Mercury in some arc crustal rocks and mantle peridotites and relevance to the moderately volatile element budget of the Earth

Dante Canil, Peter W. Crockford, Ricardo Rossin, Kevin Telmer

2015

https://doi.org/10.1016/j.chemgeo.2014.12.029

Citation for this paper:

Canil, D., Crockford, P.W., Rossin, R., Telmer, K. (2015). Mercury in some arc crustal rocks and mantle peridotites and relevance to the moderately volatile element budget of the Earth. *Chemical Geology*, 396, 134-142. https://doi.org/10.1016/j.chemgeo.2014.12.029

Mercury in some arc crustal rocks and mantle peridotites and relevance to the moderately volatile element budget of the Earth

Dante Canil[a], Peter W. Crockford[a,b], Riccardo Rossin[a,c] , Kevin Telmer[a,c]

a. School of Earth and Ocean Sciences, University of Victoria, P.O. Box 3055 STN CSC, Victoria, British Columbia V8W 3P6 Canada

b. Current Address: Department of Earth and Planetary Sciences, McGill University, 3450 University Street Montreal, Quebec, Canada H3A 0E8

c. Current Address: Artisanal Gold Council, 2675 Seaview Rd. Victoria, BC, V8N1K7

keywords - mercury, crust, mantle, chalcophile, volatile, condensation, accretion

Abstract

We measured Hg concentrations in 37 igneous rocks from an arc crustal section and in 30 mantle peridotites from ophiolite, orogenic massif and xenolith settings. Mercury is heterogeneously distributed in the igneous rocks and shows a 'nugget effect', suggesting it is concentrated in a trace phase, likely sulfide. The abundance of Hg in the crustal samples varies from 0.9 - 8 ppb and correlates with S and Cu but no other element indicative of differentiation. The average of our data produces 2.9±2.6 Hg for the bulk crust, a factor of 10 lower than previous estimates. The mantle peridotites contained 0.2 - 5 ppb Hg and a correlation of Hg with Al, Cu, S or loss on ignition (LOI) depending on sample type. Secondary uptake of Hg due to low-temperature alteration or mantle metasomatism is evident in the ophiolite and orogenic massif samples, respectively. The primitive upper mantle (PUM) contains 0.4 - 0.6 ppb Hg based on the depletion/enrichment trends in the fresh xenolith samples that demonstrably retained primary Cu/S during emplacement. During mantle melting to produce the crust, Hg behaves as a mildly incompatible element (D_{Hg} residue/melt ~ 0.1), not unlike Cu. For a chondritic abundance of 310 ppb Hg, our estimate for Hg in the mantle requires this element has a similar depletion to Se, Te or S in the bulk silicate Earth.

1. Introduction

Despite a long history in the use of Hg as a pathfinder to locate ore deposits (Fursov, 1958) the abundance of this element remains the most poorly constrained in the Earth's crust and mantle with a reported variation of an order of magnitude (Palme and O'Neill, 2003; Rudnick and Gao, 2003). The long-term recycling of crust and its role in the geochemical cycles of many elements has been well-studied, but that for Hg has rarely been quantified (Stock and Cucuel, 1934; Turekian and Wedepohl, 1961; Taylor 1964; Wedepohl 1995; Gao et al., 1998). This is partly because of analytical challenges in sample analysis and potential contamination or loss during preparation (Dissanayake and Vincent, 1975; Zintwana et al., 2012). The cycle of Hg in natural systems also remains poorly understood due to its complex behavior. Mercury is a toxic volatile metal that exists as particulate or gaseous elemental forms and can be fixed by organic components in coal and soils. Divalent mercury (Hg^{2+}) complexes with ligands forming $HgCl_2$, $Hg(OH)_2$ and other Hg halide complexes. Once dissolved into waters, biological processes can transform Hg into toxic dimethyl-mercury ($(CH_3)_2Hg$), which can bio-magnify.

There has been much study of how anthropogenic activities such as coal burning, mining and waste incineration affect the natural sources and sinks for Hg near Earth's surface (Eckley et al., 2011; Higueras et al., 2012) but less attention on its abundances and distribution in the major solid earth reservoirs – the crust, mantle and core. In this study, we estimate the abundance of Hg in the Earth's crust and mantle, to determine in a broad way how igneous or metamorphic processes control its distribution in the deeper earth. We examined a sequence of plutonic rocks related by crystal fractionation in a Jurassic-aged arc crustal section, which has a reasonably well-constrained geologic history and represents a good proxy for the bulk continental crust (Canil et al., 2010). We also measured abundances in mantle peridotites from ophiolites, orogenic massifs and as xenoliths hosted in basalt. These data are used together to estimate the crustal and upper mantle abundance of Hg and its compatibility during partial melting to form crust.

Combined with previous estimates of Hg in chondritic materials, we use the known volatility of this element to evaluate its distribution in the earth and its cosmochemical behaviour along with other volatile elements during Earth's accretion.

2. Geological Background and Samples

2.1 Bonanza Arc

The Jurassic Bonanza arc section on Vancouver Island, Canada was exhumed in the Paleogene and consists of an upper extrusive sequence (Bonanza volcanics), underlain by felsic to intermediate plutons of the Island Plutonic Suite, and intermediate to mafic plutons of the West Coast Complex (DeBari et al., 1999) that can related to one another by crystal fractionation of mostly olivine, amphibole and plagioclase (Larocque and Canil, 2010). The Bonanza arc has a structural thickness of ~ 15 km and an overall bulk average composition of basaltic andesite (56wt% SiO_2, Mg/Mg+Fe (Mg#) = 50 – Canil et al, 2010, 2013) similar to other estimates for bulk continental crust (Gao et al., 1998; Rudnick and Gao, 2003). Mercury concentrations were made in 37 rock samples from various plutonic and volcanic rocks of the arc (Table 1). Ancillary major and trace element data for these samples are given in Larocque and Canil, (2010).

