

Evaluating the diffusive gradients in thin films technique for the detection of multi-element anomalies in soils

INTRODUCTION

Soil sampling and chemical analysis is widely evaluated and applied by researchers and by mining companies for the purpose of geochemical exploration (Kelley *et al.* 2006). This sampling is usually undertaken as a first-pass evaluation of potential for mineralisation, and has become increasingly important due to the need for simple, low-cost methods that detect the presence or absence of mineralisation concealed by transported overburden (Kelley *et al.* 2006; Anand *et al.* 2007; Cohen *et al.* 2010). However, questions remain regarding the mobility and speciation of key elements in soils (Ma & Rate 2009), as these elements can exist in a variety of forms, including discrete phases (e.g. as minerals or salts) or as complexes adsorbed on to mineral surfaces. A variety of analytical methods can be used to determine the concentrations and fixation of elements in soils, including: Mobile Metal Ions™ (MMI), (Mann *et al.* 1998), Enzyme Leach © (Clarke 1993) and sequential extractions (Tessier *et al.* 1979; Chao 1984). While these methods are broad in scope and diverse in results (Mazzucchelli 1996; Hall 1998; Kelley *et al.* 2006; Cohen *et al.* 2010), the main objective remains the same: to correctly define any anomaly related to mineralization and enhance its expression (Cameron *et al.* 2004). Partial extraction techniques have been demonstrated to better highlight anomalies as compared to total digestion techniques (Cohen *et al.* 2010). The use of more rigorous statistical analyses of geochemical results to enhance signal detection has also gained prominence in recent years (Garrett *et al.* 2008). However, separating geochemical signals related to underlying mineralisation from the background continues to pose a challenge, despite the growing array of tools available to exploration geochemists.

One of the inherent difficulties with using methods such as partial extractions for determining the mobility and speciation of trace elements in soils, and thereby the presence

or absence of geochemical anomalies, is the effect of the analytical techniques on the soils and on the aqueous environment immediately surrounding the wetted particles of soil, i.e. the soil solution (Zhang *et al.* 1998). Ideally, mobility and speciation measurements in soil solution should be *in situ*, facilitated by procedures that minimise disturbance of the soil solution. Chemical separation techniques not

only alter the spatial variability of soil-solution properties (Sposito 2008), but can also affect the distribution of elemental species in solution (Zhang *et al.* 1998); therefore such an analysis does not represent a natural, undisturbed soil system. For example, the widely-used sequential extraction procedure as outlined by Tessier *et al.* (1979) examines the soil sample as a combination of five separate fractions which require a specific chemical attack in order to evaluate the geochemistry of the sample. Selective partial extractions can provide better anomaly contrast as compared to total element determination methods

(Filipek & Theobald Jr. 1981), provide information on the mode-of-occurrence of elements (Chao 1984), and may allow discrimination between metal enrichment mechanisms and determination of whether the elements are natural or anthropogenic in origin (Hall 1993). There have been a number of modifications to sequential extraction methods over the years, including variations in the steps required e.g. concentrations of reagents, pH used, time required per step, the fractions targeted and the extractants used (Hall *et al.* 1996; Gray *et al.* 1999; Reith & McPhail 2007); however, these steps rely on chemically perturbing the soil in order to elicit a response. Research on the actual mechanisms of extraction and response of the soils to the leaching agents has, to date, been limited (Cohen *et al.* 2010). To address this issue, a technique that measures element concentrations without the associated perturbations of physicochemical techniques is needed.

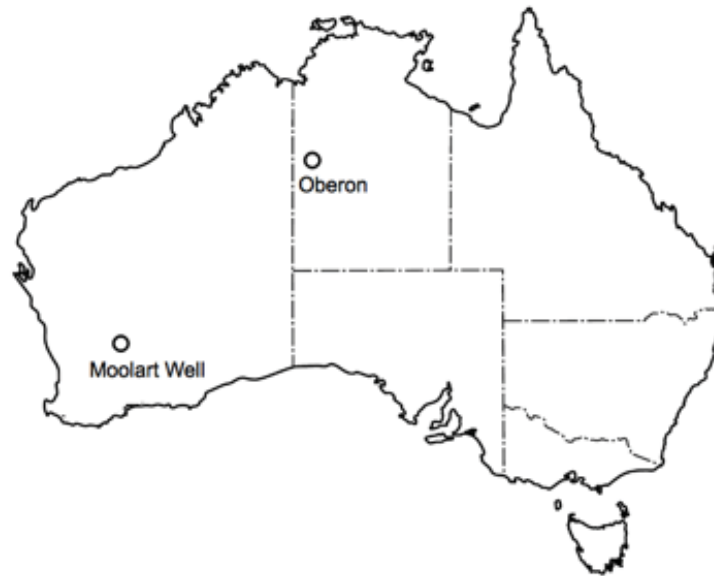


Figure 1. Location of the Moolart Well and Oberon prospects, adapted from Anand *et al.* (2007).

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President's Message

With 2014 just around the corner, this is my final President's Message. Matt Leybourne will assume the role of President of AAG and will bring a high level of professionalism to the position. Over the last decade, AAG has enjoyed a blend of Presidents representing industry (Dave Kelley, 2004-05 and Rob Howell, 2006-07), academia (David Cohen, 2008-09), provincial government (Paul Morris, 2010-11), and federal government (Bob Eppinger, 2012-13), so it is fitting that we return to a leader from industry with Matt. I wish him good luck and much success as he takes the helm.



The most obvious change for AAG in the last two years has been the creation and launching of our new website. This was a tremendous undertaking led largely by our webmaster, Gemma Bonham-Carter. Juggling duties as AAG webmaster, website coordinator, and now as a new mother (congratulations!), Gemma seeks to reduce her workload. Thus, we have been looking for a new website coordinator. Having been the website coordinator for several years, I can safely say that the role does not require website programming expertise (I have none!). Rather, it is largely a position for gathering input and ideas from AAG members, seeking new content, prioritizing Gemma's workload, and serving as a liaison between the AAG Council and webmaster/website. As you know, the website is critically important as an information source for AAG members and for the general public interested in AAG. In late-breaking news, as I write this message, Bruno Lemiere has stepped forward and has been accepted as the new Website Coordinator. Thank you Bruno! So please offer your suggestions and website content to Bruno directly (B.Lemiere@brgm.fr). One final note regarding the website: in late 2013 we will begin using PayPal for website credit card transactions such as membership renewals. We are doing this in order to adhere to e-commerce security and compliance issues. Without our own dedicated server, this is the simplest solution for AAG to maintain security aspects of online transactions.

Because of publication timelines, I am writing this message prior to AAG's 26th IAGS in Rotorua, New Zealand. Based on the pre-meeting organization to date, I am sure the meeting will be a successful event and a good opportunity for applied geochemists worldwide to reconnect at a stimulating meeting in a beautiful venue. I thank Tony Christie and his New Zealand colleagues for organizing and running the event and David Cohen as AAG's Symposium Committee Chair for keeping the AAG Council informed of progress along the way. Announced in Rotorua, the next IAGS will be in Tucson, Arizona, USA in 2015. This symposium is being organized by Erick Weiland with help from many AAG members. It has been a while since an IAGS was held in a desert environment and Tucson is a great choice. As of this writing, no one has stepped forward with proposals for hosting the 2017 IAGS. If you have a venue in mind and are willing to help organize one, now is the time to formulate a proposal. Details are found on AAG's website.

In looking over Paul Morris' final President's Message, I see that some things remain the same. To quote Paul, "As you are all aware, AAG continues to thrive due to the commitment of its members, especially those who take on roles associated with running the Association. A subset of the latter are the 'old hands' who have been doing their jobs (often quite varied within AAG) for a number of years, and have accordingly not only served us all well, but also accrued a large amount of corporate knowledge, which is an invaluable asset in terms of guiding new members. In the past few years, we have been fortunate in recruiting some new council members from a younger demographic, and I am hopeful that many of these will hang around AAG and become new 'old hands' as the existing 'old hands' move on." Paul's words are still pertinent. I thank our 'old hands' for helping to guide me over the last two years and am sure they/we will be around to help Matt in his new role. For brevity of space, I am not listing these people individually—just look at the inside cover of the back page of **EXPLORE** to see their names. But I must make an exception and thank three who have been here the longest: Gwendy Hall (Treasurer and GEEA Editor), Dave Smith (Secretary), and Betty Arseneault (Business Manager). Thank you for your MANY years of service to AAG! And thank you to the 'new hands' for strengthening and expanding the goals of AAG. We look forward to your leadership.

Bob Eppinger *President*



Notes from the Editor

The December 2013 issue of **EXPLORE** features one technical article by Andrew Lucas, Andrew Rate, Ursula Salmon, Nathan Reid, and Ravi Anand that describes the use of thin films for the detection of multi-element anomalies in soils. The research described in this article was funded, in part, by the Association of Applied Geochemists through our *Student Support Initiative*. **EXPLORE** thanks all other contributors and reviewers for this fourth issue of 2013: Steve Amor, Betty Arseneault, Charles Butt, David Cohen, Bob Eppinger, Philippe Freyssinet, Bob Garrett, Ian Jonasson, Erick Weiland, and Peter Winterburn. **EXPLORE** gratefully acknowledges our four corporate sponsors in 2013, Actlabs, ALS Minerals, Geosoft, and SGS, as well as our advertizers for their continuing financial support. Sarah Lincoln (**EXPLORE** Business Manager) and I wish all AAG members a safe holiday season and a successful 2014.

