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Editorial: The marine iodine cycle, past, present and future

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Editorial on the Research Topic The marine iodine cycle, past, present and future

Iodine is a redox-active element that exists in multiple oxidation states and phases in the oceans, and is taken up and transformed by living organisms. The dominant forms in seawater are the dissolved anions iodide (Γ) and iodate (IO_3^-), along with smaller fractions of dissolved organic iodine (DOI), and particulate iodine (Chance et al., 2014). It plays an important role in atmospheric chemistry, impacting air quality and climate. Reaction with iodide-iodine at the ocean surface is a major sink for tropospheric ozone, a pollutant gas, and the main driver of the sea-air iodine flux. Understanding the distribution and drivers of marine iodine speciation is necessary to accurately quantify sea-air iodine fluxes and the marine ozone sink. Another key motivation for understanding the modern marine iodine cycle is the use of iodate-iodine abundance in ancient carbonate minerals as a proxy for oxygenation in the paleo-ocean (Lu et al., 2010). Refinement of this proxy to be more quantitative requires an improved understanding of the marine iodine cycle and how it responds to changes in redox conditions. Finally, iodine species, including anthropogenic radioisotopes, are also proposed as tracers of water masses and sedimentary inputs.

In this Research Topic, we bring together ten articles from the diverse research communities interested in the marine iodine cycle, including paleoceanographers, atmospheric chemists, and biogeochemists. The physical chemistry underpinning iodine's chemical speciation and transformations in the ocean is reviewed by Luther; this paper provides a theoretical basis for the field observations presented in this Research Topic.

Three observational papers report present-day iodine speciation in the Pacific, Atlantic and Indian Oceans. New profiles of iodide and iodate concentrations from the vicinity of station ALOHA (A Long-term Oligotrophic Habitat Assessment) in the subtropical North Pacific (§treangă et al., 2023) and station BATS (Bermuda Atlantic Time-series Study) in the Atlantic (Schnur et al., 2024) are in good agreement with observations made more than 30 years earlier (Campos et al., 1996), suggesting long term temporal stability in the distribution of iodine species. In addition, these two papers both use radiotracers as a powerful tool to probe iodine transformations. By incubating seawater spiked with ¹²⁹I, §treangă et al. find evidence for an intermediate iodine pool that is rapidly converted to iodate, and Schnur et al. are able to place an upper limit of <2.99 nM day⁻¹ on the iodide

oxidation rate. Meanwhile, Chance et al. present sea surface iodide concentrations from ~12°N to ~70°S in the Indian Ocean and the Indian sector of the Southern Ocean, a historically undersampled ocean basin. The measurements confirm the trend of higher iodide at lower latitude seen elsewhere (Chance et al., 2014). Two extremely high iodide concentrations (~1000 nM) were encountered in the Bay of Bengal and are thought to be associated with sedimentary inputs under low oxygen conditions.

Shi et al. and Jones et al. each present time series observations of iodine speciation in coastal, temperate waters. Time series measurements of iodine speciation are scarce, so these data sets will be invaluable for incorporating seasonal variation into iodine parameterizations and models. Shi et al. present measurements made over 4.5 years in a fjord in Nova Scotia, Canada, and demonstrate that existing parameterizations for sea surface iodide are not accurate for this location. Jones et al. explore the drivers of seasonal changes in surface water iodine speciation in the English Channel. They find that while iodate reduction is associated with seasonal changes in biological productivity, an additional, possibly sedimentary, process affecting the total iodine budget may also be operating.

Speciation of iodine in the marine atmosphere is considered by Droste et al., who report iodine speciation in aerosol samples collected during four cruises in the East and West Pacific and Indian Oceans. Soluble organic iodine (SOI) was a relatively constant proportion of the total (~20%), while iodide and iodate were inversely related. Iodate reduction was attributed to aerosol acidity, which is greater in smaller particles and air masses influenced by anthropogenic emissions. Meanwhile, iodide and SOI were correlated, suggesting that SOI may be a source of aerosol iodide.

Carbonate-iodine abundance (as I/Ca ratios) has been used as a paleoredox proxy across essentially the entire geologic time scale (e.g., Hardisty et al., 2014; Lu et al., 2018; Hess et al., 2023). In this Research Topic, three studies have scrutinized the validity of various carbonate archives as records of marine iodate levels. Specifically, the archives studied were planktic foraminifera (Winkelbauer et al., 2023), deep-sea bamboo and scleractinian corals (Sun et al., 2023), and ancient bulk carbonate rocks (He et al., 2022). An important finding is that, while benthic and planktic foraminifera from core-tops are known to record iodate variations of the overlying water column (reviewed in Hoogakker et al., 2024), foraminifera from plankton tows demonstrated littleto-no iodine incorporation regardless of local iodate abundance (Winkelbauer et al., 2023). This finding highlights the need for future work to address at what stage - between living, postmortem, and diagenesis - iodate is incorporated into foraminiferal tests. In contrast, Sun et al. are the first to demonstrate abundant iodate incorporation in deep-sea corals across a range of localities. Deep-sea corals may thus prove to be an important, relatively high-resolution record of recent oxygen minimum zone (OMZ) dynamics. Finally, He et al. address the influence of diagenetic processes on I/Ca in bulk carbonate samples by directly comparing I/Ca to lithology in Devonian-aged bulk carbonate. In addition to proxy calibration, this study provides evidence for potential paleoredox variations across this critical interval in environmental and biological evolution.

Several papers in this Research Topic showcase new analytical techniques. Both Shi et al. and Jones et al. use ion chromatography to measure iodine species, including DOI. These methods are less labour-intensive than the electrochemical and spectrophotometric techniques that have commonly been used in the past, and their development allows higher temporal and/or spatial resolution studies to be conducted. <u>Streangă et al.</u> used anion exchange chromatography coupled with isotope dilution inductively coupled plasma mass spectrometry, which offers improved precision over conventional methods.

In summary, this Research Topic demonstrates the broad range of activity in marine iodine research. Analytical advances are allowing more extensive and detailed observations of iodine speciation, including less abundant but potentially important intermediate forms such as DOI, and helping to constrain the rates of iodine transformations. The I/Ca paleoredox proxy continues to be refined and applied across a wide range of time scales and carbonate archives.

Author contributions

RC: Writing – original draft, Writing – review & editing. GC: Writing – original draft, Writing – review & editing. DH: Writing – original draft, Writing – review & editing. AM: Writing – original draft, Writing – review & editing.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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