2.2 Mantle Peridotites

We measured Hg in 30 samples of mantle peridotites (Table 2) from two ophiolites and an orogenic massif exhumed in the northern Canadian Cordillera (Canil et al, 2003; 2006) and in xenoliths hosted in a Quaternary alkali basalt lava flow in central British Columbia (Canil and Russell, unpubl. data). The ophiolite and orogenic massif samples are variably serpentinized (0 – 50%) but retain coherent major and trace element trends consistent with partial melt extraction (Canil et al 2003; 2006; Babechuk et al, 2010). The alkali basalt hosted xenoliths are completely fresh except for one sample (TM53) containing olivine that was extensively hematized by Fe-oxyhydroxides during emplacement in the lava flow. That sample was purposely chosen to investigate the effects of emplacement and subaerial oxidation on its Hg and other chalcophile abundances.

3. Analytical Methods

Rock samples were sawn into 1 cm thick slabs using a diamond saw, and trimmed of any surface alteration. The slabs were crushed to cm-sized fragments in a steel jaw crusher and then reduced to a powder by crushing in an alumina ball mill. Crushing steps were done in short durations (1 min steps, 5 min total), to limit frictional heating and avoid any potential volatilization of Hg. A separate set of rock slabs were crushed by hand in a steel mill and agate mortar/pestle to check for contamination, and to test if unintentional heating during crushing in the steel mill affected the abundances of Hg.

Mercury concentrations were determined for the rock powders using a customized LUMEX RA-915+ Analyzer employing thermal decomposition Zeeman corrected atomic absorption spectrometry (TDZ-AAS) for analysis. For each analysis, between 2 and 42 mg of rock powder was loaded in a quartz boat and fired in different temperature steps to ~ 800 °C in an air stream flowing at 5.5 L/min from a furnace into the analyzer. The signal for Hg was integrated over several heating steps, which ensured that all Hg volatilized was incorporated in the bulk analysis.

We initially calibrated the LUMEX instrument with synthetic standards prepared by weighing out $HgCl_2$ salt to a known aqueous concentration that was then injected into a spoon, weighed, evaporated, and analysed. Using that calibration method, we analysed

JB-2 basalt and JGB-1 gabbro standards as unknowns and obtained results similar to those reported in the literature (JB-2 - 4.78 ppb; JGB-1 2.1 – 4.2 ppb). We then calibrated the instrument for our rock samples over a range of Hg concentrations by using varying weights of the standard material JB-2. The calibration curve created with different weights of basalt JB-2 is linear, fully bracketed the Hg concentrations of our unknowns, and tus required no extrapolation. After calibration using different weights of JB-2 basalt, we analysed reference material JGB-1 gabbro between every two to three unknown samples to check for precision, drift, and accuracy. The average of multiple analyses (n=17) for JB-2 was 2.54 ppb - close to the lower reported value in GeoReM for thsi standard (http://georem.mpch-mainz.gwdg.de/). We determined instrument blanks using preheated quartz sand. Because the thermal decomposition method integrates the total signal, preheating samples assures zero Hg blanks. For example, for low level Hg in peridotite sample TM49 (< 0.6 ng/g) we measured an integrated area for Hg that is over 35 times that of the preceding blank on quartz sand. A conservative detection limit for our method is 0.11 ng/g based on 3σ of the standard deviations of analyses for five separate 50 mg aliquots of TM49.

Between four to six separate aliquots (each weighing 3 to 45 g) of each rock sample powder were analyzed to test for homogeneity. Results reported in Table 1 for each sample are the average and standard deviation of the four to six aliquots. Carbon and S abundances for the samples were measured using an ELBA elemental analyzer at the University of British Columbia or the LECO method at McGill University (Tables 1, 2).

4. Results

4.1 Bonanza Arc Crustal Rocks

We found no systematic differences in Hg concentrations of crustal rocks in crushing either by hand or by alumina ball mill (Fig. 1). A similar range in Hg concentrations within a sample is measured using both crushing methods, which suggests that the variability in abundances within and between samples is not due to volatility or contamination during sample preparation.

There is a notable difference in Hg concentrations in the arc rocks depending on aliquot size for analysis. For example, most of the samples measured using 5 mg aliquots contain more than 6 ppb, up to the highest concentration observed (69 ppb), whereas all but one of the samples using 30 mg aliquots contained less than 6 ppb (Fig. 2). The variations within the samples, as measured by the relative standard deviation (RSD) is between 2 to 55 %, illustrating significant variability in some samples, but little in others (Table 1). The highest RSD are consistently observed for the samples that used 5 mg aliquots (Fig. 2) making those data appear less accurate if not more suspect.

In the arc rocks, the abundances of Hg in large sample aliquots (> 30 mg) vary by an order of magnitude from 0.6 to 9 ppb (Table 1). The abundance of Hg in the arc rocks shows no correlation with any lithophile element or loss on ignition (LOI). We observe a positive correlation of Hg with Cu in analyses based on large aliquots ($r = 0.64$, $p = 0.024$), but more scatter with small ones (Fig. 3a). An even stronger positive correlation ($r = 0.842$, $p = 0.017$) is observed between Hg and S in the analyses using large aliquot sizes (Fig. 3b).

