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Biogeosciences Discussions

Interactive comment on "Implications for chloro- and pheopigment synthesis and preservation from combined compound-specific $\vec{\delta}^{13}$C, $\vec{\delta}^{15}$N, and $\vec{\Delta}^{14}$C analysis" *by* S. Kusch et al.

Anonymous Referee #1

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General comments The paper submitted by Kusch et al. introduces paired analyses of compound-specific stable isotope (13C, 15N) and 14C of bulk sediment, chlorophyll and chlorophyll degradation products from sediments and sediment extracts of the Black Sea. These novel data are used to discuss influences on the original isotope composition of chlorophyll, and to search for transformations and their duration by comparing the original signal with that of presumed degradation products in the same samples. In my opinion, the paper should be accepted for publication, but only after a solid reworking and resubmission for review. This suggestion is motivated by the very innovative approach and novel data on the one hand, and on flaws (or at least alternative ways to interpret the data) in the interpretations on the other hand. The manuscript

certainly addresses relevant scientific questions within the scope of BG, but can in my opinion not be published in its present form. It is very difficult to read, in part because the text is overly concise is many instances, glosses over obvious inconsistencies in other places, and often makes assertions where to me there were lots of unresolved issues remaining. The paper would certainly also gain by a thorough work-over in terms of language and writing style: Some of my problems with understanding the meaning may have originated from long sentences and imprecise choice of words.

Specific comments The approach used here is new and these are the first data in that combination for that particular group of related molecules. The authors thus cannot look for help in interpreting their – in part unexpected - data in the light of other studies. In many respects, the paper thus is devoted to rationalising data that often deviate from expectations: As suggested by the title, I assume that the intention of the entire research effort was indeed to explore the use of three isotope systems in tracking changes in isotope composition from the origins (marine autotrophs assimilating nitrate of known composition) in the chlorophyll of marine algae or bacteria to sedimentary signals (too bad that there apparently have been no analyses of suspensions in the euphotic zone or of sediment trap materials....). As is often the case in natural systems, it appears as if the source-product line in the same samples of surface sediments is not as straightforward as one would wish in the case of the Black Sea. The individual data sets presented are complex already, and in unison make for some seriously confusing and ambiguous observations that the authors chose to acknowledge by offering series of possible explanations why the various observations deviate from expectations. Intriguingly, some explanations immediately came to my mind that may arise from the study area with its non-standard carbon, radiocarbon and nitrogen isotope properties, and from source and product mixing in each sediment sample (authors do acknowledge, but dismiss this simple explanation in the Discussion, but not entirely convincingly so). Another explanation that came to me (and is also briefly discussed, but dismissed in the text) is whether the results reflect superpositions of sources and processes. I would expect such a mixture in a natural system that has diverse sources (land plants from a river, marine phytoplankton and presumably also cyanobacteria) and conditions of preservation (anoxic and oxic sea floors, diverse sedimentation rates etc.). Unfortunately for such a bold and new effort, the Black Sea appears to be far from ideal to tackle the problem the paper set out to explore. The attempt to cover all bases in terms of explaining the possible reasons why the properties and ages do not follow expected lines results in a discussion where no substantial conclusions are offered or even can be offered: Although I agree with the last sentence in the conclusions that asserts that “the method can delineate biogeochemical and diagenetic processes (in surface waters?) and simultaneously assess the timescales of these processes”, I wonder if that is what is described in the text. In the same vein, the title clearly reflects the ambitious goals, but in my opinion overstates the messages given. The same holds for the abstract, which indeed is a description of the contents, but gives no indication of the Ifs and Whens discussed in the body of the text. In my opinion, the paper should be rewritten to be more cautious (some examples outlined below), and the possibility of mixed sources and products. But I don′t have a really good idea on how to improve the flow of arguments. In any event, the writing needs to be improved on the way: Many sentences wind on and on, and sometimes the language is so complicated as to completely obscure the meaning. This is even though apparently the things that authors want to say are quite simple (for example, the last sentence before the Conclusions). This all makes reading the text overly tedious.

