HISTORICAL VARIATIONS OF MERCURY STABLE ISOTOPE RATIOS RECORDED IN HIGH ARCTIC SNOW.

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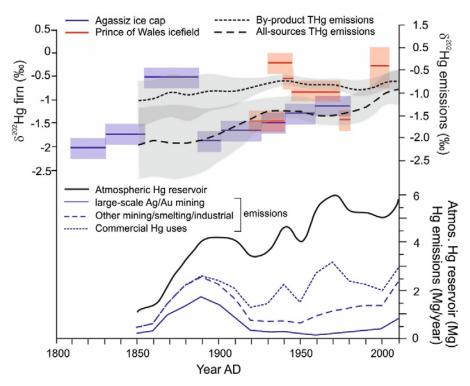
Introduction

Owing to its reactivity and volatility, mercury (Hg) can be dispersed globally via the atmosphere or oceans, and contaminate remote, high-latitude environments and ecosystems (AMAP, 2011). Stable Hg isotope ratios measured in environmental media provide a new way to identify the emission source(s) and processes involved in Hg pollution (Blum et al., 2014). In this study, we used Hg isotope ratios in glacier cores from the Canadian Arctic to investigate past and recent source(s) and trends of atmospheric Hg deposition.

Methods

We used archived glacier firn (compacted snow) and ice cores recovered between 1994 and 2005 on four Canadian Arctic ice caps (latitudes 67.2 to 80.7 °N). The samples range in age from recent decades to $>10^4$ years. We carefully removed the outer layers of cores, and determined total Hg concentrations ([THg]) by CV-AAS, and stable Hg isotope ratios (δ^{202}Hg, δ^{199}Hg, δ^{200}Hg) by MC-ICP-MS in the melted samples.

Results

 The [THg] in High Arctic firn increased from close to or < 0.5 ng/L in pre-industrial time to ~0.8-1.2 ng/L in the past 200 years, implying a ~two-fold enhancement (or larger) during the modern industrial era. The mass-independent fractionation of Hg (δ^{199}Hg) in most samples was close to 0 ‰ and much less than in snow impacted by atmospheric Hg depletion events (Sherman et al., 2012), which suggests these events contribute little Hg accumulation on Arctic glaciers. The range of Hg isotopic compositions (δ^{202}Hg, δ^{199}Hg) in firn and ice overlaps with that of several possible known sources, some natural (e.g., Arctic seawater) and some anthropogenic (e.g., coal burning) but it is presently impossible to unambiguously discriminate between these sources (or source-regions) using Hg isotopes alone. However, variations of δ^{202}Hg recorded in High Arctic firn cores display a gradual positive shift of ~1 ‰ from the 19th to late 20th century (Fig. 1), which parallels the estimated trend in the δ^{202}Hg of industrial by-product THg emissions to the atmosphere over the same period (Sun et al., 2016). We hypothesize that the δ^{202}Hg of firn reflects the isotopic evolution of the atmospheric Hg pool in the High Arctic in response to growing anthropogenic emissions. If this is correct, it offers one of the most unequivocal lines of evidence obtained so far of the far-reaching impact of anthropogenic Hg emissions in the remote Arctic atmosphere.

Figure 1. Top: Measured δ^{202}Hg in firn cores from two Canadian High Arctic ice caps (red, blue; shading: ± 2σ) compared with modeled historical variations in the δ^{202}Hg of anthropogenic THg emitted to the atmosphere either as a by-product, or from all emission sources (after Sun et al., 2016; shading: 95 % C.L.). Bottom: Reconstructed changes in global Hg emissions to the atmosphere since 1800 from various sources, and simulated changes in the size of the atmospheric Hg reservoir based on these emissions (Streets et al., 2011; Amos et al., 2013; Horowitz et al., 2014).

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