Ultra-trace analysis of Hg in alkaline lavas and regolith from James Ross Island

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Abstract: Polar regions represent a unique environment for the study of mercury cycling in the global ecosystem. Our research was focused on the assessment of the origin and mobility of mercury in the geochemical cycle in Maritime Antarctic (James Ross Island) by means of atomic absorption spectrometry. Mercury content in a set of extrusive (subaerial, subaqueous) and intrusive (dyke) alkaline basalts ranged between 1.6 µg kg^{-1} (for samples without xenoliths) and 8 µg kg^{-1} (for samples containing crustal xenoliths). The mercury content in alkaline basalts indicates a very low concentration of mercury in peridotitic mantle sources. Samples of regolith from James Ross Island were subjected to a comprehensive analytical procedure proposed for ultra-trace mercury concentrations involving fractionation and thermal analysis. Total mercury contents in regolith (2.7–11.3 µg kg^{-1}) did not deviate from the natural background in this part of Antarctica. Additionally, the obtained results are about two orders of magnitude smaller than values formerly assumed for primary mercury contents in basaltic lavas. Our results from Antarctica were compared with mercury contents in basaltic rocks from Greenland and the findings were confirmed. It seems that the input of mercury of geological origin into the polar ecosystem is apparently lower than expected.

Introduction

Contamination of the Antarctic ecosystem by pollutants from lower latitudes is one of the main research topics concerning Antarctica (Bargagli 2008). Although Antarctica is isolated by the circulation of air masses and ocean currents, the concentration of metals and persistent compounds in environmental samples indicate long-range transport of pollutants from continents of the Southern Hemisphere (Bargagli 2008). These pollutants include mercury, which concentrates in polar regions after deposition and re-emission cycles (Bargagli *et al.* 2007, Brooks *et al.* 2008a). Antarctica is contaminated less than the Arctic by mercury from anthropogenic activities (Pfaffhuber *et al.* 2012). The main sources of mercury in Antarctica are marine aerosols, volcanic activity and atmospheric deposition (Bargagli *et al.* 1998). Contaminants are also introduced into the terrestrial ecosystem by seabirds nesting on the shore (Nie *et al.* 2012).

Polar coastal ecosystems seem to be cold traps for global atmospheric mercury burden (Bargagli 2005). Atmospheric mercury consists mainly of the elemental

