

GEOCHEMICAL SURVEY OF SEDIMENTARY ROCKS AND THE WATER COLUMNS S AND SE CRETE / MEDITERRANEAN SEA: PRELIMINARY REPORT

E. Rahders*, P. Halbach*, M. Quednau*,
M. Maggiulli* and G. Anastasakis**

ABSTRACT

During RV METEOR M 25/3 cruise in July 1993 sediment cores, unconsolidated hemipelagic surface sediments, conglomeratic sandy hard rocks, and water samples, were recovered from selected areas in the realm of the Hellenic Trench.

In the water column salinity, pH, Eh, T, O₂, CH₄, SO₄ and Cl were measured. The water column in all areas reveals a nearly uniform physico-chemical distribution pattern. However, significantly enhanced amounts of methane (max. value 717 nl/l) were detected in the bottom water column above the sediments in a pull-apart basin south of Kasos Island. Although all collected bottom waters are defined by oxic conditions, no oxygen minimum zone was discovered.

Sedimentary core material was sampled in three different tectonic domains: a pull-apart basin south of Kasos, a perched basin near the Ptolemy mountains and a plateau south of Crete, the latter, undisturbed sequence serving as reference core.

To characterise the sedimentary sequence in the piston cores geochemically, the element distribution of C_{org}, S, Fe, Mn, Ba, Cu, Mo, and As were measured. Although most sediment layers are reworked and disturbed, it was surprising to observe similar distribution profiles of C_{org}, S_{tot}, Mn, Fe, and As in all cores. Organic carbon, S_{tot}, Cu, As, Ba, and Mo are significantly enriched in the sapropels. In all cores maximum contents of C_{org}, S_{tot}, and As are detected at the base of the uppermost sapropel. In contrast, Mn as highly redox sensitive element, is enriched in the oxic sediments, just above the top of the sapropels. Remarkable in general is the erratic element distribution pattern of the multiple turbidite sapropel compared to the sapropel material from areas with less disturbed sequences. In all cores, characteristic element distributions are primarily influenced by diagenetic processes.

INTRODUCTION

During a cruises in July 1993 with the German research vessel Meteor, samples from hemipelagic, sedimentary rocks and the overlying water column were recovered. The study and sampling areas of the M 25/3 cruise are

* FU Berlin, Institut für Geologie, FR Rohstoff- und Umweltgeologie, Malteserstr. 74-100, 12249 Berlin, Germany.

** NCMR National Centre For Marine Research, 16604 Hellenikon-Athens, Crece.

located south of Crete as well as southeast of Crete and south of Kasos, to obtain sediment cores general regions were restricted but undisturbed autochthonous sedimentation (perched basin), as well as with slumped turbidic sediment filling (steep depressions). Such redeposited sediments can dominate the sediment accumulation in continental-margin basins over long periods of time so we can learn and increase our understanding of how material fluxes proceed from the continental shelf to the deep sea and thereby which role local marginal basins may play.

This complete region is characterised by active tectonic domains, with strong vertical and lateral crustal movements at the margin of the Aegean microplate (McKenzie 1972, Le Pichon and Angelier 1979, Mascle et al. 1986, Jongsma 1987, Meulenkamp et al. 1988, Finetti et al. 1991). The aim of the current investigation is to examine the bulk chemistry of the water columns and sediments in order to compare these data obtained from locations defined by different tectonic styles, i.e. pull-apart structure, perched basin and a plateau with "normal" hemipelagic sedimentary conditions. All three tectonic regimes were sampled (see Fig. 1, A1, L2, L4):

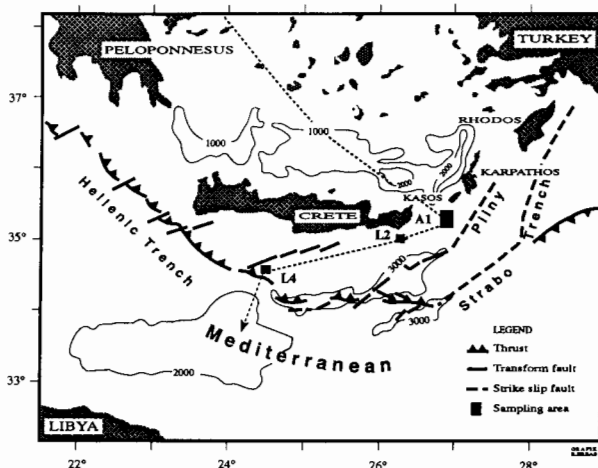


Fig. 1: Track of Meteor Cruise M 25/3. Area A1 and locations L2, L4 are shown.

