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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 [1], Ricardo Rossin [2], Kevin Telmer [2]

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

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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 to 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 have 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., 2013) 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

* Corresponding author.
[1] Current address: Department of Earth and Planetary Sciences, McGill University, 3450 University Street Montreal, Quebec H3A 0E8, Canada.
[2] Current address: Artisanal Gold Council, 2675 Seaview Rd. Victoria, BC V8N1K7, Canada.

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(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 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 (56 wt.% 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 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 was 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+ Analyser 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 analyser. The signal for Hg was integrated over several

Table 1
Mercury abundances in Bonanza Arc crust samples.

Sample	Unit	Rock type	Hg ppb[a]	sd	Sample wt	Hg ringmill	sd	Hg handcrush	sd	C (ppm)	S (ppm)	LOI (wt.%)	Cu (ppm)	SiO_2 (wt.%)
JL06-038	BONV	Volcanic	4.03	0.11	30							1.80	108	49.9
JL06-050	BONV	Basalt dyke	3.50	0.35	5							1.12	132	49.3
JL06-053	BONV	Basalt dyke	1.18	0.16	30	1.0	21.7	3.7				3.42	90	53.1
JL06-061	BONV	Volcanic	10.46	2.11	5							4.36	92	47.6
JL06-077	BONV	Volcanic	7.22	2.54	5							2.75	7	64.6
JL06-090	BONV	Volcanic	2.77	0.21	5							3.55	82	55.5
JL06-092	BONV	Volcanic	4.97	0.28	5	5.0	5.6	7.4	6.4			4.77	65	48.4
JL06-093	BONV	Volcanic	0.23	0.08	5							6.51	31	51.5
JL06-002	IPS	Granodiorite	3.30	0.32	30	3.3	15.5	1.2	6.1	121		0.76	6	70.7
JL06-040	IPS	Granodiorite	0.88	0.03	30	0.9	3.8	0.5	12.5	94		1.18	12	69.8
JL06-041	IPS	Granodiorite	1.31	0.03	5					124	422	1.97	35	55.4
JL06-076	IPS	Granodiorite	11.98	2.16	5					904	2101	1.30	50	60.7
JL06-107	IPS	Felsic dyke	2.50	0.24	30	2.5	31.8	2.4	21.9	102	405	1.71	37	61.3
JL06-003	WCC	Diorite	4.19	0.66	5					174	1362	1.34	24	60.4
JL06-006	WCC	Diorite	3.33	0.61	30					323	1897	0.99	291	50.3
JL06-009	WCC	Gabbro	12.60	5.10	5					187	2171	0.89	218	43.4
JL06-010	WCC	Diorite	8.55	1.03	5					92	1524	1.46	82	49.3
JL06-011	WCC	Gabbro	5.66	1.66	5	5.7	29.2	3.0	34.7	216	539	0.77	309	40.3
JL06-013	WCC	Diorite	3.71	0.46	5					200	539	1.53	12	56.0
JL06-017	WCC	Gabbro	47.45	8.45	5					145	836	1.58	157	50.4
JL06-020	WCC	Diorite	0.72	0.16	30					282	315	1.69	15	49.6
JL06-022	WCC	Basalt dyke	2.10	0.07	30	2.1	1.8	3.5	4.6	125	1038	3.29	57	49.9
JL06-044	WCC	Diorite	1.52	0.22	5					609	2702	1.67	103	45.9
JL06-066	WCC	Diorite	1.25	0.31	5	1.2	26.2	0.9	23.2	189	749	1.34	71	52.5
JL06-103	WCC	Gabbro	6.66	1.49	5					508	2117	1.43	147	47.4
JL06-104	WCC	Gabbro	2.81	0.42	5					230	1965	0.91	96	46.7
JL06-108	WCC	Gabbro	13.50	1.25	5	13.5	18.8	17.7	4.2	932		2.36	36	53.3
JL06-005	WCC	Hbl peridotite	0.44	0.04	30	0.3	26.8	0.7	7.0		301	6.14	10	40.6
JL06-021	WCC	Hbl peridotite	2.48	0.28	30						902	4.62	33	42.3
JL06-029	WCC	Hbl peridotite	0.84	0.08	5						252	1.58	20	42.0
JL06-042	WCC	Pyroxenite	5.37	1.24	30							4.68	142	45.6
JL06-043	WCC	Hbl peridotite	1.84	0.35	5						1908	7.04	102	39.5
JL06-067	WCC	Gabbro	3.38	0.31	5					89	1716	1.72	169	44.5
JL06-068	WCC	Pyroxenite	1.38	0.25	5							2.52	41	50.0
JL06-101	WCC	Hbl peridotite	6.36	1.47	5						1352	1.89	170	44.9
JL06-105	WCC	Pyroxenite	68.51	12.41	5					4244	795	3.16	138	48.4
JL06-106	WCC	Hbl peridotite	0.95	0.19	30						690	2.24	28	42.6

sd — one standard deviation of the mean of analyses for five aliquots.
5 mg — sample aliquots of ~5 mg.
30 mg — sample aliquots of ~30 mg.
BONV — Bonanza Group volcanic rocks.
IPS — Island Plutonic Suite.
WCC — West Coast Complex.
[a] Mean of analyses for five separate aliquots.