Beth McClenaghan *Editor*



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The diffusive gradients in thin films (DGT) technique

The diffusive gradients in thin films (DGT) technique potentially offers a new tool in the assessment of element speciation in soils for the purpose of geochemical exploration. The technique uses a device containing a binding resin gel (e.g. Chelex®-100 in a cross-linked polyacrylamide gel), diffusive gel (polyacrylamide or agarose, 0.8 mm thick) and

filter membrane (cellulose-nitrate, 0.45 μm porosity, 0.13 mm thick) in a specially-designed plastic housing (Davison & Zhang 1994). The device, depicted in Figure 2, can be placed in either waters or wetted soils. The diffusive hydro-gel limits the rate at which the flux of dissolved inorganic and organic species are captured by the resin layer (Zhang & Davison 1995). In soils, the technique removes labile

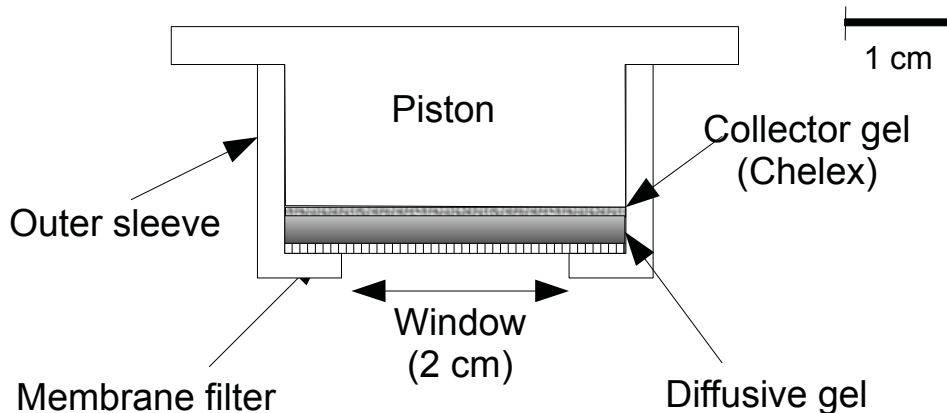
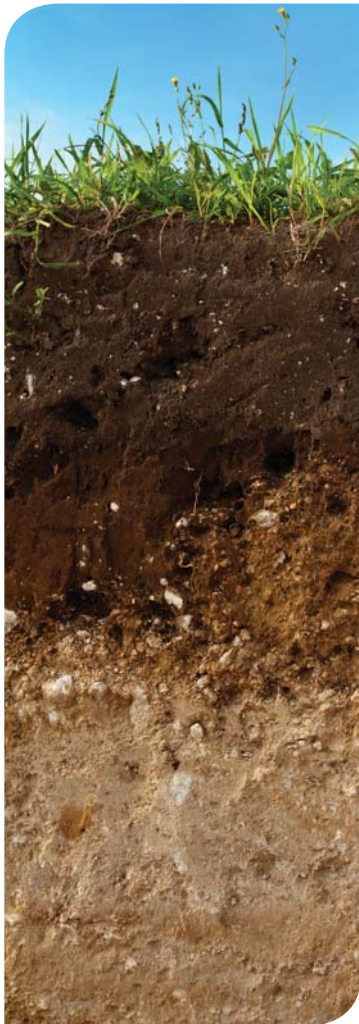


Figure 2. Schematic of the DGT device (Zhang & Davison 1995).

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elements from soil solutions and thus induces desorption or dissolution of the elements from solid phases, as depicted in Figure 3 (Zhang *et al.* 1998).

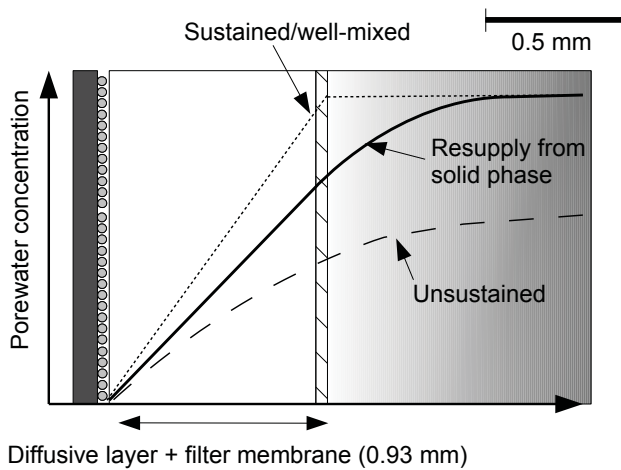


Figure 3. Schematic cross section through the DGT device and the adjacent soil solution (Zhang *et al.* 1998). The dotted line illustrates uptake by the DGT device in well-mixed solutions (e.g. flowing waters). The large-dashed line shows uptake when supply to the DGT device is by diffusion only. Commonly, there is some resupply from the solid phase, as depicted by the solid line.

The DGT technique presents several advantages for measuring element concentrations in soils, namely that the technique: pre-concentrates metals via diffusive transport through the soil solution (Zhang *et al.* 1998); induces resupply from elements bound to the solid phase (Harper *et al.* 1998); has very good sensitivity, especially when deployment times are extended (Davison & Zhang 1994); does not significantly alter the soil either chemically or physically; and has been demonstrated to behave analogously to plant roots for a variety of trace elements, including Cu (Zhang *et al.* 2001) and Zn (Koster *et al.* 2005). These last two features are of particular interest to geochemical exploration due to the uncertainty regarding the role of vegetation in generating surficial anomalies of mineralisation and associated uptake mechanisms (Ma & Rate 2009). While these features of DGT have been extensively evaluated for the purpose of environmental monitoring of soils (Harper *et al.* 1998; Zhang *et al.* 2001; Bade *et al.* 2012), no research has been carried out to date on assessing the suitability of the technique for mineral exploration using soil geochemistry.

The concentration of elements measured by DGT is determined using equation 1:

$$C_{\text{DGT}} = \frac{M \Delta g}{(D t A)} \quad (1)$$

where C_{DGT} is the concentration of target element in the soil solution, M is the mass of that element accumulated onto the resin gel, Δg is the thickness of the diffusion layer, D is the diffusion coefficient of the element, t is the deployment time and A is the area of the DGT device window. The

following elements are known to be detectable using the Chelex DGT: Co, Ni, Cu, Zn, Cd, Pb, Al, Mn, Ga, as well as the rare earth elements over a wide range of pH values and ionic strengths (Garmo *et al.* 2003). However, Chelex DGT performance is known to be pH-dependent for the following elements: V, Cr, Fe, U, Mo, Ti, Ba, and Sr (Garmo *et al.* 2003), and poor for the following elements: Li, Na, K, Rb, Mg, Ca, B, Tl, P, S, As, Bi, Se, Si, Sn, Sb, Te, Zr, Nb, Hf, Ta, W, Th, and Ag (Garmo *et al.* 2003).

This study tested soils with anomalous Au contents but focused on elements other than Au as part of a typical multi-element exploration or research program. The current study aimed to evaluate DGT as a 'first-pass' technique for soils obtained from two Au prospects in Australia (Fig. 1), with a focus on the following metals of interest: Al, Cd, Co, Cu, Mn, Ni, U and Zn. Note that Al, while not necessarily an element of interest for Au exploration, is both detectable by DGT and the subject of scrutiny regarding its bioavailability in soils (Violante *et al.* 2010). As DGT uptake is known to be analogous to plant uptake for a number of metals (Zhang *et al.* 2001), we have therefore included Al in this study. The first set of soils was obtained from an archived collection derived from a prospect that exhibited a vegetation anomaly (Anand *et al.* 2007) while the second set of soils were obtained as a part of two studies examining hydrogeochemical and biogeochemical anomalies for Au (Reid & Hill 2013; Lucas *et al.* 2013, in preparation). It is hypothesized that standard DGT soil deployments (Chelex-based units deployed for 24 hours) can be used to identify multi-element anomalies in residual or transported soils over mineralisation, thereby supplementing current methods for geochemical exploration using soils.

METHODS

General procedures

For laboratory work, all plastic containers (70 ml transparent polypropylene, Sarstedt®) and pipette tips (1 ml, Sarstedt®) used were acid-washed (10% HCl) for at least 24 hours prior to rinsing with milli-Q water (Millipore, 18.2 MΩ cm). All reagents used were analytical grade. All experiments were undertaken in duplicate where possible, with some experiments not replicated due to an insufficient quantity of soil. Quality control during analysis included regular calibration of equipment, as well as analysis of solution blanks and standards of known concentration (Intertek Genalysis, Perth). Chelex DGT devices were purchased from DGT Research Ltd (www.dgtresearch.com). Four Chelex DGT devices were separately analysed as manufacturing blanks. A series of experimental blanks were also run in conjunction with the main experiment, using acid-washed sand instead of soil.

Soils

Soils used in this study are from two prospects located in Australia (Fig. 1). The prospects were: 1) the Moolart Well prospect, located in the northern Yilgarn Craton of Western Australia (27° 37' S, 122° 20' E), for which both

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TABLE 1. Physical characteristics of soils used in this study

Soil location	Code	Soil description	Mean pH	Mean E.C. ($\mu\text{s}/\text{cm}$)	Total Organic C %	Total N %
Oberon	OB	Sandy ferruginous, fine	5.99	60.1	0.15 – 0.27	0.017 – 0.025
Moolart Well topsoil	MW	Ferruginous clayey sand	5.64	25.0	0.86 – 1.36	0.069 – 0.132
Moolart Well subsoil	MA	Gravelly sandy clay	6.23	56.7	0.08 – 0.15	0.015 – 0.028

surface samples (7 samples, 0–20 cm depth, MW-series) and subsoil (13 samples, 0.5 – 1.5 m depth, MA-series) samples were obtained; 2) the Oberon prospect, located in the Tanami desert in the Northern Territory (20° 16' S, 129° 59' E), for which only surface soils (9 samples, 0–20 cm depth, OB-series) were obtained. Physical characteristics of these soils were determined using standard techniques (SSSA 1996), and total organic carbon and nitrogen contents of the soils were determined using an Elementar vario MACRO instrument (www.elementar.de). The soils were obtained from at least one transect across each prospect. The OB samples are from a NW-SE diagonal transect over mineralisation, and were sourced from the same sites as previous samples used to study the use of DGT deployed in boreholes (Lucas *et al.* 2013, in preparation). The MW surface soils were obtained from two separate E-W transects, with one transect overlying mineralisation and the second transect over background distal to known mineralisation. The MA subsurface soils were collected from three E-W closely spaced transects; again, some of the soils overlie mineralisation, and the remainder overlie background areas. In the results section below, the data are plotted according to E-W alignment, as this provides the best indication of element responses over mineralisation.

