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Geochemistry of an exotic sediment layer above sapropel S-1: mud expulsion from the Urania Basin, eastern Mediterranean?

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Abstract

In a gravity core from the eastern Mediterranean Sea, a chemically and mineralogically distinct, 5.5-cm-thick layer is present above sapropel S-1 and overlain by hemipelagic marls. Calcite is completely absent in this exotic layer, dolomite is present only in small amounts, and the Cr concentrations are significantly enhanced. The layer was deposited primarily under reducing conditions, but the distributions of redox-sensitive elements show that a large part of the exotic layer is now oxidised by a downward-progressing oxidation front. Sediments from within the nearby anoxic, hypersaline Urania Basin are similar to those from the exotic layer, in particular in S-, C-, and O-isotope distributions of pyrite and dolomite, as well as increased Cr concentrations. Mud expulsion due to expansion of gas-rich mud is proposed to explain the presence of the exotic layer outside the Urania Basin. The deposition of an anoxic layer above S-1 shielded the sapropel from oxidation which resulted in the rare occurrence of a complete preservation of S-1 and provides the first minimum age for the start of anoxic mud accumulation in the Urania Basin.

Author Keywords: brine basin; sediment; accretionary complex; diagenesis; sapropel; eastern Mediterranean

1. Introduction

In compressional tectonic regimes like accretionary wedges, fluid migration within the sediments is commonly observed, and upwards migrating gas- and fluid-rich muds may result in mud volcanoes and mud diapirs which are most prominent seafloor expressions in such areas. Along the crest and the inner part of the Mediterranean Ridge, overpressured, fluid-rich sediments escape from the decollement zone or from higher levels of the accretionary wedge due to the compressive tectonic regime (Camerlenghi et al., 1992; Cita et al., 1989 and Robertson and Kopf, 1998). The Urania Basin is one of the few known depressions in the eastern Mediterranean Sea filled with anoxic, highly saline brines (De Lange and Ten Haven, 1983; Scientific Staff of Cruise Bannock 1984-12, 1985; MEDRIF Consortium, 1995 and De Lange et al., 2001). The basin is located about 200 km west of Crete on the Mediterranean Ridge (Fig. 1), at the boundary of the accretionary complex and the so-called Inner Plateau of the ridge (Lallemant et al., 1994). The anoxic sediments of the basin contain abundant dolomite, elemental sulfur and gypsum, and a thermal anomaly of up to 45°C was detected in the western part of the Urania Basin (Corselli et al., 1996). Accordingly, the transport of warm fluids (and possibly sediment) from a deeper source to the Urania Basin is attributed to the compressional regime of the ridge. Outflow of Urania brine or deposition of Urania Basin mud outside the basin has not been reported thusfar.

Fig. 1. Location of the Urania Basin in the eastern Mediterranean. Coring locations are indicated as well as the approximate brine-filled area of the basin (shaded grey). The dashed line is the profile line (A–B) of Fig. 4.

In this paper, we discuss the mineralogical, geochemical and C-, O- and S-isotope inventory of the uppermost 23 cm of a gravity core taken in the vicinity of the Urania Basin, containing an exotic sediment layer. The core consists of hemipelagic marls with several intercalated sapropel layers representing the usual succession of the eastern Mediterranean. However, as a special feature, a partly anoxic sediment layer poor in carbonate (the carbonate is dominantly dolomite; Table 1) is present above the youngest sapropel S-1 (Fig. 2). Being significantly different from the overlying hemipelagic marls as well as from the underlying sapropel in colour and carbonate content, this layer was considered to be exotic in the normal hemipelagic succession of core 6SL. By comparing the mineralogy and geochemistry of the exotic layer with sediments which accumulated within the Urania Basin under anoxic and hypersaline conditions, we present evidence that the exotic layer of our core is genetically related to the Urania Basin sediment/brine system. It is peculiar to find brine basin sediments about 40 m above the present brine interface, so the possible mechanisms for the upward transport or other processes responsible for the emplacement of this exotic material are discussed. The age of the eastern Mediterranean brine basins is poorly known and so far spanning from 2000 yr for the Discovery Basin (Wallmann et al., 1997) to 176 000 yr (Scientific Staff of Cruise Bannock 1984-12, 1985). For the Urania Basin, no data are available to date, thus the age correlation of the exotic layer is significant in providing the first minimum age of the start of anoxic mud accumulation in the Urania Basin area.

