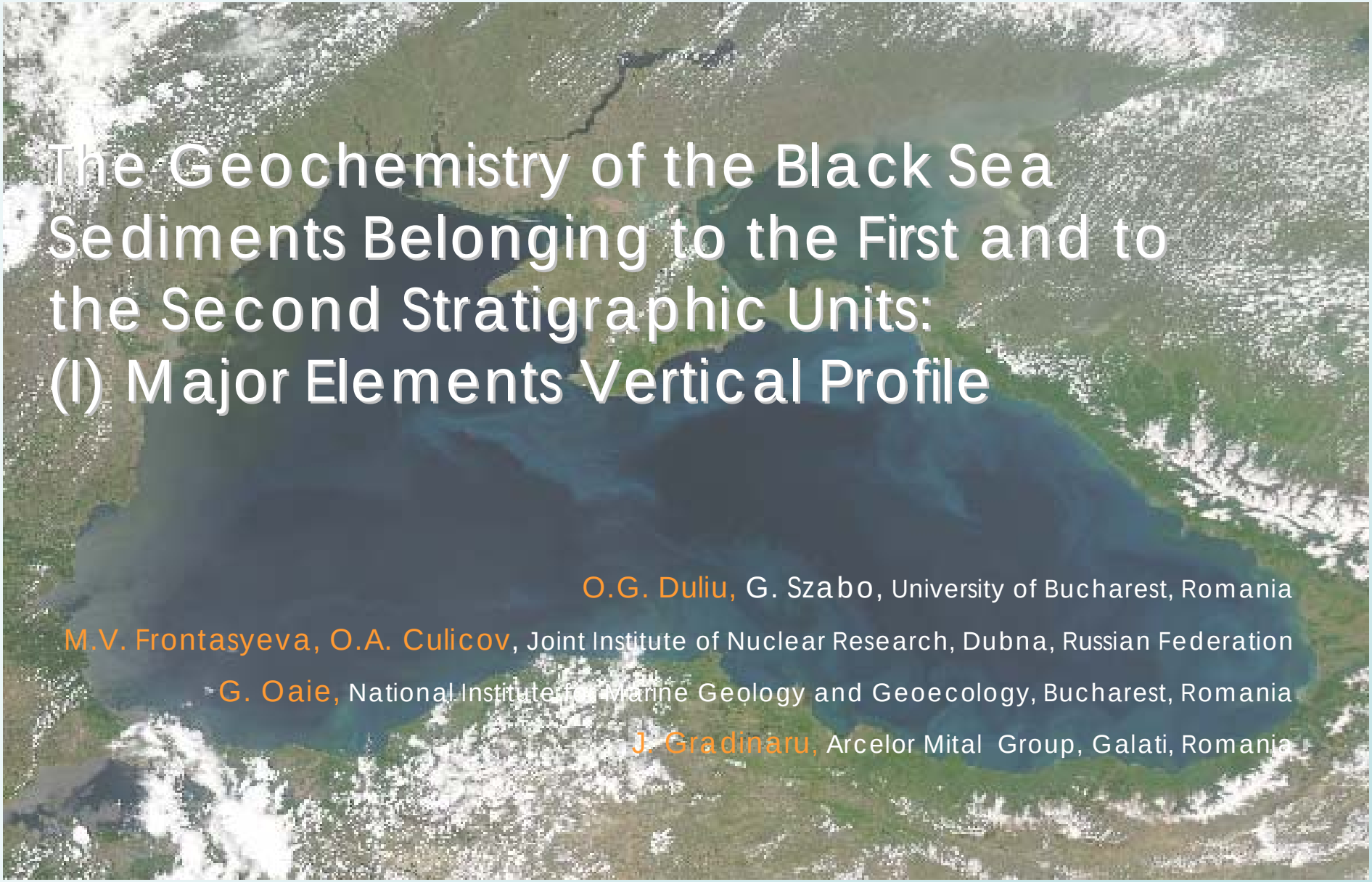

The Geochemistry of the Black Sea Sediments Belonging to the First and to the Second Stratigraphic Units: (I) Major Elements Vertical Profile

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The Black Sea is a large inland sea (422,000 km^2 with maximum depth of 2212 m) situated between southeastern Europe and Asia Minor.

It communicates in the southwestern corner with the Mediterranean Sea by the Strait of Bosphorus, the Sea of Marmara and the Strait of Dardanelles, and in the North with the Sea of Azov by the Strait of Kerch.

