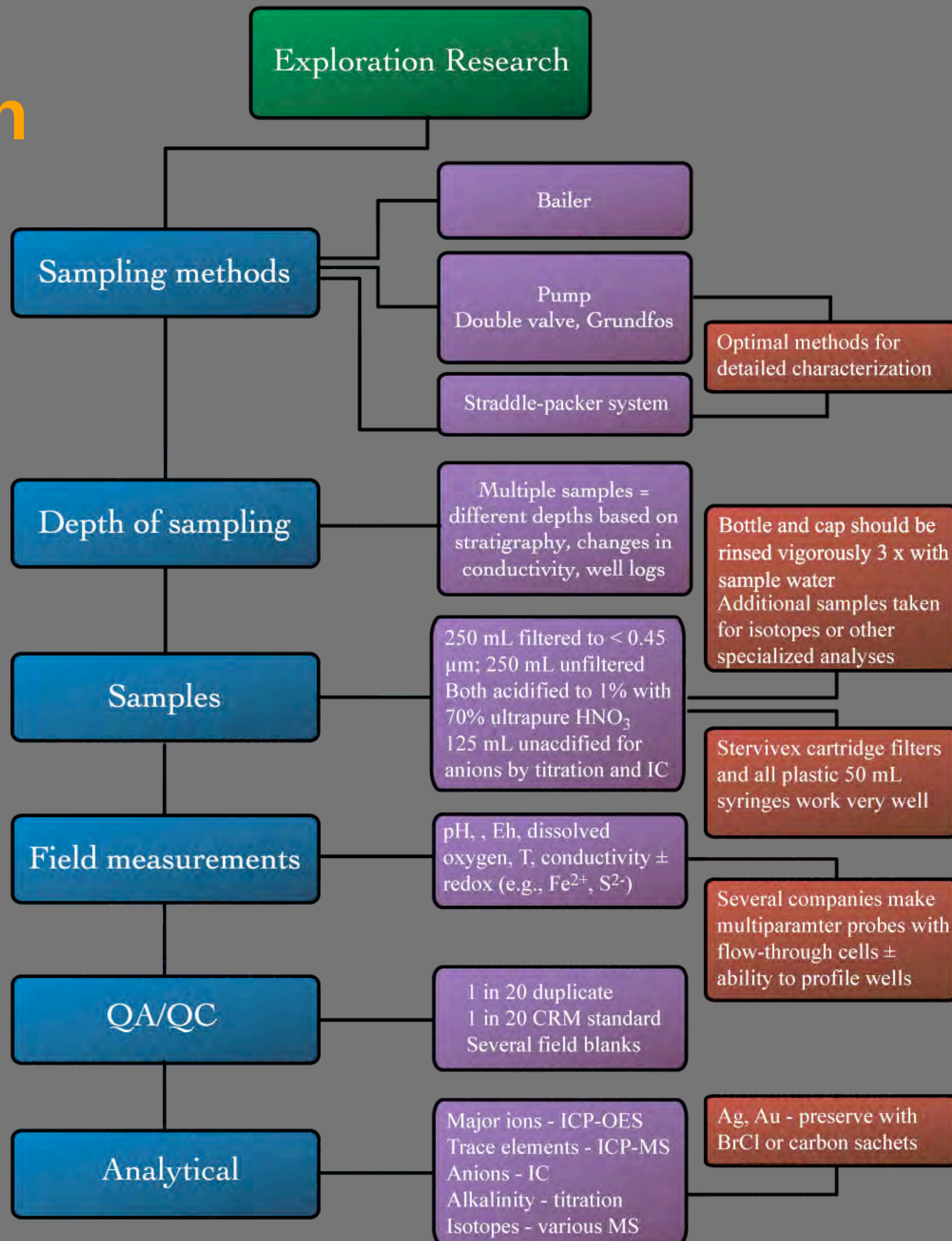




Routine Exploration



Exploration Research



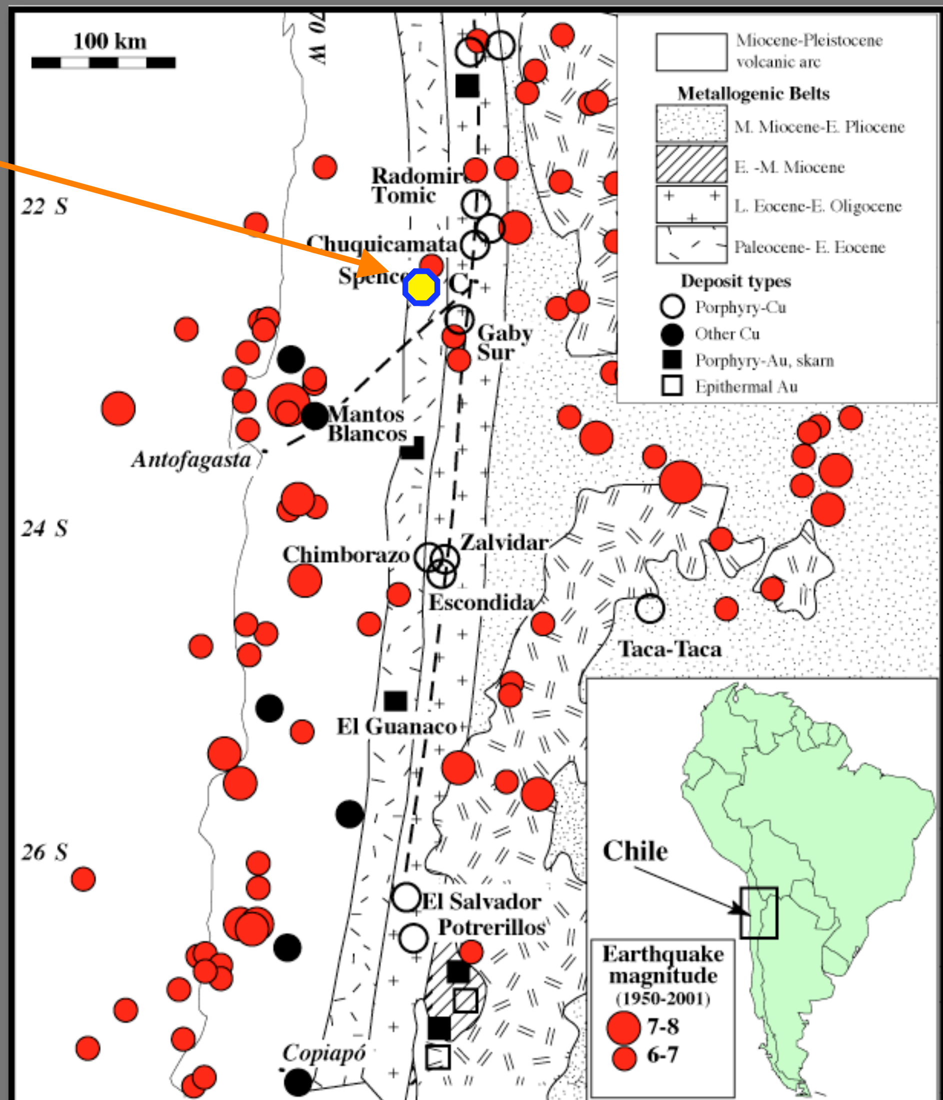
Case studies

Type of deposit	Major components	Minor components	Labile components[A]	Relatively immobile components[B]
VMS	Fe, S, Cu, Zn, Pb	Cd, Hg, Au, As, Sb, Ba, Bi, In	Fe, S, Zn, Cu, As, Cd, Hg, Sb	Pb, Bi, In, Au, Ag, Ba
Porphyry Cu ± Mo	Cu, Mo, S	Fe, Ag, Au, Se, Re, As	Cu, Mo, S, Fe, Se, As, Re	Ag, Au
SEDEX	Fe, S, Cu, Zn, Pb	Ag, Au, Ba, Cd	Fe, S, Zn, Cu, Cd	Pb, Ba, Au, Ag
Gold (vein)	Au, Ag	As, Sb, Se, Te, S, Hg	S, Se, As, Hg, Te, Sb	Au, Ag
Ni-Ci-PGE	Ni, Cu, PGE	Cr, Co, S	Cu, S, PGE	Co, Ni, Cr
Kimberlite (diamond)	Sr, Nb, Ba, Cr, Ni	LILE, HFSE, REE	Sr, LILE	Ba, HFSE, Nb, Ba, Cr, Ni, REE
Unconformity uranium	U	Se, Mo, V, Cu, Pb	U, Se, Cu, Mo	U, Pb, V

A. Under oxidizing and near neutral conditions
B. Under normal conditions; e.g., Ba is immobile in the presence of S as SO_4 owing to insolubility of barite.
LILE, large ioon lithophile elements; HFSE, high-field strength elements; REE, rare earth elements
Table modified after McMartin and McClenaghan (2001)

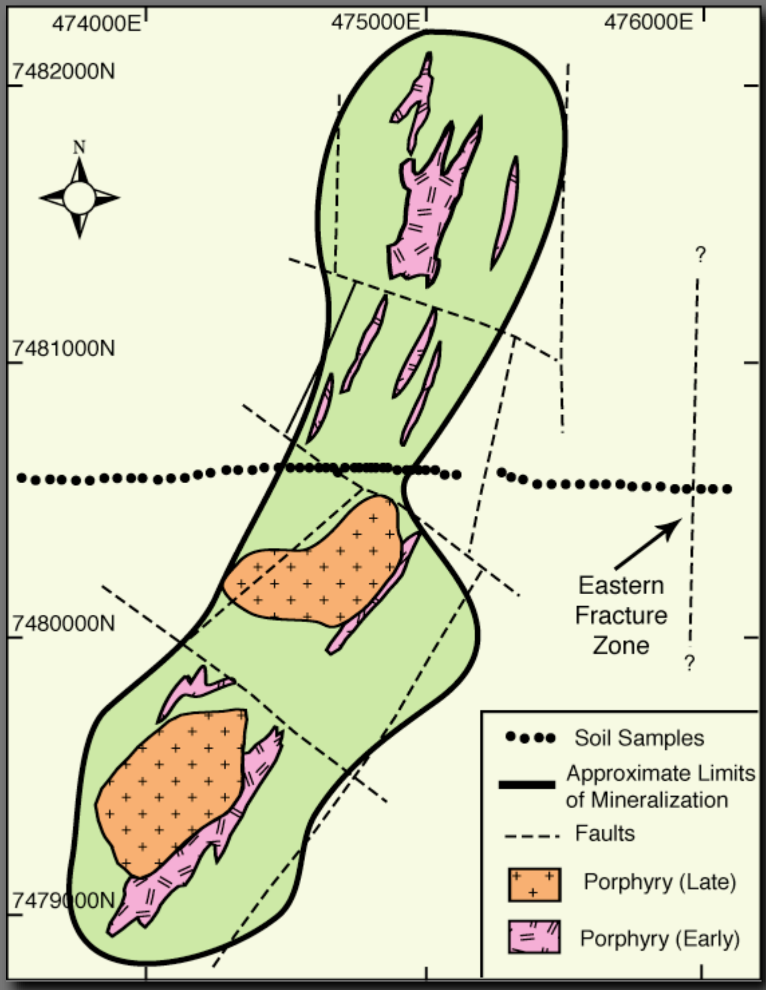
Case study: porphyry copper (Chile)

Spence deposit



Case study: porphyry copper (Chile)

- **Porphyry copper deposit, with 74.8 Mt @ 1.24% oxide Cu, 238 Mt of sulfide Cu @ 1.03%**
- **Hosted in andesitic volcanic rocks, associated with three quartz-feldspar porphyries**
- **Supergene alteration prior to mid-Miocene, produced leached cap - enriched oxide zone over supergene and hypogene sulfides**



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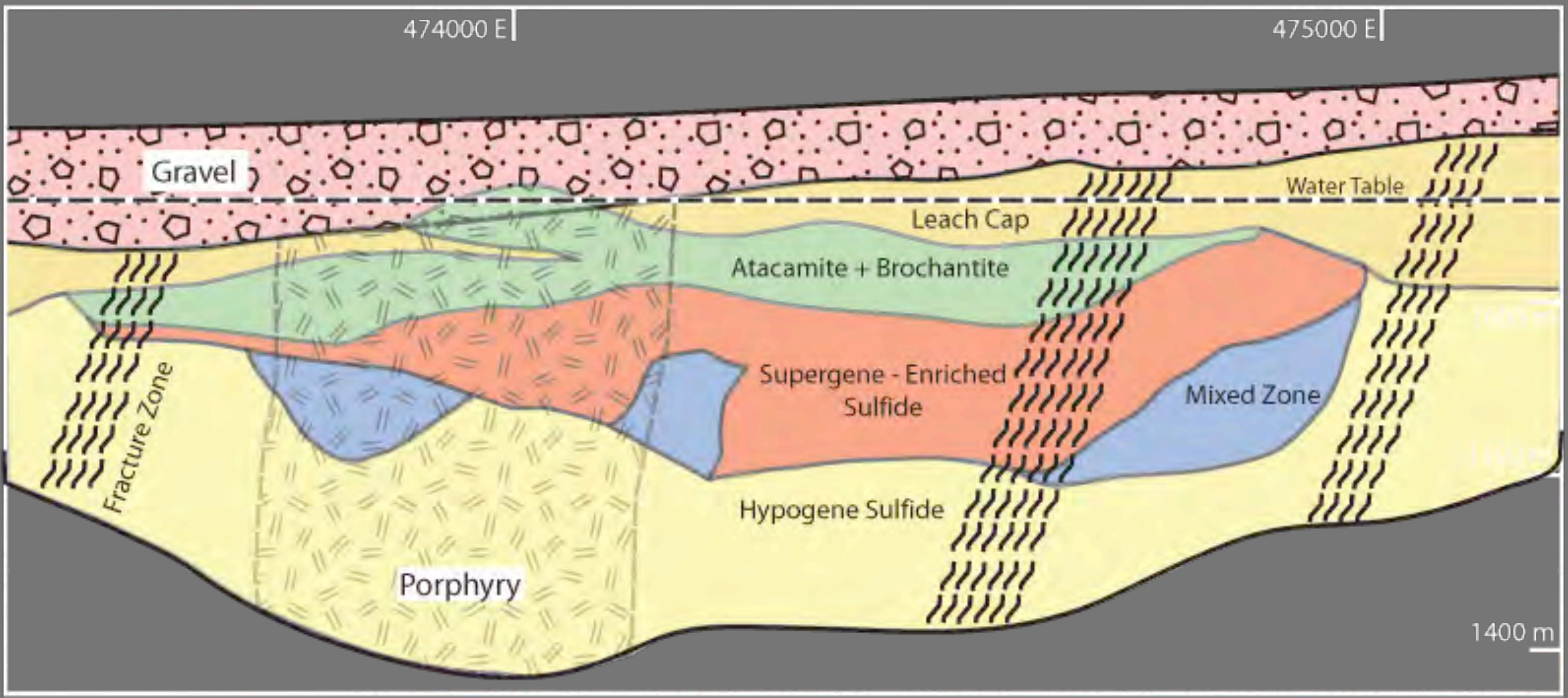

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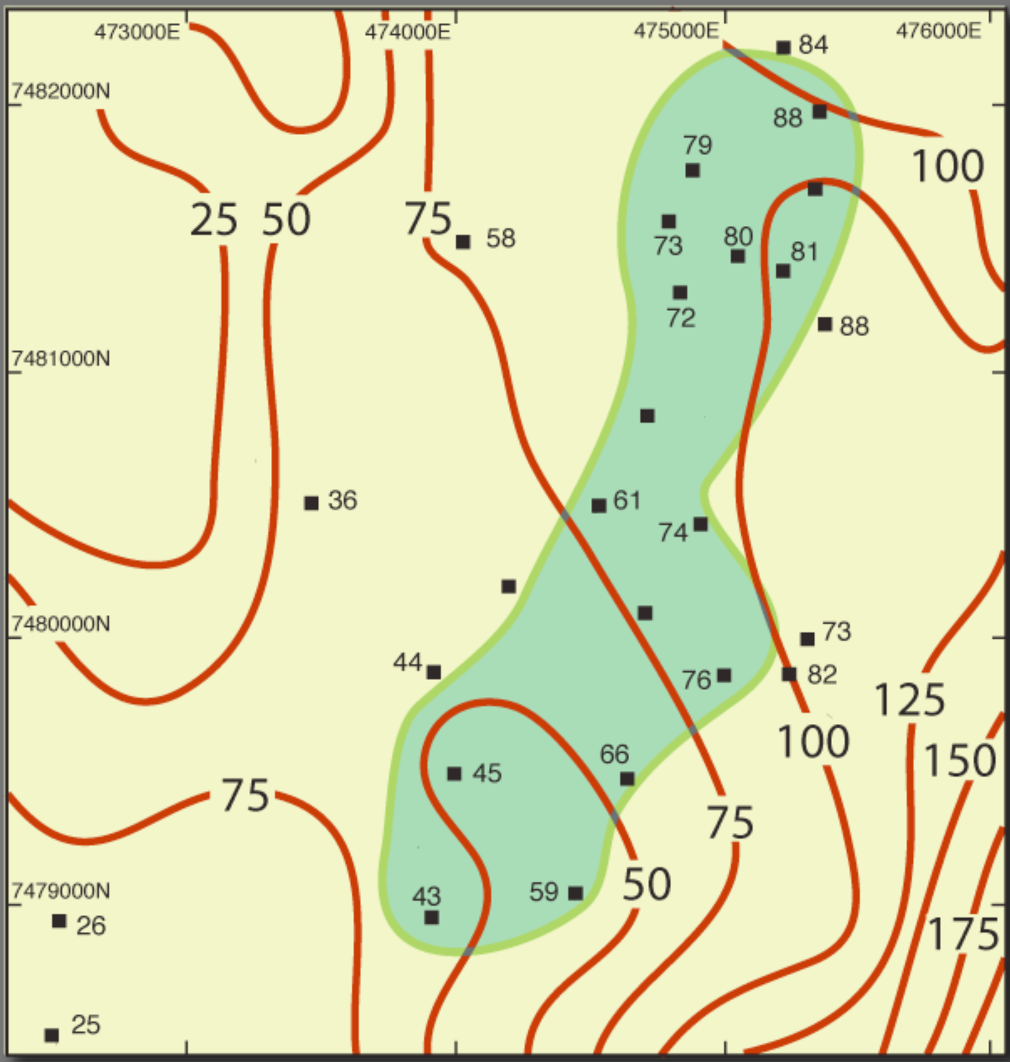

