



GEOTRACES

Mediterranean Planning Workshop

4-6 October 2010, Nice, France



## EARLY DIAGENESIS AND BENTHIC FLUXES IN ADRIATIC AND IONIAN SEAS

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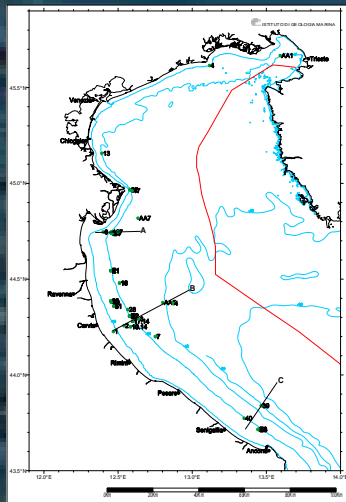
<sup>2</sup>Istituto Scienze Marine, CNR, Bologna, Italy

# Early diagenesis processes and benthic fluxes in the Adriatic and Ionian sea as resulting from various research projects carried out from 80s to present

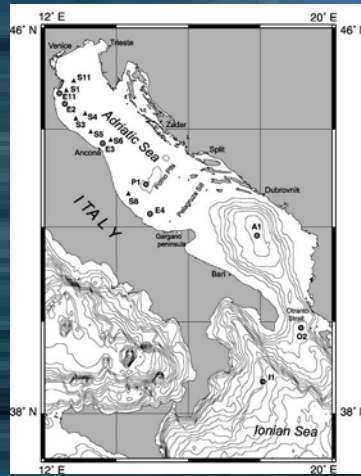
- Early projects of the Institute of Marine Geology of Bologna (Italy), (1980-1989) Giordani P., Hammond D., Frascari F.;
- MAST, (1995-1997) Giordani et al.;
- EUROMARGE, (1997-2000) Giordani et al.;
- PRISMA1, (1993-1996) Frascari F., Spagnoli F., Bergamini M.C., Marcaccio M.;
- PITAGEM, (2001-2004) Spagnoli F., Bartholini G., Giordano P.;
- VECTOR, (2006-2009) Spagnoli F., Giordano P., Ravaioli M.

# Sampling sites of previous researches

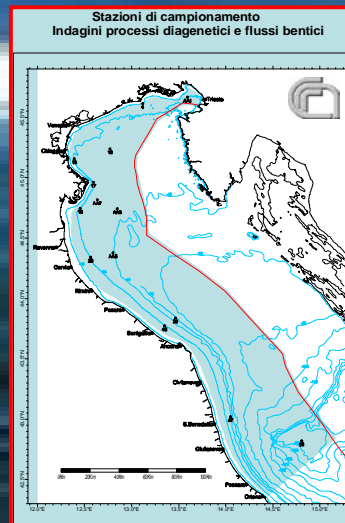
Old IGM-CNR projects



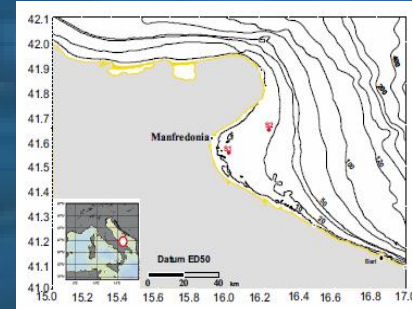
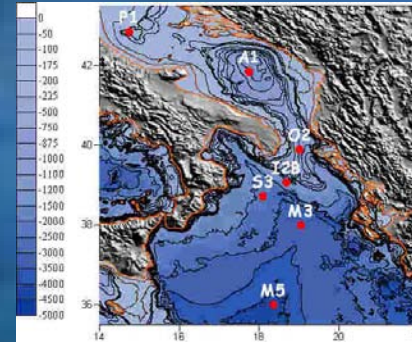
MAST, EUROMARGE



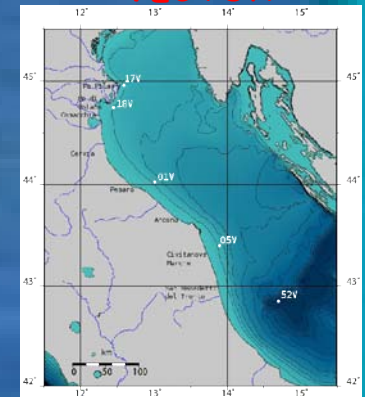
PRISMA1



PITAGEM



VECTOR



# Methods

- **Early diagenesis**

- Pore water and solid phase analyses in sediment cores;



