Questioning Dark Oxygen Production in the Deep-sea Ferromanganese Nodule Field

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Previous studies have concluded that the natural process where oxygen is consumed as decomposition of organic matter that supplied from shallow waters occurs on the deep-sea floor. Sweetman et al.[1] presented the surprising observation that deep-sea ferromanganese nodules generate oxygen, which they labelled as dark oxygen production. The authors claimed that oxygen was generated through the electrolysis of seawater by ferromanganese nodules. If true, it represents the discovery of a significant unknown energy source. Consequently, it may have an impact comparable to that of the discovery of submarine hydrothermal systems and the ecosystems that live there. However, regarding this interesting discovery and claim, I raise the following three main concerns: (1) the lack of evidence for electrolysis, (2) the improbability of the energy source, and (3) inconsistency with existing research.

1. Lack of evidence for electrolysis

During the electrolysis of water, the oxygen generation reaction on the anode side proceeded simultaneously with the hydrogen generation reaction on the cathode side. Sweetman et al.[1] confirmed oxygen generation in an “ex situ” experiment using ferromanganese nodules. Based on this, the authors presumed that the cause of oxygen generation was ferromanganese nodules. If this assumption is correct, it is inevitable that hydrogen generation will also occur simultaneously within the ferromanganese nodules, which must be detected. However, the reason for hydrogen generation has not yet been investigated or confirmed.

Furthermore, during seawater electrolysis, chlorine is generated simultaneously with oxygen on the anode side, depending on the voltage applied during the electrolysis[2]. If this could be confirmed, it would provide strong evidence of electrolysis as a cause of dark oxygen production (DOP).

2. Improbability of the energy source

Although the authors used the presence of voltage potentials on the surface of ferromanganese nodules as evidence of electrolysis, electrolysis requires energy in addition to a potential difference. Water electrolysis requires 237 kJ/mol H_2O (474 kJ/mol O_2) of energy even under thermodynamically ideal conditions, and the voltage of 1.23 V is only the theoretical minimum decomposition voltage derived from this energy requirement.

If DOP of 1.7–18 mmol O_2/m^2/day is actually occurring, the energy required for it could reach 8.53 kJ/m^2/day. This value is comparable to the crustal heat flux at almost all ocean floors except near the mid-ocean ridges (4.32–8.64 kJ/m^2/day)[3]. It would have been surprising if such a large energy source had been overlooked in the long history of ocean observations.

One possible process that produces electrical energy on the seafloor is a redox reaction. It has been confirmed that electrical energy is generated in seafloor hydrothermal vents, where reducing hydrothermal fluids and oxidising seawater coexist[4]. However, unlike sulfide chimneys, which precipitate from hydrothermal fluids, ferromanganese oxides/hydroxides, which comprise ferromanganese nodules and crusts, are minerals formed by precipitation from oxidised seawater or relatively oxidised pore water in surface sediments[5]. Thus, these minerals are in equilibrium with the seawater, resulting in the fact that nodules and crusts remain stable on the seafloor for tens of million years[5]. Consequently, it is unlikely that ferromanganese nodules generate large amounts (large fluxes) of energy through redox reactions with seawater.

Furthermore, ferromanganese nodules are found only in waters with low bioproductivity, resulting in a poor supply of organic matter[6]. Therefore, a supply of biogenic reducing substances cannot be expected, and it is highly unlikely that exergonic redox reactions large enough to match crustal heat fluxes occur on the surface or inside the ferromanganese nodules.

3. Inconsistency with existing research

Sediment community O_2 consumption (SCOC) observations:

Studies on the oxygen uptake associated with organic matter decomposition on the seafloor have been active since the 1970s[7]. These studies, including the study by Sweetman et al.[1], placed isolated chambers on the seafloor to measure the changes in oxygen concentrations. To date, no anomalous oxygen generation has been reported in the enormous amount of research conducted over more than half a century, including in and around the ferromanganese nodule field.

A recent data compilation confirmed that all Sediment community O_2 consumption (SCOC) data show a clear exponential decrease with increasing water depth[8]. This is consistent with the fact that, except for areas such as seafloor hydrothermal vent sites, the deep ocean (including nodule distribution areas) biosphere is supported by scarce photosynthetically derived organic matter supplied from the shallow ocean[9].