4.2 Mantle peridotites

Based on results of measurements of the crustal rocks, only large (> 30 mg) sample aliquots were used for the mantle peridotite measurements. The Hg abundances in ophiolite and orogenic massif samples vary from 0.2 to 4.7 ppb, on the low end of the overall range in crustal rocks (Figs. 3c, Table 2). The fresh anhydrous xenolith samples have overall less depleted major element composition (Al_2O_3 wt%) and contain markedly less Hg as a group than do the more depleted orogenic massif and ophiolite samples (Fig. 4). There is a clear trend of decreasing Hg with depletion as measured by the Al_2O_3 content in the fresh xenolith samples ($r = 0.907$; $p = 0.013$) but no such clear trend in the ophiolite or orogenic massif peridotites. The ophiolite peridotite suite shows increasing Hg with the degree of serpentinization as signified by loss on ignition (LOI) from 0 – 10 wt% (Fig. 5a), a trend not observed in the crustal rocks. The xenolith sample TM53, with emplacement-related oxidation of olivine, shows no anomalous concentration for Hg nor depletion in Cu or S (Table 2, Fig. 4).

5. Discussion

5.1 Sample Heterogeneity

Mercury is classified as a volatile chalcophile element (Palme and O'Neill, 2003) whose abundance is expected to correlate with other chalcophile elements such as Cu or S. This has been weakly observed in a recent study of rocks from the Bushveld intrusion (Zintwana et al, 2012) and evident in samples from the Bonanza arc, but only in the analyses based on large aliquots (Fig. 3, 4). The lack of correlation of Hg with chalcophile metals and its widely varying abundance (high RSD) in smaller aliquots of crustal samples from our study (Fig. 2), suggest it is heterogeneously distributed, and likely concentrated in a trace mineral phase such as sulfide. We surmise that the small < 5 mg samples showed a wide range in Hg simply due to the presence of sulfide in some aliquots, but not in others from the same sample. This effect is obviated when sample sizes become larger, explaining both a generally lower RSD and Hg content for larger samples from our study. The concentration of Hg in trace sulfides has been recognized in meteorite samples both by petrographic observation (Caillet Komorowski et al, 2012) and by heating experiments that show peak Hg release at the thermal decomposition temperature of sulfides (Lauretta et al. 2001).

Given the occasionally erratic results for Hg in smaller aliquots, we have more confidence in, and give more emphasis to, the analyses based on larger aliquot sizes in our dataset that tend to show a strong coherent trend with other chalcophile metals such as Cu (Fig. 3, 4). The comparison of these recent data with those in the literature can be used to assess the abundance and distribution of Hg in other earth reservoirs – the crust, mantle and core.

5.2 Crustal Abundance of Hg

Despite the fact that samples in our dataset for crustal rocks range in composition from ultramafic (olivine hornblendite) to felsic (alkali feldspar granite) we found no correlation of Hg with any chemical differentiation index (i.e. MgO or SiO_2 content), or the degree of secondary alteration (LOI or C content). The range of Hg abundances is similar in each component of the arc crustal section we sampled (volcanics, felsic intrusives, intermediate/mafic intrusives) although the highest values are encountered mostly in the mafic/ultramafic rocks (Table 1) which typically contain more sulfide in the arc (Larocque and Canil, 2010), consistent with the correlation of Hg with Cu abundances (Fig 3a, 4). At a crustal scale in arc rocks related by igneous differentiation of silicate phases (olivine, hornblende, plagioclase fractionation – Larocque and Canil,

2010) the Hg content is only governed by any process that involves sulfide. The fair correlations for Hg and Cu in samples from the Bushveld and Skaergaard instrusions, which were measured using the same technique but on 100 mg sample aliquots (Zintwana et al, 2012), are also consistent with our data (Fig. 3a) and lead to similar conclusions regarding sulfide control for Hg.

In terms of comparison to other datasets it is important to note that previous analysis of Hg in rocks was mostly by wet chemical methods and spectroscopy and has traditionally been fraught with difficulty. Mercury is a contaminant in reagents and its heterogeneity in samples at low concentrations, as noted above, can give spurious results. Flanagan et al (1982) critically evaluated analyses and heterogeneity of Hg in several rock standards, and these along with data compiled by Govindaraju (1994) are compared with the Bonanza and Bushveld data in Fig. 3a. We plot Hg against Cu given the expected chalcophile nature of both elements, and the fact that the abundance and behaviour of Cu in the crust and mantle is a reasonably well-known reference.

The average and median Hg concentrations for the Bonanza arc are 2.9±2.6 ppb and 2.35 ppb. The mean and median for the Bushveld data is lower at 1.4±1.9 ppb and 0.8 ppb Hg, respectively. Our results and those for the Bushveld, using the same analytical method, are on the low end of the range of Hg contents in igneous rocks measured by all other methods. For example, geological reference rock standards that vary from felsic to ultramafic show a range of Hg from 1.8 to 240 ppb, with a mean of 30.7 and median of 8 (Govindaraju, 1994). In a compilation of analyses from more than 11,000 crustal rocks from different geologic provinces of in East China, Gao et al (1998) combined fluorescence measurements of Hg into ten composite sections, the mean of which is 15 ppb, and a median of 11.9 ppb. Both Shaw et al (1976) and Wedepohl (1995) arrived at extremely high values of > 50 ppb Hg in the crust.