ISMAR-CNR  
on deck laboratory



- **Dissolved benthic fluxes**

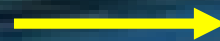
- Benthic chamber deployments;



ISMAR-CNR  
benthic chamber

- Core incubations on deck;

- Pore water profile modelization.



$$\frac{\delta C}{\delta t} = D_s \left( \frac{\delta^2 C}{\delta z^2} \right) - w(1+K) \left( \frac{\delta C}{\delta z} \right) + R_z + I_z = 0$$

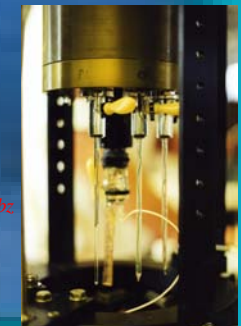
←  $R_z = \text{constant}$

←  $R_z = \text{quadratic}$

←  $R_z = \text{exponential}$

$$C = C_0 + a_1 z + a_2 z^2$$

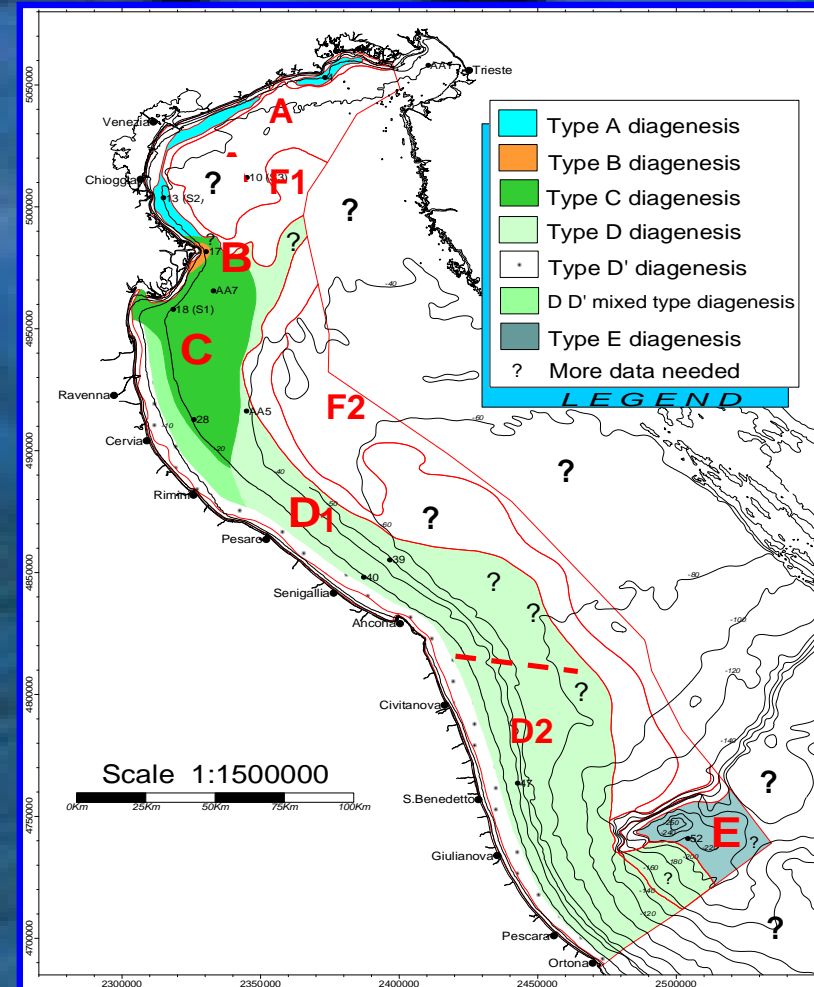
$$C = C_\infty (1 - e^{-bz}) + C_0 e^{-bz}$$



