Is abyssal dark oxygen production even possible at all?

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Physical principles need to be respected when interpreting controversial findings such as the production of abyssal oxygen. Such extraordinary claims must be analysed carefully before a large research effort is mounted and valuable human and financial resources are wasted based on flawed data. We are aware of the sensitivities around polymetallic nodules and their potential value as a source of essential metals for various applications, in particular in batteries for electric vehicles. This utility is however in conflict with the value of polymetallic nodules to deep-sea ecosystems. Although that value is unclear, the potential for damage caused by deep seabed mining must be considered in a habitat where metabolic processes are slow and recovery from damage may take centuries.

The July 2024 issue of Nature Geoscience contained a brief communication suggesting the dark production of oxygen at the abyssal seafloor.[1] This claim was soon followed by healthy scepticism.[2–4] But those critiques missed the main point, namely, that the claimed abyssal production of dark oxygen, as proposed by Sweetman et al.,[1] is simply thermodynamically impossible. In addition, Sweetman et al.'s findings contradict earlier reports,[5] but this lack of agreement was not mentioned by them.

Sweetman et al.'s suggestion that polymetallic modules contained in sediments collected from the deep-sea act like batteries that split water[1] violates the 2nd Law of Thermodynamics. Batteries operate by converting the negative change in Gibbs free energy of a spontaneous process into electrical energy. In this case, the proposed batteries would be running on a reaction which goes uphill in Gibbs free energy,

$$2\mathrm{H_2O} \longrightarrow 2\mathrm{H_2} + \mathrm{O_2} \qquad \Delta G^{\circ} = +237\ \mathrm{kJ\ (mol\ H_2O)^{-1}} \qquad \text{Reaction 1}$$

which is thermodynamically impossible. It is not surprising that Sweetman et al.[1] could measure a voltage between different spots on the nodules' surfaces. Any two different conducting materials immersed in the same electrolyte will show a potential difference and, if connected to each other, will deliver a current. But this current is necessarily provided by a chemical reaction with a negative Gibbs free energy. Typical examples are the Volta pile, in which a Cu and a Zn wire are separated (and in contact with) a cloth soaked in brine, and a pair of any two different metals stuck in a lemon or a potato. If such a battery is responsible for the oxygen detected by Sweetman et al.[1], it would require the reduction at the positive electrode of an oxidant stronger than O_2, like permanganate, ozone or fluorine, none of which seems very likely.

Of course, batteries can be used to split water, but only by playing the role of a power supply to a water electrolyser, to which they would need to supply at least the thermodynamic minimum of 1.23 eV per electron exchanged in the reaction. In reality, due to the need to overcome activation energies for the reaction to proceed at a finite rate, electrolysers do not operate at less than ca. 1.5 V. For example, two AA batteries can be connected in series to deliver 3 V and power an electrolyser. Those 3 V are delivered by a chemical reaction with a negative Gibbs free energy (e.g., in a typical alkaline battery, this will be the oxidation of zinc by manganese (IV) oxide to produce zinc (II) oxide and manganese (III) oxo-hydroxide). The energy required to split water does not necessarily have to come from a chemical reaction. In a process analogous to that of water splitting, photosynthetic organisms harvest the energy required to produce glucose and oxygen from CO_2 and water from sunlight, which plays the role of the power supply. Some organisms follow a chemosynthetic route alternative to that of photosynthesis to synthesise carbohydrates and other carbon-containing molecules from CO_2 or CH_4. But as far as we know, none of these chemosynthetic processes releases O_2.[6] On the contrary, some of them, like the hydrogen sulphide chemosynthesis, consume oxygen.

Therefore, if what Sweetman et al.[1] actually meant is that a polymetallic nodule can act as an electrolyser, the energy required to go uphill in Gibbs free energy from H_2O to O_2 and H_2 would be appearing out of nowhere, which violates the 1st law of Thermodynamics. Sweetman et al.[1] claim that the energy required for seawater electrolysis would come "from the potential difference between metal ions within the nodule layers, leading to an internal redistribution of electrons", but the question remains: where does the energy to produce that potential difference and internal redistribution of electrons come from? What is playing the role equivalent to that of sunlight in photosynthesis? Even if we admit the existence of a hidden energy source capable of generating and sustaining such a potential difference, the voltages measured between different spots on the surface of a nodule are much too small (0.9 V at most[1]) to allow for water splitting, as has already been pointed out.[2]