Table 1. Mineralogy of samples from core 6SL and representative samples from two cores from within the Urania Basin (core 3SL and 4MC).

		Q	Fsp	CC	Dol	Pyr	Selem	Gyp	Hal	Illit	Chl	Smek	Kaol
Core 6SL													
1–2 cm	hemipelagic marl	xx	x	xxx	x	–	–	–	x	x	(x)	x	(x)
3–4 cm	hemipelagic marl	xx	x	xxx	x	–	–	–	x	x	(x)	?	(x)
5–6 cm	exotic layer, brown	xxx	x	(x)	x	–	–	–	x	x(x)	(x)	?	(x)
7–8 cm	exotic layer, brown	xxx	x	–	x(x)	–	–	–	x	x(x)	(x)	x	(x)
9.5–10 cm	exotic layer, grey	xxx	x	–	–	x	–	–	x	x	x	?	(x)
13–14 cm	sapropel	xx	x	xxx	(x)	x	–	–	x	x	x	?	–
19–20 cm	hemipelagic marl	xx	x	xxx	x	(x)	–	–	x	x	x	?	–
Core 3SL													
152 cm	Urania Basin mud	xxx	–	xxx	xx	–	xx	xx	xx	x	x	x	–
Core 4MC													
38 cm	Urania Basin mud	xxx	–	xxx	xx	–	xxx	x	xx	x	x	x	–

Key: xxx, major constituent; xx, intermediate constituent; x, minor constituent. Q, quartz; Fsp, feldspar; CC, calcite; Dol, dolomite; Pyr, pyrite; Selem, elemental sulphur; Gyp, gypsum; Hal, halite; Illit, illite; Chl, chloride; Smek, smectite; Kaol, kaolinite.

Fig. 2. Geochemical profiles and schematic core log of the uppermost 25 cm of core 6SL. The exotic layer between 5 and 10.5 cm is divided into an upper brown and lower grey part. Concentrations are normalised to Al in order to account for carbonate dilution. Cadmium, Cr, Cu, V, Zn and Zr concentrations are multiplied by 1000.

2. Materials and methods

Core 6SL was recovered during Meteor cruise M40/4 from the central rise between the two branches of the anoxic, hypersaline Urania Basin, in the eastern Mediterranean Sea (Fig. 1) in a water depth of 3350 m. The 3.50-m-long core is dominated by hemipelagic marls with CaCO_3 contents of 30–40 wt%. The sediments were mainly deposited under oxic conditions, but episodically bottom water anoxia accompanied the formation of 6 C_{org} -rich layers (Fig. 2). The top 25 cm of the core were sampled in 1-cm intervals, but two samples were taken between 10–11 cm and no sample at 22 cm. The sediments from within the Urania Basin were sampled during the same cruise (gravity core 3SL, 10 m length) and during Meteor cruise M44/1 (multicorer core 4MC, 50 cm length). These cores contained grey, gas-rich, homogeneous sediments with high water contents.

