Hg in Rocks, Soils and Sediments: Speciation and Implications for Sample Processing and Analysis

Matthew I. Leybourne[1*], Lynda Bloom[2], and Brenda Coughlin[3].
[1]Department of Earth Sciences and Mineral Exploration Research Centre, Laurentian University, Sudbury ON P3E 2C6, Canada *Corresponding author: email, mleybourne@laurentian.ca; [2]Analytical Solutions Ltd., 878213 5th Line E., Mulmur, ON, Canada; [3]ALS Geochemistry, 2103 Dollarton Hwy, North Vancouver, BC V7H 0A7, Canada

INTRODUCTION

The determination of mercury contents in rocks, minerals, surficial sediments and soils is critical for a number of disciplines including the understanding of anthropogenic contributions to the environment, baseline studies, food webs, and mineral deposit formation and exploration. Many studies of Hg and Hg speciation are predicated on the basis that Hg is toxic to humans and aquatic systems, and that much of the labile Hg in the environment is of anthropogenic origin (Lacerda & Marins 1997; Martínez-Cortizas *et al.* 1999; Pirrone **et al.** 2010). Recent estimates of global Hg fluxes have suggested that anthropogenic sources are c. 2000 x 10^{6} g annually (with large variations in estimates), re-

emissions of Hg are c. 450 x 10^{6} g annually, biomass burning is c. 300 to 600 x 106 g annually, whereas geogenic sources are < 900 x 10^{6} g and < 600 x 10^{6} g annually for emissions to the atmosphere and oceans, respectively (Table 1) (AMAP/UNEP 2013). Unlike studies investigating how Hg emissions have affected the environment, the utility of Hg in exploration geochemistry is predicated on the fact that Hg occurs naturally as part of the geochemical landscape and that naturally anomalous accumulations of Hg can serve as vectors to various styles of mineralization (e.g., Goodfellow & McCutcheon 2003; Peter *et al.* 2003; Lentz 2005; Booden *et al.* 2011).

Mercury is redox sensitive, and as such occurs in a variety of forms in natural systems including elemental (Hg), ionic (Hg^+ and Hg^{2+} species, either aqueous or bound to mineral surfaces and organic complexes), sulfide minerals (cinnabar and metacinnabar; HgS), as part of Au and PGE (platinum group element) minerals, and organomercuric forms (e.g., methylmercury; CH_3Hg^+, CH_3HgCl, CH_3HgOH) (e.g., Sladek *et al.* 2002; Hall & Pelchat 2005; Al *et al.* 2006; Issaro *et al.* 2009). Understanding the speciation of Hg is important because the form of Hg controls mobility, reactivity, and bioavailability (e.g., Renneberg & Dudas 2001). A corollary is that the form and redox transformations of Hg will also influence sample treatment and analytical design for mineral exploration. There have been a large number of studies that have investigated the speciation of Hg in rocks, soils and sediments (e.g., Windmöller *et al.* 1996; Sladek *et al.* 2002; Bloom *et al.* 2003; Al *et al.* 2006; Guedron *et al.* 2009). For mineral exploration, the speciation of Hg in sediments and soils is likely to be determined in part by the mechanism by which ore-associated elements migrate or are physically transported to surface. Postulated mechanisms for metal and metalloid transport include seismic pumping of groundwater, diffusion, electrochemical induced migration, vapor transport, groundwater advection and clastic dispersal of Hg-bearing minerals; these have

Table 1. Estimated global mercury emissions

Anthropogenic emissions	2010 Emission t/y	Range t/y
Artisinal gold mining	727	410-1040
Coal combustion (all sources)	474	304-678
Oil combustion (all sources)	9.3	4.3-15.3
Natural gas combustion (all sources)	0.6	0.2-1.0
Pig iron production	45.5	20.5-241
Large scale Al, Cu, Zn, Pb and Au production	291.3	82.7-907
Hg production	11.7	6.9-17.8
Cement production	173	65.5-646
Chlor-alkali industry	28.4	10.2-54.7
Oil refining	16	7.3-26.4
Land fill waste	89.4	22.2-308
Incineration	6.2	1.5-21.9
Cremation	3.6	0.9-11.9
Contaminated sites	82.5	70-95
Other emissions		
Natural emissions from land to atmosphere		80-900
Natural emissions to the oceans		< 600
Re-emissions from land		1500-2800
Re-emissions from ocean		2000-2900
Biomass burning emissions		300-600

Data and table modified from (AMAP/UNEP 2013)

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TABLE OF CONTENTS

ADVERTISERS

Notes from the Editor

EXPLORE 171 includes one technical article about Hg
in rocks, soils and sediments written by Matt Leybourne,
Lynda Bloom and Brenda Caughlin. We are continuing
to publish a new feature "Geochemical Nuggets" with a
contribution from Ray Lett. All readers are encouraged
to contribute their stories to this new feature. **EXPLORE**
issue No. 169 (December 2015) that is posted on the AAG
web site and that was emailed to AAG members contains
updated information about the ISO accreditations in Table
1 as compared to the hard copy version that was mailed to
AAG members in early December.

We thank all those who contributed to the writing and
editing of this issue: Steve Amor, Dennis Arne, Al Arse-
neault, Lynda Bloom, Brenda Caughlin, Ray Lett, Matt
Leybourne, Ryan Noble, and Peter Outridge.

Beth McClenaghan, *Editor*

President's Message

The AAG has been busy trying to gather information to improve our Association to reflect the values of its members. Hopefully you received our online survey in February or March (if you received it in March – please pay your dues soon, thanks). Anyway, to those of you that provided feedback, thank you! An AAG committee is sorting through the information to report to Council and in turn the members. I can tell you that we had 33% of all members respond and 15% of past members also respond to the second survey that went out to a list of members from 2010 -2015. I am looking forward to seeing what your feedback was and working to use this information to improve the AAG for the future. I expect more information will be reported in the next **EXPLORE**, as this will allow the committee time to collect and report the results.

For those that read **EXPLORE** very closely, you may have noted I welcomed the "New Councillors" in the previous issue. However, this was actually our previous standing Councillors from 2015/16 and while I am thankful for their contributions, I would like to welcome our Councillors for 2016/17: Erick Weiland, Romy Matthies, Dennis Arne, Mel Lintern, and Paul Morris.

Connectivity is essential in today's global society and it is important to maintain and boost connections profession- ally. Being part of AAG can provide an opportunity to increase your connections with other geochemists, so please get the most out of your membership and join or like our LinkedIn and Facebook Groups, start discussion posts, or even just make sure to publish your science in our journal GEEA.

GEEA is the platform where your science will be most read AND used. Our membership comprises many consultants and industry employees that may not have the time or freedom to write about their own work, but they use it. They actually read about the science in GEEA and apply it. As a result, the GEEA impact factor and citations may be lower than other journals, but your paper makes more of a difference than can be measured in these metrics. I am confident that the number and value of mineral discoveries or successful mine site remediation projects that could be attributed to someone applying research written up in GEEA far exceeds that reported in a Nature-type article.

Another aspect of connectivity is to have face to face meetings or lectures. On this aspect I would like to mention two points that can enhance your professional ties.

- Attend geochemical talks in your area or look for opportunities to have the AAG Distinguished Lecturer present at your events and bring the crowd to you. Details of our current AAG Distinguished Lecturer (Dan Layton-Matthews) are available on the website or in previous **EXPLORE** articles.
- Attend our International Applied Geochemistry Symposia (IAGS). These are important events technically and socially, and a great way to establish a research network that will serve you well for the future. The next IAGS is going to be in Vancouver, Canada in June 2018 – yes, 2018 not 2017. Details will follow soon, but add this event on your "Must Go To" list.

Warm regards,
Ryan Noble *AAG President; ryan.noble@csiro.au*

Recent GSC Publications

Recent publications that are available for free download from the Geological Survey of Canada GEOSCAN website: http://geoscan.nrcan.gc.ca

- **Targeted Geoscience Initiative 4: unconformity-related uranium systems.** 2015. Potter, E.G. & Wright, D M (eds). Open File 7791.
- **Targeted Geoscience Initiative 4: Sediment-hosted Zn-Pb Deposits: Processes and Implications for Exploration.** 2015. Paradis, S. (ed.). Open File 7838.
- **Targeted Geoscience Initiative 4: Contributions to the understanding of Precambrian lode gold deposits and implications for exploration.** 2015. Dubé, B. & Mercier-Langevin, P. (eds). Open File 7852.
- **Targeted Geoscience Initiative 4: Canadian nickel-copper-platinum group elements-chromium ore systems - fertility, pathfinders, new and revised models.** 2015. Ames, D.E. & Houlé, M.G. (eds). Open File 7856.
- **Targeted Geoscience Initiative 4: Contributions to the understanding of volcanogenic massive sulphide deposit genesis and exploration methods development.** 2015. Peter, J.M. and Mercier-Langevin, P. (eds). Open File 7853.
- **TGI 4 - Intrusion Related Mineralisation Project: new vectors to buried porphyry-style mineralization.** 2015. Rogers, N (ed.). Open File 7843.

Hg in Rocks, Soils and Sediments... *continued from page 1*

been reviewed in detail elsewhere (Plouffe 2001; Cameron *et al.* 2004; Kelley *et al.* 2006).

One of the major issues with understanding the speciation, fractionation and abundance of Hg in rocks, soils and sediments is the lack of consensus on sample processing and analytical protocols. Issues include temperature, solvents used and their targets, redox changes during processing and analysis, and the impact of organic matter. For example, Issaro *et al.* (2009) reviewed selective extractions in Hg speciation analysis and reported a large number of different single and sequential extraction schemes (more than 20 combined) with a much larger number of solvents used to extract the various forms of Hg. Temperature is a contentious issue as different forms of Hg are liberated at different temperatures during pyrolysis (Windmöller *et al.* 1996; Sladek *et al.* 2002; Luo *et al.* 2011), so that sample handling and processing prior to and during analysis is potentially problematic. As a result, most commercial and research laboratories take a cautious approach to heating and drying geological samples for Hg analysis. The purpose of this paper is to review the speciation of Hg in geological media, review previous processing and analytical protocols, and make recommendations for the optimal recovery of Hg in rocks, soils and sediments. It is our view that for most samples of interest for Hg analysis in mineral exploration, there has been too much emphasis placed on handling geological samples at unnecessarily low temperatures.

Hg SPECIATION

Prior to discussing and evaluating suitable sample treatment procedures, it is important to understand the various species of Hg that may be present in sample media.

