



Down the thermodynamic ladder: A comparative study of marine redox gradients across diverse sedimentary environments



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ABSTRACT

The thermodynamic succession of electron acceptors used in microbial oxidation of organic matter and associated redox products lead to the vertical chemical zonation in diffusion-controlled marine sediments. The structure of this gradient is a key player in the recycling of organic carbon and nutrients in the marine environment. However, little attention has been given to the advection-dominated sedimentary systems where the co-existence of different reduced and oxidized chemical species is expected. In this study, performing multi-analyte Au/Hg voltammetric microelectrode profiling on cores from diverse sediment depositional settings in the Mediterranean Sea (lagoon, coastal marine, submarine canyon and shallow-water vent sediments), it is shown that there exists an excess of reducing species (H_2S , Mn^{2+} , Fe^{2+} and FeS_{aq}) in the advective shallow vent sediments compared to similar upper sediment sections of diffusion-controlled environments. The *ex-situ* upward diffusive flux of reduced species accounted for at least 26 percent of oxygen consumption in the shallow water vent sediments, and this figure is likely higher when *in-situ* advective fluxes and the oxidation of other known vent-derived reduced components are taken into account. In contrast, the upward fluxes of reduced species do not significantly contribute to oxygen consumption in the studied lagoon, coastal or submarine canyon sediments, where organic matter oxidation by oxygen likely dominates. A major implication of these findings is that the reduced substrate advection in shallow vents leads to a potential for chemoautotrophy in an otherwise oligotrophic marine system, whereas in diffusion-controlled sediments the vertical input of organic matter and its heterotrophic use is more important.

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1. Introduction

The sediment–seawater interface covers a majority of the Earth's surface. It is this steep gradient environment where exchanges of key chemical species (such as nutrients, iron, methane, nitrous oxide, etc) occur (Schulz and Zabel, 2006; Dale et al., 2011). Despite its importance, this benthic interface is still understudied mainly due to sampling difficulty and remoteness (Viollier et al., 2003; Le Bris et al., 2012). The current imperative to understand these environments is mainly driven by two factors. First, most of the organic matter arriving either from lands (Bianchi, 2011; Blair and Aller, 2012) or from the surface marine productive layer is remineralized in the surface sediments leading to the recycling of

carbon and nutrients (Sundby, 2006; Middelburg and Levin, 2009). Secondly, the early diagenetic reactions in the surface sediments influence the composition of the sedimentary material to be buried over geological timescales (Berner, 1980), which carries important proxy information for the periods in which it had formed.

From a biogeochemical viewpoint, a central feature of the surface sedimentary zone is the vertical oxidation–reduction gradient, which occurs due to the sequential use of electron acceptors by microorganisms to oxidize organic matter, the abiotic chemical reactions in sediments and transport processes (i.e. diffusion, bioturbation). As predicted by thermodynamics, the most often encountered sequence of electron acceptors is in the order of O_2 , NO_3^- , MnO_2 , FeOOH , and SO_4^{2-} . First brought to the attention of marine science by Froelich et al. (1979), this concept has been nicely termed as “thermodynamic ladder” by Bethke et al. (2011) for other geomicrobiological systems as well. The organic matter oxidation-driven stratification of chemical zones down core marine sediments was also defined as “biogeochemical

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paradigm" by Sundby (2006). These definition efforts point to the generality and usefulness of this concept in understanding natural systems. A prediction of this model is that just below the surficial sediments, mostly in a depth range of 1–10 mm for environments down to 1000 m depth, the redox conditions are anoxic and reducing, indicating that most sedimentary processes are actually occurring in the lower steps of the thermodynamic ladder. These considerations therefore have necessitated the use of tools that are capable of quantifying vertical changes in oxidants and reductants in high resolution.

In recent decades tools to measure sedimentary redox gradients have been developed but are actually underused at present. Pioneer works used amperometric microelectrodes to obtain sedimentary O_2 and H_2S gradients in coastal sediments (Jorgensen et al., 1979; Rasmussen and Jorgensen, 1992). Various electrochemical and optical techniques were also developed (see reviews by Kühl and Revsbech, 2001; Moore et al., 2009). In the late 90s multi analyte sensors have been developed, such as voltammetric gold amalgam (Au/Hg) probes capable of simultaneously quantifying O_2 , H_2S , Mn, Fe and several other redox species (Brendel and Luther, 1995; Luther et al., 2001). In the past fifteen years these probes were successfully deployed for research on continental shelf sediments (Luther et al., 1998), coastal waters and lagoons (Ma et al., 2007; Meiggs and Taillefert, 2011; Delgard et al., 2012), and anoxic-sulfidic basins (Konovalov et al., 2007). Still, most sediment voltammetric profiles reported in a particular study were confined to one type of environment, and most of these environments were diffusion-controlled marine sediments.