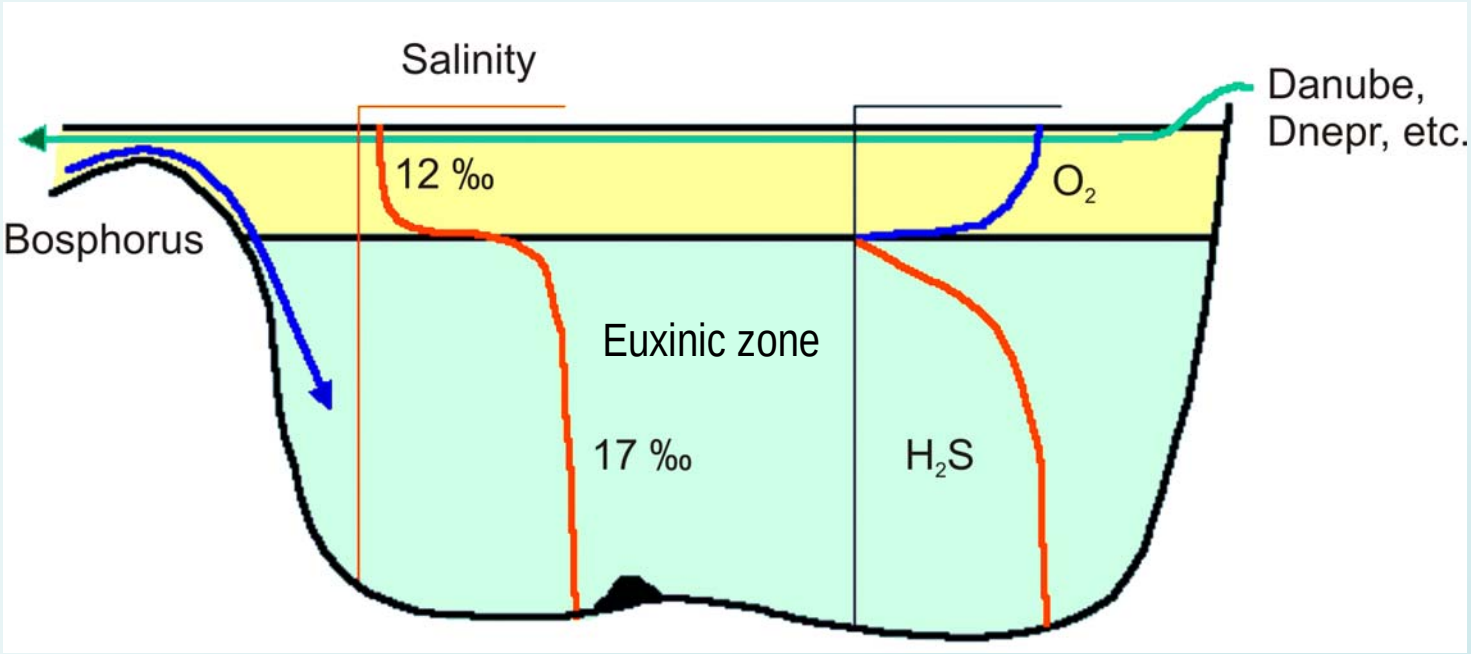
There is an inflow of freshwater from the surrounding areas, especially central and middle-eastern Europe, totaling 320 km^3 per year and a net inflow of 200 km^3 per year of seawater through the Bosphorus.

About 130 10^6 tons of solid matter are deposited annual allover the Black Sea basin with deposition rates between 0.1 mm and 0.5 cm/y.

As a result of the Mediterranean water, the Black Sea become the largest euxinic marine basin, the oxygenated water representing a thin layer of about 120 – 180 m overlying a huge volume of salt water saturated with hydrogen sulfide.

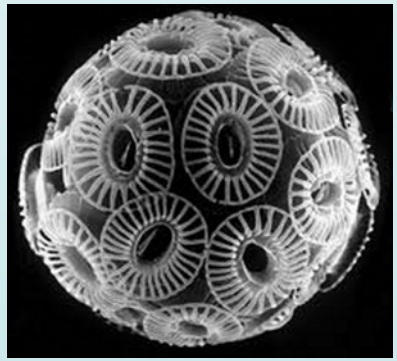
At depths varying between 120 and 180 m under the oxygenated to euxinic transition interface, there are no other living organisms able to produce bioturbation.

Therefore, the euxinic zone presents the ideal conditions to preserve their sedimentary structure for a very long time, and thus to allow a systematic reconstruction of the history of the past geological processes, especially in zones with reduced sedimentation rates.



The formation of the euxinic zone begun about 7000 years ago and ended about 3000 years ago. Before it, the Black Sea was an almost fresh to brackish oxygenated basin.

For this reason, the euxinic sediments are classified, according to the water regime in three main stratigraphic units, each of them reflecting the hydrologic and climatic conditions which governed their deposition:



- Unit I of30 to 50-90 cm (max. 3 000 y old) consists of fine alternating laminae rich in *Emiliania huxleyi* cocolites – deposited under euxinix conditions
- Unit II of variable thickness (between 3 000 and 7 000 y) – deposited under transition from lacustrine to euxinic conditions rich in sapropel and seldom aragonite
- Unit III of meter thickness (7000 to 28000 years) – deposited under oxygenated brackish conditions during the last glaciation

It is worth mentioning that the sediments transported by the Danube are come from a large drainage area in southeastern Europe consisting of Quaternary fluvial and eolian deposits, of the Hungarian and Walachian lowlands, Cretaceous and Tertiary flysch and molasse of thenorthern Carpathian Mountains as well as of the gneissand crystalline schists of the southern Carpathian Mountains while the southern drainage area is dominated by granites and crystalline schists of the Balkans and Macin mountains.

Sediment input from the regions north of the Black Sea by the rivers Dniester, Dniepr and Don reporesents only about 6% of those carried by Danube River.

Both these circumstances: A huge amount of continental sediments carried by the Danube River and an euxinic media, prone to offer ideal conditions for a perfect conservation of sediments makes the study of the Black Sea euxinic sediments extremely attractive.

These refer to the capacity of sediments to record any climatic and environmental changes.