form (Bargagli *et al.* 2005). The Northern Hemisphere has a higher mercury content (*c.* 30%) in the atmosphere than the Southern Hemisphere (Bargagli 2005). Gaseous elemental mercury can have a residence time in the atmosphere of *c.* 1 year (Martínez-Cortizas *et al.* 1999). However, in polar regions, the lifetime of Hg$^{(0)}$ in the atmosphere is shorter than at lower latitudes (Bargagli *et al.* 2005). Mercury cycling in the Antarctic environment is well described in many works (e.g. Bargagli 2005, Brooks *et al.* 2008a, Pfaffhuber *et al.* 2012). Reactive halogens in aerosols promote the oxidation and deposition of mercury in coastal areas (Bargagli *et al.* 2007). The oxidation of Hg$^{(0)}$ by bromine after the polar sunrise increases the amount of reactive gaseous mercury (Bargagli *et al.* 2005). These speciation changes increase the amount of mercury deposited in snowfall (Brooks *et al.* 2008b). A significant proportion of the deposited mercury is returned to the atmosphere by photochemical reduction (Bargagli *et al.* 2007). A portion of divalent mercury deposited on snow enters into the terrestrial ecosystem in meltwater (largely in bioavailable form), which leads to increased concentrations of total
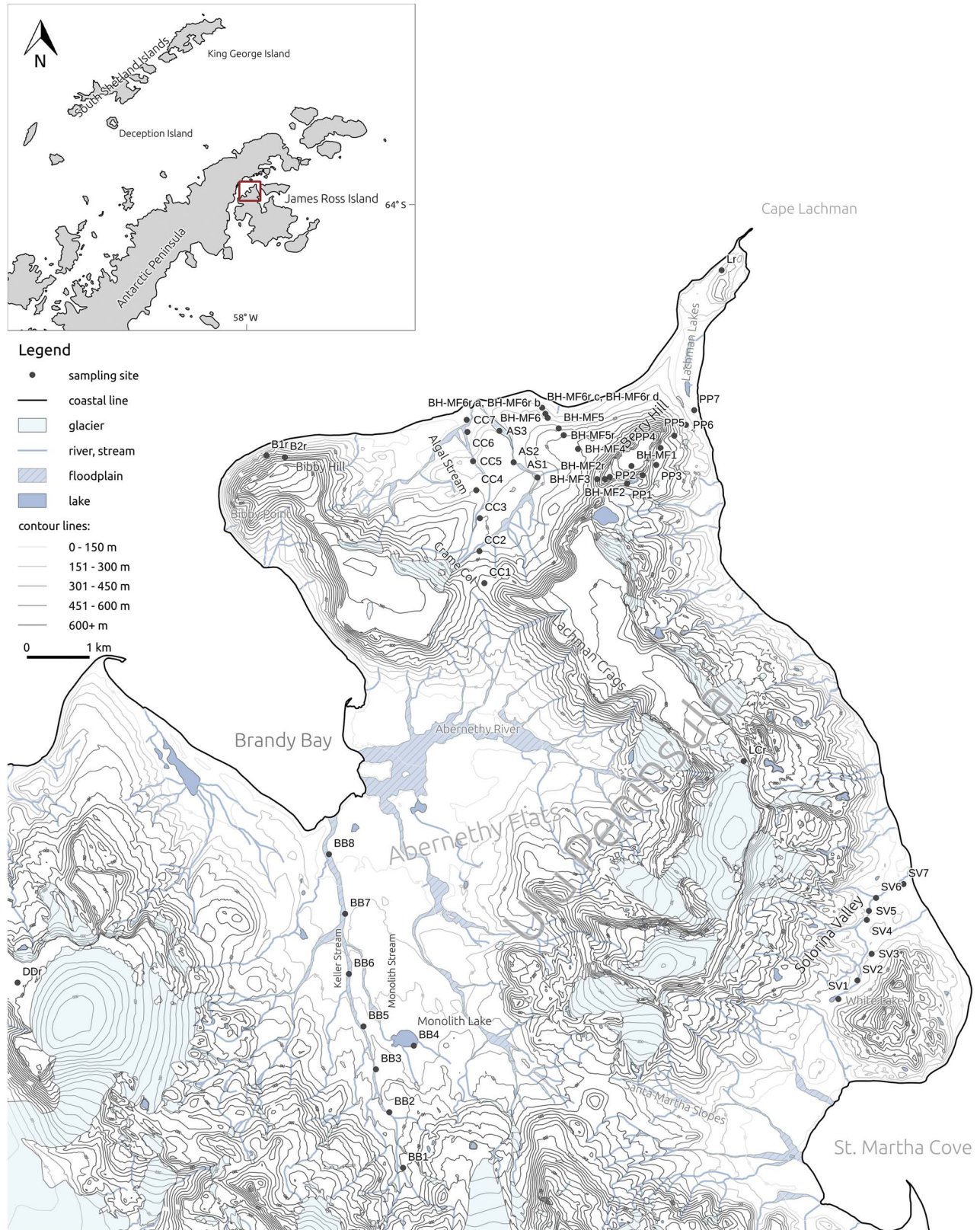
Fig. 1. Sampling sites of volcanites and weathered materials (after CGS 2009). AS = Algal Stream, B = Bibby Hill, BB = Brandy
Bay, BH-MF = Berry Hill–Mendel Formation, CC = Crame Col saddle, DD = Davies Dome, L = Cape Lachman,
LC = Lachman Crags, PP = Panorama Pass saddle, SV = Solorina Valley.

mercury in runoff (Bargagli *et al.* 2005). Nevertheless, unlike the Arctic, an increase in mercury bioaccumulation was not confirmed in Antarctica according to the analysis of sediment cores (Bargagli *et al.* 2007). The mercury content in organisms in areas close to the Antarctic Peninsula is relatively low (De Moreno *et al.* 1997). However, terrestrial environment is more susceptible to the contamination. Bioaccumulation in lichens and mosses has been observed (Bargagli *et al.* 1993, Bargagli *et al.* 1998, Bargagli *et al.* 2005).

Very few studies have been dedicated to the description of total mercury content in igneous rocks. Based on the review by Fleischer (1970), mercury content in most igneous rocks are usually below 100 µg kg^{-1}, except for alkaline basalts and kimberlites which contain several hundred µg kg^{-1} on average. Mercury is emitted into the air during volcanic eruption (e.g. Martin *et al.* 2012). Due to the effective ionic radii of Hg^{2+}, mercury might be expected to accompany Ba, Sr and Ca in rock-forming minerals, which probably accounts for the high concentrations reported for alkaline basalt rocks (Fleischer 1970). Moreover, elevated mercury content was observed in tholeiitic igneous rocks. Dissanayake & Vincent (1975) published total mercury content in whole-rocks and minerals from the layered Skaergaard Intrusion in East Greenland, which is a part of the North Atlantic large igneous province together with coeval flood basalts. The average value was 257 µg kg^{-1} determined by radiochemical neutron-activation analysis. Furthermore, the authors confirmed the hypothesis that mercury is enriched in plagioclase-rich igneous rocks.

To assess the origin, mobility and fate of mercury in the Antarctic ecosystem, information obtained by fractionation analysis can be used. The concentrations of mercury in weathered material in deglaciated parts of Antarctica may represent a background dependent on local geological conditions or may be affected by another source, such as the atmospheric deposition of mercury from distant areas. The aim of this research was to evaluate the geological influence of alkaline basaltic bedrock on the mercury content in weathered material and to consider the extent of mercury contamination in the maritime ecosystem of the Antarctic Peninsula region. Devising an appropriate analytical procedure for the determination of low concentrations of mercury forms in samples was an important task of this research.