The DOP flux reported by Sweetman et al.[1] was one to two orders of magnitude higher than that of SCOC, which is almost the only oxygen-consuming process in the deep sea. It is unlikely that such distinct oxygen production has been missed by researchers who have carefully observed oxygen concentrations on the seafloor for over fifty years.

Measurements of SCOC in several ferromanganese nodule distribution zones, including the Clarion–Clipperton Zone (CCZ), have also been conducted by research groups other than the authors of the DOP paper[10-14]. These results are consistent with previous data on SCOC values reported for deep-sea areas (Fig. 1). This suggests that either oxygen generation from ferromanganese nodules has a negligible impact on biological activity, or that no oxygen is generated.

Interestingly, studies in the CCZ, in which the lead author of the DOP paper is himself an author, also reported SCOC data consistent with the above compilation results (Fig. 1)[15,16]. If a DOP exists, these papers should be corrected (If there is more oxygen in the chamber at the end of the measurement than at the beginning, the SCOC cannot be estimated).

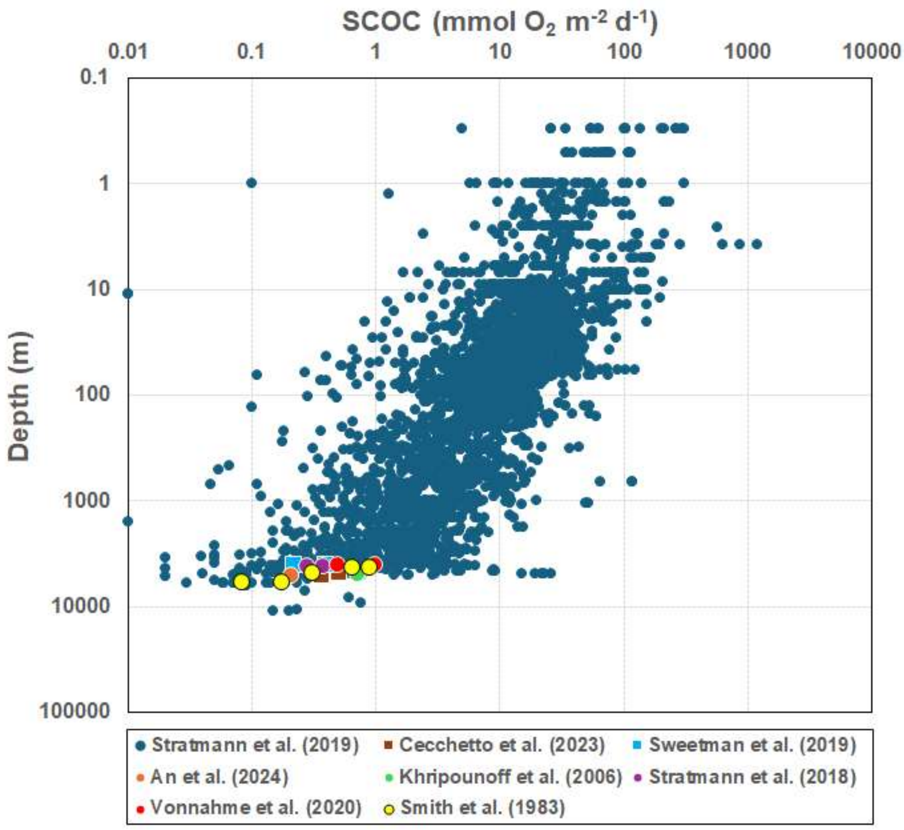

Fig. 1. SCOC vs. water depth plot for compiled data[8]. Data from ferromanganese nodule fields are plotted separately for comparison.

Ocean geochemistry

The measurement of oceanic oxygen concentration has also been a popular global research topic for a long period[17]. Recently, the GEOTRACES project (https://www.geotraces.org/) has actively measured various elements and isotopes other than oxygen, and the understanding of ocean circulation has improved.

These studies have revealed that the deep seafloor is an oxygen-rich environment and that oxygen in the deep sea is supplied by the subduction of surface water in the Arctic and Antarctic regions[18]. In fact, the observed distribution of the concentration of oxygen in ocean bottom water supports this hypothesis (Fig. 2)[6], that is, the concentration is highest in the Antarctic Ocean and the North Atlantic Ocean, where subduction of surface water occurs, and it decreases further away from these locations. This indicates that the impact of DOP on the oxygen concentration in the ocean is negligible or that such oxygen production does not occur in the first place.

