Sources and cycling of mercury in the paleo Arctic Ocean from Hg stable isotope variations in Eocene and Quaternary sediments

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Abstract

Mercury stable isotopic compositions were determined for marine sediments from eight locations in the Arctic Ocean Basin. Mass dependent fractionation (MDF) and mass independent fractionation (MIF) of Hg stable isotopes were recorded across a variety of depositional environments, water depths, and stratigraphic ages. $\delta^{202}\text{Hg}$ (MDF) ranges from -2.34‰ to -0.78‰; $\Delta^{199}\text{Hg}$ (MIF) from -0.18‰ to +0.12‰; and $\Delta^{201}\text{Hg}$ (MIF) from -0.29‰ to +0.05‰ for the complete data set (n = 33). Holocene sediments from the Chukchi Sea and Morris Jesup Rise record the most negative $\Delta^{199}\text{Hg}$ values, while Pleistocene sediments from the Central Arctic Ocean record the most positive $\Delta^{199}\text{Hg}$ values. The most negative $\delta^{202}\text{Hg}$ values are recorded in Pleistocene sediments. Eocene sediments (Lomonosov Ridge) show some overlap in their Hg isotopic compositions with Quaternary sediments, with a sample of the Arctic Ocean PETM (56 Ma) most closely matching the average Hg isotopic composition of Holocene Arctic marine sediments. Collectively, these data support a terrestrially-dominated Hg source input for Arctic Ocean sediment through time, although other sources, as well as influences of sea ice, atmospheric mercury depletion events (AMDE), and anthropogenic Hg (in core top samples) on Hg isotopic signatures must also be considered.

1. Introduction

Atmospheric deposition is a major source of mercury to the world's oceans including the Arctic Ocean (Fitzgerald et al., 2007; AMAP Assessment, 2011). It has been estimated that ~100 metric tonnes of Hg are added annually to the Arctic Ocean via atmospheric deposition, accounting for approximately half of its total modern Hg input (Douglas et al., 2012). Arctic rivers also deliver a disproportionately and increasingly large flux of Hg to the Arctic Ocean, albeit with large uncertainties regarding flux values (Outridge et al., 2008; Fisher et al., 2012; Emmerton et al., 2013; Soerensen et al., 2016). Recent studies have suggested that warming trends in the Arctic region will accelerate the release of Hg that is normally sequestered in ancient terrestrial permafrost organic matter reservoirs, thus returning more of this 'old' Hg into global circulation via enhanced Arctic river discharge (e.g., Rydberg et al., 2010; Stern et al., 2012). For example, Fisher et al. (2012) found that modern evasion rates of Hg from the surface Arctic Ocean are consistent with enhanced summer melting of active layers in Arctic permafrost and greater seasonal discharge via rivers to the Arctic Ocean of organically-bound Hg. This terrestrially-derived riverine mercury exists mainly as inorganic Hg(II) complexes which are rapidly converted to Hg(0), or gaseous elemental mercury (GEM), for release back into the global atmospheric pool once it reaches the ocean (e.g., Mason et al., 1994; Mason and Sheu, 2002; Fitzgerald et al., 2007). Thus the ongoing debate, regarding whether polar regions are in fact net global sinks for atmospheric mercury (e.g., Ariya et al., 2004; Jitaru et al., 2009; Fisher et al., 2013; Dastoor and Durnford, 2014; Zhang et al., 2015; Soerensen et al., 2016), is far from being resolved.

Because pre-anthropogenic Hg in Arctic terrestrial reservoirs is closely tied to organic matter reservoirs that are now undergoing rapid change (e.g., Cory et al., 2013), considerable

interest has begun to focus on the Arctic Hg cycle with respect to polar warming, with obvious implications of polar amplification for global biogeochemical cycling of Hg in the environment (e.g., Stern et al., 2012; Walsh, 2014). The mercury cycle in the modern Arctic environment is strongly impacted by seasonal atmospheric mercury depletion events (AMDEs; e.g., Schroeder et al., 1998; Lindberg et al., 2002; Douglas et al., 2005, 2008), which are closely linked to the seasonal cycle of polar sunrise and variations in sea ice cover. During springtime AMDEs, tropospheric Hg(0) becomes photo-chemically oxidized to Hg(II) in the presence of seawater-derived halogens (e.g., bromine) in the Arctic environment and deposited to icy surfaces in high concentrations (e.g., Douglas et al., 2012). Recognition of this process has revealed that high rates of Hg bioaccumulation in Arctic marine foodwebs could be linked to increased global atmospheric fluxes of anthropogenic Hg to the Arctic (Fitzgerald et al., 2007; Outridge et al., 2008; Kirk et al., 2012). Documentation of paleo-AMDE records is, however, lacking. With recent advances in high-precision Hg isotope ratio analysis (e.g., Bergquist and Blum, 2007; Blum, 2011; Hintelmann et al., 2012; Sonke and Blum, 2013; Wiederhold, 2015), it is now known that some of the largest photo-chemically induced fractionations in Hg isotopes are associated specifically with Arctic AMDE (Sherman et al., 2010, 2012), providing a new and potentially powerful technique for tracing Hg pathways in the Arctic environment. The objectives of this study were to investigate pre-anthropogenic Hg isotopic variations in the Arctic Ocean as recorders of Hg sources and cycling unique to the Arctic (e.g., AMDE and sea ice variations, riverine discharge etc.) using marine sediment cores.

2. Isotope geochemistry of Hg in the marine environment

The dominant species of Hg in the oceans is inorganic, oxidized Hg(II) which is mainly scavenged by particles in the water column en-route to the seafloor, or else reduced to Hg(0) in

the ocean mixed layer and evaded back to the atmosphere as gaseous elemental mercury (Mason and Sheu, 2002). Mercury is particle-reactive in the marine environment and also redox-sensitive, where it can be expected to follow trends for other metals that show strong redox behavior in marine sediments (Gehrke et al., 2009; Gobeil et al., 1999). Because Hg is rapidly exported from the surface mixed layer in open ocean settings (where the majority of ocean-atmospheric exchange occurs), Hg has short residence times, estimated to be on the order of ~10 years in the polar mixed layer of the Arctic Ocean (AMAP Assessment, 2011; Soerensen et al., 2016). Inorganic Hg(II) is the dominant Hg species found in marine sediments, and has been demonstrated to be the form of mercury dominating the total Hg pool for Arctic marine sediments (e.g., Fox et al., 2013; Soerensen et al., 2016).

Organic Hg (i.e., monomethyl-Hg; MMHg) is also produced in the oceans from inorganic Hg (Lehnher et al., 2011); this conversion occurs within the water column down to at least the oxygen minimum zone (Kirk et al., 2012; Blum et al., 2013; Fitzgerald and Lamborg, 2014; Heimbürger et al., 2015). Hg de-methylation reactions are observed in the marine environment, occurring primarily in the presence of sunlight, thus adding to the complex behavior of Hg in the oceans (AMAP Assessment, 2011). Photo-demethylation reactions involving Hg in the oceans can result in distinctive positive mass independent fractionation (MIF) in the isotopic composition of methyl-mercury, as demonstrated by measurements on fish and other marine organisms (Bergquist and Blum, 2007; 2009). These isotopic fractionations are interpreted as a signature of prior photo-degradation of a portion of the MMHg pool in the water column (e.g., Point et al., 2011; Day et al, 2012; Blum et al., 2013). Experimental results have demonstrated that photochemistry is the main driver of MIF of odd-mass Hg isotopes, primarily via the magnetic isotope effect (Bergquist and Blum, 2007; 2009; Sonke, 2011; Blum, 2011). MIF of Hg

isotopes, defined as the per mil (‰) difference relative to a standard, is expressed using cap delta notation (e.g., $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$) for measured Hg isotope ratios (see the Electronic Annex – EA, for full explanation). Large MIF effects in Hg isotopes (e.g., $\Delta^{199}\text{Hg} = -5\text{‰}$) have also been linked to inorganic Hg(II) reactions associated with AMDEs in the Arctic environment (Sherman et al., 2010, 2012). Mass dependent fractionation (MDF) of Hg stable isotopes is reported using the standard delta notation ($\delta^{202}\text{Hg}$), and occurs via a variety of mechanisms including biochemical, photochemical (abiotic), and dark (abiotic) reactions (e.g., Blum, 2012; Sonke and Blum, 2013; Wiederhold, 2015), resulting in a natural range of $\delta^{202}\text{Hg}$ values of several permil (‰) for environmental samples (Blum et al., 2014).

