High Resolution Investigation of the Geochemical and Mineralogical Composition of 1 Ky Old Euxinic Sediments of the Western Black Sea

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The Project

Goals:

- High spatial resolution distribution of major and trace elements

- Origin of sedimentary material

-Influence of euxinic environment on the geochemical imprint of unconsolidated sediments

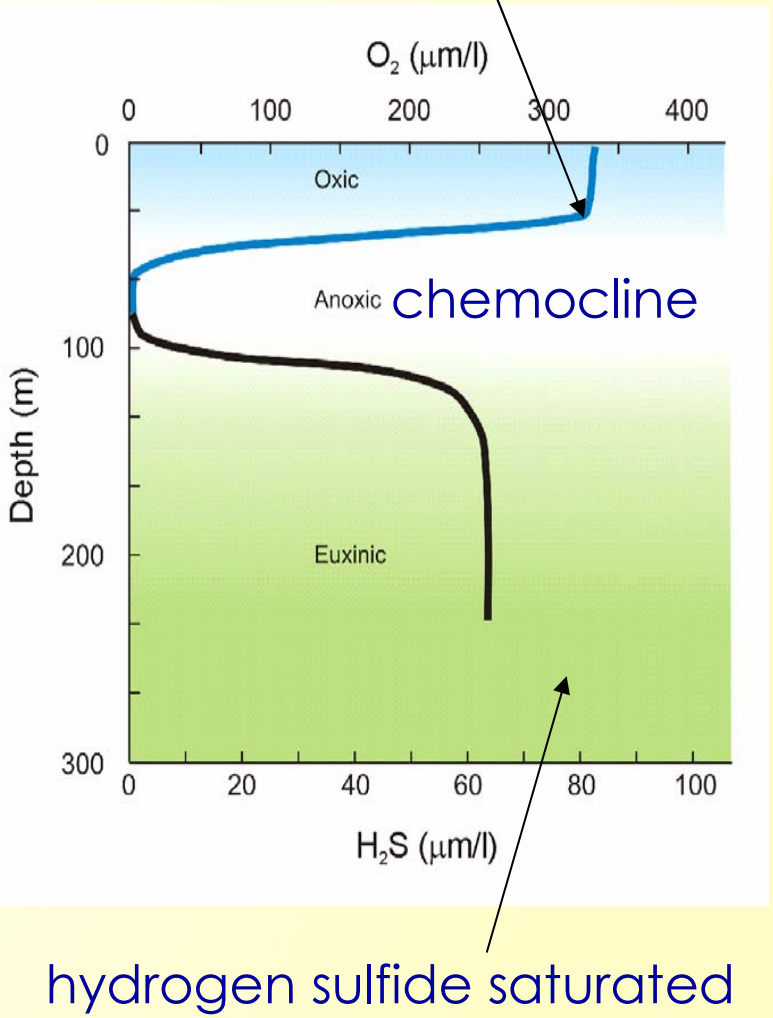
The Project

The experimental circumstances:

- the existing of a well preserved core collected from the continental platform slope from a depth of 600 m, *i.e.* at a depth well below the chemocline which marked the division between superficial oxygenated water and the bottom, hydrogen sulfide saturated ones

The Black Sea environment

As it is well known, **The Black Sea**, represents the largest meromictic basin in the world as its water consists of two layers which do not intermix



The Black Sea environment

The presence of the euxinic (anoxic and H_2S saturated) environment presents the great advantage of the absence of a bioturbation processes.

The superficial sediments are completely undisturbed allowing to investigate continuous sedimentary sequences for the last 7 ky

The Black Sea environment

The development of the euxinic environment can be dated back about 7 ky when the salted and more dense water of the Mediterranean sea entered through the Bosporus in the Black Sea which, by the end of the last glaciations, was rather a well oxygenated brackish water basin

The Black Sea environment

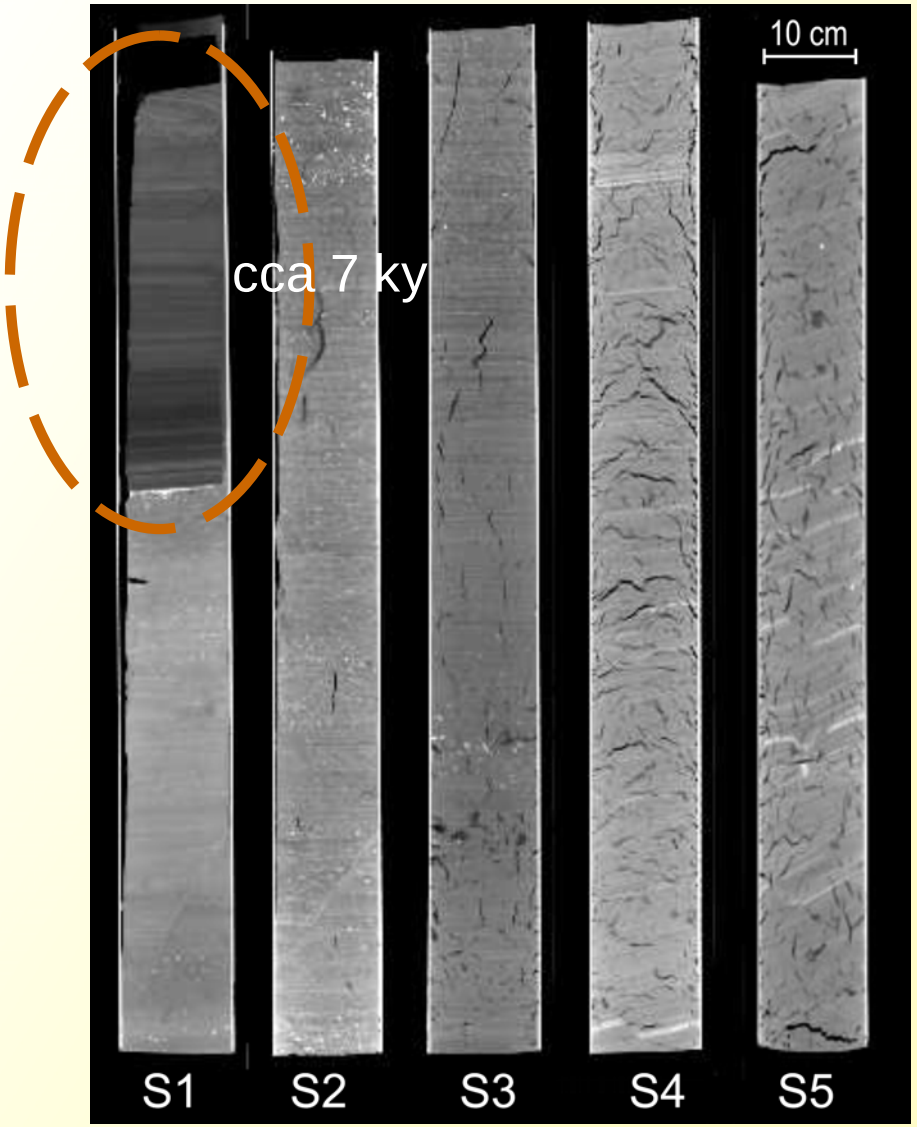
The absence of bioturbation together with a rather reducing environment could be interesting not only from the point of view of reconstructing the time shifts in the sedimentary geochemistry but also the influence of euxinic, reducing environment on the sediment chemistry