1. In core 60 PC from a pull-apart basin south of Kasos the layers appeared as a multiple turbidite sequence with expanded thicknesses.

2. From a perched basin at the Ptolemy Mountains, close to the Hellenic Trench, the recovered core 36 PC shows a more reworked sedimentary sequence.

3. Core 19 PC from a plateau south of Crete has a "normal" undisturbed sedimentation environment with low sedimentation rates.

Our core 19 PC is the "reference core" for the determination of chemical and mineralogical differences as compared to turbiditic and reworked core material. In a further step, element fluxes shall be calculated in this area of active plate boundaries in order to analyse the local development since Miocene times.

In the Eastern Mediterranean Sea the lithological sediment profile is characterised by a sequence of hemipelagic sediments, alternating with tephra and sapropel layers (Kidd et al. 1978, Sutherland et al. 1984, Pruyssers et al. 1991, Thomson et al. 1993). One of our first objectives was a geochemical inventory of these sapropels, which reflect special de-

positional conditions.

The thicknesses of the uppermost sapropel layer which was observed in the recovered cores, are varying tremendously. In core 60 PC it has an enormous thickness of 290 cm. These varying thicknesses which are due to disturbed layers and/or multiple turbiditic sequences can be explained by the local tectonic evolution. Therefore, a fundamental analysis of the main tectonic structures is necessary.

TECTONIC SITUATION

The geotectonic situation of the eastern Mediterranean Sea in particular of the region south of Crete, Kasos and Karpathos exhibits evidence of compressional as well as of extensional tectonics. This is explained by a recent to subrecent change from more orthogonal subduction of the African plate beneath the Aegean microplate in the west to more transpressive to transurrent deformation in the east of the study area resulting from incipient suturing of some microcontinental blocks against the Aegean microplate block (e.g. McKenzie 1972, Le Pichon and Angelier 1979, Jongsma 1987, Meulenkamp et al. 1988, Papazachos (1991), Anastasakis et al. 1994).

One important tectonic-morphological aspect of this region is the existence of two parallel trench features (Pliny and Strabo) which are dominated by large-scale strike-slip dislocations. In particular the eastern Pliny trench and Strabo trench segments show features which indicate both transcurrent displacement and more or less compressive northward underthrusting strike-slip tectonics, however are dominating. Jongsma (1987) described the latter trenches as narrow 3-4 km from southeast of Crete to the NE near Karpathos. The trenches consist of a series of narrow "en-echelon" troughs striking N 25°-50°. The eastern part of the Pliny trench (south of Kasos and Karpathos) becomes indistinct and it finally disappears.

Between the east of Crete and the Karpathos Island we observe a zone of E-W to NE-SW trending horsts and grabens indicating also strong vertical movements possibly combined with diapiric activity, (i.e. rapid elevation). Although this area is dominated by structural features rather attributable to extension, the nature and orientation of the ridges, basins and fault patterns show a strong link to the alignment of the eastern sector of the Pliny trench which suggests that a strike-slip modification of the former compressional regime has occurred. So our study area A1 is located in this region of sheared blocks and depressions with an orientation oblique to the strike of the adjacent eastern Pliny trench. The geometry and structural configuration of the deepest part of the A1 depression are comparable with the extensional situation of typical pull-apart basins. However, from north to northwest we observe an overthrusting and tectonic stacking of the lower slope and basin-filling sediments from the Aegean microplate (Fig. 2). In the SE of the basin a steep horst structure (seamount up to about 600 m waterdepths) is uplifted.

On the landward wall we observe furthermore a left-lateral strike-slip component which shapes the morphology of this slope significantly. This structure is possibly related to the transparent system of the eastern Pliny trench.