3. Study area

The Arctic Ocean (**Fig. 1**) is unique among modern ocean basins in its high percentage of year-round ice cover. The proportion of multi-year sea ice, along with summertime sea ice cover, has diminished dramatically over the past few decades (Polyak and Jakobsson et al., 2011), yet recent trends in ice loss are nevertheless thought to be comparable to early Holocene rates of ice loss for the Arctic Ocean (Cronin et al., 2010; Poirer et al, 2012; Jakobsson et al., 2012). Ice shelves likely extended across much of the Central Arctic Ocean during the last glacial maximum (LGM) and earlier glacial maxima, as indicated by ice scour depths down to 1000 meters (Polyak et al., 2001, 2010; Jakobsson et al., 2012, 2014). Because much of the Arctic Ocean is underlain by shallow continental shelves, sea-level drawdown during Pleistocene low-stands significantly reduced the size of the Arctic Ocean (Jakobsson, 2002; Stein and MacDonald, 2004; Darby et al., 2006; Polyak et al., 2010; Jakobsson et al., 2014). During the LGM, the Arctic Ocean was thus a substantially smaller ocean, capped with very thick ice, and exchanging with external oceans only via the deep water Fram Strait connection into the North

Atlantic (Polyak and Jakobsson, 2011). Despite its relative isolation from other oceans, strong surface salinity stratification, and historically large ice-age swings in size/volume and ice-cover, the Quaternary Arctic Ocean is nevertheless considered by most to have been a continuously well-mixed, well-ventilated ocean (Darby, 2008; Haley et al., 2008; Cronin et al., 2010; Polyak and Jakobsson, 2011).

Major Arctic rivers (e.g., Lena, Ob, Yenisei, etc.) deliver a large seasonal sediment flux of pelagic, hemipelagic, turbidite, drift and proglacial marine deposits to various shelf, slope and rise depositional environments in the Arctic Ocean (Backman et al., 2004; Stein, 2008; Darby et al., 2009; Polyak and Jakobsson, 2011). Quaternary pelagic deposits of the Central Arctic Ocean basin are dominated by fine-grained detrital muds and silts, with minor detrital carbonate content and variable amounts of ice-rafted debris, mostly deposited under oxidizing marine conditions (Jakobsson et al., 2007). These sediments are characterized by Quaternary glacial-interglacial depositional cycles with distinct compositional banding (Alexanderson et al., 2014). Jakobsson et al. (2000) correlated these cycles with the Global Marine Oxygen Isotope (MIS) record, providing a modern framework for regional stratigraphic correlation and quantification of Quaternary sedimentation rates in the Arctic Ocean (Jakobsson et al., 2000, 2001, 2003; Backman et al., 2004). Pelagic sedimentation rates in the Central Arctic Ocean are estimated at $>1\text{ cm ka}^{-1}$ for Pleistocene inter-glacials, with rates decreasing significantly (i.e, by an order of magnitude) during glacial intervals (Backman et al., 2004; Spielhagen et al., 2004; Jakobsson et al., 2000, 2001).

Eocene sediments recovered by IODP EXPEDITION 302 at Lomonosov Ridge (**Fig. 1**) in the Central Arctic Ocean Basin consist mainly of organic-rich silts and clays containing sulfidic and phosphatic components, including abundant fish debris (Stein et al., 2006; Moore et

al., 2006; Backman and Moran, 2009; Stickley et al, 2009, 2012; Gleason et al., 2009; Waddell et al., 2008). These sediments were deposited under highly reducing (anoxic/euxinic) conditions (Stein et al., 2006; Moore et al., 2006; Backman and Moran, 2009; Stickley et al, 2009, 2012; Gleason et al., 2009; Waddell et al., 2008). Paleoceanographic and paleoenvironmental reconstructions for the early/middle Eocene Arctic Ocean indicate significantly higher annual sea surface temperatures (SST) than today's (Brinkhuis et al., 2006), and a highly stratified water column with respect to both salinity and dissolved oxygen content. The ubiquitous presence of the distinctive Eocene freshwater fern *Azolla* is an indication that episodically fresh-water/brackish surface waters were a characteristic of the early-middle Eocene Arctic Ocean (Moran et al., 2006; Brinkhuis et al., 2006). Consensus has recently emerged that the Arctic Ocean was permanently ice-free prior to ~44 Ma, as indicated by the first appearance of ice rafted debris (IRD) at that time (Brinkhuis et al., 2006; Moran et al., 2006; Stickley et al, 2008; Darby, 2014). The 56 Ma PETM (*Apectodinium augustum*) interval recovered from Lomonosov Ridge represents a highly restricted paleoceanographic setting; evidence suggests it was deposited in a shallow, rapidly subsiding marginal marine basin close to 90° N paleo-latitude (Moran et al., 2006; Moore et al., 2006; Sluijs et al., 2006, 2008). A subtropical-like environment for the Arctic Ocean PETM is indicated by paleo sea surface temperature (SST) estimates (Sluijs et al., 2006, 2008; Pagani et al., 2006).

4. Arctic Ocean sediment cores used in this study

We obtained samples from sediment cores collected at eight different locations across the Arctic Ocean basin (**Fig. 1**). These include Holocene-age multi-core surface samples (HOTRAX Expedition - Darby et al., 2005; LOMROG Expedition – Jakobsson et al., 2007), Holocene and Pleistocene-age piston core samples (HOTRAX, LOMROG, Oden 96/12), and Eocene-age drill-

core samples from Lomonosov Ridge in the Central Arctic Ocean (IODP Expedition 302; Backman et al., 2006; Stein et al, 2014). Areas of the Arctic Ocean Basin sampled for Quaternary-age sediment include core locations along Lomonosov Ridge in the Central Arctic Ocean (**Fig. 1**) and other sites at various water depths along the Chukchi Margin, Mendeleev Ridge, Yermak Plateau (HOTRAX Expedition; Darby, Polyak and Jakobsson, 2009), and Morris Jesup Rise (LOMROG Expedition; Jakobsson et al., 2008). Late Quaternary piston and multi-core samples from Lomonosov Ridge (LOMROG and HOTRAX expeditions) were also obtained along with samples from the Quaternary piston core 1PC-96/12, which is a key reference core for the revised MIS-based Quaternary stratigraphy of the Central Arctic Ocean Basin (Jakobsson et al., 2000; Backman et al, 2004; Löwemark et al., 2008; 2014; Frank et al., 2008). More details of sedimentation rates, sediment lithology and age constraints can be found in Table 1 and the aforementioned papers.

5. Analytical Methods

A more complete description of the analytical methods employed in this study can be found in the Electronic Annex (EA). Mercury isotopic analysis was performed at the University of Michigan using continuous flow cold vapor generation on a Nu Instruments (Wrexham, North Wales) MC-ICP-MS (Bergquist and Blum, 2007). All samples underwent combustion/thermal decomposition, pre-concentration and purging/purification prior to Hg isotopic analysis (Biswas et al., 2008a; Lefticariu et al., 2011). Hg isotope ratios are reported using standard delta notation referenced to the NIST SRM-3133 Hg standard (Blum and Bergquist, 2007). Variations in $^{202}\text{Hg}/^{198}\text{Hg}$ ratios are reported as $\delta^{202}\text{Hg}$ (‰) for describing mass dependent fractionation (MDF) of Hg isotopes. Cap delta notation (e.g., $\Delta^{199}\text{Hg}$) is employed here to describe mass independent fractionation (MIF). For odd-numbered isotopes (^{199}Hg and ^{201}Hg), this is the

deviation from predicted $\delta^{199}\text{Hg}$ and $\delta^{201}\text{Hg}$ values based on kinetic mass-dependent fractionation law, expressed in permil units ‰ (see Bergquist and Blum, 2007). Long-term external reproducibility of Hg isotopic compositions, based on repeat analysis of the in-house Hg isotopic standard UM-Almaden (Blum and Bergquist, 2007), is $\delta^{202}\text{Hg} = -0.57\text{‰} \pm 0.10\text{‰}$ (2SD), $\Delta^{201}\text{Hg} = -0.04\text{‰} \pm 0.07\text{‰}$ (2SD), and $\Delta^{199}\text{Hg} = -0.02\text{‰} \pm 0.08\text{‰}$ (2SD). The commonly employed MESS-3 certified reference material (Beaufort Sea pelagic sediment certified at 91 ng/g Hg; NRC Canada) was processed and measured at Michigan in parallel with Arctic sediments, and yielded a mean $\delta^{202}\text{Hg}$ of $-1.90\text{‰} \pm 0.10\text{‰}$ (2SD), $\Delta^{201}\text{Hg} = -0.04\text{‰} \pm 0.05\text{‰}$ (2SD) and $\Delta^{199}\text{Hg} = 0.01\text{‰} \pm 0.05\text{‰}$ (2SD). Average recoveries (total Hg processing yields) were 92% for MESS-3 CRM and 89% for Arctic sediments. Our reported analytical uncertainty in Hg isotopic ratios is based on the long-term (2SD) reproducibility for the MESS-3 CRM (Electronic Annex - EA).

6. Results

Hg concentrations and isotope ratios were obtained for Arctic Ocean sediments ($n = 33$) having stratigraphic ages spanning 56 Ma to the present. The total range of measured Hg concentrations varies from < 5 ng/g up to 170 ng/g. $\delta^{202}\text{Hg}$ values range from -2.34‰ to -0.78‰, $\Delta^{199}\text{Hg}$ from -0.18‰ to +0.12‰, and $\Delta^{201}\text{Hg}$ from -0.29‰ to +0.05‰ (**Table 1**). Hg abundance and isotopic variations are described below for Holocene, Pleistocene, and Eocene/PETM samples, respectively.

