

## SUPPLEMENTARY MATERIALS OF

### **“The Past to Unravel the Future: Deoxygenation Events in the Geological Archive and the Anthropocene Oxygen Crisis”**

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#### **1- ECOSYSTEMIC RESPONSE TO THE PRESENT OCEAN DEOXYGENATION**

Oxygen is involved in biological and biogeochemical functions and influences life processes, from genes to properties of ecosystems (Breitburg et al., 2018). Also, deoxygenation reduces survival and growth and alters the organism's ethology (Levin et al., 2003; Diaz and Rosenberg, 2008; Rabalais et al., 2014). It causes difficulties in reproduction, such as interference with gametogenesis, neuroendocrine function, and hormone production (Thomas et al., 2015), that ultimately affects the biological population. Furthermore, oxygen deficiency affects the vision of organisms (McCormick and Levin, 2017) and confines aerobic organisms to the oxygenated part of the water column, altering migrating behavior, hugely shaping the predatory-prey dynamics (Breitburg et al., 2002), and, ultimately, the food web. One of the main challenging effects to constrain in the marine ecosystem is the response to multiple stressors (Glober and Baumann, 2016; Breitburg et al., 2015), such as warming, deoxygenation and acidification. The most glaring and impacting mechanism is that the warming is increasing the metabolic oxygen demand, while deoxygenation is reducing oxygen supply (Breitburg et al., 2018). The CO<sub>2</sub> enrichment in the seawater, which is also causing Ocean acidification, is a by-product of respiration, which is increasing following the warming (Breitburg et al., 2015). Also, warming and deoxygenation are predicted to reduce the maximum size of several fish taxa, reducing the productivity of fisheries and their economical values (Pauly and Dimarchopoulou 2022). Wind-driven upwelling systems in shelf settings are intensifying following the warming of the atmosphere, increasing marine productivity and expanding the Oxygen Minimum Zone (OMZ), the latter even becoming more acidic (Feely et al., 2008). Acidification coupled with deoxygenation can also decrease the metabolic response of invertebrates to bacterial infection (Mikulski, 2000), and have a negative effect on larvae and juvenile stage (Glober and Baumann, 2016), thus decoupling the link between increasing primary productivity and the proliferation of organism occupying a superior level in the food web.

#### **2- MODERN DEOXYGENATION SETTINGS**

The first case is marginal and/or silled lagoonal embayment systems that have a restricted water exchange with the open seas and can rapidly respond to changes in freshwater influx, evaporation, and nutrient

enrichments (Fig. 6). Elevated evaporation contributes to the formation of hypersaline water that sinks to the bottom and creates stratification, which can be enhanced by runoff and precipitation (Fig. 6). Examples of this environment are the marine karstic lakes of Mljet (42°47' N, 17°21' E; Adriatic Sea) (Wunsam et al., 1999; Sondi and Juračić, 2010) and the silled Etoliko lagoon (38°27' N, 21°20' S; Western Greece) (Koutsodendris et al., 2015). Due to their proximity to the coast, these restricted and marginal basins can be affected by eutrophication, which can further increase bottom deoxygenation (Fig. 6).

Other brine-filled basin also occurs far away from the coast; different from lagoons, in these basins brine formation derives from the dissolution of evaporites outcropping on the sea floor; however, they are equally able to create a permanent pycnocline (Fig. 6) and the consequent stratification. Some examples of this environment are the Orca Basin (Gulf of Mexico; Tribovillard et al., 2009), the Bannock Basin (Mediterranean Sea; Negri, 1996) and the Shaban Deep Basin (Red Sea; Seeberg-Elverfeldt et al., 2005).

