Mercury (Hg) in meteorites: Variations in abundance, thermal release profile, mass-dependent and mass-independent isotopic fractionation

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Abstract

We have measured the concentration, isotopic composition and thermal release profiles of Mercury (Hg) in a suite of meteorites, including both chondrites and achondrites. We find large variations in Hg concentration between different meteorites (ca. 10 ppb to 14,000 ppb), with the highest concentration orders of magnitude above the expected bulk solar system silicates value. From the presence of several different Hg carrier phases in thermal release profiles (150–650 °C), we argue that these variations are unlikely to be mainly due to terrestrial contamination. The Hg abundance of meteorites shows no correlation with petrographic type, or mass-dependent fractionation of Hg isotopes. Most carbonaceous chondrites show mass-independent enrichments in the odd-numbered isotopes ^{199}Hg and ^{201}Hg. We show that the enrichments are not nucleosynthetic, as we do not find corresponding nucleosynthetic deficits of ^{196}Hg. Instead, they can partially be explained by Hg evaporation and redeposition during heating of asteroids from primordial radionuclides and late-stage impact heating. Non-carbonaceous chondrites, most achondrites and the Earth do not show these enrichments in vapor-phase Hg. All meteorites studied here have however isotopically light Hg (δ^{202}Hg = ~−7 to −1) relative to the Earth's average crustal values, which could suggest that the Earth has lost a significant fraction of its primordial Hg. However, the late accretion of carbonaceous chondritic material on the order of ~2%, which has been suggested to account for the water, carbon, nitrogen and noble gas inventories of the Earth, can also contribute most or all of the Earth's current Hg budget. In this case, the isotopically heavy Hg of the Earth's crust would have to be the result of isotopic fractionation between surface and deep-Earth reservoirs.
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1. INTRODUCTION

Mercury (Hg) is an element of high cosmochemical interest, not least due to its unusual properties. Like a noble gas, it is highly volatile and comparatively rare in silicate matter, with abundances typically measured in parts per billion (ppb or ng/g). It has a high vapor pressure for a metal,

usually forms a mono-atomic gas (Hg$_{(0)}$) in the vapor phase, and does not easily enter chemical bonds. In contrast to noble gases, however, Hg has a strong affinity to organic matter. Mercury is the heaviest known element with more than three stable isotopes, and thus the heaviest element where internal normalization of isotope ratios can be used. Its seven stable isotopes (196, 198–202, 204) span a mass range ($\Delta M/M$) of ~4%. Both mass-dependent and mass-independent isotope fractionation processes (MDF, MIF) have been confirmed in a variety of terrestrial environments (see below). The seven isotopes of Hg have different

nucleosynthetic origins: the lightest and least abundant (∼0.15%) isotope, ^{196}Hg, is produced exclusively by the p-process, while the other six isotopes have varying contributions from the s- and r-processes (Palme and Beer, 1993; Jaschek and Jaschek, 1995; Arlandini et al., 1999). Nucleosynthetic models predict ^{196}Hg/^{198}Hg excesses on the order of several 1000‰ for supernova (SN) ejecta (e.g., Rauscher et al., 2002). Therefore, even a small fraction of SN-derived matter injected at a late stage into the solar nebula, similar to what has been suggested for short-lived radionuclides (e.g., Boss and Keiser, 2012; Brennecka et al., 2013), should lead to measurable ^{196}Hg excesses, at least if the SN-derived Hg escapes complete re-mixing with nebular Hg before incorporation into silicates. The high volatility of Hg further makes it a potential tracer for temperature-sensitive processes during all stages of planet formation: evaporation and re-condensation in the solar nebula, parent-body heating, de-volatilization and alteration, volatile loss during giant impacts (for planets), and late delivery of volatile elements to Earth and the other terrestrial planets (e.g., the "late veneer").