6.1 Holocene sediments

$\delta^{202}\text{Hg}$ values for Holocene Arctic marine sediments range from -1.77‰ to -1.06‰ (average $\delta^{202}\text{Hg} = -1.38\text{‰} \pm 0.22\text{‰}$ 1SD population; $n = 17$). Mass independent fractionation of Hg isotopes was observed in several Holocene samples (**Table 1**), which show a total range in

$\Delta^{199}\text{Hg}$ values of -0.18‰ to 0.04‰ (average $\Delta^{199}\text{Hg} = -0.05‰ \pm 0.06‰$ 1SD population; n = 17). The average bulk sediment (dry weight) Hg concentration we measured in Holocene sediments was 62 ng/g (± 32 1SD population; n = 17), with a total range of ~30 ng/g to ~120 ng/g. Holocene core top surface sediments sampled from 9 different core tops (representing 8 separate locations in the Arctic Ocean) are similar to the Holocene average (**Fig. 1; Table 1**). $\Delta^{199}\text{Hg}$ values in these core top samples range from -0.18‰ to 0.01‰ (average $\Delta^{199}\text{Hg} = -0.07‰ \pm 0.06‰$ 1SD population; n = 9). $\delta^{202}\text{Hg}$ values for the Holocene surface samples range from -1.58‰ to -1.06‰ (average $\delta^{202}\text{Hg} = -1.24‰ \pm 0.18‰$ 1SD population; n = 9). Although $\Delta^{199}\text{Hg}$ and $\delta^{202}\text{Hg}$ variations in this small (n = 9) sample subset show no clear correlation with ocean water depth or seafloor location (**Fig. 2**), four of the core top samples (two from Chukchi Sea and two from Morris Jesup Rise) have $\Delta^{199}\text{Hg}$ values that are significantly fractionated for MIF relative to the NIST3133 Hg isotopic standard (**Table 1**). Hg abundances measured in core top samples range from 31 ng/g to 120 ng/g with an average value of 63 ng/g (± 34 ng/g 1SD population; n = 9). These Hg abundances are similar to those previously reported in the literature for Arctic Ocean core top Holocene-age sediments (Gobeil et al, 1999).

6.2 Pleistocene sediments

$\delta^{202}\text{Hg}$ values for Pleistocene Arctic marine sediments range from -2.34‰ to -1.37‰ (average $\delta^{202}\text{Hg} = -1.94‰ \pm 0.29‰$ 1SD population; n = 7), and include the most negative $\delta^{202}\text{Hg}$ values that we measured for Arctic sediments (**Table 1**). Pleistocene Arctic sediments also show MIF of Hg isotopes, with $\Delta^{199}\text{Hg}$ values that range from -0.06‰ to 0.12‰ (average $\Delta^{199}\text{Hg} = 0.03‰ \pm 0.07‰$ 1SD population; n = 7). These values are slightly more positive but still overlap with Holocene $\Delta^{199}\text{Hg}$ values. Hg bulk sediment concentration measurements indicate more variability in Hg content compared to Holocene Arctic Ocean sediments. For

example, pre-Holocene Hg abundances in piston core 96/12 1pc (Lomonosov Ridge) average only ~10 ng/g total Hg at depths below 100 cm (>50 ka; **Table 2**) compared to Holocene values that average 62 ng/g.

Downcore correlations in Hg concentrations and $\delta^{202}\text{Hg}$ values are observed in several Quaternary-age sediment cores. This behavior is most pronounced in core HLY0503 18 JPC-01 (Lomonosov Ridge intrabasin; water depth 2600 m; Central Arctic Ocean). In this core, mercury concentrations decrease from 113 ng/g at the top of the core (2,690 yrs radiocarbon age; Hanslik et al., 2010) down to 27 ng/g at a depth of 25-27 cm (12,535 yrs radiocarbon age; Hanslik et al., 2010; **Fig. 3**). $\delta^{202}\text{Hg}$ values in this core appear to track Hg concentrations with depth, decreasing from -1.25‰ at the core top down to -1.97‰ at the base (**Fig. 3**). Similar, though less pronounced, downcore trends in other Quaternary cores also reveal more negative $\delta^{202}\text{Hg}$ values with increasing depth, including cores HLY0503 8 JPC-01 (Mendeleev Ridge; water depth 2792 meters), HLY0503 22 TC-01 (Yermak Plateau; water depth 798 meters), LOMROG07-TC-09 (Lomonosov Ridge; water depth 3477 meters) and PC-01 96/12 (Lomonosov Ridge; water depth 1000 meters; **Fig. 1 and Table 1**).

Six samples from the upper part of the benchmark Quaternary piston core PC-01 96/12 (Lomonosov Ridge, Central Arctic Ocean) were measured for isotopic composition (**Table 1**). $\delta^{202}\text{Hg}$ values in this core range from -2.34‰ to -1.32‰, and $\Delta^{199}\text{Hg}$ values range from -0.06‰ to +0.12‰ (**Fig. 4**). The pronounced alternations between light-colored (Mn-poor) and dark-colored (Mn-rich) bands in this core (Jakobsson et al., 2000; Löwemark et al., 2008, 2012; März et al., 2011) do not show any correspondence with either Hg abundances or Hg isotopic compositions (**Fig. 4**). Instead, both $\delta^{202}\text{Hg}$ values and Hg concentrations in PC-01 96/12 appear to decrease as a function of depth (**Fig. 4**). Bulk concentrations of metals in this core were also

obtained for (in addition to Hg) Mo, Cd, Re, U, V, Cr, Co, Ni, Cu, Zn, Fe and Mn down to 400 cm (~500 ka; **Table 2**). These data show little to no correlation between the well-documented Mn concentration banding patterns characteristic of Central Arctic Ocean pelagic sediment cores, and (non-Mn) metal abundance variations (**Table 2**; **Fig. 3**). These observations are potentially relevant to processes affecting downcore metal distributions in Quaternary sediments from the Central Arctic Ocean (e.g., Löwemark et al., 2014; März et al., 2011; Gobeil et al., 2009). Questions regarding the Mn-banding in the Central Arctic Ocean pelagic sediments, and significance for refining MIS-based glacial-interglacial Pleistocene chronologies (Jakobsson et al., 2000; Backman et al., 2004; Löwemark et al., 2014), are explored in the Discussion section.

6.3 Eocene/PETM sediments

Eight samples of early-middle Eocene organic-rich black shale recovered from IODP Expedition 302 (Lomonosov Ridge; Moran et al., 2006; Sluijs et al., 2006), and one sample of organic-rich black shale recovered from the Arctic Ocean Paleocene-Eocene Thermal Maximum (56 Ma), were analyzed for Hg concentrations and Hg isotopic compositions (**Table 1**). Hg abundances in the Eocene sediments range from 75 ng/g to 170 ng/g (average = 100 ng/g). The Hg isotope dataset for Arctic Ocean Eocene sediments reveals a narrower range of variation compared to the Quaternary sediments we measured (**Table 1**). $\delta^{202}\text{Hg}$ values range from -1.14‰ to -0.78‰ (average = $-0.98\text{‰} \pm 0.12\text{‰}$ 1SD population; $n = 8$), and $\Delta^{199}\text{Hg}$ values range from 0.08‰ to -0.08‰ (average = $0.00\text{‰} \pm 0.06\text{‰}$ 1SD population; $n = 8$). For comparison, the 2SD external reproducibility on repeat measurements of the NRC MESS-3 pelagic sediment (Beaufort Sea) reference material processed with these samples is $\pm 0.10\text{‰}$ ($\delta^{202}\text{Hg}$) and $\pm 0.06\text{‰}$ ($\Delta^{199}\text{Hg}$). One stratigraphic interval of particular interest is the early Eocene (~49 Ma) organic-rich black shale containing abundant remains of the freshwater fern *Azolla* (Brinkhuis et

al., 2006). This sample (82 ng/g Hg) has a $\delta^{202}\text{Hg}$ value of -1.04‰ and a small positive MIF anomaly ($\Delta^{199}\text{Hg} = 0.07\text{‰}$). Notably, a single analysis of the 56 Ma PETM interval (87 ng/g Hg) recovered at Lomonosov Ridge (Sluijs et al., 2006, 2008) yields a small but measureable negative MIF signature ($\Delta^{199}\text{Hg} = -0.09\text{‰}$). This sample also has a more negative $\delta^{202}\text{Hg}$ value (-1.32‰) compared to the Eocene average. We note that the Hg isotopic composition determined for the Arctic Ocean PETM ($\delta^{202}\text{Hg} = -1.32\text{‰}$; $\Delta^{199}\text{Hg} = -0.09\text{‰}$) is very similar to the Arctic Ocean Holocene sediment average ($\delta^{202}\text{Hg} = -1.38\text{‰} \pm 0.22\text{‰}$; $\Delta^{199}\text{Hg} = -0.05 \pm 0.06\text{‰}$; 1SD population; n = 17). The Hg concentrations that we determined for the Eocene/PETM samples are consistent with their relatively high organic matter content (1-5% TOC; Moran et al., 2006; **Table 1**). Quaternary sediments by contrast are lower in Hg with TOC contents < 1% (**Tables 1&2**).