Elemental Hg (Hg^0)

Mercury has three oxidation states, Hg^0, Hg^+ and Hg^{2+}. Elemental mercury (Hg^0) is the only metal that is liquid at standard pressure and temperature (Boening 2000). The high vapor pressure of Hg^0 means that it is highly volatile; the elemental form results in significant emissions from the earth's surface to the atmosphere (Pirrone *et al.* 2010). In geological systems, Hg^0 is primarily associated with magmatic systems (geothermal and hydrothermal systems) (Stoffers *et al.* 1999). However, Hg^0 is commonly associated with contaminated soils and sediments, although it is generally rapidly oxidized under surface conditions (e.g., do Valle *et al.* 2006).

Ionic forms of Hg (e.g., $HgCl_2$, Hg_2Cl_2, HgO, and $HgSO_4$)

Mercuric chloride ($HgCl_2$) is highly soluble and primarily associated with anthropogenic contamination sites such as wood treatment facilities (Bollen *et al.* 2008), natural gas extraction (Bloom *et al.* 2003) or mercury-cell chlor-alkali plants (Windmöller *et al.* 1996; Bloom *et al.* 2004; Acquavita *et al.* 2012; Baldi *et al.* 2012). Mercurous chloride (Hg_2Cl_2) is typically not expected to be present in most samples of
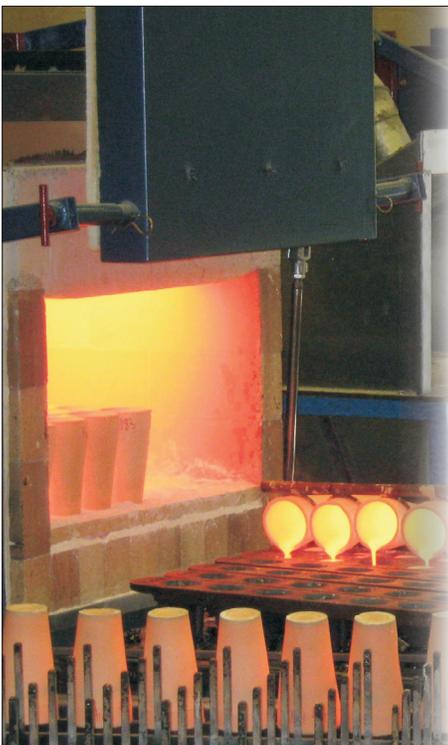
Hg in Rocks, Soils and Sediments... continued from page 5

geological interest (Bloom *et al.* 2003) although Hg$^+$ is likely an intermediary during oxidation of Hg^0 to Hg^{2+} (e.g., do Valle *et al.* 2006).

Many studies of Hg speciation involve spiking (amending) samples or simple mineral substrates with various end-member Hg species to observe changes as a function of temperature or selective leach. However, although these studies typically include HgO and HgSO$_4$ amendments (Fig. 1; e.g., Bloom *et al.* 2003), few studies have demonstrated that these species occur to any extent in rocks, soils or sediments. For example, although Sladek et al. (2002) found up to 26% HgCl$_2$ and 19% HgSO$_4 \bullet 2$HgO in Au mine and Hg mine tailings by X-ray adsorption spectroscopy (XAS), < 1% of the Hg was soluble during sequential extraction in non-tailings samples (using 0.5M NH$_4$Cl).
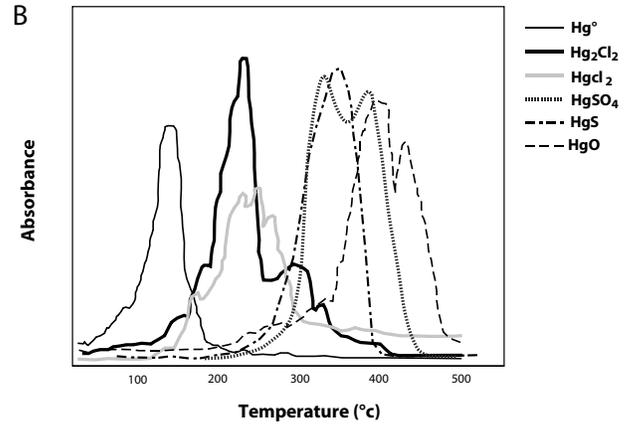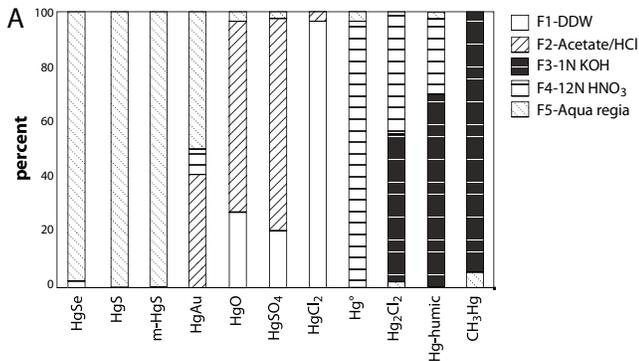
Figure 1. A) Speciation of Hg based on different sequential extractions of Hg compounds suspended in kaolinite (modified from Bloom *et al.* 2003) showing the relative insolubility of Hg^0 and the insolubility of HgS.
B) Thermograms of standard Hg species, after (do Valle *et al.* 2006) and (Bombach *et al.* 1994), showing the temperatures at which various Hg species are released.

Organically bound Hg

Although the various ionic forms of Hg noted above are possible species, in most soils and sediment, the majority of the Hg is in the form of Hg^{2+} and it is typically bound to humic and fulvic substances (Schuster 1991; Yin *et al.* 1997; Miretzky *et al.* 2005; Cattani *et al.* 2009; Zhang *et al.* 2009). Of the various components of organic matter, humic acids

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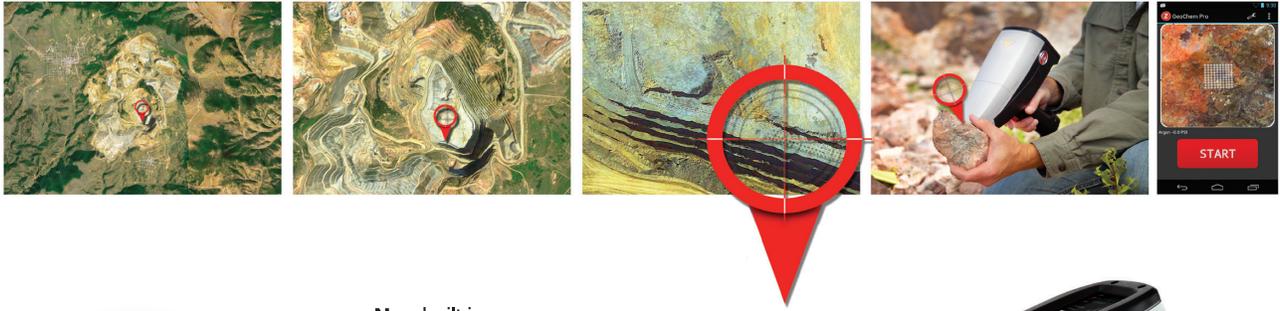
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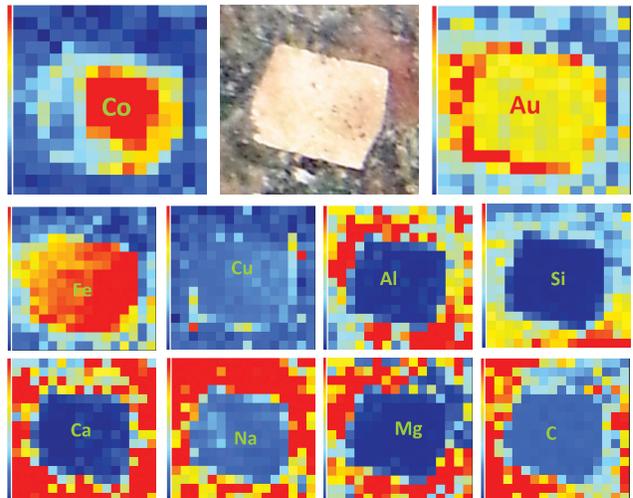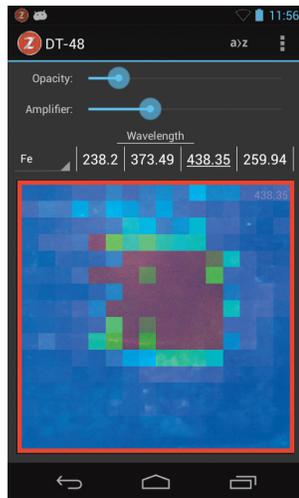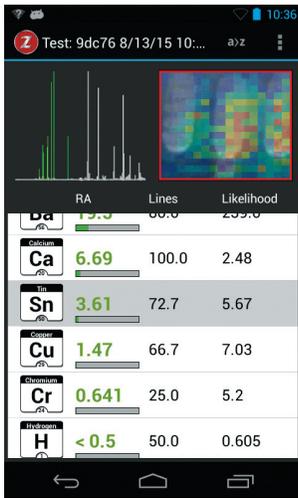
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Hg in Rocks, Soils and Sediments... *continued from page 6*

show the strongest affinity for Hg (Zhang *et al.* 2009). A recent study of a variety of forest soil types showed that close to 100% of the Hg^{2+} was bound to humic acid, whereas a smaller proportion of methylmercury (35-70%) was similarly bound (Cattani *et al.* 2009).

Hg sulfides

Sulfide forms of Hg include cinnabar (α-Hg; red, hexagonal) and metacinnabar (β-Hg; black, cubic). Cinnabar is highly insoluble in the presence of dissolved sulfide, i.e., the solubility product (K_{sp}) for cinnabar is calculated as (Schwarzenbach & Widmer 1963; Ravichandran *et al.* 1998; Boyle 2003):

$$HgS + H^+ \leftrightarrow Hg^{2+} + HS^-$$
$$K_{sp} = 10^{-36.8}$$
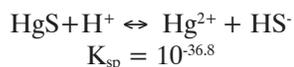
Formation of cinnabar is favored where soils and sediments are water-saturated and reduced S dominates, even if only episodically (Barnett *et al.* 1997) or during oxidation of massive sulfides, where Hg released during sulfide mineral oxidation is rapidly precipitated as cinnabar (Boyle 1995). Once formed, cinnabar is one of the most chemically resistant minerals during weathering and soil formation (Barnett *et al.* 1997; Barnett *et al.* 2001), although the presence of dissolved organic matter can enhance the breakdown of cinnabar under oxidizing conditions (Ravichandran *et al.* 1998), as can the presence of cyanide, which greatly enhances cinnabar dissolution (Leybourne *et al.* 2000). Cinnabar is relatively soft (hardness of 2-2.5), and so can be prone to grain size reduction by glacial processes (comminution). A more rare form of Hg sulfide is the mineral corderoite ($Hg_3S_2Cl_2$) (Foord *et al.* 1974). This mineral is generally formed at low pH (Paquette & Helz 1995) as a result of either supergene weathering processes (Foord *et al.* 1974) or photooxidation (Terzano et al. 2010). This mineral has been identified in contaminated soils using synchrotron methods (Terzano et al. 2010).