The samples were dried at 70°C and finely ground in an agate mortar for further analysis. Mineralogical composition of bulk sediment and of clay fraction separates was investigated with X-ray diffractometry (Phillips PW 1710). For major, minor and trace elemental analysis, 0.25 g of sediment were digested in a mixture of HClO_4 – HF – HNO_3 , and the solution was measured for Al, Ba, Cr, Cu, Fe, Mg, Mn, Ti, V, Zn and Zr by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES) (Leeman Labs Inc. PS 1000). ICP precision and accuracy were better than $\pm 5\%$. From the same solution Cd was determined using a Perkin Elmer Zeeman/3030 graphite furnace AAS (precision: $\pm 8\%$, accuracy $\pm 10\%$). Total S was determined in duplicate using a LECO CS 225 instrument. The average error of duplicates was 3% and the maximum error 8%. Total C was determined with the same instrument; the average error of duplicates was 2% and the maximum error 5%. Inorganic C was determined with a Ströhlein C-mat 500 instrument. The sample was treated with 41% H_3PO_4 at 70°C and the evolving CO_2 was measured. The average error was 3%. Organic C was calculated from the difference of total C and inorganic C. Radiocarbon ages were determined at the Leibniz-Labor AMS facility at Kiel University, following a routine procedure (Nadeau et al., 1997). The ages are given in unmodified conventional radiocarbon years according to Stuiver and Polach (1977). The hot chromium reduction procedure was used for the separation of pyrite-S (after Canfield et al., 1986). Prior to this, elemental S was removed by leaching the sample with CH_2Cl_2 . Acid volatile S (Morse and Cornwell, 1987) was <1 wt% (detection limit) in all samples. Pyrite-S was precipitated as CuS , followed by analysis of S-isotope distribution with a Micromass Optima mass spectrometer. After combustion at 1030°C, the gaseous combustion products were separated with a chromatographic column (2-m Poropak QS) prior to transferring the sample to the mass spectrometer through a 2-m steel-quartz capillary open split interface. The precision of this method is better than $\pm 0.4\text{‰}$. Accuracy was checked against NBS-127 standard which has a $\delta^{34}\text{S}$ value of $+20.3\text{‰}$ CDT. Carbonate C and O isotopic distributions of samples containing almost exclusively calcite as carbonate were determined by reacting the samples with phosphoric acid for 1 h at room temperature. The evolved CO_2 was measured as outlined below. The C- and O-isotope distributions of carbonates from the carbonate-poor layer were determined with a sequential dissolution method (after Al-Aasm et al., 1990). The sample was treated for 1 h with 100% phosphoric acid at 25°C and the evolved gas was attributed to originate from calcite. The treatment was repeated and the evolved gas was abandoned, followed by reaction for 20 h at 50°C. This gas was attributed to the dolomite fraction of the sample. Measurements were performed with a Finnigan MAT 251 at the Council of Geoscience, Pretoria, South Africa. Results were checked against in-house standards and are reported in ‰ Vienna–Pee Dee Belemnite (V–PDB); reproducibility was $\pm 0.1\text{‰}$.

3. Results

3.1. Mineralogy

The mineral inventory of the different sediment layers is presented in Table 1. Most remarkable is the almost complete absence of calcite in the samples between 5 and 10.5 cm. Minor amounts of dolomite are observed in all samples apart from the sample 9.5–10 cm (grey layer). Slightly increased dolomite reflections are present in sample 7–8 cm. Pyrite is detected only in the grey layer sample, the sapropel sample, and in the sample from below the sapropel. Elemental S is not present in any of the samples from core 6SL; halite contents are considered to be seawater derived. The clay mineral distribution in three

samples (1–2, 7–8 and 19–20 cm) was determined as: illite 52–59%, smectite 30–44%, chlorite 3–5%, and kaolinite 1–7% (normalised to 100%; Table 1).

Cores 3SL and 4MC, which were taken from within the Urania Basin, have been investigated in more detail (Hübner, 2002) and show a homogeneous mineral composition vs. core depth. For this reason, only one representative sample of each core is presented in Table 1. Important differences of these samples compared to core 6SL are their high amounts of elemental sulfur and the high concentrations of dolomite. In contrast to the calcite-poor samples between 5 and 10 cm in core 6SL, there are high contents of calcite in the Urania Basin samples. Also note the difference in pyrite among the samples from within the basin and from sample 9.5–10 cm in core 6SL.

3.2. Geochemical profiles

Carbonate contents are remarkably low in the upper part of the exotic layer (3.5–9 wt%), and even <1 wt% in the lower part (Fig. 2). This contrasts with the high carbonate contents of 29–50 wt% above and below this sediment section. C_{org} contents are 2.6–4.1 wt% from 11 to 17 cm, representing a sapropel according to the definition of Kidd et al. (1978). The Ba concentrations are also enhanced within the sapropel, whereas Mn is enriched at the top of the core and at 7–9 cm, followed by generally low values below 9 cm. In contrast, the S concentrations range from 0.2 to 0.3 wt% in the upper 9 cm of the core, increase sharply to 2.6 wt% at 9 cm, and decrease uniformly further downcore to values of ~1 wt%. Iron concentrations increase from 5 cm downcore with peak concentrations within the sapropel. The profile of Mg between 5 and 10.5 cm is very similar to the carbonate distribution, reflecting the presence of dolomite as the only carbonate phase in this layer.