The soils were separated into 'anomalous' and 'background' populations in terms of Au concentrations (CSIRO, unpublished data). Four of the seven surface soil samples obtained from MW contain low-level Au concentrations (Au > 1 ppb), although they do not indicate Au mineralisation. The remaining three samples represent the background signal (Au < 1 ppb). The thirteen deep samples from MA were all obtained from Au-rich colluvium-alluvium; three samples exhibit strongly anomalous signatures for Au (> 30 ppb) and the remaining ten exhibit what are considered to be local background signatures (Au < 15 ppb), although some of these background soils are situated over mineralisation. Of the nine soil samples obtained from Oberon (OB), two are known to have a low-level Au anomaly (Au > 1 ppb), while the remaining seven samples are indicative of the background signature (Au < 1 ppb). At all three sites, MW, MA and OB, Au anomalies measured previously in soils, vegetation and groundwater have been expressed almost directly over mineralisation (Anand *et al.* 2007; Reid & Hill 2010).

Multi-element DGT response in soils over mineralisation

Procedures for deploying DGT devices involve gradually equilibrating the soils with milli-Q water to 100% water holding capacity (WHC) over 72 hours (Zhang *et al.* 1998). Equilibrating the soils with water ensured that the DGT

devices were sampling the labile component. Note that, aside from this equilibration step, the soils do not necessarily need to be pre-sieved or pre-treated for DGT; indeed, it is preferable that the soils remain as 'natural' as possible. DGT can also be deployed *in situ* if desired, so long as soil moisture content is > 27% (Hooda *et al.* 1999). Large hand-retrievable organic material (e.g. twigs and leaves) was removed from the soils prior to use, although inorganic material (e.g. pebbles and large stones) was not removed.

The Chelex DGT devices were deployed on all soils following standard DGT soil deployment practices (Zhang *et al.* 1998; Zhang *et al.* 2006). Prior to deployment of the DGT devices, the soils were equilibrated as follows: around 20 g of soil was placed in a sealable 70 ml plastic container; the soil was wetted to 60% WHC for 48 hours and then wetted to 100% WHC and left for a further 24 hours. After the soils had been equilibrated, the DGT devices were deployed on the soils as follows: a small quantity of the soil slurry was smeared onto the DGT device face; the DGT was placed on the soil, ensuring no gaps formed between the DGT window and the soil; and the container was capped in order to minimize evaporation, but not so tightly that anoxic conditions would occur within the container. The container was then placed in a temperature-controlled laboratory at 25°C for 24 hours (the standard deployment time for DGT), after which the DGT devices were removed and thoroughly washed with milli-Q water to remove soil. The Chelex gels were removed from the DGT devices and eluted with 1 ml of 1 M HNO₃. The resulting sample was diluted to 20 ml with milli-Q water for analysis via ICP-MS (Intertek Genalysis). The method detection limit, MDL, for DGT was determined by calculating 3 × the standard deviation of the deployment blanks (Long & Winefordner 1983) and applying equation 1 for the timeframe of the deployment (Luo *et al.* 2010). The MDL for each element is shown in Table 2.

The concentrations of elements in the porewaters were also determined after the DGT devices had been removed by the following procedure: the remaining saturated soil sample was placed in a 50 ml centrifuge tube and centrifuged at 3,500 rpm for 1 hour; the porewater was extracted using a 0.2 μm graduated filter syringe; 1 ml of cold concentrated HNO₃ was added to the porewater in order to stabilise any elements present, and the solution was diluted to 20 ml with milli-Q water for analysis of elements via ICP-MS at Intertek Genalysis, Australia. All reported DGT and porewater concentrations account for volumes extracted and dilution. The instrument detection limit (IDL) of the ICP-MS is shown in Table 3, and represents the lowest concentration detectable following dilution of the sample.

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Table 2. DGT-measured concentrations of nine elements in soils, in $\mu\text{g/L}$. Soils that are known to have anomalous Au concentrations are highlighted in bold. MDL indicates the method detection limit, with values less than MDL shown by a dash. Errors are reported as +/- one standard deviation of duplicate results where applicable.

Site	Al	Cd	Co	Cu	Fe	Mn	Ni	U	Zn
MDL	2.7	0.04	0.11	1.1	14.4	1.18	2.18	0.01	4.7
OB62	14.1 ± 6.7	0.07 ± 0.01	–	1.2	–	7.7 ± 2.5	–	0.03 ± 0.003	36.0 ± 6.4
OB67	9.4 ± 0.04	0.06 ± 0.01	–	–	–	8.8 ± 2.4	–	0.03 ± 0.02	3.1 ± 2.2
OB69	24.9 ± 0.1	0.06 ± 0.02	0.2	–	33.1 ± 6.1	17.1 ± 0.8	–	0.06 ± 0.02	4.7
OB70	8.1 ± 0.05	0.06 ± 0.01	–	–	–	2.4	–	–	1.6
OB72	20.8 ± 4.9	0.05 ± 0.01	–	–	–	3.5 ± 1.7	–	0.07 ± 0.05	6.3 ± 2.4
OB73	7.4 ± 2.9	0.05	–	–	–	2.9 ± 0.8	–	–	5.5 ± 3.0
OB83	7.4 ± 4.8	0.05	–	–	–	5.9 ± 1.6	–	0.01 ± 0.005	3.1
OB86	25.5 ± 7.3	0.06	–	–	–	6.5 ± 2.5	–	0.05 ± 0.004	2.3 ± 1.1
OB89	24.2 ± 2.9	0.06 ± 0.01	–	–	–	3.5	–	0.03 ± 0.004	3.1 ± 0.8
MW9	65.9	0.09	5.2	–	4281	1735	5.4	0.15	12.5
MW10	44.4 ± 1.9	0.1	3.9 ± 0.1	1.2	1859 ± 695	734 ± 47	3.8 ± 0.8	0.10 ± 0.005	13.3 ± 0.5
MW11	45.7	0.08	3	1.7	2212	441	5.4	0.11	9.4
MW12	139 ± 16	0.12 ± 0.02	4.5 ± 0.2	2.2 ± 0.5	6291 ± 1495	652 ± 37	8.7 ± 1.5	0.3 ± 0.003	20.3 ± 0.2
MW20	264 ± 27	0.1 ± 0.01	1.1	7.5 ± 4.6	67.7 ± 38.7	726 ± 2	4.9 ± 0.8	0.16 ± 0.01	18.8 ± 4.4
MW21	106	0.12	2.3	2.5	372	887	4.4	0.22	11
MW23	78.6 ± 21.9	.22 ± 0.08	1.4 ± 0.2	2	115 ± 33	839 ± 272	2.7 ± 0.8	0.12 ± 0.03	9.4 ± 1.0
MA28	35	0.09	0.6	2.2	28.8	40.1	–	0.05	1.6
MA29	8.1	0.08	0.2	1.1	–	27.1	–	0.03	4.7
MA30	39.7 ± 20.0	0.05 ± 0.02	0.2 ± 0.08	–	40.3 ± 20.4	10.6 ± 1.4	–	0.02 ± 0.01	3.1 ± 0.01
MA31	23.5 ± 9.9	0.08 ± 0.04	0.2 ± 0.09	1.6 ± 0.7	–	10.0 ± 0.8	–	0.04 ± 0.01	3.9 ± 1.1
MA32	6.7	0.05	0.1	2.2	–	16.5	2.2	0.04	1.6
MA33	5.4	0.17	0.8	–	–	112	4.4	0.02	3.1
MA34	8.1	0.08	0.7	2.6	–	38.9	2.2	0.05	4.7
MA36	7.4 ± 0.9	0.06	0.2	–	–	14.7 ± 7.4	–	0.01 ± 0.009	3.1 ± 2.2
MA37	73.3 ± 28.8	0.06 ± 0.02	0.1	2.3	–	5.7 ± 1.7	–	0.02 ± 0.003	18.8 ± 5.6
MA38	12.8 ± 4.8	0.08 ± 0.02	0.2	–	–	15.3 ± 1.7	–	0.01 ± 0.01	7.8 ± 0.6
MA39	22.9 ± 5.9	0.06 ± 0.04	0.2	1.6 ± 0.8	–	9.4 ± 3.3	–	0.02 ± 0.01	3.9 ± 1.1
MA40	–	0.05	0.2	1.7 ± 0.8	–	8.8 ± 0.8	–	0.02 ± 0.01	1.6
MA41	4.7 ± 1.0	0.06 ± 0.02	0.5 ± 0.2	–	–	17.1 ± 4.2	–	0.02 ± 0.02	–

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Table 3. Porewater concentrations of nine elements for all soils, in $\mu\text{g/L}$. These concentrations account for both the volume of porewater extracted and dilution required for analysis. Soils that are known to have anomalous Au concentrations are highlighted in bold. IDL indicates the instrument detection limit for diluted samples, with values less than IDL shown by a dash. Errors are reported as +/- one standard deviation of duplicate results where applicable.