Methylated forms of Hg

Methylated mercury (e.g., CH_3Hg^+, CH_3HgCl, and CH_3HgOH) is generally of less interest in mineral exploration. The methylated forms of Hg are the most toxic to aquatic life and humans (Boening 2000), but are typically only a small portion of the total Hg in samples of exploration interest (Leermakers *et al.* 2005). Lake sediments with active redox cycling and abundant organic matter may contain methylated Hg and therefore may be of significance for mineral exploration. Methylation of inorganic Hg^{2+} is typically bacterially mediated, in particular by sulfate and iron reducing bacteria (Frohne *et al.* 2012), so compared to soils, lake sediments are more likely to have methylmercury present; however, the concentrations are likely to be low (i.e., < a few percent at most).

METHODS FOR DETERMINING Hg SPECIATION IN ROCKS, SOILS AND SEDIMENTS

There are three primary means of assessing the speciation of Hg in geological materials: sequential extraction, pyrolysis, and X-ray adsorption (e.g., Windmöller *et al.* 1996; Sladek *et al.* 2002; Kim *et al.* 2003; Yin *et al.* 2012; Yu *et al.* 2012).

Sequential extraction

Sequential extractions have been used in mineral exploration for several decades in an attempt to better understand where other metals are sequestered in soils and sediments (Tessier *et al.* 1979; Chao 1984; Hall *et al.* 1996). Owing to the complex redox transformations and forms that Hg takes in geological samples, the extraction procedures appropriate for metals are not applicable for understanding Hg speciation (Bloom *et al.* 2003). For a recent overview of the various Hg extraction schemes in the literature, see Issaro et al. (2009). There is little consensus regarding the best sequential extraction scheme, or on the assignment of Hg species to a particular extractant (Bloom *et al.* 2003; Issaro *et al.* 2009). However, in general the various sequential extraction schemes demonstrate that: 1) chloride, sulfate and oxide forms of Hg^{2+} are relatively labile; 2) elemental Hg, Hg^+ species, Hg bound to organic matter and methylmercury species are only moderately labile (i.e., by fairly strong acids or by a strong oxidizer such as KOH; Bloom *et al.* 2003); and 3) mercuric sulfides are immobile and require concentrated acid attack (aqua regia) to liberate the Hg (Fig. 1A). Sequential extraction methods are influenced by the amount of organic matter present in the sample and the nature of the substrate (Sladek & Gustin 2003). One of the other issues with sequential extraction is the possibility of readsorption of Hg (Hall & Pelchat 2005). Thus, one of the advantages of using an aqua regia digestion is that it is oxidizing and aggressive enough that readsorption should not be an issue.

Most studies use an aqua regia digest to determine total (or near total) Hg in geological samples (e.g., Bloom *et al.* 2003; Sladek & Gustin 2003; Hall & Pelchat 2005). Aqua regia is a strongly oxidizing acid, and will digest metals bound in carbonates, sulfides and organic matter. Aqua regia digestion thus results in only partial decomposition of the sample matrix, with silicates and crystalline oxides remaining in the residue; organic and inorganic Hg-species

Hg in Rocks, Soils and Sediments... *continued from page 8*

are oxidized and released to solution (Lomonte *et al.* 2008). Addition of H_2O_2 after aqua regia digestion was found to improve recoveries by ensuring complete oxidation of HgS (Lomonte *et al.* 2008).

Pyrolysis

Pyrolysis (i.e., thermal release) of Hg-containing samples is predicated on different species having different peak maximums as a function of temperature (Fig. 1B); the area under the peak during progressive pyrolysis is then proportional to the abundance of the Hg species (Windmöller *et al.* 1996; Durao Junior *et al.* 2009). Drawbacks of pyrolysis for determining Hg species abundance include peak overlaps and peak temperature changes as a function of heating rate (Windmöller *et al.* 1996) (Table 2). In a number of pyrolysis studies, there is a lack of consensus on the peak temperatures of Hg for different Hg species (Table 2). For example, Shuvaeva *et al.* (2008) showed that HgO, $HgCl_2$ and $HgSO_4$ were initially released at ~50 °C, with peak release at ~125-

130°C. These results are in contrast to many other studies indicating that the main species released at temperatures < 100°C is Hg^0 (e.g., Windmöller *et al.* 1996; Sladek *et al.* 2002; Durao Junior *et al.* 2009). Similarly, Reis *et al.* (2012) studied pyrolysis reactions in soils and sediments along with synthetic Hg species, and found that $HgCl_2$, was liberated in the range 125 – 225°C whereas humic acid-bound Hg was liberated at 100 – 240°C (Table 2). However, in general, these studies indicate the sequence of volatilization of Hg from soils and sediments; Hg^0 > Hg_2Cl_2 > $HgCl_2$ > organic-bound Hg > HgO and HgS.

Martínez-Cortizas *et al.* (1999) found that in some peat samples, much of the Hg budget was released when samples were heated to only 30°C. These authors also found that the proportion of Hg liberated at 30°C was a function of the climate during peat formation. Peat formed during cold climate intervals released a greater proportion of Hg at low temperature. By contrast, peat formed during warmer climate intervals over the last 4,000 years released a greater

Table 2. Temperature ranges and peak temperature of Hg release for various Hg species.

Mercury species	Temperature range (°C)	Peak temperature (°C)	Reference
Hg°	< 80		(Watling et al., 1972)
	< 150		(Bombach et al., 1994)
		100	(Windmöller et al., 1996)
	30-160	120	(Luo et al., 2011)
	Room-200	~150	(do Valle et al., 2006)
Hg_2Cl_2		170	(Watling et al., 1972)
		140-160	(Windmöller et al., 1996)
		~230	(do Valle et al., 2006)
$HgCl_2$	< 250		(Table 1 in Windmöller et al., 1996)
		220	(Watling et al., 1972)
		263-276	(Windmöller et al., 1996)
	55-175	125	(Shuvaeva et al., 2008)
	125-225		(Reis et al.)
	60-400	200	(Luo et al., 2011)
	150-320	~260	(do Valle et al., 2006)
	50-150	85	(Lopez-Anton et al., 2011)
HgO	270-535		(Table 1 in Windmöller et al., 1996)
	160-495		(Watling et al., 1972)
	50-180	130	(Shuvaeva et al., 2008)
	280-450	~400	(do Valle et al., 2006)
CH_3HgCl	150-200		(Shuvaeva et al., 2008)
$HgSO_4$	50-180	130	(Shuvaeva et al., 2008)
		570	(Lopez-Anton et al., 2011)
Hg-humic	100-240		(Reis et al.)
	190-340	270	(Luo et al., 2011)
		300	(Windmöller et al., 1996)
HgS		320	(Windmöller et al., 1996)
	225-325		(Reis et al.)
	230-350	310	(Luo et al., 2011)
		265	Metacinnabar; (Lopez-Anton et al., 2011)
		290	Cinnabar; (Lopez-Anton et al., 2011)

Hg in Rocks, Soils and Sediments... *continued from page 10*

proportion of Hg at higher temperatures, above 105°C.

Roos-Barraclough *et al.* (2002) also studied Hg in peat. Their study included heating samples in several steps (air, 30, 60, 90 and 105°C) to determine potential losses of Hg. Although they calculated trend lines for these experiments, the data do not appear to be statistically robust. Further, they suggested that milling of the peat samples resulted in loss of Hg because milling generates heat, although they do not present any data on the temperatures attained during milling. Cragin and Foley (1985) dried soil samples using 5 different methods: air drying at 23°C, freeze drying at -15°C, oven drying at 60°C for 2.5 hours, and oven drying at 105°C and 150 °C for 1 hour. They found that there were significant differences in the Hg content of soils for most samples for the 150°C drying and for some samples also for the 105°C. However, over all four samples, there were no statistically significant differences in Hg content between air dried, freeze dried and oven dried at 60°C. Drying may impact Hg determinations by changing how Hg is bound to surfaces. A weak digestion may give different results for samples dried at low temp versus high temperature. But this may not be because Hg was volatized; it is because the Hg might be trapped, for example in collapsed clay minerals that is then resistant to weak extractions. However, with a strong digestion, such as aqua regia, this difference would be unlikely to be apparent.

X-ray adsorption spectroscopy (XAS)

Both sequential extraction techniques and pyrolysis suffer from a number of problems in understanding Hg speciation, including: 1) they are indirect measures of speciation; 2) require extensive sample modification; 3) have problems of readsorption during extraction; 4) there are potential changes to Hg speciation during extraction; and 5) inconsistencies in data interpretation (Bernaus *et al.* 2005; Jew *et al.* 2011). To overcome these issues, many studies have in recent years focused on x-ray adsorption spectroscopic (XAS) techniques. XAS techniques rely on x-ray radiation produced within a synchrotron (Bernaus *et al.* 2005), and include x-ray adsorption fine structure spectroscopy (XAFS) and near edge structure (XANES) (e.g., Sladek *et al.* 2002; Kim *et al.* 2003; Terzano *et al.* 2010; Jew *et al.* 2011). XAS techniques yield critical speciation information and have the advantage that minimal to no sample pretreatment is required prior to analysis. However, XAS methods are limited primarily by the requirement of minimum Hg contents of generally >100 mg/kg. μ-XAS techniques have more recently been used to overcome the detection limit problem of bulk sample XAS analyses, by focusing the synchrotron energy to small areas of interest (i.e., elevated Hg) with a spatial resolution of around 20 μm focused on regions of elevated (> 100 mg/kg) Hg (Terzano *et al.* 2007).