Concentrations of Cu are significantly higher in the sapropel in contrast to the surrounding sediment. Above the sapropel, Cu concentrations increase slightly towards the top of the core. Chromium concentrations are high within the whole carbonate-poor sediment layer, without any shift in concentrations at the boundary at 9 cm; within the sapropel the concentrations are intermediate and in the background sediments above the carbonate-poor layer and below S-1, Cr contents are low. Like Cr, V shows a similar uniform distribution across the whole carbonate-poor layer, as well as low concentrations in the background sediments; however, within the sapropel V concentrations are distinctively higher. Zinc concentrations within the sapropel are higher compared to the background sediment layers and the upper carbonate-poor section.

3.3. Radiocarbon dating

Two bulk sediment samples of the uppermost sapropel in core 6SL were dated using AMS radiocarbon analysis. For the top of the sapropel at 11 cm, an age of 6675 ± 35 BP was determined, and for a sample from 14 cm, 7780 ± 35 BP.

3.4. S-isotope distribution

Samples from the grey part of the exotic interval have rather different $\delta^{34}S$ compared to the underlying S1 interval but are similar to those in Urania Basin sediments (Table 2).

Table 2. S-isotope distributions (δ notation) of pyrite-S of different samples from core 6SL and of sediments from within the Urania Basin (cores 3SL and 4MC)

	$\delta^{34}\text{S}$ (pyrite)
Core 6SL	
10 cm (grey layer)	-10.9
15 cm (sapropel S-1)	-34.7
20 cm (below S-1)	-45.6
Urania Basin pyrite (average, $n=6$, standard deviation in parentheses)	-7.1 (1.3)

Values are given in ‰ (V–CDT).

3.5. C- and O-isotope distribution

Two samples from within the carbonate-poor layer and two samples from above and below (hemipelagic marl, 2 and 20 cm) were analysed for C- and O-isotope distributions (Fig. 3). Additionally, data are presented for dolomite from sediments of the Urania Basin which were treated with the sequential dissolution method. Dolomite samples from the brown part of the exotic layer show similar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compared to dolomite from the Urania Basin and are quite different from the calcite isotope distributions from hemipelagic marls above and below the exotic layer.

Fig. 3. Distributions of C and O isotopes of calcite and dolomite from core 6SL (sample depth is labelled to the respective samples) and from sediments of the Urania Basin. For different sample treatment, see text. Values are reported in ‰ relative to V–PDB.

4. Discussion

4.1. The exotic layer: mineralogical and geochemical constraints

The eastern Mediterranean seafloor is dominated by the sedimentation of hemipelagic marls, mainly composed of two components: terrigenous detritus (detrital carbonate and non-carbonate phases) and settling biogenic carbonate tests. Carbonate contents of these sediments are usually in the range of 30–70 wt% (Venkatarathnam et al., 1972). To produce carbonate-depleted sediments as observed between 5 and 10.5 cm in core 6SL, several potential explanations are possible: (1) the exotic layer represents a tephra interval; (2) it is a turbidite from a carbonate-poor area; (3) it results from a former highstand of brine in the basin; (4) there has been early diagenetic carbonate dissolution; (5) (re)deposition from Urania Basin carbonate-poor mud. Processes (1)–(4) cannot explain the origin of the exotic layer for the following reasons:

(1) Deposits of tephra usually have low carbonate contents, but mineralogical evidence (high amounts of crystalline SiO₂ (quartz), presence of dolomite and pyrite) precludes a tephra layer within this interval (Table 1). Additionally, the overall chemical composition of the layer is very similar in e.g. Al and Ti concentrations to the surrounding sediments, which would not be the case in a tephra layer.

(2) Turbidites from areas where mainly non-carbonate terrigenous detritus accumulates may carry carbonate-poor material into deeper waters. However, a turbiditic origin is not supported because of the lack of visible lamination or grading and the bathymetric setting of the core on a topographic high precludes gravity flow emplacement. Additionally, the source of a carbonate-poor turbidite in this region is questionable.

(3) A rise of the brine level of about 40–50 m above the present level would almost certainly drown a large part of the near surroundings of the basin. Thusfar, no indication for that has been found in cores from the vicinity of the basin. Increased brine formation during stagnant bottom water conditions was proposed by Rossignol-Strick (1987). However; since the exotic layer was clearly deposited only at the very end of such a period, a climatic control may be excluded.

