President's Message

At the beginning of my two-year term as AAG’s president, I look forward to continuing the stewardship of the outgoing president, David Cohen, and take this opportunity to thank him for his commitment to AAG during the term of his presidency. I would like to welcome AAG’s incoming councillors, Mark Arundell, Rob Bowell, Bruno Lemière, Ryan Noble, and Todd Wakefield, who bring a variety of expertise to Council. Although four councillors have finished their two-year stints (David Garnett, David Lentz, Ray Lett, and Cliff Stanley), you’ll continue to see their names associated with AAG business, as they contribute to various AAG committees.

The continued success of AAG relies on the efforts of a small group of members who make up AAG’s Council, as well as a number of ex-officio members who freely give of their advice to Council and serve on various committees. These officers, councillors and committee members are listed on the inside back cover of EXPLORE, and if you recognize many of these names, it’s probably because they have not only made contributions to AAG in various capacities over the years, but also because they are well known for their scientific contributions to applied geochemistry.

The most tangible presence of AAG for most members are its publications, and their success is in large part due to the commitment of Gwendi Hall (Editor-in-Chief of GEEA) and Beth McClenaghan (Editor of EXPLORE). The AAG website (www.appliedgeochemists.org) contains a variety of information about current and future issues related to the organization, and it has been regularly looked after by Bob Eppinger and Andrew Ransom. Gwendi Hall has had a long-term involvement with AAG’s finances as Treasurer, although some of you may not know that Eion Cameron has been looking after our investments; judging by the returns, he could well have taught a few others how to better ride out the GFC. Overseeing the day-to-day running of AAG has been the job of Betty Arsenault, whereas Dave Smith, as AAG’s long-serving secretary, keeps Council in line and informed.

Last year, the quality science of applied geochemistry was on show at the 24th IAGS in Fredericton, New Brunswick. Of the 300-odd who attended this meeting, more than one-third of the registrants were students, which shows that applied geochemistry is still a career of choice. I’m hopeful that this high student turnout and clear interest in applied geochemistry can be converted into a higher proportion of student members in AAG, which at the moment stands at only 6% of the 500-odd member total. Apart from increasing overall membership of the association, increasing the number of students will also help address the aging demographic of AAG. In terms of student interest, AAG members who hold academic positions are particularly important, as they are well placed to both foster applied geochemistry, and encourage students to join AAG.

The issue of membership numbers is not unique to our association. Recently, the Geological Society of Australia and the Australian Institute of Geoscientists went through a lengthy consultative process with members about the possibility of an amalgamation (which did not eventuate). Apart from amalgamation resulting in a large member base, economies of scale mean reduced running costs etc. However, the loss of identity has led some individuals and organizations to shy away from amalgamation; anecdotally, some in AAG have expressed their satisfaction at being a member of a small yet vibrant association with its own charter, so perhaps we should consider maintaining links with other geochemistry-focused organizations, but retain AAG in its present form.

With the beginning of the new year, it’s now just over 18 months until the next AAG symposium, which will be convened in Rovaniemi, Finland. Although August 2011 seems a little distant, I urge you to consider attending this meeting and periodically check the website (www.iags2011.fi). The IAGS meetings offer one of the few opportunities for AAG members to gather in one place, and the meeting in Finland will no doubt continue the tradition of high quality science and social activities that have characterized previous symposia. As with the day to day running of the AAG, the success of the IAGS meetings relies on the commitment of AAG members who volunteer their time to ensure the meetings are well organized and run, and I thank the Finnish local organizing committee for their efforts. A little further out is the 34th International Geological Congress (IGC), which will be held in Brisbane in August 2012 (www.34igc.org). AAG has been involved from the outset with the organization of this meeting, and its representative (David Cohen) is actively pursuing opportunities to hold AAG-hosted workshops and technical sessions at this meeting.

I look forward to keeping track of AAG members’ activities over the next two years, and hope to see many of you in Finland in 2011.

Paul Morris
AAG President
Hydrogeochemistry for mineral exploration in Western Australia (I): Methods and equipment

INTRODUCTION
The use of hydrogeochemistry for mineral exploration is increasing worldwide. Here in Western Australia, and developing in eastern Australia, junior exploration companies regularly approach us to obtain a relatively straightforward method description to conduct hydrogeochemical sampling. Although there are numerous and varied approaches for hydrogeochemical exploration available these are not easily found in the literature (e.g. Giblin 2001; Taufen 1997) or can be complex to breakdown for simpler exploration needs (i.e. EPA-type reports). To address this need we have compiled a general methodology, some basic steps (that are not regularly published as it is “common” knowledge – to hydrogeochemists) and required equipment that has been successfully applied to groundwater sampling by CSIRO in Western Australia.

Leybourne & Cameron (in press) have also recently put together a thorough and available article on the use of groundwater for geochemical exploration. Many of the sampling and analytical techniques overlap, but Australian arid and semi-arid terrains require adjustments in the methodologies of Leybourne & Cameron (in press), Giblin (2001) and Taufen (1997) or at least a different understanding of the limitations for hydrogeochemistry in these environments. Much of Western Australia has a thick regolith cover (10s of metres of transported and residual weathered material) and varied depths to the water table (~2 to 80 m). The groundwater can be relatively fresh to hypersaline, with pH ranging from 3 to 9 (Gray & Noble 2006). Even the agricultural regions of Western Australia have some extreme acid and saline groundwater chemistry, as documented by Shand et al. (2009). These conditions can make sampling, analysis and comparison to other groundwater data potentially problematic. This paper presents the methodology of groundwater sampling in Western Australia whereas Noble et al. (2010) apply the methods in case studies at various sites. This article, along with the previous references, should enable most industry explorers (with limited hydrogeochemical background) to develop a successful groundwater exploration program.