The Black Sea environment

At the same time, it should be taken into account that **The Black Sea** catchment basin, with an area of 1,864,000 km^2, covers a significant surface of central and eastern Europe so that the annual debt of solid sedimentary material of 138 $x10^6$ tons is transported from areas with different geochemical composition, which should be reflected into sediment composition

The Project

CT image of a core consisting of unconsolidated sediments collected on the Western Black Sea continental platform slope at a depth of 500 m indicating the onset of euxinic conditions



The sediments

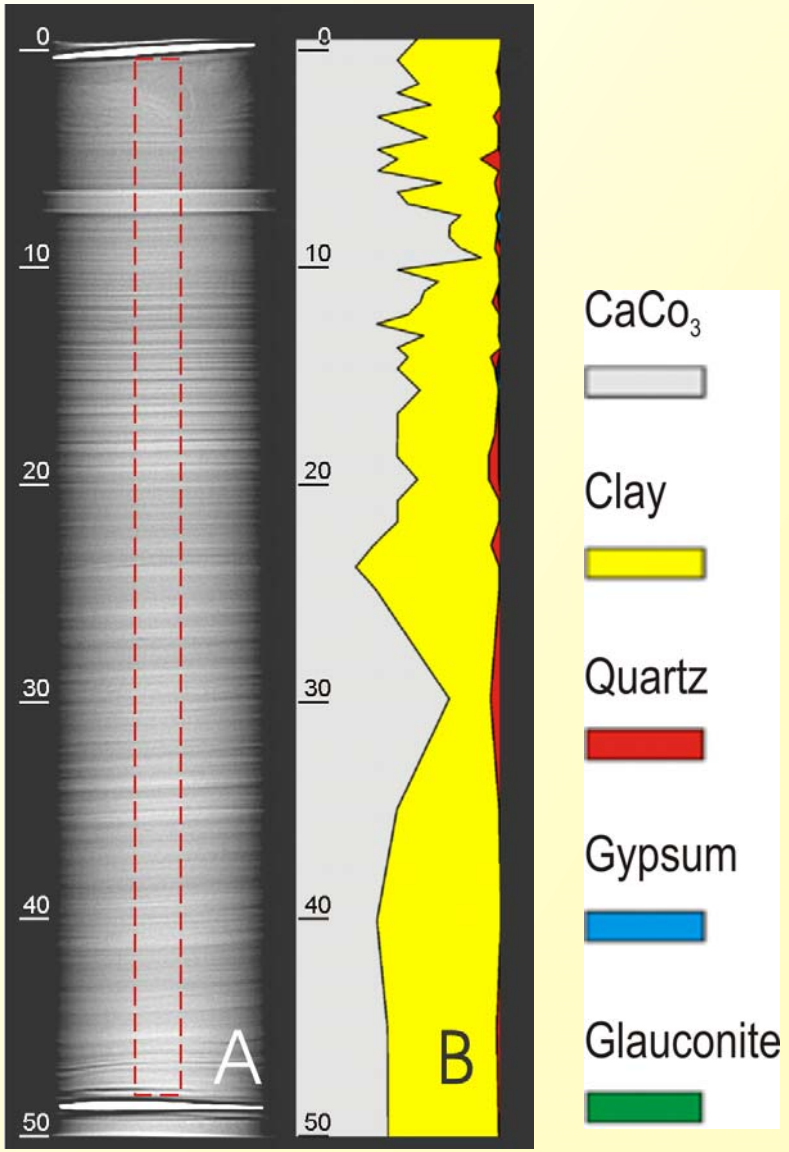
In these conditions, for the entire euxinic sediments we have investigated the vertical profile of 42 major and trace elements in the 50 cm **BS 600** core whose age we estimated to 1.02 ±0.07 ky by using synchronously both ^{137}Cs and ^{210}Pb absolute geochronology in correlation with CT image analysis

The sediments

The sediments

The BS 600 core consisted of unconsolidated detritic material: a mixture of clay and calcium carbonate.

Its CT image reveals the presence of about 250 multi-annual laminae



Elemental content

To determine the content of all major, rock forming elements we have used two different variant of the Instrumental Neutron Activation Analysis:

Epithermal Neutron Activation Analysis (ENAA) performed at the Frank Neutron Physics laboratory, Dubna (Russian Federation) and Prompt Gamma Ray Activation Analysis (PGAA) performed at the Budapest Research Reactor (Hungary)

Elemental content

To get a high resolution, the core was longitudinally split into two halves, one of them being divided into 45 segments, 5 mm to 5 cm thick.

Each segment was dehydrated at 105 °C, homogenized and divided into four aliquots, two of about 1 g for ENAA and PGAA, one of 15 to 100 g for radiometric assay and finally one of about 10 g for additional mineralogical investigations.