SAMPLE PROCESSING
Sample pulverizing/homogenization

Prior to geochemical analysis, rocks and in some cases soils or sediments are disaggregated and pulverized. Although pulverization is a routine procedure in sample preparation of geological materials, there is typically little or no information presented in the literature regarding the duration or the temperatures attained during pulverization. Thus, although most studies take a cautious approach to sample heating where Hg is to be determined, little consideration is given to the pulverizing step (Corte & Dubois 1975). In order to investigate this aspect, we performed a series of temperature measurements using a Sentry ST632 infrared thermometer on rock samples pulverized using hardened steel ring mills at ALS Geochemistry in Vancouver, BC, Canada. In commercial labs preparing rocks and soils for mineral exploration programs, two ring mill sizes are typically used to pulverize samples in which 85% passes a 75 μm sieve: 1) a small bowl that pulverizes 250 g of sample; and 2) a large bowl for 1000 g samples. In our study, temperatures attained during pulverization of the small sample size are relatively low, ranging from 56.4 to 58.4 °C. However, pulverization of larger sample volumes results in significantly higher temperatures, ranging from 84.6 to 101.4 °C. Thus, for samples with significant Hg^0 contents (> 10 ppb) sample pulverizing could potentially result in loss of Hg through volatilization.

Effect of sieving

Sieving of soil and sediment samples has two primary impacts in terms of understanding Hg abundance and speciation. First, sieving increases sample handling and exposure of samples to atmospheric oxygen, which will promote oxidation of Hg^0, if present. This is of significance for mineral exploration samples. The second more significant consequence of sieving is the influence on interpretations of Hg in the sample. Mercury is commonly associated with the <2 μm fraction of soils and sediments (Guedron *et al.* 2009a; Santoro *et al.* 2012). Sample processing that includes wet sieving and/or the extraction of the clay-sized fraction (< 2 μm; e.g., Santoro *et al.* 2012) essentially acts as a water leach similar to deionized water used as part of sequential extraction schemes to extract labile Hg (i.e., $HgCl_2$, and to a lesser extent HgO and $HgSO_4$) (Bloom *et al.* 2003).

Redox transformations

One of the defining characteristics of Hg is the number and complexity of redox transformations that can occur at surface and near-surface conditions. Many studies of Hg speciation have focused on sites with significant proximal sources of contamination, including chlor-alkali plants and mine waste sites (e.g., Windmöller *et al.* 1996; Maprani *et al.* 2003; Bollen *et al.* 2008; Durao Junior *et al.* 2009). Although the form of Hg contamination is typically $HgCl_2$ or Hg^0, these species are relatively rapidly transformed to less labile forms, in particular, complexed with organic matter or precipitated as metacinnabar (Renneberg & Dudas 2001; Malferrari *et al.* 2011). Hg^0 is volatile, but less reactive during sequential leaching than water-soluble methylated forms (Mishra *et al.* 2011), consistent with Hg^0 requiring stronger leaches to be removed from soil and sediment samples as noted above. However, Hg^0 is readily oxidized

Hg in Rocks, Soils and Sediments... *continued from page 11*

to Hg^{2+} species (do Valle *et al.* 2006; Mishra *et al.* 2011). The reverse reaction, reduction of Hg^{2+} to form Hg^0 is an important step in the process of Hg evasion from sediment to the atmosphere, owing to the volatility of elemental Hg, and this reduction can occur photolytically and microbially (Mishra *et al.* 2011). However, the study by Mishra *et al.* (2011) concluded that given a sufficient Hg:biomass value, Hg^{2+} is too strongly bound to organic matter to be readily reduced to Hg^0. Mercury may also be reduced by exposure to sunlight (photoreduction). A study of $HgCl_2$-amended soils found that this effect was limited to the uppermost couple of mm of the soil surface (Quinones & Carpi 2011). However, photoreduction of Hg^{2+} to Hg^0 is an important process in aquatic and marine systems and during artic snowmelt (Mann *et al.* 2015; Si & Ariya 2015).

Luo *et al.* (2011) noted that strongly oxidizing acids can oxidize Hg during extraction, and found that peaks in Hg during heating at ~130°C (Hg^0) and 230°C (organically-bound Hg) were removed by pre-treatment of the sample with HNO_3 prior to pyrolysis. Aqua regia digestion is commonly used in mineral exploration and is strongly oxidizing; the primary Hg transformations would be from Hg^0 and Hg^+ to Hg^{2+}, which is less volatile (Table 2). ALS Geochemistry (Method MS-MS41) has analyzed the CANMET standard STSD-4 multiple times. The provisional value from CANMET for an aqua regia digest of this standard is 930 ± 76 ppb (Lynch 1990). Over the last year, STSD-4 was analyzed by aqua regia digestion and ICP-MS with an average yield of 910 ± 80 ppb ($n \approx 1200$), indicating that recoveries for Hg are essentially the same as the provisional value, despite a relatively high temperature (115 °C) during digestion. Thus, temperature effects during aqua regia digestion do not appear to result in Hg loss by volatilization.

Lomonte *et al.* (2008) noted that USEPA (United States Environmental Protection Agency) methods stipulate hot-plate digestion (e.g., aqua regia, reverse aqua regia) temperatures to be 95 °C, just below the boiling point of dimethyl-mercury (96 °C) in order to minimize its loss. These authors also noted, however, that both cinnabar and organic-bound Hg are resistant to wet digestion, requiring higher temperatures for more complete liberation of Hg. Their analysis by aqua regia digestion of biosolids recovered only 85% of the total Hg at 95 °C, whereas at 110 °C, 100% of the Hg was recovered. At temperatures of 120 °C and above, Hg recoveries using aqua regia decreased, suggesting volatilization of Hg from the samples.

DISCUSSION AND CONCLUSIONS
Hg in rocks, soils and sediments

The use of Hg as a lithogeochemical exploration tool has recently been reviewed by Lentz (2005). Although there are a large number of papers that have investigated Hg in rocks, only a small number have specifically investigated

the speciation of Hg (Ryall 1981; Aftabi & Azzaria 1983; Rytuba 2003). More recent studies have used laser ablation ICP-MS to investigate trace element distributions in sulfide minerals associated with different styles of base and precious metal mineralization (Ulrich *et al.* 2009). Based on these studies and on the distribution of Hg within ore forming systems, the primary speciation of Hg in rocks appears to be as substitution within sulfide, telluride and sulfosalt minerals (Table 3) (Rytuba 2003), as cinnabar, or as HgS nanoparticles within other sulfide phases (Deditius *et al.* 2011). For example, Zintwana *et al.* (2012) investigated the Hg contents of mafic rocks of the Bushveld Complex, mid-ocean ridge basalts and Karoo mafic sills, and found low average Hg contents (< 6.4 ppb); Hg was primarily correlated with presence of sulfide minerals. Laser abla-

Table 3. Form of Hg associated with different styles of mineral deposit

Mineral deposit type	Hg phase
Volcanogenic massive sulfide	Hg solid solution in sphalerite (ZnS)
Sedimentary exhalitive (sedex) deposits	"Hg solid solution in sphalerite (ZnS) and cinnabar (rarely)"
Polymetallic base metal	Hg solid solution in sphalerite (ZnS) and cinnabar
Hot-spring gold	Cinnabar, HgO, corderoite ($Hg_3S_2Cl_2$)
Comstock gold–silver	Cinnabar, corderoite
High sulfidation gold–silver	Cinnabar
Sediment-hosted gold	Cinnabar, Hg in pyrite, As–Sb sulfides
Antimony–mercury	Cinnabar
Antimony	Hg solid solution in Sb sulfides, cinnabar
Mississippi Valley Tyoe	Hg solid solution in ZnS
Volcanogenic manganese	Hg adsorbed on Fe–Mn oxides
Basaltic copper	Hg–Cu amalgam
Volcanogenic uranium	Cinnabar
Bedded barite	Cinnabar
Low sulfide gold–quartz vein	Hg in sulfosalts, Au–Ag amalgam
Porphyry copper	Cinnabar

Modified from Rytuba (2003)

tion studies of the Mount Milligan porphyry Cu deposit in British Columbia, Canada found Hg contents up to 7 weight % in pyrite (LeFort *et al.* 2011). A small number of studies have suggested that chloride and sulfate Hg phases are present, based on pyrolysis studies (e.g., Aftabi & Azzaria 1983). However, in most cases not associated with contaminated sites (tailings, calcined waste), the amount of Hg liberated from sulphides in rocks at temperatures <200°C is minor (<1% e.g., Sladek *et al.* 2002).

Most soils, stream sediments, and near surface glacial sediments, exist under generally oxidizing conditions. Given the important control of redox conditions on Hg speciation, the predominant form of Hg in these geological matrices is bound to organic matter, adsorbed to oxide and clay surfaces, and as insoluble sulfide phases i.e., as Hg^{2+} species (Bollen *et al.* 2008). In unweathered glacial sediments, Hg will be present as insoluble sulfide phases. For example, do Valle *et al.* (2005) investigated the background (uncontaminated by proximal anthropogenic sources) in natural soils in Brazil and found that neither Hg^0 or Hg_2^{2+} were present i.e., Hg^{2+} species dominated. $HgCl_2$ is generally not present in soils and sediments except where proximal to wood treat-

Hg in Rocks, Soils and Sediments... continued from page 12

ment facilities (Bollen *et al.* 2008), natural gas extraction (Bloom *et al.* 2003) or mercury-cell chlor-alkali plants (e.g., Windmöller *et al.* 1996; Bloom *et al.* 2004). Under highly oxidizing and low pH conditions where there is significant Cl, $HgCl_2$ can be stable in soils (Fig. 2). However, $HgCl_2$ rapidly hydrolyses in water to form $Hg(OH)_2$ and HgClOH, depending on the activity of Cl.