# Map of the main Adriatic diagenetic environments

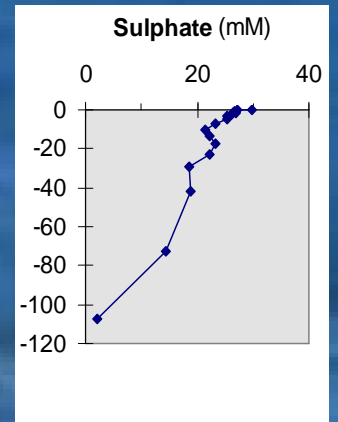
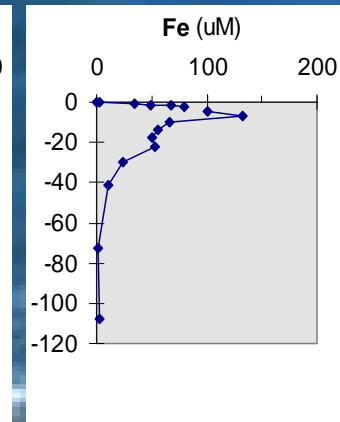
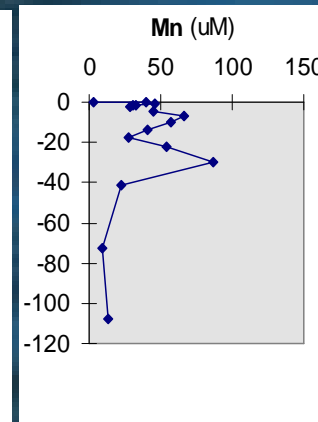
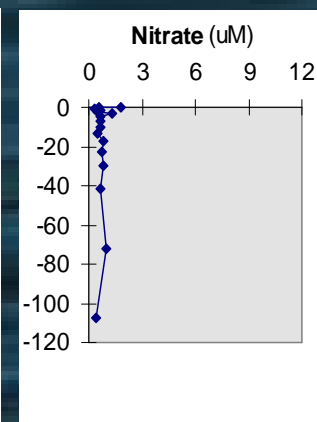
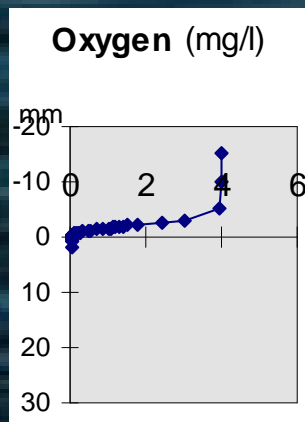
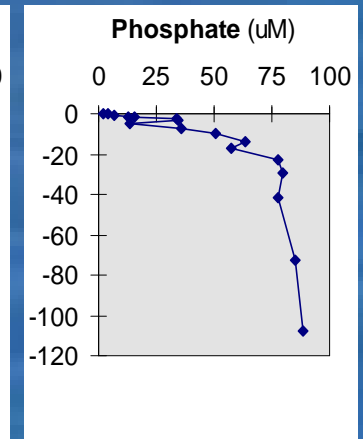
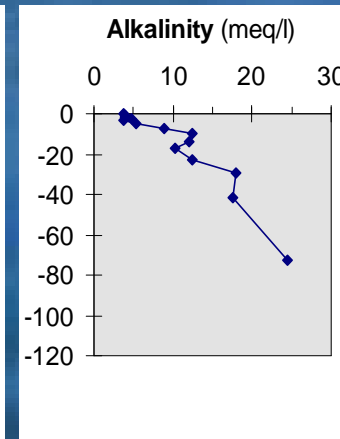
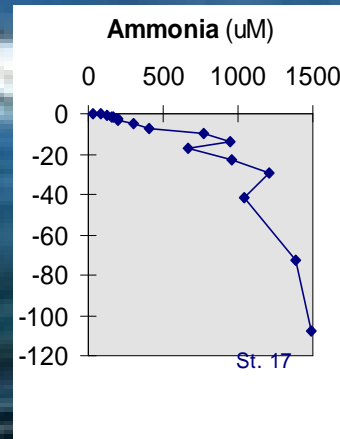
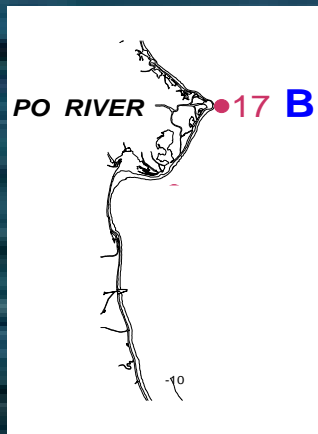
Various diagenetic environments resulted from different:

- particulate and dissolved continental inputs;
- distances from main sediment sources (mainly the Po River);
- bottom sediment composition (carbonatic or silicoclastic);
- organic matter (fresh marine and old continental organic matter);
- depths (more or less resuspension events, increasing pressure with depth);
- oxygenation of water column.



