

## Absence of Redox Potential Discontinuity in Dark Submarine Cave Sediments as Evidence of Oligotrophic Conditions

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Redox potential measurement is used to demonstrate organic input reduction from the entrance to the inner parts (40 to 100 m) of three Mediterranean submarine caves. Redox potential discontinuity gradually decreases in the inner parts of the cave. Beyond 40 to 60 m inside the caves, sediments are characterized by high redox potentials (+400 to +500 mV) and no redox potential discontinuity exists at over 15 cm in depth. Such redox profiles are evidence of low oxygen consumption and low organic matter fluxes. Submarine caves appear to be oligotrophic enclosures in coastal productive environments and some convergences can be noted with deep-sea ecosystems.

### Introduction

Early studies on Mediterranean hard-bottom benthos showed that submarine caves were occupied by two zoned communities (Pérès & Picard, 1949; Laborel & Vacelet, 1958, 1959; Vacelet, 1966; Pérès, 1982). The semi-dark cave community, found in low light, consists of a rich assemblage covering the whole of the available substratum. The inner dark cave community is characterized by a drastic decrease in biomass (Gili *et al.*, 1986; Fichez, 1989) and substrate covering, which can be less than 10% (Harmelin *et al.*, 1985). This zoned faunal decrease has also been noted in soft-bottom cave communities (Monteiro-Marques, 1981). Shortage of trophic resources was hypothesized to be the main cause of this biological decrease (Harmelin *et al.*, 1985).

Fenchel (1969) first described redox potential discontinuity as an indicator of oxygenation or of the organic matter content of a sediment. Absolute values of redox potential are difficult to interpret (Zobell, 1946). However, they are considered to be an indicator of the distribution of oxidizing compounds, such as O<sub>2</sub>, and reducing compounds, such as H<sub>2</sub>S; interstitial fauna shows a marked response to this parameter (Fenchel, 1969; Whitfield, 1969; Jorgensen, 1977b). Temporal and spatial evolutions of redox potential give useful information in benthic studies (Whitfield, 1969; Pearson & Stanley, 1979; Graf, 1986; Plante *et al.*, 1989), especially in relation to sedimentary pattern and organic loading processes. Redox potentials have thus been measured to give information on the oxido-reduction conditions in cave sediments, which made it possible to

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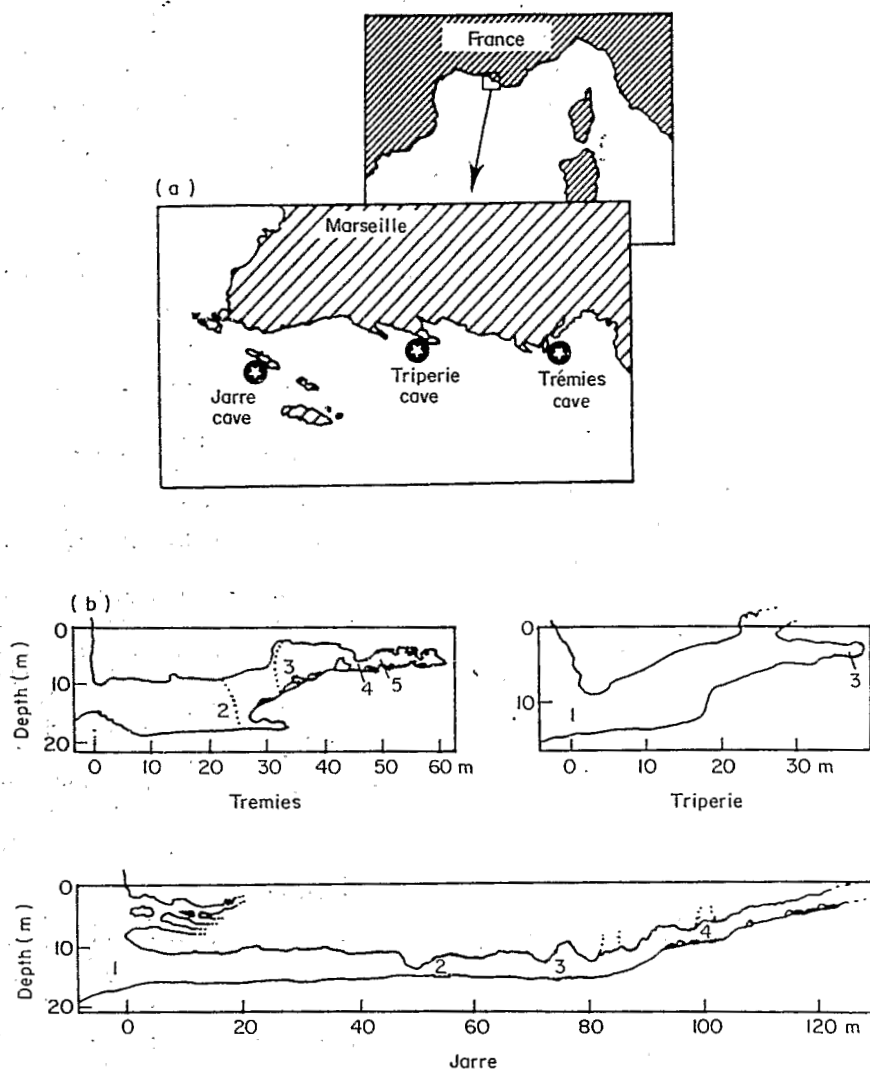