RV/Mare Nigrum - GeoEcoMar

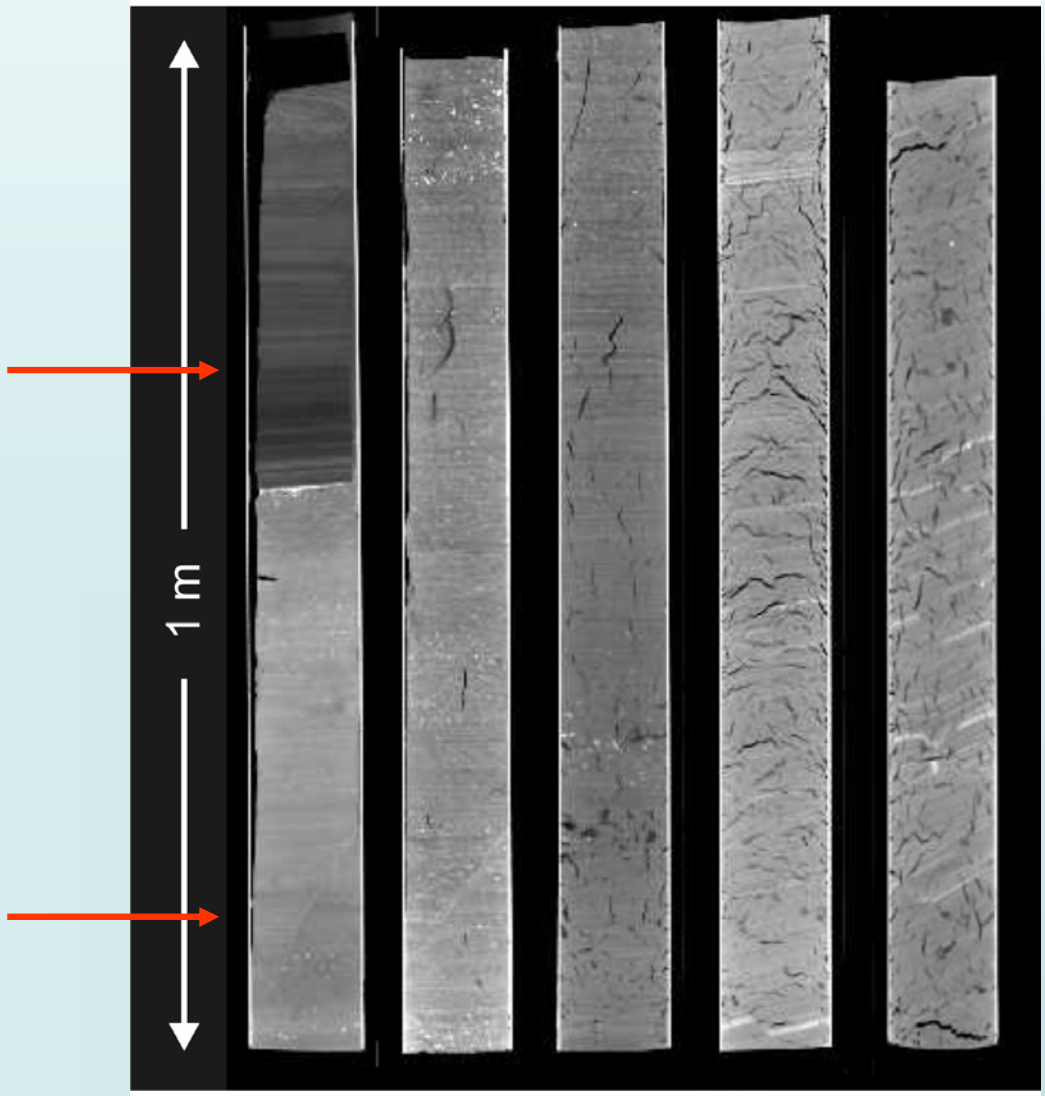
A 5 m core (Eux Ro 02) collected at a depth of 500 m from the slope of the western Black Sea Continental platform.

Collected in Summer 2011 campaign by the R/V *Mare Nigrum* of the GeoEcoMar Institute, Bucharest

Tomographic images shows with clarity at last the difference between the stratigraphic 1, with a fine alternation of dark and light laminae

and

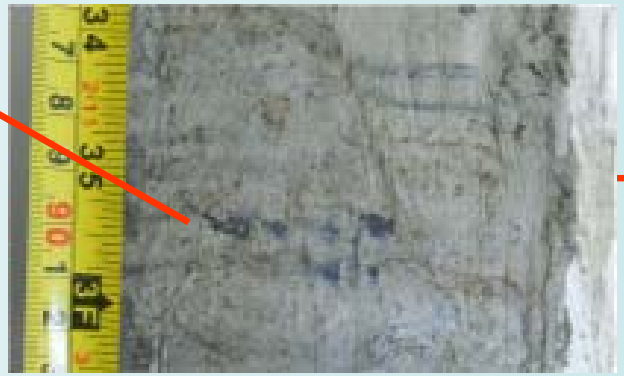
the other units, more dense, but also fine laminated sediments, mainly fine clay

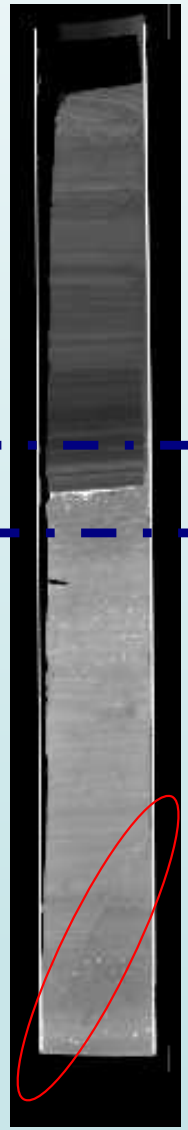


Abrupt transition to euxinic an environment ?