Elemental content

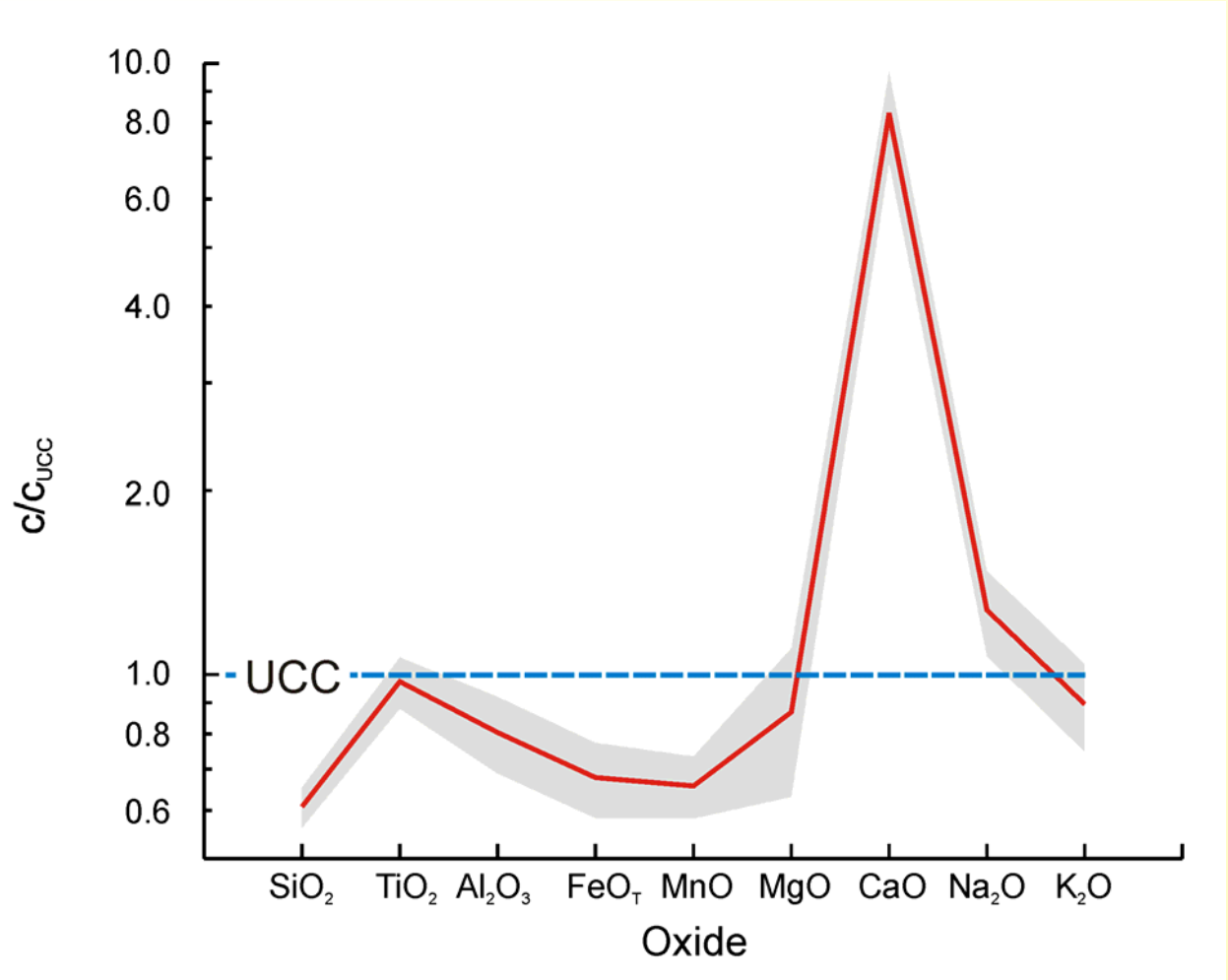
Using both methods, we have determined the vertical profile of the contents of 8 major (Na, Al, Si, Cl, K, Ca, Ti and Fe)

and 34 trace elements (B, S, Sc, V, Cr, Mn, Co, Ni, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, Hf, Ta, W, Th and U) with an accuracy better than 5 to 7 %

The accuracy was checked by NIST and IAEA reference samples as well as by an ENAA and PGAA intercomparison

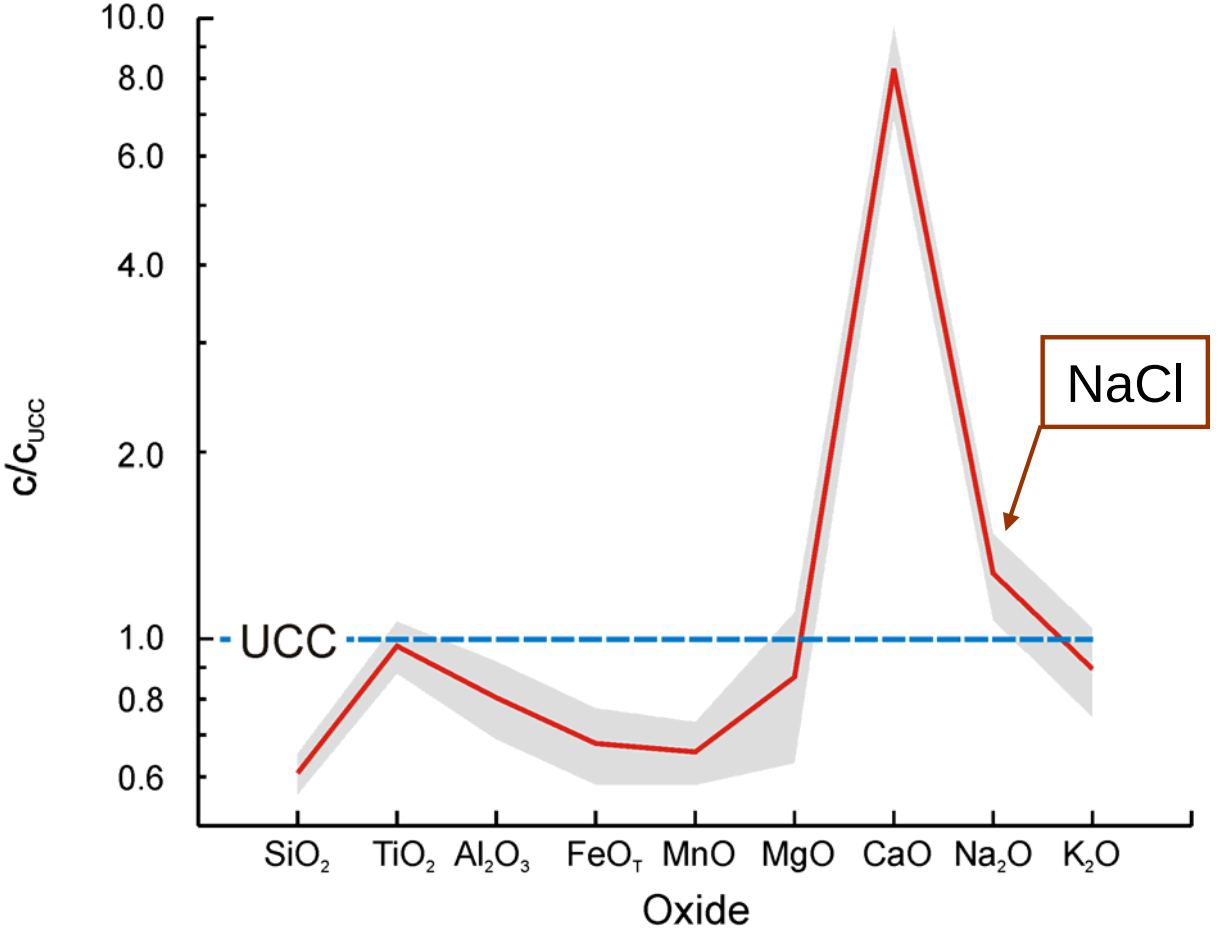
Major, rock forming elements

Spider-gram illustrating the content of major elements (as oxides) normalized to UCC