SAMPLING AREAS

The sampling locations are situated at the southern margin of the Aegean microplate. Here vigorous vertical and horizontal crustal forces result

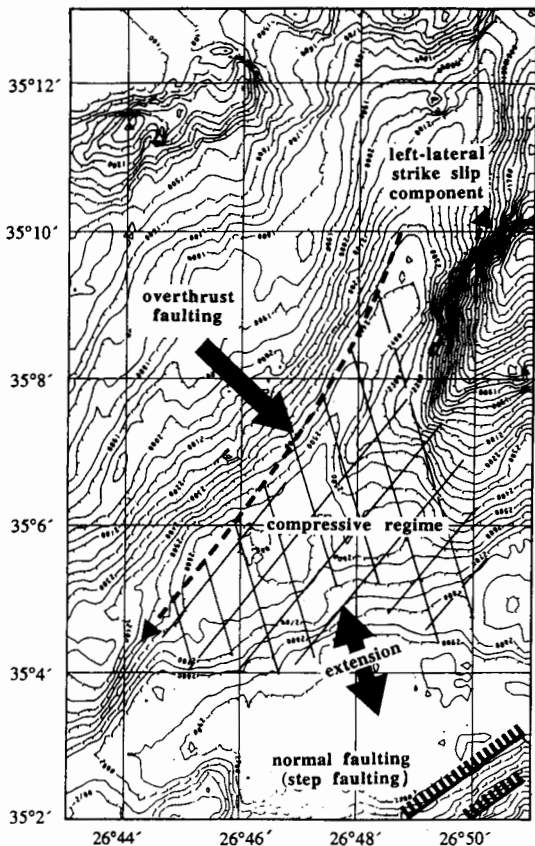


Fig. 2: Tectonic model for the evolution of area A1 ("South Kasos Basin"), interpreted as a "pull-apart basin".

in a complex tectonic pattern (Masclé et al., 1986). Sampling locations (Fig. 1) include a pull-apart basin A1, a plateau south of Crete L2 and an indicated perched basin L4.

We concentrated our research work on area A1 (Fig. 2), a basin north of the of the eastern Pliny Trench, with NE-SW striking and a maximum water depth of 2980 m.

Seismic profiles close to area A1 perpendicular to the above mentioned slip fault (Anastasakis et al., 1994) prove an analogue situation, with overthrusting from the NW, marked by landward deep faults and by sediment reflectors dipping seaward to SE.

CORE LITHOLOGY

Piston cores 19PC, 36PC, and 60PC, were recovered south and southeast of Crete from water depths of 1814 m (19PC: 34°53.41N / 26°23.10E), 229 m (36PC: 34°32.40N / 24°45.80E), and 2930 m (60PC: 35°03.07N / 26°48.01E),

respectively (Fig. 1). Their lengths are to 8.35 m (19PC), 9.25 m (36PC), and 11.20 m (60PC). All three cores were split and described onboard ship, and then sealed under nitrogen atmosphere, in order to avoid oxidation of the sapropel layers. Subsampling was carried out onboard ship in a 10-15 cm resolution for the entire cores, and later in the home laboratory in a 1-2 cm resolution for the sapropel / mud transitions.

Core 19PC (Fig. 3) reveals a yellow hemipelagic mud above the uppermost sapropel, with two volcanic ash layers intercalated at 36.5-37 cm below seafloor (bsf) and 53.5-54 cm bsf. The first sapropel, dated as S 1 (J. KELLER, pers. comm. 1994), is present at 58.5-82.5 cm bsf, exhibiting oxidised bioturbation structures. The second sapropel follows downcore in a depth of 480-495 cm beneath a sequence of gray, bioturbated ooze / mud, which itself is interrupted by volcanic ash, silt, and sand layers, at 198.5-201 cm bsf, 263.5-263.8 cm bsf, 284-288 cm bsf, and 450-455 cm bsf. A possible tephra layer (475-480 cm bsf) is present directly on top of the second sapropel. Two further, thin sapropel layers were encountered in the gray mud at 552.3-556.2 cm bsf and 568.5-574.5 cm bsf, possibly representing only one sapropel (S 4 ?). The lowermost sapropel of core 19PC is 60 cm thick (630-690 cm bsf), and shows distinct lamination in its central part as well as an intercalated, millimetric foraminiferal sand layer at 676 cm bsf. A blueish-gray redox front is developed 24 cm above the top of this sapropel. Three indistinct or possible silt-sized tephra layers were observed in the gray mud below this sapropel, at 756.5 cm bsf, 783-789 cm

bsf, and at 809-819 cm bsf. In general, no turbiditic events and no indications of reworking there are strong bioturbation structures, especially within the sapropels.