EQUIPMENT AND METHODOLOGY
Types of samples
Numerous practical options are available for collecting groundwater. Each option has advantages and disadvantages (Table 1). Farm water, water monitoring and exploration drill holes

<table>
<thead>
<tr>
<th>Sample site type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC/RAB type drill hole</td>
<td>Commonly available in the exploration area of interest</td>
<td>Potential for contamination, often not cased and may close or collapse shortly after drilling</td>
</tr>
<tr>
<td>Diamond type bore hole</td>
<td>Commonly available in the exploration area of interest, well cased and preserved</td>
<td>Commonly deep groundwater systems, generally cased to significant depth and not easily compared to other shallow samples*</td>
</tr>
<tr>
<td>Windmill</td>
<td>Easy access, no drilling costs</td>
<td>Potential for contamination if not regularly flowing, restricted available sample sites, shallow groundwater systems only</td>
</tr>
<tr>
<td>Water bore</td>
<td>Easy access, contamination unlikely</td>
<td>Uncommon, mainly shallow groundwater systems (with exceptions in areas dominated by deep water sources such as the Great Artesian Basin)</td>
</tr>
<tr>
<td>Monitoring bore</td>
<td>Easy access, contamination unlikely</td>
<td>Uncommon, shallow groundwater systems only</td>
</tr>
<tr>
<td>Open well</td>
<td>Easy access, no drilling costs</td>
<td>Potential for contamination if not regularly flowing, restricted available sample sites, shallow groundwater systems only</td>
</tr>
</tbody>
</table>

* If slotted, straddle packer system (Leybourne et al. 2000) could be employed to isolate groundwater flow at different depths to reduce decrease this disadvantage. This has not been tested in Western Australia.

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Notes from the Editor
Greetings for the New Year. We have 4 great issues planned for 2010. This March issue of EXPLORE (No. 146) includes two technical articles on groundwater sampling for mineral exploration in SW Australia. Coming in the June issue will be articles about capturing field data digitally using a hand held device and an article from Cliff Stanley on numerical methods. Scientific and technical editing assistance for this EXPLORE issue was provided by Matt Leybourne, GNS Science and Wendy Spirito, Geological Survey of Canada.

Congratulations go out to Sarah Lincoln, our EXPLORE business manager. She gave birth to a healthy baby girl on February 3. Sarah will be on leave from work for the year but will continue with her business manager duties.

Beth McClenaghan
holes (also termed “bore holes” or “bores”), and open wells are all suitable for sampling groundwater, however, detailed notes, sample preparation and data interpretation are required. Comparing similar sample types is critical. In much of Australia the lack of available springs and seeps means this type of sample has limited use.

Basic Equipment

Water collection

Table 2 shows groundwater sampling methods and some of the advantages and disadvantages of each. Bailers (Table 2, method #1) are commonly employed for rapid retrieval of water samples. Numerous types are available and clear plastic disposable types are ideal for vertical bore holes.

Disposable bailers can be reused with care and cleaning. Other heavier types (with stainless steel end caps that house the valves) can be used, particularly for angled drill holes. The added weight ensures the sample is taken from the desired depth.

Figure 1a shows two bailer types and size (one is the heavier stainless steel ended 40 mm diameter bailer with rubber flow through valves and the other is a 19 mm diameter, plastic disposable bailer that uses a plastic ball to stop water backflow). Ideally, the retrieval cord has depth markings on it to gauge water table height and sample depth (Giblin 2001), but this is not required if a depth probe is used.

Figure 1b shows two bailer types and size (one is the heavier stainless steel ended 40 mm diameter bailer with rubber flow through valves and the other is a 19 mm diameter, plastic disposable bailer that uses a plastic ball to stop water backflow). Ideally, the retrieval cord has depth markings on it to gauge water table height and sample depth (Giblin 2001), but this is not required if a depth probe is used.

Figure 1c shows two bailer types and size (one is the heavier stainless steel ended 40 mm diameter bailer with rubber flow through valves and the other is a 19 mm diameter, plastic disposable bailer that uses a plastic ball to stop water backflow). Ideally, the retrieval cord has depth markings on it to gauge water table height and sample depth (Giblin 2001), but this is not required if a depth probe is used.

Figure 1d shows two bailer types and size (one is the heavier stainless steel ended 40 mm diameter bailer with rubber flow through valves and the other is a 19 mm diameter, plastic disposable bailer that uses a plastic ball to stop water backflow). Ideally, the retrieval cord has depth markings on it to gauge water table height and sample depth (Giblin 2001), but this is not required if a depth probe is used.

Figure 1. Typical sampling gear required for groundwater sampling; a) example of bailers (with polychain cable on reel) and a dip probe for depth measurement; b) water sample bottles and activated carbon sachet (inset); c) commonly used filtration equipment for water sampling*; d) meters, probes, variable pipette and solutions required for groundwater sampling. Solutions include pH buffer, saturated KCl, distilled/DI water, conductivity check solution and high purity HNO3.

*Rubber plunger on syringe pictured is not recommended for trace metals analysis due to Zn contamination. All plastic plungers are available.

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Hydrogeochemistry for mineral exploration... continued from page 3

Table 2. Groundwater sampling methods with advantages and disadvantages of each.

<table>
<thead>
<tr>
<th>Sampling method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Direct bailing from bore holes</td>
<td>Quick and portable, mostly applicable for exploration</td>
<td>Potential for contamination, interaction of groundwater with surface water, soil, air</td>
</tr>
<tr>
<td>2. Windmill sampling directly</td>
<td>Quick and only a bucket is required for collection, applicable for exploration and generally research</td>
<td>Potential for contamination, restricted available sample sites, shallow groundwater systems only</td>
</tr>
<tr>
<td>3. Pumping (3 bore volumes) with flow through cell for measurement</td>
<td>Very consistent results, applicable for research</td>
<td>Very slow, pumping equipment is not as portable, more equipment required. Unless drill hole is properly prepared, significant mixing of aquifers</td>
</tr>
</tbody>
</table>

from actively pumping farm bores and windmills are an effective way of sampling, but not always available in areas of interest. Pumps (Table 2, method #3) can be employed, providing the most representative results, particularly if at least three bore volumes are removed initially and a flow through measuring device is used i.e. the freshly recharged groundwater is measured as it is in situ with no atmospheric contact. While valuable in some studies, the time commitment to hydrogeochemical sampling in this mode is not practical for exploration and will not be discussed. Other options for more portable pumps and comparison to bailers are discussed by Leybourne & Cameron (in press) and Leybourne et al. (2000).