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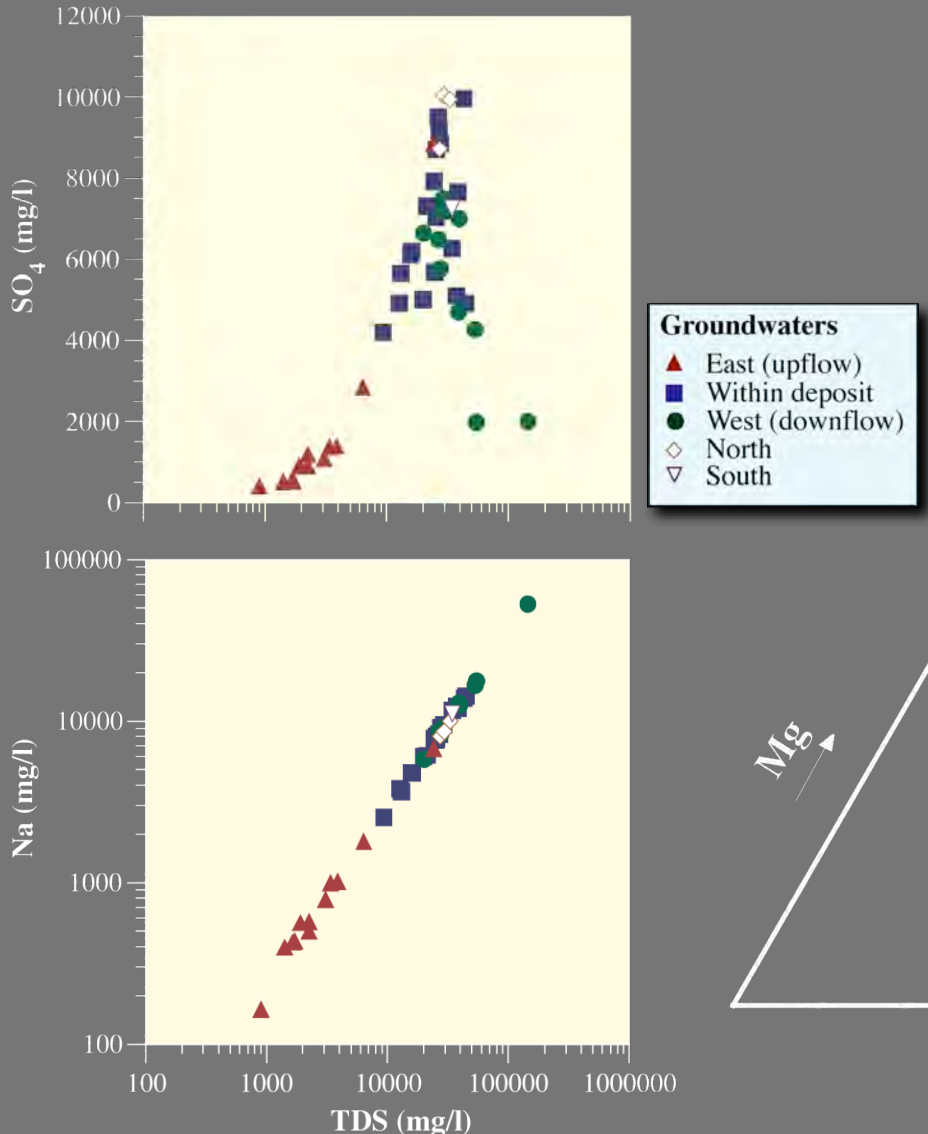

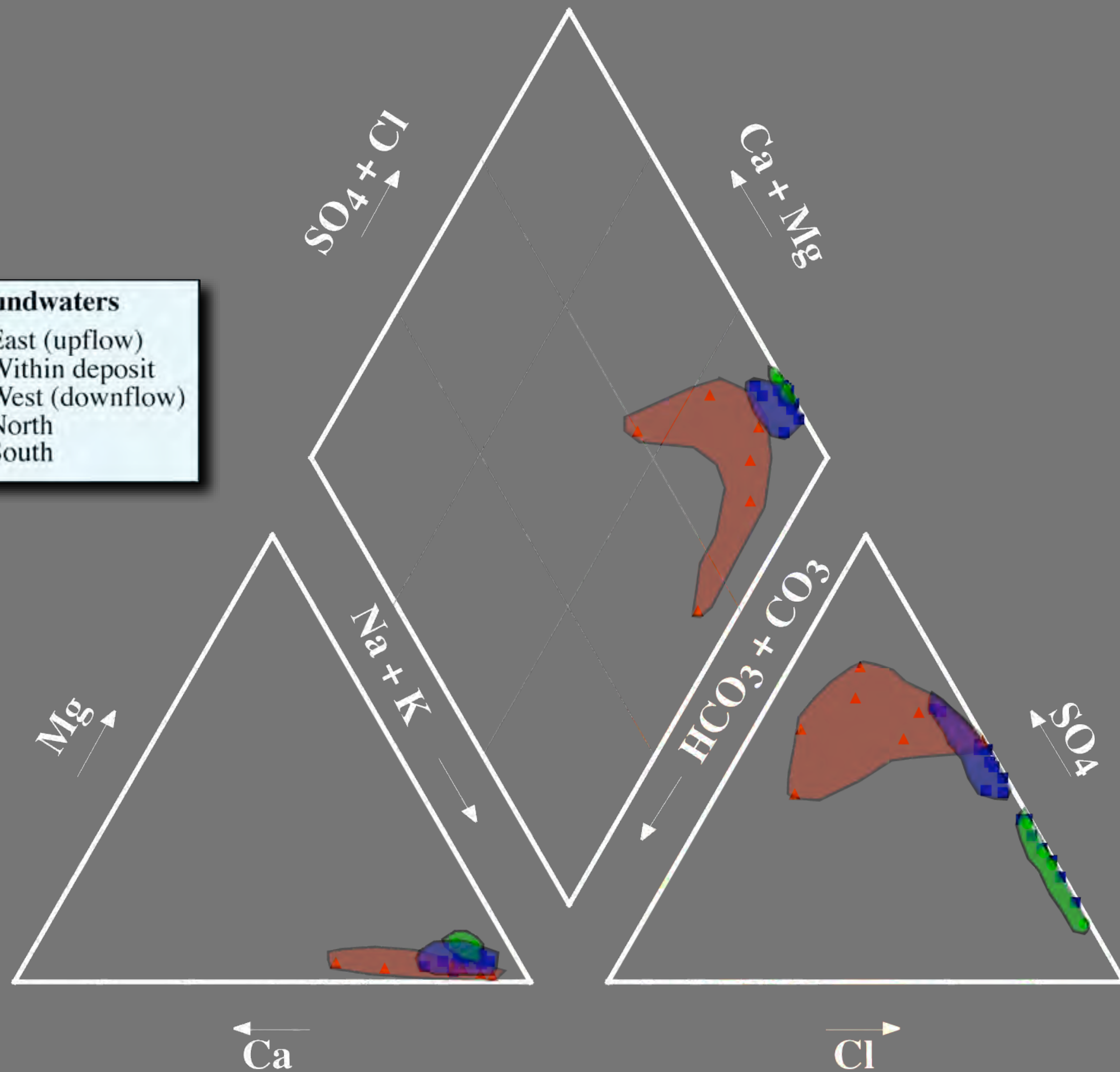

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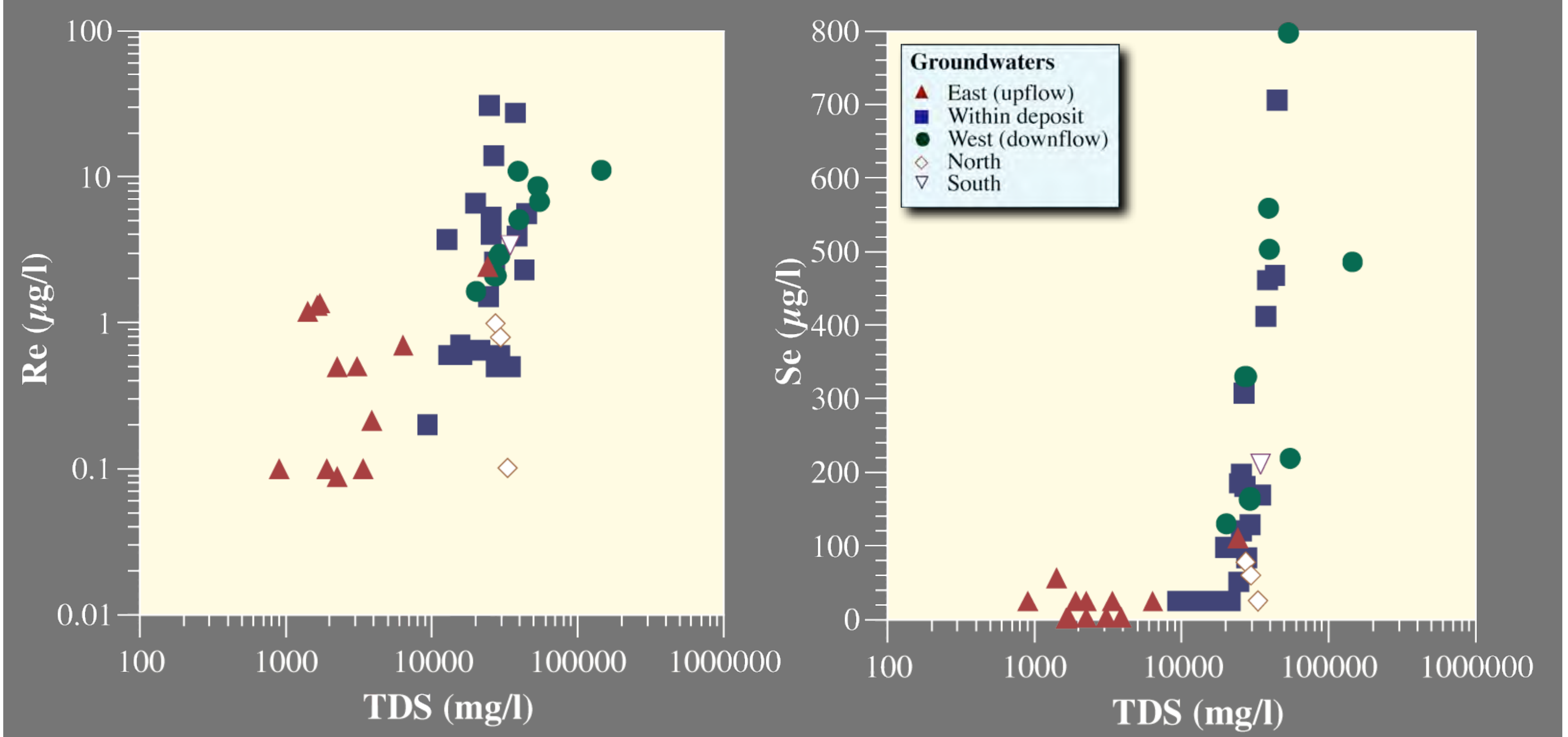

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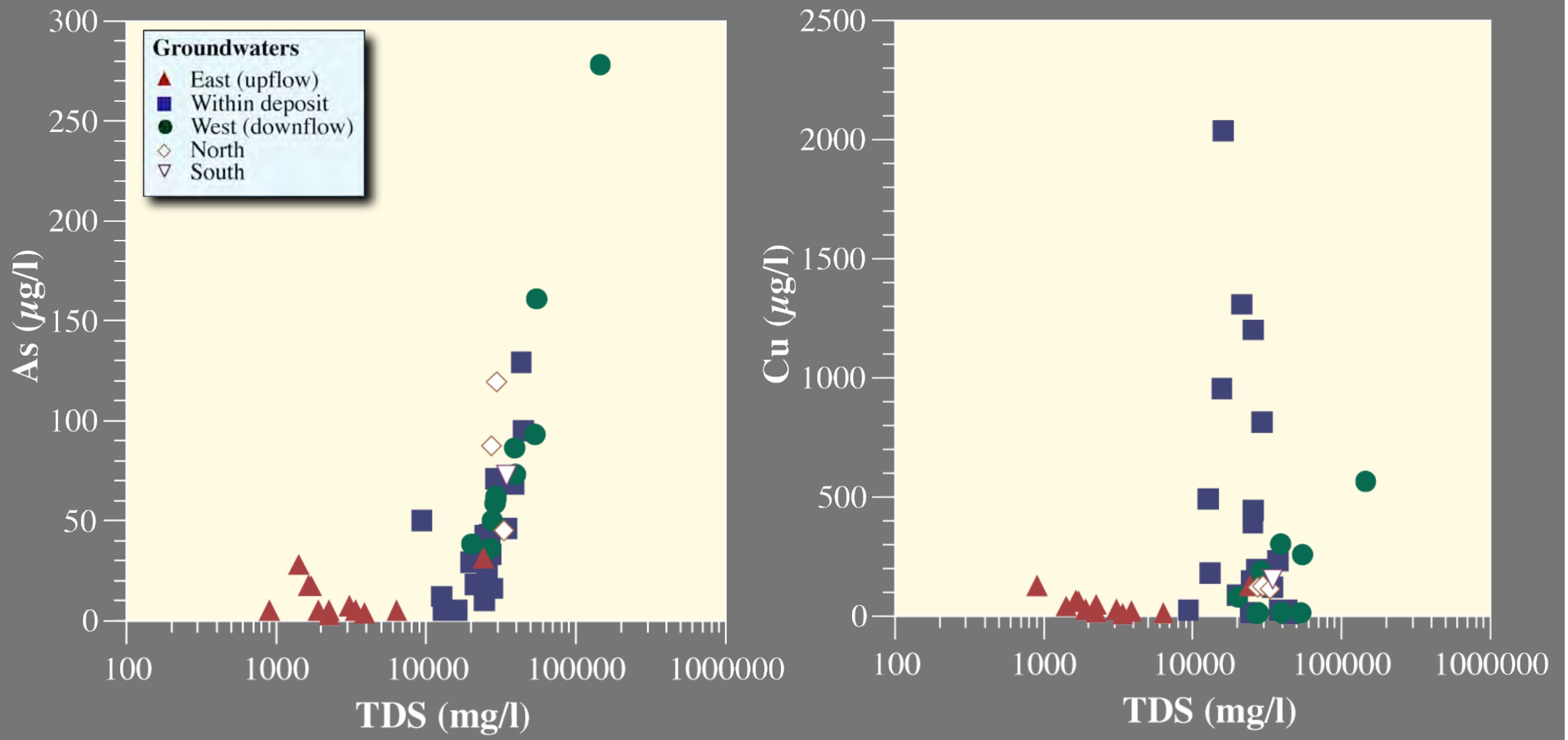

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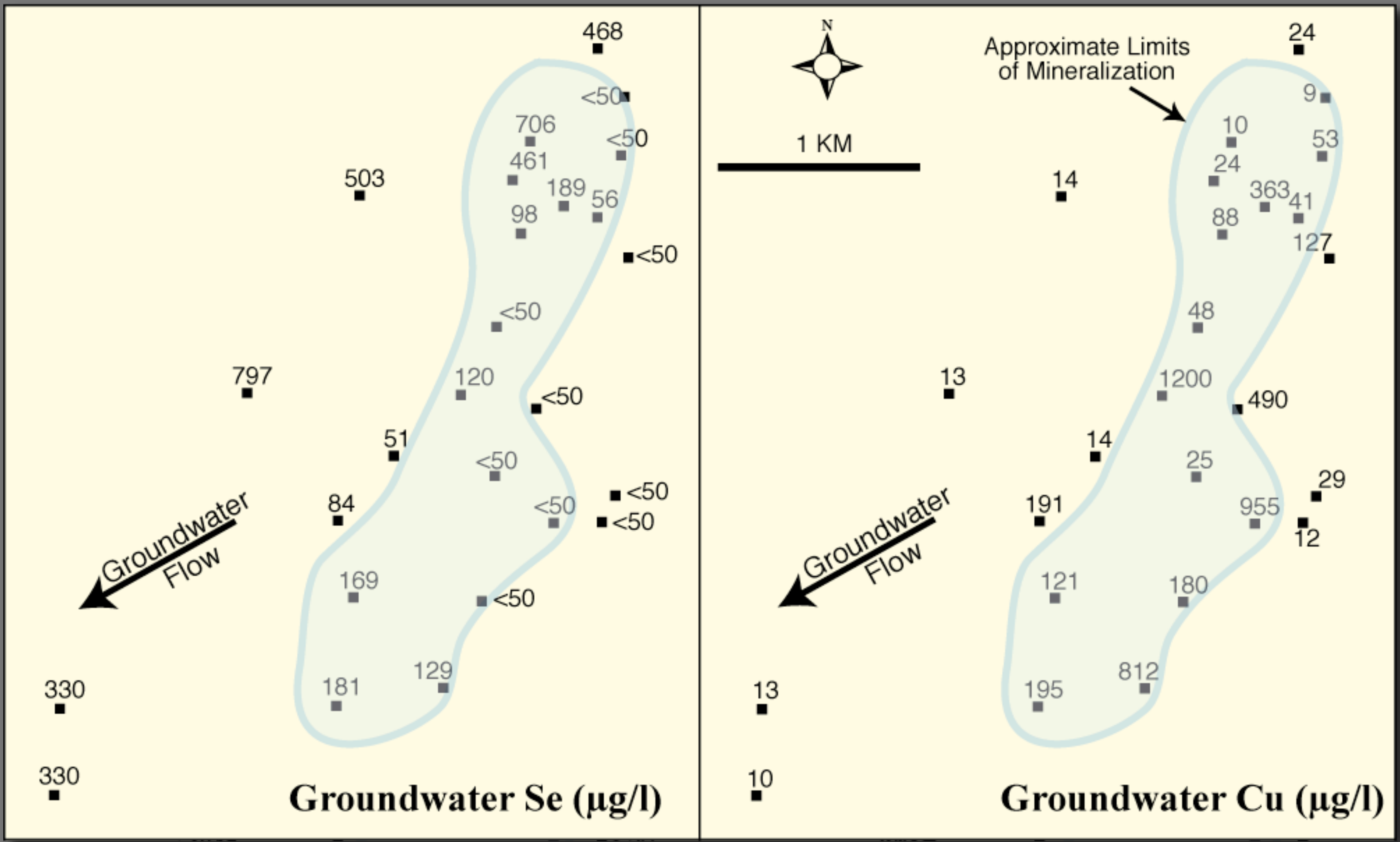