(4) Lower carbonate contents in sediments of the eastern Mediterranean are sometimes observed in sapropel layers, where CO₂ is released by the microbially mediated oxidation of organic matter coupled with sulphate reduction. Carbonate dissolution within a (former) sapropel is excluded, because this carbonate-poor layer is not a remnant of a sapropel, as becomes evident from the low Ba contents (see below, Section 4.2). Additionally, only in the early stages of sulphate reduction, a decrease in pH would be expected (Canfield and Raiswell, 1991). On the other hand, pervasive sulphate-reducing conditions will produce alkalinity that enhances the preservation of carbonate (Sholkovitz, 1973). Although dissolution through oxidation of reduced-S in the exotic interval is possible, in order to dissolve about 20–40 wt% carbonate (the difference between hemipelagic marls and the exotic layer), unrealistically high concentrations of pyrite would be required.

The expulsion of overpressured carbonate-poor mud from deeper sedimentary layers is considered to be the most likely option to explain the presence of the exotic layer in core 6SL and is discussed in more detail below. Geochemical data from the Urania Basin give evidence for the advection of the Urania brine from a deeper and hotter sedimentary reservoir below the Messinian evaporites (Vengosh et al., 1998 and Winckler et al., 1997). A thermal anomaly of up to 45°C in the western part of the Urania Basin (Corselli et al., 1996) is consistent with this interpretation. The brine and the sediments of the Urania Basin are extremely rich in gas. Brine samples have been reported to contain 2.69 mM methane at the anoxic/oxic interface (Karisiddaiah, 2000) and 11.6 mM methane in the deepest part (K. Wallmann, pers. commun.). In the pore waters of a surface sediment sample from 3435 m water depth, 2.3 mM methane was measured. Total dissolved CO₂ in the brine amounts to 57.5 mM (Halbach et al., 1998). The high gas content of the sediments is also obvious from their strong expansion when brought onboard ship. These data indicate that both higher temperatures and depressurising of gas-rich sediments contribute to the migration of fluid-rich muds in the subbottom of the Urania Basin.

The hypothesis that the exotic layer in core 6SL and the Urania Basin sediments are genetically related and possibly share a common source is supported by evidence from C- and O-isotope distributions in carbonates as well as from S-isotope distributions in pyrites. Dolomite is generally present in eastern Mediterranean deep-sea sediments with quantities up to 10% of the total carbonate fraction and is thought to be of detrital origin (Milliman and Müller, 1973 and Rutten, A., De Lange, G.J., 2002. Sequential extraction of carbonates applied to eastern Mediterranean sediments. *Geochim. Cosmochim. Acta* (submitted), Rutten and De Lange, 2002). Dolomite contents up to 1.2 wt% have also been reported from a sediment core close to the Urania Basin (Pees, 1998). Thus, the dolomite observed in most sections of core 6SL in small quantities is probably of detrital origin. However, for the dolomite observed in the carbonate-poor layer, a different origin is inferred from C- and O-isotope distributions. Dolomite from the carbonate-poor layer was found to be very similar in C- and O-isotope distribution to dolomite in sediments of the Urania Basin (Fig. 4). The latter dolomite, which is abundantly present in the Urania Basin, is thought to precipitate in situ from the evaporitic Urania Basin brine and inherits the enhanced contents of the heavy O isotope from the brine, reflecting the enrichment in evaporation brines (Sofer and Gat, 1972). The $\delta^{13}\text{C}$ value of the brine is about -4‰ (pers. commun. G. Aloisi) which corresponds well with the measured $\delta^{13}\text{C}$ of the dolomite. The striking similarity of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the Urania Basin and core 6SL dolomites (Fig. 3) suggests a common origin of these carbonates.

Fig. 4. Model of mud expulsion in the area of the Urania Basin. For profile line A–B, see Fig. 1.

Further evidence for a similar origin is obtained from S-isotope investigations. Values of $\delta^{34}\text{S}$ for pyrite-S from the Urania Basin (Table 2) are considerably more positive than usually encountered in sedimentary pyrite. Isotope fractionation in the latter range from -40 to -70‰ (Chambers and Trudinger, 1979 and Goldhaber and Kaplan, 1974), and these values are often encountered in sapropels from the eastern Mediterranean (Passier et al., 1997). The Urania Basin brine sulphate $\delta^{34}\text{S}$ is $+25\text{‰}$ (Ziebis et al., 2000).