Although soils and sediments are characterized by the dominant presence of organic and sulfide species of Hg, there are special cases where redox controls or geothermal/
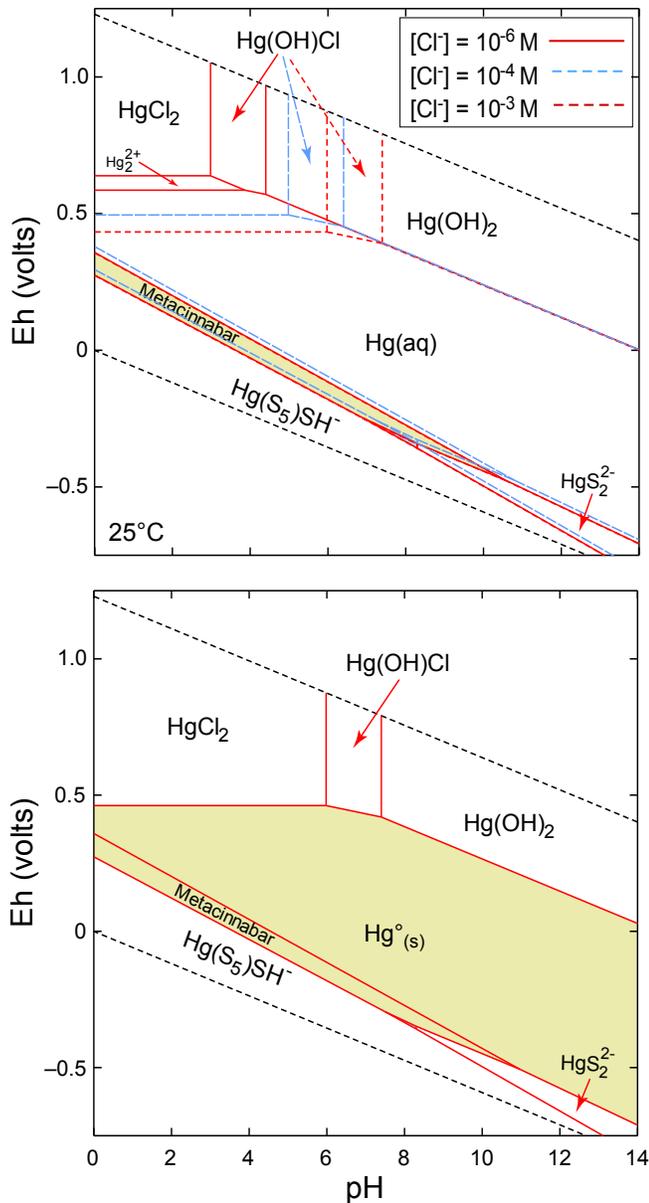
Figure 2. Eh-pH plots of mercury speciation in the presence of dissolved sulfur and chloride. Plots were generated using The Geochemists Workbench (Bethke 2002) with the following conditions: A) $[Hg2+] = 10-7$ M, $[SO42-] = 10-6$ M, $[Cl-] = 10-6$ M. Dashed lines indicate increase in $[Cl-]$ to $10-3$ M B) $[Hg2+]$ = $10-6$ M, $[SO42-] = 10-6$ M, $[Cl-] = 10-3$ M. Key points from these plots are the expansion of the mercuric chloride field as the activity of dissolved chloride increases, and formation of elemental Hg (Hg0) at elevated Hg activity.

hydrothermal inputs play a significant role. These special cases include: 1) peat bogs; 2) lake sediments; and 3) hydrothermal/geothermal upflow zones. For example, Martínez-Cortizas *et al.* (1999) studied an ombrotrophic peat bog that represented some 4000 radiocarbon years of organic matter accumulation. They found that even in pre-anthropogenic times (pre 1500 years BP), up to 50% of the Hg was lost on heating the peat samples to 30 °C; generally the majority of the Hg was stable at 105 °C.

Terrestrial geothermal and subaqueous hydrothermal systems are known to generate relatively large fluxes of Hg, in particular where hydrothermal fluids have been fluxed through continental sediments (e.g., Varekamp & Buseck 1984; Stoffers *et al.* 1999; Christenson *et al.* 2002). Hydrothermal vents off-shore of the North Shore of New Zealand, for example, contain elevated As, Sb and Hg concentrations, with the resulting hydrothermal deposits having mineralization with up to 40 volume% As, Sb and Hg sulfides (Stoffers *et al.* 1999). In these hydrothermal sediments the majority of the Hg is present as cinnabar and metacinnabar, but up to 10% of the Hg occurs as droplets of liquid Hg (Stoffers *et al.* 1999) (Fig. 3). By contrast, shallow hydrothermal vents off the coast of Mexico have elevated Hg, but only as cinnabar (Prol-Ledesma *et al.* 2002).
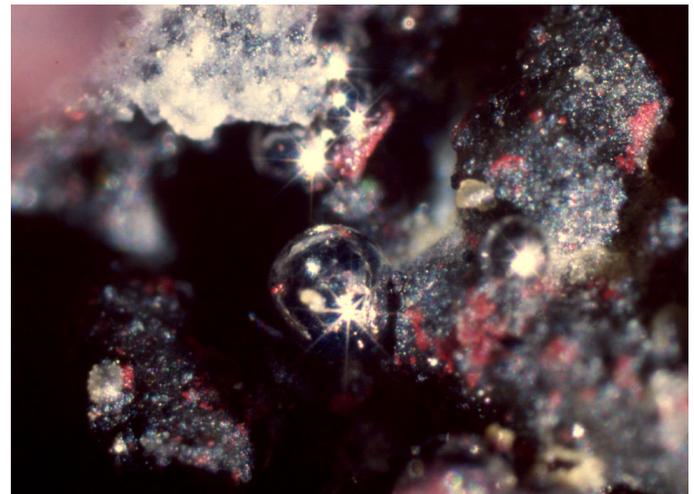
Figure 3. Native mercury droplets with cinnabar (red) and amorphous silica developed on volcanic ash, Bay of Plenty, offshore of the North Island of New Zealand, from Stoffers et al. (1999).

Impact of temperature on Hg in rocks, soils and sediments

Our review of the relevant literature indicates that Hg^0 or $HgCl_2$ are likely to be major species in samples of interest to geochemical exploration only in cases where there is anthropogenic contamination or nearby active hydrothermal or geothermal systems. Both Hg^0 and $HgCl_2$ start to volatilize at temperatures <100 °C (Table 2). Even in cases where there is obvious anthropogenic contamination, the relatively rapid redox reactions of Hg are important. For example, Biester *et al.* (2002) found that soils proximal to a Hg^0 emitting chlor-alkali plant had Hg^0 contents below detection (< 1 ppb), indicating either that Hg^0 was re-emitted from the

Hg in Rocks, Soils and Sediments... continued from page 13

soils, or that Hg^0 was oxidized to Hg^{2+}. However, where Hg^0 may be present in significant quantities, its importance can be determined using selective extraction methods; although Hg^0 is highly volatile, it is only liberated from a sample by a moderately aggressive leach, such as 12 M HNO_3 (e.g., Bloom *et al.* 2003).

A consistent result from most studies of Hg in soils is that the organic content of the soil is key (e.g., Schuster 1991; do Valle *et al.* 2005); for soils with abundant organic matter, most Hg appears to be strongly bound, especially to fulvic and humic acids (e.g., Biester *et al.* 2002). In sandy soils with low organic matter contents, however, Hg is typically present adsorbed to oxide and clay mineral surfaces (e.g., Biester *et al.* 2002). There are instances in natural systems where high concentrations of dissolved Cl and SO_4 may have an influence on Hg speciation and mobility. As an example, groundwaters in northern Chile have been shown to transport porphyry-Cu associated metals and metalloids to surface during seismic events, which upon evaporation produce significant Hg in soil geochemical anomalies (Cameron *et al.* 2002; Cameron *et al.* 2004; Leybourne & Cameron 2008). Data for a number of partial extractions (including deionized water, Enzyme Leach, MMI, hydroxylamine, and aqua regia) for soils overlying the Spence porphyry Cu in Chile deposit indicates that despite elevated Cl and SO_4 soil contents, Hg appears to be primarily associated with Fe- and Mn-oxyhydroxides in the soils; $HgSO_4$ and $HgCl_2$ appear to not be significant species (Cameron and Leybourne, unpublished data).

Recommendations for sample treatment

As discussed, we have reviewed the extensive literature on Hg speciation as determined by a variety of techniques of interest to mineral exploration. We can make the following recommendations with respect to sample handling and processing for the determination of Hg in rocks, soils and sediments. If the samples are likely to be contaminated by Hg^0 or there are visible Hg^0 droplets, then samples should not be dried or pulverized to temperatures in excess of 60°C. If Hg^0 and/or $HgCl_2$ are not present, which in geochemical exploration and baseline studies will most likely be the case, then samples can be dried and processed at temperatures of up to 105°C for around 2.5 hours. For rocks, smaller aliquots (250 g) for pulverizing appears to result in temperatures that do not exceed 105°C. Pulverizing 1000 g sample splits may result in heating samples to temperatures approaching 105°C, which could result in mercury loss and should be avoided.

Acknowledgments

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Recently Published in Elements

Volume 12, no. 2, Enigmatic relationship between silicic volcanic and plutonic rocks

The April 2016 edition of Elements explores the relationship between silicic volcanism and intrusive activity. Lundstrom & Glazner review Silicic Volcanism and the Volcanic-Plutonic Connection. This is followed by an article on the Pace of Plutonism (Coleman, Mills & Zimmerer) and another contribution with a temporal theme, The Life and Times of Silicic Volcanic Systems (Wilson & Charlier). Scaillet, Holtz & Pichavant discuss Experimental Constraints on the Formation of Silicic Magmas and Blundy & Annen discuss Crustal Magmatic Systems from the Perspective of Heat Transfer.

The final contribution is Geophysical Evidence for Silicic Crustal Melt in the Continents: Where, What Kind, and How Much? This edition of Elements should provoke some thoughts on rocks that are probably some of the first an aspiring geologist is introduced to and yet remain enigmatic.

Dennis Arne
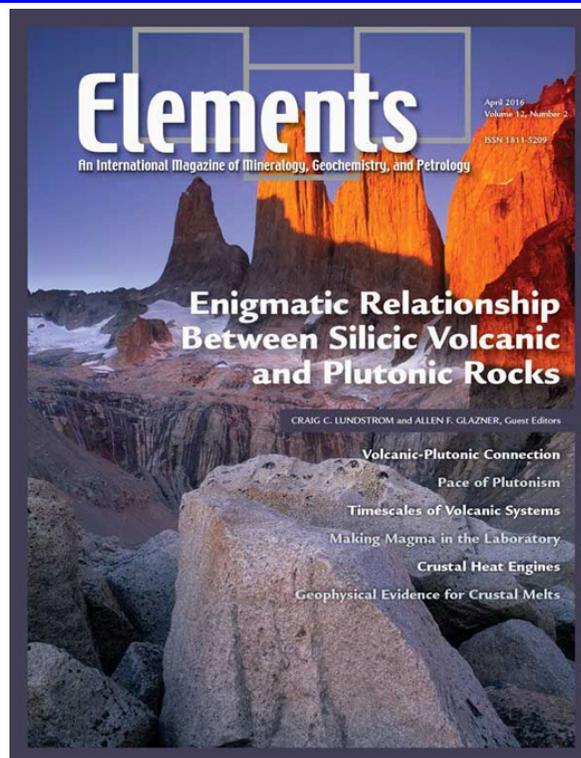
Geochemical Nuggets   *New Feature*
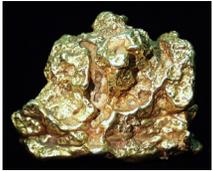
An example of till sample contamination

One of the past British Columbia Geological Survey (BCGS) regional geochemical till surveys involved the collection and analysis of over 900 samples for trace and minor elements and major oxides by a combination of instrumental neutron activation (INAA), aqua regia - inductively couples plasma emission spectroscopy (AR-ICPES) and lithium borate-metaborate-ICPES. In the field at each two samples were routinely collected, one for geochemical analysis and the other, a witness sample, for follow up analysis. The till samples for geochemical analysis were sent to an off-site preparation facility where they were dried, disaggregated and to minus 0.063 mm size fraction. No silica blank samples were sieved with the till samples during preparation.