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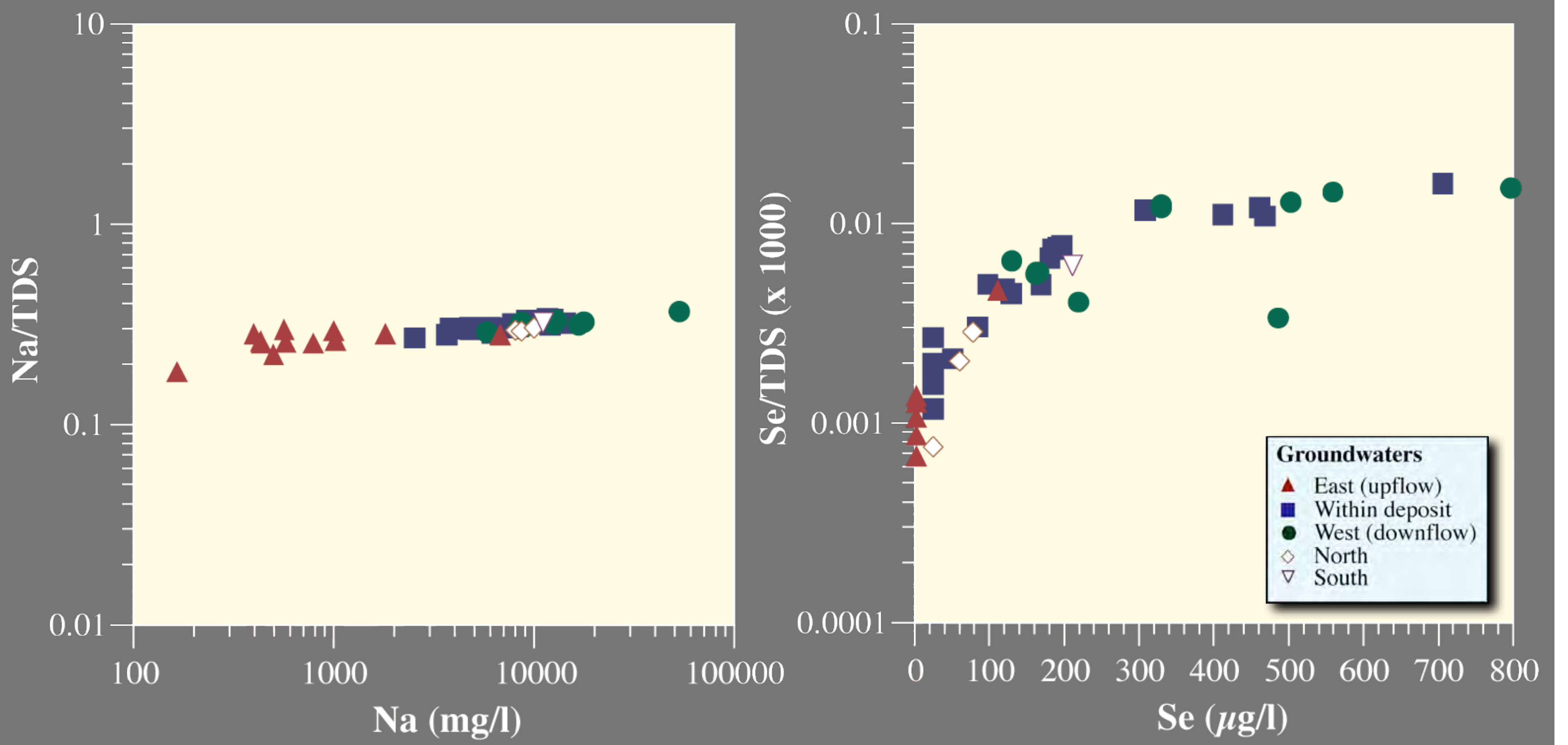

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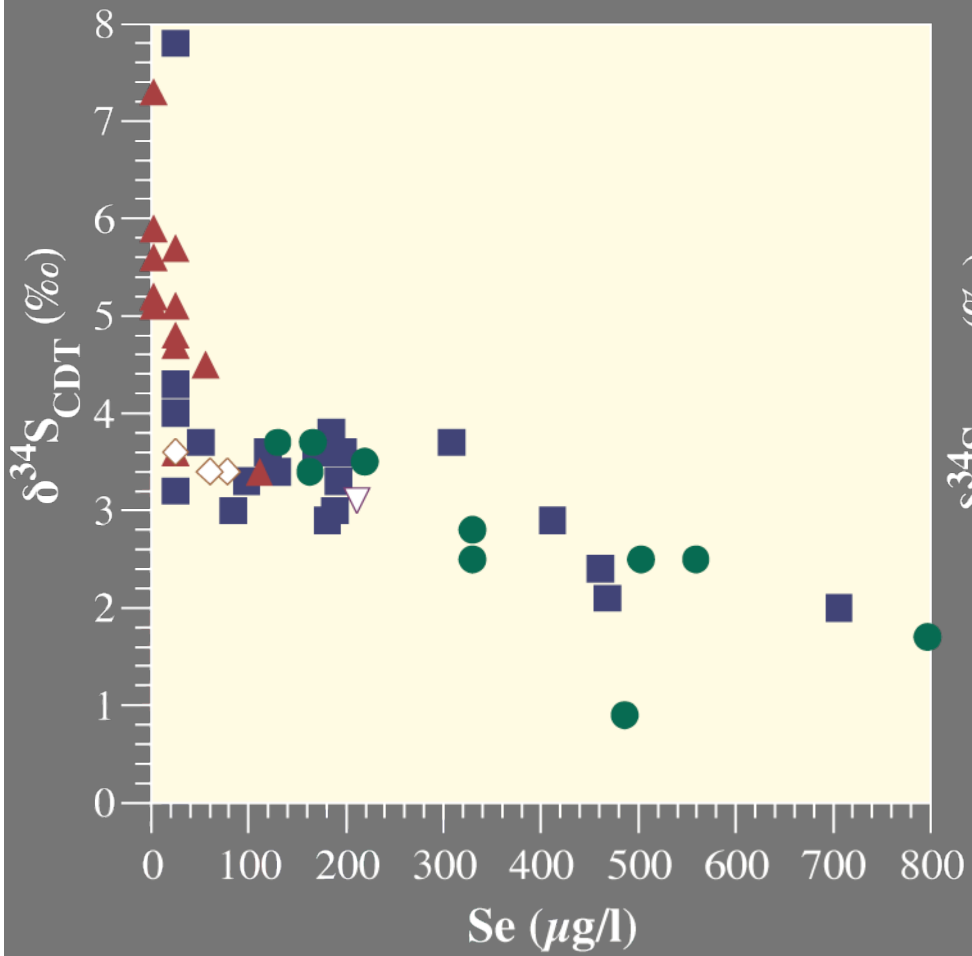

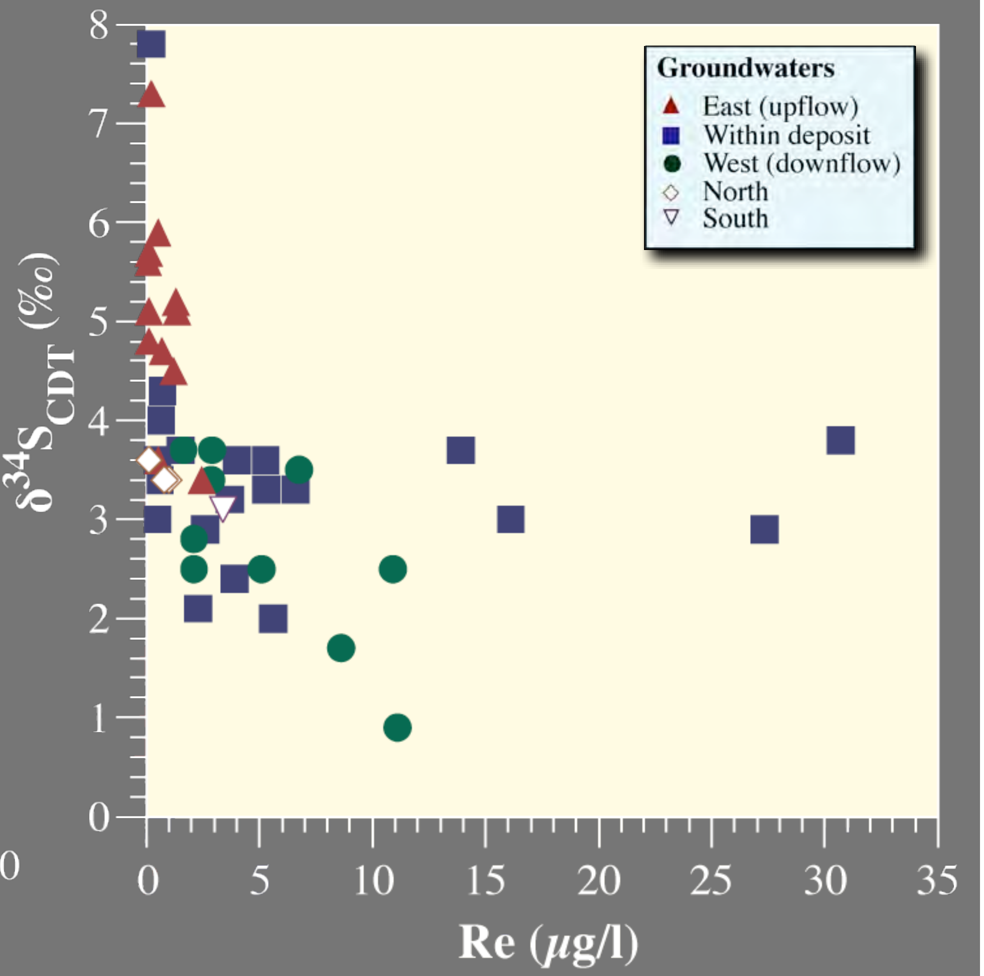

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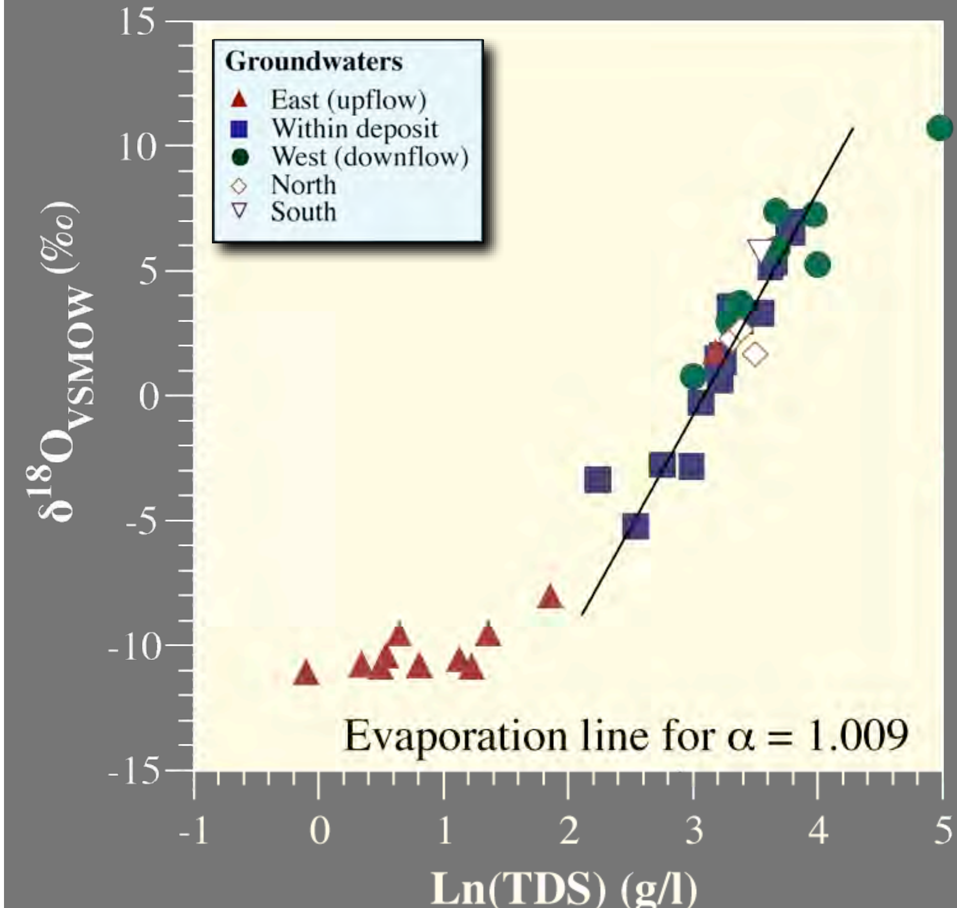