Materials and methods

Location of the study

James Ross Island (64°10'S, 57°45'W) is located on the north-eastern, leeward side of the Antarctic Peninsula (Fig. 1). Its northern part, the Ulu Peninsula (CGS 2009), is one of the largest deglaciated areas in the Antarctic

Peninsula region. The retreat of glaciers in this area occurred in the late Glacial at 12.9 ± 1.2 ka (Nývlt *et al.* 2014). The Ulu Peninsula is predominantly formed by Cretaceous marine sediments of the James Ross Basin (e.g. Vodrážka & Crame 2011) that were overlain by back-arc alkaline volcanites of the James Ross Island Volcanic Group (Košler *et al.* 2009) together with a late Miocene sedimentary sequence of terrestrial glacigenic, glaciomarine and marine sediments of the Mendel Formation (Nývlt *et al.* 2011). The ^{40}Ar/^{39}Ar age of volcanites in the Ulu Peninsula, which are created from hyaloclastic breccias, pillow-lavas and subaerial lava flows accompanied by basaltic dykes and subvolcanic plugs, is estimated to be in the range of 6–4 Ma (Smellie *et al.* 2008 and references therein).

Regarding the type of weathering processes in Antarctica, where simple mechanical disintegration predominates, the differences between parent rock and weathered material are minor (Campbell & Claridge 1987). However, compared to Continental Antarctica, the surface of James Ross Island is influenced to a significantly greater extent by liquid water, which promotes weathering and enables the mobility of dissolved minerals and nutrients. In addition, the surface at wet sites is often covered with a layer of microorganisms or moss. In these places, organic matter occurs in the upper layer of the regolith.

Collection of samples

The collection of volcanic rocks and weathered materials was performed during the Czech polar expedition at the Johann Gregor Mendel station in the summers of 2011–12 and 2012–13. In total, 11 rock samples and 33 regolith samples were collected. Considering the objectives of the research, two types of regolith were distinguished. Weathered material from dry surfaces (plateaus, hillsides and stony hillocks) was termed as type 1, whereas samples from streams (deposits in watercourses) were termed as type 2. It can be assumed that both types differ in the degree of particle leaching which may evince the mercury content. The regolith was collected using a stainless scoop; samples of type 1 were removed from a depth of 2–10 cm and type 2 from the edge of streams. The top layer of type 1 was not taken due to the potential presence of microbiota or guano. The samples were subsequently dried in the laboratory at the station for 48 hours (at *c.* 15°C) and sieved to a size fraction below 2 mm. Only this fraction was used in further investigations. The samples were stored at 4°C in polyethylene containers. The collected material was transported to the laboratory in the Czech Republic in a cooling box.

The following transects through the selected localities (Fig. 1) were suggested: Crame Col saddle, Berry Hill–Mendel Formation, Panorama Pass saddle, Brandy Bay

Table I. Samples from the comparative locality in Greenland.

Sample	GPS co-ordinates	Petrographical type
DIK01	69°15'13.536"N, 53°29'22.956"W	Olivine-phyric basalt dyke
DIK05B	69°15'56.808"N, 53°32'51.792"W	Amygdaloidal feldspar-phyric dolerite
DIK05C	69°15'56.808"N, 53°32'51.792"W	Olivine-phyric basalt lava
DIK06	69°15'15.480"N, 53°30'48.636"W	Amygdaloidal olivine basalt clast from hyaloclastite breccia
DIK07	69°15'10.836"N, 53°29'45.276"W	Feldspar-phyric basalt lava
DIK08	69°15'39.060"N, 53°27'35.604"W	Olivine-phyric basalt lava
DIK09	69°15'44.532"N, 53°31'58.044"W	Olivine and feldspar-phyric lava

and Solorina Valley. Additionally, samples from Algal Stream were also taken. The Berry Hill–Mendel Formation transect included the sampling of erratic granite and microgranite pebbles from the Mendel Formation, as well as hyaloclastite breccias and massive basalts above the Mendel Formation. Due to the assessment of mercury content in alkaline volcanites of the Ulu Peninsula, various petrographical samples out of the transects were also collected. Subvolcanic plugs and dykes formed by Na-rich basalt–hawaiite were sampled along the northern slope of Bibby Hill. Basalt pillow lava was collected on Cape Lachman, while subaerial dolerite lava was sampled on exposed upper parts of the Lachman Crags and Davies Dome.

With respect to the low levels of mercury detected in basaltic lavas from the James Ross Island Volcanic Group, an additional polar field campaign focused on the sampling of Palaeocene flood basalts was performed. Exposed basalts in the vicinity of the Arctic Station (University of Copenhagen) in Qeqertarsuaq, Disko Island, West Greenland (e.g. Larsen & Pedersen 2009) were chosen as a comparative locality. Sampling sites and the petrographical features of the collected material are defined in Table I.