Both minus and plus 0.063 mm size fractions were returned to the BCGS Laboratory where the minus 0.063 mm size fraction of each field duplicate sample was split into a sub-sample to monitor analytical variability. This sample together with the field duplicate and a standard reference material sample were inserted into batches of twenty samples for analysis. These samples were carefully split and one sub-sample sent for INAA analysis for gold and 32 minor and trace elements at a commercial laboratory. The other sub-sample was sent to a second commercial laboratory for AR-ICPES and lithium borate-metaborate-ICPES analysis.

In time the results were delivered by the two analytical laboratories to the BCGS where an examination of data generated from analysis of standard reference materials, field and analytical replicate samples revealed that the data were within acceptable quality control guidelines. However, closer inspection of the gold results provoked considerable excitement because one till sample from an area where no bedrock gold mineralization had been previously reported contained more than 10 ppm Au and two had over 2 ppm. The samples also contained more than 50 ppm As. The high Au values were corroborated by INAA and AR-ICPES analysis although the Au detection limit by AR-ICPES was 1000 ppb. Closer inspection of the results in the data tables revealed a suspicious trend in that INAA gold concentrations declined progressively from the peak value to a point where they were below detection (Fig. 1). In fact, they rather resembled the classic down-ice geochemical profile observed through the dilution of mineralized material in till samples collected down-ice from concealed bedrock mineralization. The investigating geologist noted, however, that the spatial distribution of the high gold values did not follow any reasonable pattern, as the sample sites with elevated gold were widely scattered around the map area and not clustered.
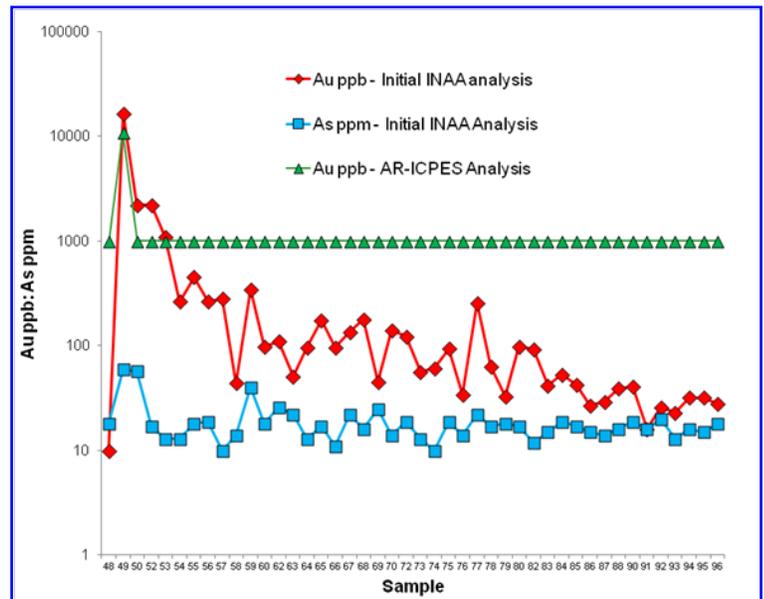
Figure 1. Gold and As by INAA and Au by aqua regia-ICPES in the original till samples.
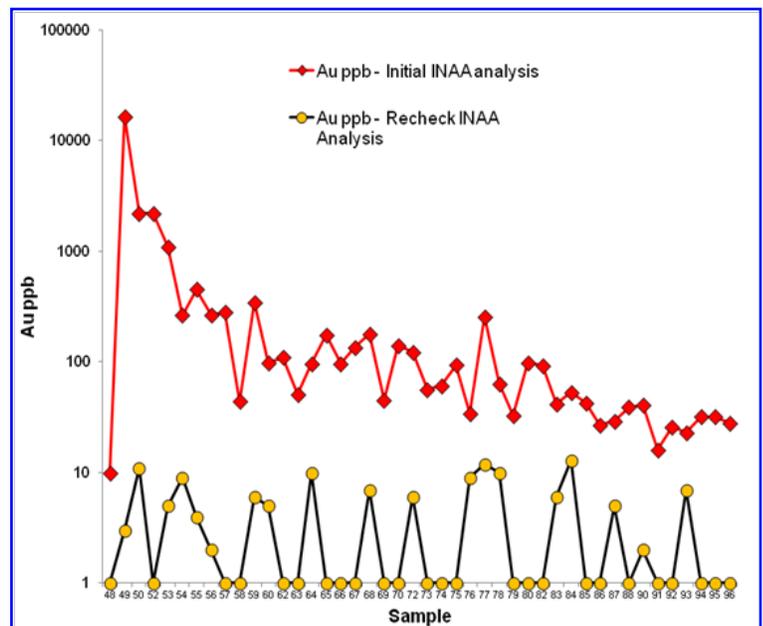
Figure 2. Results of INAA Au analysis of the original and a witness till sample for Au.

Caution prevailed and a portion of the witness material for the samples with high Au values was dried, disaggregated, sieved to the minus 0.063 mm size fraction in the BCGS laboratory and the samples, with reference standards, were sent for commercial INAA analysis. When the results from these witness sample INAA analyses were received the

An example of till sample contaminatio... *continued from page 18*

>2 ppm Au anomaly was found to have disappeared (Fig. 2). Clearly there had been gold contamination at the preparation facility during the initial sieving of the till samples. Although no explanation was given it was suspected that mineralized rock sample crushing and till sample sieving were being carried out at the same time at nearby locations within the preparation facility. The As content of the initial and witness samples is almost identical (Fig. 3) indicating no obvious As contamination during the till sample preparation.

Ray Lett,
Victoria, B.C., Canada

Figure 3. Results of INAA analysis of the original and witness till samples for Au and As.
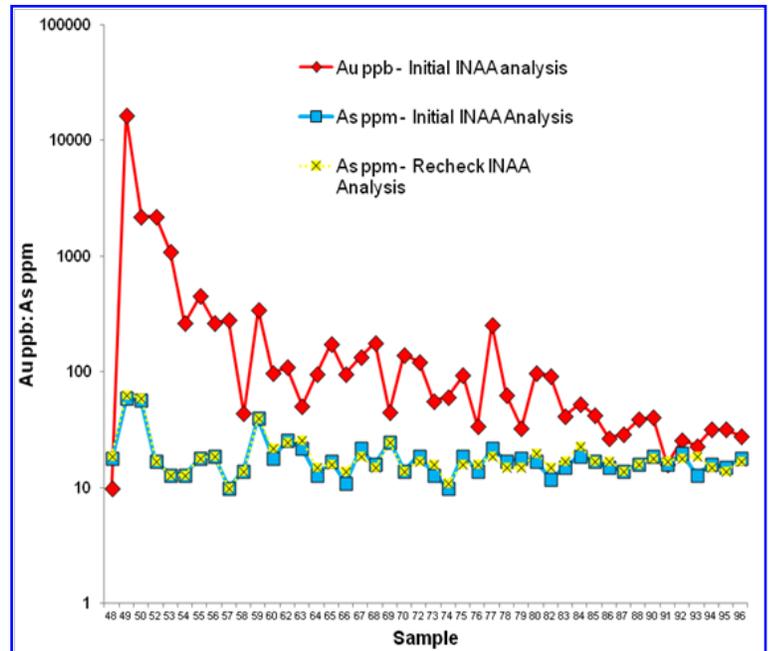
2016-2017 Regional Councillors

Dennis Arne

Dennis Arne is Principal Consultant – Geochemistry and Director of CSA Global Canada. He has been a principal geochemical consultant for the last seven years based primarily out of Vancouver, initially with ioGlobal (now Reflex Geochemistry) and then with a small consulting group, Revelation Geoscience Ltd, prior to their merging with CSA Global in 2012. Before moving to Canada he was a contract Senior Geochemist and consultant for Geoscience Victoria, Australia where he undertook orientation studies in lithogeochemistry, partial extraction soil geochemistry, hydrogeochemistry and hyperspectral analysis as part of the Gold Undercover initiative. He ran his own geological and environmental consultancy for nearly a decade in Australia where he worked in mineral exploration as well as undertaking geotechnical and land capability assessments. He was previously Senior Lecturer in Applied Geochemistry and Economic Geology at the Western Australian School of Mines, Curtin University and Lecturer in the same areas at the University of Ballarat, Australia. Dennis was a Killam post-doctoral Fellow at Dalhousie University in the early 1990s where he applied thermochronological methods to petroleum maturation and tectonic studies and prior to that worked for several years as a consultant to the global petroleum industry. He has completed a Graduate Diploma in Hydrogeology and Groundwater Management at the University of Technology, Sydney, a PhD in thermochronology applied to mineral deposits at The University of Melbourne, a MSc in economic geology at Lakehead University, and a BSc Honours at the University of Regina. He has worked extensively in Canada and Australia, with occasional forays into South America, Africa and Antarctica. Dennis has served on the AAG Council for the last two years and is currently the AAG coordinator for the Society News section of Elements magazine.

Mel Lintern

Mel Lintern is a research geochemist for CSIRO Mineral Resources in Australia. His expertise lies in the application of geochemistry, including biological media and calcrete (a common soil component in arid Australia) for mineral exploration. Mel's research is enabling mining companies to explore with more confidence when tackling greenfield areas where sedimentary cover dominates, particularly in arid and semi-arid regions of Australia. Since 2002, at least

2016-2017 Regional Councillors ... *continued from page 20*

two large mines have opened (Tropicana and Challenger) as a result of using his calcrete research for exploration; the gold from these mines alone equates to over A$12 billion dollars. He is currently leading projects on laser ablation, biogeochemistry, environmental geochemistry and calcrete geochemistry. He is passionate about geochemistry and is keen to promote its use to exploration companies and the community at large.