Core 36PC (Fig. 3) has a relatively similar lithology to 19PC, with comparable sapropel and tephra units: the uppermost sapropel was encountered under-

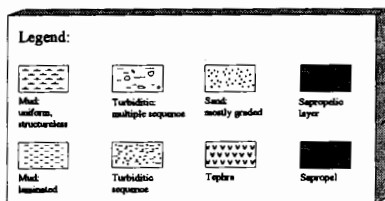
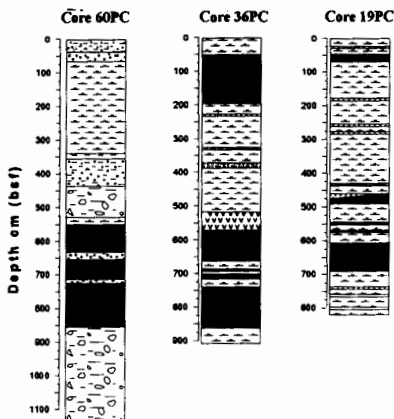


Fig. 3: Simplified core-logs of the recovered piston cores

present in 552-575 cm bsf, in 36PC in a depth of 696-719 cm bsf, and here the upper sapropel layer is connected to a 3 mm thin, bluishgray redox front about 5 cm above it. Probably, also these two sapropel layers in 36PC belong to only one sapropel (S 4 ?), because they are only separated by 5.5 cm of oxic mud. Like all other sapropel layers in 36PC they are also regarded as reworked deposits, which is also true for the lowermost sapropel in 36PC. This is 128.2 cm thick (743.6-871.8 cm bsf), and related to an other millimetric bluish-gray redox front 7 cm above its top in the gray mud. At least four bioclastic turbidites are intercalated in this sapropel, and below it some lamination was observed in the mud (900-906 cm bsf).

Core 60 PC (Fig. 3) is distinctively more turbiditic than both other cores. At its top, a 47 cm thick turbiditic sequence is present, composed of coarse - grained layers with wood fragments, silt, and turbiditic mud (BOUMA layers Td to Te). Underneath, a uniform, structureless and extremely fine-grained turbiditic mud was observed down to 312 cm bsf. A 2 m thick sequence of alternating, up to 77 cm thick turbidites, partly cut-off at their bases, follows down. Below this multiple turbidite sequence is a sapropelic mud (539-621 cm bsf) was encountered, which itself includes several fine-grained, thin turbidites. Between sapropelic mud and the first and only, 208 cm thick reworked sapropel, another 19 cm thick turbi-

dite exists, and also the sapropel (640-848 cm bsf) is interrupted by a non-sapropelic turbidite at 704-711 cm bsf. Furthermore the sapropel contains numerous cm-thick clayey, silty, and sandy intercalations which are also partly upward-graded. Underneath the thick sapropel a frequent alternation of turbidites (BOUMA layers Tb to Tc), up to about 10 cm thick and partly composed of graded volcanic sands and silts, was observed forming another prominent multiple turbidite sequence at the base of this core (848-1120 cm bsf). Here also thin band of Mn staining are present.