All the igneous rocks from large samples in this study show a generally good positive correlation with Cu (Fig. 3a). There is more scatter with other measurements of igneous rocks of the crust in the literature, varying up to two orders of magnitude, with maximum values of ~ 20 ppb, but most values are < 10 ppb. Recent measurements on two MORB samples (5.8-6.9 ppb Hg - Zintana et al, 2012), are similar to four other basalt rock standards (mean = 5.7±1.7 ppb - Govindaraju et al 1994). Assuming a mean Hg of 2.9±2.6 ppb (Table 1) and 40 ppm Cu in the upper continental crust (Canil and Lacourse, 2010) produces a crustal Cu/Hg ratio of ~ 13,000. That ratio is similar to the MORB reservoir assuming it contains 5.8 - 6.9 ppb Hg and 80 ppm Cu, respectively (Zintana et al, 2012; Jenner and O'Neill, 2012). In a general way, Cu and Hg may show a similar fractionation between crust and mantle, an inference that can be tested given information on the Hg content of the mantle.

5.3 Mantle Abundance of Hg

Palme and O'Neill (2003) derived a PUM abundance of 6 ppb Hg based on the assumption that Hg is chalcophile and geochemically follows Se. Using a Hg/Se of 0.075 for the crust from Gao's et al (1998) data for East China, Palme and O'Neill (2003) obtained 6 ppb Hg in the mantle, assuming the Hg/Se ratio is preserved during melting. That value is not unlike that of McDonough and Sun (1995) of 10 ppb Hg in PUM. As shown in our study (Fig. 3a), Gao et al's (1998) Hg estimate is much higher than all crustal rocks from this study and from the Bushveld rocks of Zintwana et al (2012). Mercury abundances of 6 – 10 ppb in the mantle, when coupled with data for igneous rocks of the crust from this study (Fig. 3), would require the surprising result that the partition of Hg between crust and mantle ($D_{Hg}^{crust/mantle}$) be near or less than unity.

Prior to this study only one dataset existed for Hg abundances in mantle rocks. Garuti et al (1984) measured Hg for orogenic mantle peridotites from three massifs in the Ivrea zone, Italy, by hydride generation atomic absorption. Their results show Hg abundances of up to 320 ppb, with a mean of 49±63, notably higher than observed in crustal rocks (Fig. 3b). Palme and O'Neill (2003) discounted these data as spurious. Nevertheless, Garuti et al (1984) employed a technique that uses large amounts of sample (500 mg), obviating the 'nugget effect', and that at the time was shown to reproduce Hg in rock standards well (Sighinoli et al 1984). Furthermore, we find in a compilation that high Hg is also observed in other peridotites used as reference standards (UCC1 and DTS1) analysed by many different laboratories, with consistently high values of 15 and 31 ppb (Govinidaraju, 1994). The Ivrea mantle peridotite data would suggest an Hg abundance of ~ 20 to 50 ppb for the mantle. This gives a maximum crust/mantle ratio for Hg of 0.3 to 0.5, much less than unity and similar in behaviour to Se as assumed by Palme and O'Neill (2003). Intriguingly, the Garuti et al (1984) data would suggest Hg is more compatible in the mantle than crust.

The mantle peridotites in this study have maximum values of 5 ppb Hg, orders of magnitude lower than observed by Garuti et al (Figs. 3, 4). Garuti et al (1984) did not report Al_2O_3 contents for their samples, but using Ni as a depletion parameter shows that over a similar range in depletion the Ivrea peridotites are clearly inflated in Hg compared to those from this study (Fig. 6). Both Cu and S have similar distribution in the mantle, mainly controlled by sulfide behaviour during partial melting or post-melting metasomatism in the mantle lithosphere (Lorand, 1989; Lorand et al 2003). The high Hg in Ivrea peridotites are over a similar range in Cu, S and level of depletion as samples from our study (Figs. 3b, 4). Thus, the difference between the Ivrea peridotites and those in this study cannot be due to geologic setting or to the behaviour of sulfides during melting or metasomatism in the mantle. Rather, the Ivrea peridotites have Hg levels that have been grossly inflated by secondary processes or contamination.

The freshest rocks in our dataset are the anhydrous spinel peridotite xenoliths. These samples show clear igneous trends for Hg with Al_2O_3 and Ni (Figs. 4, 6) assuming the abundances of the latter two elements represent indices of either partial melt extraction or enrichment in the lithosphere (Canil, 2004; Leroux et al, 2007). We anticipated that Hg, being volatile, may behave similar to S in the xenolith samples, and show low and/or erratic abundances affected by secondary processes associated with high-temperature subaerial emplacement, as has been inferred for many other mantle xenoliths (e.g. Lorand, 1990; Handler et al, 1999). Remarkably, even the visibly altered sample TM53, with completely oxidized olivine (coloured by Fe-oxyhydroxides during supergene alteration on eruption), plots along the ‘depletion/enrichment’ trend (Fig. 4), suggesting that Hg is robust during heating or oxidation of the xenoliths in their host magma during emplacement. Furthermore, the xenoliths from this study do not show any of the depletions in S or Cu characteristic of other xenoliths for which the signature of secondary oxi-hydration of mantle-derived sulfides has been inferred (Lorand, 1990). In contrast, the xenoliths all have Cu/S values less than 0.2 (Fig. 7), identical to fresh massif peridotite samples and to the current estimate for PUM (Lorand, 1989; Handler et al, 1999). Given the evidence for well-preserved Cu and S in the xenoliths, we view their chalcophile element trends as robust and primary, suggesting 0.4 - 0.6 ppb Hg in PUM, depending on its assumed Al content (Fig. 4, 7).