Site	Al	Cd	Co	Cu	Fe	Mn	Ni	U	Zn
IDL	2	0.02	0.1	1	10	1	2	0.1	1
OB62	57.5	0.77 ± 0.06	–	–	–	–	–	–	–
OB67	30.6	0.72 ± 0.06	–	–	–	–	–	–	–
OB69	43	0.62 ± 0.08	–	–	–	–	–	–	–
OB70	28.7	0.65 ± 0.11	–	–	–	–	–	–	–
OB72	86.3 ± 13.6	0.77	–	–	–	–	–	–	–
OB73	70.4 ± 30.1	0.63 ± 0.04	–	–	–	–	–	–	–
OB83	92	0.81	–	–	–	–	–	–	–
OB86	53	0.71	–	–	–	–	–	–	–
OB89	–	0.7	–	–	–	–	–	–	–
MW9	907	0.46	15.6	9.2	5095	5434	27.5	0.53	18.3
MW10	1581	0.43	18.5	28.6	4265	3269	38.2	0.77	38.2
MW11	513	0.45	16.2	18	5130	2565	36	0.59	27
MW12	849 ± 118	0.50 ± 0.02	9.9 ± 1.4	24.9 ± 0.9	4998 ± 948	1276 ± 251	37.3 ± 1.4	0.76 ± 0.11	30.9 ± 7.6
MW20	1710 ± 528	0.65 ± 0.06	7.1 ± 0.25	35.5 ± 1.2	694 ± 193	2394 ± 50	35.5 ± 1.2	0.89 ± 0.06	53.0 ± 6.5
MW21	1251	0.64	7.7	12.8	1315	1532	–	0.68	12.8
MW23	660 ± 17	0.73 ± 0.11	2.8 ± 1.7	14.9 ± 2.1	511 ± 112	956 ± 309	–	0.28 ± 0.67	–
MA29	–	0.53	–	10.5	–	21	–	0.09	–
MA31	57.5	0.77	–	–	–	–	–	–	–
MA32	–	0.4	–	–	–	30.3	–	0.5	–
MA33	45.9	0.76	–	–	–	198.7	–	–	–
MA34	–	0.85	–	17	–	17	–	–	–
MA36	–	0.64 ± .017	–	–	–	14.2	–	–	–
MA37	–	0.67 ± 0.14	–	–	–	–	–	–	–
MA40	–	0.69 ± 0.11	–	–	–	–	–	–	–

Statistical analysis

The determination of significant differences between known anomalous soils and background soils can be undertaken using a two-sample Welch's t-test for data obtained from each site. Welch's t-test, an adaptation of Student's t-test, can be used when the sample sizes and the variances between datasets are not equal (Welch 1947). The t-statistic can be evaluated using equation 2:

$$t = \frac{(X_1 - X_2)}{\sqrt{\frac{s_1^2}{N_1} + \frac{s_2^2}{N_2}}} \quad (2)$$

where t is Student's t-distribution for the data, X_1 and X_2 are the means of each sample set, s_1 and s_2 are the standard deviations for each sample set and N_1 and N_2 are the sample sizes for each data set. The degrees of freedom for testing can be determined from the Welch-Satterthwaite equation (equation 3):

$$d.f. = \frac{\left(\frac{s_1^2}{N_1} + \frac{s_2^2}{N_2}\right)^2}{\frac{s_1^4}{N_1^2 d_1} + \frac{s_2^4}{N_2^2 d_2}} \quad (3)$$

where $d.f.$ is the degrees of freedom, s_1 and s_2 are the standard deviations for each sample set, N_1 and N_2 are the sample size and d_1 and d_2 are the degrees of freedom for each sample set, (determined as $N_1 - 1$ for each N). Data obtained in this study were analysed using the software package *R* (R Core Team 2012), which was used to apply Welch's t-test for each set of elements compared and provided both $d.f.$ and the relevant p-value for the t -statistic determined in equation 2. For this work, the testing was undertaken per site for each element.

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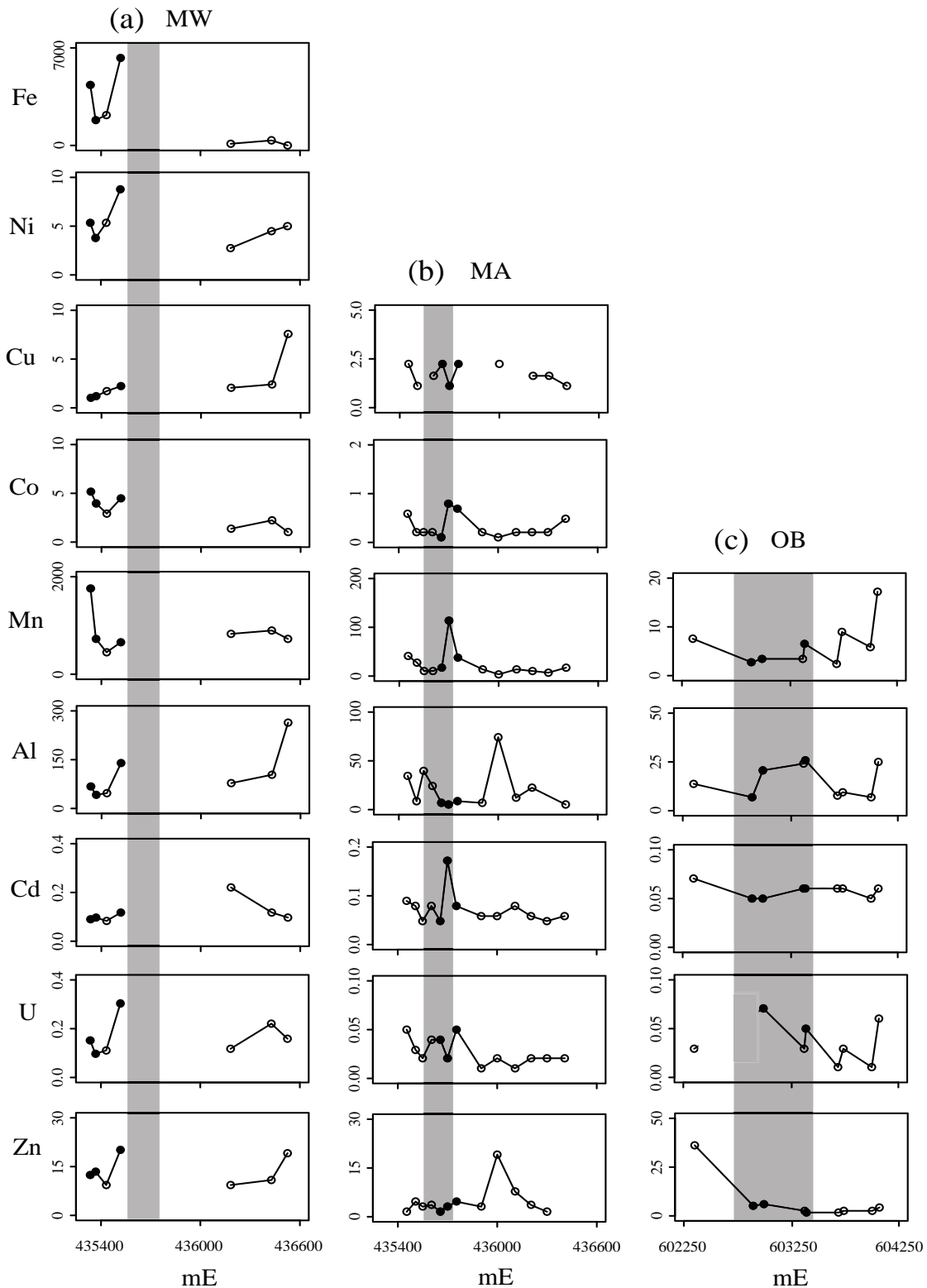


Figure 4. Transects showing concentration of elements as measured by DGT at (a) MW, (b) MA, and (c) OB. All concentrations are shown in µg/L. The OB transect is roughly 20° 16' S, 129° 59' E. Both MW and MA transects are roughly 27° 37' S, 122° 20' E. The y-axis scale for each prospect is adjusted to highlight detail, and the grey shading indicates the approximate vertical projection of gold mineralisation. Soils with known anomalous Au concentrations are shown as black circles, and background soils are shown as clear circles.

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RESULTS

Broad geochemical characteristics of the soils

The pH, electrical conductivity (EC), and percentage of total organic carbon and nitrogen of the soils are shown as ranges in Table 1. The soils are acidic, with the lowest mean pH being 5.64 for soils sourced from MW, and the highest mean pH being 6.23 for soils sourced from the MA hardpan layer. The mean EC values of the soils ranged from 25.0 $\mu\text{S}/\text{cm}$ to 60.1 $\mu\text{S}/\text{cm}$. Both the OB and MA soils had very low total organic carbon contents with that of the MW surface soils being slightly higher, at up to 1.36%. This higher quantity of organic matter in the MW surface soils is also reflected in the nitrogen content of these soils when compared with the OB and MA samples.

DGT-measured concentrations

The data for the concentrations of elements detected by DGT are shown in Table 2, and are also plotted on the soil sampling transects, along with the zones of known Au mineralisation, in Figure 4. Table 2 shows that a range of elements (Al, Cd, Co, Mn, Zn and U) were detected by DGT in almost all soils. The values for Cu are close to the detection limit of the technique; these less than detection limit values might be increased in future deployments by extending the deployment time (Zhang *et al.* 1995; Zhang *et al.* 1998). As stated previously, the measurement of Fe and U with Chelex DGT is pH dependent. This was taken into account following the methods of Garmo *et al.* (2003). Table 2 shows that there is a clear difference in the concentrations of elements measured at each of the sites in that

higher concentrations of all elements were detected in the MW samples than in either the OB and MA samples, by both the DGT and porewater methods. For example, the DGT-determined concentrations of Fe and Mn in the MW surface samples are greater than an order of magnitude higher than the concentrations in the OB and MA soils. Nickel was not detected at all in the OB soils, and was detected in only three MA samples. Interestingly, these same three MA samples are also known to be anomalous for Au, likely as a consequence of the mineralisation at Moolart Well being hosted in ultramafic greenstones.