Water bottles and general equipment

High density polyethylene (HDPE) bottles are commonly used and suitable for groundwater samples (Hall 1998; Reimann et al. 1999; U.S. E.P.A. 1983), but these should be monitored using blanks to ensure no contamination occurs from the plastic (Reimann et al. 2007). Two sizes are used by CSIRO for sampling in Western Australia; 125 mL for the measurement of cations, anions and alkalinity and 1000 mL for the measurement of Au and PGEs (Fig. 1b). Other ancillary equipment is documented in Giblin (2001 Appendix 1).

Filtration gear

A variation on the method of Giblin (2001) is that field
Hydrogeochemistry for mineral exploration... continued from page 4

filtration is necessary for collecting the most representative “dissolved” fraction of elements. Cameron et al. (1997) determined filtration was unnecessary in Canadian surface waters that have very little particulate matter, but in semi-arid Australia the large quantities of sediment and organic debris that is frequently present in bailed samples need to be filtered out immediately.

Commonly the term “dissolved” refers to the water and its constituents that pass through a <0.45 μm filter membrane (Hall et al. 1996). Some clays and colloids are much smaller than this and will be analysed as “dissolved”, but minimising the interference from larger solids is desired. As discussed later, there is little difference between 0.45 and 0.1 μm filtration for all elements tested, except Fe and Al. Multiple options for filtering water samples exist. The commonly available Nalgene® units of 250 mL capacity are ideal for most exploration projects. The filter unit uses a mixed cellulose, nitrocellulose or polyethersulphone filter paper (all of which are suitable). The pore size should be 0.45 μm or less and the filter diameter is dependent on the unit size. A comparison of two filter pore sizes is documented later. The unit shown in Figure 1c requires 47-50 mm diameter filter papers. A pump is required with these filter units to ensure filtration is not overly time consuming. Other options include syringe filters that attach to a syringe which then provides positive pressure to filter (Fig. 1c). Syringe filters are best used for small volume sampling (<50 mL). All-plastic syringes should be used as the rubber parts used in some syringes contain significant quantities of Zn and can contaminate water samples.

Field measurement equipment and chemicals

Essential field measurements for groundwater include pH, Eh and temperature. Electrical conductivity (EC) is beneficial, but can also be done in the laboratory later. Alkalinity measurements can be done in the laboratory for convenience if the sample bottle is properly sealed and there are low dissolved concentrations of elements such as Fe and Al. These elements can oxidize, generate acid and following neutralization of this acid by consuming bicarbonate, lower the alkalinity concentration from that of the original groundwater conditions.

Some pH/mV and conductivity electrodes and meters have a specific range of measurements, so it is important to ensure the equipment is suitable for the sampling area. For example, sampling in southern Australia requires conductivity meters that can measure up to 200 mS/cm. The electron potential or redox electrodes (Eh) are effective in Western Australian groundwater where the Fe2+ and Fe3+ couple are the dominant redox sensitive ions. The use of Eh measurements should be interpreted with care, and in other regions obtaining useful and stable Eh measurements is not possible. Measurement error is commonly 10-100 mV, which across a potential range of greater than 1200 mV is still acceptable in obtaining information of the groundwater characteristics (e.g., Fe oxide, Mn oxide or sulfide dominated). The Pt electrodes have proven to be robust in measuring groundwater in semi-arid and arid Australia. Associated with the measurement electrodes are solutions required for calibration, reference and storage (Fig. 1d). The Eh electrode will require a check solution such as Zobell’s or Quinhydrone to standardise against the theoretical hydrogen electrode. Conductivity meters also have standard solutions based on type and range of measurements for calibration. Finally, saturated KCl is often used to store the probes in, but this may vary based on the type of electrode.

Other chemicals required are a high purity concentrated (69%) nitric acid for preservation of the cations sample and DI water (Fig. 1d). Acid is required (for one subsample) to ensure metals and metalloids remain in solution. This is particularly important for Fe2+ that may precipitate in the surface, oxygen-rich environment as Fe2+ oxyhydroxides, and in doing so adsorb other dissolved constituents biasing the results. Addition of acid can be done later in the laboratory to reduce potential for contamination. Samples should be kept cool and out of direct sunlight. We have not observed any problems from samples that were stored between 4°C and 35°C for periods less than two weeks.

Carbon sachets

Carbon sachets weighing approximately 1 g (Fig. 1b inset) have been used in Australia to adsorb and concentrate certain metals from the water resulting in the low level (ng/L) detection of Au and PGE (Giblin 2001; Gray & Noble 2006). Direct analysis (Leybourne & Cameron in press) can be used with other fresh water samples, but the detection limits required are not consistently achieved in Australian saline samples. These sachets are presently manufactured by CSIRO (construction details are available from the authors). Exchange resins have been tested, but have not been used as extensively or as successfully as the carbon sachets (Gray & Noble 2006). A case study using the carbon sachets is presented in Noble et al. (this issue).

Generalized Sampling Method and Analysis

Not all sites are suitable for groundwater sampling. Site investigation is the first critical step to obtaining acceptable samples. Record notes on location, type of sample, type of casing (PVC or metal, open or closed, slotted) and potential contaminants, i.e. Fe from rusted pipe casing, excessive organics, drilling grease or dead animals in the water. It is important to note this or even exclude contaminated samples. A flow chart of the following sampling method is depicted in Figure 2.

Calibrate instruments

Calibration of instruments should be performed daily and checked if conditions change or irregular measurements are shown. The electrodes and meters should be checked against their required reference standards. Ensure the correct storage solutions for each electrode is used for probe longevity and accurate measurements.