Figure 1. (a) Sampling area location, detailed map of the coastline between Marseille and Cassis and location of studied caves. Stars represent cave sites with associated names. (b) Topography of the three studied caves (vertical profile) with sampling station (numbers). Number 1 is for open sea sampling points, number 2 is for semi-dark area sampling points and numbers 3, 4 and 5 are for dark area sampling points.

suggest some theories about the importance of organic inputs and degradative processes occurring at the benthic boundary layer.

## Materials and methods

### Sampling area

Three submarine caves were studied along the Mediterranean coastline near Marseille (Figure 1). Each of these three caves opens at a depth of 15 m by a single entrance (blind cave) and present ascendant slopes. Blind caves differ from tunnel caves by a reduction

in water circulation and are therefore characterized by a stonger biological decreasing gradient (Riedl, 1966).

Trémies cave [Figure 1(a)] is 60 m long and 35 m at its widest. The entrance and outside bottom are composed of a mass of sediment-free fallen rocks. The floor of the semi-dark area (800 m<sup>2</sup>) is covered with a grey muddy sediment. The floor of the dark area includes rocks and large patches of brown muddy sediment and is separated from the semi-dark area by an 8- to 10-m rise (rocky step). Eighty per cent of mud is composed of fine particles (less than 63 µm) (Monteiro-Marques, 1981).

Jarre cave is more than 130 m long and less than 9 m wide. The first part is a 60-m long straight tunnel covered with grey muddy sediment (60–25% fine particles) (Monteiro-Marques, 1981). The second part, situated more than 65 m from the entrance, consists of an irregular narrow upward-sloping gallery covered with rocks, gravel and some brown muddy sediment patches.

Triperie cave is 40 m long and 10 m wide. The whole cave bottom is composed of hard substratum with the exception of two places. At the entrance, the hard bottom is partly covered with a sandy sediment bearing strong ripple marks. In the terminal dark part of the cave, 40 m from the entrance, a 2-m<sup>2</sup> patch of a 10-cm deep brown muddy sediment can be found.

#### Sampling

At each sampling point sediment cores (8–30 cm long) were hand-collected by SCUBA using transparent tubular plexiglass corers (inner diameter 2.7 cm). These corers were handled vertically to avoid any disruption in stratification. Determination of redox potential profile was performed on-board. The aim of this study was to observe whether any redox potential change could be noticed, and whether this could be correlated with the biological decrease. Sampling points were chosen along longitudinal transects from the entrance to the end of the three caves. Station 1 corresponds to entrance sediments, station 2 to semi-dark section sediments and stations 3 to 5 to dark section sediments.

#### Redox potential measurement

The  $E_H$  measurement was made immediately after coring in order to minimize temperature influence. The recording potentiometer (PVRTC pH meter Ponselle) was fitted with both a calomel reference electrode and a platinum measurement probe. The measurement probe was composed of a 30-cm long and 0.5-cm diameter metallic rod with a terminal platinum wire sealed in glass. The reference electrode was placed in the overlying water and the measurement probe, fixed to a stand, could then be slowly and carefully wound down into the sediment core. Potentiometer calibration was made with pH buffer solution for the reference electrode and +250 mV solution for the measurement probe. The +250 mV solution was used to control calibration stability between each measurement. The stabilization of redox potential measure, which could vary from a few minutes to more than 1 h (Frenchel, 1969; Plante *et al.*, 1989), was followed using a graphic recorder. In our case, the highest stabilizing times were reached in the redox potential discontinuity area (up to 20 min). Direct reading on the potentiometer was corrected for hydrogen reference by adding +250 mV (temperature = 15 °C).