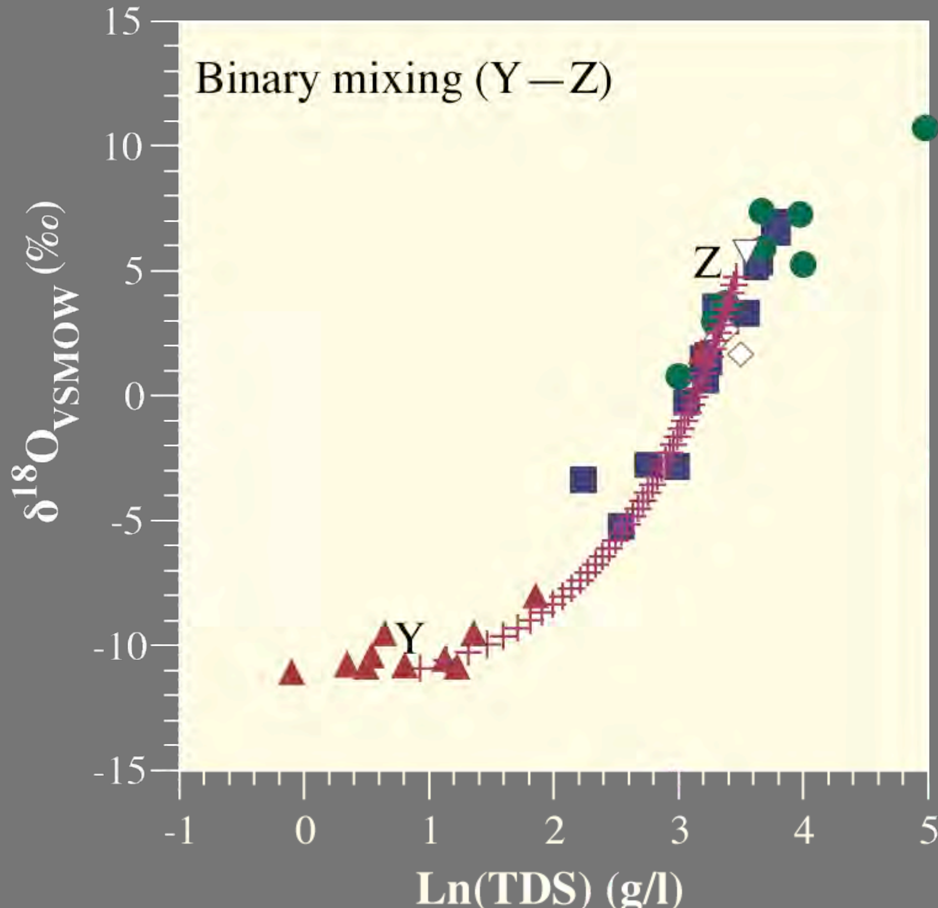

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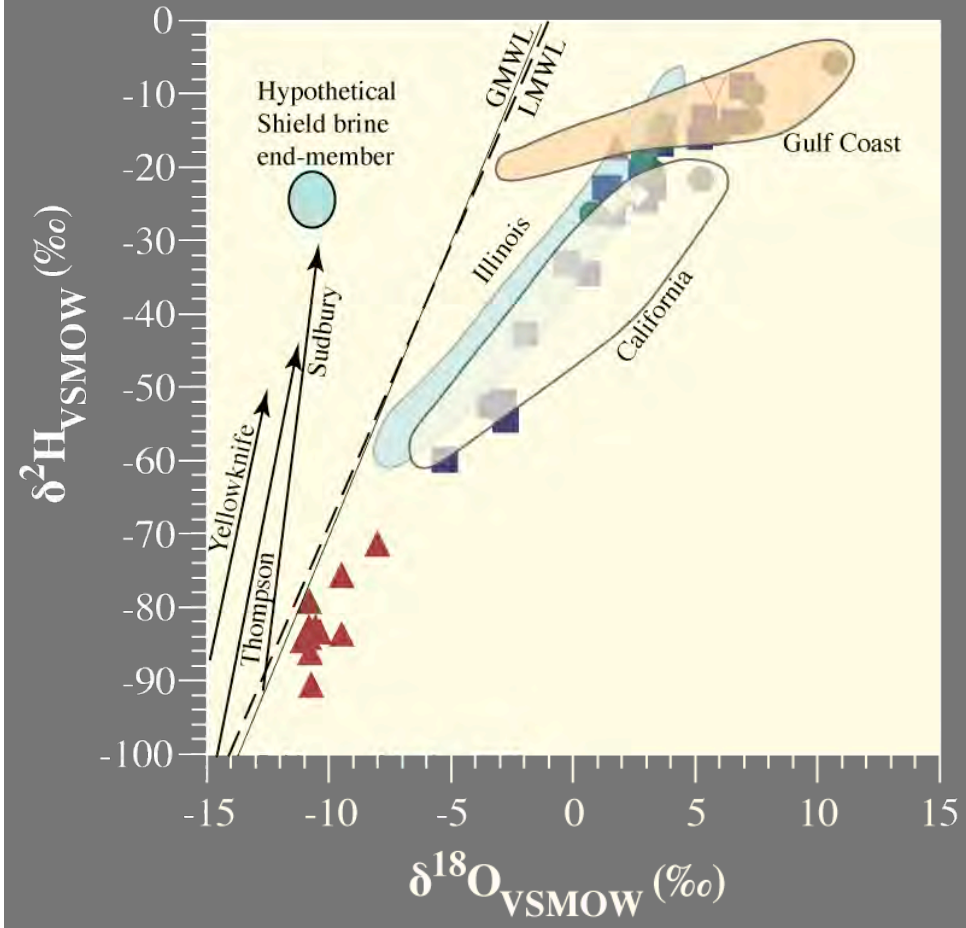
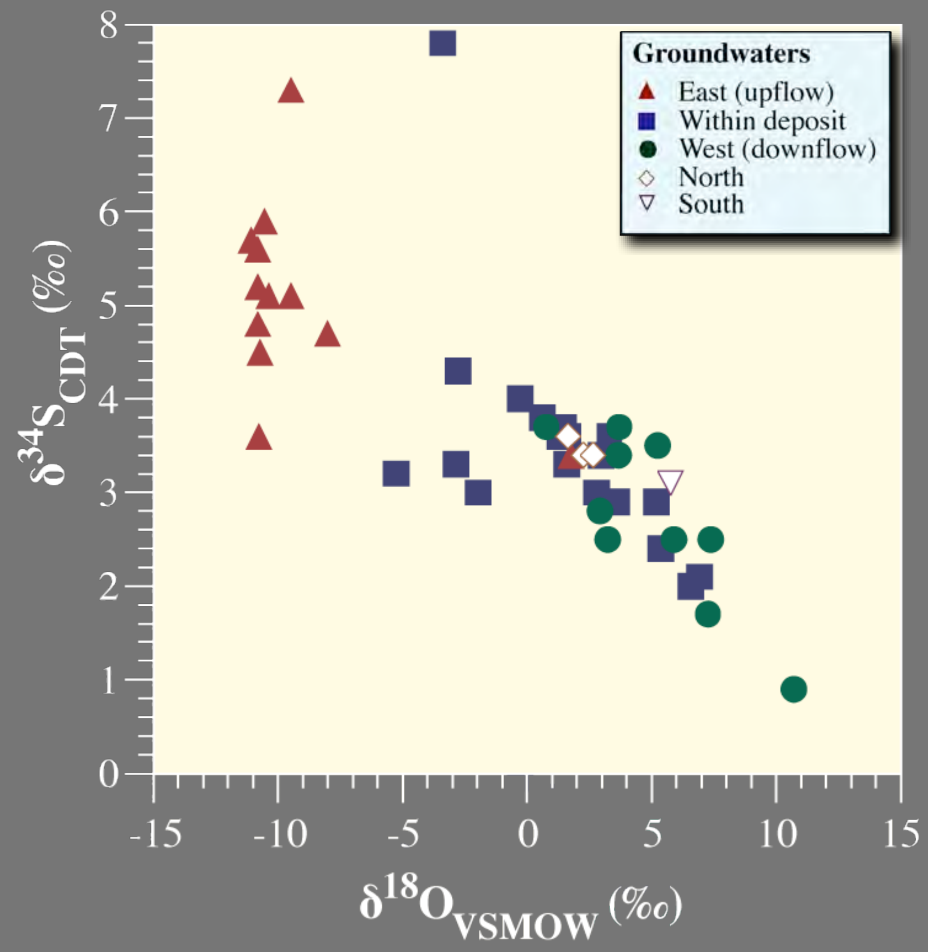
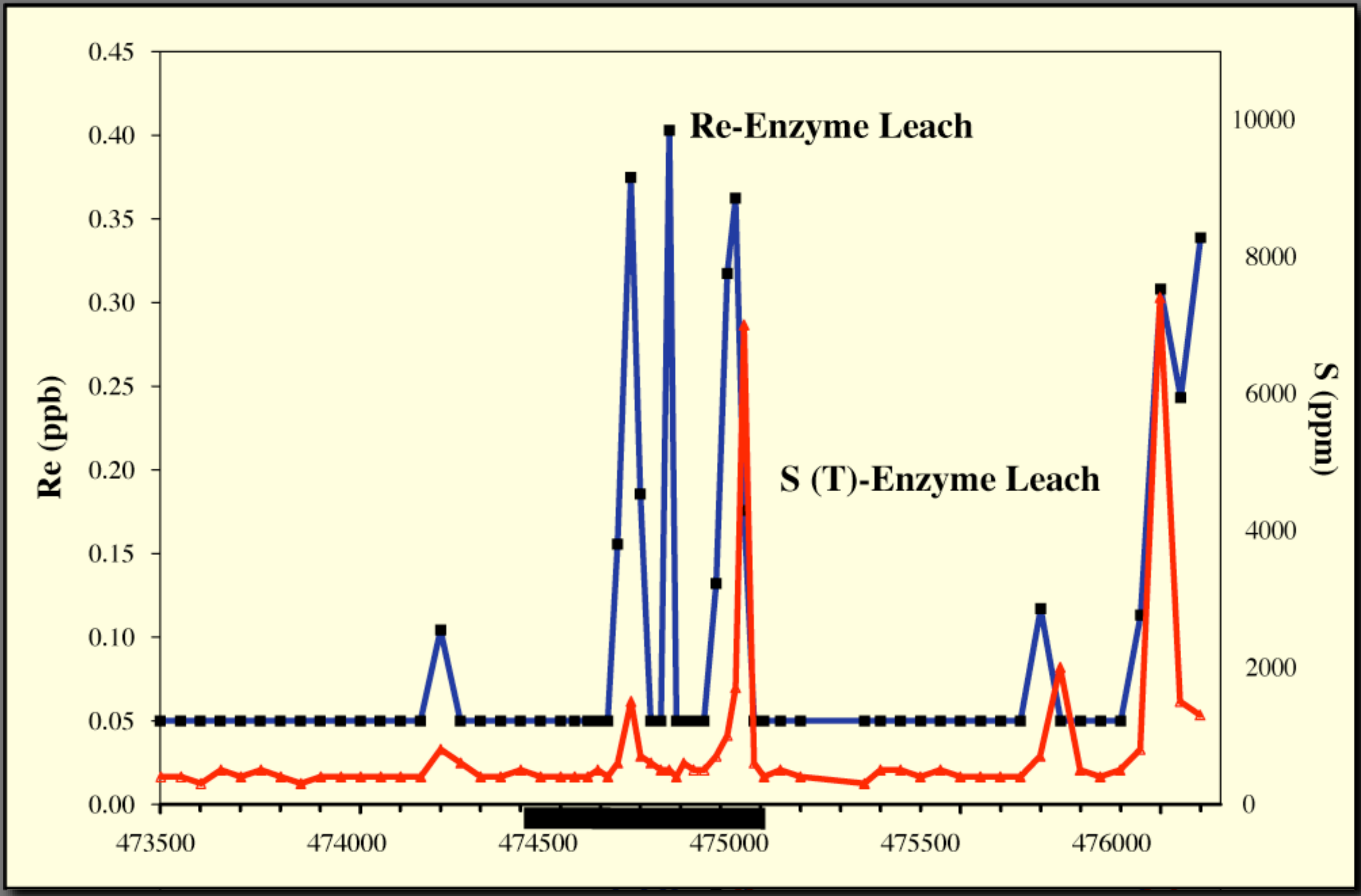




Lessons from Spence groundwater - soil geochemical anomalies



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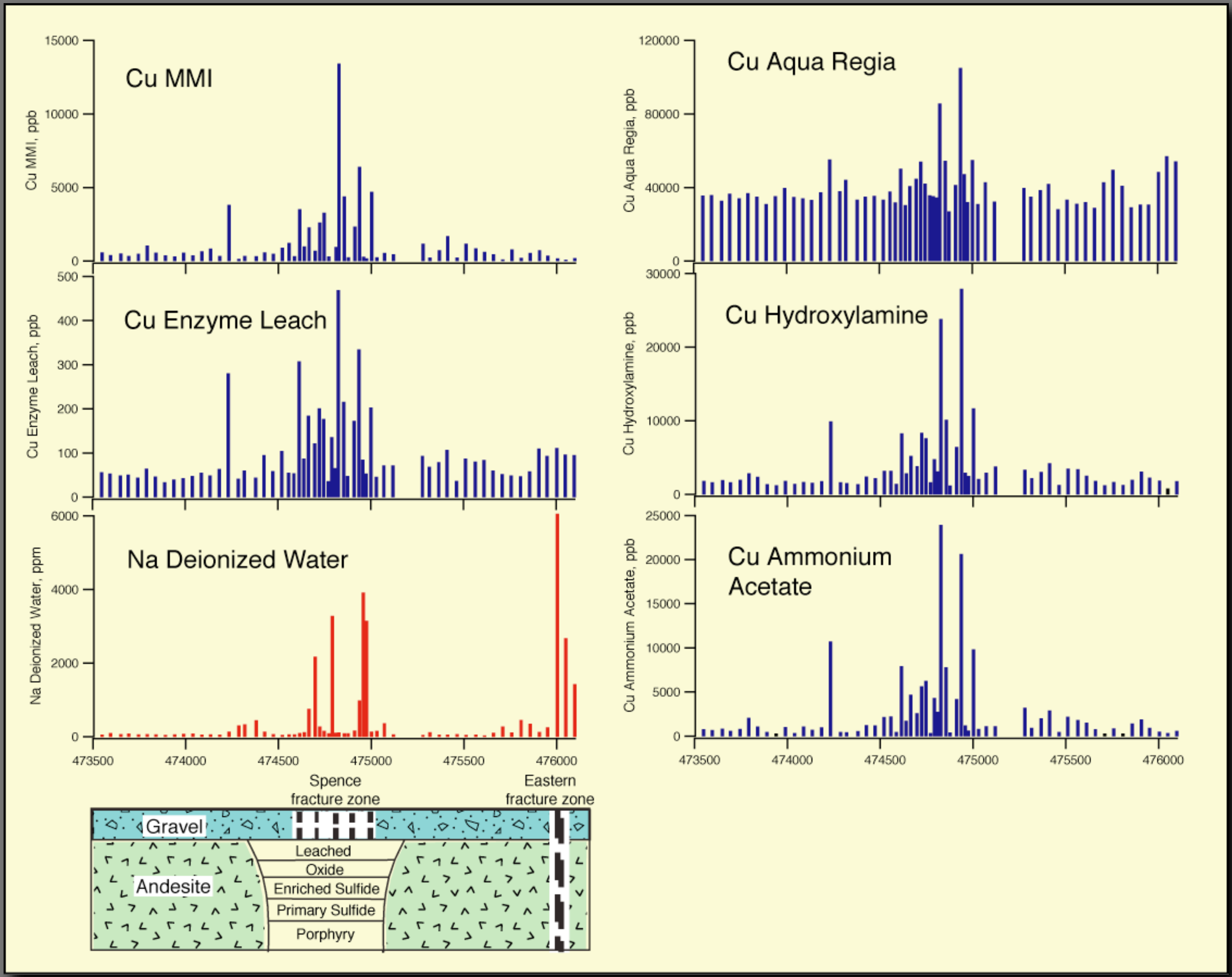
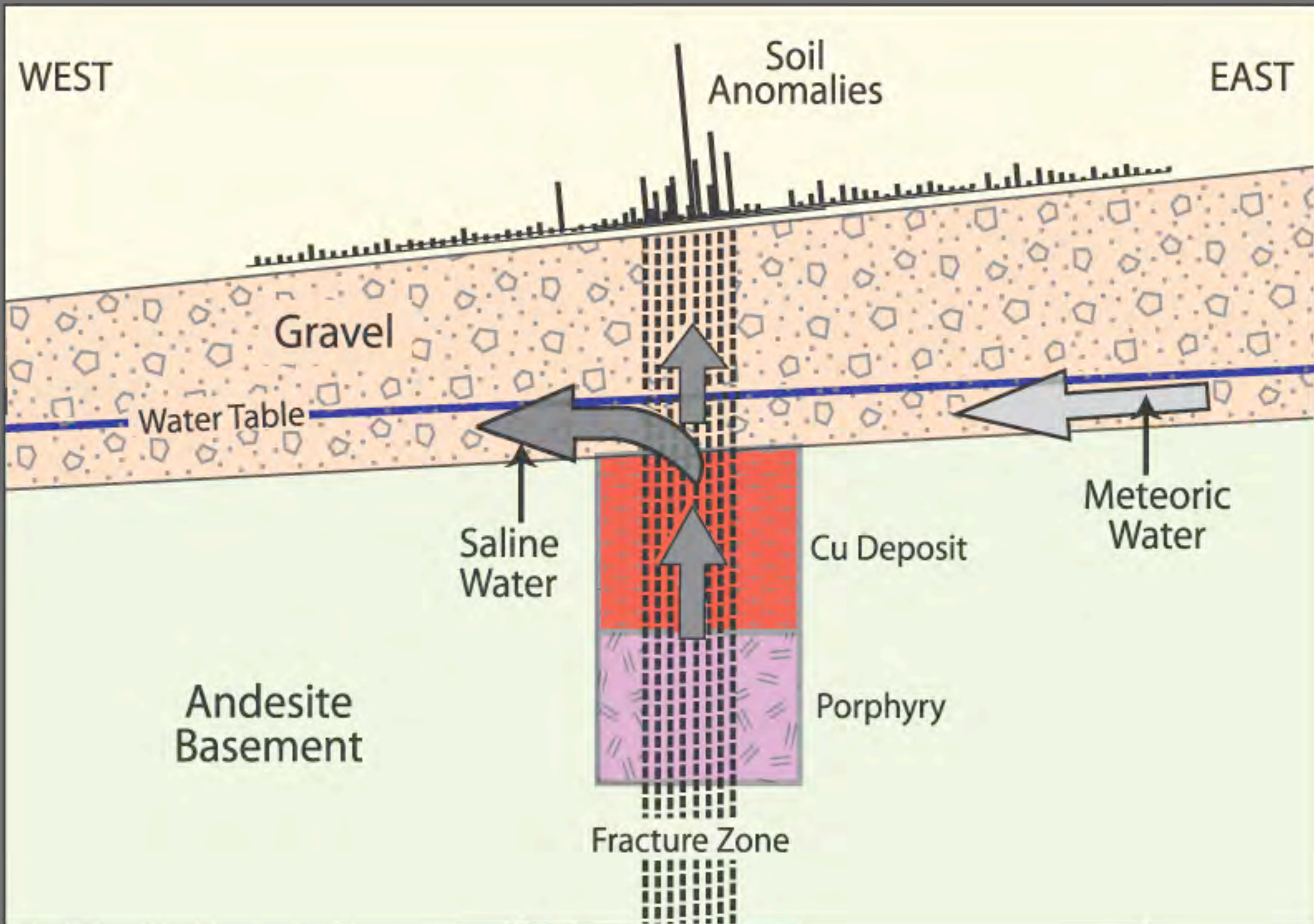
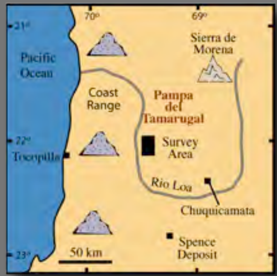
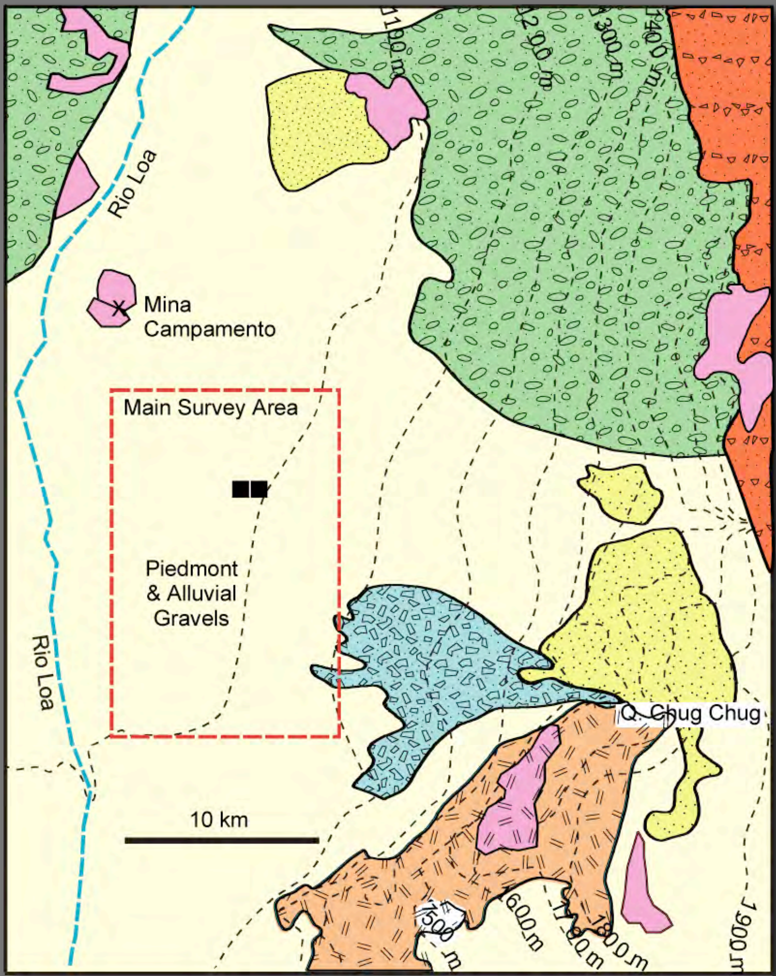


