

Interactive comment on “Diagenetic control of nitrogen isotope ratios in Holocene sapropels and recent sediments from the Eastern Mediterranean Sea” by J. Möbius et al.

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We thank Prof. Frans Jorissen for the review and for his very helpful suggestions.

Regarding the specific comments:

p. 1134: the authors compare modern Eastern Med $\delta^{15}\text{N}$ data with S1 ones, and conclude that both systems have strikingly low values in common. However, the recent EM values are still considerably higher than S1 values.

We agree and differentiate the statement in our revision.

p. 1135, lines 2-17: The idea that today's low $\delta^{15}\text{N}$ values are due to incorporation of

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15N-depleted atmospheric NO_x is largely based on a single paper (Mara et al., 2009). I wonder whether the authors really need this for their interpretation of the sapropel signals?

One of our motives for looking into the modern situation (and motive for the Mara-study) was that we could not think of a plausible reason aside from the atmospheric deposition for the low surface-sediment d15N. We did not agree with other authors that the present-day N-cycle is dominated by N₂-fixation, because the high N:P ratios in dissolved nutrients in our opinion argued against this. Other publications (e.g. Preunkert et al., 2003 ; Krom et al., 2004; Emeis et al., under review) also evidence a strong influence/imprint of atmospheric NO_x on the N-cycle and $\delta^{15}\text{N}$ of the Mediterranean Sea. This isotopically depleted source is unambiguously apparent in atmospheric precipitation samples as well as in the dual isotopic composition of N and O in the surface water nitrate of the Eastern Mediterranean Sea (Emeis et al., under review). On the other hand, the evidence for N-fixing bacteria is scarce or questionable, respectively. From our perspective atmospheric precipitation is the major external N-source in the recent Eastern Mediterranean Sea and must be considered if we compare recent to ancient processes. In the case of the Mediterranean, the present is not key to the past.

p. 1135, line 22-24: pristine $\delta^{15}\text{N}$ values have been obtained in diatom frustules, foram shells and biomarkers. What are the results of these analyses?

Pristine $\delta^{15}\text{N}$ values in foram shells and diatom frustules have been achieved in other parts of the world ocean. We clarified this. Sachs and Repeta (1999) determined an enrichment of 5.7‰ during early diagenesis in the Eastern Mediterranean Sea by analyses of $\delta^{15}\text{N}$ in chlorins and bulk N. We acknowledge this now and also cite a new publication on chlorin $\delta^{15}\text{N}$ (Higgins et al., 2010).

p. 1135, line 25 – p. 1136, line 3. The authors argue that “reoxygenation would most seriously compromise the reliability of as a proxy in environments with low sedimenta-

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tion rates”. I admit that in many Mediterranean areas sedimentation rates are very low, but the ultimate conclusion is that the reliability of $\delta^{15}\text{N}$ has to be questioned everywhere! And, rather surprisingly, in view of the predominance of records in settings with well oxygenated sea floors, at present, the sapropel records are difficult to interpret, because the original signal is exceptionally well perfectly!

We tried to respond to this comment as much as possible in the revision.

p. 1136, lines 5-7. The authors suggest that they can sort things out by looking at nitrogen isotopes, Ba/Al ratios, total nitrogen, and bulk organic carbon at the same time. Later in the paper it turns out that this is not true, since they argue that all these parameters are strongly affected by the anoxic bottom waters!

The reviewer is correct, and we changed the introduction to reflect our doubts now.

p. 1139, sediment traps. The info on these trap data is really very limited. It would be interesting to know whether there is a seasonal variability in $\delta^{15}\text{N}$! There is a difference of 1.4‰ between the extreme average values. Do the authors have any idea why?

The $\delta^{15}\text{N}$ of sinking material shows no pronounced and no recurrent seasonality. We consider the $\delta^{15}\text{N}$ in the sediment traps to be driven by differences in preservation as the linear relationship suggests. Preservation may be variable due to sinking speed and total flux. Minor differences may be assigned to variable N-sources, because the atmospheric input does have some seasonal variation in both isotopic composition and mass/unit area, or to variable N-utilization.

p. 1141, paragraph 4.1. The authors are faced with the apparent contradiction of a significant decrease in the Corg flux between their traps at 1500 and 2500 m depth, which is not resulting in a significant change in the Corg quality (as expressed by DI). They explain this as “disaggregation and disintegration of sinking material without compoundspecific fractionation. It is difficult to understand why the loss of 75% would not lead to a change in $\delta^{15}\text{N}$ and DI, whereas further, quantitatively less important, losses

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at the sediment–water surface would cause a large shift in these proxies. Perhaps the authors can give a quantitative estimate of the Corg losses at the sediment-water interface (compared to the losses during the transit of the water column).