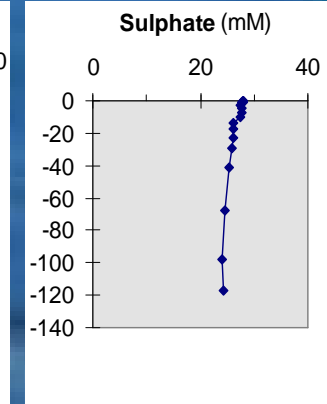
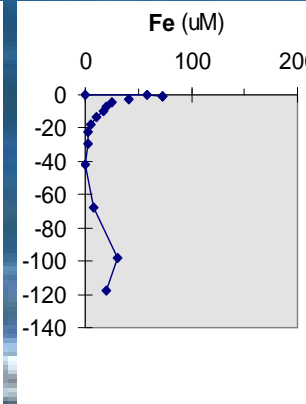
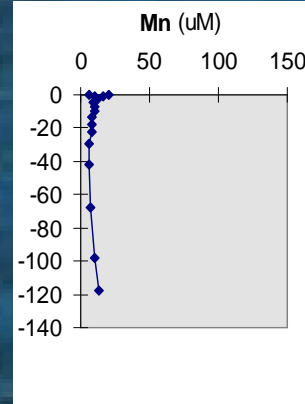
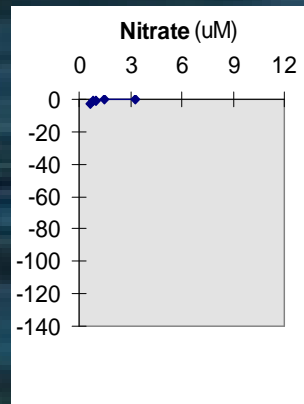
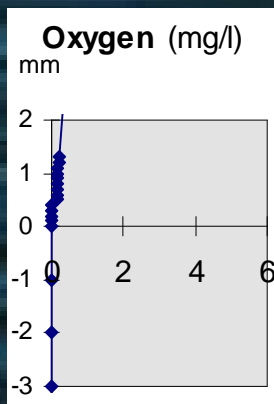
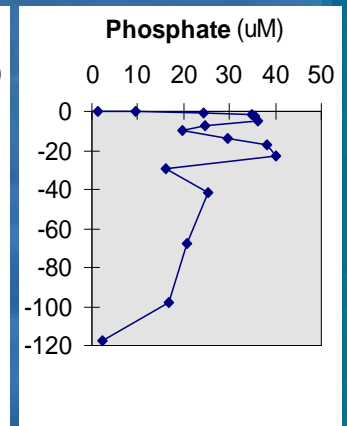
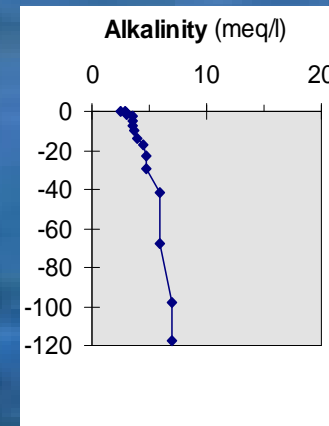
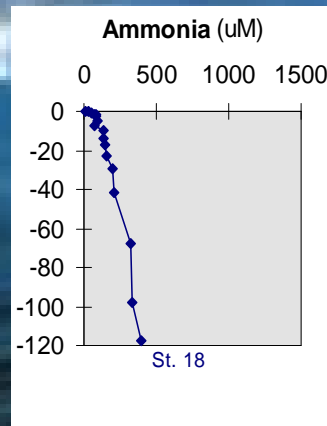
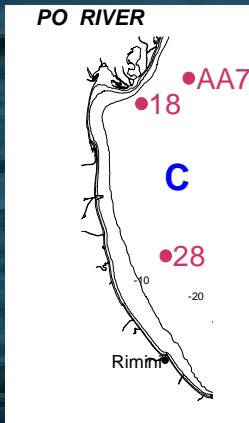
# Early diagenesis Process: type B

Silicoclastic sediments, high sedimentation rates, high reactive and degraded organic matter contents, high Fe-oxy-hydroxide contents, very high benthic fluxes ( $\text{NH}_4$ ,  $\text{PO}_4$ , DIC) for degradation of high organic matter contents, anoxic-non sulfidic-methanic environments



# Early diagenesis Process: type C

Silicoclastic sediments, autochthonous organic matter, high Fe-oxi-hydroxides, medium sedimentation rates, medium benthic fluxes ( $\text{NH}_4$ , DIC,  $\text{Si}(\text{OH})_4$ ) for degradation of reactive organic matter in anoxic conditions, anoxic-non sulfidic-partially post oxic environments, high phosphate fluxes for Fe oxy-hydroxide dissolution.