7. Discussion and Interpretation

7.1 Sources of Hg to the paleo Arctic Ocean from bulk sediment Hg isotope geochemistry

$\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values for Arctic Ocean sediments (**Fig. 5**) overlap with previously published marine sediment data (pre-industrial) including mid-Pleistocene Mediterranean sapropels from the Tyrrhenian Basin (Gehrke et al., 2009), pre-anthropogenic (Holocene) sediment from the Portuguese Atlantic margin (Mil-Homens et al., 2012), and pre-anthropogenic (Holocene) sediment from the Adriatic Sea (Foucher et al., 2009). Gehrke et al. (2009) observed that Hg isotopic compositions measured in a sequence of alternating organic-rich sapropel (high Hg) and organic-poor (low-Hg) mid-Pleistocene sediments from the Mediterranean Tyrrhenian Basin were nearly invariant, perhaps a surprising result given the strong cyclicity in Hg concentrations, redox conditions and paleo-productivity recorded in this sequence. A strong relationship between total organic carbon (TOC) and Hg abundances was noted by these authors

who concluded, based on water column mass balance estimates, that inorganic Hg(II) was being removed quantitatively from seawater via particulate organic matter (POM) into sediments (Gehrke et al., 2009). The modest range in $\delta^{202}\text{Hg}$ signatures was therefore thought to be relatively independent of the magnitude of TOC and Hg depositional rates recorded in this marine environment; from this the authors concluded that the measured sapropel Hg isotopic compositions were an accurate proxy for Hg isotopic compositions of mid-Pleistocene Mediterranean seawater, as well as the sources supplying that Hg (Gehrke et al., 2009).

In the context of the Arctic Ocean sediments studied here, it is noteworthy that the mid-Pleistocene Mediterranean sapropel (Tyrrhenian Sea) Hg isotope signatures (average $\delta^{202}\text{Hg} = -0.84\text{‰} \pm 0.17\text{‰}$ 1SD; $\Delta^{199}\text{Hg} = +0.08\text{‰} \pm 0.04\text{‰}$ 1SD) measured by Gehrke et al. (2009) partly overlap Hg isotopic compositions determined for the Arctic Ocean sediment dataset (**Fig. 5**). High TOC Eocene Arctic Ocean sediments (average $\delta^{202}\text{Hg} = -0.98\text{‰} \pm 0.12\text{‰}$ 1SD; $\Delta^{199}\text{Hg} = 0.00\text{‰} \pm 0.06\text{‰}$ 1SD) show strongest overlap with Mediterranean sapropel isotopic compositions (**Fig. 5**). Pleistocene Arctic Ocean sediments (average $\delta^{202}\text{Hg} = -1.94\text{‰} \pm 0.29\text{‰}$ 1SD; $\Delta^{199}\text{Hg} = 0.03\text{‰} \pm 0.07\text{‰}$ 1SD), though they have a similar range of $\Delta^{199}\text{Hg}$ values, are significantly shifted toward more negative $\delta^{202}\text{Hg}$ values (**Fig. 5**). Holocene Arctic Ocean sediments (average $\delta^{202}\text{Hg} = -1.38\text{‰} \pm 0.22\text{‰}$ 1SD; $\Delta^{199}\text{Hg} = -0.05\text{‰} \pm 0.06\text{‰}$ 1SD) are also offset relative to Mediterranean sapropels, with a slight overlap in isotopic compositions but trending toward significantly more negative $\Delta^{199}\text{Hg}$ values (**Fig. 5**). As noted above, the Arctic PETM ($\delta^{202}\text{Hg} = -1.32\text{‰}$; $\Delta^{199}\text{Hg} = -0.09\text{‰}$) is virtually identical in its Hg isotopic composition to the average for Arctic Ocean Holocene sediment measured here ($\delta^{202}\text{Hg} = -1.38\text{‰} \pm 0.22\text{‰}$; $\Delta^{199}\text{Hg} = -0.05 \pm 0.06\text{‰}$; 1SD population; $n = 17$). In accordance with the inferences of Gehrke et al. (2009) regarding sources of Hg in Mediterranean sapropels, we propose that terrestrial

sources for Hg have had a significant influence on the Hg isotopic composition of Arctic Ocean sediments over time, though with some additional complexities unique to the Arctic environment, which we explore below.

Cenozoic Arctic Ocean sediments also show significant Hg isotopic overlap with known global terrestrial Hg pools, including: 1) hydrothermal, volcanic and other geologic sources (i.e., geogenic); 2) modern marine, lake and river sediments; 3) peatland and coal deposits; and 4) modern terrestrial foliage and vegetation (**Fig. 6**). These observations suggest collectively that terrestrial Hg source inputs to the Arctic marine environment could have been a key influence on Hg isotope signatures observed in Arctic Ocean sediments of different ages. The small but significant negative $\Delta^{199}\text{Hg}$ MIF values observed in some Arctic marine sediments match closely the isotopic signatures of many terrestrial-dominated Hg sources, including Holocene peat (Barrow, Alaska), which overlaps the Hg isotopic compositions of Arctic Ocean Holocene sediments (Biswas et al., 2008a,b) (**Fig. 6**). It is tempting from this observation alone to draw a direct connection between the terrestrial Arctic peat Hg pool and Arctic Ocean sediment Hg reservoirs; however, it is also likely that the isotopic variations observed in Arctic Ocean sediments reflect significant Hg inputs from a wider variety of sources. For example, the Cenozoic Arctic Ocean would have received direct input from atmospheric Hg via both wet and dry deposition in addition to terrestrial surface Hg discharge via Arctic rivers (e.g., Fisher et al., 2012; Douglas et al., 2012; Dastoor and Durnford, 2014; Zhang et al., 2015; Soerensen et al., 2016; Strok et al., 2015). For comparison, Blum et al. (2013) inferred Hg isotopic signatures for the mixed layer central North Pacific inorganic Hg pool to be similar to oxidized tropospheric Hg delivered directly to oceans via wet/dry deposition (see **Fig. 6**), consistent with previously inferred sources of Hg in remote open ocean settings. Direct isotopic measurements of modern

atmospheric Hg (e.g., GEM, precipitation etc.) are available (see **Fig. 6**), though with the caveat that these measurements reflect significant contributions of anthropogenic Hg (e.g., Mason et al., 1994; De Simone et al., 2016). Strok et al. (2015) concluded that Hg sources in the modern Arctic Ocean are approximately evenly distributed between terrestrial (i.e., fresh water river discharge incorporating DOM/POM-bound Hg) and direct atmospheric inputs (both wet and dry deposition), based on directly measured Hg isotopic compositions in Arctic Ocean surface waters (**Fig. 6**). Our data allow for upwards of 80% terrestrially derived Hg in Arctic Ocean sediments, which is the upper limit estimated by Strok et al. (2015) for Arctic Ocean waters based on their direct seawater measurements. In making this comparison, we do not take into account processes within the water column, or within deposited sediments, that could potentially induce further isotopic fractionation of the marine inorganic Hg pool, e.g., photoreduction/evasion from the water column, or *in situ* (i.e., post-depositional) processes that are potentially capable of inducing isotopic fractionation of Hg between sediment-bound Hg and seawater (Yin et al., 2015). Despite these uncertainties, the general conclusion that Cenozoic Arctic marine sediments contain 50-80% Hg delivered largely from terrestrial land sources via Arctic rivers is supported by known hydrologic mass balance for the Arctic region, and consistent with the strongly particle-reactive geochemical behavior of Hg in these environments (AMAP, 2011).

Also compatible with this conclusion is the observation that, despite order of magnitude variation in TOC values, the $\delta^{202}\text{Hg}$ MDF signature in Arctic Ocean sediments is shifted by less than 1 per mil between high-TOC (~3%) Eocene samples and low-TOC (~0.3%) Quaternary samples (**Figs. 6,7**). Sequestration of highly particle-reactive inorganic Hg(II) onto particulate organic carbon (POC) in marine sediments was proposed by Gehrke et al. (2009) to explain the relatively homogeneous Hg isotopic signatures they observed for mid-Pleistocene Mediterranean

sediments (TOC = 0.2% to 4.5%). Varying proportions of Hg from atmospheric deposition vs. terrestrial/geogenic sources delivered by rivers could potentially account for some of the variations observed in the Hg isotopic compositions of Quaternary Arctic Ocean sediments. Arctic rivers of today deliver a disproportionate amount of freshwater runoff (~10% of global total; Amos et al., 2014) to the Arctic Ocean, which is smaller both in total area and volume compared to other ocean basins (Douglas et al., 2012). This implies that Hg derived from permafrost regions during the summer thaw season should be disproportionately represented in the uppermost (~50m) part of the water column mixed layer (AMAP, 2011). Although particle export of Hg in the Central Arctic Ocean is believed to be low (Douglas et al., 2012), the impact of local terrestrially derived Hg on the isotopic composition of Central Arctic Ocean pelagic sediments should still be higher than for other oceans, where atmospheric sources of Hg (see **Fig. 6**) are expected to predominate (Fitzgerald and Lamborg, 2014). The observation that low TOC and low (i.e., more negative) $\delta^{202}\text{Hg}$ values converge in Pleistocene sediments of the Central Arctic Ocean may therefore be a consequence of other factors, which we explore below.