Major, rock forming elements

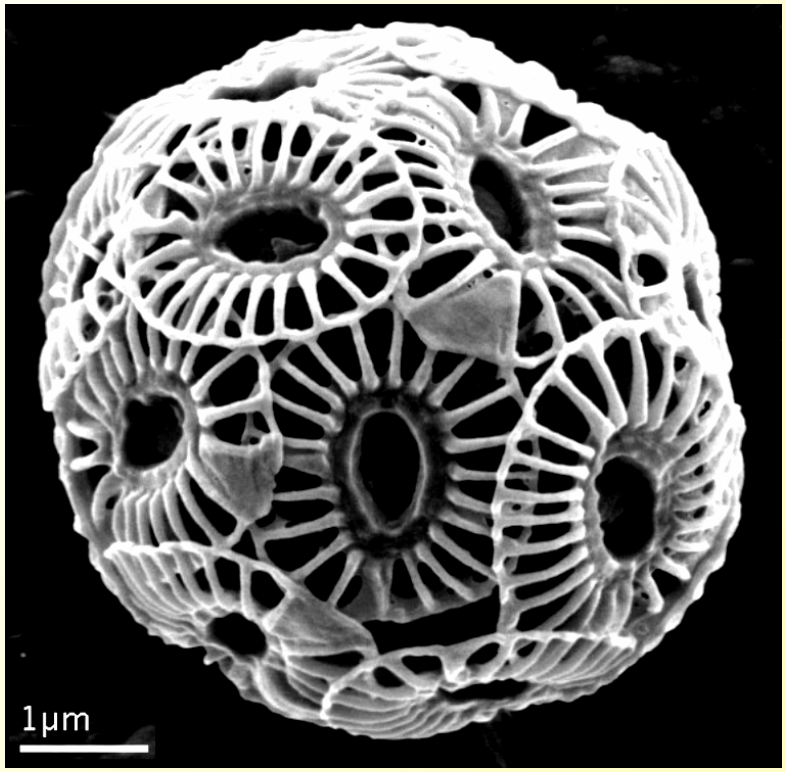
It is evident that the average content of Ca is about 9 times higher than the Upper Continental Crust



Major, rock forming elements

One possible explanation could be related to an increased content of natural carbonates, coccolithes of the calcareous microscopic algae *Emiliania huxleyi* being one of the possible source

http://www.mikrotax.org/Nannotax3/index.php?taxon=Emiliania%20huxleyi%20B%20group&module=Coccolithophores



Major, rock forming elements

	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
TiO_2	**0.816**								
Al_2O_3	**0.429**	0.346							
FeO	**0.572**	**0.503**	**0.799**						
MnO	-0.133	-0.093	**0.555**	0.378					
MgO	-0.142	-0.251	-0.368	-0.264	-0.231				
CaO	**-0.839**	**-0.638**	**-0.636**	**-0.783**	-0.027				
Na_2O	0.212	0.167	-0.125	0.206	-0.283	0.022	**-0.429**		
K_2O	**0.520**	0.363	0.311	0.511	-0.078	-0.045	**-0.704**	**0.564**	
Cl	0.211	0.149	-0.025	0.186	-0.149	0.036	**-0.438**	**0.889**	**0.423**

clay

clay

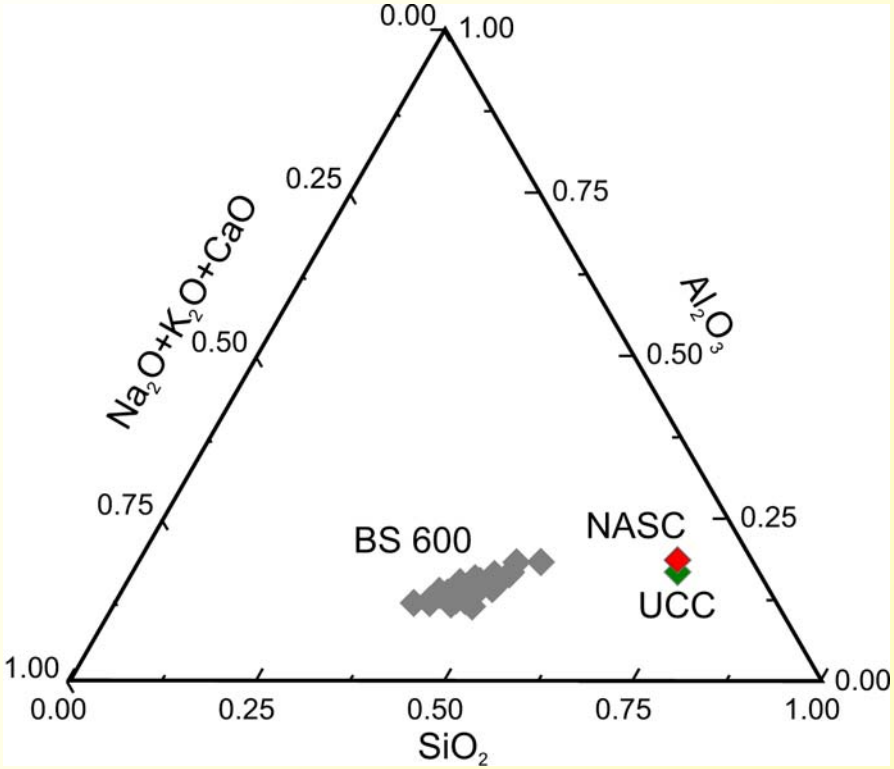
Carbonates

NaCl, KCl

The Spearmans' ρ correlation coefficients table (bold correlation at $p < 0.01$) in good agreement with the mineral composition of the sediments.

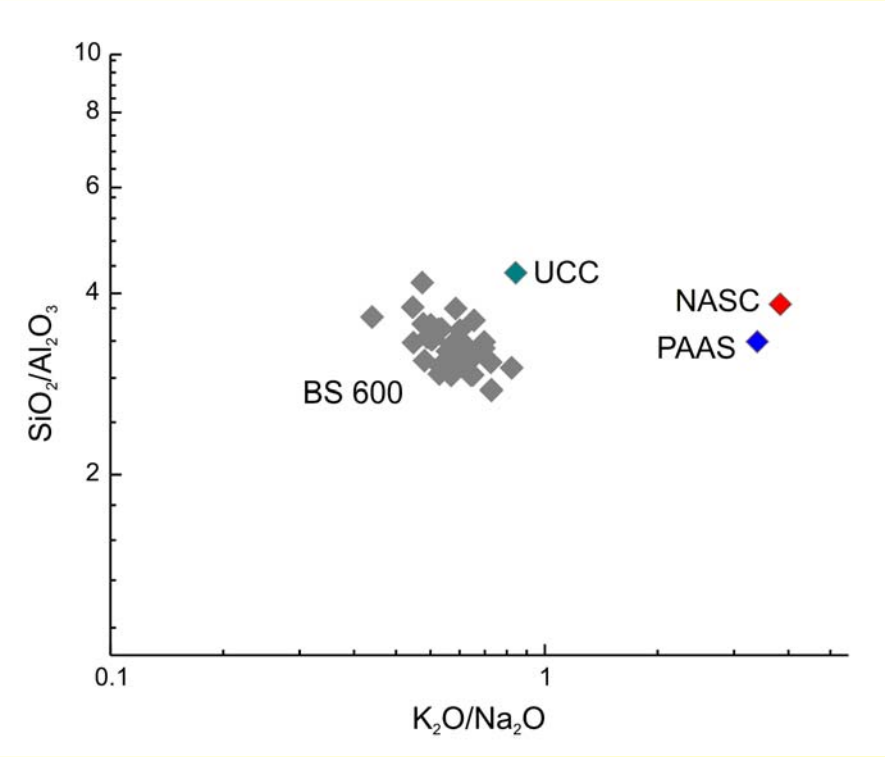
Major, rock forming elements

Although the sedimentary material originates from the continent, the significantly high content of carbonates makes the difference between BS 600 sediments and Upper Continental Crust (UCC) and North America Shale Composite (NASC)