Cocolithic laminae

Sapropel

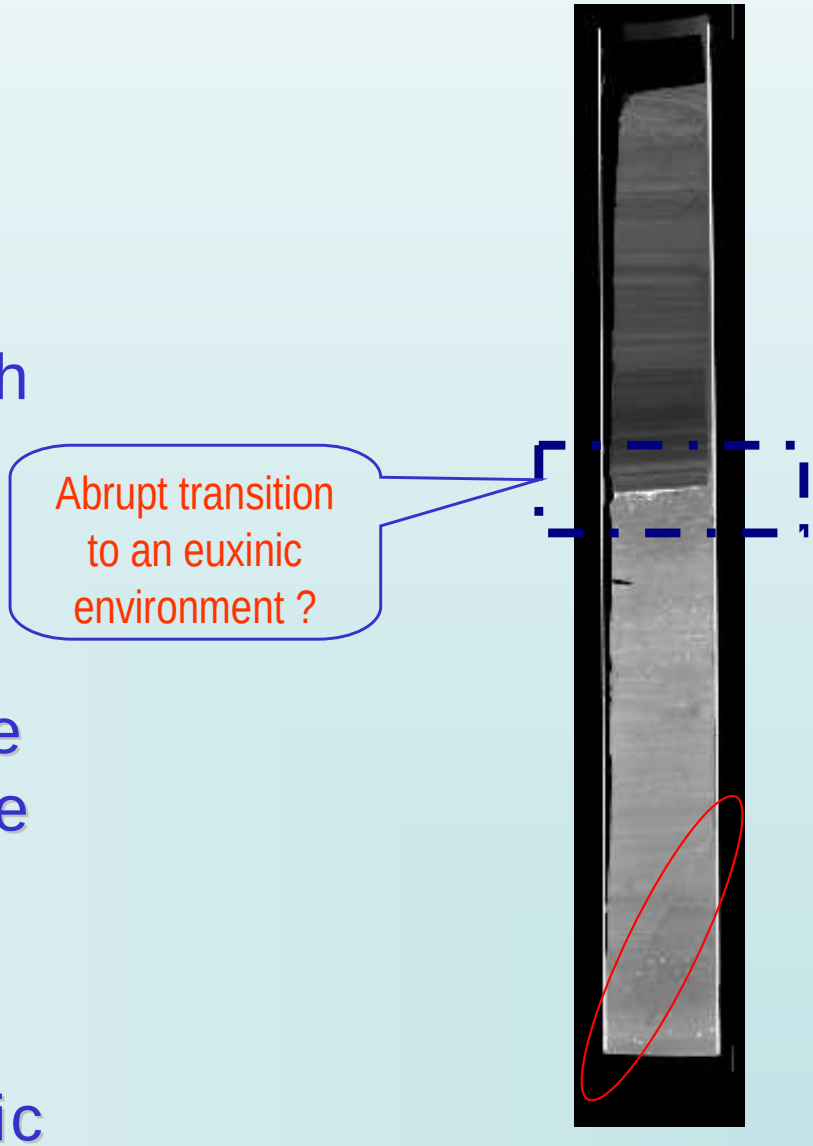




A small fault (during collection ?)

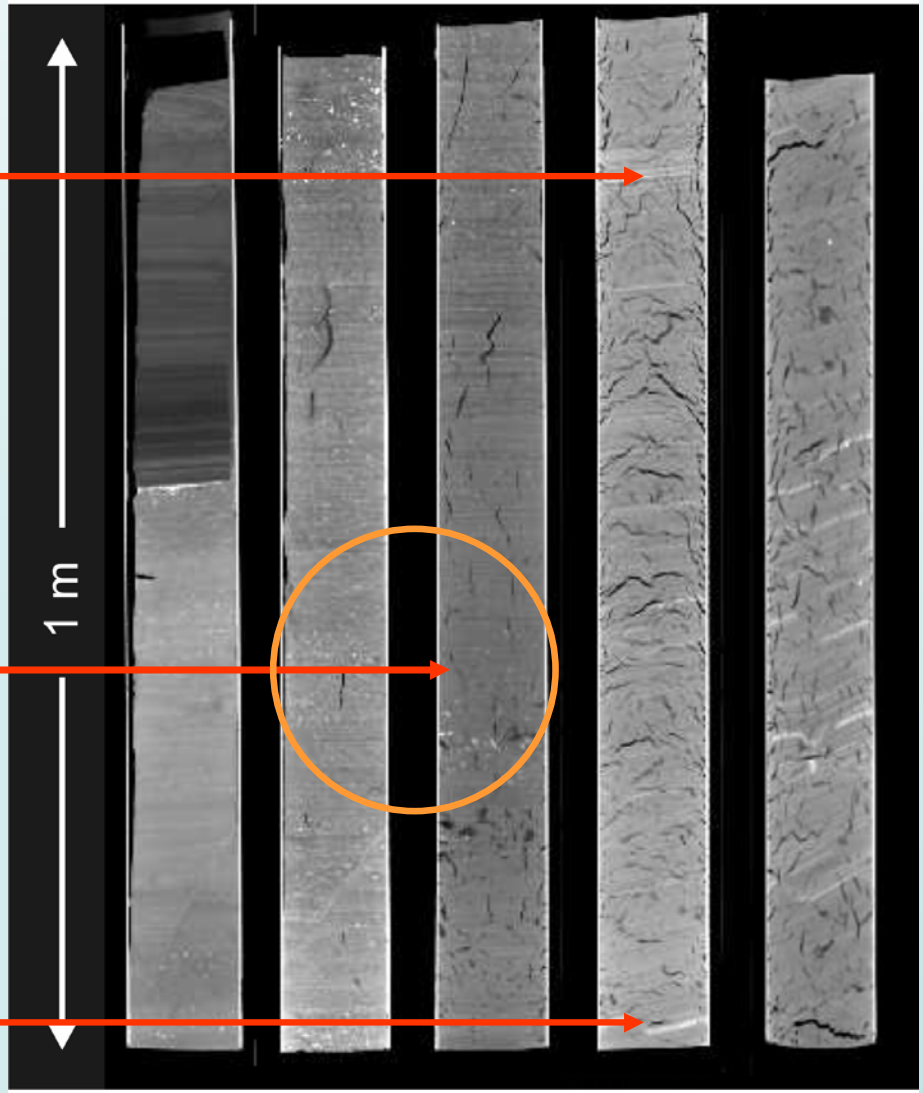
To find an answer to this question it needs more data regarding first of al the geochemistry of both major – rock forming elements and trace elements ones.

Such study needs to take into account the fact the sedimentary material comes from a large and diverse area, with different geomorphologic features