Analytical procedures

Thin sections of representative rock were prepared for detailed petrographical investigation (structural/textural characteristics, identification of the constituent mineral phases). Photographs were acquired using an Olympus BX 51 polarizing microscope equipped with a Canon EOS 1100D digital camera.

Prior to analysis, the rock samples were ground to a size fraction below 2 mm. Afterwards, all samples of rock and regolith were milled to a size fraction below 63 µm using short durations of milling to prevent sample heating. The total mercury content in all samples was determined using an AMA-254 Analyzer (Altec, Czech Republic). This atomic absorption spectrometer incorporating thermo-oxidative decomposition of the sample allows the measurement of liquid and solid samples and the pre-concentration of mercury atoms on a gold amalgamator. Three parallel analyses were performed for each sample.

The determination of total mercury in solid samples was verified by means of the certified reference material CRM 020 Trace Metals – Sandy Loam 2 (RTC, USA). The limit of quantification for all measurements was 0.3 µg kg^{-1}.

The samples from the transect in Brandy Bay were subjected to fractionation analysis. The following procedure of sequential extraction was designed for the determination of low concentrations of mercury forms. Total mercury was fractionated into mobile mercury (extracted in 0.5 mol l^{-1} HCl), mercury bound to organic matter (extracted in 0.2 mol l^{-1} KOH), elemental mercury (extracted in 50% HNO$_3$) and residual mercury (the content in solid residue after extraction in HNO$_3$). The extraction was carried out using a return shaker at laboratory temperature, with a solid/liquid ratio of 100 mg of sample to 10 ml of extractant; the time of extraction was 18 hours for each step. Extracts were separated by centrifugation; solid residues were dried at 30°C. The determination of individual mercury forms from the solid residues was performed after each extraction step (for the entire weight of each sample). The concentrations of the mercury forms were calculated from the differences in mercury contents between the steps. Therefore, a new portion of the sample was required for each step of the extraction. Three parallel extractions were performed; thus, one sample was extracted in nine repetitions. The measurement of solid samples allows the determination of lower mercury concentrations than the measurement of liquid extracts.

The content of Hg$^{(0)}$ in samples from Brandy Bay was also determined using thermal desorption. The Hg$^{(0)}$ was calculated from the difference in mercury contents before and after heating at 105°C for 48 hours (Coufalík *et al.* 2014). In addition, the thermal stability of mercury in samples from Brandy Bay was also studied. Samples were heated in an oven from 50–250°C, with the temperature increasing in steps of 50°C over 2 hours. The determination of mercury content in the samples was performed at each temperature step.