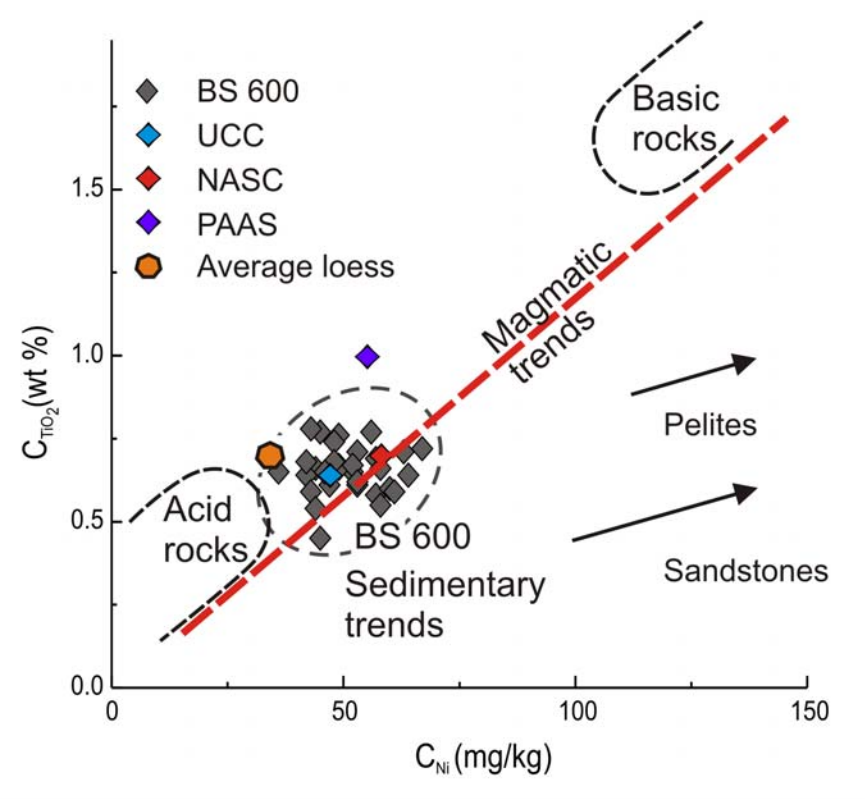
Major, rock forming elements

The continental origin is also confirmed by the SiO_2/Al_2O_3 vs. K_2O/Na_2O bi-plot where all points form a cluster in the vicinity of the Upper Continental Crust (UCC), North America Shale Composite (NASC) and Post Achaean Australian Shale (PAAS)



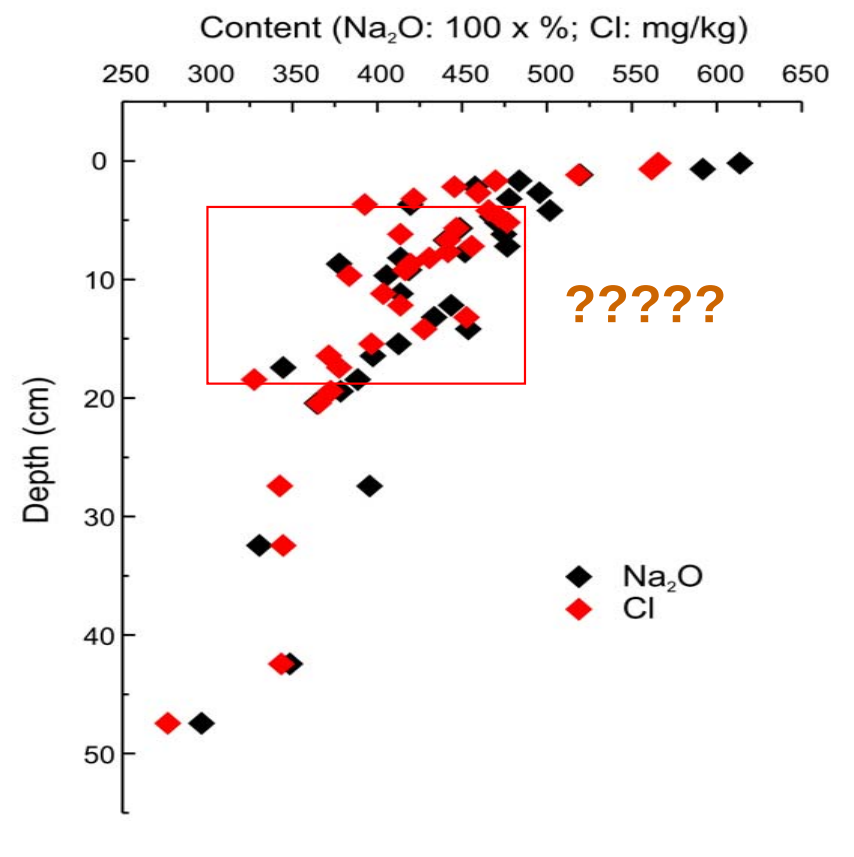
Major, rock forming elements

A possible major contribution of the continental material to the BS 600 sediments is sustained by the TiO_2 (Wt %) vs Ni (mg/kg) bi-plot where the BS 600 material lies very close to UCC, NASC, PASS and average loess



Major, rock forming elements

Elemental composition is constant or show little variation with depth except Na_2O and Cl, which present an almost exponential decrease most probable related to the salt sea water diffusion