7.2 Origin of downcore trends in $\delta^{202}\text{Hg}$ for Quaternary Arctic Ocean sediments

Gobeil et al. (1999) observed a systematic decrease in bulk sediment Hg concentrations with depth in Arctic Ocean sediments, which they interpreted as having a diagenetic origin related to mobilization of Hg along redox gradients tied to iron reactivity within the sediments. We observe a similar trend in Hg concentrations with depth for Quaternary core HLY0503 18 JPC-01 (Lomonosov Ridge Intrabasin; water depth 2598 m). In addition to the Hg abundance trend, $\delta^{202}\text{Hg}$ values in this core are also correlated with depth (**Fig. 3**). $\delta^{202}\text{Hg}$ values decline with increasing depth, from -1.25‰ to -1.97‰, while Hg abundances decrease from 113 ug/g to 22 ug/g (**Table 1**). Several other cores, including Quaternary piston core PC-01 96/12

(Lomonosov Ridge; water depth 1003 meters), also show decreasing $\delta^{202}\text{Hg}$ values with increasing depth (**Table 1**); however, for these cores the trends are not systematically correlated with Hg abundances. In PC-01 96/12, for example, $\delta^{202}\text{Hg}$ values decline from -1.32‰ (surface) to -2.34‰ (~90 ka), while Hg concentrations remain high (31-90 ug/g; average = 50 ± 21 ug/g); however, at greater core depths (e.g., 100-500 ka), Hg concentrations fall below 10 ± 5 ug/g (**Table 2**). Although we were unable to obtain reliable Hg isotopic data for the deepest core depth intervals in PC-01 96/12, metal concentrations that we measured in this core demonstrate that there is no correlation between Hg and other metal abundances, including Mn (**Table 2**).

Jakobsson et al. (2000) concluded that the Mn-rich dark banding in this and other cores from the Central Arctic Ocean correspond closely in time to periods of increased terrestrial riverine dissolved load, which would equate to warmer interglacial/interstadial periods when the Arctic hydrologic cycle was much more active. During times of sea level high-stand, Arctic rivers deliver a larger flux of Mn and other metals to the Arctic Ocean (Polyak and Jakobsson, 2011; Löwemark et al., 2014). During times of sea level low-stand the Arctic Ocean loses much of its shelf area (~50% by area of the Arctic Ocean Basin), which significantly changes redox conditions and limits the storage capacity of Mn in shelf sediments, minimizing delivery of Mn to the Central Arctic Ocean (MacDonald and Gobeil, 2012). Although downcore Hg isotopic compositions and Hg concentrations in PC-01 96/12 are uncorrelated with Mn cycles, the fact that Hg concentrations, $\delta^{202}\text{Hg}$ values and TOC all generally decline with core depth (**Table 2**) suggests a strong connection between TOC and Hg behavior in Central Arctic Ocean sediments.

In detail, of six intervals measured for Hg isotopes in PC-01 96/12, the two youngest (Holocene) have average $\delta^{202}\text{Hg} = -1.37\text{‰} \pm 0.06\text{‰}$ (1SD), whereas the two oldest (80-90 ka) have average $\delta^{202}\text{Hg} = -2.15\text{‰} \pm 0.26\text{‰}$ (1SD), in general agreement with the observation that

the less negative $\delta^{202}\text{Hg}$ values correspond to intervals with higher organic carbon content (**Table 2**). Sample depth 167-168 cm (ca. 70 ka) has the highest (i.e., least negative) $\delta^{202}\text{Hg}$ value (-1.37‰) that we measured for Pleistocene sediments (average $\delta^{202}\text{Hg}$ = -1.94‰), and so is anomalous in this regard. This is an interval previously demonstrated to have undergone diagenetic alteration and loss of Mn due to resorption of Mn oxyhydroxides under reducing conditions (e.g., Alexanderson et al., 2014; März et al., 2011), consistent with interval 167-168 cm in PC-01 96/12 also having the highest TOC of all the Pleistocene sediments that we analyzed (**Table 2**). The close correspondence between low TOC and low $\delta^{202}\text{Hg}$ values in Pleistocene sediments of the Central Arctic Ocean (**Fig. 7**) suggests a connection between Hg isotope signatures and Hg sources that is possibly related to organic inputs. Holocene surface sediments by contrast have higher $\delta^{202}\text{Hg}$ values (average = -1.24‰ $\pm$ 0.18‰ 1SD), higher Hg concentrations, and higher TOC levels (Table 1). As an alternative to the source input hypothesis, *in situ* fractionation of Hg stable isotopes (e.g., diagenetic effects in sediments) could also potentially shift $\delta^{202}\text{Hg}$ towards higher or lower values in sediments. In light of this, we consider below four possible explanations for the observed down core $\delta^{202}\text{Hg}$ variations:

- 1) changes in Hg isotopic composition linked to Arctic Ocean bio-productivity or variable Pacific and Atlantic Ocean surface/deep water inflow through time
- 2) variable chemical sorption reaction rates between Hg(II) and mineral/POM surfaces during sedimentation, causing changes in MDF of Hg isotopes in sediments
- 3) migrating redox fronts near sediment-water interface influencing MDF of Hg isotopes
- 4) changing source apportionment (e.g., atmospheric vs. terrestrial Hg) with time

We consider the last three possibilities first. Sorption reactions can potentially produce measureable mass dependent fractionation of Hg isotopes of less than 1‰ $\delta^{202}\text{Hg}$ (Jiskra et al.,

2012), with the mobile Hg (II) fraction being enriched in heavier isotopes, and the sorbed Hg (II) pool (e.g., iron oxides) enriched in lighter isotopes. While such processes may fractionate Hg isotopes in the water column (Yin et al., 2015), there appears to be no correlation with Fe or with the abundances of other reactive metals and Hg isotopic compositions in the sediments we analyzed. MDF of Hg isotopes has also been measured in experiments exploring binding behavior between Hg (II) and thiol groups in organic matter (Wiederhold et al., 2010), which can also produce a small amount of MIF in Hg isotopes via the nuclear volume effect (e.g., dark abiotic reduction). Alternatively, *in situ* redox (e.g., diagenetic) reactions in Arctic Ocean sediments (e.g., Gobeil et al., 1999; März et al., 2011) combined with open system behavior and evasion of Hg in sediments may result in MDF of Hg isotopes. However, we suggest that the overall lack of any correlation between $\delta^{202}\text{Hg}$, Hg concentrations and other redox sensitive metals (in all but one core) would seem to argue against an *in situ* mechanism for explaining the down core variation observed in $\delta^{202}\text{Hg}$. Regardless, any measurable shift in the Hg isotopic composition of bulk sediment by diagenesis would require that a large fraction of an isotopically fractionated Hg pool be removed from the sediment, which seems unlikely for Hg(II). Yet another possibility involves changes in the apportionment of tropospheric Hg to the Arctic Ocean with time (e.g., Stern et al., 2012). With considerably less sea ice cover and much greater surface area exposed to direct atmospheric inputs during sea level high stands (e.g., Polyak and Jakobsson et al., 2011), the Arctic Ocean would be expected to receive a larger flux of direct atmospheric Hg inputs compared to times of Pleistocene glacial maxima; however, riverine inorganic Hg inputs to the Arctic Ocean should also scale up during times of warming climate associated with glacial minima, maintaining the balance in source apportionment as reflected in Hg isotopic compositions. Increased evasion of total Hg from more ice-free surface waters

(Soerensen et al., 2016; Stern et al., 2012) would also likely counterbalance greater input of Hg from the atmosphere. We conclude that changing proportions of atmospheric Hg delivered to the Arctic Ocean does not explain the observed variations recorded in $\delta^{202}\text{Hg}$ of sediments.

Another possible explanation for the observed $\delta^{202}\text{Hg}$ downcore variations is that during times of sea-level high-stand, significant introduction of low-salinity Pacific Ocean waters (e.g., Outridge et al., 2012; Haley et al., 2014) may result in enhanced organic productivity of Arctic Ocean surface waters, accompanied by more efficient drawdown of Hg in the water column from sinking organic matter. $\delta^{202}\text{Hg}$ of Hg(II) in the water column is impacted by photo-reduction of Hg(II) to Hg(0) (Bergquist and Blum, 2007); equilibrium isotopic effects also fractionate Hg isotopes between organic ligands (thiol-bound Hg) and dissolved Hg(II) (Wiederhold et al., 2010). The competing effects of these processes on $\delta^{202}\text{Hg}$ signatures of inorganic Hg (II) in the Arctic Ocean should vary with time depending on the inter-related (and relative) influences of water column organic flux vs. % light penetration. Sea ice conditions affect surface water productivity and water clarity, the magnitude of riverine flux of Hg, the % organics derived from terrestrial Hg reservoirs, and also the % exchange of marine surface waters with oceans external to the Arctic Ocean Basin (e.g., Pacific Ocean). These could all have been influences on the variability in Hg isotopic compositions seen in the Quaternary record.