Figure 4 shows the concentrations of DGT-measured elements along the sampled transects. More element concentrations were reported to be greater than detection limit by DGT at MW (a total of 9) than at either MA (7) or OB (5). At MW (Fig. 4a), Al, Fe, Ni, U, and Zn follow a similar trend over the length of the transect, with the highest concentrations of these elements (excluding Al) being found over mineralisation. Element concentrations over background, indicated on the eastern side of the figure, appear to be flatter than those over mineralisation, with the exception of Cu and Al. At MA (Fig. 4b) Co, Mn, and Cd follow a similar trends over the length of the transect, with the highest concentrations of these elements over mineralisation. Both Al and Zn show elevated concentrations to the east of mineralisation, with concentrations decreasing still further towards the east. For the OB soils (Fig. 4c), Al and U show a marginal elevation over mineralisation; the remaining elements do not show significant variation over mineralisation.

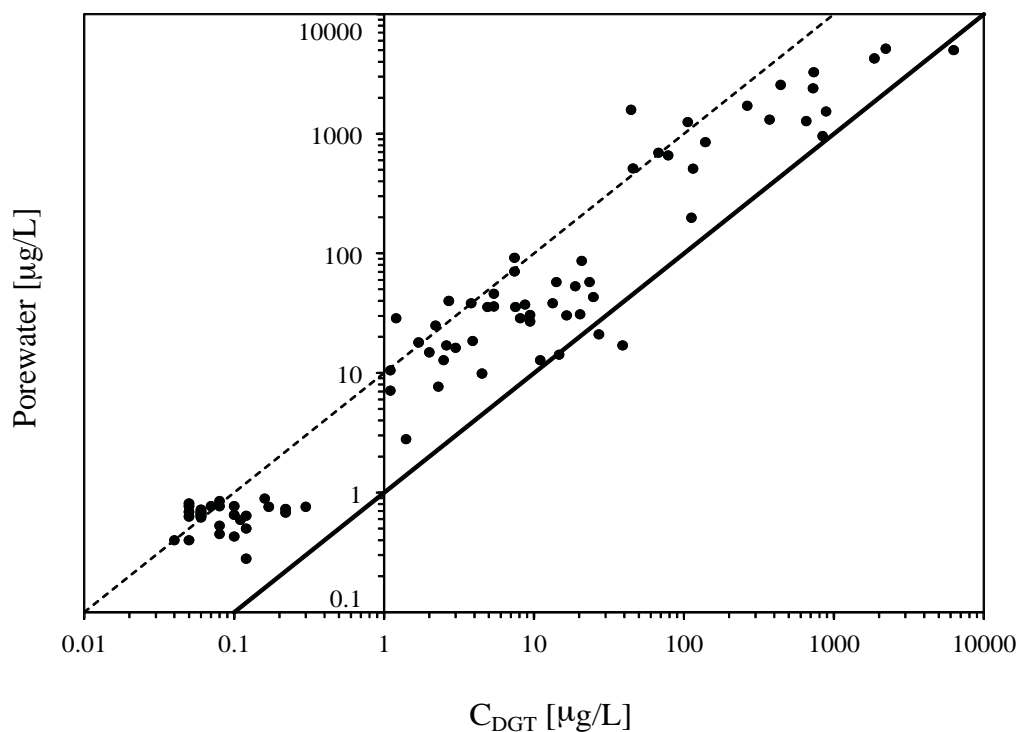


Figure 5. Log-log plot of all porewater concentrations vs. C_{DGT} for all elements detected by both techniques. The solid line represents a 1:1 relationship, and the dashed line represents a factor of 10 greater than the 1:1 line.

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Porewater concentrations

The concentrations of elements in the soil “porewaters” (post-DGT deployment) are shown in Table 3. Difficulties were encountered in extracting a sufficient quantity of porewater for analysis. This was particularly true for both the sandy OB soils and the highly lateritic MA soils with five MA soils – MA28, MA30, MA38, MA39 and MA41 – generating insufficient volumes for analyses. Porewater volumes extracted from the soils were often <0.2 ml, due to low initial WHC. In addition, the porewater concentrations of elements from these sites were more often below the detection limit. The overall distribution of metal concentrations in porewater mirrors that of the DGT-measured concentrations (Fig. 5), although concentrations in the porewaters are often greater than an order of magnitude higher than DGT values. The reasonable correlation suggests that DGT is a suitable method for assessing porewater element concentration trends along these transects, and furthermore, as the concentrations were more often measurable (due to the lower detection limit of DGT than porewater analysis), DGT would appear to constitute a methodological improvement over porewater centrifugation.

Statistical interpretation of results

Table 4 shows the results of the Welch’s t-testing of concentrations of elements between soils that are anomalous for Au (highlighted in bold in Tables 2, 3, and 4) and the background soils (plain text in Tables 2, 3, and 4). Note values that were below detection limit were excluded from testing, as opposed to assigning an arbitrary or statistically derived value. In the DGT dataset Welch’s t-testing shows that: Mn concentration is significantly different between anomalous and background samples in the OB soils; Co and Fe concentrations are significantly different in the MW soils; and Al concentration is significantly different in the MA soils where it is likely due to a pH anomaly existing in these soils (Table 1). For porewater data, only Al and Cd concentration were above detection limit for the OB soils, neither of which were significantly different between anomalous and background samples. In the MW soils, both Co and Fe concentrations were significantly different between anomalous and background soils as with the DGT dataset. However, for the MA soils, both Cd and Co concentrations were significantly different between anomalous and background soils, which contrasts with the DGT dataset.

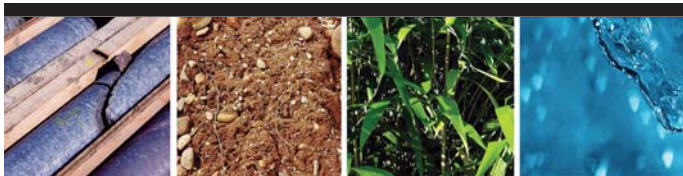
DISCUSSION

The main objective of this study was to assess whether DGT was capable of being used as a tool for geochemical exploration as a ‘first-pass’ technique, with the hypothesis that DGT was able to determine multi-element anomalies in soils that relate to underlying mineralisation. On the limited selection of soils tested, the DGT technique appears to have both successfully met the objective and confirmed the hypothesis. In particular, DGT is more sensitive at detecting labile elements in porewaters than conventional porewater extractions due to the preconcentration of elements onto the Chelex resin. In this discussion, we assess the DGT technique on the basis of its use as a tool for geochemical exploration in soils, and as a tool for simultaneous detection of multi-element anomalies.

Using DGT as a tool for exploration

As a general tool for geochemical exploration in soils, the DGT technique is simple to prepare and deploy, either in laboratory-based studies such as this one or *in situ*. The analysis of the resin gels is also straightforward; an elution step with concentrated acid, which can be undertaken at any stage after the deployment, minimizes the risk of contamination. This feature would be particularly advantageous in *in situ* field deployments. The pre-concentration of elements onto a resin gel ensures low detection limits, which become even lower when deployment times are extended (Davison & Zhang 1994; Zhang *et al.* 1998).

We can broadly compare the DGT technique to the better-known exploration tool of partial extractions. The first part of most soil partial extraction techniques usually



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Table 4. Significance testing between background soils and Au-anomalous soils, using unpaired 2-sample Welch's t-test. A p-value ≤0.05 indicates a significant difference between the background soils and anomalous soils.

Testing is inclusive of all replicates.

	DGT			Porewater			
	Element	p-value	degrees of freedom	Significantly different?	p-value	degrees of freedom	Significantly different?
OB	Al	0.86	6.3	No	0.17	7.7	No
	Cd	0.32	13	No	0.98	13.8	No
	Fe	0.23	1.2	No	-	-	No
	Mn	0.03	17	Yes	-	-	No
	U	0.36	3.9	No	-	-	No
	Zn	0.37	14.1	No	-	-	No
MW	Al	0.42	6.4	No	0.83	8.8	No
	Cd	0.49	5.2	No	0.1	6.4	No
	Co	>0.01	8.8	Yes	0.03	8.9	Yes
	Cu	0.19	5.3	No	0.82	9	No
	Fe	0.02	4.9	Yes	0.01	6.6	Yes
	Mn	0.51	5.2	No	0.24	5.3	No
	Ni	0.19	5.6	No	0.98	4.5	No
	U	0.41	5.2	No	0.39	7.1	No
MA	Zn	0.33	9	No	0.96	5.5	No
	Al	0.01	16.3	Yes	0.35	4.2	No
	Cd	0.45	2.1	No	0.01	8.8	Yes
	Co	0.33	2.1	No	>0.01	8.7	Yes
	Cu	0.62	2.7	No	0.95	3	No
	Mn	0.28	2	No	0.07	2.5	No
	U	0.19	2.6	No	0.69	6.5	No
	Zn	0.29	17.1	No	0.99	5.7	No

extractions, there is scope to expand the DGT technique to include chemical modification of the soil, but this was beyond the scope of this initial study.