#### Results

In Trémies cave, redox potentials recorded in the water and immediately above the sediment surface ranged from +378 to +540 mV [Figure 2(a) and (b)]. The semi-dark

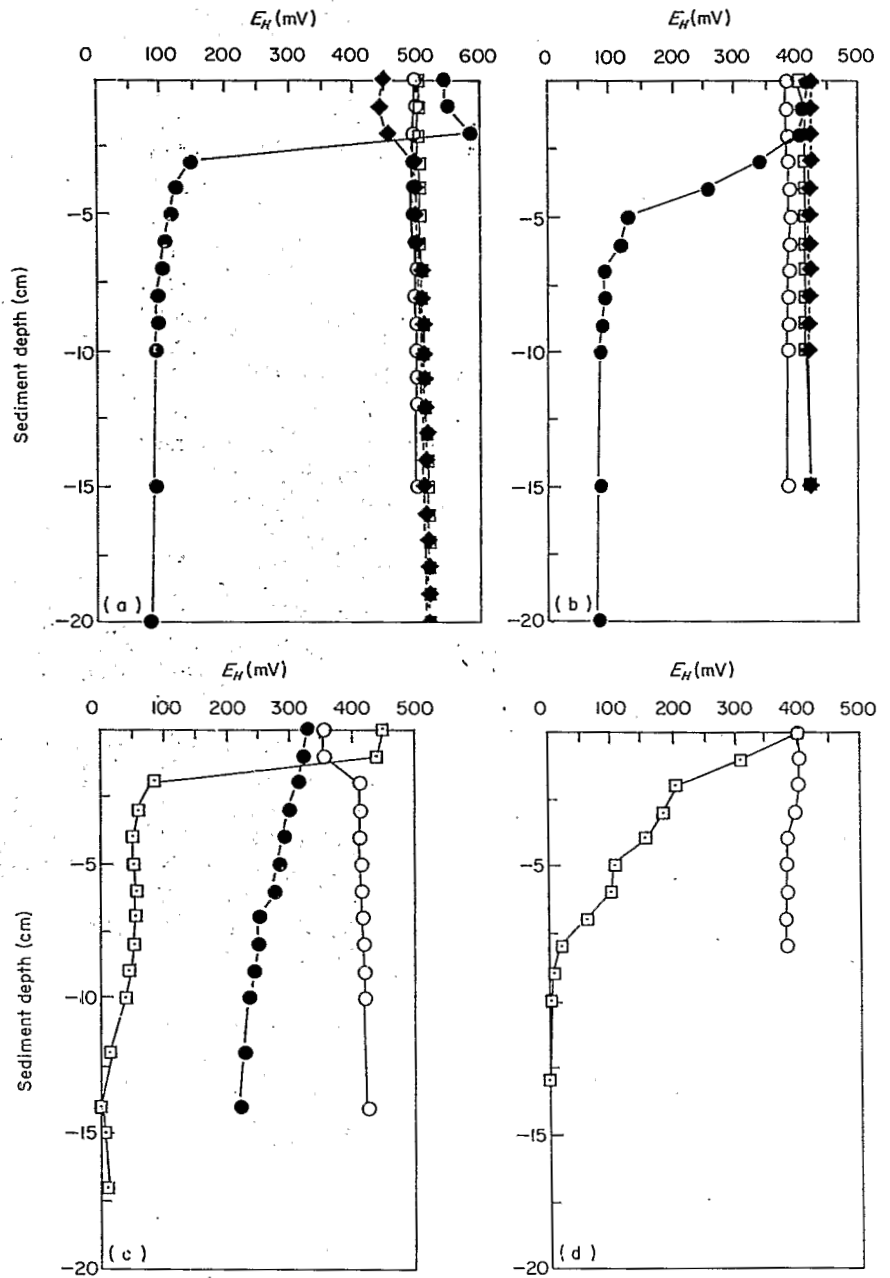


Figure 2. Profile of  $E_H$  values down the sediment column in (a) Trémies cave 14 May 1987, (b) Trémies cave 16 February 1988, (c) Jarre cave 16 February 1988, (d) Triperic cave 16 February 1988. Station 1 is located close to the entrance, station 2 is the semi-dark area and stations 3, 4 and 5 are in the dark area. —□—, Station 1; —●—, station 2; —○—, station 3; —□—, station 4; —◆—, station 5.

area sediment showed a well marked redox potential discontinuity between 2 and 5 cm in depth. Values decreased from +403 mV and +540 mV at 0 cm to +132 mV and +117 mV at 5 cm.  $E_H$  was +100 mV at a depth of 6–7 cm giving the upper limit for the

occurrence of free hydrogen sulphide and indicating anoxic layers. The dark area sediment presented straight-line profiles with high redox potential values ranging from +440 to +525 mV in May 1987 and from +377 to +430 mV in February 1988. Lack of any redox potential discontinuity appeared to be typical at any sampling point in the dark area.