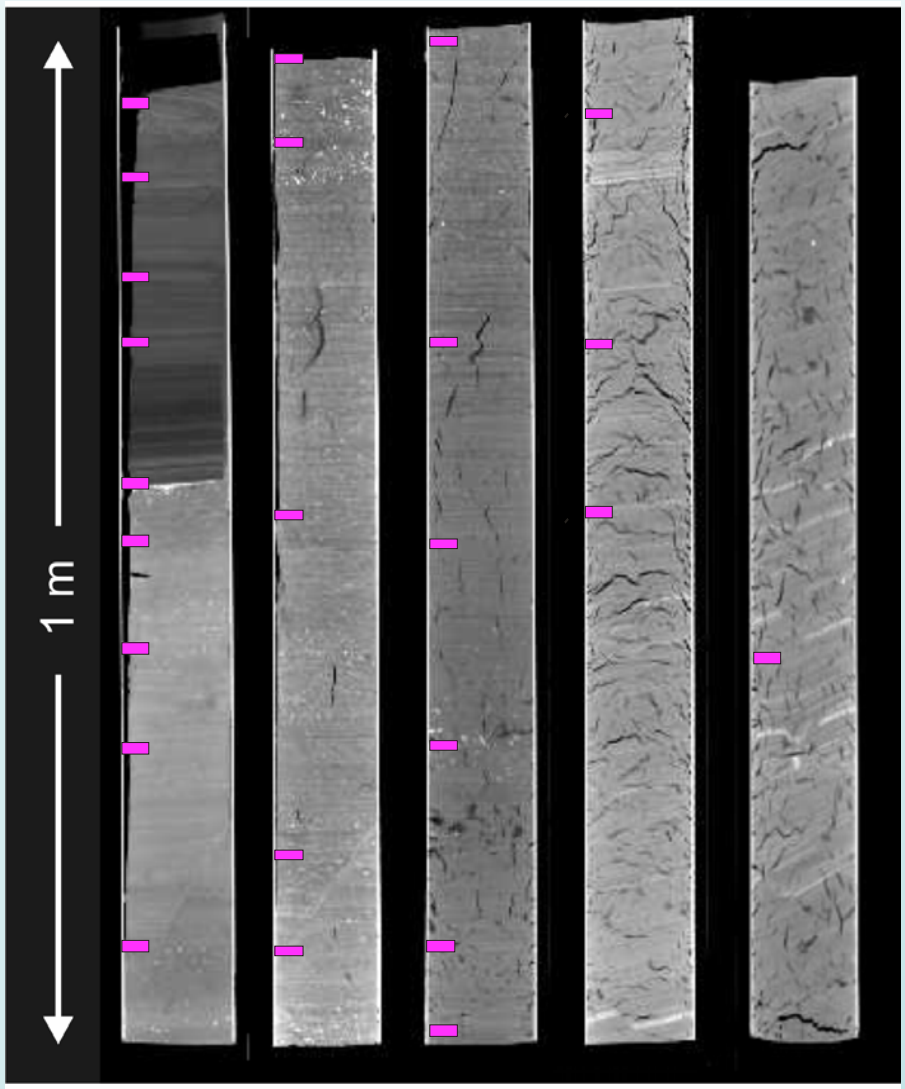
Because, as tomographic images shows excepting this discontinuity, the rest of the core display almost the same features, *i.e.* almost equal spaced laminae and some grains of pyrite.

Only at higher depth one cloud remark few intercalations of a denser material.



For this reason we have investigated the vertical profile of 11 elements, *i.e.* Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, FeO, MnO as well as P and SO_3.

For this study we have chosen 32 points along the entire 5 m core.



All measurements were performed by XRF as the content of all elements was higher the order of magnitude of percents.

For WDXRF measurements we have used an ARL 9900 Thermo Scientific X-ray fluorescence sequential spectrometer provided with Thermo Scientific™ OXSAS™ Software.

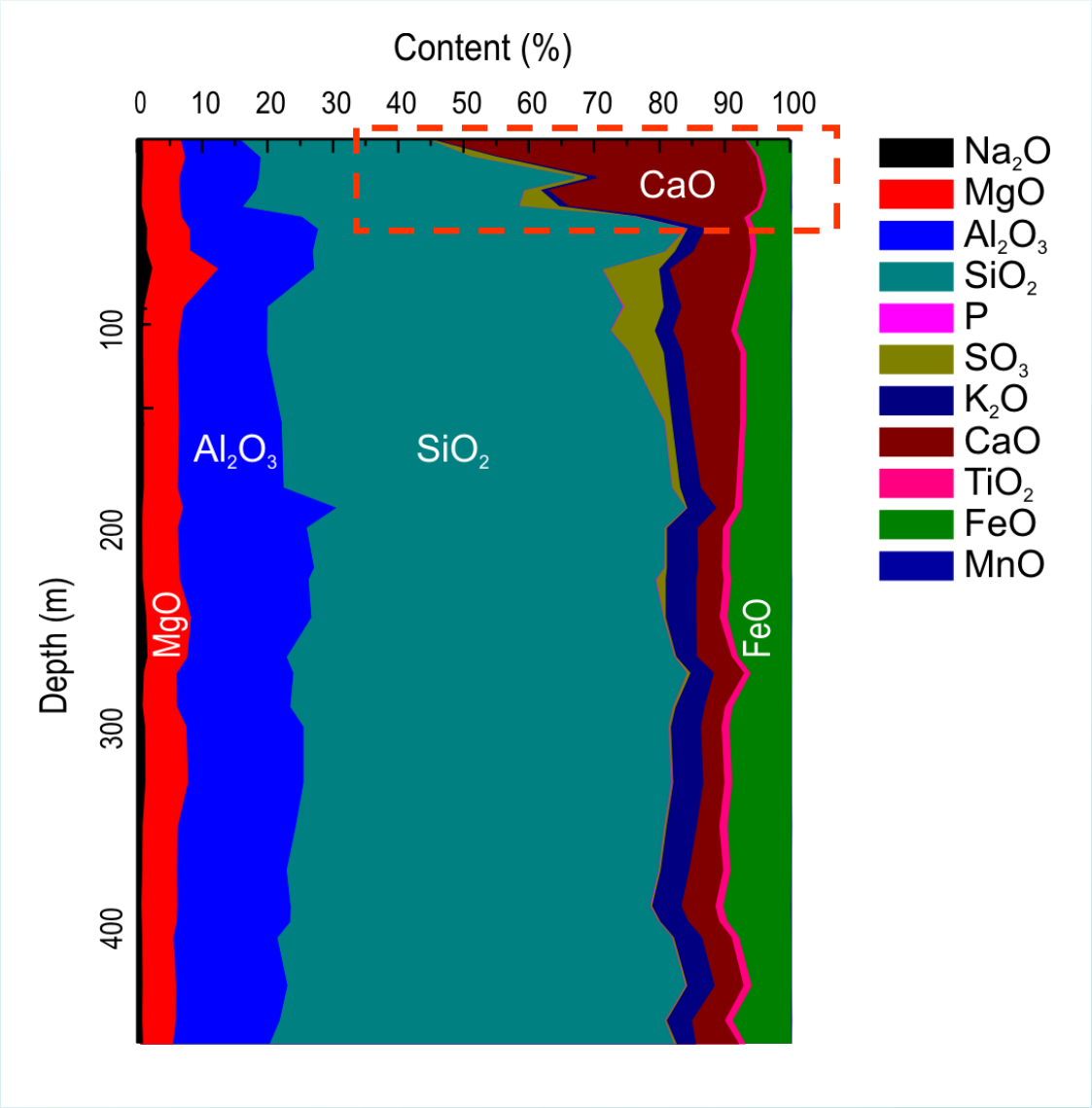
The presence of a built-in calibration system and of an appropriate soft allow obtaining final data without a need for standard samples.

