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

Field methods

**Sample return**
- N₂ gas to sample head
- N₂ gas to packers
- Sample head
- 1 psi cracking valve
- Upper packer
- Groundwater flow
- Groundwater flow
- Sample entry chamber (with 45 μm in-line filter)
- Lower packer
Field methods
Packer versus bailer
The best way to sample groundwater!
pH and Eh
Redox
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

Log[H+]^2 + log[Cl]^2 vs. Log P_{CO2}

- Atacamite: Cu_4(OH)_6Cl_2
- Azurite: Cu_3(OH)_2(CO_3)_2
- Tenorite: CuO
- Malachite: Cu_2(OH)_2CO_3

SI_atacamite vs. [Cu^{2+}] (μM)

[Image of graphs showing the relationship between chemical speciation and modeling parameters.]

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Speciation and modeling

![Graph showing the relationship between SI_Anglesite and Pb (μg/L)]

- Halfmile Lake
- Restigouche
- Mines
Routine Exploration

- Sampling methods
  - Bailer
  - Pump
    - Double valve, Grundfos

- Depth of sampling
  - One sample = at least 5 m below water table
  - Multiple samples = different depths based on stratigraphy, changes in conductivity, well logs

- Samples
  - One aliquot
    - 250 or 500 ml Nalgene

- Field measurements
  - pH, conductivity

- QA/QC
  - 1 in 20 duplicate
    - 1 in 20 CRM standard
    - Several field blanks
  - Major ions - ICP-OES
  - Trace elements - ICP-MS
  - Ag, Au require other preservation
    - Store cold

- Analytical
  - Ag, Au - preserve with BrCl or carbon sachets
# Case studies

<table>
<thead>
<tr>
<th>Type of deposit</th>
<th>Major components</th>
<th>Minor components</th>
<th>Labile componentså</th>
<th>Relatively immobile componentsβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>VMS</td>
<td>Fe, S, Cu, Zn, Pb</td>
<td>Cd, Hg, Au, As, Sb, Ba, Bi, In</td>
<td>Fe, S, Zn, Cu, As, Cd, Hg, Sb</td>
<td>Pb, Bi, In, Au, Ag, Ba</td>
</tr>
<tr>
<td>Porphyry Cu ± Mo</td>
<td>Cu, Mo, S</td>
<td>Fe, Ag, Au, Se, Re, As</td>
<td>Cu, Mo, S, Fe, Se, As, Re</td>
<td>Ag, Au</td>
</tr>
<tr>
<td>SEDEX</td>
<td>Fe, S, Cu, Zn, Pb</td>
<td>Ag, Au, Ba, Cd</td>
<td>Fe, S, Zn, Cu, Cd</td>
<td>Pb, Ba, Au, Ag</td>
</tr>
<tr>
<td>Gold (vein)</td>
<td>Au, Ag</td>
<td>As, Sb, Se, Te, S, Hg</td>
<td>S, Se, As, Hg, Te, Sb</td>
<td>Au, Ag</td>
</tr>
<tr>
<td>Ni-Ci-PGE</td>
<td>Ni, Cu, PGE</td>
<td>Cr, Co, S</td>
<td>Cu, S, PGE</td>
<td>Co, Ni, Cr</td>
</tr>
<tr>
<td>Kimberlite (diamond)</td>
<td>Sr, Nb, Ba, Cr, Ni</td>
<td>LILE, HFSE, REE</td>
<td>Sr, LILE</td>
<td>Ba, HFSE, Nb, Ba, Cr, Ni, REE</td>
</tr>
<tr>
<td>Unconformity uranium</td>
<td>U</td>
<td>Se, Mo, V, Cu, Pb</td>
<td>U, Se, Cu, Mo</td>
<td>U, Pb, V</td>
</tr>
</tbody>
</table>

A. Under oxidizing and near neutral conditions
B. Under normal conditions; e.g., Ba is immobile in the presence of S as SO₄ owing to insolubility of barite.

LILE, large ion 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 porphyrries
- Supergene alteration prior to mid-Miocene, produced leached cap - enriched oxide zone over supergene and hypogene sulfides
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Groundwaters
- East (upflow)
- Within deposit
- West (downflow)
- North
- South

Evaporation line for $\alpha = 1.009$

Binary mixing ($Y - Z$)
Case study: porphyry copper (Chile)
Lessons from Spence groundwater - soil geochemical anomalies
Lessons from Spence groundwater - soil geochemical anomalies
Conceptual model
Lessons from Spence groundwater - Tamarugal
Lessons from Spence groundwater - Tamarugal

![Graphs showing δ^2H and δ^18O vs. TDS with annotations and data points]

- Fritz et al. (1981)
- Tamarugal
- Spence waters:
  - East of deposit
  - Within deposit
  - West of deposit
  - North of deposit
  - South of deposit