Rinse equipment and set up filtration unit

The bailer or other water collection device should be rinsed with DI water prior to collection of each sample. Filtration equipment should also be thoroughly rinsed.
Hydrogeochemistry for mineral exploration... continued from page 5

Place a new filter paper or syringe filter for each sample, being careful not to introduce dirt or contamination into the unit. Use a vacuum pump or syringe to filter the solution. Commonly, a two-person team should be used for groundwater sampling, with one person collecting the water and the other performing the “clean” work of the filtration, sample preparation and measurements.

**Label bottles**

A complete set of chemical analysis will require four bottles (isotope work is more specialized and not considered here). The bottles should be labelled with an identification number and the type of future analysis on the cap, shoulder of the bottle and main body of bottle.

- **Bottle 1** will be used for anion analysis (125 mL bottle filled with ~ 50 mL)
- **Bottle 2** will be used for alkalinity (125 mL bottle completely filled)
- **Bottle 3** will be used for cation analysis (125 mL bottle filled with 125 mL)
- **Bottle 4** will be used for carbon Au/PGE analysis (1 L bottle filled with ~1 L)

**Sample groundwater**

A bailer is lowered down a hole until the sampler hears or feels (the fall rate will slow) the top of the water. The depth to the water table should be recorded. This

Figure 2. Flow chart of general method for hydrogeochemical sampling in Western Australia.

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**Assays**

- Biogeochemistry
- Hydrogeochemistry
- Lithogeochemistry
- Selective Extractions
- Trace Element Geochemistry

- A new Bioleach option designed to help identify metals associated with SGH anomalies

... and more
measurement can be completed separately and more accurately with the depth probe. Lower the bailer to the desired sampling depth or until refusal (bottom of hole) and retrieve the water sample. Consistency is the key to representative sampling, previous research by others has sampled, where possible, at least 5 m below the water table to avoid the chemical oxidation changes which occur close to the surface (Gray & Noble 2006; Giblin 2001 Appendix 2). The first water collected is a rinse for the bailer and also used to rinse the measurement electrodes. Repeat the bailing procedure until approximately 2 L of water is collected (excluding the first rinsed sample).

**Groundwater measurement**

Place the initial bailer rinse-water in a container with the electrodes on and start the devices, but do not record numbers. Tip the remaining water out of bailer. The second sample of water is used to contain the water in the container to measure water parameters (tip out initial rinse). Record Eh, pH and EC over 5-15 minutes until stabilized. In some cases Eh may still vary up to 50 mV. Ideally, Eh measurements should be made in a flow-through cell to avoid the introduction of air into the sample that can cause erroneous measurements. For exploration purposes this is not often practical, but it is important to measure the water quickly after it is retrieved and not let to stand for more than 15 minutes. Reduced groundwater (measured < 200 mV) readings may decrease and then begin to rise. The minimum value is the most important for later data processing with this type of sample. A comparison of bailed versus pumped groundwater and the Eh differences are reported in Leybourne & Cameron (in press). For EC, pH (and Eh in most samples) the stable measurements are used. It is good practice to record all measurements over time.

**Filtered samples**

Initially filter approximately 50 mL of water. After all the water has passed through the filter membrane, pour the filtrate into the 125 mL bottle (bottle #1) for anions analysis. This sample is filtered, but not acidified. Pour another 150 mL of water into the top of the filter unit and filter. Pour approximately 5 mL into the bottle for cations analysis, cap and shake vigorously for 10 seconds. Discard this water. Finally fill the cations analysis sample bottle (bottle #3) with the remaining filtered water. This sample is acidified later with high purity nitric acid to 0.2% v/v or greater to ensure there are no Fe precipitates. Greater concentrations of acid can be used if precipitates remain after the initial aliquot of acid is added. Continue to add acid incrementally every few days until the Fe is dissolved.

The sample that is not acidified (bottle #1) is analysed for major anions by Ion Chromatography (IC) and independently for dissolved organic C and PO₄. The acidified sample (bottle #3) is analysed for major, minor and trace metals using by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and ICP-Optical Emission Spectrometry (ICP-OES) for the full suite of elements available.

### Table 3. Elements/compounds with general detection limits and the analytical instrument or method used for Western Australian groundwater analyses.

<table>
<thead>
<tr>
<th>Element</th>
<th>Units</th>
<th>Method</th>
<th>Detection limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>ng/L</td>
<td>ICP-MS Carbon</td>
<td>5</td>
</tr>
<tr>
<td>Al</td>
<td>mg/L</td>
<td>ICP-OES</td>
<td>0.002</td>
</tr>
<tr>
<td>As</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
</tr>
<tr>
<td>Au</td>
<td>ng/L</td>
<td>ICP-MS Carbon</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>mg/L</td>
<td>ICP-OES</td>
<td>0.1</td>
</tr>
<tr>
<td>Ba</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
</tr>
<tr>
<td>Bi</td>
<td>ng/L</td>
<td>ICP-MS Carbon</td>
<td>0.5</td>
</tr>
<tr>
<td>Br</td>
<td>mg/L</td>
<td>IC</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/L</td>
<td>ICP-OES</td>
<td>0.1</td>
</tr>
<tr>
<td>Cd</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
</tr>
<tr>
<td>Ce</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>mg/L</td>
<td>IC</td>
<td>10</td>
</tr>
<tr>
<td>Co</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
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<tr>
<td>Cu</td>
<td>μg/L</td>
<td>ICP-MS</td>
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<td>mg/L</td>
<td>DOC analyser</td>
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</tr>
<tr>
<td>F</td>
<td>mg/L</td>
<td>IC</td>
<td>0.01</td>
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<tr>
<td>Fe</td>
<td>mg/L</td>
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<td>0.004</td>
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<td>Ga</td>
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<tr>
<td>HCO₃⁻</td>
<td>mg/L</td>
<td>Titratin</td>
<td>1</td>
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<tr>
<td>K</td>
<td>mg/L</td>
<td>ICP-OES</td>
<td>0.08</td>
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<tr>
<td>La</td>
<td>μg/L</td>
<td>ICP-MS</td>
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<td>ICP-MS</td>
<td>0.01</td>
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<td>Na</td>
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</tr>
<tr>
<td>Ni</td>
<td>μg/L</td>
<td>ICP-MS</td>
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</tr>
<tr>
<td>NO₃⁻</td>
<td>mg/L</td>
<td>IC</td>
<td>1</td>
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<tr>
<td>Pb</td>
<td>μg/L</td>
<td>ICP-MS</td>
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</tr>
<tr>
<td>Pd</td>
<td>ng/L</td>
<td>ICP-MS Carbon</td>
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<tr>
<td>PO₄³⁻</td>
<td>mg/L</td>
<td>Titratin</td>
<td>0.009</td>
</tr>
<tr>
<td>Pt</td>
<td>ng/L</td>
<td>ICP-MS Carbon</td>
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<tr>
<td>Rb</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
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<tr>
<td>Sb</td>
<td>μg/L</td>
<td>ICP-MS</td>
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<tr>
<td>Si</td>
<td>mg/L</td>
<td>ICP-OES</td>
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<td>Sn</td>
<td>μg/L</td>
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<td>SO₄²⁻</td>
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<td>Sr</td>
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<tr>
<td>W</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
</tr>
<tr>
<td>Zn</td>
<td>μg/L</td>
<td>ICP-MS</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Detection limits vary depending on salinity levels, with more saline samples having higher detection limits due to increased dilution requirements. Many of the rare earth elements (REE), Au and PGE are below detection in groundwater samples from Western Australia, hence the use of the activated carbon sachet to concentrate Au and PGE to enable detection of these elements. Table 3 shows the full suite of elements, analytical instrument and achieved detection limits used by CSIRO for arid and semi-arid Australian groundwater. In other regions of Australia and the world the groundwater is fresher, requiring little or no dilution for analysis. In these environments much lower detection limits are achieved (0.1-1 ng/L) without the use of carbon for concentration.