Major, rock forming elements

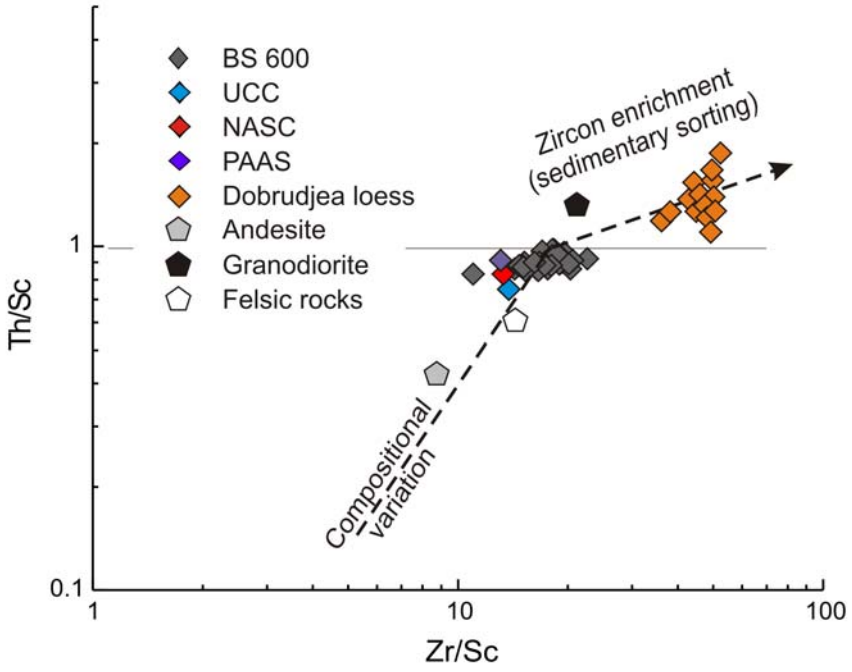
The final data resulting by analyzing the content and the distribution of **the major, rock forming elements** suggest that the BS 600 sediments have a predominant terrigenous component, close to the continental crust one, and, an important fraction of calcium carbonate related to the sedimentation of the exoskeletons of the Emiliania huxleyi coccolithophore

Trace elements

Among the 32 analyzed trace elements, the most important information concerning sedimentary material was mainly provided besides V and Ni, by incompatible and insoluble element such as Sc, Zr, REE, Hf, and Th while the redox sensitive elements **Fe, Mo** and **U** constitute excellent proxi for euxinic environments

Trace elements

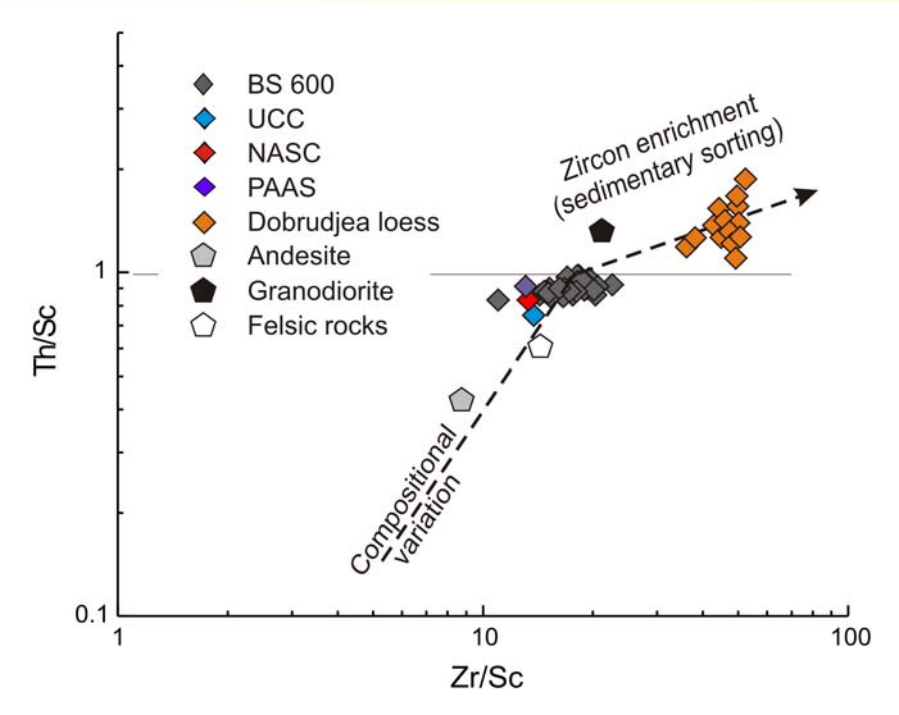
Zircon is very resilient to abrasion, the T/Sc vs. Zr/Sc diagram may give some information concerning material recycling.



In the BS600 case, the material appears less rec7cled as in the case of neighboring Dobrogea loess

Trace elements

This results as well as the similarity to UCC, NASC and PAAS, suggests that the BS600 material come from a significant larger area uncovered by loess source, in good correlation with **The Black Sea** large hydrogeological catchment basin



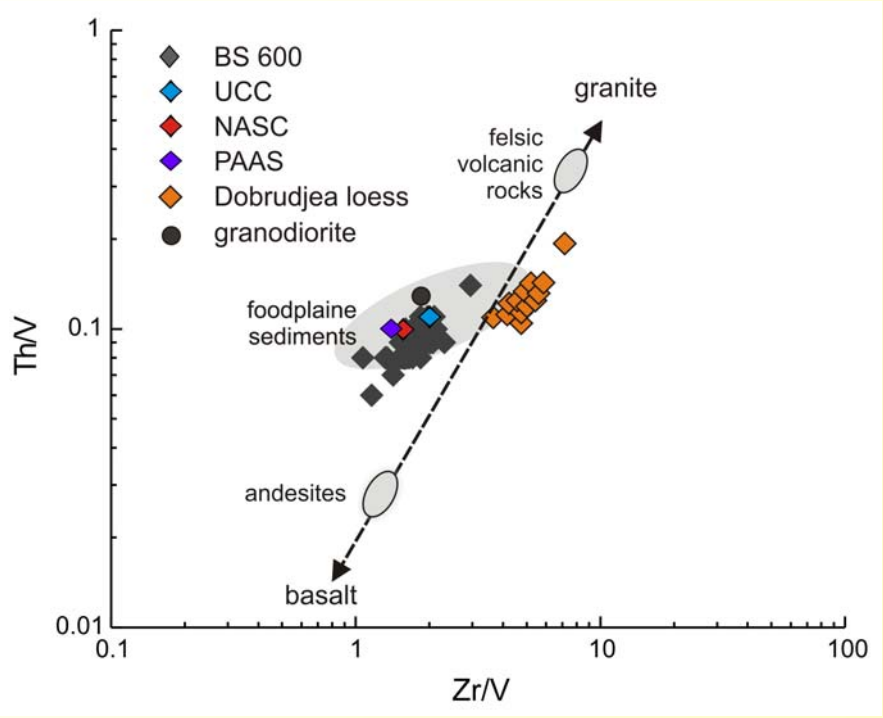
Trace elements

http://www.envirogrids.net/index.html?option=com_content&view=article&id=5&Itemid=16