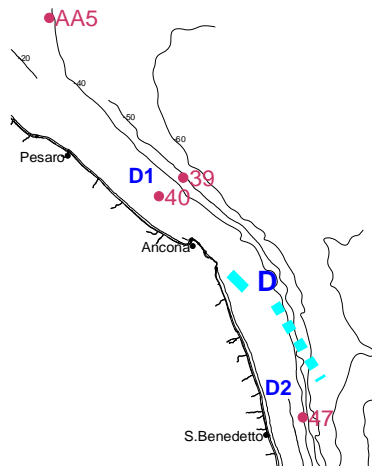


# Early diagenesis Process: type D

Mixed silicoclastic sediments, weak sedimentation rates, weak reactive organic matter for repeated reworking and low primary production, higher oxygenation of water column:

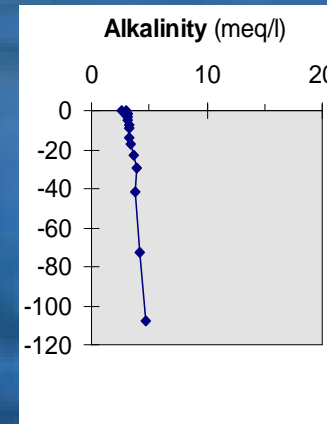
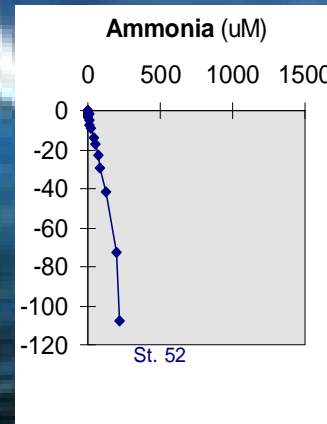
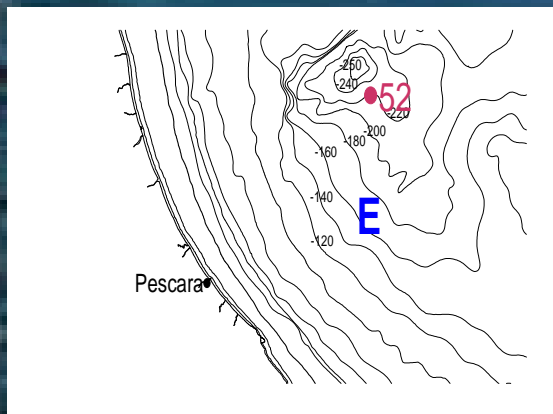
·D1) weak benthic fluxes for low reactive organic matter, anoxic-non sulfidic-post oxidic environments;

·D2) medium benthic fluxes for local higher organic matter inputs, anoxic-non sulfidic-partially post oxidic environments.



# Early diagenesis Process: type E

Basin area, greater depths and far away from main continental inputs, low sedimentation rate, fine sediment highly reworked, low reactive organic matter contents, main degradation at sediment-water interface, oxic environments up to 10 cm, very weak diagenetic processes and benthic fluxes, Fe and Mn oxy-hydroxides precipitation on first centimetres.

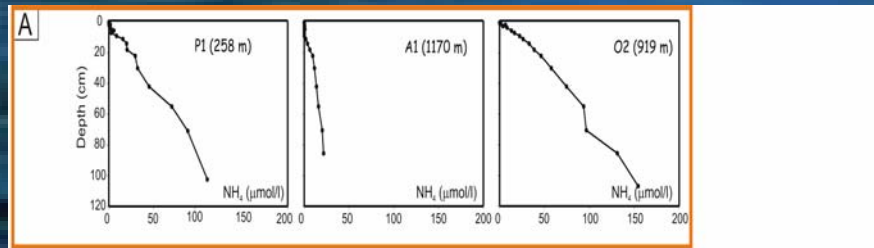


# South Adriatic and Ionian Sea

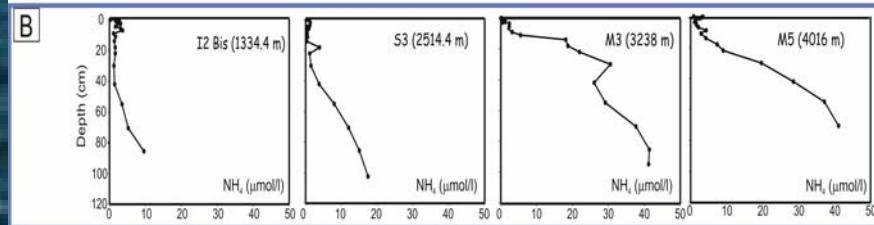
Very low organic Matter degradation product concentrations for low reactive organic matter inputs