The depositional environment for Eocene Arctic Ocean sediments provides an end-member comparison for the relative influences of these factors, during a time in the past when the Arctic Ocean was ice-free and actively exchanging with Pacific Ocean surface waters (e.g., Moran et al., 2006; Gleason et al., 2009). The high contents of reduced-sulfur and organic-matter in the Arctic Eocene/PETM sediments minimizes the possibility of significant post-depositional Hg mobility; in addition, the MDF signature of Hg isotopes in the Eocene sediments suggests

that sulfide precipitation did not result in significant isotopic fractionation of Hg (e.g., Smith et al., 2015), since the $\delta^{202}\text{Hg}$ values have a very narrow range (average $\delta^{202}\text{Hg} = -0.98\text{‰} \pm 0.12\text{‰}$ 1SD). The relatively small isotopic differences we observe between the Eocene dataset and Pleistocene dataset also suggest to us that *process* was subordinate to *source* as the key driver of isotopic variability in Arctic Ocean sediments. The more negative downcore $\delta^{202}\text{Hg}$ values in Quaternary sediments appear to equate to times of lower productivity (e.g., sea level low stand, or Pleistocene stadials), corresponding to times of increased sea ice cover in and around the periphery of the basin, and less mixing of Pacific surface waters into the Arctic Ocean Basin. During these times, dust and/or snow-dominated atmospheric Hg deposition to ice-covered surfaces would have been accompanied by a diminished hydrologic input of Hg into a smaller ocean basin having a dramatically reduced continental shelf area (Polyak and Jakobsson, 2011; Jakobsson et al., 2014). While these conditions would not specifically explain the apparent shift in MIF of Hg isotopes toward more positive $\Delta^{199}\text{Hg}$ values for these intervals (**Fig. 5**), we postulate that the best explanation for Quaternary downcore $\delta^{202}\text{Hg}$ variability is that changes in the average isotopic composition of terrestrial Hg being delivered to the Arctic Ocean occurred between glacial maxima and minima. The average terrestrial signal of mixed biomass + geogenic Hg may have been impacted by additional factors during the Holocene, which we discuss next.

Hg isotopic signatures and Hg abundances in Holocene Arctic peat samples indicate that the atmospheric Hg flux delivered to Arctic tundra sites has been increasingly influenced by anthropogenic Hg since the industrial era (Biswas et al., 2008a,b). However, it is unlikely that this anthropogenic Hg flux to terrestrial environments is reflected in the composition of the Holocene Arctic Ocean surface sediments that we measured, as they integrate many centuries worth of deposition (**Table 1**). The % anthropogenic Hg in our surface sediment samples is

calculated conservatively at 20% but is probably much less for most of our samples, based on integrated sedimentation rates, known anthropogenic Hg isotopic compositions and industrial era Hg fluxes. We acknowledge that dry deposition of atmospheric Hg dominates the Hg input to modern peat bogs, with complex biological interactions governing Hg isotopic compositions in these environments (Enrico et al., 2016). Given this, it seems best to view the Arctic Ocean Hg pool as an integral component of a greater Arctic Hg cycle, where Hg is obtained from and released again to the atmosphere on various time scales as a function of marine-cryosphere-atmosphere-biomass Hg residence times. It is revealing that both Arctic Ocean sediment and Arctic terrestrial peat datasets overlap with the Hg isotopic compositions measured for a wide range of global terrestrial carbon- and Hg-rich reservoirs including boreal soils (Jiskra et al., 2015), peatlands, coal deposits and modern vegetation (e.g., Biswas et al., 2008a; Lefticariu et al., 2011; Sun et al., 2014; Yin et al., 2010, 2015; Demers et al., 2013; Blum et al., 2014; **Fig. 6**). In this context, the origin of Hg isotope MIF signatures for this dataset turns out to be especially difficult to evaluate, because of the limited variation in measured $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ values. Despite the large uncertainties in the $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratios for individual samples, average $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ values for Arctic marine sediments grouped by age plot on a line with slope close to ~1 (see Electronic Annex – EA), similar to many commonly known terrestrial reservoirs including Arctic peat (Biswas et al., 2008a,b). As established by Bergquist and Blum (2007), this is the signature of photo-reduction of Hg(II) to Hg(0), associated with DOM in aquatic systems and is also a characteristic of photo-chemical processes governing MIF of Hg isotopes in vegetation (Demers et al., 2013).

The small but nonetheless significant $\delta^{202}\text{Hg}$ variations that we measured, and their correspondence with organic content variability in Arctic marine sediments grouped by age, was

suggested above to be a potential water column productivity signature related to Pacific water inflow. Modern Arctic Ocean circulation (e.g., Stein and McDonald, 2004; Stein, 2008; Outridge et al., 2008; Haley and Polyak, 2013; Jakobsson et al., 2014) allows for significant mixing of low salinity Pacific Ocean waters into the western (Canadian) basin and to a lesser extent the eastern (Eurasian) basin (**Fig. 1**). Increased export of organic carbon into Arctic Ocean sediments is compatible with times of diminished ice cover (Gobeil et al., 2001) and appears to be associated with Hg in sediments having less negative $\delta^{202}\text{Hg}$ delivered to the seafloor. We thus view Arctic Ocean Quaternary $\delta^{202}\text{Hg}$ variations as being fundamentally tied to ice age climate swings which, in contrast to the Pleistocene Mediterranean Sea case, produce Hg source input signatures that are isotopically more variable over time. North Atlantic inflow delivers a significant flux of Hg to deep waters in the Arctic Ocean (e.g., Soerensen et al., 2016), and would be expected to dominate the ocean-exchange mass balance during glacial maxima, when exchange with the Pacific Ocean was effectively shut down, likely contributing to some of the isotopic variability incorporated into the sedimentary record. Finally, the % Hg contribution from Arctic rivers that is transferred to the marine sediment Hg pool through time is also governed by the organic chemistry of Arctic rivers and the ‘source to sink’ binding behavior of Hg, as it travels from terrestrial freshwater environments into environments governed by marine Hg geochemistry. Ultimately, the $\delta^{202}\text{Hg}$ signature of Hg exported to Arctic Ocean sediments must reflect not only river chemistry, but also changing proportions of riverine Hg versus the Hg delivered to the Arctic Ocean via Pacific/Atlantic Ocean inflow across climate transitions.

8. Conclusions

New mercury isotope data suggest a strong commonality of sources, pathways and processes governing the isotopic composition of Hg in paleo Arctic Ocean sediments over the

course of Cenozoic time. Terrestrial, organic carbon-rich Hg sources (peatland/soil/permafrost Hg) appear to have dominated the Hg isotopic composition of sediments deposited in the Arctic Ocean since the Eocene. Some photo-reduction of Hg(II) is indicated by a small but measurable mass independent fractionation signature of Hg isotopes in Arctic Ocean sediments; however, we discern no clear signature of Hg that has been transformed by paleo AMDE in Arctic Ocean sediments, nor is there any clear signal of anthropogenic Hg detectable in surface sediments at the resolution studied. A single analysis of the Central Arctic Ocean PETM interval (IODP Expedition 302, Lomonosov Ridge) is similar in its Hg isotopic composition to Holocene sediments, reinforcing the overall consistency of Hg isotopic signatures observed over a range of depositional environments, water depths, stratigraphic ages, and climatic regimes. Quaternary downcore $\delta^{202}\text{Hg}$ trends are interpreted as a provenance signal tied to ice age glacial cycles, and not sedimentary diagenetic effects.

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10. Tables

Table 1. Hg concentrations and isotopic compositions of Arctic Ocean sediments.

Table 2. Piston Core PC-01 96/12 Hg and other metal abundances.

11. Figures

Figure 1. Bathymetric map of the Arctic Ocean Basin (Jakobsson et al., 2012). Core top surface sediment $\delta^{202}\text{Hg}$ values (‰) are indicated for 8 core locations (see Table 2). Locations include Lomonosov Ridge (Central Arctic Ocean), Yermak Plateau and Morris Jesup Rise (Eurasian Basin), Mendeleev Ridge and Chukchi Plateau (Amerasian Basin).

Figure 2. $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values vs. water depth in meters below sea level for nine Arctic Ocean surface sediment (core top) samples. Sample locations shown in Fig. 1. Error bars are 2SD replication (external reproducibility) of MESS-3 CRM (see text).