Black Sea catchment basin

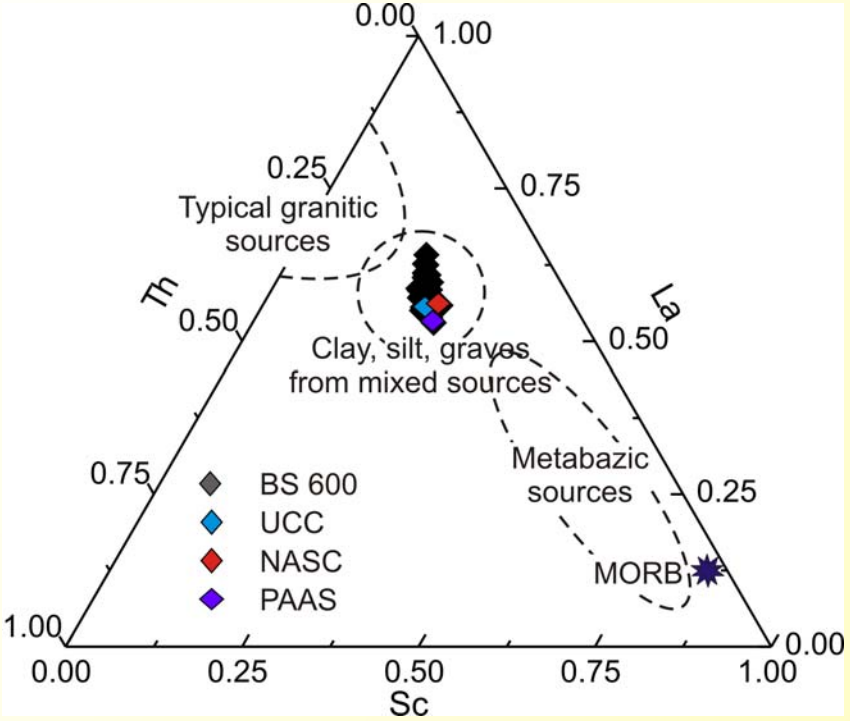
Trace elements

In this regard, the Th/V vs. Zr/V bi-plot was very useful in sustaining the hypothesis according which a significant fraction of BS 600 sedimentary material comes from the plains, as they cover significant area of the **Black Sea** catchment area



Trace elements

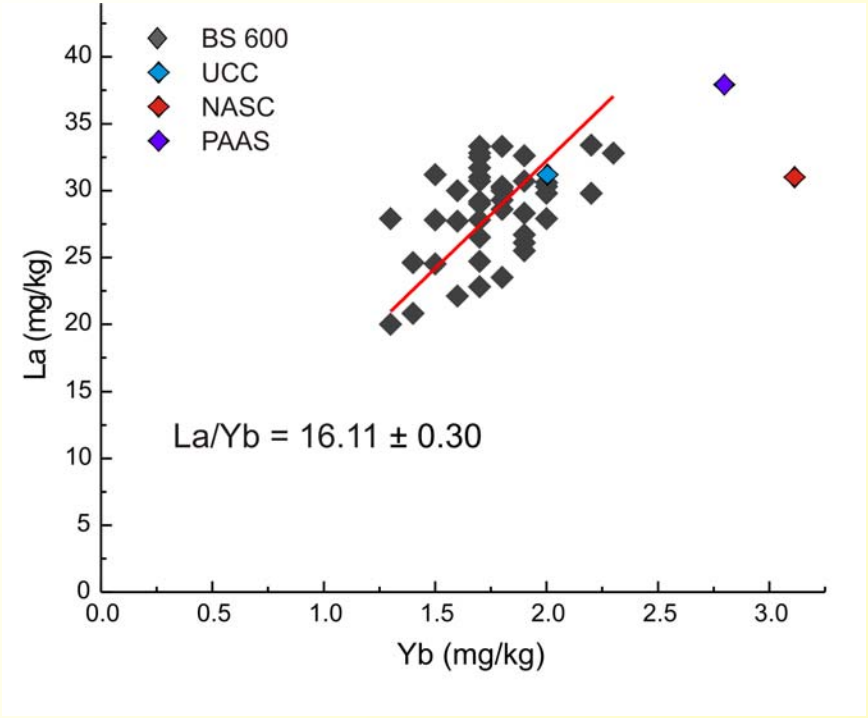
The content of incompatible elements Sc, La and Th ternary diagram suggest that the BS 600 material is very close



to the sedimentary material which enter in the composition of the UCC, NASC and PAAS

Trace elements

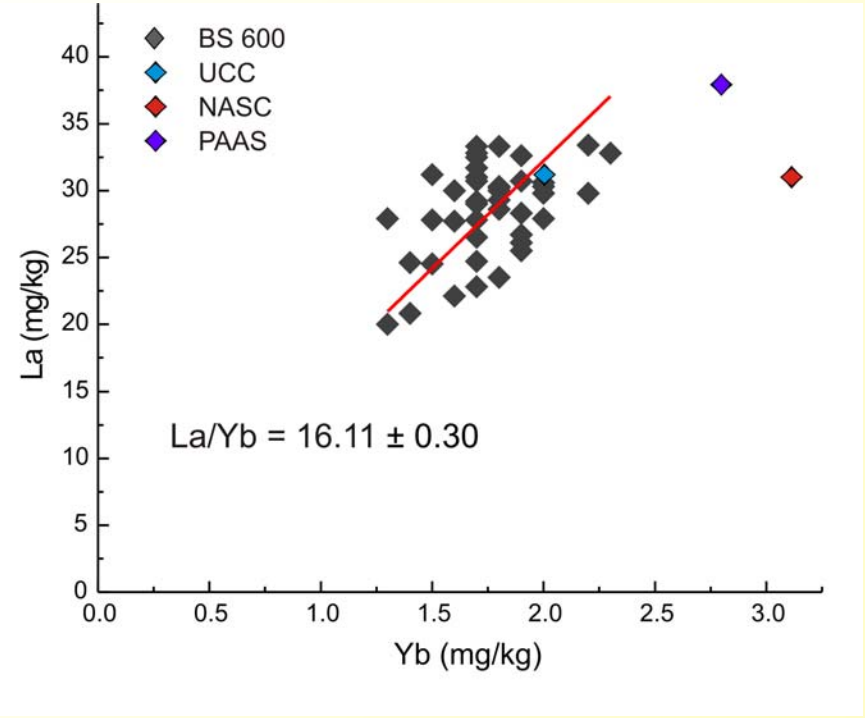
La/Th as well as La/Yb ratio are good indices concerning the investigated system. In our case, these values of 2.92 ± 0.04 and 16.1±0.3



respectively were closer to the UCC (2.96 and 15.1) than to NASC (2.48 and 10) and PAAS (2.60 and 13.6)

