EXPLORE
NUMBER 171 JUNE 2016
Newsletter for the
Association of Applied Geochemists

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

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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).

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)

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

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https://doi.org/10.70499/VUXW1148

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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

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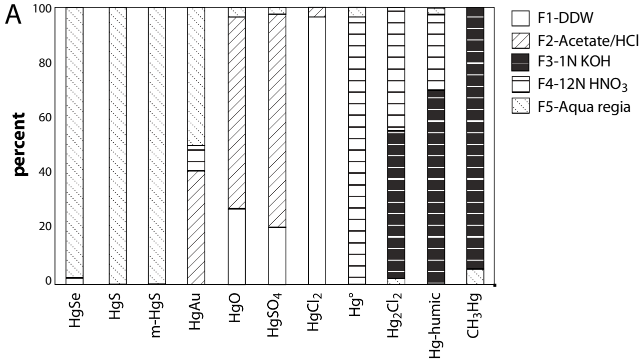
geological interest (Bloom *et al.* 2003) although Hg^+ is likely an intermediary during oxidation of Hg^0 to Hg^{2+} (e.g., do Valle *et al.* 2006).

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% $HgSO_4 \bullet 2HgO$ 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_4Cl).



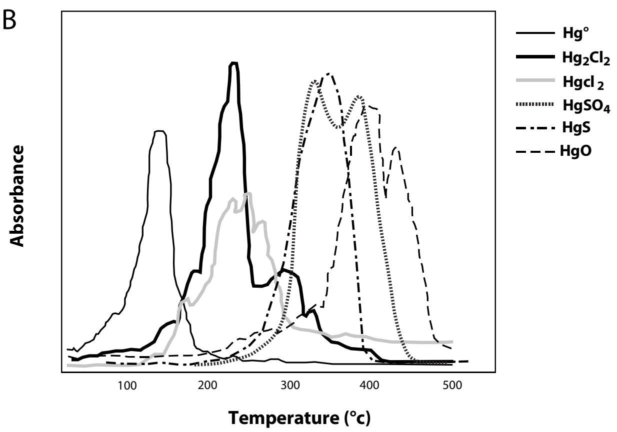


Figure 1. A) Speciation of Hg based on different sequential extractions of Hg compounds suspended in kaolinite (modified from Bloom *et al.* 2003) showing the relative insolubility of Hg^0 and the insolubility of HgS.
B) Thermograms of standard Hg species, after (do Valle *et al.* 2006) and (Bombach *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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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

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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)

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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 Hg0 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

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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 dimethylmercury (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 ablation 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).

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)

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 $Hg2^{2+}$ were present i.e., Hg^{2+} species dominated. $HgCl_2$ is generally not present in soils and sediments except where proximal to wood treat-

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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/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.

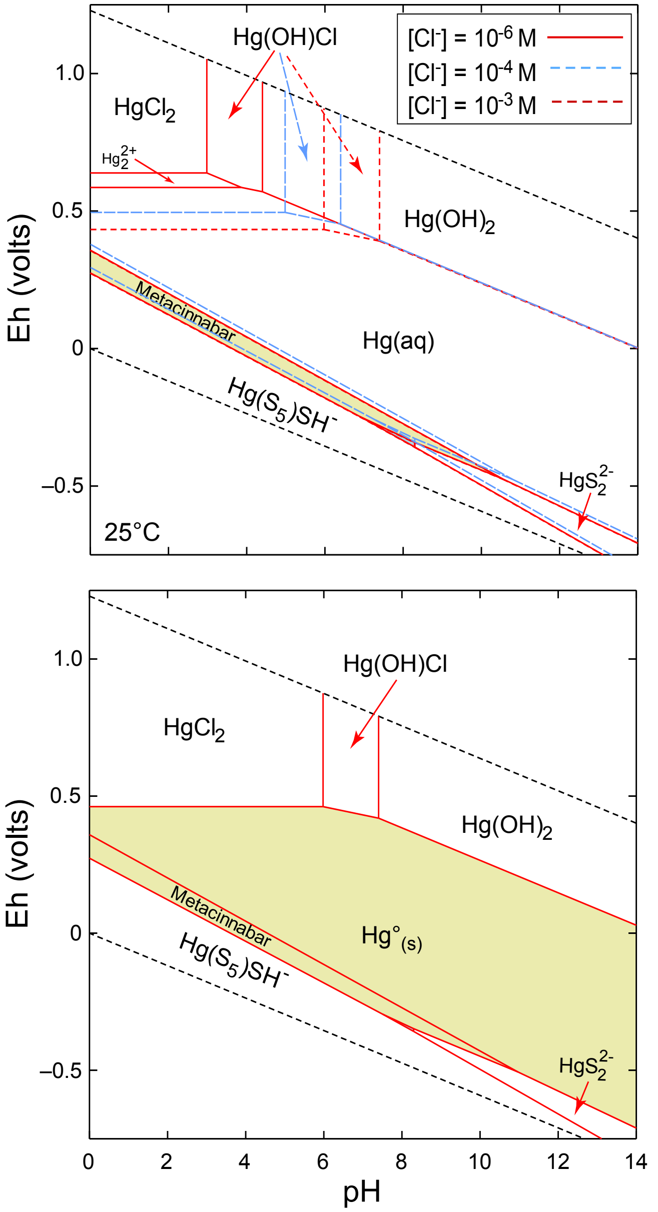

Figure 2. Eh-pH plots of mercury speciation in the presence of dissolved sulfur and chloride. Plots were generated using The Geochemists Workbench (Bethke 2002) with the following conditions: A) [Hg2+] = 10-7 M, [SO42-] = 10-6 M, [Cl-] = 10-6 M. Dashed lines indicate increase in [Cl-] to 10-3 M B) [Hg2+] = 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.

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).

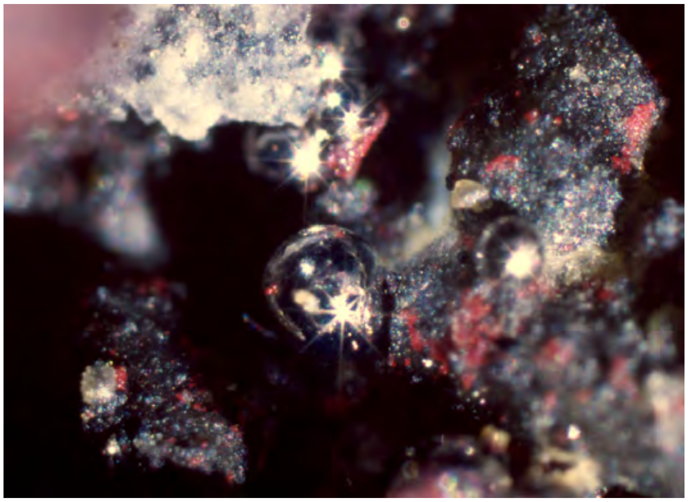

Figure 3. Native mercury droplets with cinnabar (red) and amorphous silica developed on volcanic ash, Bay of Plenty, offshore of the North Island of New Zealand, from Stoffers et al. (1999).

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

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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

Dr. Karen Johannesson (Tulane University) is thanked for generating the Eh-pH diagrams. Dr. Mark Hannington (University of Ottawa) is thanked for the image of liquid mercury droplets from the Bay of Plenty, New Zealand. Peter Outridge and Beth McClenaghan are thanked for careful and insightful comments on an earlier version of the manuscript.

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