The use of DGT to detect multi-element anomalies

As stated in the introduction, one of the objectives of a soil sampling program is to assess whether an anomalous signal related to mineralization can be separated from background values. In this study, we obtained soils that have previously been determined to contain either an anomalous or background signature for Au and examined other elements to see whether anomalies could be detected by Chelex DGT. As a tool for the simultaneous detection of multiple elements in soils, the DGT technique was limited for Cu and Ni in the soils (Table 2), likely due to the negligible amount of a labile fraction of these elements in the soils generally. Cadmium was detected in almost all soils, but the concentrations were barely above the detection limit. Measured concentrations of a number of

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focuses on the water-soluble or ion-exchangeable fraction, and uses a small portion of soil (e.g. 5 g) with a known volume of leaching agent (e.g. 90 ml) such as water (Reith & McPhail 2007), MgCl₂ or CH₃COONH₄ (Tessier *et al.* 1979; Gray *et al.* 1999). This fraction is likely to contain the lowest concentration of elements, and is the fraction that has been previously assumed to correlate best with bio-availability (Peijnenburg *et al.* 2007). There are at least two issues with this assumption however. First, the proportion of soil to extractant used (e.g. 1:8 or greater) effectively ensures that concentrations of elements measured will be low. This limitation could potentially be alleviated by use of a pre-concentrating agent e.g. an ion-exchange resin. Second, the partial extraction procedure does not ensure the soil is unperturbed; speciation measurements cannot be easily made as the separation of solution and solid phases disrupts the physicochemical equilibrium, which affects the distribution of species in solution (Zhang *et al.* 1998). The DGT technique avoids both issues by: 1) pre-concentrating elements at a well-defined rate of uptake *via* diffusion, and; 2) minimally disturbing the soil porewater and thus allowing for an assessment of speciation.

While the DGT technique does not rely on chemical leaching, the uptake of elements through the diffusive layer, coupled with the associated dynamics of the soil solution, not only provides specific information regarding the exchange dynamics within the soil but also provides a tool for evaluating bioavailability. By analogy with partial



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elements were, however, more likely to exceed detection limits for DGT than for porewater extraction and analysis.

Elements such as As and Cu are known to exhibit pathfinder behavior for Au (Ashton & Riese 1989); however, As was not examined in this study due to poor uptake by the Chelex resin, and concentrations of Cu in both DGT and porewater were very low. Both of these issues are also relatively easy to address with DGT for future experiments. First, DGT devices equipped with either ferrihydrite gels or mixed binding layer gels are able to detect As (Mason *et al.* 2005; Panther *et al.* 2008), and second, increasing the sensitivity of the DGT technique for elements like Cu may simply be a matter of increasing the deployment time (Zhang & Davison 1995). There are some considerations with regards to increasing deployment times: firstly, the ion holding capacity of the Chelex resin needs to be accounted for, as exceeding the resin's sorption capacity by an excessively long deployment will invalidate equation 1 (Zhang & Davison 1995); secondly, other processes, such as changes to redox conditions and increased biological activity within the soil, may affect the lability of elements in the soil solution (Ernstberger *et al.* 2002). A deployment time of 24 hours is recommended for DGT when these other processes need to be avoided (Hooda *et al.* 1999); however, for exploration purposes, reducing the limit of detection is advantageous, and longer DGT deployments are recommended as long as the possibility of a change in soil conditions is accounted for.

In this study, we demonstrate the variation in element concentrations over mineralisation, and have ascertained that there is an observable multi-element difference between soils over mineralisation and soils from background areas. This difference, namely that anomalous values are higher than background values, can be seen both visually in Figure 4 as well as statistically in Table 4 for elements such as Co and Mn (and Cd for MA). The Chelex DGT devices used in this study do not sample for Au (Lucas *et al.* 2012); however, the DGT has recently been modified for uptake of Au through the use of activated carbon as an adsorbent (Lucas *et al.* 2012), and evaluation of Au-DGT in soils is currently underway.

This study did not include an analysis of the total concentrations of elements and metals in the soils; instead, only the DGT-detectable and porewater-extractable fractions were evaluated. A comparison of total elements with the DGT-detectable fraction, which can be considered as approximation to bioavailability, *c.f.* Mann *et al.* (2012), may help shed light on the interaction and exchange of elements between the biosphere and the lithosphere, and a better understanding of the surficial expression of mineralisation.

As mentioned in the introduction, the DGT technique for soils was originally developed to assess toxicity and plant uptake for environmental monitoring and regulation. The detection of highly elevated concentrations of elements such as Cu and Cd in soils was not to be viewed as a positive result; if anything, excessive quantities of these

elements have implications ranging from the health of vegetation and ecosystems to human health and food security (McLaughlin *et al.* 2000; Zhang *et al.* 2006). Although an evaluation of the technique in a wider range of prospective soils and environments is required, this study demonstrates a new field of application of the DGT technique to low-level measurement of elements for the detection of mineralisation.

CONCLUSIONS

The DGT technique shows potential as a tool to augment current geochemical exploration efforts. The technique is relatively simple to apply, and is very sensitive for a range of elements even when deployments are restricted to 24 hours. The initial potential shown by DGT soil deployments at two Australian Au prospects suggests that further evaluation of DGT as a geochemical exploration tool would be a productive direction for research in other environments.

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2013 STUDENT PAPER PRIZE



Pim van Geffen

The Association of Applied Geochemists and SGS are pleased to announce Pim van Geffen as the winner of the 2012 SGS-AAG Student Paper Prize. This prize is awarded for the best paper published in GEEA by a student, on work performed as a student and published within three years of graduation, which addresses an aspect of exploration geochemistry or environmental geochemistry related to the mining industry. His winning paper is based on research that Pim undertook for his PhD at Queen's University, Kingston.

His award-winning paper is entitled 'Till and vegetation geochemistry at the Talbot VMS Cu-Zn prospect, Manitoba, Canada: implications for mineral exploration' which was published in 2012 in *Geochemistry: Exploration Environment Analysis*, 12:67–88, and was co-authored by Kurt Kyser, Christopher Oates and Christian Ihlenfeld. The abstract of the paper is:

"The Proterozoic Talbot VMS occurrence in the Flin Flon-Snow Lake terrane is buried under more than 100 m of Palaeozoic dolomites and Quaternary glacial till. Structurally controlled anomalies of Zn, Cu, Ag, Pb, Au, Mn, Hg, Cd, Co, Bi and Se in the clay fraction of till depth-profiles indicate upward element migration from the buried volcanogenic massive sulphide mineralisation and near-surface chemostratigraphic deposition. Principal component analysis and molar element ratios indicate that separation of the <2 µm clay fraction reduces chemical heterogeneity and increases trace-element yield relative to the <250 µm fraction of the till. The greatest anomalies

occur at or below 30 cm depth and over faults, suggesting that elements were deposited in the till after upward migration through structures. The ratio Zn/Al in the <250 µm fraction can be used as a proxy for Zn in the clay fraction, producing high-contrast anomalies. Carbon isotopic compositions indicate that these anomalies are related to organic carbon in the clay fraction. Humus, moss and black spruce bark are of limited use for exploration in this environment, because they accumulate atmospheric Pb and Cd, most likely from the Flin Flon smelter at 160 km NW. Black spruce tree rings that formed before smelter operations commenced indicate Zn and Mn anomalies in an uncontaminated sampling material. Much of the initial vertical migration of elements to the surface at the Talbot prospect was driven by upward advection of groundwater through fractures in the dolomite, resulting from a combination of subsurface karst collapse and remnant hydrostatic pressure during glacial retreat."

Pim received a \$1,000 cash prize from SGS, a two-year membership of the Association of Applied Geochemists, together with our journal, *Geochemistry: Exploration, Environment, Analysis* and newsletter, *Explore*, and a certificate of recognition.

The Association of Applied Geochemists would like to thank SGS for, once again, generously supporting this prize.

D.R. Cohen
Chair, Student Paper Competition Committee





CALENDAR OF EVENTS

International, national, and regional meetings of interest to colleagues working in exploration, environmental, and other areas of applied geochemistry. These events also appear on the AAG web page at: www.appliedgeochemists.org.

9-13 December 2013. AGU Fall Meeting San Francisco CA USA Website: fallmeeting.agu.org/2013

2014

6-11 January 2014. 2014 Winter Conference on Plasma Spectrochemistry. Amelia Island FL USA. Website: tinyurl.com/ck2s5eu

27- 30 January 2014. Mineral Exploration Roundup 2014. Vancouver BC Canada. Website: www.amebc.ca/roundup/overview-2014.aspx

16-20 February 2014. The Minerals Metals & Materials Society 2014: Linking Science and Technology for Global Solutions. San Diego CA USA. Website: www.tms.org/meetings/annual-14

23-28 February 2014. 2014 Ocean Sciences Meeting. Honolulu HI USA. Website: www.sgmeet.com/osm2014

2-5 March 2014. Prospectors and Developers Association of Canada Annual Convention. Toronto ON Canada. Website: www.pdac.ca/pdac/conv

20-21 March 2014. North Atlantic Craton Conference 2014. St. Andrews UK. Website: www.nac-conference2014.org.uk

31 March – 2 April 2014. EAGE Workshop on Integrated Interpretation of Seismic, EM and Geochemical Data. Singapore. Website: tinyurl.com/obbztfo

27 April – 2 May 2014. European Geosciences Union General Assembly 2014. Vienna, Austria. Website: www.egu2014.eu

11-16 May 2014. 5th International Congress on Arsenic in the Environment. Buenos Aires Argentina. Website: www.as2014.com.ar

21-23 May 2014. GAC/MAC Annual Meeting. Fredericton NB Canada. Website: www.unb.ca/conferences/gamac2014

8-12 June 2014. 20th World Congress of Soil Science. Jeju Korea. Website: www.20wcss.org

9-13 June 2014. Goldschmidt 2014. Sacramento CA USA. Website: goldschmidt.info/2014

15-19 June 2014. 2nd International Symposium on Ethics of Environmental Health. Ceske Budejovice, Czech Republic. Website: www.iseeh2014.org

17-20 June 2014. 38th International Symposium on Environmental Analytical Chemistry. Lausanne Switzerland. Website: tinyurl.com/p4q2qgd

21-26 June 2014. Euroscience Open Forum. Copenhagen Denmark. Website: esof2014.org