Given this potential, it is surprising how little is actually known about the abundance and isotopic composition of Hg in meteorites, despite more than half a century of study. Even the solar system abundance remains unclear since Hg cannot be detected in the solar photosphere (Grevesse, 1970; Grevesse et al., 2015). The Hg content in CI chondrites (Ivuna-type; e.g. Orgueil), which has in most cases been measured by either neutron activation analysis (NAA) or wet chemistry, is of little help in that respect, as it varies by up to three orders of magnitude between different CI chondrites, and even between individual samples of the same CI chondrite (Lauretta et al., 1999). From nuclear reaction cross-sections, and the known abundance of elements with similar masses, Beer and Macklin (1985) calculate a Hg abundance of 0.34×10^{-6} atoms of Hg per atom of Si (given by these authors without uncertainty), which corresponds to an "expected" concentration of 260 ppb Hg for CI chondrites (Lauretta et al., 1999). It is currently not clear how Hg was incorporated into meteorites, i.e., we do not know whether we should indeed expect 260 ppb Hg in CI chondrites. Lauretta et al. (1999) suggested a model of chemisorption of Hg onto Fe-grain surfaces in the solar nebula, which is capable, for certain temperatures and Fe-grain sizes, to condense the full solar nebula content of Hg. In the following, we will simply assume that the solar abundance of Hg was initially fully condensed into meteorites. We will call this initial abundance of 260 ppb Hg the "bulk solar system silicates value", or Hg$_{BS3}$.

Meteorites with abundances significantly above the Hg$_{BS3}$ value would thus have experienced some process of additional Hg acquisition, while lower values require either Hg loss or inefficient initial acquisition. Whether these processes happened on Earth (terrestrial "contamination" and "loss") or in space (e.g., through thermal processes on the parent body) is unclear. Some authors have dismissed the exceptionally high Hg abundances measured in Orgueil

(up to 500,000 ppb) as due to terrestrial contamination (e.g., Palme and Beer, 1993). For the majority of the meteorites analyzed so far, the Hg concentration was measured using NAA, which can detect only two of the seven isotopes, ^{196}Hg and ^{202}Hg. Strong variations in the ^{196}Hg/^{202}Hg ratio (of up to a few 1000‰, both positive and negative) have been reported in many early NAA studies (see summary by Lauretta et al., 1999). However, Ebihara et al. (1998), Lauretta et al. (1999) and Kumar et al. (2001) have suggested that interference from ^{75}Sn and ^{203}Hg might have compromised the Hg signal in NAA studies, leading to both an overestimation of the total Hg content, and spurious isotopic variation in the measured ^{196}Hg/^{202}Hg ratio. Lauretta et al. (2001) analyzed the carbonaceous chondrites Murchison (Mighei type; CM) and Allende (Vigarano type; CV), for which large isotopic variations in ^{196}Hg/^{202}Hg had previously been reported in NAA studies. They used single- and multi-collector inductive-coupled plasma mass spectrometry (SC-ICP-MS and MC-ICP-MS, respectively) to find that the Hg isotopic composition of these meteorites was compatible with terrestrial Hg within 0.2–0.5‰, except for a small unexplained deficit in ^{200}Hg in Murchison. Lauretta et al. (2001) also reported a Hg concentration of 294 ± 15 ppb and 30.0 ± 1.5 ppb Hg for Murchison and Allende, respectively, which is within the lower range of values determined by NAA for these meteorites.

The development of cold vapor (CV) MC-ICP-MS (Klaue et al., 2000), and the pioneering work by Lauretta et al. (1999, 2001), have inspired a large number of ICP-MS studies of Hg in Earth- and environmental science (Blum et al., 2014). Mass-independent isotopic fractionations (MIF) of Hg isotopes have since repeatedly been discovered in terrestrial environments, with both the even- and odd-numbered Hg isotopes affected (e.g., Chen et al., 2012; Demers et al., 2013). These MIFs allow the identification and quantification of different sources and processes contributing to the Hg measured in terrestrial samples, e.g., atmospheric, industrial and urban Hg (Estrade et al., 2010) or Hg from compact fluorescent lamps (Mead et al., 2013). Strong MIF of up to several permil have been observed in such unlikely seeming reservoirs as freshwater and marine fish (e.g. Bergquist and Blum, 2007), and Arctic snow (Sherman et al., 2010). A recent review of terrestrial Hg measurements and the processes thought to be responsible for the observed MIFs is given by Blum et al., 2014.

There are two processes inducing MIFs in the odd-numbered Hg isotopes (^{199}Hg, ^{201}Hg): The "magnetic isotope effect" (MIE), which is due to the odd-numbered isotopes carrying a magnetic moment, resulting in a slightly different behavior during chemical reactions involving radicals; and the "nuclear volume effect" (NVE), where the slightly different ion radii of the odd-numbered isotopes are thought to result in isotopic fractionation during evaporation and condensation, such that the Hg vapor phase is enriched both mass-dependently in the light isotopes and mass-independently in the odd isotopes, with a Δ^{199}Hg/δ^{202}Hg slope of ~-0.1 (Ghosh et al., 2013). Here, δ^{xxx}Hg = $(((^{xxx}$Hg/^{198}Hg$_{measured}$)/