This results in an exceptionally small S-isotope fractionation of only 32‰ during the conversion of sulphate to dissolved sulfide and subsequent precipitation of pyrite, assuming negligible fractionation during pyrite formation from dissolved reduced S (Price and Shieh, 1979). Small S-isotope fractionations are often related to closed system environments in terms of sulphate availability (Calvert et al., 1996); however, the high amounts of dissolved sulphate in the brine of the Urania Basin (Vengosh et al., 1998) rather point to an open system.

Culture experiments with sulphate-reducing bacteria yielded significantly lower fractionations than observed in most natural systems (Kaplan and Rittenberg, 1964), and the larger fractionations observed under natural conditions are explained by the disproportionation of intermediate S-species thiosulphate and/or elemental sulfur (Canfield and Thamdrup, 1994). Growth inhibition of disproportionating bacteria, high sulphate reduction rates, or a specific population of sulphate reducers were put forward to account for the small S-isotope fractionation in the Urania Basin (Ziebis et al., 2000). Regardless of the exact mechanism responsible, the $\delta^{34}\text{S}$ values are comparable to the sample from the grey layer in core 6SL. In contrast, $\delta^{34}\text{S}$ of pyrite from the underlying sapropel S-1 and from below the sapropel show significantly lower values than the sample of the exotic carbonate-poor layer. This shows that the conditions of pyrite formation differed dramatically in the exotic layer compared to the S-1 and marl samples in core 6SL. The similarity of $\delta^{34}\text{S}$ from within the basin with the sample from the exotic interval in core 6SL leads us to suggest that pyrite was formed under similar, hypersaline and hypersulfidic conditions.

Apart from S concentrations and concentrations of carbonate-related elements (Ca, Mg, Sr), major, minor and trace element concentrations of Urania Basin sediments agree very well with hemipelagic marls of core 6SL, which is surprising in view of the extremely different accumulation environments (hypersaline and anoxic vs. normal marine salinity and oxic conditions) of the two sediment types. The only clear exception to this is Cr (Table 3). Chromium exists in natural waters in two main oxidation states, Cr(VI) and Cr(III) (Elderfield, 1970). In anoxic basins, Cr(VI) appears to be rapidly reduced to the Cr(III) state and is removed from solution, probably by the adsorption of $\text{Cr}(\text{OH})_2^+$ on particle surfaces (Emerson et al., 1979). The reduction of Cr(VI) may be coupled to the oxidation of Fe(II), organic compounds or H_2S . Kinetic investigations showed that high H_2S concentrations of 1 mM accelerate the reduction to Cr(III) significantly (Pettine et al., 1994). Thus the formation of insoluble Cr species in the sediment appears to take place during the ascent of fluidised anoxic, hypersaline mud. The Cr distribution points to an origin of the exotic layer from a deep source. The reason for this is the observation that Cr is enriched in the Urania Basin sediments and the exotic layer, but not in the hemipelagic marls.

Table 3. Median values of selected elements from core 6SL (only samples that are not sapropels were considered) and from two cores from within the Urania Basin (cores 3SL and 4MC, Hübner, 2002)

	Al	Fe/Al	K/Al	Ti/Al	Ba/Al
6SL without Sap (n=100)	42600	0.61	0.28	0.060	0.0041
3SL (n=27)	34035	0.63	0.33	0.056	0.0053
4MC (n=9)	35682	0.67	nd	0.052	0.0044
	Cu/Al	Cr/Al	Mn/Al	V/Al	Zn/Al
6SL without Sap (n=100)	0.0014	0.0021	0.023	0.0018	0.0014
3SL (n=27)	0.0009	0.0036	0.020	0.0017	0.0016
4MC (n=9)	0.0014	0.0030	0.018	nd	0.0016

Units: Al, ppm; Fe/Al and Ti/Al, ppm/ppm; all others, ppm/wt%. Abbreviation: nd, not determined.