The ophiolite and massif peridotites show higher Hg than the xenoliths for a given level of partial melt depletion (Fig. 4). Compared to the anhydrous xenoliths, the serpentinized ophiolite peridotites show a clear, statistically significant positive correlation of increasing Hg (r=0.644, p=0.003), and decreasing S, with increasing LOI (Fig. 5c). In peridotite, S can be gained during higher-temperature serpentinization or hydrothermal processes, or lost during low-temperature supergene alteration (Lorand et al, 2003; Lorand and Alard, 2010). If Hg is chalcophile and controlled by sulfide behaviour, the concomitant uptake in Hg but loss of S in the ophiolite samples (Fig. 7) could have resulted from a low-temperature overprint. Serpentinization of ophiolite peridotites in the Canadian Cordillera proceeded to low temperatures, and may even be active in the present day (Power et al, 2009). Pronounced low-temperature uptake of Hg is not evident in the orogenic massifs (Fig. 5), which are in contrast higher in S than the fresh xenoliths, despite having a higher level of depletion (Fig. 3b). The high S contents in the massif samples could reflect higher-temperature serpentinization (Lorand et al, 2003) or more likely metasomatic enrichment when they were part of the lithosphere (Lorand and Alard, 2010). Their higher Hg contents (compared to the xenoliths) may also be metasomatic in origin. Low temperature alteration and Hg uptake could also explain the anomalously high Hg in the Ivrea peridotites of Garuti et al (1984), but the state of alteration of LOI in those rocks were not reported to test that idea.

Unlike S, the Cu abundances in most of the peridotites in our study do not show a marked trend with LOI (Fig. 5b), but follow a coherent trend with Hg (Fig. 3, 8). The trend in Cu/Hg in serpentinized ophiolite peridotites with depletion merges with four samples of the fresh anhydrous spinel peridotite xenoliths (Fig. 8). Extrapolation of the fitted trend in the ophiolite samples to an assumed Al_2O_3 content in PUM of 3.5 to 4.4 wt.% suggests a Cu/Hg value of between ~ 35,000 - 50,000. This Cu/Hg value is identical to that calculated for PUM using its inferred Cu contents of 20 – 30 ppm (Fellows and Canil, 2012) and Hg of 0.4 - 0.6 ppb from anhydrous peridotite xenoliths in this study (Fig. 4). The uptake of Hg by low temperature alteration appears to correlate with Cu in the ophiolite samples. If Hg and Cu are not decoupled during the alteration of the ophiolite peridotites, and their partial melting or metasomatism signature is preserved, we can constrain the compatibility of Hg relative to Cu, whose behaviour in the mantle is fairly well known. For example, Cu is a mildly incompatible element with D_{Cu} mantle/melt of ~0.2 (Fellows and Canil, 2012) broadly similar to the Cu content of PUM divided by its MORB complement (~0.25). A similar exercise with Hg, assuming 0.4-0.6 ppb in PUM (Fig. 4) and 5.8 – 6.9 ppb in MORB (Zintwana et al, 2012) would suggest a bulk $D_{Hg}^{residue/melt}$ ~0.1, making Hg about twice as incompatible as Cu during melting.

5.4 Earth's depletion in Hg and the 'late veneer'

Estimates of the element abundances of the Earth's mantle and crust, or bulk silicate earth, bear on the condensation history of elements in planetary materials and on planetary accretion processes (Palme and O'Neill, 2003). For example, the abundances of lithophile elements in Earth's mantle follow a fairly regular trend that scales with their 50% condensation temperatures or 'volatility' (Fig. 9). This volatility trend continues for some moderately volatile chalcophile elements such as Cu, Cd and Pb, but does not hold for similar metals S, Se and Te, which although chalcophile at low pressures, can become siderophile at high pressure and temperature (Rose Weston et al, 2009). The latter three elements show pronounced depletions away from the volatility trend of other chalcophile elements (Fig. 9). In a similar way to the highly siderophile elements (HSE), however, the depletion of S, Se and Te in the mantle cannot have been set by high pressure-temperature equilibration with metal during core formation as they are not commensurate with levels expected from metal-silicate partitioning (Palme and O'Neill, 2003; Rose Weston et al, 2009; Brenan and McDonough, 2009). Like the HSE, the depletions in S, Te and Se in the earth require addition of a 'late veneer' of chondritic materials of unconstrained composition (Kimura et all, 1974). The percentage of 'late veneer' added to the earth after its accretion is estimated to be near ~ 0.5% of its mass (Holzheid et al, 2000; Brenan and McDonough, 2009).

Being volatile elements, the abundances and ratios between S, Se and Te could bear on the composition of the 'late veneer' and the delivery of volatiles to the Earth, though such an application is controversial (Konig et al, 2011, 2014; Wang and Becker, 2013). Mercury is a chalcophile but strongly volatile element with a low 50% condensation temperature from a solar nebula of < 350 K (Lodders, 2003; Lauretta et al, 2001). For this reason, Hg should be strongly depleted in the earth, but whether it follows the trend of other moderately volatile chalcophiles (Cu, Cd, Pb) or like S, Te and Se can be siderophile at high T and P and perhaps depleted by core formation, is unclear.

The abundances and distribution of Hg in chondritic meteorites confirm its chalcophile behaviour (Lauretta et al, 1999; 2001) but there are no experimental data on the partitioning of Hg to test whether it can also be siderophile, especially at higher T - P conditions inferred for earth's accretion. Our study provides constraints on Hg abundances in the Earth’s mantle but the analytical difficulties and unique properties for Hg have made its abundance and cosmochemical behaviour in meteorites somewhat enigmatic (Anders and Grevesse, 1989; Lauretta et al, 1999; Caillet Komorowski et al, 2012). For example, if we use the commonly assumed chondritic abundance of 310 ppb Hg (Palme and ONeill, 2003), our estimate for PUM produces a chondrite-normalized depletion for Hg that is nearly identical to that of S, Se and Te, and displaced from the ‘volatility’ trend of other elements (Fig. 9). This leads to the intriguing possibility that Hg, although a volatile element like Se, Te and S, was also siderophile during accretion.