There is one additional issue that was overlooked by Sweetman et al.[1] Seawater electrolysis is notably difficult due to the presence of chloride. Although the standard potential of the Cl_2/Cl^- couple is more positive (1.36 V) than that of the O_2/H_2O couple (1.23 V), the faster kinetics of the chlorine evolution reaction (CER):

$$2\mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2 + 2e^- \qquad \text{Reaction 2}$$

allow it to outcompete the oxygen evolution reaction (OER),

$$2\mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{O}_2 + 4\mathrm{H}^+ + 4e^- \qquad \text{Reaction 3}$$

resulting in the production of H_2 and Cl_2

$$2\mathrm{H}_2\mathrm{O} + 2\mathrm{Cl}^- \longrightarrow \mathrm{H}_2 + \mathrm{Cl}_2 + 2\mathrm{OH}^- \qquad \text{Reaction 4}$$

when attempting to electrolyse a chloride-containing aqueous solution. For that reason, and despite seawater being a much more abundant and stable resource than scarce and fluctuating supplies of fresh-water, current water splitting technologies require access to the latter. The observations reported by Sweetman et al. not only suggest that the material in the nodules is capable of splitting seawater at a voltage smaller than the minimum imposed by thermodynamics, but it is also uniquely capable of oxidising water to oxygen in the presence of chloride without evolving chlorine. None of these two problems is going to be improved by the high pressures and low temperatures of the abyssal depths. The dependence of the Gibbs free energy of any process on T and P is given by:

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \qquad \text{Equation 1}$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \qquad \text{Equation 2}$$

Because water splitting converts 2 mol of liquid water into 3 mol of gas (Reaction 1), it is associated to a huge change in volume. In other words, according to Eq. 1, it will result in a large increase of the (positive) reaction's Gibbs free energy. Although the reaction is associated with a positive change in entropy that should result, according to Eq. 2, in a slightly less positive Gibbs free energy at the low abyssal temperatures, this will be more than overcome by the large increase in ΔG due to the higher pressure. Furthermore, that increase will not be as large for Reaction 4 as for Reaction 1, because in the former 2 mol of liquid water become 2 mol of gas. Any eventual improvement in the kinetics of the OER at abyssal pressure and temperature is irrelevant, because kinetics cannot make possible what is thermodynamically impossible.

Ascribing a novel and potentially critical function to polymetallic nodules will alter the already heated debate around the projected impact of deep seabed mining and therefore needs to be scrutinised carefully before it is used to inform decisions. Evaluation of claims with such a high potential to influence extremely important claims must be done with respect to well-established scientific knowledge and, quoting Einstein, thermodynamics is "the only physical theory of universal content which [we] are convinced that [...]will never be overthrown".[7] Unless the presence of some very strong oxidant or of a hidden energy source is demonstrated, the claim of abyssal dark oxygen production is thermodynamically impossible, as shown by the reasoning above. If such oxidant or energy source cannot be identified, further investigation of an impossible process can negatively affect the way in which scientific findings inform that decision-making process.

Competing Interests

The authors declare no competing interests

References

1. Sweetman, A. K. *et al.* Evidence of dark oxygen production at the abyssal seafloor. *Nat Geosci* **17**, 737–739 (2024).
2. Denny, A., Svellingen, W. & Trellevik, L.-K. L. (PDF) Review of 'Evidence of Dark Oxygen Production at the Abyssal Seafloor' by Sweetman et al. https://www.researchgate.net/publication/383037889_Review_of_Evidence_of_Dark_Oxygen_Production_at_the_Abyssal_Seafloor_by_Sweetman_et_al?channel=doi&linkId=66b9a3908f7e1236bc508962&showFulltext=true#fullTextFileContent (2024) doi:10.13140/RG.2.2.30239.37289.
3. Voosen, P. Claim of seafloor 'dark oxygen' faces doubts. *Science* **385**, 1258–1259 (2024).
4. Downes, P. *et al.* Contributions to the discussion of novel detection of dark oxygen production at the abyssal seafloor. (2024) doi:10.31223/X5WB0X.
5. Khripounoff, A., Caprais, J.-C., Crassous, P. & Etoubleau, J. Geochemical and biological recovery of the disturbed seafloor in polymetallic nodule fields of the Clipperton-Clarion Fracture Zone (CCFZ) at 5,000-m depth. *Limnol Oceanogr* **51**, 2033–2041 (2006).
6. *Fundamentals of Ecosystem Science, Second Edition* (Academic Press, 2021). doi:10.1016/B978-0-12-812762-9.00005-8.
7. Albert Einstein. Autobiographical Notes. in *Albert Einstein: Philosopher-Scientist* (ed. Schilpp, P. A.) (Library of Living Philosophers, Evanston, Ill, 1949).