In summary, core 60PC seems not comparable lithologically to the two other cores because of its composition mainly of turbiditic sequences, which were found in the very thick sapropelic and sapropel layers, too. Also a 275 cm thick layer of uniform structureless mud (47-312 cm bsf) is considered to be of turbiditic origin, and no autochthonous tephra layer could be detected in this 11.2 m long core. Core 36PC seems partly comparable to core 19PC in terms of lithology and lithostratigraphy although the uppermost tephra layer of 19PC (encountered above sapropel S1) is not present in core 36PC. Also, in contrast to 19PC, all sapropels of 36PC are reworked deposits, and a number of turbiditic events were observed in the oxid mud as well as in the sapropels. But the top of the uppermost sapropel (probably S 1 in both cores) was encountered in a similar subsurface depth of 44.5 cm in 36PC and 58.5 cm in 19PC (resulting in a sedimentation rate of 6.4-8.4 cm/ky for the last 7,000 years at both sites. On the other hand, all sapropels in core 36PC are much thicker than the sapropels in core 19PC, which is also true for the prominent tephra layer in 36PC (503.5-552 cm bsf) compared to its possible equivalent in 19PC (475-480 cm bsf). Therefore, core 19PC seems to represent the "normal" hemipelagic sedimentary conditions (= palaeofluxes of particles and elements) in the Eastern Mediterranean Sea much more than all other cores recovered during the M25/3 cruise.

SAMPLING TECHNIQUES AND ANALYTICAL METHODS

Water chemistry was investigated especially regarding the contents of O₂ and salinity (CTD multisonde), CH₄ (gas chromatography), and Mn (polarography) for on-board determination. The samples were obtained with ten 5 l Niskin bottles per station. Sediments were sampled by long piston cores and the sedimentary cover was collected by box corer. The sediment sample material was dried at 105 °C. Carbon and sulphur were analysed by infrared spectrometry (SECO Inc.). CaCO₃ contents were calculated after determination of C_{tot}. The contents of Corg were calculated after heat-treatment (over 2 hours) of the samples at 500 °C. Ba, Mn, Fe, Mo, and Cu concentrations were analysed by ICP-AES. For ICP analysis the statistical error was less than 5%. Arsenic contents were measured by hydride AAS.

GEOCHEMISTRY OF THE WATER COLUMN

Nearly constant values of O₂ (5-7 Mg/l), a pH of 8.3, and a salinity of 38-39 ‰ were measured throughout the whole water-column at every station. A small increase of temperature was noticed with increasing water-depth, starting with 13.8 °C at a depth of 300 m increasing to 14.45 °C at 2900 m. In area A1 a slight increase is detected for manganese concentrations from less than 0.2 ppb to 2.6 ppb. Also in the bottom water methane contents in area A1 display increasing values toward the seafloor: at station 2 MS the CH₄ concentration was 274 nl/l in a water-depth of about 600 m, increasing

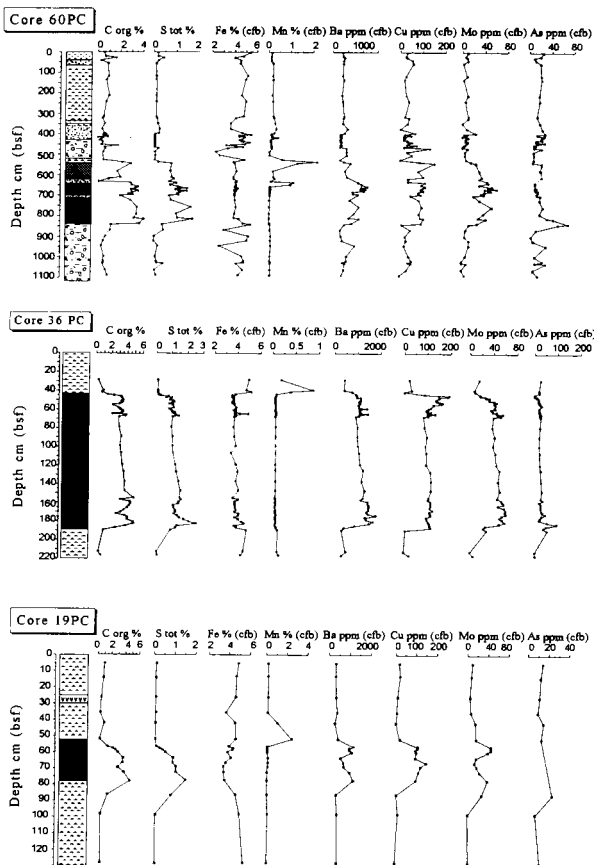


Fig. 4: Concentration / depth profiles for the cores 60PC, 36 PC, and 19PC.
For signatures see the legend at Fig. 3.

to 604 nl/l at about 1390 m and to 717 nl/ml in 2923 m. The background of methane in the eastern Mediterranean seawater is 20-60 nl/l.