## Ammonia

Adriatic



Ionian



- low concentration layer in first cms (oxic layer, nitrification processes):

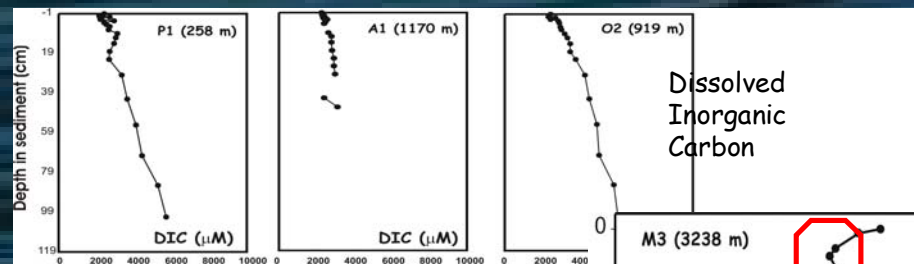
- thinner in Adriatic stations (higher organic matter inputs and sedimentation rates):

- thinner in Ionian basin stations respect to slope stations:

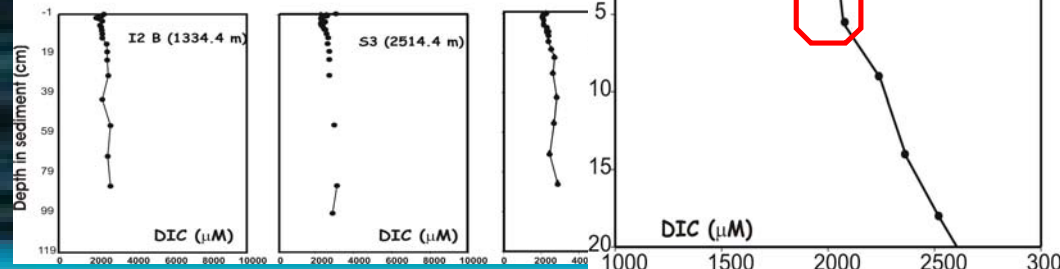
- Deeper layers characterized by NH<sub>4</sub> increase, stronger in Adriatic Sea (higher reactive Organic Matter and sedimentation rates).

## DIC

Adriatic



Ionian



## Adriatic Sea:

Higher concentrations respect to Ionian Sea Station:

- DIC concentrations increase about linearly with depth:

- slow degradation processes, low reactive OM.

## Ionian Sea:

- DIC concentrations decrease below sediment-water interface, and increase beyond 5-10 cm (CaCO<sub>3</sub> precipitation in the uppermost cms);

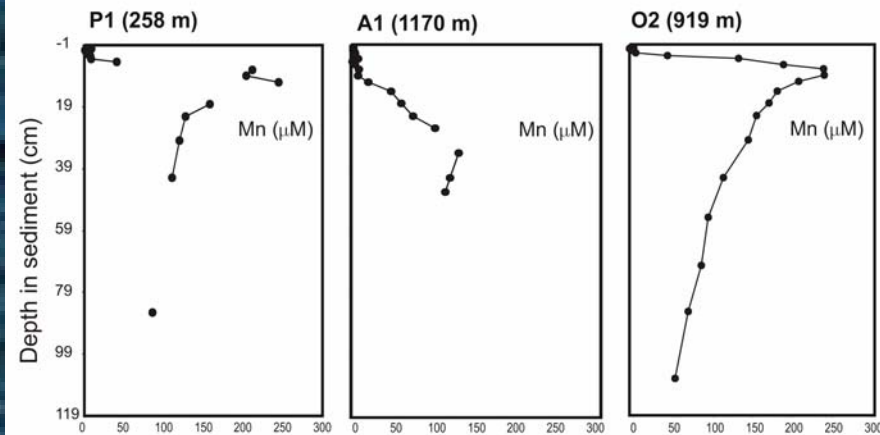
- lower values respect to Adriatic stations;