Mel joined CSIRO in 1980 and has since achieved numerous scientific breakthroughs that have had a direct impact on mineral exploration. He has translated the science of biogeochemistry, gold's mobility in the surficial environment and how abiotic-biotic geochemical anomalies form into robust mineral exploration tools used by industry to find new mineral deposits.

In the last ten years, he has led a number of large, multi-client externally-funded projects involving more than 40 domestic and international exploration companies, geological surveys and academic institutions. Mel's research has demonstrated that vegetation creates detectable surficial geochemical anomalies in calcrete, even where there are significant thicknesses of transported cover such as sand dunes. With others he found tiny gold nuggets precipitated inside gum leaves showing that deep rooted plants can uptake and precipitate gold and thereby create geochemical anomalies for exploration. He discovered that gold occurs in both ionic and metallic forms within calcrete, which has helped explain the chemical mobility of gold in soil and allows partial extraction analysis to be confidently applied by mineral explorers to detect mobile surficial gold anomalies. Mel holds the following qualifications: PhD Applied Geology, Graduate Diploma in Environmental Science and Bachelor of Science (Zoology)

Romy Matthies

Romy Matthies has been an AAG Fellow since 2009 and holds a Ph.D. from Newcastle University (UK, 2010), a M.Sc. from the University of Leon (Spain, 2007) and a Diploma (M.Sc. equivalent, Germany, 2005) from the Technical University Mining Academy of Freiberg. Romy worked three years as a mining consultant (SRK Chile S.A., SRK UK Ltd.) before moving into research (Newcastle University, UK; Waterloo University, Canada; Tohoku University, Japan). She is currently working for the R&D – Mineral Resources section of the GUB Ingenieur AG in Germany. Romy is member of the Awards and Medals Committee of the AAG and was previously Council member during two terms. Her main expertise lie in the fields of metal(loid) geochemistry, mine water prediction, transport modeling, and remediation.

Paul Morris

Paul Morris holds a BA (Geography) and a BSc (Hons: Geology) from the University of Otago, and a PhD in geology from Victoria University of Wellington. He has held post-doctoral research and teaching positions at the University of Sydney, and Shimane University (Japan). Since 1988, he has been employed by the Geological Survey of Western Australia, and has been Chief Geochemist since 1996, responsible for GSWA's regional regolith geochemistry and mapping program, acquisition of all geochemical data, and design, implementation and maintenance of GSWA's corporate geochemical database.

Paul joined the then AEG in 1999, and has held several positions, including Symposium Coordinator (2003-2007), AAG vice president (2008-2009), AAG president (2010-2011), Awards and Medals Committee chairman (2012-2003), AAG Councillor (2014-2005), AAG Education Committee Chairman (2011-). He was also co-chair of AAG's International Applied Geochemistry Symposium, held in Perth, Australia in 2005.

Erick Weiland
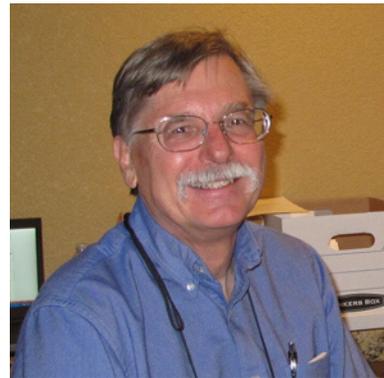
An internationally respected geochemist with over forty years of professional experience and technical knowledge across multiple disciplines, Erick has successfully completed projects in fourteen (14) countries. His expertise include: mining/mineral geochemistry, rock/waste characterization, environmental impact assessments, water quality and soil remediation investigations, material characterization, geochemical evaluation of surface water, groundwater, and mineral interactions, and assessing the acid generation potential (acid rock drainage) with associated leaching of potentially hazardous constituents from natural materials. He is an expert in the application of geochemistry supporting exploration, engineering, and environmental projects including site characterization, feasibility studies, permitting, remediation, water quality, soil remediation, evaluation of acid mine drainage, waste rock dumps and tailings dam engineering/design, and mine closure activities.

Erick has successfully designed, implemented, and

2016-2017 Regional Councillors ... *continued from page 20*

evaluated field and laboratory investigations related to geochemical processes in the surface and sub-surface environments. Projects include: attaining and maintaining compliance with federal and state permits; environmental assessment, safe recharging of surface and waste waters to groundwater aquifers, monitoring and cleanup; CERCLA emergency clean-up actions; risk assessment; fate and transport analysis of metals and non-metals within the natural environment; hydrological modeling; geochemical and contaminant transport modeling; and environmental analysis.

Erick is currently the Manager of Source & Migration Control projects within the Freeport-McMoRan Environ-

mental Technology / Life Cycle Analysis Team. This team identifies, evaluates, develops, and deploys emerged or emerging technologies that can be applied to risk and liability management at existing mining and processing sites, closure and reclamation of mining operations, and remediation of legacy sites. He joined the association in 1978 and has been an active member ever since. He has participated as an AAG Councilor, President, Database Chairman, Editorial Board member, Canadian and Australian Geosciences Council representative, Symposium Chair, and other miscellaneous duties over the past 37 years.

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AAG Fellow (Voting)

Mark C. Pirlo
Senior Research Fellow (Geochemist)
WH Bryan Mining & Geology Research Centre
(BRC), Sustainable Minerals Institute,
The University of Queensland, St Lucia
PO Box 12930, George Street
Brisbane, QLD 4003 AUSTRALIA
Membership # 3644

Regular Members (Non-voting)

Mr. Chuandong Zhao
Inst. of Geophysical and Geochemical Exploration
84 Jinguang Road
Langfang, Hebei 13, CHINA 13 065000
Membership # 4316

Mr. Ted Erdman
P.O. Box 82
North Fork, ID USA 83466
Membership # 4317

Yulia Uvarova
Senior Geochemist, CSIRO
26 Dick Perry Ave
Kensington, WA AUSTRALIA 6151
Membership # 4318

Dr. Tom Meuzelaar
Senior Consultant,
Geology and Geochemistry
Golder Associates, Inc.
2470 South Deframe Street
Lakewood, CO USA 80228
Membership # 4319

Jeff Havig
Postdoctoral Fellow and Adjunct Faculty
University of Cincinnati
4133 Ballard Ave.
Cincinnati, OH USA 45209
Membership # 4320

Jacques Houle
P. Eng. Mineral Exploration Consulting
6552 Peregrine Road
Nanaimo, BC CANADA V9V 1P8
Membership # 4321

Mr. Zhixuan Han
Institute of Geophysical and Geochemical Exploration
84 Jinguang Road
Langfang 13 Hebei CHINA 065000
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Mr. Shanfa Xu
Institute of Geophysical and Geochemical Exploration
84 Jinguang Road
Langfang 13 Hebei   CHINA 065000
Membership # 4326

Mr. Qingqing Liu
Institute of Geophysical and Geochemical Exploration
84 Jinguang Road
Langfang 13 Hebei CHINA 065000
Membership # 4327

Dr. Carmina Jorquera
Senior Geochemist, Barrick Gold
La Capitania 171, d.96
Santiago CHILE 758001
Membership # 4328

Mr. Serge Perreault
Principal Geochemist
Soquem Inc.
120 des Saules
Val-d'Or, QC CANADA J9P 4G1
Membership # 4329

Student Member

Mrs. Ismahane Chaouche
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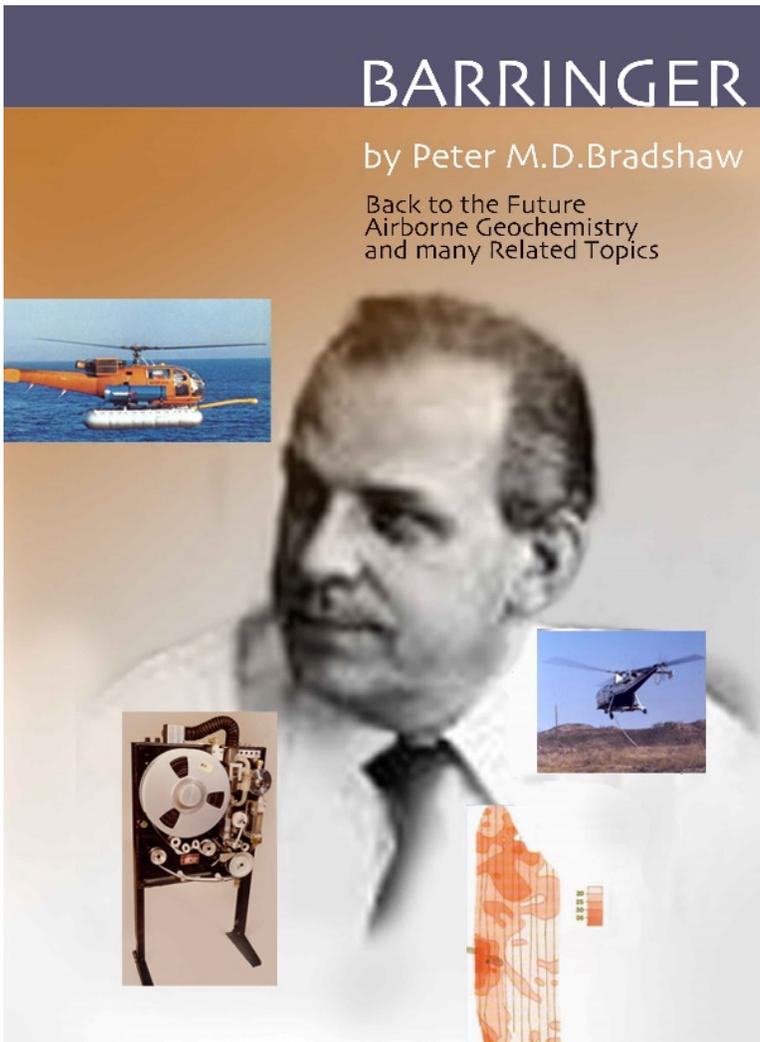
BARRINGER - THE BOOK

Exploration, Remote Sensing, Environment, Analysis, Security

The 1960's and 70's were marked by an explosion in mineral exploration and remote sensing technology. A leader throughout this period was Dr. Anthony (Tony) Barringer and his team at Barringer Research Ltd. (BRL). The highly successful airborne geophysical methods created at BRL are well known while the contributions to exploration geochemistry and many other fields are not. This book documents the many advances in geochemical theory, as well as the ground, airborne and remote sensing techniques plus analytical methods that were conceived and developed under the leadership of Tony Barringer. Innovative concepts backed by pioneering research funded by BRL on the movement of metals in rock, soil and vegetation remain important areas of investigation. Tony Barringer's ability to bring together a diverse team including geologists, geochemists and physicists with electrical, optical and aeronautical engineers under one roof, provide leadership, a highly stimulating environment and financial support, was truly remarkable. This led to ground breaking advances in a number of different fields, including: exploration geochemistry for minerals and oil and gas; environmental monitoring from the ground, aircraft and space; and civilian and armed forces security. The underlying scientific principles for many of the inventions, now upgraded with modern electronics, are still considered state of the art. One of the many inventions from the BRL "incubator" described in this book is Ionscan, the drug and explosive screening device used in most airports today, which was conceived and developed by BRL in conjunction with technology for the detection of mineral deposits.