**Unfiltered samples**

A 125 mL bottle (bottle #2) for alkalinity analysis is filled with sample water, making sure to exclude all bubbles and leaving no air space at the top. The 1000 mL bottle (bottle #4) for Au and PGE analysis is filled with unfiltered water to within 2 cm of the top. Using plastic tweezers, a carbon sachet is added to this bottle along with 10 g NaCl. This method varies from that reported in Giblin (2001) as her use of cyanide powder in the field was considered to be too hazardous for general use.

The alkalinity sample is titrated with a known concentration of acid (e.g. 0.01M HCl) to an endpoint at pH = 4.3. Commercial laboratories can conduct this analysis, but it can also be performed in the field with a burette, stirrer and pH meter. A field alkalinity titration is a time consuming step in the field, making it less practical, and is often better done as soon as possible in a laboratory setting. Detection limits for the titration are approximately 5 mg/L.

The carbon sachet analysis is carried out at a commercial laboratory (presently Ultra Trace Ltd laboratories in Canning Vale, Western Australia). Sachets should be left in the sample bottle for at least 4 days and preferably placed on a bottle roller or shaker. The sachet is weighed (dry; 3 decimal places) and then the metals are determined by ashing, dissolution in aqua-regia and measurement using ICP-MS. The element suite is Au (0.1 μg/L), Pt (1 μg/L), Pd (1 μg/L), Ag (5 μg/L), with the reported lower detection limits in brackets. Using the sample weight and solution volume the final calculated values are an order of magnitude lower (ng/L). The analytical method described above has been previously tested for Au and PGE recovery in varying salinities, with activated carbon, with a recovery of ~95% (unpublished data). Field and analytical blanks, as well as

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**Figure 3.** Chloride, Ca, Mo, U, Si and V concentrations compared from the 0.1 and 0.45 μm filtration treatment methods. The blue line represents a 1:1 correlation and with no differences between pore size. Error bars are applied based on the detection limit of the analysis (Gray & Noble 2006).
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**Filter size comparison**

A key consideration for the previously described sampling methods is the influence of pore size in filtration. Studies by Hall et al. (1996) and Kennedy et al. (1974) have investigated the influence from filter pore sizes, but the samples tested were not from groundwater collected using the previously described methods. Clay minerals are commonly much smaller than 0.45 μm and theoretically could pass through a filter and adsorb metal in solution prior to analytical determination or release elements on acidification. A comparison between 0.1 μm and 0.45 μm pore size filters was conducted on 18 groundwater samples from a fresh to saline environment in the central Yilgarn and 11 fresh groundwaters from the NE Yilgarn Craton. Both gave similar results, with the later test described in detail below.

The results for U, Mo, Si and S show no difference between the two pore sizes (Figs. 3 & 4), similarly to the patterns for major anions and cations (Fig. 3). Vanadium,
Hydrogeochemistry for mineral exploration... continued from page 10

W and Cu and to a lesser extent Ni (not shown) and Zn also indicate no difference (Fig. 4), but there are fewer samples for comparison as many samples were below detectable concentrations. Greater salinity increases the required dilution and in turn increases the detection limits. However, Al and Fe show significant, random variability. Aluminum concentrations are higher in the 0.1 μm pore size filter samples as compared to 0.45 μm pore size filter. This higher concentration for the finer pore size does not support the idea that small clay minerals (aluminosilicates) are passing through the 0.45 μm filter and being retained by the 0.1 μm filter. In comparison, the near-perfect correlation between filter sizes for Si suggests the greater dissolved Si concentrations are not influenced by the comparatively smaller concentrations of Al and Fe silicates that may pass through the filter membranes. The lack of significant difference between filter sizes for the trace elements suggests they are not influenced by Al and Fe colloids i.e. Al and Fe do not irreversibly adsorb the dissolved trace metals. Based on these data, Gray & Noble (2006) concluded the use of either tested filter pore size is acceptable for groundwater exploration in the NE Yilgarn. The more widely available, faster filtering and less expensive 0.45 μm pore size is preferred.

CONCLUSIONS

Groundwater sampling methods are easy to use and are accessible to most industry explorers (with limited hydrogeochemical background) to develop a successful groundwater exploration program with the general procedure of this paper and associated literature references. This method is most useful in the arid and semi-arid regions of Western Australia where access can be difficult and the groundwater is highly variable in pH, salinity and depth (from the surface).