There is a loss of 75% in total flux from the shallow trap to the deep trap; however, the composition of total sinking matter does not change much. The relative contribution of organic carbon (see table 3), total N etc. is the same in all traps. At the same time, amino acid spectra suggest no differences in decomposition and the $\delta^{15}\text{N}$ did not change either. These results match observations and considerations from previous work (e.g., Altabet and Francois, 1994; Altabet, 1996; Gaye-Haake et al., 2005). We think that these data support our assumption that physical disintegration of aggregates is the main mechanism: This would make the totals amount sinking progressively smaller, while maintaining chemical and isotopic characteristics. The loss between 1000 m above bottom and the sediment-water interface might be much lower as it decreases with increasing water depth (and travelling time) but we are not able to provide solid loss estimate for the material reaching the sediment-water interface.

p.1143, lines 7-10. I fail to understand this argument. Why would the fact that recent fresh Corg has a similar isotopic signature as S1 Corg mean that the $\delta^{15}\text{N}$ of primary produced Corg was the same in both periods? This is only logical when we admit that absolutely no alteration has occurred in sapropel times. But this conclusion comes only later in the paper! Since DI is higher in S1 than in recent sediment trap material, Corg would be (slightly) better preserved during S1 times. This would then suggest slightly higher $\delta^{15}\text{N}$ values of recent PP Corg compared to sapropel times.

The reviewer is right and we clarified this.

p. 1143: line 23: “the protosapropel that developed under suboxic conditions”. Several papers (e.g. Passier et al., 1996) have suggested that the protosapropel has been deposited under fully oxic conditions, and that the grey color is due to a downward migration of sulphides, leading to the formation of pyrite. In most sapropel records,

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the onset of anoxic conditions is almost instantaneous (at most 1-2 centuries). The lower $\delta^{15}\text{N}$ of the 2 protosapropel samples in fig. 4 could be due to a shortening of the residence time in oxic conditions (at the sea floor) due to the onset of anoxic conditions AFTER the deposit of these sediments. However, in order to know whether such a hypothesis can be envisaged, it is necessary to know at what exact level (with respect to the sapropel basis) these protosapropel samples were taken!

We agree and also mention the other scenario for the onset of the sapropel. The exact level of the samples in relation to the sapropel base level cannot be determined because no age determinations have been carried out. In our opinion, however, it would not make a big difference for the interpretation of the data. There appears to be some indication (from highly-resolved benthic foram records in rapidly accumulating cores; G. Schmiiedl, pers. comm..) of an increase in productivity (possibly at declining oxygen levels) immediately below the (visible) sapropel, and normally TOC% also increases below the visible sapropel, which has strongly elevated %TOC.

p. 1144, line 56: The authors should better explain how they arrive at +2‰

We arrive at 0 to 2‰ just by shifting the data points of highly degraded and ^{15}N enriched sediments on the regression line of $\delta^{15}\text{N}$ vs. DI to DI values of the well preserved OM in the sapropels. The range of 0 to 2‰ is given by the values analyzed in the sapropel and is estimated conservatively.

p. 1145, line 27 – p. 46, line 2. The authors write that the higher $\delta^{15}\text{N}$ values in three S1 records are due to the fact that the northern sub-basins have not been fully anoxic. They cite Kuhnt et al. (2007) to justify this statement (Kuhnt et al., 2008, should not be cited, since they do not present faunal data). Several shallower Aegean records (e.g. Abu-Zied et al., 2008) confirm the presence of benthic foraminiferal faunas during S1. However, this is not the case for the Adriatic Sea, where no S1 records below 800 m depth contain benthics foraminifera. Therefore, such a scenario can not explain the maximum $\delta^{15}\text{N}$ values found in S1 of the Adriatic Sea.

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We deleted Kuhnt et al., 2008 from the manuscript. Regarding the abundance of benthic forams in the deep Adriatic Sea S1 sapropel we have good reasons for our statement. The foram record in AD91-17 almost drops close to zero but is never zero (Giunta et al., 2003). Furthermore short-scale (annual) variability in oxygenation may in our opinion not be reflected in the abundances of benthic foraminifera, because they need more time to recolonize the substrate; but the reviewer will probably know better. . . .

p. 1145: comparison S5, S6 and S1. Line 24: during S5, “PN was uncharacteristically depleted”. I don’t understand what the authors mean. In the lines before they suggest that primary produced PN had the same composition in all sapropels, which is logical. So I guess this statement pertains to sediment PN?! But I do not see why it is uncharacteristic. Following the reasoning of the authors, the negative $\delta^{15}\text{N}$ values could simply be indicative of a perfect preservation, since we are not outside the range of -2 to +1‰ for PN resulting from N_2 -fixation.

The reviewer is absolutely right and we clarified this.

Lines 25-28: the authors suggest that the differences between the sapropels must be due to “variable degrees of anoxia”. First, anoxia means zero oxygen, there is no such a thing as “variable anoxia”. Next, since the sea floor was anoxic for all three sapropels, the difference must be in the water column. Unfortunately, earlier in the paper, the authors argue that the water column transit has no impact on $\delta^{15}\text{N}$, which is largely determined by diagenetic processes at the sea floor. This is an apparent contradiction (the arguments for both opinions are valid), which should be mentioned. This gives an extra argument to the alternative mechanism, proposed in paragraph 4.5!

This is a good point and we consider and discuss this contradiction in our revision.

Details:

We followed all suggestions.

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