In addition, the organic carbon content in samples from Brandy Bay was determined after the previous removal of carbonates by HCl. Measurements were performed on a Vario TOC Cube Analyzer (Germany).
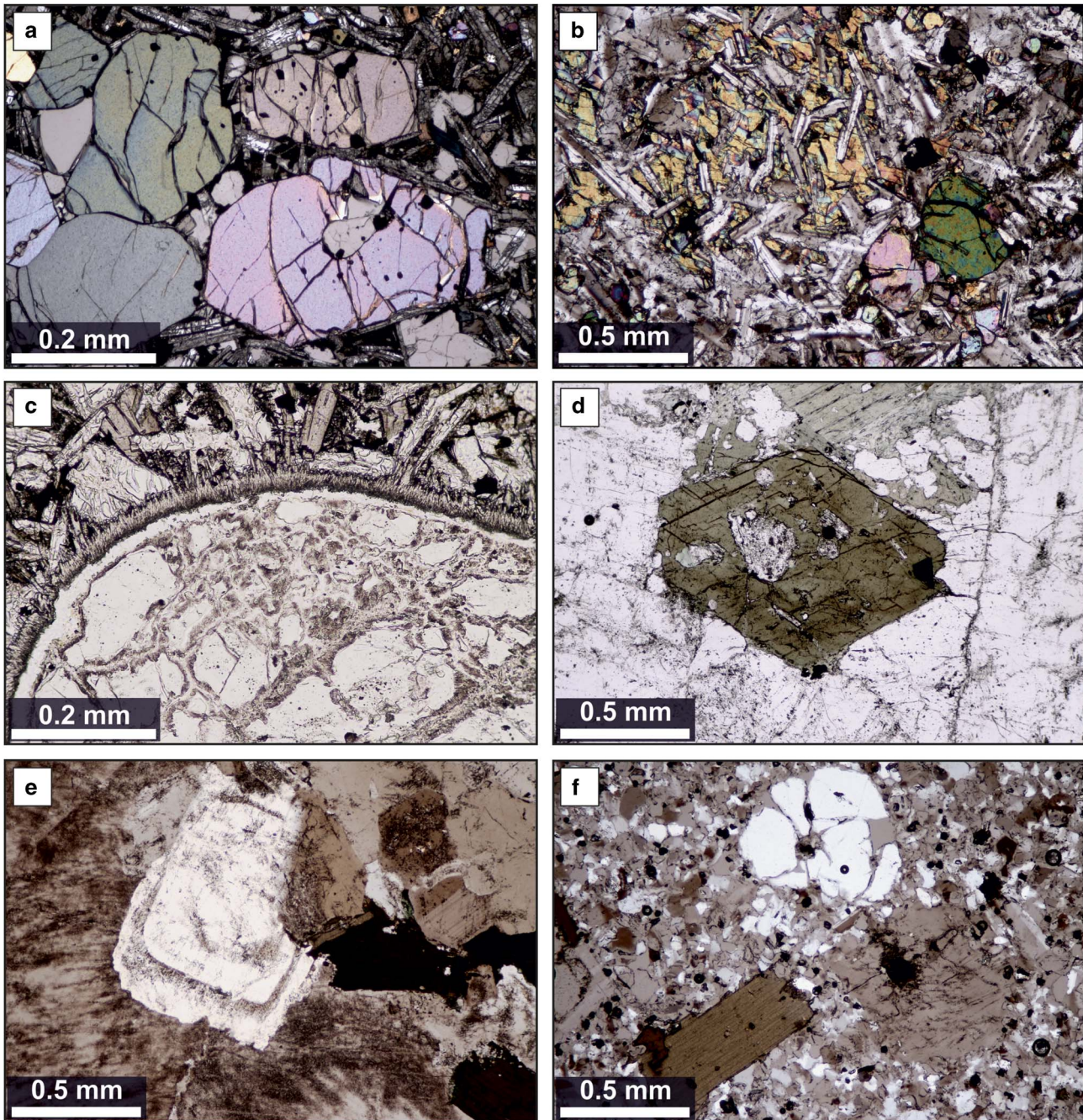
Fig. 2. Photomicrographs of the analysed rocks. **a**. Glomeroporphyritic olivine containing euhedral Cr-spinel (B2r, hawaiite, Bibby Hill; crossed polars). **b**. Plagioclase laths enclosed in anhedral clinopyroxene (BH-MF5r, platy basalt flow above the Mendel Formation; crossed polars). **c**. Reaction rim around quartz xenolith (B2r; parallel polars). **d**. Amphibole from mafic enclave in granite (BH-MF6r_b, pebble from the Mendel Formation; parallel polars). **e**. Plagioclase with compositionally different zones highlighted by selective sericitization (BH-MF6r_d, granite pebble from the Mendel Formation; crossed polars). **f**. Quartz, feldspar and biotite in a felsic fine-grained matrix (BH-MF6r_c, pebble of porphyric microgranite newly identified from the Mendel Formation; crossed polars).

Results

Petrography of the parent rocks

The bedrock of most of the transects is represented by alkaline olivine basalts and dolerites of the James Ross Island Volcanic Group. The sampled sites covered products with textural features of both subaerial and subaqueous volcanic activity. Among the primary minerals, volcanites contain phenocrysts of euhedral olivine, occurring as individual crystals and as glomeroporphyritic aggregates (Fig. 2a). Olivine crystals contain inclusions of spinel group minerals. Olivine is

Table II. Total mercury content in rock samples in µg kg^{-1}.

James Ross Island Sample		Greenland Sample	
BH-MF2r	1.9	DIK01	3.2
BH-MF5r	8.0	DIK05B	1.3
BH-MF6r a	4.0	DIK05C	1.7
BH-MF6r b	1.8	DIK06	3.8
BH-MF6r c	2.9	DIK07	1.5
BH-MF6r d	0.7	DIK08	1.1
B1r	1.6	DIK09	2.0
B2r	2.6		
Lr	8.0		
LCr	3.4		
DDr	2.8		

Table III. Total mercury content in regolith in µg kg^{-1}.

Sample	Type 1	Type 2	Sample	Type 1	Type 2
CC1	4.5		BB1	7.6	7.2
CC2	9.8		BB2	8.3	5.3
CC3	8.2		BB3	9.4	9.1
CC4	4.7		BB4	7.9	6.3
CC5	5.0		BB5	7.3	7.2
CC6	4.9		BB6	8.3	5.5
CC7	5.4		BB7	10.3	4.3
AS1		7.8	BB8	11.0	5.2
AS2		7.6	SV1	3.8	6.3
AS3		5.5	SV2	3.0	4.6
BH-MF1	5.5		SV3	5.6	5.2
BH-MF2	11.3		SV4	4.1	
BH-MF3	5.6		SV5		4.2
BH-MF4	5.6		SV6	3.6	4.5
BH-MF5	6.7		SV7	2.7	3.8
BH-MF6	5.6				
PP1	8.0				
PP2	5.1				
PP3	7.2				
PP4	5.4				
PP5	8.4				
PP6	3.1				
PP7	4.3				

also present in the matrix, where it is accompanied by laths of plagioclase with ophitic to trachytic arrangements. Plagioclase crystals can be enclosed in subhedral to anhedral clinopyroxene (Fig. 2b). Additionally, a variable amount of glass can also be found in quickly chilled samples. The majority of accessory minerals are formed by magnetite and ilmenite. Secondary minerals include alteration products of olivine, zeolite group minerals in amygdules, and the palagonitic alteration of glass in hyaloclastic breccias. A characteristic textural feature of the studied basalts is the presence of xenoliths from underlying Cretaceous sediments of the James Ross Basin (Fig. 2c).