GEOCHEMISTRY OF THE SEDIMENTS

Core 19PC was geochemically analysed to a depth of 1.2 m, core 36 PC up to 2.2 m and core 60 PC in its whole length (Fig. 4). However in core 19 PC and 36 PC only the uppermost sapropel and in core 60 PC one thick sapropel sequence is thus covered. Consequently we always refer to the uppermost sapropel in each core.

For *organic carbon* (= C_{org}), obtained from the recovered surface samples, the regional background value is approximately 1 %. In the oxic environments of the recovered cores (Fig. 4), i.e. turbiditic sequences and structureless mud, the amount of Corg is generally similar to the background. Only in core 60 PC three layers show Corg contents of 1.6 %, 1.85 %, and 3 %, respectively (Fig. 4). The multiple turbiditic sequences of core 60 PC is reflecting the same irregular distribution pattern of Corg as the less disturbed cores 36 and 19 PC. In core 60 PC in sapropel S1 organic carbon varies between 2.1 to 4.2 %. Core 19 PC has a max. value of 4.4 % in S1 (Fig. 4). In core 36 PC Corg varies between 1.5 % and 4.8 %. Sa-

propels are defined as organic-rich layers with Corg contents of more than 2 (Kidd et al. 1978). In all three cores Corg is enriched at the base of S1.

Sulphur generally is enriched in the sapropels compared to the oxic environment. A sharp boundary reflects the change between the various redox conditions. The Stot concentration generally varies between 0.053-0.065 % in the oxic environment (Fig. 4). However, an enhanced value of 0.43 % Stot is detected immediately below sediment-water interface. Within the sapropels S-contents increase to 0.8 % (max. value 1.75 %). There is an obvious trend of enrichment toward the base of the uppermost sapropels. A similar behaviour is recognisable in the cores 36 PC and 19 PC.

Carbonate was additionally determined. CaCO₃ has max. Contents of 75.4 % in the oxic sediments and less contents in the uppermost sapropels with 26-47.5 %. To avoid dilution effects by an extensive amount of carbonate minerals all metal contents were normalised to a carbonate free basis (=cfb).

Manganese (cfb) has comparable distribution patterns in all three cores (Fig. 4), but the concentrations of the compared cores are not uniform. Mn is, as one the most redox sensitive elements, typically enriched immediately above the uppermost sapropels with 2.19 % (60 PC), 0.87 % (36 PC), and 2.5 % (19PC). In general Mn appears significantly depleted in the sapropels (min. value of 0.06 % in 36 PC), and is 5-14 times enriched in the oxic environment just above the sapropels.

Iron, a typical redox-sensitive element does not reveal a significant distribution pattern similar to above-mentioned Mn. Regarding core 60 PC Fe-concentrations (cfb) start with 5.38 % and vary in a wide-spanned range of 2.32 % - 5.5 % (Fig. 4). In the sapropelic environment of core 60 PC Fe-contents in the oxic part remain relatively constant. Regarding the cores 36 PC and 19 PC Fe-contents appear slightly depleted in the sapropels. In the central part of the 36 PC-sapropel, vertical distribution is more or less homogenous. Iron concentrations do not exceed 5 % in the sampled section of core 19 PC. Although generally depleted compared to the oxic parts of the cores, Fe values seem to increase towards the top of the sapropel.

Barium (cfb) is a typical nutrient type element. Regarding core 60 PC the vertical distribution is defined by a uniform range of contents: 300-397 ppm. In the sapropelic layer Ba concentrations increase up to 1200 ppm. Generally, in all three cores Ba is enriched at the top and bottom of the uppermost sapropel. Ba distribution has no relationship to organic carbon. Secondary redistribution signals, as mentioned by Van Os et al. (1991) i.e. re-enrichment above the reducing environment cannot be detected.