Other than by increasing the bottom water salinity and density, many marine marginal basins undergoing stratification are those receiving a relatively larger proportion of continental over marine waters, therefore being sensible to deoxygenation. This is the case of the Northern Adriatic Sea, a shallow basin with a maximum water depth around 50 m receiving the Po River runoff, which drains the heavily anthropized North Italy (Justić et al., 1987). Also, the Chesapeake Bay, on the NE coast of North America (39°32'35.02" N -76°04'32.02" W), is usually reported as one of the most outstanding cases of eutrophication-driven deoxygenation in marginal and restricted settings (Kemp et al., 2005). In the restricted and marginal basins, also the role of wind is crucial, as in the case of Tokyo Bay. In this shallow setting (average water depth of 15 m) the wind blowing from the northeast enhances the exchange with the open Ocean; conversely, the wind blowing from the southwest suppresses the exchange with the open Ocean, promoting deoxygenation. However, if the southwest wind exceeds the threshold of  $10 \text{ m s}^{-1}$ , a recovery from the hypoxia can occur (Sato et al., 2012; Nakayama et al., 2010, 2013). Stratification-driven deoxygenation is also occurring in fjord systems, where stratification, due to the less dense superficial waters provided by runoff, is enhanced by the seasonal ice formation, which creates dense brine sinking beneath the fresher (and lighter) water mass (Dugan et al., 2011).

Marginal basins can be quite large, as is the case of the Baltic Sea, characterized by a narrow gateway connected to the marine Nordic Sea and by a high freshwater input from the numerous rivers draining the Scandinavian peninsula and Northeastern Europe. The freshwater mainly enters from the north-eastern area flowing west and southward and exit through the Danish strait into the North Sea, while marine water comes from the North Sea to the Danish strait. The density difference of the water column results in stratification of the water column separated by a halocline located at ~56 m. The increase in human-induced eutrophication and the warming trend during the last century triggered deoxygenation events by stimulating primary productivity and stratification, respectively (Cartensen et al., 2014).

Silled basins typically develop anoxic bottom waters. The largest, deeper, and best example of a silled, anoxic and stratified basin is the Black Sea (2200 m water depth). Below 100-150 m, the Black Sea is euxinic and devoid of metazoan life (Tyson and Pearson, 1991). In this setting, the stratification is due to the narrow and shallow sill at the Bosphorus Strait, which limits the exchange of marine water and by the huge continental runoff which provides freshwater. Due to the expansion of urban agglomerate and industrial development, the nutrients loading of the Black Sea is higher than that commonly observed in the coastal zone (Wollast, 1998), causing large phytoplankton bloom that only contributes to increasing the organic carbon accumulation in the sediment (Pitcher et al., 2021), but it is not responsible for oxygen consumption, which is already low due to stratification. A similar case is represented by the marginal Cariaco Basin (1400 m water depth), a tectonic depression on the Venezuela continental shelf. This basin is characterized by several sills located around 120 – 150 m depth, which limit the deep-water exchange favoring deoxygenation (Pitcher et al., 2021).

A completely different environmental setting is that of the OMZ occurring below the photic zone and related to the remineralization of the sinking organic matter (Fig. 1 and Fig. 6; Helly and Levin, 2004). These zones are typically nutrient-enriched due to the natural upwelling of deep waters. Historically, this mechanism has provided food and economic resources to the population inhabiting the adjacent coasts, because of the high abundance of fish. However, deoxygenation can be considered a harmful by-product depending on the magnitude of export products (Schimmelman et al., 2016). If the OMZ impinges the sea floor, benthic life is mostly suppressed, and the preservation of organic carbon is enhanced. The most important OMZ impingements can be found along the slopes in the Eastern Pacific Ocean, South-eastern Atlantic and Northern Indian Ocean (Fig. 1). From 1960 onward, the OMZ expanded both vertically and horizontally and the trend is predicted to continue during the near future, under the climate change.

### **3 - PALEOXYGENATION PROXIES**

A suite of different tools can be used for reconstructing past oxygen content at the sea bottom and in the water column. The paleo-oxygen proxies can be divided in two group: biological and geochemical.

The main biological proxy is the benthic foraminiferal assemblage, since these organisms live in and on the sediment bottom and their abundance and variation in the assemblage reflect the oxygen content at the bottom (Murray, 2006). Recently, a transfer function to convert features of benthic foraminifera assemblage in dissolved oxygen value has been proposed (Kranner et al., 2022). The feature of the external wall, such as the dimension and concentration of the pores, can provide further information about the oxygen content (Kaiho, 1994; Tetard et al., 2017; Kranner et al., 2022).