Experimental uncertainties less then 3%

Vertical profile

The most important feature:

The disbalance between CaO and SiO_2 un the upper part of sediments which corresponds to the **euxinic zone**



For this reason we have instigated the vertical profile of the Al/Ti, Ca/Ti and K/Ti as proxies related both to the abundance of terrestrial materials and to paleoclimate records.

At the same time, as mentioned earlier, the Black Sea turned about 3000 y into an euxinic basin which drastically modified the oxi-reduction conditions of the about 90% of bottom turning them, due to the presence of hydrogen sulfide into a reduction one.

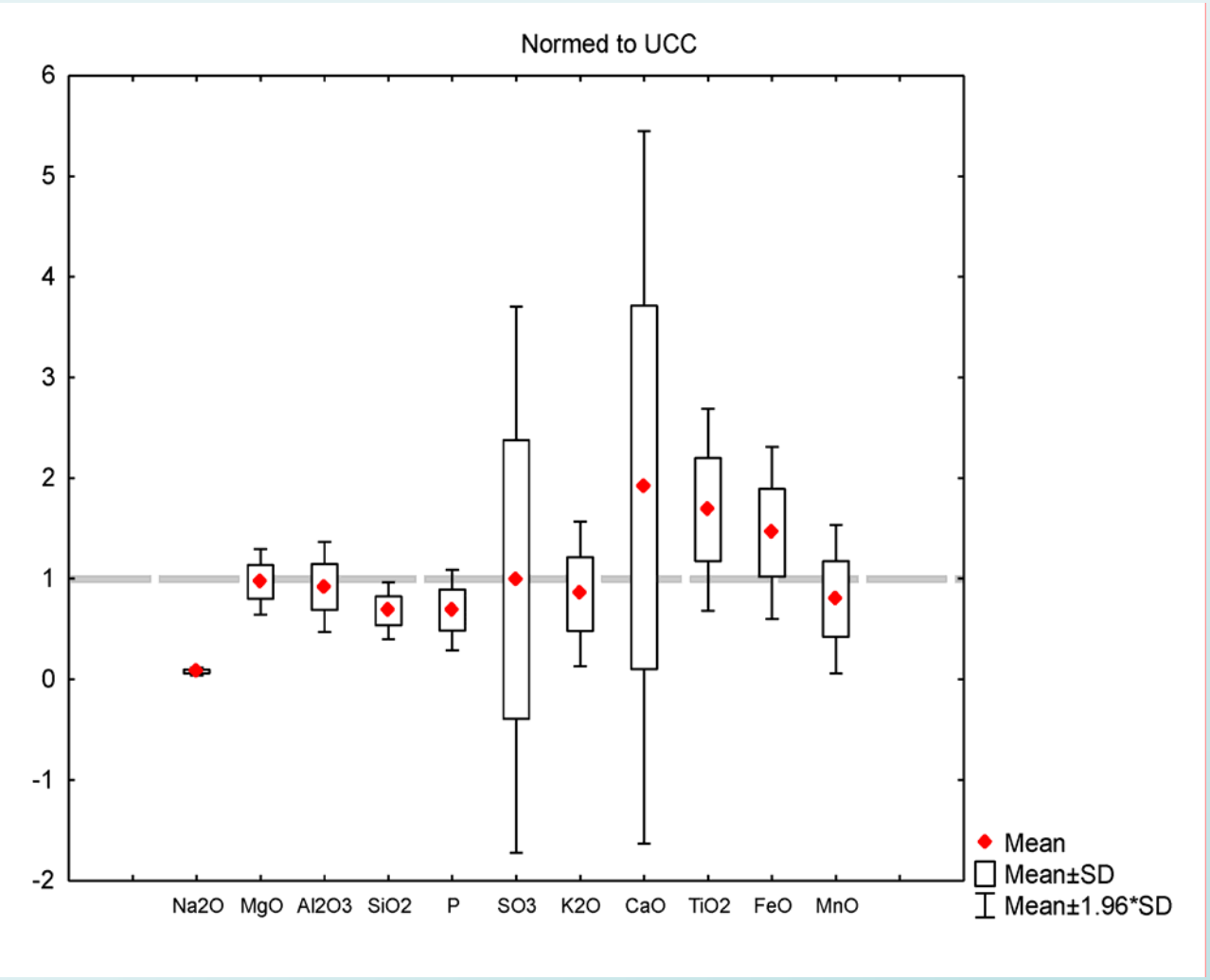
This fact should be also reflected by the sediments geochemistry.

Results in correletion with the Upper Continental Crust (UCC) excepting P in correlation with the pelagic sediments

Element (oxide)	Eux Ro 2	UCC
Na_2O	3.0 ± 0.7	3.9
MgO	2.1 ± 0.4	2.2
Al_2O_3	14.0 ± 3.5	15.2
SiO_2	45.5 ± 9.4	66.9
P	0.06 ± 0.02	0.07
SO_3	1.3 ± 1.8	-
K_2O	2.9 ± 1.2	3
CaO	8.1 ± 7.5	4.2
TiO_2	0.8 ± 0.3	0.5
FeO	6.6 ± 2.0	4.5

Results in normed to Continental Crust (UCC).