Tests have shown the 0.45 μm pore size filters were cost effective and of sufficiently small pore size for groundwater sample preparation. Activated carbon sachets added to 1000 mL of unfiltered groundwater can be routinely used for Au and PGE analysis, successfully lowering detection limits by up to three orders of magnitude in saline groundwater. Improving detection for elements in saline samples will enhance the chances for exploration success in the future.

ACKNOWLEDGEMENTS

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Hydrogeochemistry for mineral exploration in Western Australia (II):
Case Studies

INTRODUCTION

Mineral deposits are becoming more difficult to find and greater emphasis is being placed on exploring through deep (>30 m) transported cover and into basin terrains. Groundwater interacts with mineralized rocks and can display a geochemical signature with a much greater footprint than other sampling media, as groundwater is mobile (Cameron 1978; Giblin & Dickson 1992; Leybourne & Cameron 2005). The larger size of groundwater geochemical anomalies can reduce the required drilling density needed to explore in a region, an important consideration for cost-effective exploration in covered terrains.

The application of hydrogeochemistry for mineral exploration is valuable in Western Australia and other parts of the world, and is particularly useful for early-stage exploration and development of regional targets (Gray et al. 2009; de Caritat et al. 2005; Taufen, 1997). Research by Carey et al. (2003), Gray (2001), Gray & Noble (2006) and Gray et al. (2009) has advanced the use of exploration hydrogeochemistry in Western Australia, while Kirste et al. (2003), Pirlo & Giblin (2004) and de Caritat et al. (2005) have successfully applied groundwater exploration methods in other parts of Australia. Outside of Australia, extensive groundwater research for mineral exploration has been conducted in North America (Boyle et al. 1993; Gillis et al. 2004; Leybourne et al. 2000; Phipps et al. 2004), South America (Cameron et al. 2002; Cameron & Leybourne 2005; Leybourne & Cameron 2006) and elsewhere (de Caritat et al. 2009; Pauwels et al. 2002). This paper presents results from a number of sites used for hydrogeochemical investigations in Western Australia (Fig. 1). The groundwater was collected and analysed by the procedures of Noble & Gray (2010).

CASE STUDIES

Harmony Au Deposit – A local scale investigation of Au

The Harmony Au deposit is located within a depositional plain approximately 9 km west of Peak Hill and 90 km north of Meekatharra in Western Australia (Fig. 1). The region is arid, with low, irregular rainfall averaging 240 mm per annum (Bureau of Meteorology, 2008). The sparse vegetation consists largely of mulga (Acacia aneura), and drought-resistant shrubs and grasses. The deposit was discovered in 1991 by RAB drilling to saprolite and fresh rock, although, in retrospect, sampling of groundwater, buried laterite and the basement-cover interface would have also been successful (Robertson 2001; Robertson & Gray 2003).

The site is located in the Palaeoproterozoic Bryah Basin. The mineralization is on the contact between the Ravelstone and Narracoota Formations. The Ravelstone Formation is a thick turbidite sequence of fine-grained, mafic, feldspathic and lithic wackes. Folded ultramafic and mafic volcanics comprise the Narracoota Formation. The sequences are metamorphosed to lower to middle greenschist facies (Pirajno & Occhipinti 1995; Pirajno et al. 1995). Primary mineralization is associated with hematitic quartz veins and carbonate-filled breccia, with Au and Ag occurring as inclusions in pyrite with associated pyrrhotite, pentlandite, chalcopyrite and scheelite. Trace element signatures in the mineralized rocks include As, Te, Zn and Pb, with Au and W the most useful pathfinders (Harper et al. 1998).

The deposit has been weathered to ferruginous saprolite and covered by colluvium-alluvium. Colluvium-alluvium in the area is 7-12 m thick, but directly over the deposit (a palaeo-high) it is 1-3 m thick. The upper few metres of the colluvium-alluvium are silicified to a red-brown hardpan. Below this, the material is similar, but finer grained and un cemented. Adjacent to the deposit, but beneath the colluvium-alluvium, the deposit is flanked by a lateritic

continued on page 13
duricrust of approximately 8 m thickness. A palaeochannel drains from 1 km south of the deposit in a northwest direction (Fig. 2). The palaeochannel is filled with 10-24 m of mottled, thick, puggy, clay-rich sediments (Robertson 2001).

The shallow aquifer groundwater <2 km from the Baxter deposit has a neutral pH, is fresh and generally similar to those from the northern Yilgarn Craton. The groundwater flows southeast towards the channel. Approximately 40 samples were collected from drill holes over a 6 km² area. Dissolved Au concentrations are low (2-11 ng/L) and ~100 times less than in mineralized areas around Kalgoorlie. Despite these low concentrations, dissolved Au is a good pathfinder for mineralization in the Baxter region (Fig. 2).

Some groundwater has concentrations of Au below detection over mineralization that may indicate inconsistencies in Au mobility in this environment. Additionally, Sc, Mo (Fig. 2), W and possibly Rb have elevated groundwater concentrations in areas of Au mineralization and are more consistent pathfinders than Au itself in groundwater at this local scale. This elemental suite is similar, though more limited, to those observed elsewhere in the NE Yilgarn for detecting Au mineralization.

Figure 2. Dissolved Au (top) and Mo (bottom) concentrations in groundwater at the Baxter/Harmony gold deposit (dots) superimposed on maximum Au concentrations in the regolith at the interface between colluvium and residuum at a depth ranging between 1 and 12 m. The pit outline is shown towards the centre. The palaeochannel outline and the direction of ground water flow are also depicted.
Chromium in groundwater may be used to indicate underlying ultramafic lithologies in this region (Gray & Noble 2006). Chalcophile elements (e.g. As, Mo, Ag, Sb, W, Tl and Bi) are commonly enriched and more mobile in neutral groundwater in direct contact with weathering sulfides, suggesting regional groundwater sampling may be effective at locating these types of deposits.