Mercury is the most volatile non-gaseous element, and only H, C, N and the rare gases have lower condensation temperatures. The Hg abundances could thus be used as a constraint on the early history and delivery of atmophile elements to the Earth. Unlike S, Te or Se or other HSE, the abundance of Au in the mantle is consistent with simple equilibrium metal silicate fractionation to form the core (Brenan and McDonough, 2009). Assuming 148 ppb and 0.88 ppb Au in PUM and chondrites, respectively (Palme and O’Neill, 2003) we obtain Hg/Au in PUM of 0.7, lower than the chondritic value of ~2 (if chondrites contain 310 ppb Hg). Using data from this study and that of Wang and Becker (2013), the chondrite-normalized ratios of S, Se or Te relative to Au for PUM ($[S, Se, Te/Au]_{PUM}/[S, Se, Te/Au]_{C1}$) are between 0.62 – 0.94 but that for Hg is more depleted ($[Hg/Au]_{PUM}/[Hg/Au]_{C1} = 0.22 - 0.33$). Mercury was either more siderophile than S, Te or Se during core formation, or more volatile than these elements during any late veneer stage. There is evidence for metallic Hg in meteorites but only in samples inferred to have altered or accreted at low temperature (Caillet Komorowski et al, 2012). Future experiments could test whether Hg can be siderophile at the high pressures and temperatures envisaged for Earth's accretion and core formation.

Isotopic data for Ag in terrestrial rocks suggest that Earth accreted a considerable fraction of material with high contents of moderately volatile elements (Schönbächler et al, 2010). Alternatively, as has been recently suggested for S, Te and Se (Konig et al, 2014), the abundances of Hg in mantle rocks could simply be a consequence of melting and metasomatism involving various sulfide components, and that its posited abundance in PUM is simply a construct that has nothing to do with accretion and differentiation to form Earth's mantle.

Acknowledgements – We thank T. Lacourse for some help with statistics, and are grateful to H. Becker and H. Palme and for their reviews of our manuscript. This research was supported by NSERC of Canada Discovery Grants to DC and KT.

References

Anders, E., Grevesse, N., 1989. Abundances of the elements: Meteoritic and solar. Geochim. Cosmochim. Acta, 53, 197-214.

Babechuk, M. G., Kamber, B. S., Greig, A., Canil, D., Kodolanyi, J., 2010. The behaviour of tungsten during mantle melting revisited with implications for planetary differentiation time scales, Geochim. Cosmochim. Acta 74, 1448-1470.

Brenan, J.M., McDonough, W.F., 2009. Core fromation and metal-silicate fracitonation of osmium and iriduum from gold, Nature Geosci. doi:10.1038/NGEO658

Caillet Komorowski, C. El Goresy, A. Miyahara, M., Boudouma , O., Mae, C., 2012. Discovery of Hg–Cu-bearing metal-sulfide assemblages in a primitive H-3 chondrite: Towards a new insight in early solar system processes, Earth Planet. Sci. Lett., 349-350, 261-271.

Canil, D., Lacourse, T., 2011. An estimate for the bulk composition of juvenile upper continental crust derived from glacial till in the North American Cordillera, Chem. Geol., 284, 229-239.

Canil, D., Johnston, S.T., Evers, K., Shellnutt, J.G., Creaser, R.C., 2003. Mantle exhumation in a Paleozoic passive margin, northern Cordillera, Yukon. J. Geol., 111, 313-327.

Canil, D., Johnston, S.T. , Mihalynuk, M., 2006. Mantle redox in Cordilleran ophiolites as a record of oxygen fugacity during partial melting and the lifetime of mantle lithosphere. Earth Planet Sci. Lett., 248: 91-102.

Canil, D., Styan, J., Larocque, J., Bonnet, E., Kyba, J., 2010. Thickness and composition of the Bonanza arc crustal section, Vancouver Island, Canada. Geol. Soc. Amer. Bull., 122, 1094-1105.

Canil, D., Johnston, S.T., Larocque, J.P. Friedman, R., Heaman, L., 2013. Age, construction and exhumation of intermediate mid-crust of the Jurassic Bonanza arc, Vancouver Island, Canada. Lithosphere, 5, 92-97

DeBari, S. M., Anderson, R. G., Mortensen, J. K., 1999. Correlation among lower to upper crustal components in an island arc: the Jurassic Bonanza arc, Vancouver Island, Canada. Can. J. Earth Sci., 36, 1371-1413.

Dissanayake, C. B., Vincent, E. A., 1975. Mercury in rocks and minerals of the Skaergaard intrusion, East Greenland. Mineral. Mag, 40, 33-42.

Eckley C.S., Gustin M., Marsik F., Miller M.B., 2011. Measurement of surface mercury fluxes at active industrial gold mines in Nevada USA. Science of The Total

Environment, 409, 514–522

Fellows, S.A., Canil, D., 2012. Experimental study of the partitioning of Cu during partial melting of Earth's mantle. Earth Planet. Sci. Lett., 337, 133-143.

Flanagan F.J., Moore R., Aruscavage P.J., 1982. Mercury in geologic reference samples, Geostand. Newslett., 6, 25-46.

Fursov, V.Z., 1958. Halos of dispersed mercury as prospecting guides at Achisai lead-zinc deposits. Geokhimica, 3, 338-344.

Gao, S., Luo, T. C., Zhang, B. R., Zhang, H. F., Han, Y. W., Zhao, Z. D., Hu, Y. K., 1998. Chemical composition of the continental crust as revealed by studies in East China. Geochim. Cosmochim. Acta, 62, 1959-1975.