Figure 3. $\delta^{202}\text{Hg}$ values and Hg concentrations vs. core depth in cm below sea floor, for piston core HLY0503 JPC18-01 (Central Arctic Ocean, Lomonosov Ridge intrabasin, water depth 2600 meters). $\delta^{202}\text{Hg}$ downcore trend is indicated by solid line with open symbols. Downcore trend in Hg (ng/g) indicated by solid symbols. 2SD error bar indicates uncertainty in $\delta^{202}\text{Hg}$ values (‰). Hg concentrations range from 22 ng/g to 113 ng/g ($\pm 5\%$ 1SD; Table 1).

Figure 4. $\delta^{202}\text{Hg}$ values (‰) and Hg concentrations (ng/g) vs. stratigraphic age (ka) for piston core 01PC - 96/12.

Figure 5. $\Delta^{199}\text{Hg}$ vs. $\delta^{202}\text{Hg}$ for Arctic Ocean sediments, grouped according to stratigraphic age. Arctic Ocean PETM indicated by solid circle. Other marine sediment Hg compositions shown for comparison: a) mid-Pleistocene Mediterranean sapropels (open triangle; Gehrke et al., 2009); b) Holocene (pre-industrial) Atlantic margin, Portugal (open circle; Mil-Homens et al., 2011).

Figure 6. $\delta^{202}\text{Hg}$ vs. $\Delta^{199}\text{Hg}$ for Arctic Ocean sediments compared with Arctic sea ice and snowpack AMDE Hg isotopic compositions (Sherman et al., 2010, 2012), modern Arctic coastal seawater Hg (Strok et al., 2015), and non-Arctic atmospheric Hg (precipitation data from compilation of Blum et al., 2014). Boxed precipitation value represents estimated remote open ocean atmospheric GEM isotopic composition of North Pacific region (Blum et al., 2013). Note that modern atmospheric Hg isotopic values reflect anthropogenic influence. Approximate range of Hg isotopic values is indicated for various terrestrial Hg reservoirs including vegetation, soil, peat, and coal (Blum et al., 2014; Demers et al., 2013; Biswas et al., 2008a, Lefticariu et al., 2011; Yin et al., 2010; Sun et al., 2014; Jiskra et al., 2015). Hg isotopic composition of two Alaskan peat samples (Biswas et al., 2008a) indicated by green triangle symbols. Average isotopic composition of Holocene peat samples from Barrow, Alaska (including anthropogenic influenced) indicated by star symbol (Biswas et al., 2008b). Average boreal forest soil Hg isotopic composition is from Jiskra et al. (2015).

Figure 7. Total Organic Carbon (% TOC) vs. $\delta^{202}\text{Hg}$ values for a subset of Arctic Ocean sediments, for which TOC values are available (data from Table 1). Eocene sediments have higher average % TOC and Hg compared to Quaternary sediments, which show a larger range in $\delta^{202}\text{Hg}$ trending towards more negative values (see text for discussion).

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Table 1

Table 1. Mercury stable isotopic compositions of Arctic Ocean sediments (56 Ma to present) determined by CV-MC-ICPMS for this study.

Quaternary Samples	Ship/Expedition	Piston, Trigger or Multi-Core	Location	Water Depth (meters)	Core Depth (centimeters)	Age (yrs)	REFS ¹	Hg (ng/g)	δ ²⁰² Hg‰	Δ ¹⁹⁹ Hg‰	Δ ²⁰⁰ Hg‰	Δ ²⁰¹ Hg‰	Δ ²⁰⁴ Hg‰	Lat.	Long.	TOC%	Lithotype ²
Holocene	Healy-Oden/HOTRAX 05	HLY0503 18 JPC-01	Lomonosov Ridge Intrabasin	2598	0-2	2690	1	113	-1.25	-0.02	0.01	-0.12	0.03	88° 27' N	146° 34' E		1,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0503 18 JPC-01	Lomonosov Ridge Intrabasin	2598	5-7	7220	1	67	-1.34	-0.03	-0.01	-0.09	-0.02	88° 27' N	146° 34' E		1,4,5
<i>duplicate combustion</i>	Healy-Oden/HOTRAX 05	HLY0503 18 JPC-01	Lomonosov Ridge Intrabasin	2598	5-7	7220	1	67	-1.33	-0.05	0.00	-0.09	0.02	88° 27' N	146° 34' E		1,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0503 18 JPC-01	Lomonosov Ridge Intrabasin	2598	10-12	8795	1	55	-1.61	-0.05	-0.02	-0.09	0.00	88° 27' N	146° 34' E		1,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0503 18 JPC-01	Lomonosov Ridge Intrabasin	2598	15-17	10240	1	22	-1.77	0.04	0.00	-0.08	-0.04	88° 27' N	146° 34' E		1,4,5
Pleistocene	Healy-Oden/HOTRAX 05	HLY0503 18 JPC-01	Lomonosov Ridge Intrabasin	2598	20-22	11890	1	47	-1.92	-0.04	-0.01	-0.07	0.04	88° 27' N	146° 34' E		1,4,5
Pleistocene	Healy-Oden/HOTRAX 05	HLY0503 18 JPC-01	Lomonosov Ridge Intrabasin	2598	25-27	12535	1	27	-1.97	0.00	0.01	-0.07	0.02	88° 27' N	146° 34' E		1,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0503 8 JPC-1	Mendeleev Ridge	2792	0-2	3981	2,10	55	-1.06	0.01	0.00	-0.05	-0.03	79° 36' N	172° 30' W	0.45	1,4,5
Pleistocene	Healy-Oden/HOTRAX 05	HLY0503 8 JPC-1	Mendeleev Ridge	2792	22-24	15000	2,10	55	-1.95	0.08	0.01	-0.01	-0.05	79° 36' N	172° 30' W	0.30	1,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0503 22 TC-01	Yermak Plateau	798	0-2	<i>Holocene</i>	8	55	-1.25	-0.08	-0.02	-0.13	0.01	80° 29' N	172° 30' W		2,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0503 22 TC-01	Yermak Plateau	798	9-11	<i>Holocene</i>	8	45	-1.42	-0.01	0.00	-0.10	0.00	80° 29' N	172° 30' W		2,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0503 22 TC-01	Yermak Plateau	798	21-23	<i>Holocene</i>	8	48	-1.55	-0.03	0.00	-0.09	0.09	80° 29' N	172° 30' W		2,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0503-03MC	Chukchi Sea (Northwind Ridge)	583	0-1	<i>Holocene</i>	9	46	-1.42	-0.10	0.00	-0.16	-0.01	77° 15' N	157° 03' W		2,4,5
Holocene	Healy-Oden/HOTRAX 05	HLY0501-04MC	Chukchi Sea (Chukchi Plateau)	462	0-1	<i>Holocene</i>	9	79	-1.14	-0.11	0.02	-0.12	0.08	77° 42' N	157° 22' W		2,4,5
Age (ka)**																	
Holocene	Oden/Arctic 96	96/12 TWC	Lomonosov Ridge	1003	0-1	4	3	31	-1.32	0.01	-0.01	-0.02	-0.03	87°05.9'N	144°46.4'E	0.26	1,4,5
Holocene	Oden/Arctic 96	96/12 TWC	Lomonosov Ridge	1003	1-2	7	3	33	-1.41	0.02	0.00	0.05	0.06	87°05.9'N	144°46.4'E	0.26	1,4,5
Pleistocene	Oden/Arctic 96	96/12 1PC	Lomonosov Ridge	1003	100-101	48	3	49	-2.08	-0.06	0.03	-0.03	-0.02	87°05.9'N	144°46.4'E	0.30	1,4,5
Pleistocene	Oden/Arctic 96	96/12 1PC	Lomonosov Ridge	1003	167-168	70	3	47	-1.37	0.02	0.00	-0.06	-0.12	87°05.9'N	144°46.4'E	0.37	1,4,5
Pleistocene	Oden/Arctic 96	96/12 1PC	Lomonosov Ridge	1003	194-195	79	3	90	-1.97	0.12	0.02	-0.04	0.00	87°05.9'N	144°46.4'E	0.12	1,4,5
Pleistocene	Oden/Arctic 96	96/12 1PC	Lomonosov Ridge	1003	199.5-200.5	90	3	50	-2.34	0.09	-0.01	-0.01	0.03	87°05.9'N	144°46.4'E	0.13	1,4,5
Age (yrs)*																	
Holocene	Oden/LOMROG II 09	LOMROG09-TC-09	Lomonosov Ridge	3477	0-1	786	5	120	-1.58	-0.05	-0.03	-0.12	0.03	89° 26' 51" N	128°54'22" W		1,4,5
Holocene	Oden/LOMROG II 09	LOMROG09-TC-09	Lomonosov Ridge	3477	1-2	1661	5	112	-1.56	-0.07	-0.02	-0.11	-0.02	89° 26' 51" N	128°54'22" W		1,4,5
Holocene	Oden/LOMROG II 09	LOMROG09-TC-09	Lomonosov Ridge	3477	2-3	2247	5	105	-1.64	0.00	0.00	-0.09	0.00	89° 26' 51" N	128°54'22" W		1,4,5
Holocene	Oden/LOMROG I 07	LOMROG07-TC-08	Morris Jessup Rise	1038	0-1	9291	4	31	-1.10	-0.12	-0.04	-0.18	0.02	85° 19.19' N	14° 51.45' W	0.41	1,4,5
Holocene	Oden/LOMROG I 07	LOMROG07-PC-08	Morris Jessup Rise	1038	0-1	<i>Holocene</i>	4	37	-1.07	-0.18	-0.04	-0.29	-0.03	85° 19.19' N	14° 51.45' W	0.44	1,4,5
Age (Ma)***																	
Eocene Samples		Site, Drillcore															
Middle Eocene	IODP Exp 302 (ACEX)	M0002a, 48x	Lomonosov Ridge	1209	208	44	6,7	169	-0.84	0.06	0.01	0.02	-0.01	87.92118° N	139.36501° E		3,6
<i>duplicate combustion</i>	IODP Exp 302 (ACEX)	M0002a, 48x	Lomonosov Ridge	1209	208	44	6,7	169	-0.78	0.08	0.00	0.00	0.03	87.92118° N	139.36501° E		3,6
Middle Eocene	IODP Exp 302 (ACEX)	M0002a, 53x	Lomonosov Ridge	1209	225	45	6,7	91	-1.00	-0.01	0.01	-0.07	-0.02	87.92118° N	139.36501° E	2.81	3,6
Middle Eocene	IODP Exp 302 (ACEX)	M0002a, 57x	Lomonosov Ridge	1209	245	46	6,7	76	-0.96	-0.02	0.00	-0.07	0.01	87.92118° N	139.36501° E		3,6
Middle Eocene	IODP Exp 302 (ACEX)	M0004a, 07x	Lomonosov Ridge	1288	280	47	6,7	96	-0.92	0.03	0.02	-0.05	-0.09	87.86658° N	136.17735° E		3,6
Middle Eocene	IODP Exp 302 (ACEX)	M0004a, 10x	Lomonosov Ridge	1288	295	48	6,7	95	-1.08	-0.06	-0.05	-0.07	0.00	87.86658° N	136.17735° E	3.38	3,6
Early Eocene - Azolla	IODP Exp 302 (ACEX)	M0004a, 11x	Lomonosov Ridge	1288	300	49	6,7	82	-1.04	0.07	0.03	0.02	0.05	87.86658° N	136.17735° E		3,6
Early Eocene	IODP Exp 302 (ACEX)	M0004a, 23x	Lomonosov Ridge	1288	345	52	6,7	105	-1.03	-0.06	-0.03	-0.03	0.01	87.86658° N	136.17735° E	2.84	3,6
Early Eocene	IODP Exp 302 (ACEX)	M0004a, 27x	Lomonosov Ridge	1288	370	54	6,7	110	-1.14	-0.08	0.00	-0.11	0.07	87.86658° N	136.17735° E		3,6
PETM	IODP Exp 302 (ACEX)	M0004a, 30x	Lomonosov Ridge	1288	380	56	6,7	87	-1.32	-0.09	-0.04	-0.12	-0.04	87.86658° N	136.17735° E	3.04	3,6
*radiocarbon years																	
**Mn-based stratigraphy																	
***biostratigraphic ages																	
¹ References			² Lithologic type														
1	<i>Hanslik et al., 2010</i>		1 - pelagic clay/silty clay														
2	<i>Adler et al., 2009</i>		2 - hemipelagic clay/silty clay														
3	<i>Jakobsson et al., 2000</i>		3 - organic-rich clay/silty clay														
4	<i>LOMROG I cruise report</i>		4 - ice rafted debris (IRD) present														
5	<i>LOMROG II cruise report</i>		5 - detrital carbonate present														
6	<i>IODP 302 Proceedings</i>		6 – sulfidic														
7	<i>Backman et al., 2008</i>																
8	<i>HOTRAX I cruise report</i>																
9	<i>HOTRAX II cruise report</i>																
10	<i>Yamamoto & Polyak, 2009</i>																