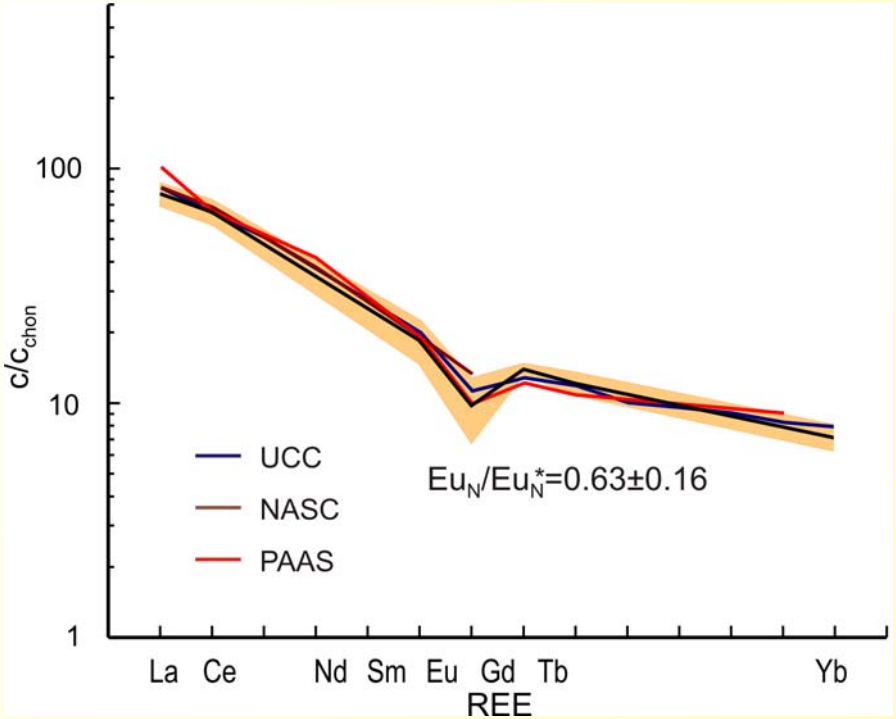
Trace elements

REE represent a group of 15 incompatible elements with similar chemical properties and which presence is very helpful in establishing the origin and the evolution of different rocks including the **Black Sea** unconsolidated sediments



Trace elements

The REE chondite normalized diagram (8 REE as determined by ENAA and PGAA) shows a typical for sedimentary rocks distribution characterized by negative Eu anomaly, a characteristic for all UCC formations



Trace elements

The second goal of this study consisted of investigating the influence of the euxinic conditions on the sediments geochemistry during the past 1 ky, *i.e.* the age of the BS 600 sediments, as previously derermined by ^{137}Cs and ^{210}Pb geochronology

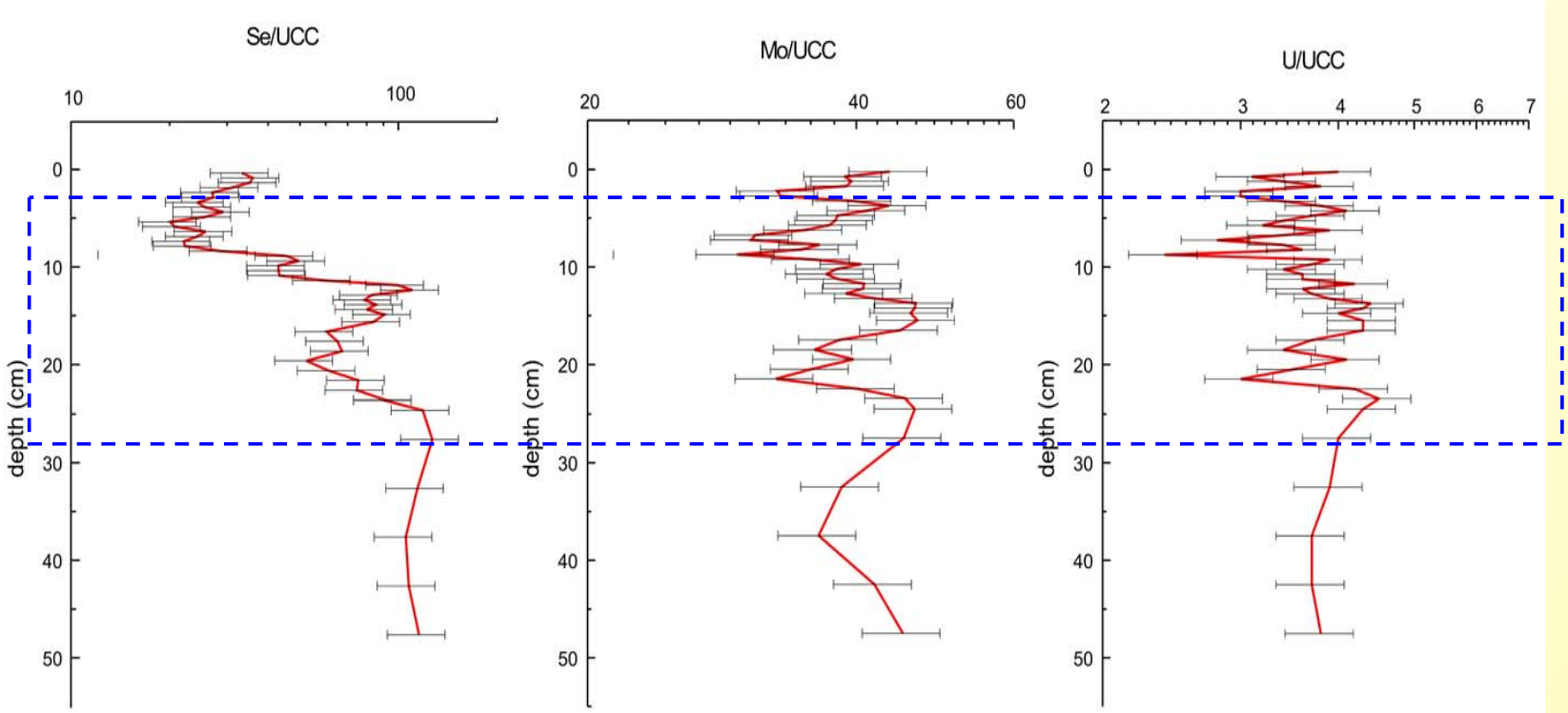
Trace elements

Fe, Se, Mo, Cd, Re and U are redox sensitive elements which content increase in euxinic environment.

INAA allowed determining only the content of Fe, Se, Mo, and U

All of them interacts with the H_2S by forming insoluble sulfides which are traped by sediments

Trace elements



We have noticed that only Se, Mo and U contents overpassed the UCC ones by about 60, 40 and less then the four times respectively

Trace elements

In all cases we have used the UCC as reference as all previous data suggested a significant similarity of the BS 600 sediments geochemistry with those of the UCC one.

Concluding remarks

Contrary to literature date, the iron content remained comparable with the UCC one.

In this case It is possible that

- the Fe content of sediments to be diluted by the high productivity and sedimentation of the coccolith skeletons which increases carbonate fraction

- the main rivers (Danube for this core) bringin sediments with low Fe content.

Concluding remarks

The distribution of eight major and 26 trace elements in a 50 cm core containing unconsolidated euxinic sediments collected from the western slope of the **Blak Sea** continental platform proved the continental origin of the sedimentary material significantly enriched in organic calcium carbonates as well as a significant steadiness of the euxinic environment during the past 1 ky

Acknowledgments

This project was accomplished only with the contribution of my colleagues form **Romania**: Prof. dr. Emil Constantinescu, dr. Carmen Cristache, dr. Gheorghe Oaie to whose memory this presentation is dedicated, **Austria**: dr. Ana-Voica Bojar, and **Russian Federation**: Dr. Otilia-Ana Culicov and Dr. Marina Frontasyeva

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