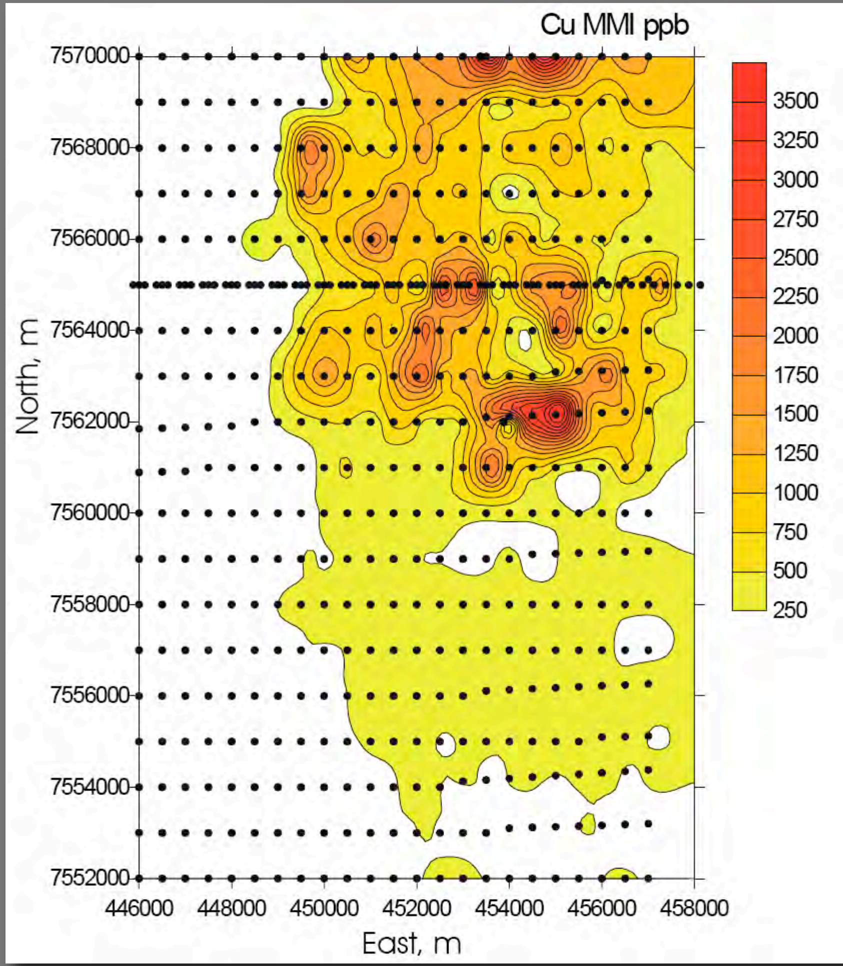
Conceptual model



Lessons from Spence groundwater - Tamarugal







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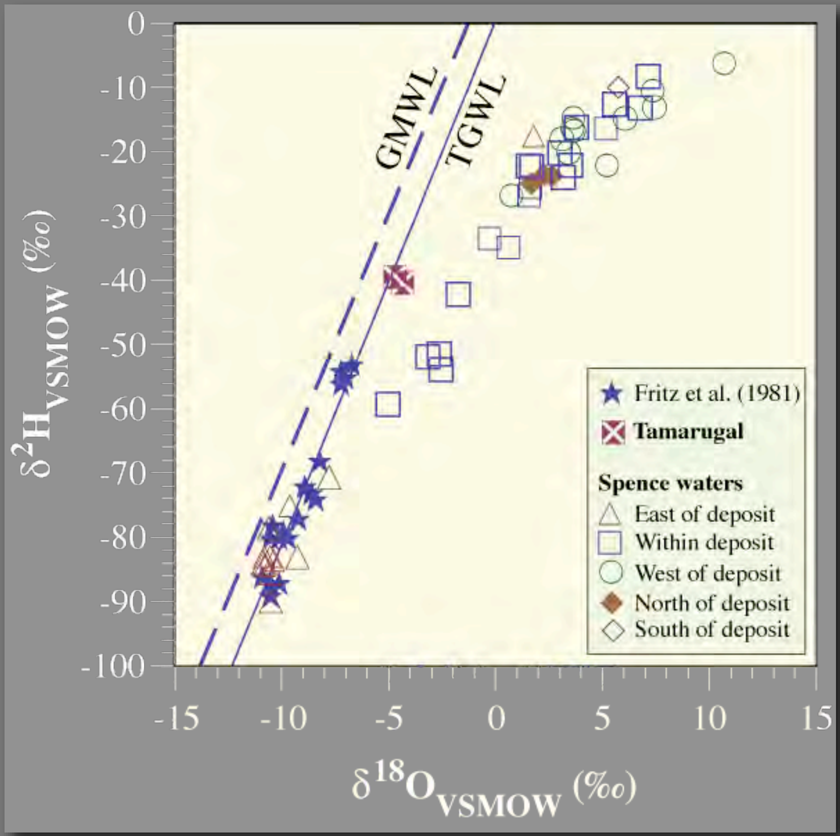
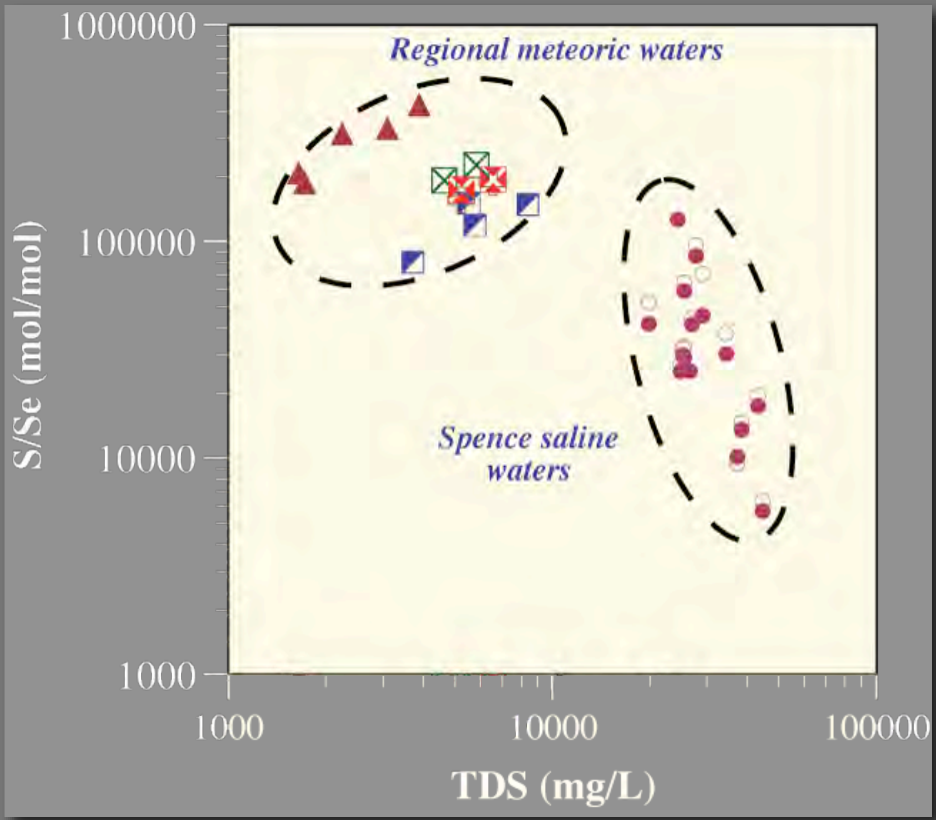
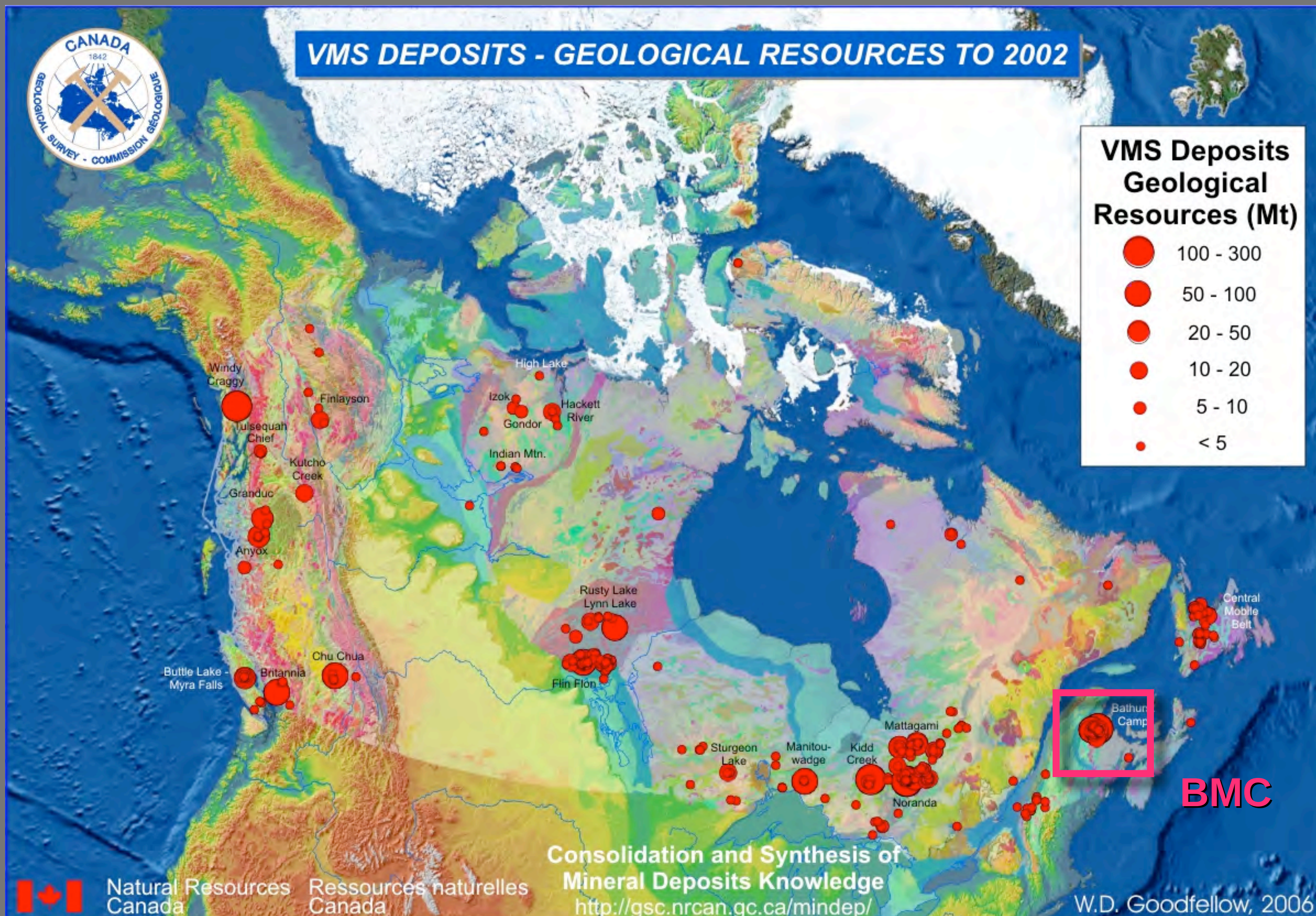




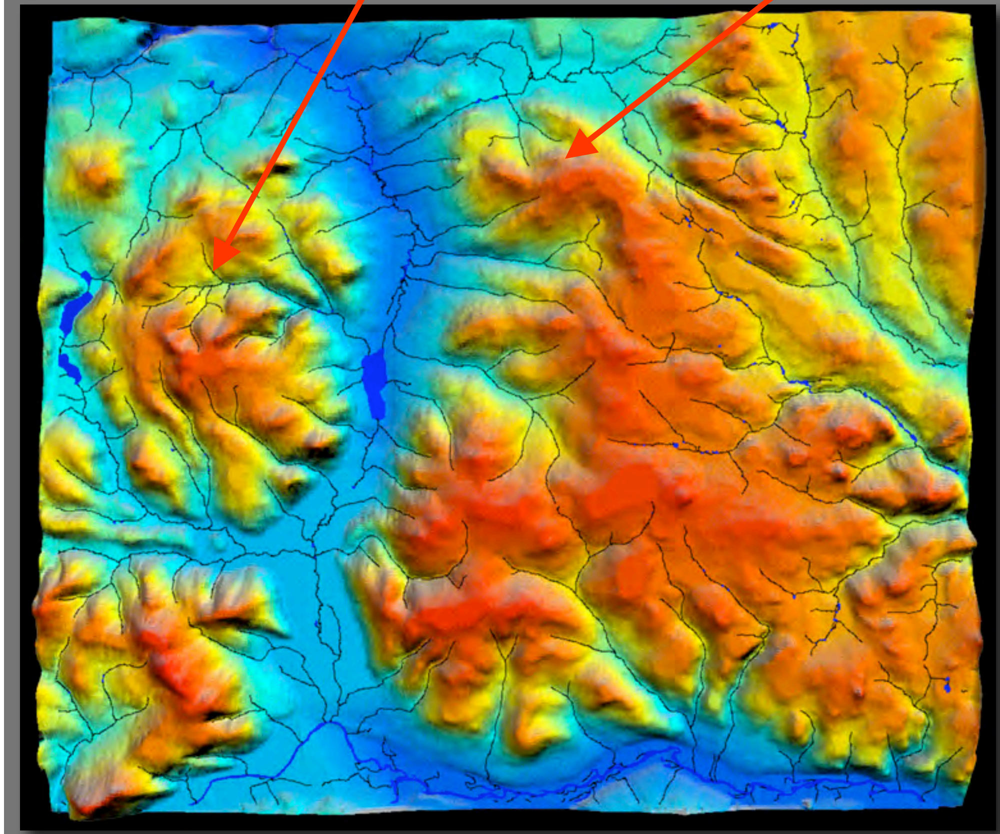
Case study: VMS (Bathurst Mining Camp)

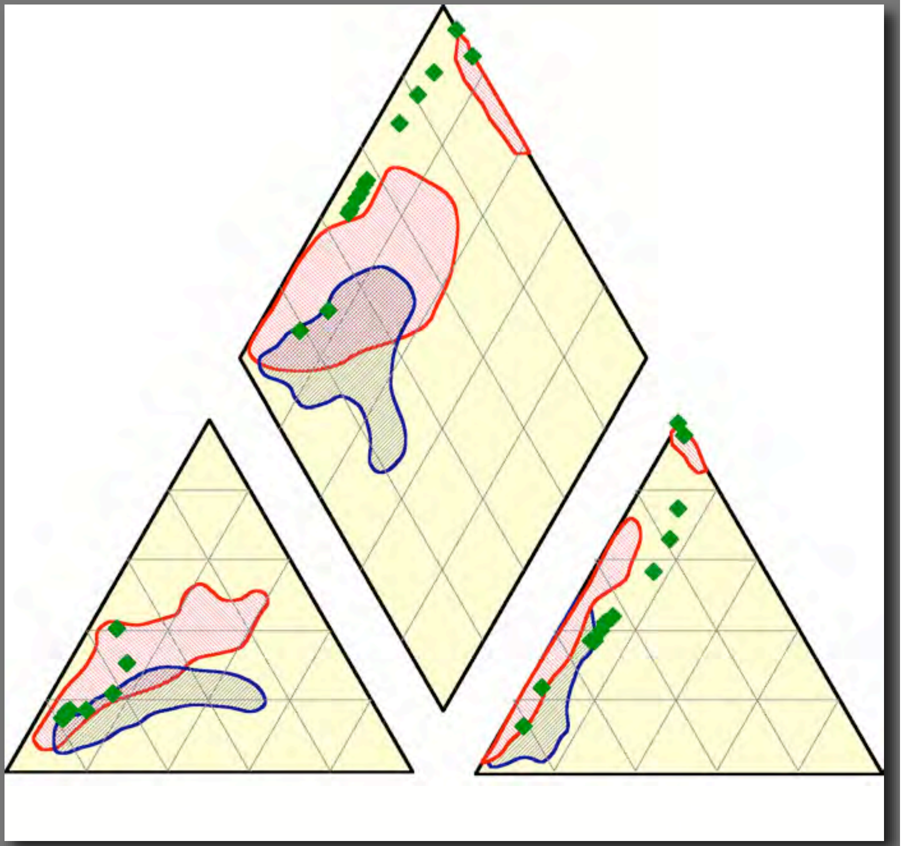


Case study: VMS (Bathurst Mining Camp)

Restigouche deposit

Murray Brook deposit





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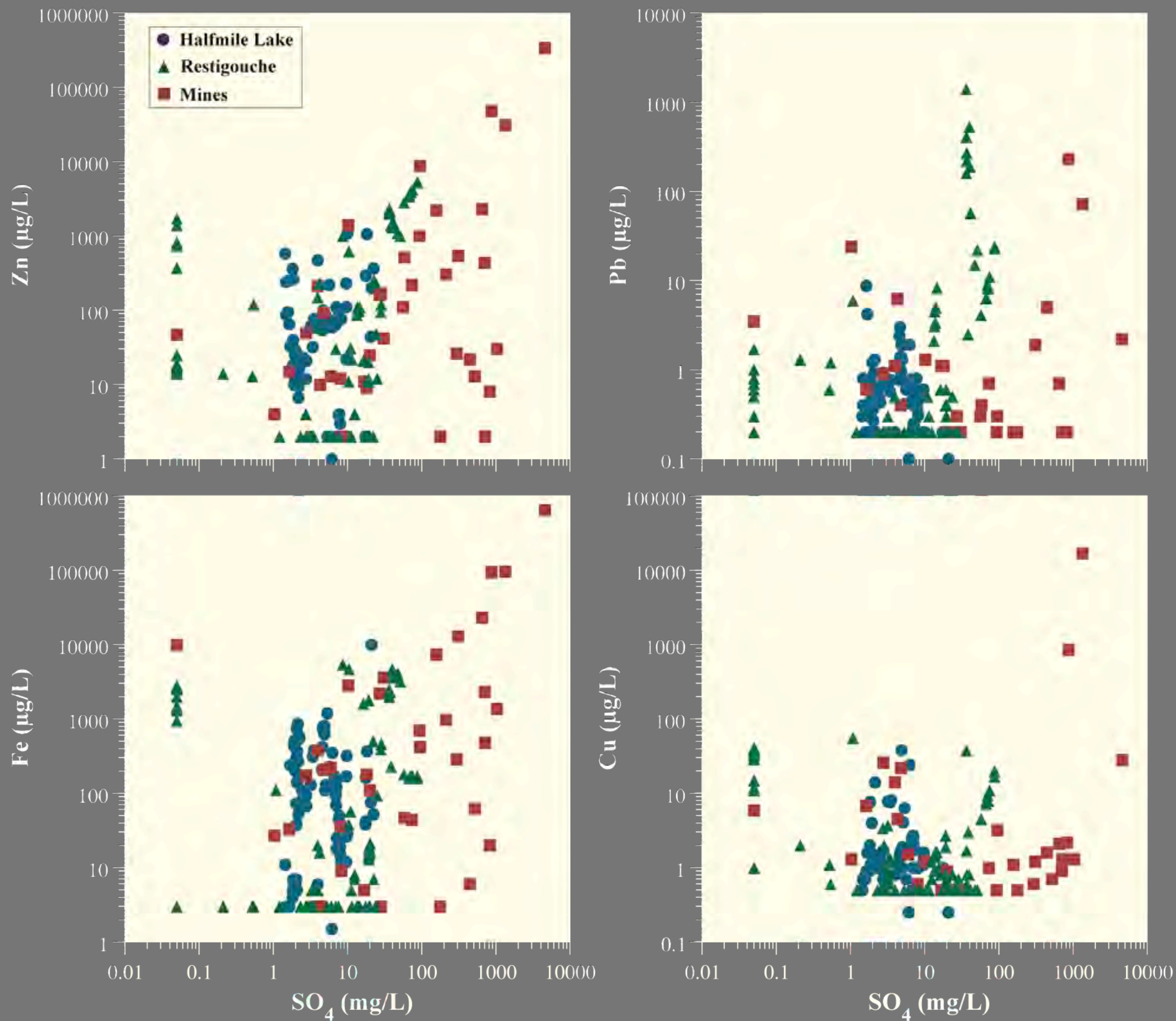