29 June - 2 July 2014. 2nd International Conference on 3D Materials Science. Annecy France. Website: www.tms.org/Meetings/2014/3DMS2014

7-10 July 2014. Australian Earth Sciences Convention. Newcastle NSW Australia. Website: www.aesc2014.gsa.org.au

14-19 July 2014. Earth Sciences and Climate Change: Challenges to Development in Africa. Nairobi Kenya. Website: www.aawg.org

29-30 July 2014. Sampling 2014 (AusIMM). Perth WA Australia. Website: www.ausimm.com.au/sampling2014

3-7 August 2014. Microscopy & Microanalysis 2014. Hartford CT USA. Website: tinyurl.com/mrtf48v

5-12 August 2014. 23rd Congress and General Assembly of the International Union of Crystallography. Montreal QC Canada. Website: www.iucr2014.org

11-13 August 2014. 4th International Conference on Environmental Pollution and Remediation. Prague Czech Republic. Website: icepr.org

11-14 August 2014. XII International Platinum Symposium Yekaterinburg Russia. Website: tinyurl.com/qyle4lp

19-22 August 2014. 14th Quadrennial IAGOD Symposium Urumqi China. Website: www.14iagod.org/en

25 August – 3 September 2014. EMU School 2014: Planetary Mineralogy. Glasgow UK. www.eurominunion.org

1-5 September 2014. 21st General Meeting of the International Mineralogical Association (IMA2014). Johannesburg South Africa. www.ima2014.co.za

17-19 September 2014. ERA12: An International Symposium on Nuclear & Environmental Radiochemical Analysis. Bath UK. Website: tinyurl.com/on9vn9p



CALENDAR OF EVENTS

continued from page 17

21-25 September 2014. Uranium Mining and Hydrogeology 2014 International Conference. Freiberg Germany. Website: tu-freiberg.de/umh-vii-2014

21-26 September 2014. IWA World Water Congress and Exhibition. Lisbon Portugal. Website: www.iwa2014lisbon.org

24-27 August 2014. 7th International Conference on Environmental Catalysis. Asheville NC USA. Website: www.efrc.lsu.edu/ICEC

1-5 September 2014. 21st General Meeting of the International Mineralogical Association (IMA2014). Johannesburg South Africa. Website: www.ima2014.co.za

24-26 September 2014. XX Congress of Carpathian Balkan Geological Association. Tirana Albania. tinyurl.com/kxegt8 (Facebook)

27-30 September 2014. SEG 2014: Building Exploration Capability for the 21st Century. Keystone CO USA. Website www.seg2014.org

19-22 October 2014. GSA 2014 Annual Meeting. Vancouver BC Canada. Website: www.geosociety.org/meetings/2014

2015

19-24 April 2015. 27th International Applied Geochemistry Symposium. Tucson, AZ, USA. Website: www.27IAGS.com

27 July -2 August 2015. 19th INQUA Congress (Quaternary Perspectives on Climate Change, Natural Hazards and Civilization). Nagoya, Japan. Website: inqua2015.jp

8-14 August 2015. Geoanalysis 2015. Leoben, Austria. Website: geoanalysis.info

2016

27 August – 4 September 2016. 35th International Geological Congress. Cape Town South Africa. Website: www.35igc.org

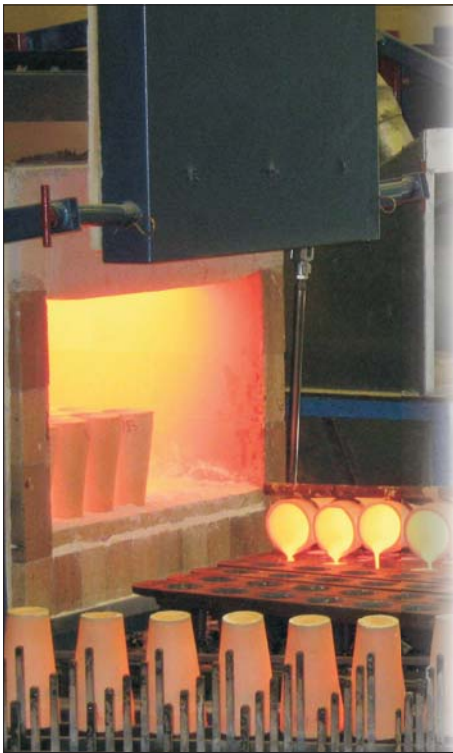
Please let us know of your events by sending details to:

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OBITUARY**HUBERT ZEEGERS (1942-2013)**

Hubert Zeegers, formerly International Director of the Bureau de Recherches Géologique et Minières (BRGM) in Orléans, France, died suddenly in July 2013. He was a knowledgeable and widely respected exploration geologist and geochemist who for some 40 years had worked extensively in West Africa, South America and SE Asia, undertaking projects ranging from regional geochemical surveys to more detailed site investigations. Hubert was able to combine practical, commercially-focussed exploration experience with research interests, and encouraged his staff to adopt a similar approach.

Hubert Zeegers was born in Belgium and graduated with a PhD in geology from the Louvain Catholic University in 1969. After graduation, he spent five years in mineral exploration projects with the United Nations Development Program based in Burkina Faso (then Upper Volta). It was during this period that he developed his interest in multi-element geochemical exploration techniques.

Hubert joined the BRGM in 1974, when the organization was undertaking large regional geochemical surveys in many parts of the world. He continued to work in savanna and rainforest terrains, mainly in West and Central Africa (Mali, Cote d'Ivoire, Burkina Faso and Gabon), but also in South America, especially French Guiana. BRGM at that time had the complex and sometimes seemingly conflicting roles of geological survey and scientific research organization, geological and geochemical service contractor to overseas governments, and semi-autonomous private exploration company. These activities gave Hubert experience in exploration in many different environments, and presented him with the opportunity to identify important research problems, particularly those relating to exploration in deeply weathered, lateritic terrain. There was considerable scientific discussion about the processes of weathering and lateritization and, particularly, whether geochemical signals in laterites were truly autochthonous and representative of the underlying bedrock. It was also a creative period when multi-element ICP-ES analysis and computer-aided data handling were being developed, providing further exploration and research opportunities. Hubert was very keen to import and apply these new technologies to geological issues and he stimulated considerable research and development on these topics. He formed collaborative links with universities working on soil science, weathering processes and geomorphology of these regions, notably with Yves Tardy at the University of Strasbourg and Daniel Nahon at the University of Poitiers, with a view to relating geochemical dispersion to the history of the landscape. The combination of scientific concepts from soil science, analytical geochemistry and economic geology was very fruitful. He presented an early paper on this subject at an IGCP Symposium in India in



1979. Similar ideas being pursued by CSIRO in Australia were presented by Charles Butt at the same Symposium and this was the starting point for a long and productive collaboration. In 1987, Hubert and Etienne Wilhelm were co-conveners of the 12th International Geochemical Exploration Symposium, hosted by BRGM in Orléans. This was a peak period for regolith exploration geochemistry with the boom gold exploration and interest in supergene gold deposits. Collaboration between BRGM and CSIRO continued as Hubert and Charles combined to compile a volume in the series Handbook of Exploration Geochemistry (Regolith exploration geochemistry in tropical and sub-tropical terrains), which was published in 1992.

Gold was still the major focus of exploration and the collaboration between the two organizations included exchange visits of research students Philippe Freyssinet and Louisa Lawrance, both then studying aspects of gold dispersion in lateritic terrain, in Mali and Western Australia, respectively. Hubert visited Australia whilst working on the Handbook, taking advantage of the difference in seasons to stock up on quantities of surfing fashions, for himself and his son Yves, which in France lagged 6 to 18 months behind the scene in Australia! In the days before the internet, Hubert always travelled with a powerful radio receiver to keep in touch with home news and during his visit to Perth in 1987, he was somewhat dismayed by the difference in reporting of the Chernobyl nuclear reactor crisis between Australia and France.

Hubert and Etienne Wilhelm co-managed a dynamic team of geologists and geochemists whose work led to several discoveries mostly in Mali, Guinea and Côte d'Ivoire. These regions were poorly explored in the early eighties and many of the exploration projects he managed in this region remain as important sources of information.

In 1994, BRGM transferred its commercially-oriented mineral exploration activities into La Source Compagnie Minière, a joint venture with the Australian company Normandy Exploration. Hubert was appointed as head of the international activities of BRGM, a position he held until La Source was dissolved in 2004. He then resigned from the BRGM and became an independent consultant.

Hubert had a real passion for Africa, particularly West Africa, not only for its geology, but also for its peoples and ethnic culture. He particularly wanted to help African geologists, to which end he became Director of CIFEG (Centre International pour la Formation et les Echanges en Geosciences), a foundation sponsored by UNESCO and the French government. Through CIFEG, he devoted his energy to boosting aid projects aimed at developing training and cooperation in earth sciences in Africa.

Hubert died after a short illness at his home in Trebeurden, a small village in Brittany. He was 71. He is survived by his wife Françoise, and by his children Yves and Anne-Françoise.

Philippe Freyssinet and Charles Butt
October 2013



OBITUARY

PATRICE LAVERGNE (1929-2013)

Pat Lavergne was one of the unsung heroes of applied geochemistry, he worked at the Geological Survey of Canada for 50 years, retiring in 1997, and died in August at the age of 84. He was one of the first employees hired by Hal Steacey (later Curator of the National Mineral Collection) to work in the Radiometric Laboratory of the GSC's Mineral Deposits Division, September 20, 1947. At that time the search was for uranium deposits, his task was to scan samples submitted by prospectors and the public with a Geiger counter to identify those that were uraniferous. Pat's later, and major work, after he joined the recently formed Geochemistry Section in 1960, was in sample preparation, an often unacknowledged task, working over the years on all the materials in the geochemist's catalogue. What he excelled at were mineral separations, he could perform incredible feats with his heavy liquids, modified Superpanner and Frantz separator. This was particularly valuable to the mineral studies of both Bob Boyle and Ian Jonasson for over 35 years. Pat was the only Survey employee to receive a 50 year service gold-plated medal and citation signed by the Prime Minister of Canada. It was presented to a very shy and embarrassed Pat at a special meeting on his retirement, October 1, 1997. He was seen to bite it, just to make sure it was gold. He retired a month later, he had achieved his goal.