- very slow OM degradation processes

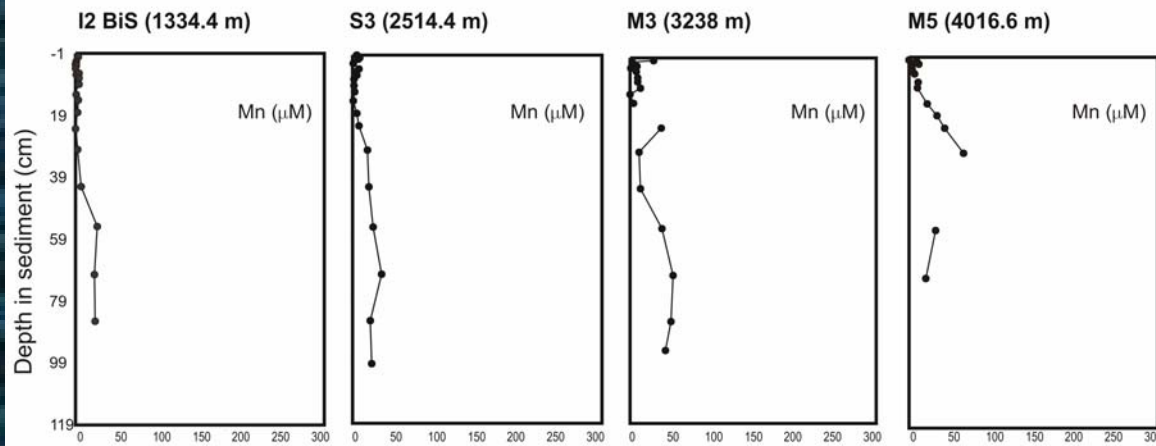
# South Adriatic and Ionian Sea

Electron final acceptors: dissolved Mn pore water profiles  
oxic and anoxic non-sulfidic post oxic environments

Adriatic



Ionian



Oxic layer increases southward from Adriatic to Ionian stations.

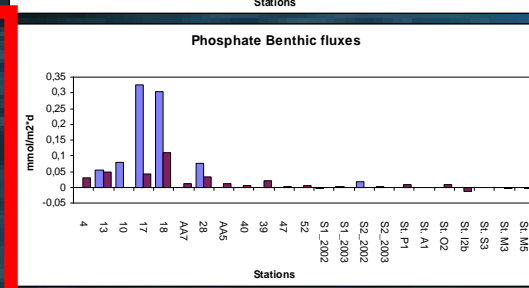
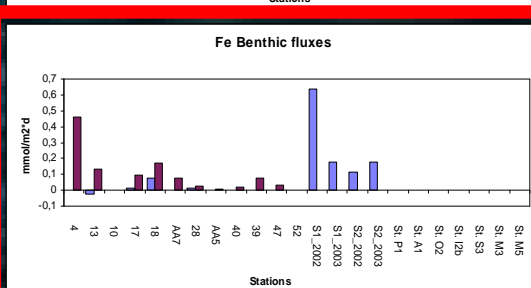
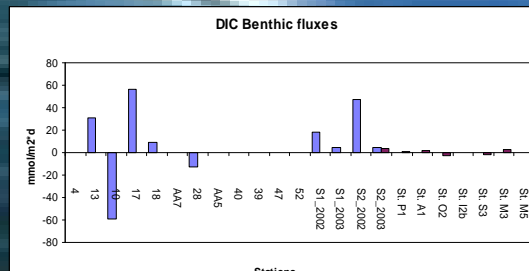
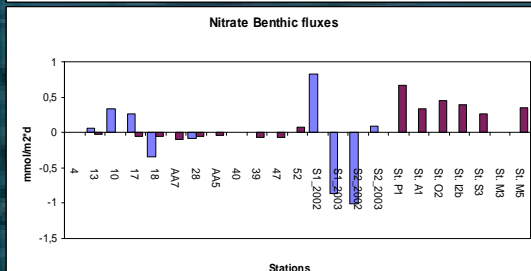
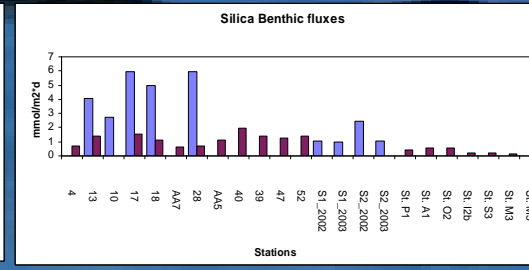
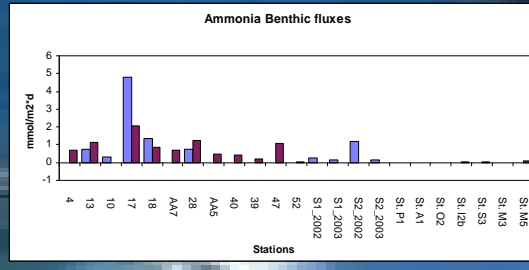
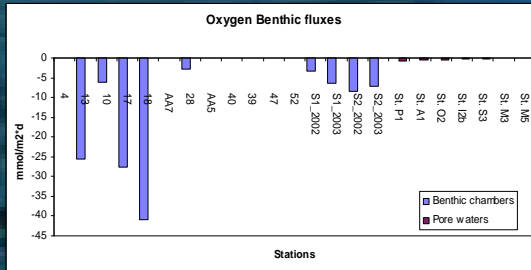
Different thickness for different organic matter inputs and sedimentation rate (basin area in Ionian Sea).