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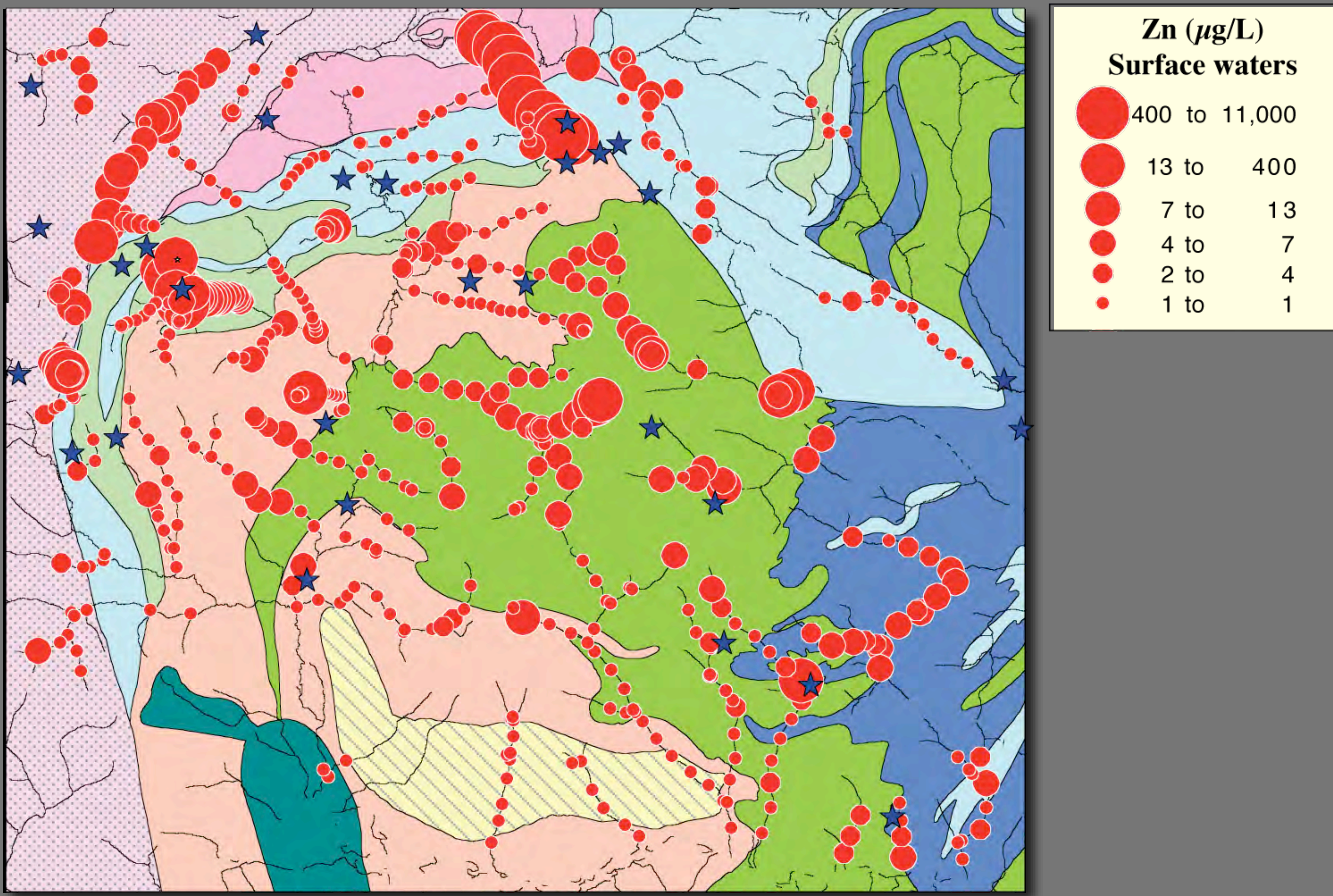

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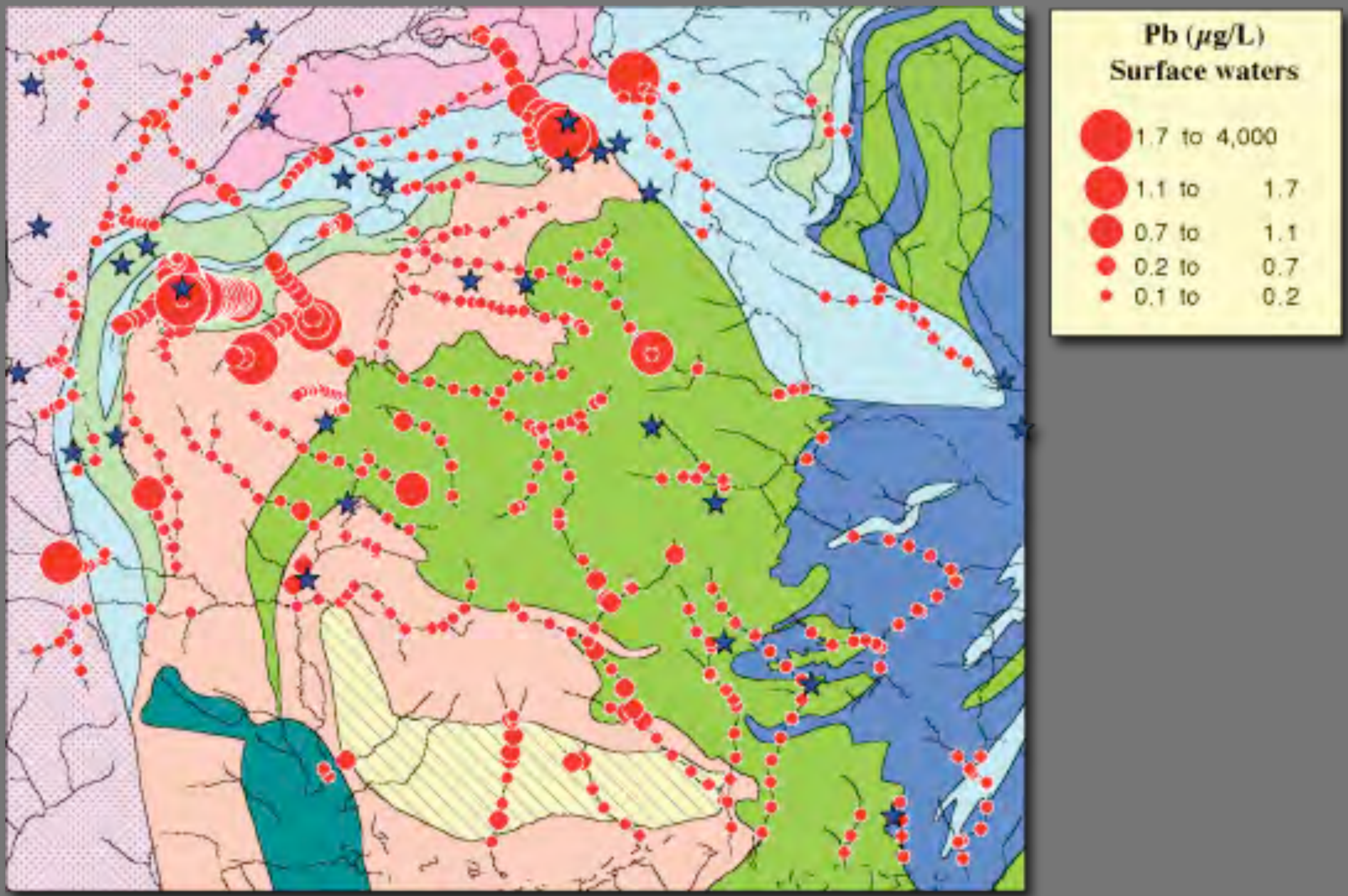

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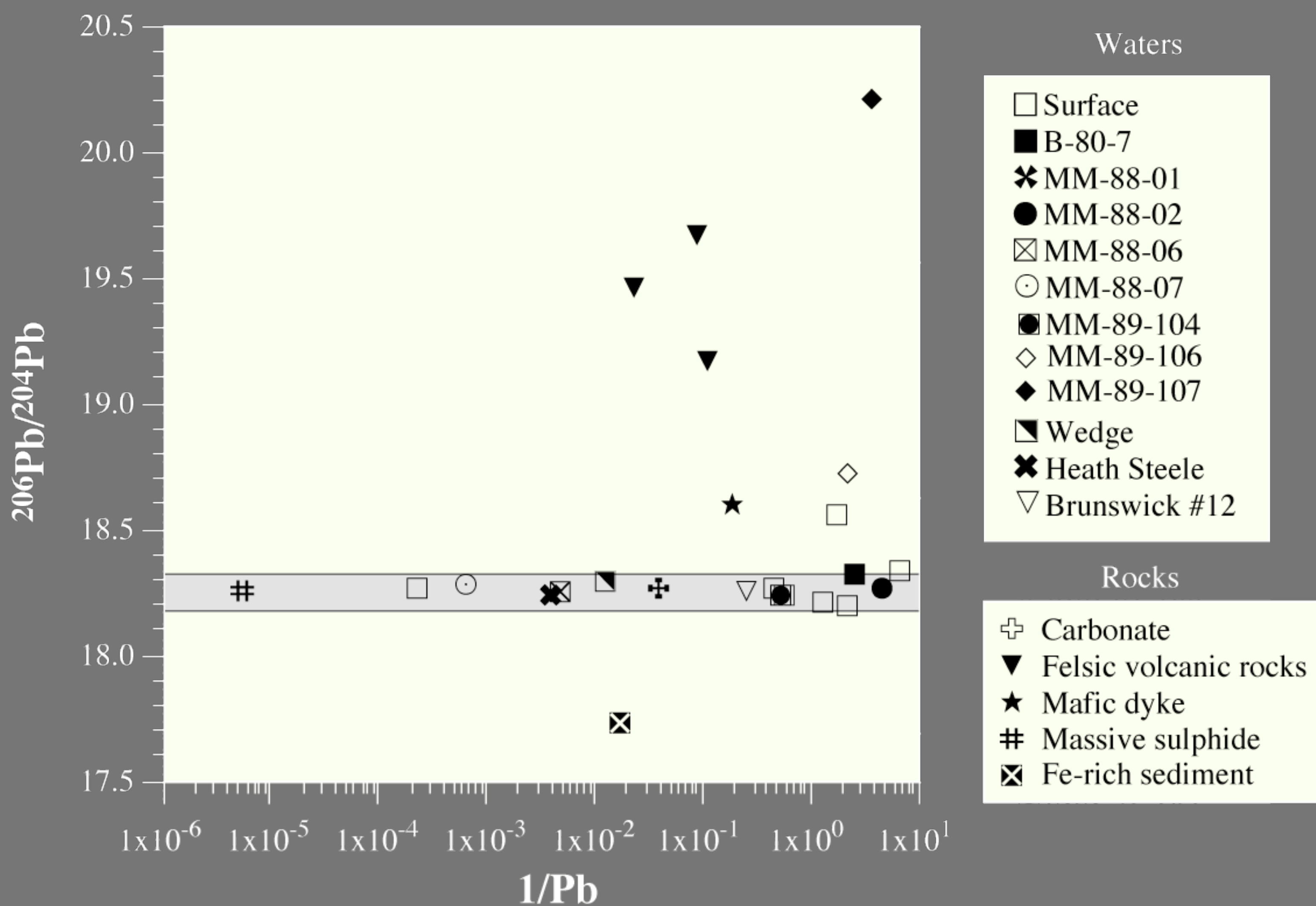

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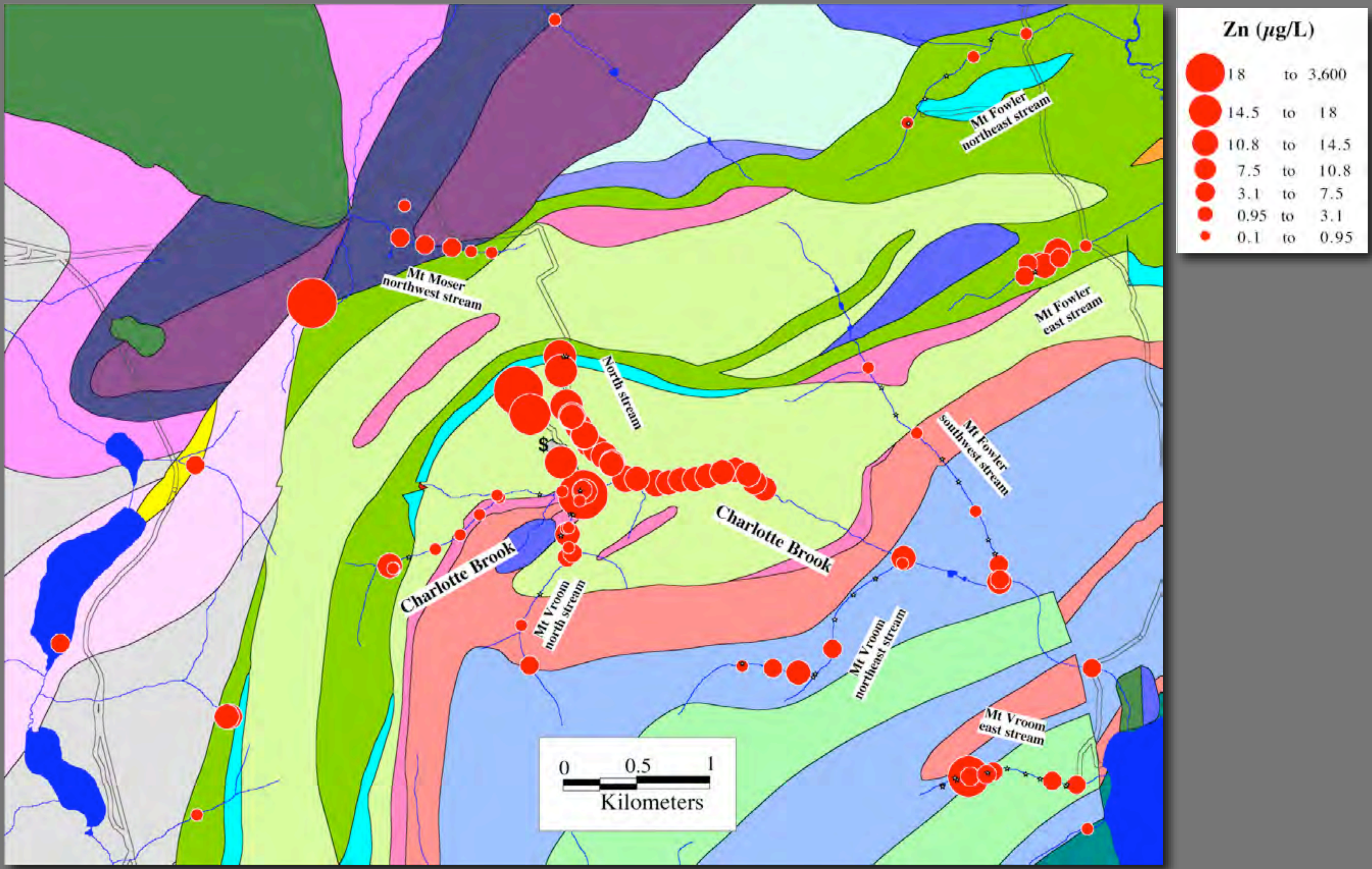

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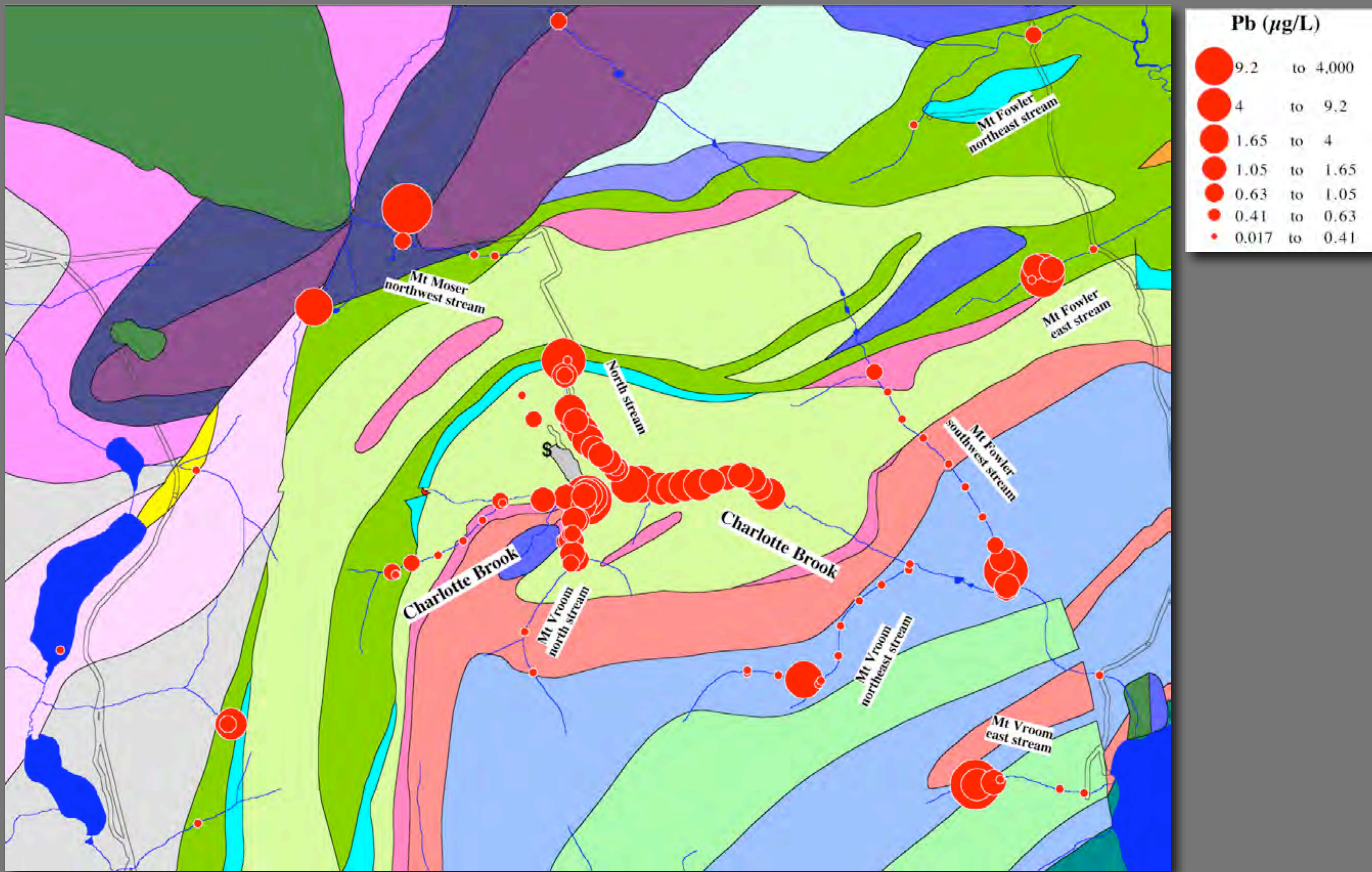
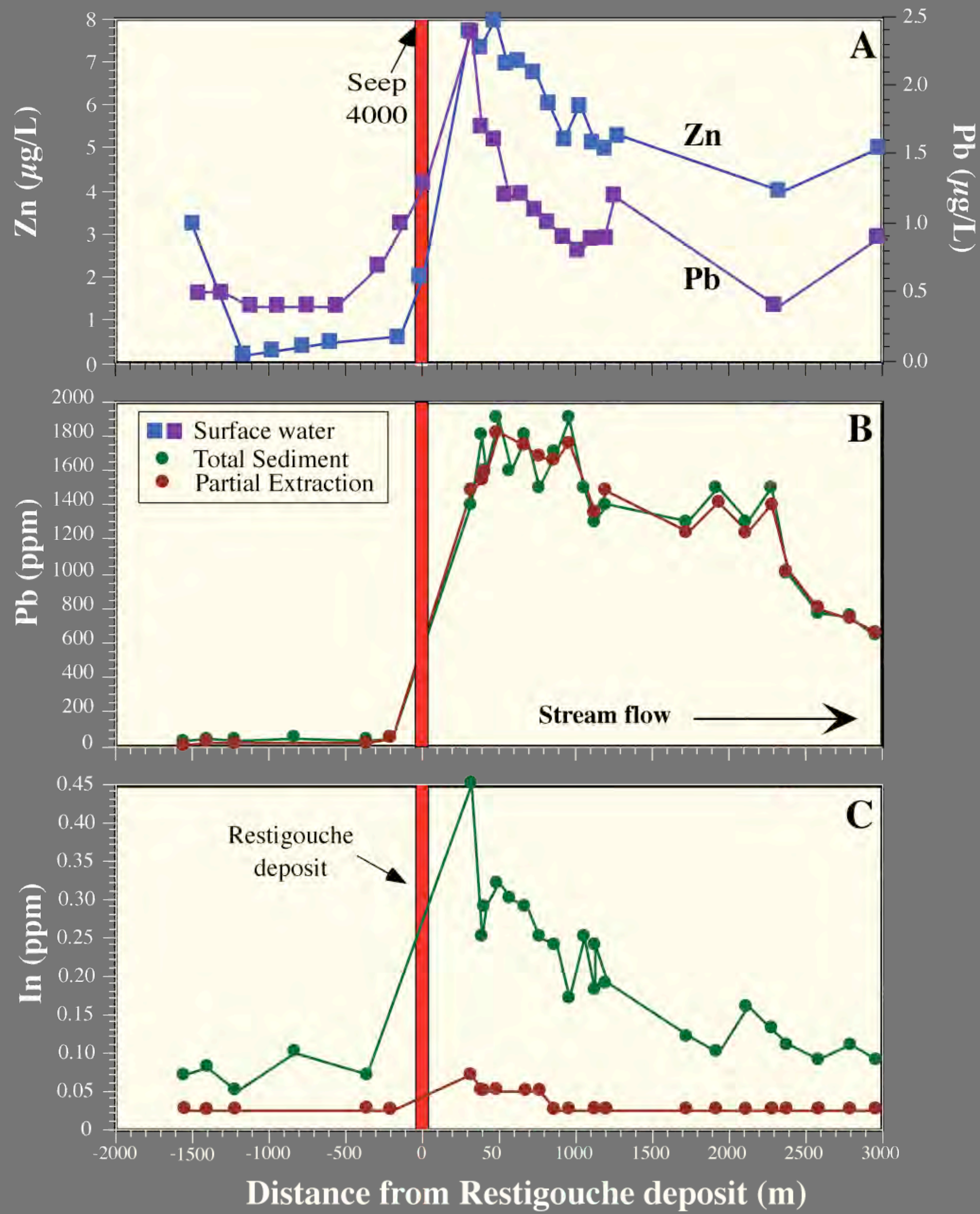