Meanwhile, an increasing number of studies have showed that exceptions to the ideal biogeochemical stratigraphy in marine sediments can be induced by advection of porewaters (Boudreau et al., 2001; Huettel et al., 2003). Several types of advection can occur, such as wave-induced porewater displacement that can influence oxygen dynamics in settings such as permeable shelf sands (Huettel et al., 1996, 1998; Reimers et al., 2004). Bioturbation is known to alter biogeochemical rates in the upper parts of the sediments (Meysman et al., 2006), while groundwater flow through sediments can change porewater geochemistry (Charette and Sholkovitz, 2006; Santos et al., 2012). Tidal flow also can induce co-occurrences of oxidized and reduced solutes in coastal sediments as shown by Taillefert et al. (2007) and Meiggs and Taillefert (2011) using an *in-situ* Au/Hg voltammetric profiler. A final type of advection is the upward seepage of cold or high-temperature fluids that originate from the deep subsurface, mostly bringing reduced solutes towards the upper parts of the sediment (de Beer et al., 2006; Grünke et al., 2011). Two or more of these types of advection can co-occur, adding to the complexity of sediment biogeochemistry.

In this context, this study is focusing on a comparative assessment of redox species distributions between diffusion-controlled, biogeochemically stratified marine sediments and a specific type of advective environment, i.e. coastal sediments affected by shallow water hydrothermal venting. Specific hypotheses to be tested are (1) due to advection, the sediments of the shallow hydrothermal environment are more reduced compared to their diffusion-controlled, biogeochemically stratified counterparts (2) the oxidation of advectively transported vent-derived reduced species can elevate diffusive oxygen fluxes in an oligotrophic coastal setting, and this rate may approach those in relatively organic-rich coastal sediments. In order to address these issues, multi-analyte Au/Hg voltammetric microsensor profiling is applied to different sediment cores sampled across diverse environments in the Mediterranean Sea, including previously understudied (submarine canyons, coastal lagoons) or virtually unexplored environments such as

sediments around shallow-water hydrothermal systems. While the detailed dynamics of each system will remain out of the scope of this study, the emphasis will be on a comparative assessment of the drivers of upper sediment porewater redox processes in different marine settings.

2. Materials and methods

2.1. Sediment sampling from diverse environments

The studied sedimentary regions, shown in Fig. 1a, can be grouped into two. The first group lies along a transect in the Northwestern Mediterranean Sea, starting from coastal lagoons of Southern France, passing through coastal marine sediments and extending down to 510 m depth in a submarine canyon (Fig. 1b). A second group of cores were sampled from the hydrothermalism-affected, shallow water sediments at Milos Island, Greece, in the Eastern Mediterranean Sea (Fig. 1c). All the sampling was performed with 100 mm diameter, 500 mm long plastic core liners, manipulated either by SCUBA for shallow depths or attached to a multicorer for deeper environments.

Cores representing organic-rich shallow lagoon environment were sampled from two sites in Southern France, Salse-Leucate and Canet (also known as Saint-Nazaire) Lagoons, in September 2012 at about 1 m depth. Salse-Leucate Lagoon is a relatively open system with three outlets to the Gulf of Lions. Canet Lagoon is an environment with a more restricted access to the sea (Fig. 1b) and subject to eutrophication (Mouillot et al., 2007). Another set of push-cores representing a more coastal, but not so shallow environment was taken in September 2012 from offshore Banyuls-sur-mer (southern France), at 37 m depth, by SCUBA diving. This environment is relatively organic-poor (0.5–1% organic matter, Dr. Audrey Pruski personal comm.) as compared to the lagoons nearby. Finally, as a representative of deep-water sediments, samplings were performed at the Lacaze-Duthiers submarine canyon, which is one of the submarine channels that links the continental shelf of the Gulf of Lions to the deeper basin. The head of the canyon starts at offshore Banyuls-sur-mer (Fig. 1), at about 300 m depth and the channel extends down to 1000 m depth. The sampling site was located at 510 m depth and the sediment samples were taken with a multicorer aided by live video feeds from a ROV (COMEX, Inc.) in May 2011.

As a representative of hydrothermalism-affected, advection dominated sedimentary environment, cores were taken around the shallow hydrothermal vents at Paleochori Bay, Milos Island, Greece. This environment is a sandy bay characterized by frequent spots of hydrothermal venting starting from depths of 3 m up to at least 300 m (Dando et al., 2000). The specific vent area targeted for this study was situated at 10 m depth at the eastern part of the bay. The surface sediment temperature associated with the hottest part of venting was close to 50 °C and the surface sediment temperature gradually decreased to 20 °C of the surrounding environment. Here, push-cores were collected by SCUBA in May 2012 along a transect whose center was the hottest area, and cores were collected at 50 and 150 cm away from this central area and from an unaffected area.

2.2. Voltammetric profiling of the sediment cores

The redox chemical species in the porewaters of the sediment cores were measured with a three-electrode voltammetric sensor setup with the gold amalgam (Au/Hg) voltammetric glass micro-electrode as the working electrode. These electrodes are capable of simultaneously measuring sedimentary redox species such as O_2 , HS^-/H_2S , $S_2O_3^{2-}$, S_x^{2-} , S^0 , Mn^{2+} , Fe^{2+} and qualitatively detecting the presence of soluble FeS_{aq} and Fe^{3+} (Brendel and Luther, 1995;

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