Govindaraju K., 1994. Compilation of working values and sample description for 383 geostandards. Geostandard. Newslett. 18 Special Issue., 158pp.

Garuti , G., Corgoni, C, Sighinolfi, S., 1984. Sulfide mineralogy and chalcophile and siderophile element abundances in the Ivrea-Verbano mantle peridotites, Western Italian Alps, Earth Planet. Sci. Lett. 70, 69-87.

Handler, M,R., Bennett, V.C., Dreibus, G. 1999. Evidence from correlated Ir/Os and Cu/S for late-stage Os mobility in peridotite xenoliths: Implications for Re-Os systematics. Geology, 27, 95-98.

Higueras, P., Oyarzun, R., Lillo, J., Morata, D., 2013. Intraplate mafic magmatism, degasification, and deposition of mercury: The giant Almadén mercury deposit Spain. revisited. Ore Geol. Rev. 51, 93-102.

Holzheid, A., Sylvester, P., O'Neill, H. S. C., Rubie, D. C., Palme, H., 2000. Evidence for a late chondritic veneer in the Earth's mantle from high-pressure partitioning of palladium and platinum. Nature, 406, 396-399.

Jenner, F.E., O’Neill, H.S., 2012. Analysis of 60 elements in 616 ocean floor basaltic glasses. Geochem. Geophys. Geosyst. 13,11-31.

Kimura, K., Lewis, R.S., Anders, E., 1974. Distribution of gold and rhenium between nickel-iron and silicate melts: implications for the abundance of siderophile elements on the Earth and Moon, Geochim. Cosmochim. Acta ,38, 683-701.

Konig, S., Luguet, A., Lorand, J.-P., Wombacher, F., Lissner, M., 2012. Selenium and tellurium systematics of the Earth’s mantle from high precision analyses of ultradepleted orogenic peridotites. Geochim. Cosmochim. Acta 86, 354–366.

Konig, S., Luguet, A., Lorand, J.-P., Pearson, D.G., 2014. A non-primitive origin of near chondritic S-Se-Te ratios in mantle peridotites: implications to the earths late accretionary history. Earth Planet. Sci. Lett, 385, 110-121.

Larocque, J., Canil, D., 2010. The role of amphibole in the evolution of arc magmas and crust: the case from the Jurassic Bonanza arc section, Vancouver Island, Canada. Contributions to Mineralogy and Petrology, 159, 475-492.

Lauretta, D. S., Devouard, B., Buseck, P. R., 1999. The cosmochemical behavior of mercury, Earth Planet. Sci. Lett., 171, 35-47.

Lauretta, D. S., Klaue, B., Blum, J. D., Buseck, P. R., 2001. Mercury abundances and isotopic compositions in the Murchison (CM) and Allende (CV) carbonaceous chondrites. Geochim. Cosmochim. Acta, 65, 2807-2818.

Le Roux, V., Bodinier, J.L.,Tommasi, A., Alard, O., Dautria, J.M., Vauchez, A., Riches, A.J.V., 2007. The Lherz spinel lherzolite: Refertilized rather than pristine mantle. Earth Planet. Sci. Lett. 259, 599–612.

Lodders, K., 2003. Solar system abundances and condensation temperatures of the elements. Astrophys. J. 591, 1220–1247.

Lorand, J.P., 1989. Abundance and distribution of Cu-Fe-Ni sulfides, sulfur, copper and platinum-group elements in orogenic-type spinel lherzolite massifs of Ariege Northeastern Pyrenees, France.. Earth Planet. Sci. Lett., 93, 50-64.

Lorand, J. P., 1990. Are spinel lherzolite xenoliths representative of the abundances of sulfur in the upper mantle? Geochimica et Cosmochimica Acta, 54, 1487–1492.

Lorand, J. P., Alard, O., 2010. Determination of selenium and tellurium concentrations in Pyrenean peridotites, Ariege, France.: new insight into S/Se/Te systematics in the upper mantle. Chem. Geol. 278, 120–130.

Lorand J. P., Alard O., Luguet A., Keays R. R., 2003. Sulfur and selenium systematics of the subcontinental lithospheric mantle: inferences from the Massif Central xenolith suite France.. Geochim. Cosmochim. Acta 67, 4137–4151.

Lyubetskaya, T., Korenaga, J., 2007. Chemical composition of Earth's primitive mantle and its variance: 1. Method and results, J. Geophys. Res., 112, B03211

McDonough, W.F., Sun, S. S.,1995. The composition of the Earth. Chem. Geol., 120, 223-253.

Palme, H., O'Neill, H.St.C., 2003. Cosmochemical estimates of mantle composition. pp. 1-38. In: The Mantle and Core (ed. R.W. Carlson) vol. 2 Treatise on Geochemistry (eds. H.D Holland and K.K. Turekian), Elsevier –Pergamon, Oxford.

Power, I.M., Wilson, S., Thom, J.M., Dipple, G.M., Gabites, J.E., Southam, G., 2009. The hydromagnesite playas of Atlin, British Columbia, Canada: A biogeochemical model for CO_2 sequestration, Chemical Geology, 206, 302-316.

Rose-Weston, L., Brenan, J.M., Fei, Y.W., Secco, R.A., Frost, D.J., 2009. Effect of pressure, temperature and oxygen fugacity on the metal-silicate partitioning of Te, Se and S: implications for earth differntiation. Geochim. Cosmochim. Acta, 73, 4598-4615.