Case study:
VMS (BMC)



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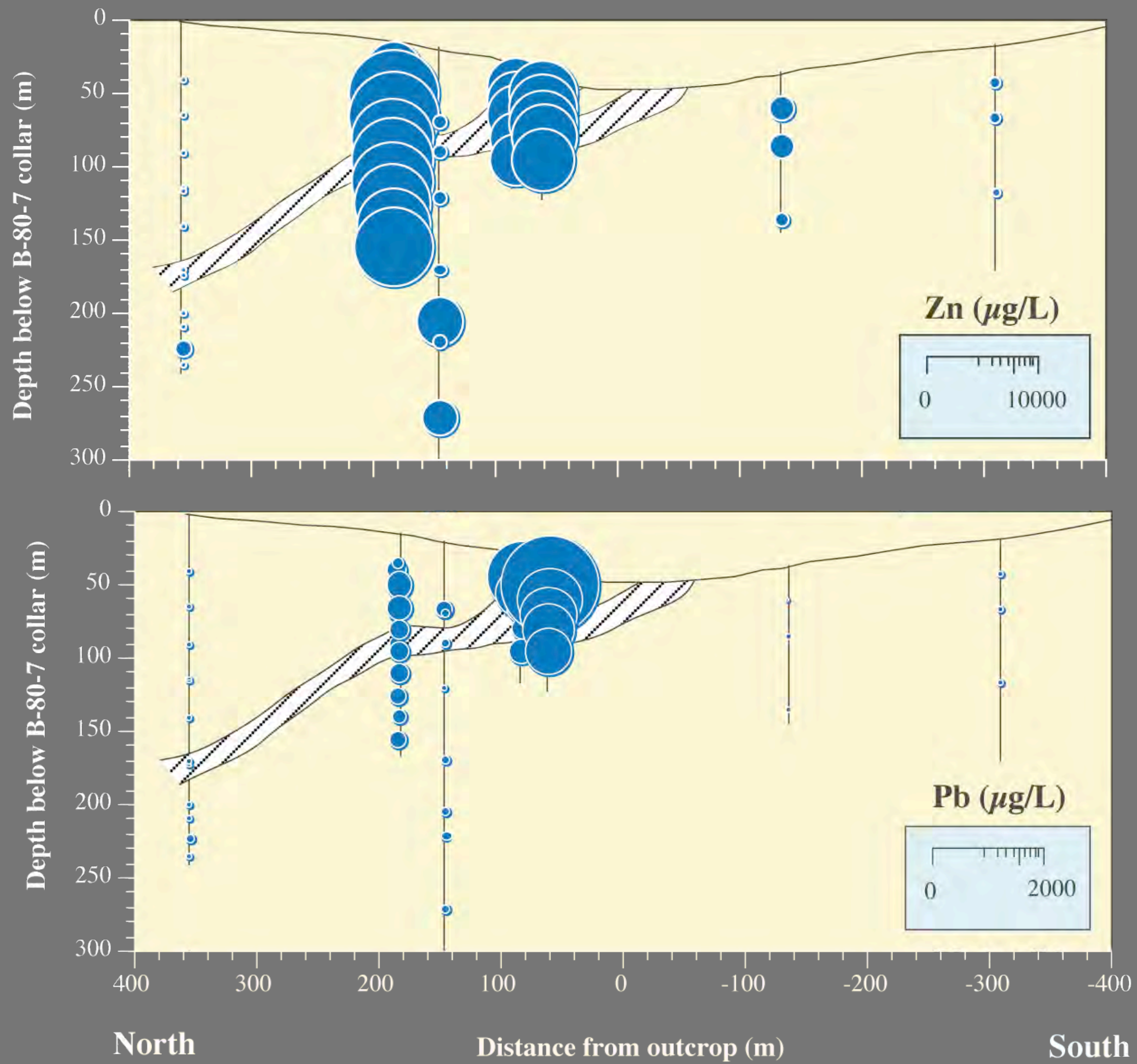
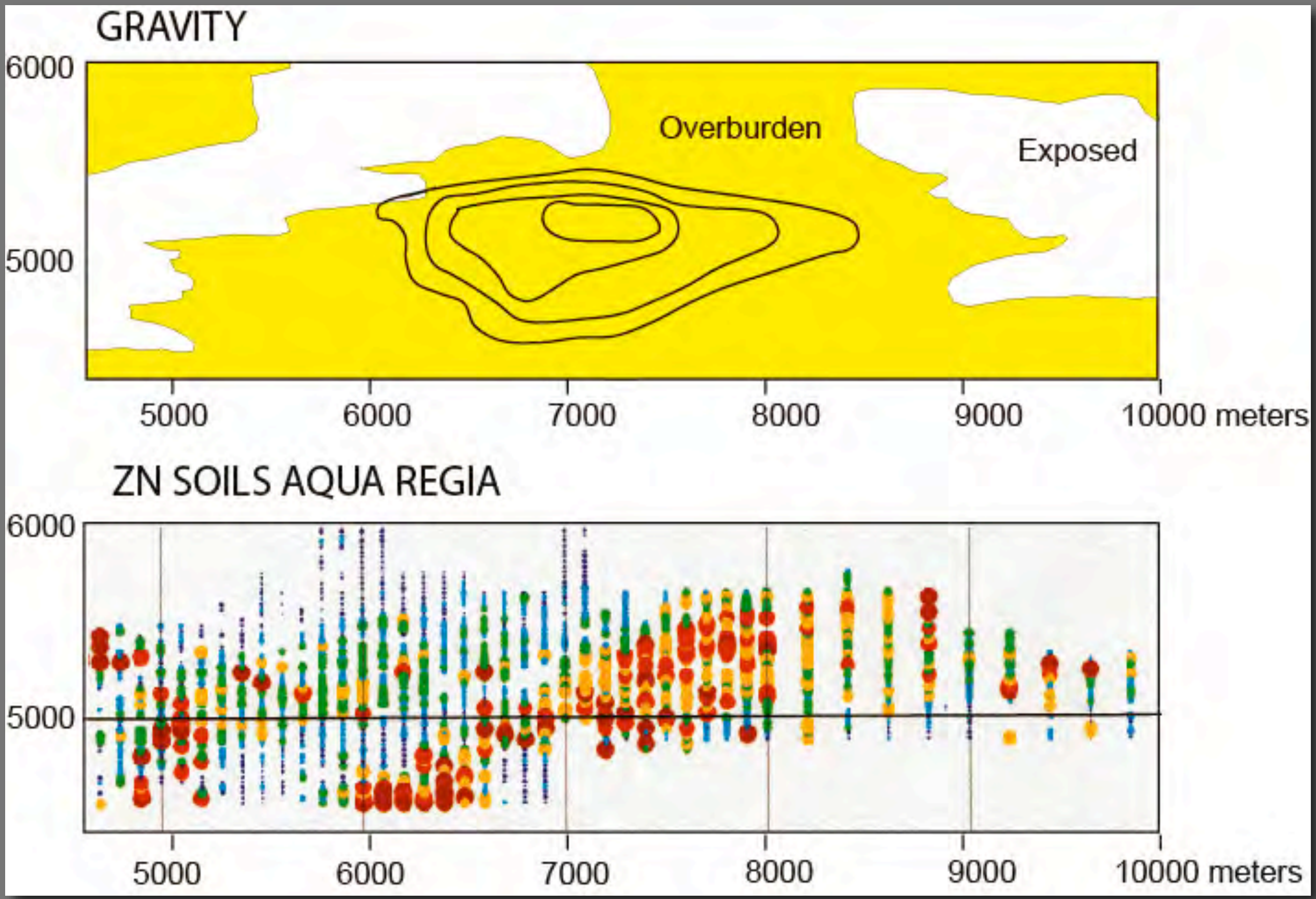


Duc Prospect Melville Peninsula



Cameron, E.M., 1998, Deep-penetrating geochemistry: Canadian Mining Industry Research Organization (CAMIRO) Report 97505, 117 p.

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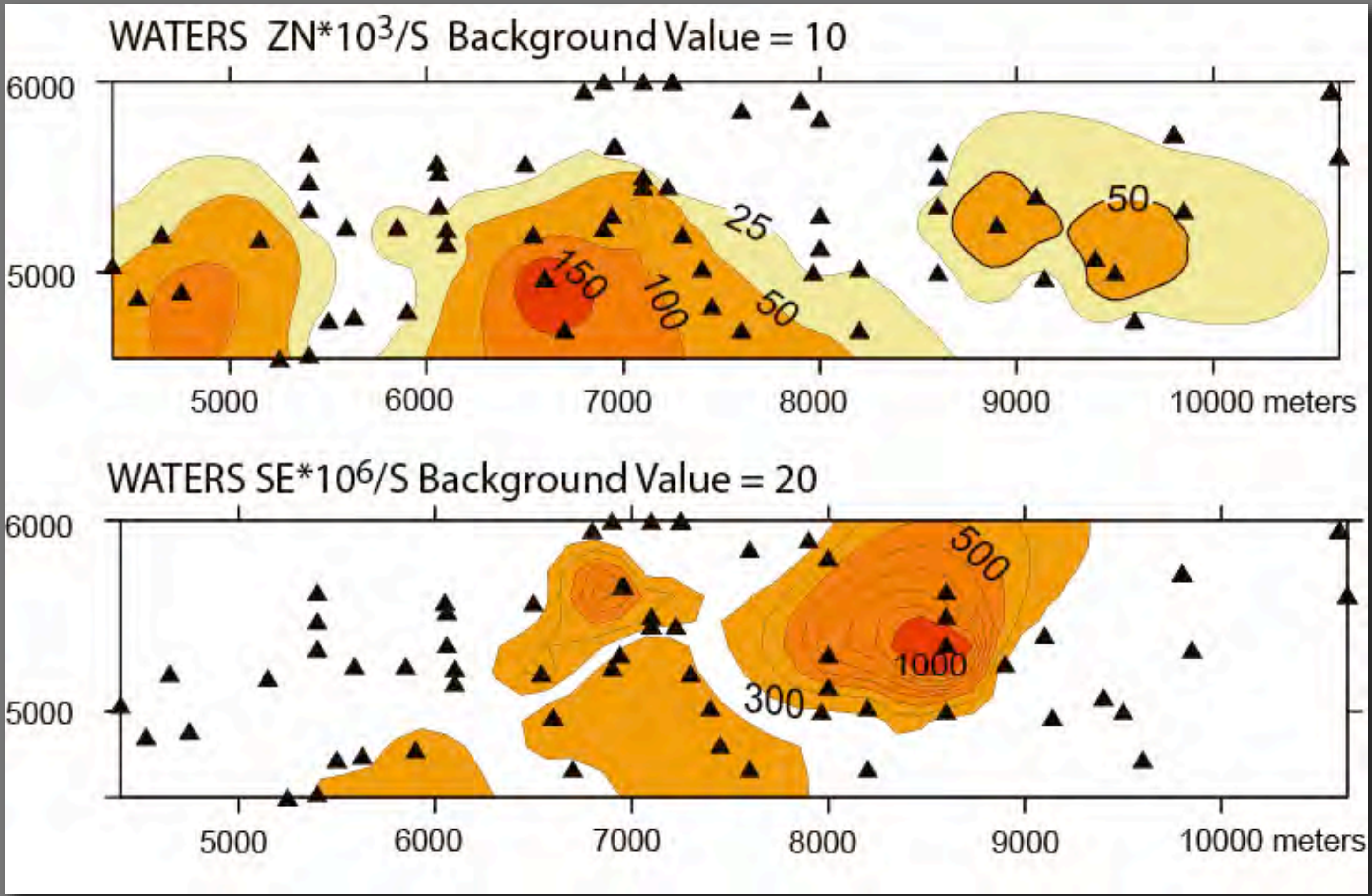

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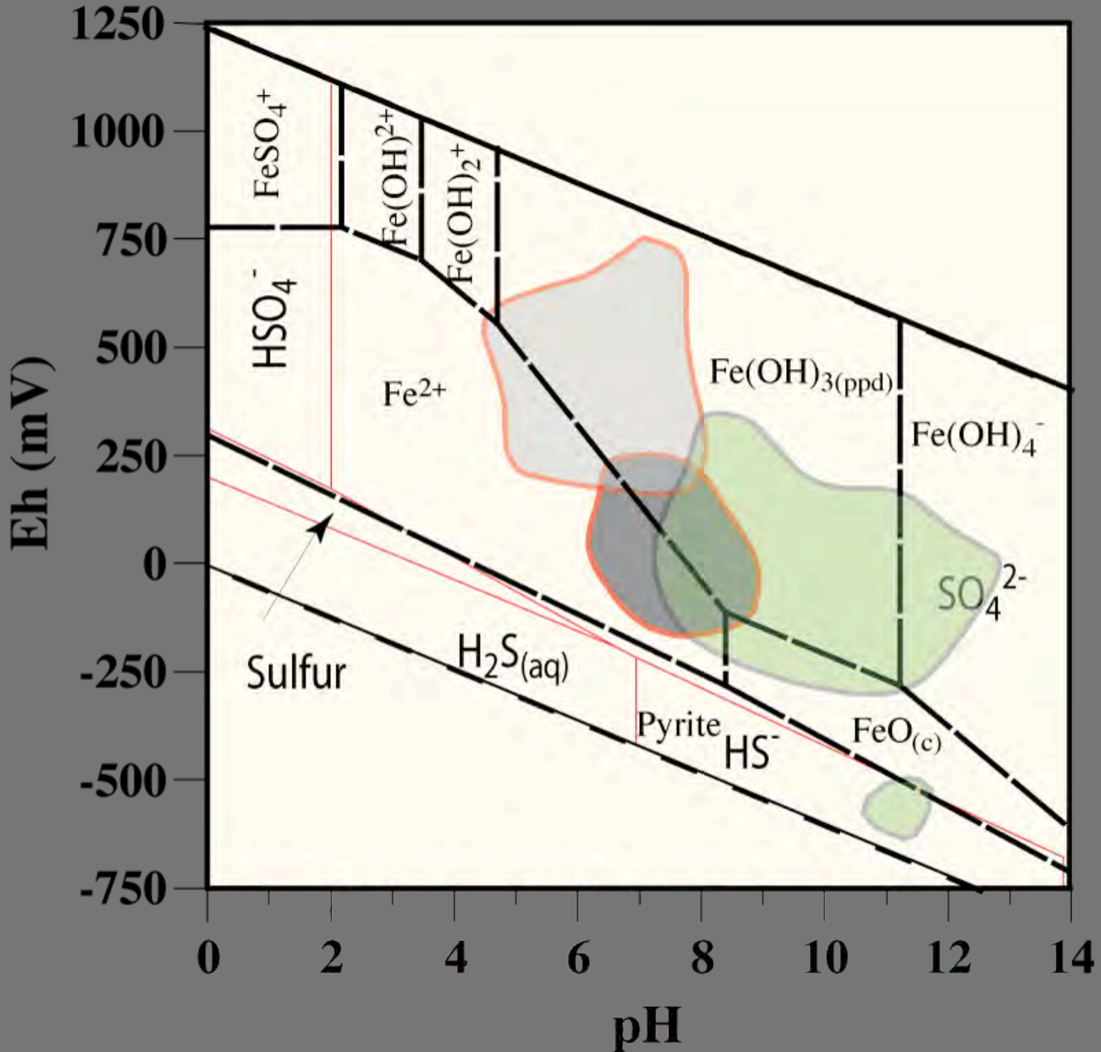
Kimberlites