Urania Basin sediments may be viewed as a mixture of material from three sources: (1) sediment transported from deeper levels; (2) hemipelagic marls slumping from the margins into the basin and being introduced by normal background sedimentation; and (3) minerals added by authigenic processes within the brine. These sediments thus show the features of all three sources: enhanced Cr contents

(presumably deep-source derived), high amounts of calcite (slumping and background sediment 'rain') and abundant dolomite, gypsum and elemental S (authigenic). The exotic layer in core 6SL could then be considered to represent the deep-source endmember of the Urania Basin sediments (Fig. 4) for the following reasons. (1) Similar to Urania Basin mud, the exotic layer shows enhanced Cr concentrations. (2) The lack of calcite is explained by fast emplacement of the layer during a single event of mud outflow. Thus, hemipelagic sediments settling through the water column were not incorporated. Additionally, emplacement on a topographic high prevents slumping of hemipelagic marls from nearby. (3) Authigenic gypsum, elemental S and dolomite are thought to originate in the hypersaline, anoxic brine of the Urania Basin. Since the water column above the exotic layer during its emplacement was normal seawater, these minerals are absent or scarce.

4.2. Diagenesis

The carbonate-poor layer is divided into an upper part from 6 to 9 cm and a lower part from 9 to 10.5 cm, displaying major differences in colour, Mn and S contents (Fig. 2). The Mn-rich, but S-poor upper part is coloured brown, reflecting the presence of Mn oxides particles, whereas the lower part is grey due to the presence of fine-grained pyrite. The enhanced pyrite concentrations and the low Mn contents indicate that reducing conditions prevail in the grey layer, whereas the upper part is presently oxic. The shape of the Mn profile between 6 and 9 cm leads us to postulate that the whole section between 6 and 10.5 cm, i.e. the complete carbonate-poor layer, was initially reducing, followed by subsequent oxidation of the upper part by downward diffusing oxygen. The concept of the oxidation of reducing sediment layers by the downward migration of an oxidation front has been postulated before for turbidites (Wilson et al., 1985) and for sapropel S1 (e.g. De Lange et al., 1989 and Van Santvoort et al., 1996).

Iron contents show little change across the oxic/anoxic boundary within the exotic layer, opposed to a sharp increase of S concentrations in the anoxic part (Fig. 2). The average Fe/Al ratio for recent sediments from the Mediterranean is 0.49 (Rutten and De Lange, 2002). Taking this ratio as the background ratio (lithogenous clays have a similar Fe/Al ratio), it is possible to calculate the 'excess' (=non-detrital) amount of Fe in the grey layer samples. Applying this value to S concentrations suggests that 50% of the excess S in the grey layer is present as FeS₂. Upon oxidation of the upper part of the exotic layer, pyrite-S was liberated and diffused away as porewater sulphate. Iron, however, was precipitated rapidly as Fe-oxyhydroxide and stayed in place. Thus, the increased Fe content in the oxidised part of the exotic layer represents at least in part the former excess Fe present as pyrite.

Due to the presence of dissolved reduced sulphur in anoxic sedimentary environments, chalcophile elements like Cd, Cu and Zn may form sulphides. Other elements like Cr and V are immobilised under anoxic condition by forming less soluble species (for a review, see Calvert and Pedersen, 1993). Although they share the chalcophile character, Cd, Cu and Zn show different behaviours in the carbonate-poor layer. The peak concentrations of Cd and Zn just below the redox boundary within the exotic layer are interpreted as evidence that the reactive fraction of these elements has repeatedly been mobilised to porewater solution by oxidation, migrated downwards by diffusion and has been fixed in the solid phase again below a downwards progressing redox front. Since mobilised ions may diffuse upwards as well as downwards, the downward concentration gradient must be significantly greater than the upward one, implying a rapid removal of these elements from solution when reducing conditions below the oxidation front are re-encountered. The position of the trace metal peaks below the solid phase Mn enrichment at 9 cm is in accordance with the different oxidation/reduction potentials of the respective elements, leading to a succession of concentration peaks along a redox gradient (Thomson et al., 1993). Apart from this, the Zn distribution in the oxidised part of the exotic layer is coupled to the Fe distribution. The fact that Cu does not show any enrichment either in the oxic or in the anoxic part of the exotic layer is probably due to its lack of enrichment in this whole interval. The hypersaline conditions in the porewaters possibly prevented precipitation of Cu sulphides due to changed solubilities. The V distribution downcore resembles the Fe distribution, which reflects the geochemical affinity of V to Fe-phases.