The geochemical proxies can be further divided in organic and inorganic. The organic geochemical proxies, sometimes referred as biomarker, is represented by the record of isorenieratene. This molecule is an aromatic carotenoid produced by the anaerobic, photolithotrophic green sulphur bacteria belonging to the family Chlorobiaceae, that requires both sulphide and light. Therefore, the record of isorenieratene provides information about the vertical extent of anoxia in the water column. The inorganic geochemical proxies are represented by the redox-sensitive elements, the  $\delta^{13}\text{C}_{\text{carbonate}}$  and trace elements measured on foraminifer test. The redox-sensitive elements used in the paleo-oxygen reconstruction are Mn, I, Cr, Mo, Re, Fe U and V: these elements have different solubility and affinity at varying redox conditions in the sediment, which in turn are related to the redox condition during the sedimentation or early diagenesis (Piper and Calvert, 2009; Bennett and Canfield, 2020). The redox condition in marine sediments mostly reflect changes in the organic carbon respiration and the organic carbon flux to the seafloor; these parameters are reflected by  $\delta^{13}\text{C}$  of the benthic foraminiferal shell. The organic carbon shows a typical  $\delta^{13}\text{C}$  value (i.e., -22%), and the release of  $^{13}\text{C}$ -depleted carbon during the remineralization of organic matter mainly controls the  $\delta^{13}\text{C}$  distribution in the sediment pore-waters. Therefore, using different benthic foraminiferal taxa which live at different depth in the sediment (e.g., the shallow epifaunal versus the deep infaunal) is possible to reconstruct the  $\text{O}_2$  gradient in the sediment (Jorissen et al., 2007).

One of the most promising proxies for paleo-oxygen is the I/Ca measured on benthic foraminifera calcite. The rationale of this proxy resides in the redox-sensitive nature of iodine and its inorganic forms of dissolved iodine in seawater (i.e.,  $\text{I}^-$  and  $\text{IO}_3^-$ ): the ratio between  $\text{I}^- / \text{IO}_3^-$  has a reduction potential close to that of  $\text{O}_2/\text{H}_2\text{O}$ , therefore the I/Ca is thought to be sensitive to oxygen scarcity in seawater (Glock et al., 2014; Lu et al., 2010). Among the trace element on foraminifera, uranium is getting attention in its potential for reconstructing redox conditions. Uranium precipitates in any substrate in marine sediment during reducing condition (Anderson et al., 1989; Tribollivard et al., 2006), therefore reflecting the redox state (Gottschalk et al., 2020). The foraminifera calcite has a negligible amount of U in the crystal lattice compared to the authigenic coating, therefore the measurement of the U/Ca on foraminifera reflects oxygen concentration. Global and regional core top calibration between  $\text{U}/\text{Ca}_{\text{foraminifers}}$  and bottom oxygen content is available (Hu et al., 2023; Costa et al., 2023), allowing a semi-quantitative and quantitative reconstruction.

Proxy	Rationale	Environmental indication	Reference
Benthic foraminiferal assemblage	Taxa have different tolerance for oxygen deficiency	Oxic, sub-oxic, anoxic	Murray, 2006; Morigi et al., 2001; Jorissen et al., 2007
Benthic foraminiferal pores density and morphology	Pores serve as oxygen exchange channel with the surrounding environments	Quantitative, from 0 to 6.0 ml/l $\text{O}_2$	Kaiho, 1991; Kranner et al., 2022

Isorenieratene	By-products of anaerobic bacteria that requires both light and sulphide	Shallow euxinia in the water column	Passier et al., 1999; Nijenhuis and De Lange, 2000; Marino et al., 2007
Redox-sensitive elements	Different solubility along a redox gradient	Oxic, sub-oxic, anoxic	Piper and Calvert, 2009; Bennet and Canfield, 2020
$\delta^{13}\text{C}_{\text{carbonate}}$	Carbon fixation and respiration patterns	Oxic, sub-oxic, anoxic and redox-cline	Fontainer et al., 2017
Trace elements of foraminiferal shells	Different solubility along a redox gradient	Oxic, sub-oxic, anoxic	Anderson et al., 1989; Glock et al., 2014; Gottschalk et al., 2020

Tab. S1: Main proxies used in the paleoenvironmental reconstruction of past oxygen conditions.

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