The broad petrographical variability of the bedrock of James Ross Island is represented by the erratic fraction of Mendel Formation sediments (Berry Hill–Mendel Formation transect). Among the prevalent basaltic lavas and tephra of local origin, there are also present gravel-to-boulder clasts of magmatic (granitoids, diorites and gabbros) and metamorphic (cherts, phyllites, biotite gneisses, orthogneisses and amphibolites) rocks with a presumed origin from the Antarctic Peninsula Batholith and the surrounding crystalline basement. Various types of medium-grain granites (both porphyric and epigranular) are the most abundant. Granites exhibit textures of interaction with basic melt demonstrated by the presence of abundant mafic microgranular enclaves of dioritic composition rich in green amphibole and biotite (Fig. 2d). Even granites without visible mafic microgranular enclaves show evidence of magma mixing, as they contain feldspar crystals with

Table IV. Content of mercury forms in samples from Brandy Bay in µg kg^{-1}.

Sample	Organic carbon (%)	Sequential extraction				Thermal desorption
		Mobile Hg	Organic bound Hg	Hg^0	Residual Hg	Hg^0
BB1$_{type1}$	0.45	1.7	2.8	2.7	0.4	2.7
BB1$_{type2}$	0.41	1.9	1.7	3.3	0.3	1.8
BB2$_{type1}$	0.31	2.4	3.3	2.2	0.4	2.4
BB2$_{type2}$	0.28	1.8	1.3	1.9	0.3	0.9
BB3$_{type1}$	0.31	5.1	1.8	2.0	0.5	1.7
BB3$_{type2}$	0.21	4.4	0.7	2.8	1.2	2.5
BB4$_{type1}$	0.45	2.2	3.1	2.1	0.5	1.8
BB4$_{type2}$	1.24	1.4	3.0	1.5	0.4	1.2
BB5$_{type1}$	0.24	3.6	1.5	1.6	0.6	1.1
BB5$_{type2}$	0.49	2.2	3.0	1.6	0.4	1.5
BB6$_{type1}$	0.32	4.9	0.7	2.2	0.5	1.4
BB6$_{type2}$	0.30	3.1	0.4	1.6	0.4	1.2
BB7$_{type1}$	0.38	6.3	0.6	3.0	0.4	1.9
BB7$_{type2}$	0.23	2.1	–	1.9	0.3	1.6
BB8$_{type1}$	0.60	4.4	4.3	1.6	0.7	1.7
BB8$_{type2}$	0.22	1.4	2.1	1.2	0.5	1.1

– = below the limit of quantification.
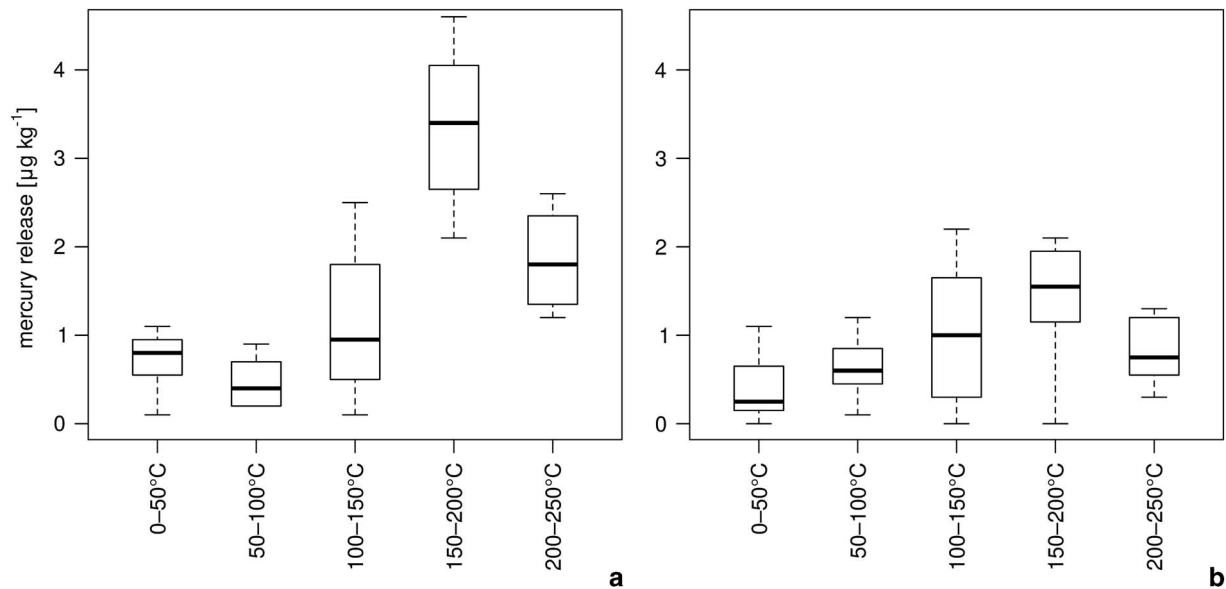
Fig. 3. Release of mercury from samples from Brandy Bay. **a.** Type 1. **b.** Type 2.