Close to the entrance in Jarre cave a strong decrease in redox potential was recorded in the upper 2 cm (from +465 to +84 mV) [Figure 2(c)]. At the end of the semi-dark area 50 m from the entrance, sediment showed a low regular decrease in  $E_H$  values from +330 mV at the boundary layer to +226 mV at a depth of 15 cm. In the dark area (85 m from the entrance), the  $E_H$  sediment profile increased from +364 mV at the boundary layer to +413 mV at a depth of 1.5 cm and to +435 mV at a depth of 15 cm.

Superficial sediments from Triperie presented  $E_H$  values close to +400 mV in each station [Figure 2(d)]. At the cave entrance, values regularly decreased from +414 mV at a depth of 0.5 cm to +22 mV at 8 cm. Beyond 8 cm, a slow decrease led to a value of +3 mV at a depth of 13 cm close to the hard-bottom substratum. The  $E_H$  profile for Triperie dark area sediment was approximately linear, decreasing weakly from +404 mV at the surface to +375 mV at a depth of 8 cm.

### Discussion and conclusion

In cave entrances a redox potential discontinuity was observed at a depth of 2 cm delimiting an anoxic layer ( $E_H \leq +100$  mV). Both high sedimentation rates and low sediment porosity induced oxygen consumption and low oxygen diffusion leading to anoxic conditions. This redox potential profile is a general feature in low-energy coastal marine sediments which are characterized by a reduced environment covered by a thin oxidized surface layer (Fenchel & Riedl, 1970; Jorgensen, 1977b) and a large part of the degradation processes can occur through sulphate reduction (Jorgensen & Fenchel, 1974; Jorgensen, 1977a). A progressive decrease in  $E_H$  values, observed in the sandy entrance sediment of the Triperie cave, can be explained as resulting from both a high porosity of coarse-grained sediment which made a high oxygen diffusion rate possible and the recent rearrangement of sediment by strong hydrodynamic action which has been followed by a progressive recovering of reduced conditions.

Redox discontinuity was gradually attenuated in the semi-dark area and disappeared in the dark area giving evidence of the decrease of the inputs and the associated decomposition rates of organic carbon which leads to low oxygen consumption. In most isolated areas, low inputs (Fichez, 1989, 1990) prevented the formation of an anoxic layer and the development of anaerobic metabolism. Under such conditions degradative processes only occurred through aerobic metabolism (Van Es, 1984) and were mainly concentrated at the benthic boundary layer. These organic-limiting conditions support the biological and biomass decrease of cave communities. Under aphotic conditions benthic heterotrophic metabolism principally depends on organic inputs to the sea-floor which require lateral advection. Horizontal transport involves significant losses of particulate material, both through sedimentation and degradation of particles. Redox potential appears to be a good index of the mean oligotrophic state of this ecosystem as it provides information on long-term inputs of organic matter. Oxygen conservation in 15-cm deep sediment layers attests to the presence of carbon-limiting systems mainly encountered in deep-sea ecosystems (Emerson *et al.*, 1985).

Redox potential profiles comparable with those encountered in dark cave sediments have been registered in deep-sea Atlantic sediments (Daumas *et al.*, 1978). More recently

de Lange (1986) has pointed out the high nitrate concentration (meaning high redox potential) in an 8-m sediment layer in the Atlantic abyssal plain in slowly accumulating, pelagically deposited sediments (Emerson *et al.*, 1980) and he postulated an organic flux limitation. The low amount and the degradation state of the organic matter reaching the sediment interface exclusively support weak aerobic processes (Marty *et al.*, 1989). However, this analogy between redox profiles from deep-sea and cave sediments is obviously not proof of a real analogy between these two ecosystems because of the differences (e.g. temperature, salinity, pressure, sedimentation, organic matter composition) and heterogeneous conditions in deep-sea ecosystems.

However, the purpose of this study is to demonstrate that submarine caves appear to be strong oligotrophic enclosures in coastal environments. High  $E_H$  values and the lack of redox potential discontinuity attest to weak degradative processes and demonstrates that carbon-limiting conditions in dark oligotrophic caves result in a simplification of the biogeochemical processes. These conditions, associated with the channelled transport of resources from the open-sea productive waters to the inner non-productive waters of the cave, allow a simple evaluation of food cycling (in terms of carbon or energy for example). Submarine caves could then be considered to be interesting heterotrophic models of food-limited ecosystems and used to study the influence of oligotrophy on heterotrophic metabolism. Furthermore, results on cave investigations might be useful to studies on the energetic outflow and transformation processes from the neritic productive zone to the bathyal benthic system.

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