There was not a single GSC geochemist or mineral deposit geologist that did not benefit from his quiet diligence and inventiveness working in the background to support our research studies. His lab contained a collection of equipment accumulated over the years, much of which he had modified to improve its performance or make it easier to clean so as to avoid cross-contamination. He wrote two excellent papers to impart his very specialized knowledge of sample preparation and mineral separation. He preferred to work quietly away on the top, eighth, floor of the Geological Survey building on Booth Street. The 1988 Open File is a complete set of instructions for establishing a sample preparation facility in the lab or field that is still a valuable contribution today. Behind the scenes he contributed to hundreds of papers and Open File reports by the Ottawa geoscientists.

As an example of Pat's versatility and inventiveness there is the story of the refrigerator rescued from the Whitehorse, Yukon, dump in 1965 for use in Operation Keno led by Chris Gleeson and Bob Boyle. Why the refrigerator was rescued is lost to history, but Pat got it up to Keno Hill and running again in its propane mode, where it was used to keep the dithizone cold and away from light to be used each day for the Bloom (1955) field test for heavy metals in stream sediments and waters. At the end of the field season it was shipped back to Ottawa where it continued to work in its electrical mode. In the late 1960s it was in the Room 733, the Section meeting room, being used to keep lunches, and the like, cold. Eventually it found its way to the Operations Room on the fifth floor. It continued to run until 2007 before it finally died, probably after some 50



years of service. Pat was contacted, but a second resuscitation proved impossible. They simply don't make them like they used to. And the same can be said of Pat Lavergne.

Thank you Pat for your dedication and all the work you did for the Ottawa geochemists.

Bob Garrett and Ian Jonasson,
Geological Survey of Canada
Ottawa, Ontario.

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North Atlantic Craton Conference 2014

The North Atlantic Craton:
A craton specific approach
to exploration targeting



University of St Andrews, 20th-21st March 2014

Sponsoring Institutions:

- Cardiff and St. Andrews University Chapters of the Society of Economic Geologists
- Applied Mineralogy Special Interest Group of the Mineralogical Society of Great Britain and Ireland
- The Mineralogical Society of Great Britain and Ireland
- The British Geological Survey
- The Geological Survey of Denmark and Greenland

Confirmed Keynote Speakers: Dr. Graham Begg (Minerals Targeting International), Dr. Jochen Kolb (GEUS), Prof. Chris Hawkesworth (University of St Andrews), Dr. Richard Goldfarb (USGS), Prof Sarah-Jane Barnes (l'Université du Québec)

Conference abstracts

Abstract submissions for both oral and poster presentations

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22nd - 26th March 2014, price: £450*

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A field trip to the Lewisian Gneiss Complex, an Archaean gneiss terrane and a marginal part of the North Atlantic Craton. Field locations to include Gairloch, Loch Maree, Loch Borralan, Scourie and Loch Loyal.

*Price includes all travel, hotel accommodation, food (breakfast, lunch & dinner) and field guidebook

EXPRESSION
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1. The geology and formation of the NAC
2. Cratonic structure and regional controls on mineralisation
3. Mantle metasomatism and influences on SCLM geochemistry
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5. Breakup of the NAC - effects of the opening of the Atlantic and Labrador Sea
6. Ni-Cu-PGE potential of the NAC
7. New developments and discoveries in exploration
8. Applied mineralogy
9. Future exploration and potential for academia-industry collaboration

Icebreaker Wednesday 19th March

Conference dinner & ceilidh Thursday 20th March

Registration opens October 2013

Early[†] registration fee £192 / Student fee £54**

**Includes abstract volumes, refreshments, lunch and icebreaker

[†] Early bird registration until 15th January 2014

NOTE: Late registration fees £228 (student rate £60)



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www.nac-conference2014.org.uk



27th INTERNATIONAL APPLIED GEOCHEMISTRY SYMPOSIUM

We have had a GREAT time in Rotorua NZ, now is time to look to the next IAGS, submit your abstracts, and ready your travel plans.

The 27th IAGS will be held:
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Registration for the 27th IAGS begins April 2014.

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*Visit the 2015 IAGS website
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for detailed information.*



AAG Student Support Initiative Analytical Support for BSc (Hons), MSc and PhD Students in Applied Geochemistry

In 2011, AAG implemented a coordinated program with analytical laboratories to provide In-Kind Student Support for applied geochemical research projects. We are off to an exciting start with several students currently being assisted, multiple laboratories participating, and the first student paper published in EXPLORE #157: "Particle size fractionation and chemical speciation of REE in a lateritic weathering profile in Western Australia". Ms. Xin Du is from University of Western Australia with Genalysis Laboratory Services (Intertek) sponsoring the analyses. The latest Student/Laboratory match-up is Markham Phillips from the University of Otago in New Zealand who is being supported by ALS Geochemistry in Vancouver, Canada on his research into "*Granite host and it's alteration suites as well as geochronology of gold bearing sulphide minerals*" in New Zealand.

Investment in Applied Geochemistry

The AAG Council believes that securing both the future of the Association and that of applied geochemistry requires attracting more students to the science. As an investment in the future, the AAG wishes to encourage and support students whose area of study is Applied Geochemistry. For students of applied geochemistry, a major cost component in any research is the geochemical analyses. AAG believes that by identifying appropriate students, using a set of simple criteria, and coordinating with analytical laboratories that are willing to offer support in terms of geochemical analyses, high quality research and training in fundamental geochemical principles can result. The research is then published through the AAG journal (*Geochemistry: Exploration, Environment, Analysis*) or the *EXPLORE* newsletter.

Laboratories Participating in the In-Kind Student Support Initiative

Four laboratories generously signed on to provide the analytical support to students during 2012; committing over \$35,000 in terms of analytical support:

- Becquerel Laboratories Inc., Mississauga, Ontario, Canada
- ALS Geochemistry, North Vancouver, BC, Canada
- Genalysis / Intertek, Gosnells, Western Australia
- Ultratrace / Bureau Veritas, Canning Vale, Western Australia

If your laboratory or student is interested in being a part of this program, please contact the chair of AAG's Education Committee, Erick Weiland (education@appliedgeochemists.org), who can provide you with details of this program. Student applications and instructions may also be found on the AAG web site: <http://www.appliedgeochemists.org/> student's page under the Student Support link.

Education Committee

Eric Grunsky, Ray Lett, Ryan Noble, Nigel Radford, Erick Weiland (Chair)





ioStipend



In-kind Analytical Research Fund for BSc(Hons), MSc and PhD students

Much has been said and written about the broadening gulf between the demand for qualified explorationists and the supply coming out of our colleges, technical institutes and universities. One merely has to attend any geo-conference and gaze out over the sea of grey to fully grasp the situation our industry faces. This is all the more evident in the field of exploration geochemistry whose members have always been in short supply.

As consultants and service industries, we owe our livelihood to mining and exploration and thus have a vested interest in its development. We believe that any aid to promote fresh faces into our sector is helping to secure our future.

Acme Analytical Laboratories Ltd. and **ioGlobal** are taking the bold initiative of directly aiding students in the geosciences via the **ioStipend**. The **ioStipend** is a grant available to students conducting exploration-related geochemical studies at a recognized educational institution. The grant is in the form of analytical services using any package provided by Acme Analytical Laboratories Ltd. Students and/or their teachers/advisors can apply for the grant by submitting the application to ioGlobal who will vet the proposals.

The grant is intended to promote the collection of high quality, base-line data for comparison with more “esoteric data” (eg, isotopic data, partial digests, non-standard sample media) generated during the course of research, and to promote broad training in fundamental geochemical principals across the geosciences.

The **ioStipend** allows for amounts of approximately \$5,000 (AUD, CAD or equivalent) for in-kind analytical work. Successful applicants will also be provided with 3 academic licences of **ioGAS**, the new exploratory data analysis software package available from ioGlobal.

The application form is available at www.ioglobal.net.

It is envisaged that three or four of these awards will be made each year.

Applications are reviewed by an expert group of ioGlobal’s geochemists

Eligibility Criteria

Preference will be given to:

- students with no other source of funding
- students working on exploration geochemistry projects
- projects no or very minimal confidentiality requirements

The ioStipend is international. Applications are welcome from qualified institutions globally.

Some technical input may be provided by ioGlobal on request.

Requirements for receiving the ioStipend

Firstly, there are minimal strings attached. Recipients would have to agree to

1. Have their project promoted on the ioGlobal web site in an area devoted to R&D carried out under the program (couple of passport photo shots, brief description)
2. Acknowledge ACME Labs and ioGlobal for support in technical and public presentations of results
3. Write a short article for Explore describing the project outcomes, and allow this to be published on the ioGlobal web site.

David Lawie, John Gravel



EXPLORE

Newsletter No. 161

DECEMBER 2013

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Manuscripts should be double-spaced and submitted in digital format using WORD. Photos and figures (colour or black and white) should be submitted as separate digital files and as high resolution jpeg or PDF files. Tables should be submitted as separate digital files in EXCEL format. All scientific/technical articles will be reviewed. All contributions may be edited for clarity or brevity.

Formats for headings, abbreviations, scientific notations, references and figures must follow the Guide to Authors for *Geochemistry: Exploration, Environment, Analysis* (GEEA) that are posted on the GEEA website at: http://www.geolosc.org.uk/template.cfm?name=geea_instructions_for_authors

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