4.3. Sapropel age and geochemistry

Extrapolation of the radiocarbon ages (at 11 and 14 cm) to the base of the sapropel at 17 cm results in an age of 8.9 kyr BP for the beginning of sapropel (S-1; Cita et al., 1977) deposition. This matches perfectly

with other published ages of the base of S-1: an average age of 8.97 kyr ($n=7$) was published by Fontugne et al. (1994); and an age of 8.9 kyr by Thomson et al. (1995). In contrast to the good age agreement for the beginning of sapropel formation, a wide range of published radiocarbon ages exists for the top of S-1. Dark, C_{org}-rich material from the top of S-1 was dated from 6.37 to 8.05 kyr (Fontugne et al., 1994); this wide range was interpreted reflecting oxidation of different amounts of organic matter in the upper part of the sapropel (Fontugne et al., 1994 and Pruyssers et al., 1991). Using a faunistic approach based on benthic foraminiferal investigations in an Adriatic core, the end of anoxic bottom water conditions was placed at 6.3 kyr by Rohling et al. (1997). However, the interpretation of Mn, Fe and Ba profiles within and above S-1 and the radiocarbon dating of an 'upper Mn/Al peak maximum' suggested deep water reventilation and the end of the S-1 accumulation at about 5.3 kyr (Thomson et al., 1995). Our age of 6.67 kyr for the top of S-1 is older than both proposed ages of not, vert, similar 6.3 and 5.3 kyr. Usually, such a finding would be explained by the reduction of sapropel thickness by early diagenesis. One result of that process is low C_{org} contents, but still elevated Ba concentrations in the oxidised part of the sapropel. Barium has been used as a palaeoproductivity indicator (Bostroem et al., 1973), and excess Ba above a mainly detrital background is present in a broad peak within several investigated S-1 units (Thomson et al., 1995 and Van Santvoort et al., 1996). Since this excess Ba, in contrast to C_{org}, is resistant to oxidation by downward diffusion of oxygen, it provides a quantitative proxy for the detection of oxidised sapropels.

All so far published data on S-1 from deeper waters indicate diagenetic burn-down of the upper part of the sapropel. Based on the interpretation of our C_{org} and Ba profiles, we report here for the first time geochemical evidence for a deep-water S-1 which is unaltered by diagenesis: Ba correlates well with C_{org} and does not show higher concentrations above the section which displays high C_{org} contents (Fig. 2). The simultaneous decrease in C_{org} and Ba concentrations towards the top of S-1 (Fig. 2) indicates that the deposition of the exotic layer above S-1 occurred at a time when the accumulation of S-1 was in its waning phase. The sapropel was not diagenetically altered by 'burn-down', but instead was shielded from post-depositional oxidation by the accumulation of an equally anoxic sediment layer. Since no redeposition is detected in the S-1 layer, the timing of the emplacement of the exotic layer is well constrained and provides for the first time a minimum age for the start of anoxic mud deposition in the Urania Basin area.

5. Conclusions

- (1) The exotic sediment layer overlying sapropel S-1 in a gravity core from the eastern Mediterranean differs in colour, geochemistry and mineralogy from the sapropel and the overlying hemipelagic marls. Furthermore, the exotic layer shows similarities with sediments from within the nearby anoxic, hypersaline Urania Basin. These sediments have similar $\delta^{34}\text{S}$ of pyrite as well as C- and O-isotopic distributions in dolomite. Also, enhanced Cr concentrations indicate a common origin of the exotic layer and Urania Basin sediments.
- (2) For the emplacement of the exotic layer we propose outflow of liquid, anoxic mud with a primarily low carbonate content, either directly at or near the coring site. The sediments of the Urania Basin (and presumably in the subbottom of the basin) are extremely gas charged, which provides a driving force for upwards migration of overpressured mud.
- (3) The emplacement of the exotic layer in the waning phase of sapropel S-1 deposition is well constrained by radiocarbon dating of the top of the sapropel S-1.
- (4) Early diagenetic oxidation has altered the upper part of the originally completely anoxic exotic layer. The deposition of anoxic mud directly above sapropel S-1 shielded this sapropel from oxidation, resulting in the rare occurrence of a complete preservation of S-1.

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