Groundwater PGE for nickel exploration – a greenstone belt investigation

The Norseman-Wiluna greenstone belt extends through the NE Yilgarn Craton (Fig. 1) and hosts numerous major Ni deposits. The area is semi-arid to arid and has a Mediterranean climate with hot, dry summers and cool, wet winters. Mean annual rainfall is between 200-300 mm, similar to the Harmony study site (Bureau of Meteorology 2008). Mulga dominates the vegetation with minor drought-resistant shrubs and grasses. The primary land use is cattle grazing and mining.

Greenstones, including ultramafic and mafic volcanics, are enclosed within granitoids. This greenstone belt is abundantly mineralized, hosting numerous Ni sulfide deposits, including Cosmos, Honeymoon Well (Wedgetail, Corella, Harrier, Hanibals), Harmony, Mt Keith, Perseverance, Prospero, Rocky’s Reward, Sinclair, Waterloo, Weebo and Yakabindie (Six Mile Well/Goliath). Most mineralization is in stratiform volcanic-hosted deposits, related to komatiite flows (Morris & Sanders 2001). The mineralization is varied massive, disseminated, matrix and remobilized stringer and breccia hosted sulfide mineralization of pentlandite and pyrrhotite. The sulfides also contain significant concentrations of Platinum Group Elements (PGE). A comprehensive review of the geology and Ni mineralization styles and settings is given by Barnes (2006).

The topography is broadly flat with ancient alluvial transported cover of varied thickness (a few metres to tens of metres). Soils are dominantly acidic, sandy with red-brown hardpans and lack significant calcrite horizons except in channels. A comprehensive review of the regolith and geomorphology of the region is given by Anand & Paine (2002). The watertable along the greenstone belt is 10-40 m below surface.

The groundwater study included approximately 300 samples from in and around eight deposits along 160 km of the Norseman-Wiluna greenstone belt between Leonora and Wiluna. Gray & Noble (2006) investigated the evolution of groundwater and the hydrogeochemical signature related to sulfide weathering. The concentration of Pt and Pd in the groundwater was determined as part of this study using preconcentration onto activated carbon sachets (Noble & Gray 2010; Giblin 2001; Gray 2001). This method showed Pt and Pd (and W) are a useful vector to Ni mineralization (Fig. 3). The concentrations of PGE in the NE Yilgarn groundwater is very low (commonly <1 ng/L), making the use of these elements as pathfinders difficult. Samples of >1 ng/L (detection) are considered anomalous. Results show that higher concentrations of Pt, as well as any detectable Pd, are found mostly within 2 km of mineralization (Fig. 3). At Honeymoon Well, the four mineralized zones are all delineated with detectable Pt (>1 ng/L, Fig. 3).

The deposits all have elevated, but sporadic, Pt concentrations in the groundwater around the deposits. The lack of a PGE groundwater signature does not indicate an absence of Ni sulfide mineralization (i.e. could be a false negative), but a positive PGE result is a strong indicator of mineralization. The groundwater around the Jaguar VMS Zn deposit (Fig. 3) is also enriched in PGE, indicating that PGE in groundwater may be indicators of several different types of sulfide mineralization. The Ni sulfide mineralization in the Norseman-Wiluna greenstone belt contains significant PGE concentrations, but the weathering rates and mobility of PGE means concentrations are expected to be limited. Regardless, the use of PGE is more effective than the direct measurement of the target element (Ni for NiS deposits and Zn and Cu for the VMS deposits) alone. Nickel, Zn and Cu in groundwater are commonly adsorbed by clays and Fe-oxides and, as a result, the soluble concentrations are erratic, and often below detection, and do not commonly produce coherent anomalies around the sulfide mineralization.

Improving the detection limit for PGE in groundwater may significantly enhance exploration success using hydrogeochemistry for Ni sulfides and VMS in Australia.

Groundwater U from farm wells and bores – a regional scale investigation

Previous work has demonstrated that groundwater geochemistry can provide large geochemical signatures (Gray & Noble 2006; Cameron & Leybourne 2005). Uranium is...
generally mobile in groundwater and surface water and, in previous work, has shown geochemical haloes around U mineralization (Cameron 1980; Mann & Deutscher 1978; Peuraniemi & Aario 1991). A research project by the CSIRO Minerals Down Under Flagship assessed the value of low-density groundwater sampling (>5 km sample spacing) for mineral exploration and environmental management (Gray et al. 2009). The groundwater project objectives and spacing are similar to the successful laterite geochemistry project of the Yilgarn Craton (Cornelius et al. 2008) that showed large geochemical signatures in laterite, but spatially the two projects have only a minor overlap. This paper will only discuss some of the U results from the regional groundwater study.

The northeast Yilgarn Craton consists of Archaean granites and granitic gneiss and extensive northeast oriented, elongate greenstone belts (Williams 1975; Myers 1997). Cassidy et al. (2006) summarises the tectonic evolution of the Yilgarn Craton. The granitic rocks comprise deformed and metamorphosed granodiorite-monzogranite. The greenstones generally comprise mafic and ultramafic volcanic rocks underlain by quartzite, banded iron formation and minor felsic volcanics.

The climate and landforms are similar to those mentioned in the previous case studies. The northeast Yilgarn regional study covered approximately 470 x 250 km or 92 000 km² (Fig. 1) with numerous Ni (sulfide and laterite), Au (orogenic) and U (secondary carnitite) ore systems, as well as several Zn (VMS) deposits (including the area of the previous greenstone belt case study).

Secondary carnitite style deposits (calcrite uranium) are prevalent along the drainage systems throughout the region, and include the world class Yeelirrie deposit, Lake Maitland, Centipede, Lake Way and the Cogla Downs/Hilveiv prospects (Fig. 4).

Groundwater samples (1420) were collected from farm wells and bores on ~5 km spacing where available. Regionally, the groundwater is relatively fresh and of neutral pH. Salinity tends to increase towards the drainages and valley floors where, in many cases, there are salt lakes. This is also the region where soluble U precipitates as carnitite.