Rudnick, R. L., Gao, S., 2003. Composition of the continental crust. pp. 1-64. In: The Crust (ed. R. Rudnick) vol. 3 Treatise on Geochemistry (eds. H.D Holland and K.K. Turekian), Elsevier –Pergamon, Oxford.T

Schönbächler, M., Carlson, R. W., Horan, M. F., Mock, T. D., Hauri E. H., 2010. Heterogeneous accretion and the moderately volatile element budget of Earth, Science, 328, 884-887.

Sighinolfi, G.P., Gorgoni, C., Santos, A.M., 1980. Atomic absorption determination of ultratrace elements in geological materials by vapor, hydride-forming techniques, I. Mercury. Geostand. News. 4, 223-227.

Stock, A., Cucuel, F., 1934. Die verbreitung des Quecksilbers. Naturwissenschaften, 22, 390-393.

Taylor, S. R., 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta, 28 8., 1273-1285.

Turekian, K. K., Wedepohl, K. H., 1961.. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Amer. Bull., 72, 175-192.

Wang, Z., Becker, H. 2013. Ratios of S, Se and Te in the silicate Earth require a volatile-rich late veneer. Nature, 499, doi:10.1038/nature12285

Wedepohl, H. K., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta, 59, 1217-1232.

Zintwana, M. P., Cawthorn, R. G., Ashwal, L. D., Roelofse, F., Cronwright, H., 2012. Mercury in the Bushveld Complex, South Africa, and the Skaergaard Intrusion, Greenland. Chem. Geol., 320-321, 147-155.

Figure Captions

Figure 1 - Comparison of Hg concentrations in samples crushed by hand in an agate mortar with those crushed in a steel ring mill. Error bars are one standard deviation. Line is the 1:1 correlation.

Figure 2 - Plot comparing the percentage relative standard deviations (RSD) and Hg contents for large and small aliquots of crustal rocks. Note break in axis.

Figure 3 – Mercury abundances for samples from this study compared with other chalcophile elements. (a) Covariation of Cu and Hg in both large and small sample aliquots of the Bonanza arc igneous rocks, compared with intrusive rocks of the Bushveld Intrusion (Zintwana et al, 2012), East China crustal composites (Gao et al, 1998) and mafic geologic reference materials (Govindaraju, 1994). (b) Covariation of S and Hg in the Bonanza arc igneous rocks, compared with data for mantle peridotites form this study (ophiolites, orogenic massifs, xenoliths) and from the Ivrea zone orogenic massifs (Garuti et al, 1994). The very good correlation of the arc crustal samples (dashed line, $r = 0.842$, $p = 0.017$) passes near the xenolith data. (c) Plot of Cu versus Hg in the mantle peridotites from this study (labelled as in (b)) and from the Ivrea zone (Garuti et al, 1994). Also shown are the data for the large aliquot arc crustal samples with a good correlation (dashed line, $r = 0.64$, $p = 0.024$) that passes through most xenolith samples.

Figure 4 – Covariation of Al_2O_3 (wt%) with Hg in peridotite samples. Note the excellent positive correlation (dashed line, $r = 0.907$; $p = 0.013$) for the fresh xenolith samples, but higher Hg and lack of correlation in ophiolite and orogenic massif samples for a given degree of depletion. The grey bracket shows the range of Al_2O_3 (wt%) estimated for

primitive upper mantle (PUM) (after McDonough and Sun, 1995; Lyubetskaya and Korenaga, 2007).

Figure 5 – A comparison of Hg, S and Cu contents in peridotites from this study with loss on ignition (LOI wt%). The latter can be used as a measure of degree of alteration. In the ophiolite samples note the positive correlations of LOI with Hg (r=0.644, p=0.003) but little or no correlation with Cu or S.

Figure 6 - Covariation of Ni (ppm) with Hg in peridotite samples. Note the inflated Hg at a given degree of deletion (as defined by Ni content) in the ophiolite and orogenic massif samples, compared to xenoliths. Also shown for comparison are data for orogenic massifs from the Ivrea zone (Garuti et al, 1984).

Figure 7 – Plot of the Hg contents compared with Cu/S in the mantle samples. The xenoliths and some of the massif samples have retained their primary Cu and S during emplacement, to values near that for PUM and other unaltered orogenic massif peridotites (Lorand, 1989). In contrast, the ophiolite peridotites show uptake of Hg that correlates with higher and disturbed Cu/S values.

Figure 8 – Comparison of the ratios of Cu and S to Hg in peridotite samples for this study as a function of partial melt depletion as measured by Al_2O_3 (wt%). The fitted trend for Cu/Hg for the serpentinized ophiolite samples (r = 0.76) extrapolates through four of the six fresh xenolith samples, giving a Cu/Hg of 30,000 – 38,000 for PUM, depending on its assumed Al_2O_3 content (grey bracket - after McDonough and Sun, 1995; Lyubetskaya and Korenaga, 2007).

Figure 9 – Plot of the C1 chondrite-normalized abundances in PUM: $(\text{element}/\text{Mg})_{PUM}/(\text{element}/\text{Mg})_{C1}$ of the moderately volatile chalcophile elements Cu, S,

Te, Se, Pb, Cd, Hg) plotted against their 50% condensation temperatures from a solar nebula. The condensation temperatures for Hg are from Lauretta et al (2001) and all others from Lodders (2003). The volatility trend and the abundances for Cu, Cd, Pb and S in PUM, and Hg in chondrite, are from Palme and O'Neill (2003). Data for Se and Te in PUM are from Wang and Becker (2013). The data points for Hg show two different cases: (1) Hg in PUM from this study (filled symbol) and (2) Hg in PUM from Palme and O'Neill (2003) (open symbol).