rounded zones resembling those grown under magma-mixing conditions. Growing zones are highlighted by selective alteration (Fig. 2e). Dyke equivalents of granites–porphyric microgranites, which are characterized by phenocryst of quartz, alkaline feldspars and biotite (Fig. 2f), were newly recognized within the Mendel Formation.

Total mercury contents

The studied samples of regolith and bedrock from James Ross Island cover various petrographical types. Therefore, the relatively low range of total mercury content (0.7–11.3 μg kg^{-1}) was unexpected (Table II and Table III). The relative standard deviation (RSD) of the determination was within 3% for all samples.

The determined concentrations of total mercury in rock samples from James Ross Island and Greenland are presented in Table II. While the results obtained for granites and microgranites of the Mendel Formation (0.7–4.0 μg kg^{-1}) were in the expected range, the very low mercury content found in the alkaline volcanites (1.6–8.0 μg kg^{-1}) were quite unexpected. The results obtained for mineralogically and texturally similar basaltic lavas from Greenland were also in the low range (1.1–3.8 μg kg^{-1}). Since volcanites in polar regions are not strongly affected by chemical weathering, these results can be considered as reliable and significant.

Fractionation analysis and thermal desorption

Fractionation analysis was performed on samples with the highest mercury content, i.e. those from the transect in Brandy Bay. Results of the determination of individual mercury forms together with organic carbon content

are presented in Table IV. Elemental mercury was determined using both sequential extraction and thermal desorption. The RSD of the determination was up to 8% for all mercury forms. The decrease in mercury content in samples from Brandy Bay with increasing temperature (in steps) for both regolith types is presented in Fig. 3.

Discussion

Total mercury content

The results of older studies (cf. Fleischer 1970, Dissanayake & Vincent 1975) were not confirmed. Similarly, Zintwana *et al.* (2012) found significantly lower mercury concentrations for the Skaergaard Intrusion than in previous measurements, and the authors found no evidence of mercury enrichment in plagioclase-rich igneous rocks, as was reported previously. Zintwana *et al.* (2012) attributed this difference to the inaccurate analytical methodology of early measurements.

Rudnick & Gao (2003) published the following mercury contents in the Earth's crust: 50 μg kg^{-1} for the upper continental crust, 8 μg kg^{-1} for the middle continental crust and 6 μg kg^{-1} for the lower continental crust. The mercury content in the primitive mantle is estimated to be 6 μg kg^{-1} (Palme & O'Neill 2003). Nevertheless, it seems that these estimates are being reduced with increasing data. The relatively high range of mercury content determined for basalts from James Ross Island in comparison with Greenland samples is probably the result of contamination of basaltic melt by crustal material. Numerous findings of xenoliths from the underlying Cretaceous sedimentary rocks represent evidence of this contamination. The influence of

sediments on the composition of lavas on James Ross Island is also recorded in the Li isotope system (Košler *et al.* 2009). The homogeneous distribution of mercury in the primitive mantle cannot be expected. Thus, mercury content in the primitive mantle could even be lower.

Concentrations of total mercury in regolith samples from all transects are presented in Table III. The transects were designed to run through the geological layers along with the change in altitude. A trend of mercury accumulation with a drop in altitude or a significantly higher concentration in some localities was not observed. The determined concentrations were relatively low in relation to published data. The lowest mercury content (0.5 µg kg^{-1}) was determined in sediments from Deception Island, outside fumaroles (De Ferro *et al.* 2014). Higher mercury concentrations were found in other parts of Antarctica, mostly up to 100 µg kg^{-1} (Bargagli *et al.* 1993, 1998, 2005, Nie *et al.* 2012), compared to those found for James Ross Island (this study).

The total mercury content in samples may be considerably affected by speciation. Mobile mercury forms are subjected to the influence of external conditions, i.e. leaching from particles of weathered material; thus, the mercury content in geological layers increases at lower elevations. The secondary enrichment of material by mobile forms is noticeable in the case of samples from Solorina Valley (type 2). However, this form of enrichment caused by mercury transport via surface water cannot be compared to the effect of bio-vectors such as penguins or seals (Nie *et al.* 2012).