Molybdenum contents of all cores vary between 0 to 20 ppm (cfb) regarding the oxic environment. A sharp increase of Mo-contents can be detected in the uppermost sapropels in all cores. As a rule Mo is about 4-5 times enriched compared to the non-sapropel units. In cores 60 PC and 36 PC maximum values are 60 ppm; core 19 PC has a maximum value of

Copper distribution varies among a wide range: 0.85 up to 75 ppm (cfb) considering all oxic sequences in the cores. In the uppermost sapropels of the cores the mean value ranges between 90-120 ppm. Below the uppermost sapropel Cu contents decrease immediately.

Arsenic has a similar distribution pattern as sulphur regarding oxic and anoxic layers. In the upper parts of the uppermost sapropel As-contents are not different from those in the oxic layers. Only at the base of the sapropel there is a sharp significant increase of arsenic contents. This behaviour can be identified in all three cores.

CONCLUSIONS

For the interpretation of the preliminary results it has to be considered that the surveyed locations are situated in a very active tectonic region in the realm of the Hellenic Trench (e.g. Jongsma 1987). Remarkable is are A1, with relatively fast subsidence resulting in an enormous gravity-driven sediment supply. Sedimentation rates of up to 1 m/ky were calculated for the sequences above the S1 sapropel in core 60 PC.

The recent tectonic activities in area A1 produced pathways for upward migrating gas phases such as methane with max. values of 717 nl/l in the bottom water. This anomaly is obviously not caused by degassing of the very thick turbiditic upper sapropel layer encountered in core 60 PC, because the complete sequence of fatty acids is still present in this sapropel (pers. comm., C. Vale, Lisbon). Therefore, it is proposed here that the methane source (other thick sapropel layers) lies below the studied sapropel.

The sedimentary profile reveals a characteristic geochemical contrast between the oxic layers and the sapropels. The organic-rich sapropels are effective geochemical traps, enriching a number of trace elements. After deposition of the sediment the primary element distribution changed due to diagenetic processes, as previously discussed e.g. by Pruyssers et al. (1993). In these processes oxidation fronts are involved as an effective mechanism of element transport and redistribution.

The interpretation of the geochemical results obtained from two of the sediment cores is complex because of the extremely disturbed sequences. In these cores the uppermost sapropel appears as a multiple turbidite (60 PC, pull-apart basin), or as a reworked horizon (36 PC, perched basin). Another, piston core is the reference of a "normal" sedimentation (19 PC, plateau situation). In general there are only small but significant geochemical differences between the various cores regarding the uppermost sapropel.

The amount of Corg defines sapropels, at least 2.1 - 4 wt, % we measured. In the reference core PC 19, Corg-values (Fig. 4) decrease significantly from the base to the top of the sapropel, probably because of downward oxygen diffusion and subsequent "burning down" of the sapropel material. This supports the hypothesis that post-depositional diagenesis can distort the distribution of organic carbon significantly. In the other two piston cores (Fig. 4) this decrease in organic carbon from the base to the top of the uppermost sapropel is not quite as obvious, probably due to the strong reworking in core 36 PC, and the multiple turbiditic deposition in core 60 PC.

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Sulphur and As have a similar distribution pattern as Corg. The downward moving redox-front is also clearly expressed by As with a sharp maximum peak at the base of the sapropels in all three cores.

The nutrient-type elements Ba (and Cu), and the conservative element Mo seem not to be affected by subsequent diagenetic processes. The concentration/depth profiles for these elements display no individual concentration maxima which may be expected in the oxic environment. Ba, Cu and Mo appear to be conserved as primary signals. The distribution of these three elements within the 290 cm thick sapropel layer in core 60 PC with its turbiditic characteristic and its interlayers is more erratic than in the other two cores. Nevertheless, a significant similarity of all three profiles could be stated regarding e.g. the relative enrichment of Corg, As and S at the base, overall decrease of Fe, and the enrichment of Mn immediately above the sapropel.

Consequently, vertical element flux in the sediments appears to be affected by reducing diagenetic activities caused by mass flow induced by strong tectonics. When an oxidation front moves downward the most redox-sensitive elements appear to be mobilised.

The progress of diagenesis which may be responsible for the re-distribution of less mobile phases may be stopped by sudden input of a new elemental budget by gravity driven mass flow. Previous oxidation processes stop and chemical re-equilibration has to be organised anew. According to specific reaction kinetics a selective mobilisation can be assumed.

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