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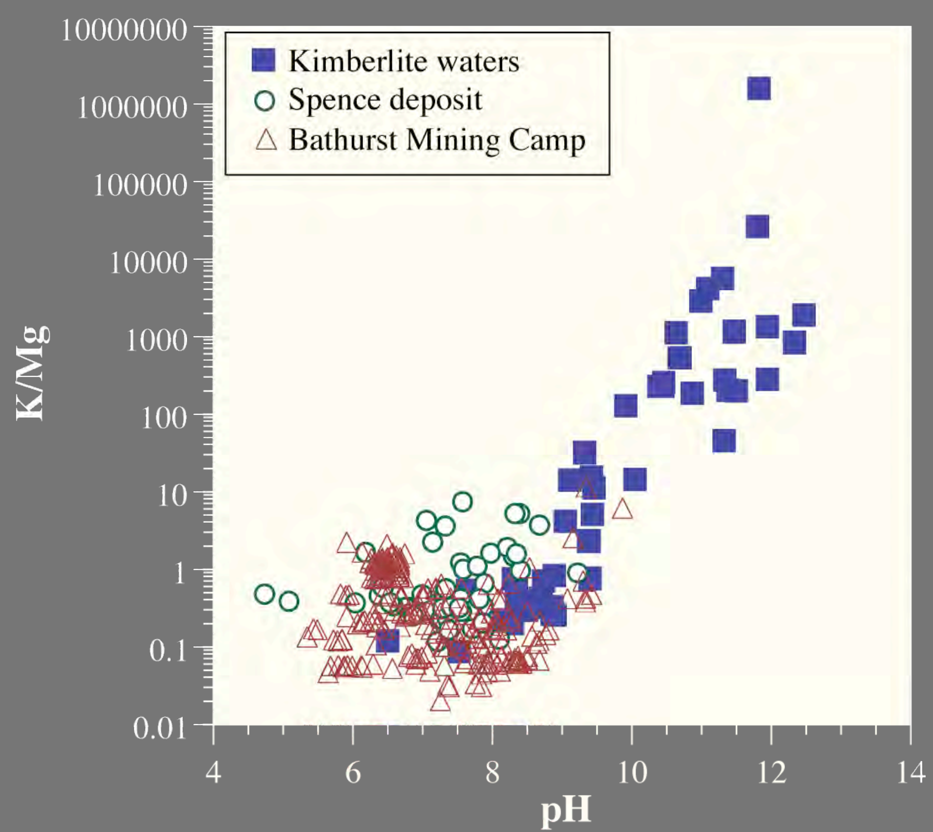
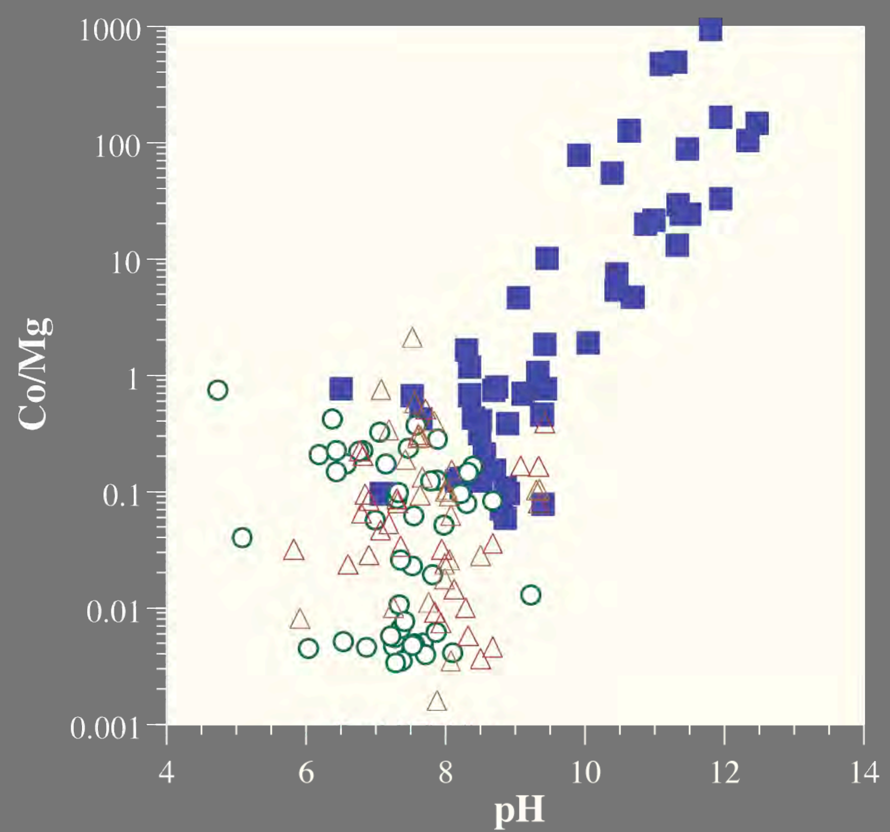
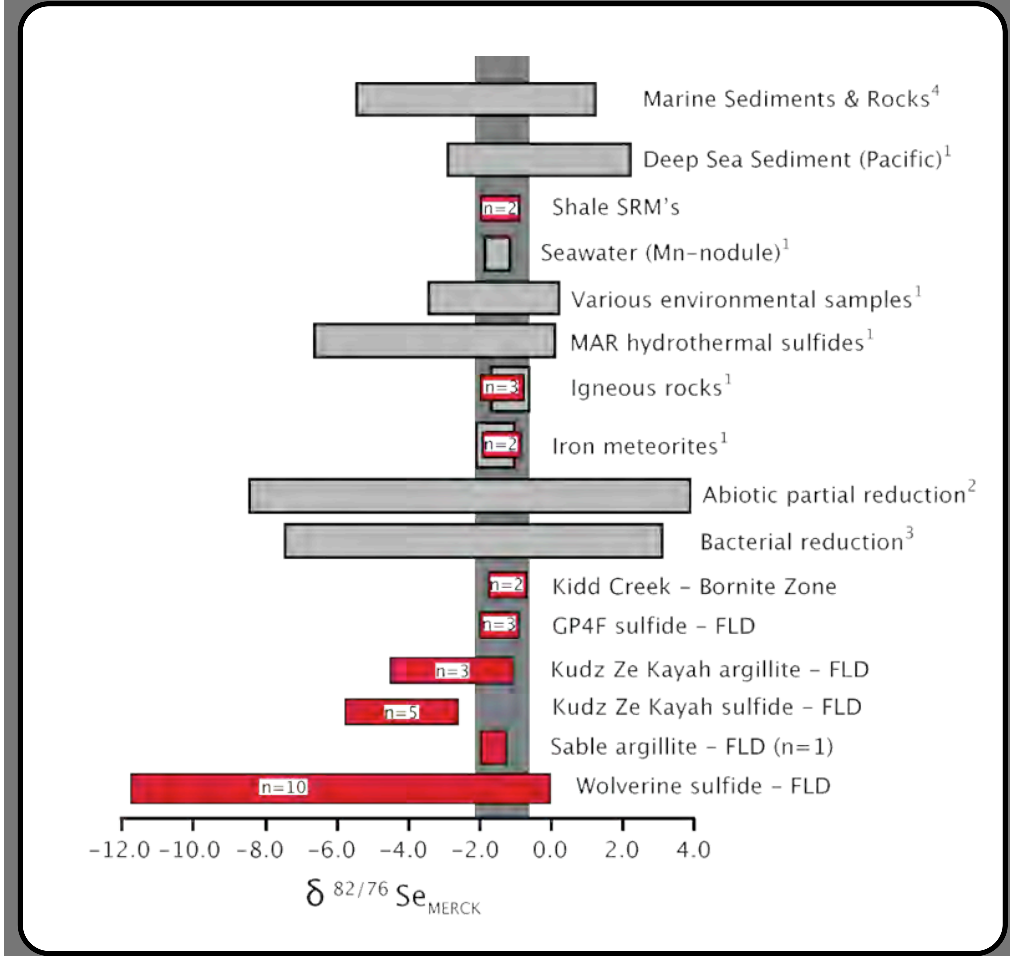


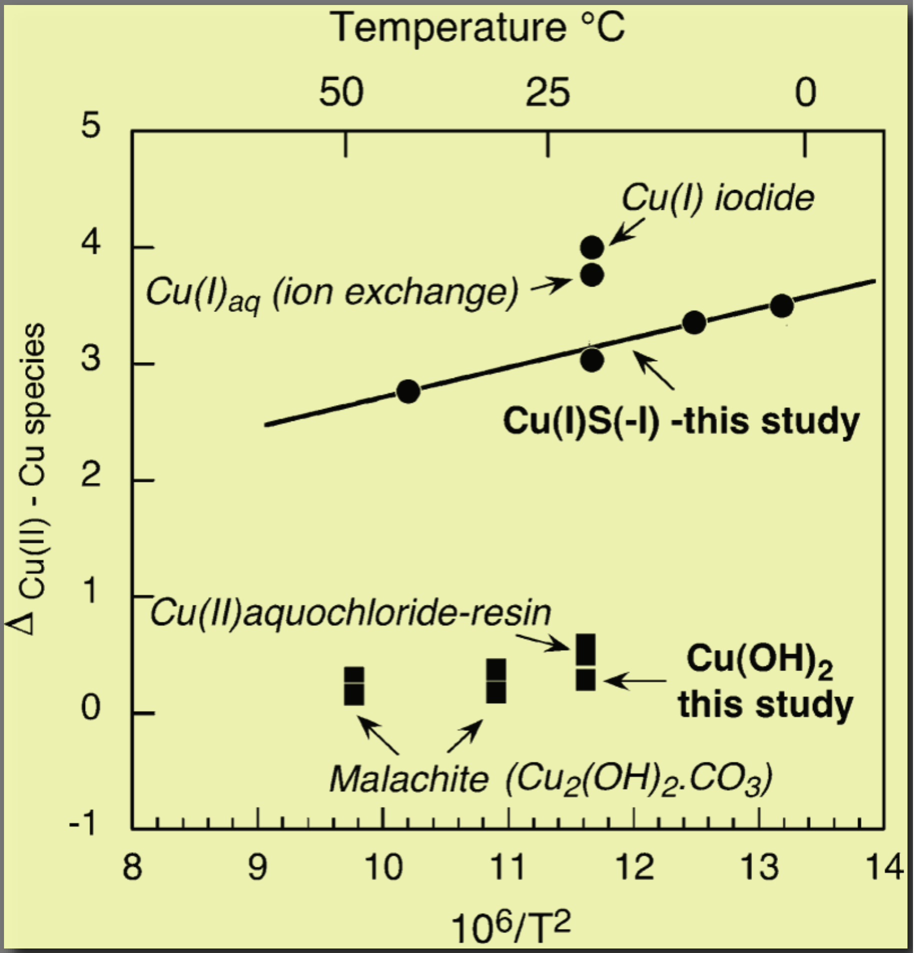


Future directions

- Incorporation of isotopic methods; sourcing, fingerprinting
- Widespread availability of quadrupole-based ICP-MS and increasing penetration of MC-ICP-MS should result in:
    - Non-traditional isotopes being used in exploration
    - Rapid and cheap analysis of more well characterized systems such as Pb, Sr, S

Future directions

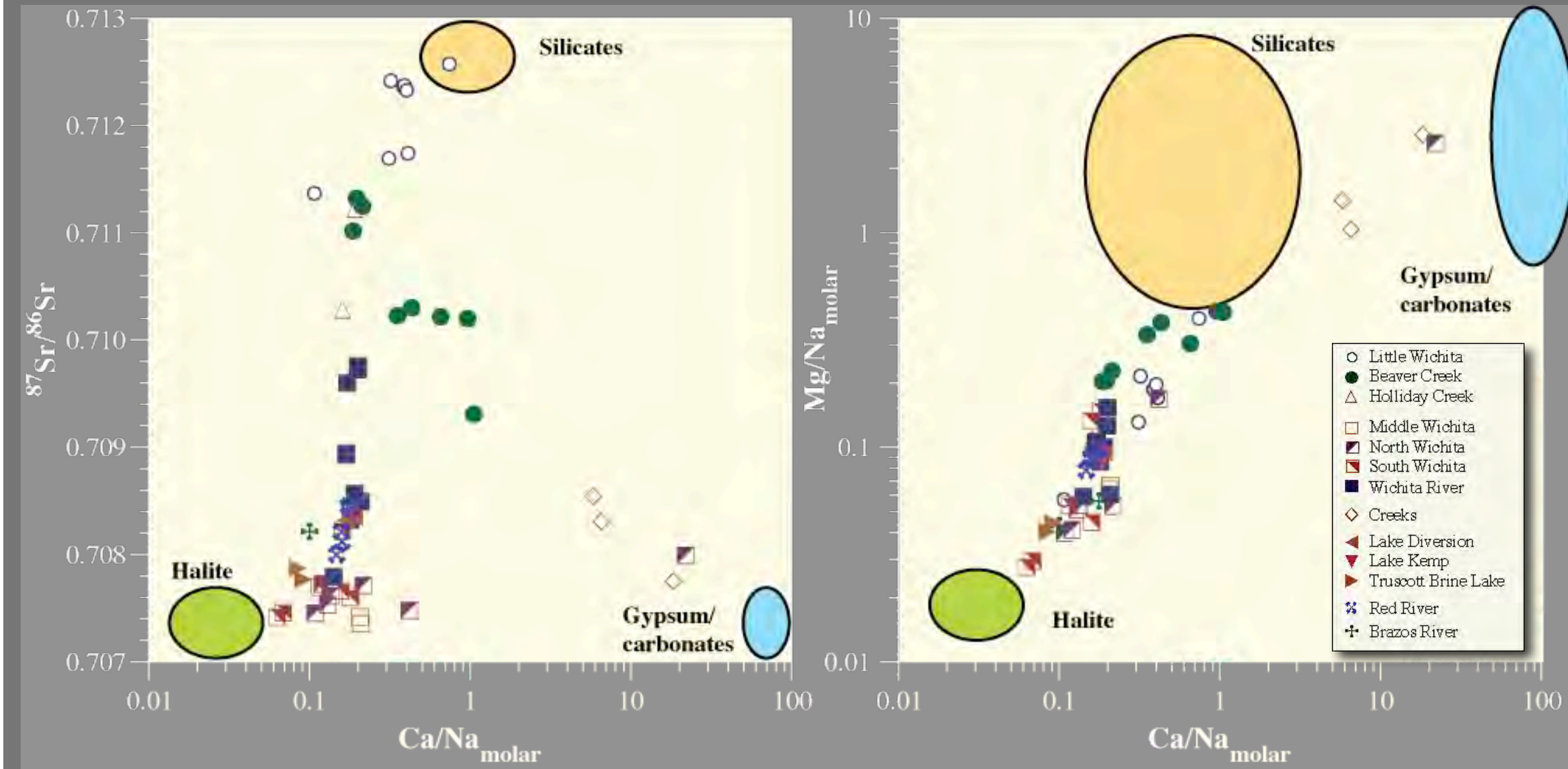




Layton-Matthews et al., 2006; in prep

Ehrlich et al., 2004. Experimental study of the copper isotope fractionation between aqueous Cu(II) and covellite, CuS. Chemical Geology, 209, 259-269

Future directions



Future directions

- Better understand the role of bacteria in sulfide oxidation and silicate hydrolysis
- Development of better models to understand metal migration in different environments
- Development of better models to distinguish between real and false anomalies (to what extent can we really use species not specifically ore-related?)
- More systematic application of hydrogeochemical methods in prospective but areas but without known mineralization

Where to find out more

Type of deposit	Main pathfinders	Secondary pathfinders	Key analytical methods	Key publications	Notes
VMS	Zn	Low pH, Pb, SO_4,	ICP-MS – metals IC, ICP-OES - S	Cameron, 1978; Leybourne et al., 2003; Leybourne and Goodfellow, 2003	Sulfide-Pb sources typically isotopically distinct; Pb isotopes can fingerprint ore versus non-ore Pb
Porphyry Cu ± Mo	Distal – Se, Re, Mo, As Proximal - Cu	Pb, Zn	ICP-MS – metals IC, ICP-OES - S	Cameron and Leybourne, 2005; Cameron et al., 2002; Leybourne and Cameron, 2006, in press	S isotopes also useful as a complimentary vector
SEDEX	Zn	Ag, Au, Ba, Cd	ICP-MS – metals IC, ICP-OES – S TIMS, MC-ICP-MS – Pb isotopes	Goodfellow, 1983; Jonasson et al., 1987; Kelley and Taylor, 1997	Sulfide-Pb sources typically isotopically distinct; Pb isotopes can fingerprint ore versus non-ore Pb
Gold (vein)	Au	Se, As, Sb	Activated carbon preconcentration or BrCl (see text) ICP-MS, NAA	Carey et al., 2003; Giblin, 2001; Gray, 2001	
Cu-Ni-PGE	Ni, Cu, Pd	As, Cr, Co, S, PGE	ICP-MS – metals IC, ICP-OES - S	Hattori and Cameron, 2004	Pd mobility is enhanced under alkaline conditions relative to other pathfinders
Kimberlite (diamond)	Low Mg, elevated K/Mg, pH » 10	Ni, Co, Cr, high Co/Mg and Ni/Mg	ICP-MS – metals IC, ICP-OES - S	Sader et al., 2003, 2007	Also, formation of Mg hydroxides (brucite), silicates (serpentine) and carbonates (magnesite)
Unconformity uranium	Oxidizing – U, radon Reducing – Se, Mo	Se, Mo, As, V, Cu, Pb	ICP-MS – metals IC, ICP-OES – S TIMS, MC-ICP-MS – Pb isotopes	Deutscher et al., 1980; Dickson and Giblin, 2006; Earle and Drever, 1983; Giblin and Snelling, 1983; Langmuir and Chatham, 1980	Radiogenic $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ but non-radiogenic $^{208}Pb/^{204}Pb$ should prove useful

Summary - Aqueous geochem the simple way

- Regional - lake and stream waters
- Lake waters can be collected by helicopter
- No preservation, no field testing, no filtering
- Analyze rapidly to ensure no loss of metals to the bottle walls or to precipitates that form during transport to the lab
- Groundwaters can be collected using plastic bailers
- Analysis by multi-element ICP-MS only

Summary - Aqueous geochem the less easy way

- Exploration companies may choose the easy way, but:
- Dual-use programs (exploration and environmental baseline) would require more adherence to environmental guidelines
- Characterization/pilot studies require more detailed sample collection and analytical approaches
- More closely spaced samples
- In field testing, especially for pH, redox, alkalinity
- Filtering in situ; acid preservation
- Isotopes

Thanks!

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