The calculated baseline concentration of mercury (without an anthropogenic contribution) on King George Island (South Shetland Islands) is 13 µg kg^{-1} (Lu *et al.* 2012). Mercury content in rock and regolith samples did not differ significantly. The determined concentrations in James Ross Island could be considered as a background in this part of Antarctica. Nevertheless, the possible contamination of the area by long-range transport is not excluded. Mercury deposition from the atmosphere may not be evident in these inorganic samples.

Fractionation analysis and thermal desorption

Determination of the mobility (i.e. bioavailability) and thermal stability (i.e. inclination towards re-emission) of mercury in material is essential for the assessment of mercury fate in the Antarctic environment. A proportion of mercury releasable in water exhibits a considerable variability depending on the location. It may be caused by the adsorption of ions onto particles after the evaporation of meltwater (Bargagli *et al.* 2007). In this case, the first extraction step also consisted of mercury bound to alkaline components of the material. The content of mobile mercury varied between 23–61% of the total

content in samples. Mercury in surface soil is mostly bound to organic matter or clay (Bargagli *et al.* 2005). In general, the content of organic material in Antarctic soils and sediments is very low (Campbell & Claridge 1987), as can be seen here (Table IV). A soil poor in carbon may have an excess of metal with respect to the number of bonding groups in organic material, which increases the soluble fraction (Bargagli *et al.* 2007). Mercury bound to organic matter formed up to 53% of total mercury content. This is probably the result of strong interactions between mercury and organic matter, even if the mercury content did not correlate with the content of organic carbon (Bargagli *et al.* 1998). A direct correlation of mercury levels with carbon was confirmed for samples with higher carbon content (Bargagli *et al.* 1993) or in the case of ornithogenic sediments (Nie *et al.* 2012). Elemental mercury constituted 15–47% of the mercury in samples. Residual mercury formed 4–14%; this fraction consists of insoluble and immobile mercury forms, such as mercury sulfide.

The results of Hg$^{(0)}$ determination obtained by thermal desorption and sequential extraction evinced a sufficient degree of conformity in relation to low concentrations. The values determined thermally were equal to or lower than the concentrations determined by the extraction. A difference of at least 1 µg kg^{-1} was observed for the BB1 and BB2 samples (type 2) and for the BB7 sample (type 1). Thus, the extraction of amalgams or complex compounds together with elemental mercury could be expected for these samples in this extraction step.

Mercury, which condenses in areas with a cold climate, tends to have low thermal stability (Martínez-Cortizas *et al.* 1999). Mercury re-emission from the surface depends on the intensity of metal interaction with the matrix, the surface of the particles and the thermal stability of the mercury species contained. Thermal stability may also be enhanced by adsorption to internal surfaces of the particles (Coufalík *et al.* 2014).

Significant mercury release was not observed up to 50°C, which may be the result of the relatively high temperature of the deglaciated surface of James Ross Island during sunny days in the summer period. The proportion of mercury with low thermal stability (up to 100°C) was lower than that of thermally determined Hg$^{(0)}$. Thus, a portion of elemental mercury is not free and is adsorbed in pores of the particles. The highest mercury release was observed between 150 and 200°C; the mercury released here was the divalent form, which is not bound to organic matter. The remaining content after the heating of samples to 250°C can be defined as thermally stable mercury. This proportion was always higher for type 2 than for type 1 and formed up to 43% of the total content. The content of residual mercury (Table IV) was very low. For this reason, thermally stable mercury was not comprised only of mercury sulfide but also contained

other divalent mercury forms, such as the mercury bound to organic matter (Coufalík *et al.* 2014).

Based on the results obtained, the following mercury cycle in the Antarctic Peninsula region could be expected. Low mercury concentrations which are released from the bedrock by weathering processes represent the background. The input of additional mercury from the atmosphere is probable, which may increase the amount of mobile divalent mercury in the ecosystem. A proportion of deposited mercury is subjected to re-emission. Transport and adsorption occur at temperatures above 0°C. Generally, the content of organic matter and mineral particles in regolith is very low. Thus, insignificant capture by particles of material poor in carbon occurs and a substantial portion of the mercury migrates. For this reason, there is no obvious contamination in inorganic components of the environment. Mercury can accumulate by adsorption to the finest particles (e.g. in lakes) or flow out into the sea. The degree of contamination of the environment in this area cannot be determined on the basis of the analysis of inorganic samples. The solution may consist of the analysis of living organisms. To assess Hg^0 input from the atmosphere, the analysis of lichens can be suggested; the analysis of cyanobacterial coatings could be proposed to evaluate the extent of mercury accumulation in the aquatic environment.

Conclusion

Mercury content in basaltic lavas is significantly lower than previously considered, which indicates a very low mercury concentration in the peridotitic mantle source. Background concentrations of mercury in regolith in Antarctica are dependent mainly on the concentrations in parent rocks, especially because of the low retention capacity of weathered material with a low content of organic matter and particles with a large surface. It seems that mercury deposition from the atmosphere occurs in the region of the Antarctic Peninsula. However, its extent cannot be evaluated on the basis of the analysis of inorganic samples.

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