# Adriatic and Ionian Benthic fluxes

## Electron acceptors

## O.M. degradation products

## Silica



# Early diagenesis and benthic fluxes in the GEOTRACES Programme

Information on the isotopic alteration in sediments during early diagenesis will enhance the ability to use stable isotope abundances from sedimentary records as proxy indicators for past changes of environmental conditions.

- Trace element stable isotopes affected by early diagenesis:
  - $\delta^{98/95}\text{Mo}$  (McManus et al. 2002),
    - Early diagenesis reactions fractionate Mo isotopes: lighter ratio in oxic pore water environment (2.1‰ pw, 2.3‰ sw) produced by Mn-oxide dissolution, heavier ratio in reducing sediments (3.5‰), net sink of isotopically light dissolved Mo that explains the heavier sea water (2.8‰);
    - Low temperature hydrothermal systems are sources of light Mo in the ocean (0.8‰);
  - $\delta^{56}\text{Fe}$ ,
    - Decreasing values in pw by Fe-oxide dissolution, increasing with depth in pw for sulfide precipitation;
  - $\delta^{74}\text{Ge}$  (Rouxel et al. 2006),
    - Which is the segregation of Germanium isotopes in early diagenesis (opal dissolution and Ge precipitation)? Sea water >3‰, BSE ~1.3‰, authigenic marine sediments 3‰, mesozoic deep sea chert 0.7-2‰. How does the  $\delta^{74}\text{Ge}$  change with climatic change in sea water (both with Ge/Si and Si isotopes)?
- other stable element isotopes:
  - $\delta^{13}\text{C}$  (Lehmann et al. 2002), decreasing value in O.M. during oxic and anoxic early diagenesis (1.6‰), decreasing values in pw (from -1 to -20‰) for degradation of O.M. or increasing value for CH<sub>4</sub> production (Nissenbaum et al. 1972);
  - $\delta^{15}\text{N}$ , decreasing value in O.M. during anoxic early diagenesis (3‰), no distinguishable trend in oxic degradation
  - $\delta^{34}\text{S}$ , increasing in pw by consuming of SO<sub>4</sub> and producing of S.
- Early diagenesis and benthic fluxes are poorly investigated in the Mediterranean (Golfe du Lion et des Baléares, Rouibah & Cauwet, 1993; Picon & Buscail, 2000; Denis, Grenz, 2003; Local Iberian seas, Vidal & Morgui, 1998; Gómez-Parra and Forja; Ortega, Ponce, Forja and Gómez-Parra, 2002; Aegean Sea, Ozkan, Kocatas and Buyukisik, 2008)
- Studies related to early diagenesis isotope fractionation are not many in the Mediterranean (some early data of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  from Langone et al. 2009) so that investigation in this field could be very interesting.

# ISMAR-CNR vessel facilities for GEOTRACES

Website: <http://www.cnr.it/sitecnr/UPO/gestione/infoce/navi/UPOnavi.html>

Available for GEOTRACES programme by scientific agreement with ISMAR-CNR scientists:

- 2011: in already scheduled cruises (Adriatic Sea, Ionian Sea, Sicily Strait);
- 2012: by application of scientific proposals.



## RV Urania

Operator: CNR - National Research Council  
Country: Italy  
Vessel Type: Multipurpose Research Vessel  
Vessel Class: Regional  
Operational Area: Mediterranean Sea  
Endurance: 45 days

**Scientist berths: 20**  
**Length: 61.3m**



## M/N Dallaporta

Operator: CNR - National Research Council  
Country: Italy  
Vessel Type: Off shore research activity vessel  
Operational Area: Mediterranean Sea

**Length: 33.30 m**

Width: 7.65 m  
Speed: 14 knots  
Crew: 6

**Scientists 11**