![Graph showing S/Se vs. TDS with annotations]

- Regional meteoric waters
- Spence saline waters

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Case study: VMS (Bathurst Mining Camp)
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Restigouche deposit

Murray Brook deposit
Case study: VMS (Bathurst Mining Camp)
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Exploration Geochemistry - Basic Principles and Concepts
Case study: VMS (Bathurst Mining Camp)
Case study: VMS (Bathurst Mining Camp)
Case study: VMS (BMC)
Case study: VMS (Bathurst Mining Camp)

Exploration Geochemistry - Basic Principles and Concepts
Duc Prospect Melville Peninsula

Duc Prospect Melville Peninsula

Kimberlites
Kimberlites
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

Exploration Geochemistry - Basic Principles and Concepts
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

<table>
<thead>
<tr>
<th>Type of deposit</th>
<th>Main pathfinders</th>
<th>Secondary pathfinders</th>
<th>Key analytical methods</th>
<th>Key publications</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>VMS</td>
<td>Zn</td>
<td>Low pH, Pb, SO₄,</td>
<td>ICP-MS – metals IC,</td>
<td>Cameron, 1978;</td>
<td>Sulfide-Pb sources typically isotopically distinct; Pb isotopes can fingerprint ore versus non-ore Pb</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>ICP-OES - S</td>
<td>Leybourne et al., 2003; Goodfellow, 2003</td>
<td></td>
</tr>
<tr>
<td>Porphyry Cu ± Mo</td>
<td>Distal – Se, Re,</td>
<td>Pb, Zn</td>
<td>ICP-MS – metals IC, IC,</td>
<td>Cameron and Leybourne, 2005; Cameron et al., 2002; Leybourne and Cameron, 2006, in press</td>
<td>S isotopes also useful as a complimentary vector</td>
</tr>
<tr>
<td></td>
<td>Mo, As</td>
<td></td>
<td>ICP-OES - S</td>
<td></td>
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<tr>
<td></td>
<td>Proximal - Cu</td>
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<tr>
<td>SEDEX</td>
<td>Zn</td>
<td>Ag, Au, Ba, Cd</td>
<td>ICP-MS – metals IC, IC,</td>
<td>Goodfellow, 1983; Jonasson et al., 1987; Kelley and Taylor, 1997</td>
<td>Sulfide-Pb sources typically isotopically distinct; Pb isotopes can fingerprint ore versus non-ore Pb</td>
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<td>ICP-OES – S TIMS, MC-ICP-MS – Pb isotopes</td>
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<tr>
<td>Gold (vein)</td>
<td>Au</td>
<td>Se, As, Sb</td>
<td>Activated carbon preconcentration or BrCl (see text)</td>
<td>Carey et al., 2003; Giblin, 2001; Gray, 2001</td>
<td></td>
</tr>
<tr>
<td>Cu-Ni-PGE</td>
<td>Ni, Cu, Pd</td>
<td>As, Cr, Co, S, PGE</td>
<td>ICP-MS – metals IC, IC,ICP-OES - S</td>
<td>Hattori and Cameron, 2004</td>
<td>Pd mobility is enhanced under alkaline conditions relative to other pathfinders</td>
</tr>
<tr>
<td>Kimberlite</td>
<td>Low Mg, elevated K/Mg, pH &gt; 10</td>
<td>Ni, Co, Cr, high Co/Mg and Ni/Mg</td>
<td>ICP-MS – metals IC, IC,ICP-OES - S</td>
<td>Sader et al., 2003, 2007</td>
<td>Also, formation of Mg hydroxides (brucite), silicates (serpentine) and carbonates (magnesite)</td>
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<td>Unconformity uranium</td>
<td>Oxidizing – U, radon</td>
<td>Se, Mo, As, V, Cu, Pb</td>
<td>ICP-MS – metals IC, ICP-OES – S TIMS, MC-ICP-MS – Pb isotopes</td>
<td>Deutscher et al., 1980; Dickson and Giblin, 2006; Earle and Dreyer, 1983; Giblin and Snelling, 1983; Langmuir and Chatham, 1980</td>
<td>Radiogenic $^{207}\text{Pb}$/$^{206}\text{Pb}$ and $^{208}\text{Pb}$/$^{204}\text{Pb}$ should prove useful</td>
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<td>Reducing – Se, Mo</td>
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</tbody>
</table>
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!

• Beth McClanaghan
• Jan Peter, Wayne Goodfellow
• Jamil Sader, Clinton Rissmann
• Stew Hamilton, Dan Layton-Matthews, Gwendy Hall
• CAMIRO
• BHP-Billiton, NSF, TGI, EXTECH
• Dan Boyle
• GNS Science