The amount of oxygen supplied to the deep sea by the sinking surface water in the Arctic and Antarctic regions is estimated to be 3×10^{14} mol O_2/year[18]. This is thought to be distributed throughout the entire deep-sea (1×10^{14} m^2)[19], and thus the amount of oxygen supplied by ocean circulation to the deep seafloor is estimated to be 3 mol O_2/m^2/year. If the authors' estimate of the amount of DOP is correct, the amount would be 0.6 to 6.6 mol O_2/m^2/year. This would have the same level of impact on the deep ocean of the manganese nodule field, including the CCZ, as oxygen is brought to the deep sea via ocean circulation.

Therefore, if the DOP level that the authors claim occurs universally, it should have a significant impact on the oxygen concentration in the deep water of nodule distribution areas, including the CCZ,. However, the existence of such areas of high oxygen concentration have thus far not been identified,. In addition, no areas of abnormal oxygen concentration have been observed in the CCZ NORI-D area (https://www.eisconsultationnauruun.org/). This clearly indicates that the impact of DOP on oceanic oxygen concentration levels is negligible, or that such oxygen generation does not occur in the first place.

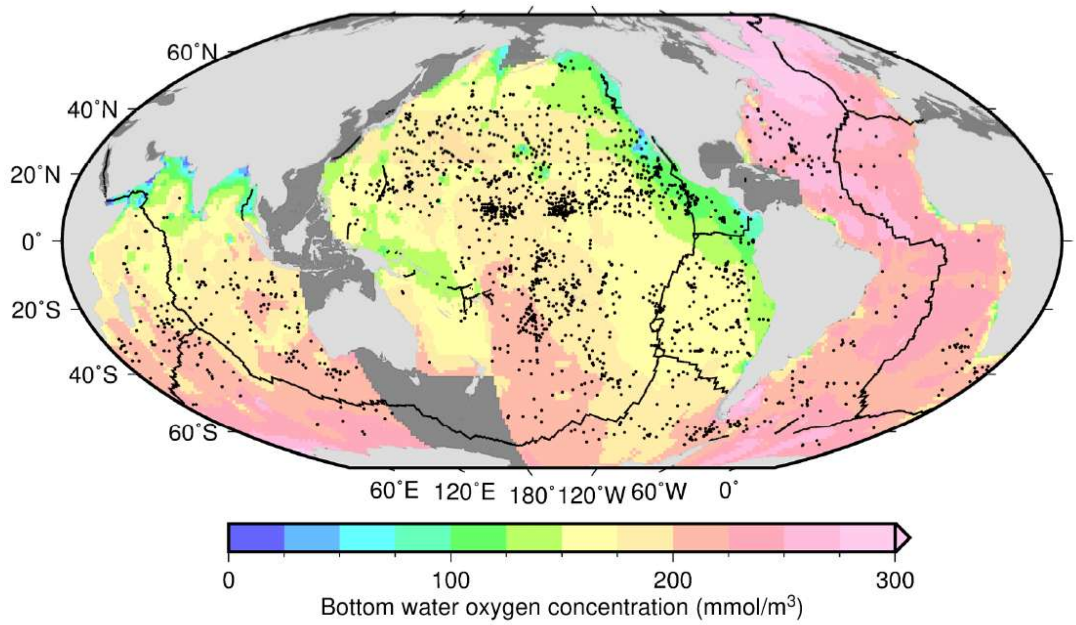

Fig. 2. Map showing bottom water oxygen concentration, with nodule occurrence as black dots (from Dutkiewicz et al.[6]).

Climatologists and oceanographers have long warned that global warming will reduce the oxygen concentration in the ocean, which will have a significant impact on the marine ecosystem[20]. Furthermore, recent simulation studies of ocean circulation have shown that global warming is weakening the Atlantic meridional overturning circulation, which is the main pathway responsible for oxygen supply to the deep ocean. If global warming continues, the sinking of surface water in the Atlantic Ocean may cease in the next few decades[21]. Based on this knowledge of the impact of ocean circulation on deep-sea oxygen concentrations, it is clear that the weakening or halting of ocean circulation will lead to a significant decrease in oxygen concentrations on the deep seafloor, and this impact will undoubtedly cause irreparable damage to deep-sea ecosystem. Thus, it is clear what humanity must do to protect marine ecosystems.

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