Note: TOC (%) values are taken from references listed above; Hg concentrations are CV-AAS values (±5%) from this study (see also Table 2).

Table 2

Core Depth (cm)	Sr ng/g	Mo ng/g	Cd ng/g	Ba ng/g	Re ng/g	U ng/g	V ng/g	Cr ng/g	Co ng/g	Ni ng/g	Cu ng/g	Zn ng/g	Hg* ng/g	Age** ka	MIS	Color	TOC %	Na ₂ O wt%	MgO wt%	Al ₂ O ₃ wt%	K ₂ O wt%	CaO wt%	TiO ₂ wt%	MnO wt%	Fe ₂ O ₃ wt%
0-1 TWC													31	4			0.26								
1-2 TWC													33	7			0.26								
100	160	12.5	0.21	573	0.0054	1.8	90	68.0	12.6	24.1	17.0	57.0	49	52	3.3	Dark	0.30	2.36	1.28	12.65	2.80	0.71	0.653	0.221	5.35
167	144	2.2	0.31	495	0.0069	2.3	148	44.7	19.1	42.5	23.9	85.2	47	70		Light	0.37	2.60	2.19	14.61	3.15	1.67	0.708	0.051	6.68
194	188	5.3	0.19	490	0.0068	1.8	118	42.4	97.4	53.4	50.3	73.7	90	79	5.1	Dark	0.12	2.86	2.17	14.86	3.02	2.80	0.733	0.348	6.10
199.5	147	1.6	0.18	482	0.0070	2.0	123	87.6	17.6	41.2	31.0	87.3	50	90		Light	0.13	2.68	2.22	15.19	3.11	1.55	0.711	0.090	5.85
204.5	157	3.5	0.20	532	0.0071	2.2	140	41.9	47.5	45.9	25.1	87.7	7	97	5.3	Dark	0.13	2.61	2.17	15.39	3.16	1.60	0.722	0.240	6.24
210	132	2.0	0.18	490	0.0068	2.1	135	71.6	22.5	36.8	23.5	84.3	14	106		Light	0.16	2.61	2.89	15.53	3.11	2.31	0.728	0.149	6.08
221	177	4.2	0.20	516	0.0070	2.1	136	74.6	61.3	48.9	29.1	82.8	6	122	5.5	Dark	0.15	2.73	2.24	15.43	3.05	2.16	0.729	0.331	6.22
260	167	4.4	0.19	496	0.0080	2.1	129	74.1	44.9	48.6	26.9	79.9	18	194	7.1	Dark	0.14	2.94	2.00	15.02	2.95	1.62	0.711	0.343	6.04
280.5	150	8.6	0.25	540	0.0073	2.3	147	42.4	52.3	61.7	34.3	94.7	6	236	7.5	Dark	0.13	2.83	2.24	16.30	3.22	1.13	0.813	0.473	6.84
290.5	134	2.2	0.19	524	0.0069	2.2	138	71.2	17.7	35.8	23.8	86.6	19	277		Light	0.14	2.90	2.02	16.31	3.39	0.95	0.745	0.135	6.31
298.5	154	8.3	0.24	542	0.0070	2.2	136	71.7	44.1	48.2	29.2	82.3	13	309	9.1	Dark	0.11	2.85	2.07	15.69	3.14	0.84	0.762	0.420	6.23
387.5	145	10.2	0.26	506	0.0070	2.3	149	45.8	38.0	42.0	28.4	79.9	6	481	13.11	dark	0.10	2.76	1.83	15.61	3.04	0.65	0.753	0.309	6.32
402.5	137	6.0	0.22	534	0.0067	2.3	140	47.0	25.2	35.5	22.9	86.6	5	500	13.13	light	0.11	2.85	1.87	15.93	3.33	0.68	0.746	0.199	6.27
BCR-2 (CRM)	272	234.6	1.95	541	0.0173	1.5	358	11.8	32.0	9.8	13.0	103.2						3.09	3.44	13.21	1.78	6.88	2.160	0.192	13.47
BCR-2 certified	346	248.0		683		1.7	416	18.0	37.0		19.0	127.0						3.16	3.59	13.50	1.79	7.12	2.260	0.196	13.80
MAG-1 (CRM)	120	1.2	0.27	398	0.0090	2.6	122	91.1	19.3	43.1	22.6	104.0						3.70	2.69	14.83	3.36	1.28	0.627	0.091	6.37
MAG-1 certified	150	1.6	0.20	480		2.7	140		20.0	53.0	30.0	130.0						3.83	3.00	16.40	3.55	1.37	0.750	0.098	6.80
MESS-3 (CRM)													94 (±5)												
MESS-3 certified													91 (±10)												

*All data based on bulk sediment acid digests except for Hg concentrations by thermal decomposition CV-AAS

**interpolated age based on Mn age model of Jakobsson et al. (2000) except for TWC samples based on C14 calibrated age

TWC = trigger weight core sample

MIS = marine isotope stage

Note: non-Hg metals abundances determined by magnetic sector ICP-MS (Element 2, Thermo Fisher Scientific) at the University of Michigan.

Figure 1.

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7