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A Digest-purge-trap method for Mercury Isotope Measurements of Natural Carbonates

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Sedimentary carbonate rock is a potential archive of mercury cycling in freshwater and seawater. However, the ultra-low mercury content in carbonate rocks, such as marine corals and terrestrial speleothems, hampers the exploration of their mercury isotopic composition. In this study, we developed a new digest-purge-trap method for separating and preconcentrating Hg from carbonates for isotope analysis. By performing multiple optimizations, we found that a mass ratio of 1:2:4 for carbonate sample: acid mixture: MQ followed by a reduction by 20% $SnCl_2$ at the 200 ml/min argon flow rate could give the best Hg recovery. This protocol as validated by the synthetic carbonate with varying Hg loadings and certified carbonate rocks had a Hg recovery of 95 ± 4% (n = 30, 1SD) and 101 ± 1% (n = 4, 1SD), respectively. Repeated measurements of synthetic carbonate spiked with different Hg standards exhibited no significant isotope fractionation during the whole preconcentration process. Our protocol has the advantages of a short sample processing time (~30 min), low procedure blank (39 pg of Hg, n = 2), and limited matrix interferences on Hg isotopic analysis. This protocol was then applied to natural carbonate rock samples with a recovery of 100 ± 6% (n = 22, 1SD). Coral carbonate skeletons in South China Sea had a mean δ^{202}Hg (representing mass-dependent fractionation, MDF) value of -2.82 ± 0.10‰ (n = 3, 2SD), which was significantly lower than co-located surface seawater. In contrast, their Δ^{199}Hg (representing mass-independent fractionation, MIF) values were comparable within analytic uncertainty. This suggests that the marine MIF rather than MDF has been conserved in coral skeletons This highlights the potential use of MIF signatures in fossil corals to reconstruct the past marine Hg cycling. A bulk stalagmite from South China displayed a mean δ^{202}Hg value of -1.26 ± 0.16‰ and a mean Δ^{199}Hg value of -0.19 ± 0.04‰ (n = 2, 2SD), which are similar to those of terrestrial ecosystems. This suggests that the Hg isotope signatures in stalagmite may represent those of terrestrial ecosystems, which in turn could be used to inform past atmospheric Hg deposition pathways over terrestrial ecosystems.