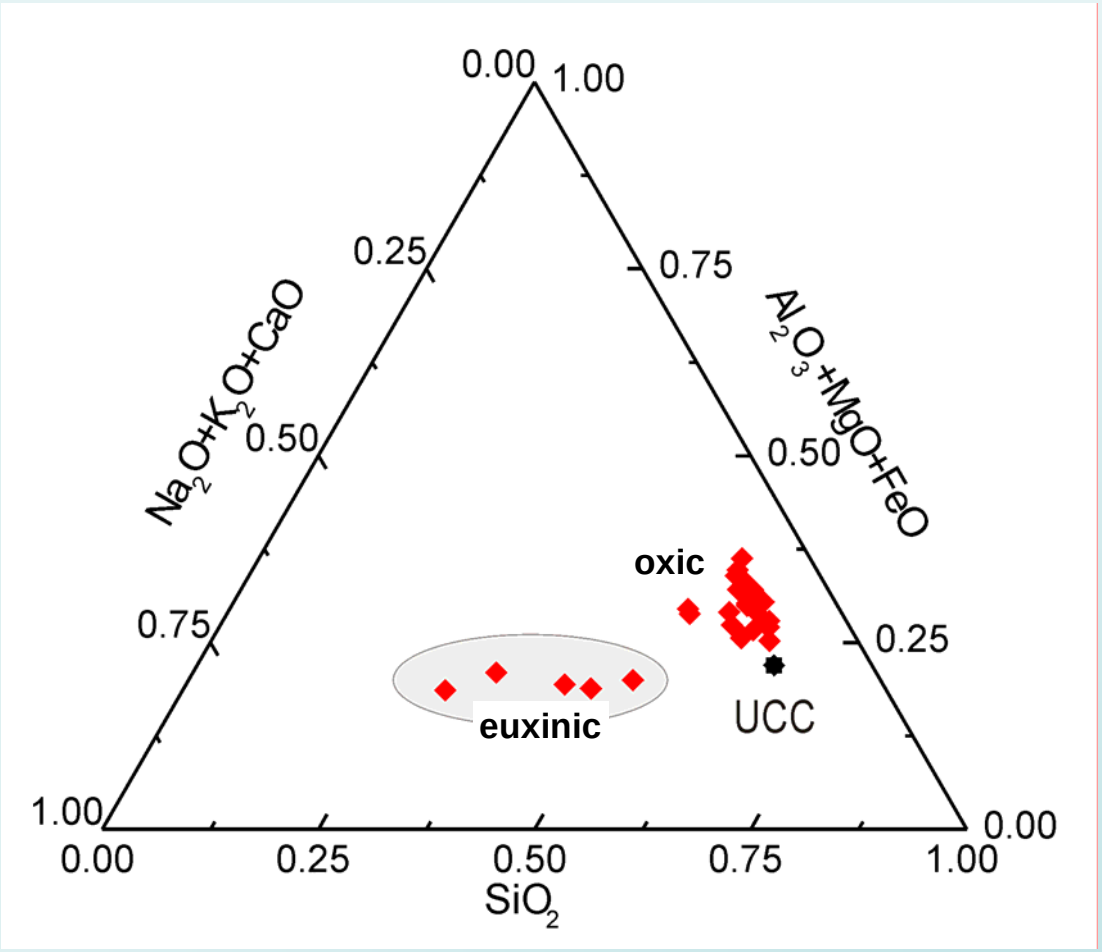
Normal terrigenous material excepting whose abundance is affected by the coccoliths



Two categories of sediments:

Siliciclastic, argilaceous one, close to UCC

Rich in coccolithic carbonates



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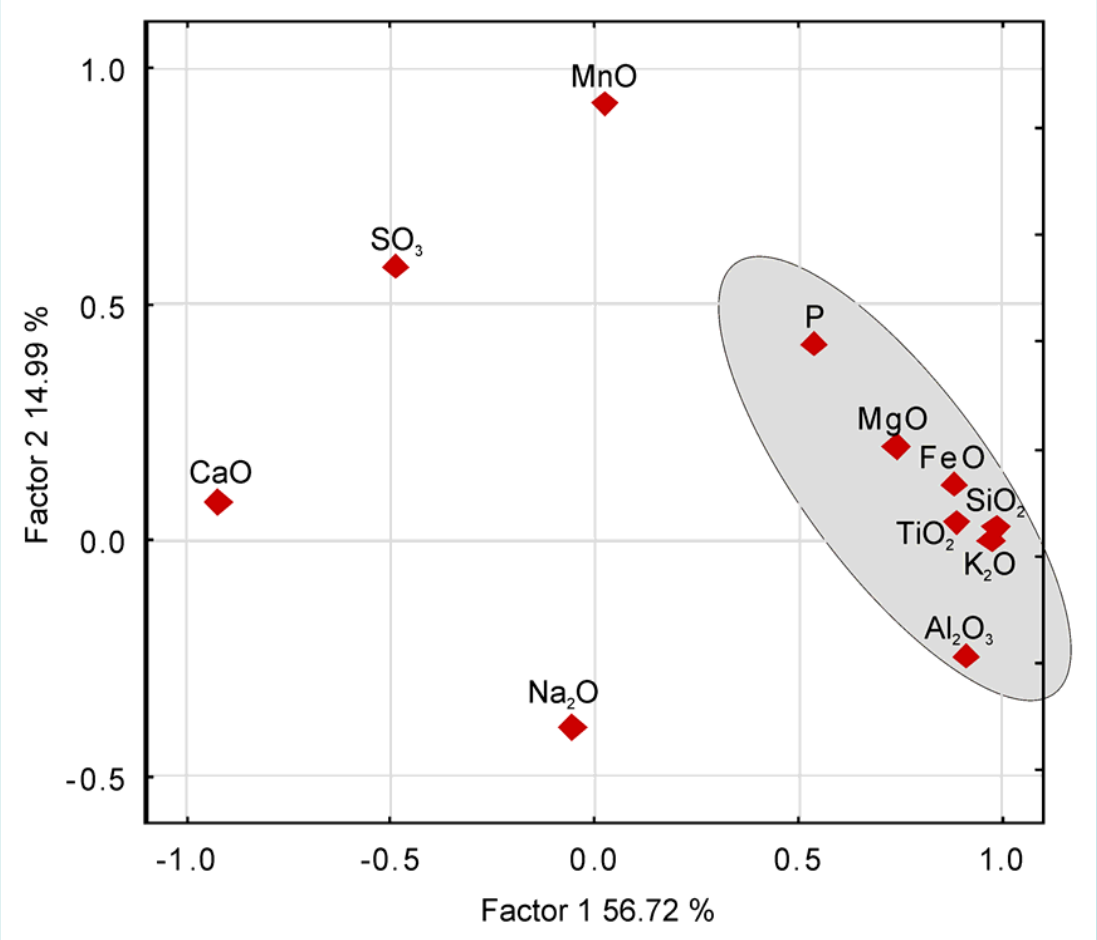