Dissolved U alone is a reasonable targeting element on the ~5 km sample spacing, confirming the findings of Cameron (1980) and Mann & Deutscher (1978). Uranium concentrations in the northeast Yilgarn range from 1 to 700 μg/L (Fig. 4). In particular, the greatest U concentrations are close to the Yeelirrie deposit (along the drainage flow), identifying the Yeelirrie area as the strongest target (Fig. 4). Other known deposits also have elevated U concentrations compared to the background, with most of the known deposits occurring close to the larger (>100 μg/L) U groundwater concentrations. These larger U concentrations are consistently in the topographically lower parts of the landscape (drainage channels). Exceptions to this are the

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**Figure 4.** Northeast Yilgarn groundwater U concentrations. Major U deposits are labelled. Coloured polygons indicate major greenstone (green), granite (pink), felsic (yellow) and sedimentary (brown) lithologies. Black lines are faults.
Hydrogeochemistry for mineral exploration... continued from page 15

second and third largest concentrations of U >297 μg/L towards the southwest of the study area in the Youanmi region (Fig. 4), which occur adjacent to the drainage divide and are in regionally elevated terrain. This particular area of elevated U concentrations in groundwater is unrelated to the palaeochannel/playa style deposits, and more likely reflects a primary ore source (this area does not show a surface radiometric response).

Uranium concentration alone does not strongly identify the second largest known deposit, at Lake Maitland, but this deposit is unusual because it occurs over greenstone bedrock (Fig. 4). Mineral saturation indices directly compute the activity of various chemical species, incorporating master variables such as pH and Eh of the system and, in turn, determine if the water is over- or under-saturated with respect to specific minerals. The carnotite saturation index (SI) is a direct measure of the potential for such deposits to form in palaeochannel or playa deposits. Spatially, the carnotite SI is more predictive than the U concentration and predicts most of the known deposits and prospects. The SI results for carnotite, reported in Gray et al. (2009), show the gradation of groundwater approaching saturation along the channels that corresponds to the location of the deposits. The carnotite SI also indicates that the groundwater upstream from Lake Maitland is close to saturation.

CONCLUSIONS

Groundwater sampling provides significant exploration potential at different scales in Western Australia, even where highly weathered rocks are over lain by transported material. Target and pathfinder element signatures may be much broader than geochemical haloes in other media and extension of hydrogeochemical exploration to sediment obscured Craton margins could be a cost-effective and viable technique for exploration in these areas. Comparison studies between sample media are required and the relationships between the laterite geochemistry data (Cornelius et al. 2008) and the groundwater data (where the two sets overlap) are statistically analyzing results. We also offer technical support for choosing the RM jars and 30g, 50g, 100g sachets for laboratories and exploration geologists.

An added benefit of mineral exploration using groundwater is that it provides additional data for monitoring human and livestock drinking water supplies, baselines for future hydrogeochemical exploration and environmental management (e.g. mine closure).

In addition to the groundwater regional study (Gray et al. 2009), a biogeochemical mapping project using 1400 mulga (A. aneura) samples has been started and will be completed by late 2010. This project will investigate the links between the regional groundwater chemistry and vegetation chemistry in the northeast Yilgarn, and provide the first large scale biogeochemical map in Australia. For additional information please contact the authors.

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Rob Bowell

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Todd Wakefield received a B.Sc. in geology from the University of Redlands in 1986, and a M.Sc. in geology from the Colorado School of Mines in 1989. While at CSM, Todd worked for Westmont Mining, exploring for gold in Nevada. Upon graduation, Todd joined Newmont Mining Company, where he worked as an exploration geochemist for the next 13 years on exploration and mining projects in Nevada, Southeast Asia, and South America. For the past five years Todd has worked for AMEC, an international engineering services company, as Principal Geologist and for the past year as US Manager of Consulting. For AMEC, he has worked on over 50 mining projects, including significant gold, copper, nickel, iron, vanadium, aluminum, and uranium projects in North America, South America, and Australia. He has published over 20 NI 43-101 Technical Reports on projects in North and South America, and has presented papers at technical conferences on subjects related to exploration geochemistry and mineral resource estimation. Todd’s interests include reconnaissance exploration, blind deposit exploration, and exploration data quality related to mineral resource estimation. Todd is a Fellow and past Councilor of the Association of Applied Geochemists, and is a member of the Australasian Institution of Mining and Metallurgy (AusIMM), Society of Mining Metallurgy and Exploration (SME), and the Geological Society of Nevada (GSN). He is currently based in Reno, Nevada.
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**RECENT PAPERS**

This list comprises titles that have appeared in major publications since the compilation in EXPLORE Number 144. Journals routinely covered and abbreviations used are as follows: Economic Geology (EG); Geochimica et Cosmochimica Acta (GCA); the USGS Circular (USGS Cir); and Open File Report (USGS OFR); Geological Survey of Canada papers (GSC paper) and Open File Report (GSC OFR); Bulletin of the Canadian Institute of Mining and Metallurgy (CIM Bull.): Transactions of Institute of Mining and Metallurgy, Section B: Applied Earth Sciences (Trans. IMM). Publications less frequently cited are identified in full.

Compiled by L. Graham Closs, Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401-1887, Chairman AEG Bibliography Committee. Please send new references to Dr. Closs, not to EXPLORE.


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Director General
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Expressions of interest and nominations are being sought for the chief scientific and administrative officer of ICENS. The mission of ICENS (http://www.icens.org) is the interdisciplinary application of science and technology to Jamaica’s development.

The scientific agenda emphasises integrated research programmes based on environmental geochemistry and because of the extraordinary levels of several elements, in certain Jamaican soils the present focus is on elemental transfers and potential consequences thereof in the system:

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Further details can be obtained by email at: icens@uwimona.edu.jm, by telephone at (876) 935 8288 or by mail addressed to: Search Committee c/o Ms. Verna Lumsden, ICENS, 2 Anguilla Close, University of the West Indies Mona, Kingston 7, Jamaica.

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