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Review

Trends and advances in mercury stable isotopes as a geochemical tracer

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ABSTRACT

Mercury (Hg) stable isotope geochemistry is a rapid emerging research field. During the past decade, mercury isotope geochemistry has become an essential part of mercury science, and has played an important role for a wide variety of scientific progresses relating to this metal. Recent studies have demonstrated that Hg isotopes can be systematically fractionated during specific environmental processes (*e.g.*, biotic, abiotic and photochemical). Mercury can have both mass-dependent fractionation (MDF) and mass-independent fractionation (MIF). Each fractionation process imparts a diagnostic pattern of isotopic variations on the earth's geochemical reservoirs, and thus Hg isotope ratios can be used to unravel the sources and complex biogeochemical pathways for Hg. Large variations (∼10‰) of both MDF and MIF signatures have been detected in different environmental compartments. The observation of MIF in natural samples suggests that photochemical reaction of Hg species plays an important role in the global cycle of Hg. This paper reviews the analytical methods, the contrasting isotope fractionation during Hg geochemical transformation, the isotopic signatures of different geochemical reservoirs, and the potential uses of Hg isotopes in the future.

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1. Introduction

Mercury is a globally distributed and toxic trace metal [1–4]. The geochemical cycling of Hg (Fig. 1) involves direct emissions, atmospheric transport, deposition to land and ocean, and re-volatilization [3]. The atmosphere plays a cardinal role in the global dispersion and deposition of mercury [4]. Mercury is released to the atmosphere through natural, anthropogenic and secondary emissions [5] in the form of gaseous elemental Hg (Hg^0_g), gaseous oxidized Hg (Hg^{II}_g) and particulate/aerosol bound Hg (PHg_g). Hg^0_g is the most abundant (>95%) atmospheric Hg form with an extensive life-time of ~1 yr [1,2]. Hg^0_g is subjected to atmospheric long-range transport, and is subsequently the predominant source of Hg in pristine remote areas [6,7]. Hg^0_g is oxidized to Hg^{II}_g by ozone and reactive halogen species [8]. Hg^{II}_g and to a lesser extent Hg^0, can be associated with aerosols and particulate matter in the form of PHg_g, which is effectively removed from the atmosphere through wet and dry deposition [9]. Oceanic Hg emissions contribute to the long-range transport of atmospheric Hg through a "multi-hop" mechanism as atmospheric Hg is deposited to the ocean and then reemitted to the atmosphere [10]. Once deposited into aquatic environments, Hg undergoes complicated transformation both by biological and non-biological processes [11]. Mercury exists in the ocean mainly in inorganic forms, *e.g.*, dissolved divalent Hg (Hg^{II}_{aq}), particulate Hg (PHg_{aq}) and dissolved gaseous elemental Hg (Hg^0_{aq}) [2]. Reduction of Hg^{II}_{aq} to Hg^0_{aq} in natural waters may proceed thermally or induced by actinic radiation in the presence of suitable ligands [12]. Oceanic waters generally exhibit significant degrees of supersaturation with respect to Hg^0_{aq} [13]. The subsequent loss of Hg^0_{aq} is thought to be rapid and extends the atmospheric lifetime of Hg [14]. Conversely, Hg can exit the water through conversion of Hg^{II}_{aq} to PHg_{aq} followed by gravitational settling. The ultimate sink of PHg_{aq} is burial into the deep-ocean sediments, which occurs very slowly [11]. Bioavailable Hg^{II}_{aq} may also convert to methylmercury (MeHg), a toxin that can be effectively bio-accumulated through aquatic food webs, eventually posing a serious threat to humans and wild life [1]. Humans have altered the biogeochemical cycle of Hg by a factor of ~3. As a consequence of past and present intensive human activities and given the sluggish transfer time of ~3000 yr to sediments, an increased amount of Hg is circulating in the land-ocean-atmosphere system [3].

Research into Hg stable isotope biogeochemistry is offering new insight into the behavior of Hg [15–19]. Recent experimental work demonstrated fractionation of Hg isotopes during various processes (*i.e.*, biological [20–23] and non-biological physiochemical [24–36] processes) known to be a part of the global and regional Hg biogeochemical cycles. Large variations of both mass-dependent (MDF, represent as δ^{202}Hg) and mass-independent fractionation (MIF, represent as Δ^{199}Hg) (range of ~10‰ for both) are found among different source materials on the earth [15–19]. Variations in the natural abundance of Hg isotopes have shed lights on many long-standing problems in Hg science including: (1) label of Hg isotope fractionation factors to discriminate important biotic and abiotic reactions [20–36]; (2) tracing potential sources of Hg in the environment compartments [37–57]; and (3) determination of environmental materials to reveal specific geochemical processes of Hg [58–72] (Fig. 2).

Since the first precise measurement of Hg isotopes in natural samples in 2000 [73], to the Special Issue titled with "Advances in

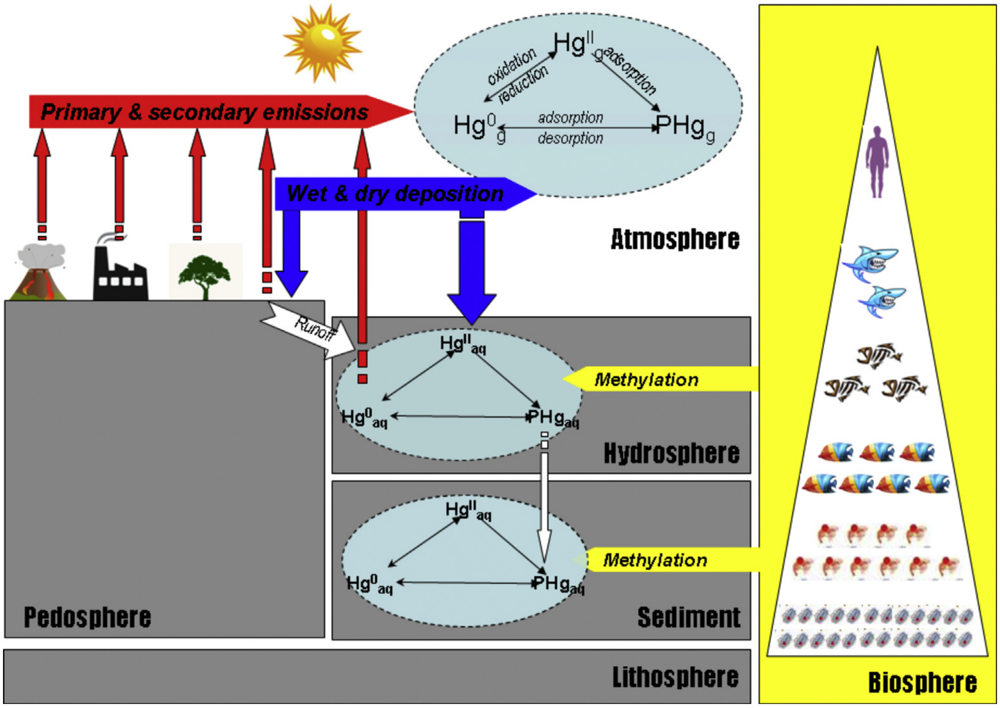

Fig. 1. Conceptual view of the global Hg biogeochemical cycle.