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Email: StephenAmor@gov.nl.ca   Tel: +1-709-729-1161

2016

19-23 JUNE	6th International Congress on Arsenic in the Environment. Stockholm Sweden. Website: www.as2016.se
19-24 JUNE	Geochemistry of Mineral Deposits. Les Diablerets, Switzerland. Website: tinyurl.com/h7xvh2b
26-30 JUNE	Australian Earth Sciences Convention. Adelaide SA Australia. Website: aesc2016.gsa.org.au
26 JUNE-1 JULY	Goldschmidt 2016. Yokohama Japan. Website: www.geochemsoc.org/programs/goldschmidtconference/
4-8 JULY	32nd International Conference of the Society for Environmental Geochemistry and Health. Brussels, Belgium Website: segh-brussels.sciencesconf.org/
10-13 JULY	3rd International Conference on 3D Materials Science. St. Charles IL USA. Website: tinyurl.com/psr55at
10-13 JULY	9th International Conference on Environmental Catalysis. Newcastle Australia. Website: tinyurl.com/pts5mtv
11-15 JULY	4th International Workshop on Highly Siderophile Element Geochemistry. Durham UK. Website: community.dur.ac.uk/hse.ws
17-22 JULY	Eurosoil 2016. Istanbul Turkey. Website: www.eurosoil2016istanbul.org
19-21 JULY	39th International Symposium on Environmental Analytical Chemistry. Hamburg Germany Website: tinyurl.com/pnaswjw
23-27 JULY	Euroscience Open Forum 2016. Manchester UK. Website: www.esof.eu
24-28 JULY	Microscopy & Microanalysis 2016. Columbus OH USA. Website: tinyurl.com/pdyxkpz
24-29 JULY	Organic Geochemistry (Gordon Research Conference). Holderness NH USA. Website: tinyurl.com/jrmsafs
25-27 JULY	5th International Conference on Earth Science & Climate Change. Bangkok Thailand. Website: earthscience.conferenceseries.com
27-28 JULY	8th International Congress of Environmental Research. Lübeck Germany. Website: www.icer16.jerad.org
30 JULY- 3 AUG.	6th International Maar Conference. Changchun, China. Website: tinyurl.com/ju74yn9
7-12 AUGUST	Annual Meeting of the Meteoritical Society. Berlin Germany. Website: www.meteoriticalsociety.org
14-18 AUGUST	11th International Conference on the Environmental Effects of Nanoparticles and Nanomaterials. Golden CO USA. Website: tinyurl.com/qa5kzyl
14-20 AUGUST	Joint International Conference on Environment, Health, GIS and Agriculture. Galway Ireland. Website: www.nuigalway.ie/iseh2016
20-21 AUGUST	6th International Conference on Environmental Pollution and Remediation. Budapest Hungary. Website: icepr.org
21-25 AUGUST	33rd International Geographical Congress. Beijing China Website: www.igc2016.org
27 AUGUST – 4 SEPTEMBER	35th International Geological Congress CapeTown South Africa. Website: www.35igc.org
28-31 AUGUST	3rd International Symposium on Ethics of Environmental Health. Budweis Czech Republic. Website: iseeh.org
4-7 SEPTEMBER	IAP 2016: Interfaces Against Pollution. Lleida Spain. Website: www.iap2016.org
4-7 SEPTEMBER	15th Workshop on Progress in Trace Metal Speciation for Environmental Analytical Chemistry. Gdansk Poland. Website: chem.pg.edu.pl/tracespec
5-9 SEPTEMBER	13th International Nickel-Copper-PGE Symposium. Fremantle WA Australia. Website: www.iagod.org/node/58
11-15 SEPTEMBER	2nd European Mineralogical Conference. Rimini Italy. Website: emc2016.socminpet.it/
12-15 SEPTEMBER	18th International Conference on Heavy Metals in the Environment. Ghent Belgium. Website: www.ichmet2016.ugent.be/
17-22 SEPTEMBER	28th International Meeting on Organic Geochemistry. Florence Italy. Website: www.houseofgeoscience.org/imog/
18-24 SEPTEMBER	Association of Environmental & Engineering Geologists 58th Annual Meeting. Kona HI USA. Website: aegannualmeeting.org/
25-28 SEPTEMBER	SEG 2016 Conference: Tethyan Tectonics and Metallogeny. Çeşme Turkey. Website: www.seg2016.org
25-28 SEPTEMBER	Geological Society of America Annual Meeting. Denver CO USA. Website: www.geosociety.org/meetings/2016
9-13 OCTOBER	World Water Congress & Exhibition. Brisbane QLD Australia. Website: tinyurl.com/pgrbkwu
10-11 OCTOBER	Annual International Conference on Geological & Earth Sciences (GEOS 2016). Singapore. Website: www.geoearth.org

CALENDAR OF EVENTS
continued from page 23

16- 21 OCTOBER   Water Rock Interaction 15. Évora Portugal. Website (pdf): tinyurl.com/lch75x8

5-9 DECEMBER   American Exploration and Mining Association Annual Meeting. Sparks NV USA. Website: www.miningamerica.org

12-16 DECEMBER   AGU Fall Meeting. San Francisco CA USA. Website: fallmeeting.agu.org/2016/

2017

23-26 JANUARY   Mineral Exploration Roundup 2017. Vancouver BC Canada Website: www.amebc.ca/roundup/about-roundup

2-3 MARCH   6th International Conference "Ecological & Environmental Chemistry-2017". Chisinau Moldova. Website: eec-2017.mrda.md

5-8 MARCH   Prospectors and Developers Association of Canada Annual Convention. Toronto ON Canada. Website: www.pdac.ca/convention

14-18 MAY   Geological Association of Canada/Mineralogical Association of Canada Annual Meeting. Kingston ON Canada. Website: www.kingstongacmac.ca/

16-21 JULY   13th International Conference on Mercury as a Global Pollutant Providence RI USA. Website: mercury2017.org/initial/index.php

12-17 AUGUST   21st World Congress of Soil Science. Rio de Janeiro Brazil. Website: 21wcss.org/

13-18 AUGUST   Goldschmidt 2017. Paris France. Website: goldschmidt.info/2017

21-25 OCTOBER   Exploration '17. Toronto ON Canada. Website: www.exploration17.com

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THE ASSOCIATION OF APPLIED GEOCHEMISTS
P.O. Box 26099, 72 Robertson Road, Ottawa, Ontario K2H 9R0 CANADA • Telephone (613) 828-0199
www.appliedgeochemists.org

OFFICERS
January - December 2016

Ryan Noble, *President*
CSIRO
P.O. Box 1130
Bentley, Australia 6102
TEL: +61 8 6436 8684
email: ryan.noble@csiro.au

Steve Cook, *Vice-President*
Teck Resources Limited
Suite 3300, 550 Burrard Street
Vancouver, BC
Canada V6C 0B3
email: stephen.cook@teck.com

David B. Smith, *Secretary*
U.S. Geological Survey
Box 25046, MS 973
Denver, CO 80225, USA
TEL: (303) 236-1849
email: dbsmith13@gmail.com

Gwendy E.M. Hall, *Treasurer*
110 Aaron Merrick Drive
Merrickville, ON K0G 1N0
Canada
TEL: +1-613-269-7980
email: gwendyhall@gmail.com

COUNCILLORS

2015-2016
Dave Cohen
Ray Lett
Tom Molyneux
Juan Carlos Ordóñez Calderón
Peter Winterburn

2016-2017
Dennis Arne
Mel Lintern
Romy Matthies
Paul Morris
Erick Weiland

Brazil
João Larizzatti
joao.larizzatti@cprm.gov.br
Chile
Brian Townley
btownley@ing.uchile.cl
China
Xueqiu Wang
wangxueqiu@igge.cn

Northern Europe
Pertti Sarala
pertti.sarala@gtk.fi
Southern Europe
Benedetto De Vivo
bdevivo@unina.it
Southeast Asia
Iftikar Malik
malik.iftikhar@gmail.com

Southern Africa
Theo Davies
theo.clavellpr3@gmail.com
UK and Republic of Ireland
Kate Knights
kknights@hotmail.com

AAG COMMITTEES

New Membership
Nigel Radford,
nradford@iinet.net.au

Awards and Medals
Bob Eppinger
eppinger@usgs.gov
Chris Benn
Pertti Sarala
Romy Matthies

Admissions
Nigel Radford,
nradford@iinet.net.au

Education
Paul Morris
paul.morris@dmp.wa.gov.au

Symposia
David Cohen,
d.cohen@unsw.edu.au

AAG COORDINATORS

AAG Student Paper Prize
David Cohen, d.cohen@unsw.edu.au

AAG Website
Gemma Bonham-Carter, webmaster@appliedgeochemists.org
Coordinator:
Bruno Lemiere, b.lemiere@brgm.fr

Geoscience Councils
David Cohen, d.cohen@unsw.edu.au

GEEA
Kurt Kyser, kyserk@queensu.ca

EXPLORE
Beth McClenaghan, beth.mcclenaghan@canada.ca

ELEMENTS
Dennis Arne, dennis.arne@csaglobal.com

AAG Regional Councillors
Stephen Cook,
stephen.cook@teck.com

Al Arseneault, *Business Manager*
P.O. Box 26099, 72 Robertson Road, Ottawa, ON K2H 9R0 CANADA,
TEL: (613) 828-0199 FAX: (613) 828-9288,
e-mail: office@appliedgeochemists.org