Factor 1

Elements directly connected with sediments mineralogy: carbonates, feldspars, clay

Factor 2

Elements more connected with anaerobic-reducing environment media

	Factor 1	Factor 2
Na_2O	0.0005	0.0954
MgO	0.0869	0.0236
Al_2O_3	0.1337	0.0366
SiO_2	0.1266	0.0009
P	0.0469	0.1048
SO_3	0.0378	0.2056
K_2O	0.1523	0.0000
CaO	0.1367	0.0039
TiO_2	0.1550	0.0005
FeO	0.1236	0.0086
MnO	0.0001	0.5201

As Al and Ti content in seawater is very low due to their extremely reduced solubility, these elements reflects the terrestrial materials in marine sediments.

This means their content in marine sediments also could reflect the weathering and transportation processes which took part on terrigenous source.

On the other hand, K, which is one of the major cations in seawater and tends to be absorbed by clay minerals in marine sediments, is still associated with terrestrial materials.

The same thing we can say about Ca, which also are actively bonded by some marine microscopic algae as well as by some invertebrates exoskeleton.

For this reason we have instigated the vertical profile of the Al/Ti, Ca/Ti and K/Ti as proxies related both to the abundance of terrestrial materials and to paleoclimate records.

At the same time, as mentioned earlier, the Black Sea turned about 3000 y into an euxinic basin which drastically modified the oxi-reduction conditions of the about 90% of bottom turning them, due to the presence of hydrogen sulfide into a reducing one.

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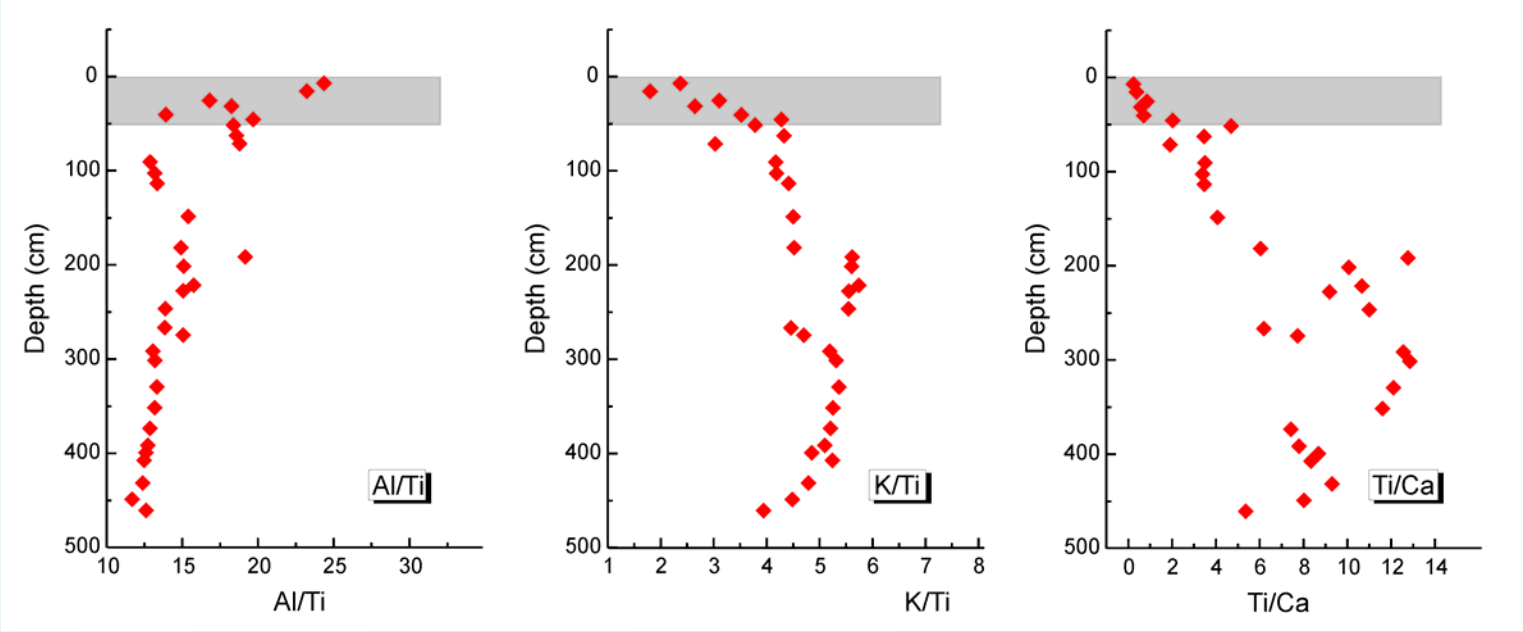

Again, the uprmost layer, deposited in anaerobic-reducin (euxinic) media differ with respect with the lower layers, deposited under oxic conditions

Some Concluding Remarks

The Black Sea sediments, deposited either under euxinic or oxic conditions, show remarkable features, not only regarding the deposition media but also the entire recent history of the Black Sea.

This study was a first part of our project, the second part regarding the distribution of trace elements in under work.

Acknowledgement

The present work was done within the protocol

4322-4-14/16

between the Joint Institute for Nuclear Research – Dubna and the University of Bucharest

Thank you for your attention !