Detailed comments: Page 6268: I don′t know if the statement that chlorophyll a undergoes several diagenetic processes is correct. It is a molecule that undergoes specific chemical reactions: Cell senescence, grazing etc. may affect the cells that contain chlorophyll a, but not the molecule..... Page 6271: The reference for the new EA-MS method (Ogawa et al., 2010) is incomplete and not easily accessible. There should at least be a short description here. Line 15: How do you analyse the stable isotope composition of bulk sediment on an IR-MS? With an EA periphery? Line 20: The samples were evacuated and flame-sealed? How? Page 6272: Stuiver et al. 2010 missing in reference list In the 2.4 Surface DIC model formula, I did not find the term “z” which is

explained 2 lines below. The "my" term (time constant of the first-order loss and gain term) is enigmatic to me. In general, I am not entirely sure why you need the model in this text in the first place, and why it could not go into the ancillary materials entirely. If you decide to keep it here, please devote some text to results of the model and possibly some discussion. Also, explain what the purpose is to non-specialists (not apparent to me from the following text, but maybe I missed something). On page 6279 you reference existing data, whereas the model is introduced to alleviate the lack of data..... Page 6274: What is “pre-aged terrigenous organic matter” (also in other places)? Do you mean “older” or indeed “artificially aged”? Line 19: “....consistent with less bomb 14C in deeper water”? Page 6275, line 11: Different from what? This entire paragraph is one that threw me off, because each station/sample apparently is different from the others, and even repeated analyses of one sample appear to diverge significantly (or am I wrong?)? Are differences of duplicate analyses on one sample of the same magnitude as inter-sample differences? The title of part 4.1. is very ambitious (I don′t believe that the data are suited to shed light on the ecology of the photoautotrophic community!) and this entire part of the discussion makes several statements that I do not agree with.

Page 6275 lines 22 ff: The statements that ïĄď13C values < -26‰ “reflect a marine phytoplanktonic origin” is somewhat puzzling and unconvincing; low values such as these may occur in phytoplankton in the area (I don′t know the references cited in support), but it certainly is a range of values that does not exclude a terrestrial origin. In the following lines, a series of reasons for inter-pigment differences in d13C are listed and all may be able to explain the discrepancies. But what does a long list like that of possible reasons do to help explain the differences in some samples, whereas the differences are apparently not seen in other samples? This entire paragraph needs to be reworked.

Page 6276 line 14: I do not agree with that statement, because other observations tell another story: Water column profiles of suspended matter δ15N show a slight enrichment from ca. 4‰ in the upper mixed layer to up to 8‰ at the oxycline. Below the oxycline in the Black Sea, however, δ15N values shift dramatically to extremely depleted values (-8‰ at the top of the anoxic water body. A simultaneous increase in the mass of total SPON implies that 15N-depleted OM must be newly produced there. This was attributed to newly produced OM by the biomass of chemoautotrophic bacteria utilizing NH4+ as their dominant N source (Coban-Yildiz et al., 2006). Coban-Yildiz, Y., Altabet, M. A., Yilmaz, A. and Tugrul, S.: Carbon and nitrogen isotopic ratios of suspended particulate organic matter (SPOM) in the Black Sea water column, Deep-Sea Res. II, 53, 1875-1892, 2006. See also Fry, B., Jannasch, H. W., Molyneaux, S. J., Wirsen, C. O., Muramoto, J. A. and King, S.: Stable Isotope Studies of the Carbon, Nitrogen and Sulfur Cycles in the Black-Sea and the Cariaco Trench, Deep-Sea Res. I, 38, 1003-1019, 1991.

Line 20 ff: You are comparing nitrate d15N values (don't say "heavy" d15N but "high" d15N) at an unknown stage of assimilation (when in the year was the cruise anyway? Overall low nitrate concentrations indicate that assimilation may be advanced and may have enriched what nitrate remained. One concentration sticks out: I guess that the upper layer near the coast may have a high d15N of nitrate due to admixtures of land-derived nitrate?) with the assimilation products in sediments 0-2 or 0-3 cm.

Page 6276: The entire discussion here is an illustration for the fact that one can find any number of reasons why data differ from expectations. What do we learn from the long list of possible reasons? Line 15 ff: The sediments and pigment/chlorophyll extracts certainly integrate over at least one entire seasonal cycle or several years, so that arguments about late-season origin of chlorophyll are in my opinion meaningless. Also, the inference of increasing diazotrophic N2-fixation with distance from the river mouth is based on conjecture only and me need to be phrased more cautiously. To my knowledge there has been no experimental or observational evidence for diazotrophic N2 fixation in the Black Sea. Does synechococcus (see citation Uysal, 2000) produce the pigments analysed here? That N2 fixation is indeed a significant input at least to the

nitrate pool is unlikely in my opinion considering the nitrate d15N values: The average d15N of nitrate in the upper layer above the chemocline (no nitrate below, of course) appears to be 7-8 permil. This is significantly higher than open ocean deep-water nitrate (of course no connection with the Black Sea) and nitrate in the intermediate water of the Mediterranean Sea. But it is known that rivers draining fertilized catchments bring nitrate enriched in d15N (>8 permil), which may set the level of nitrate d15N in the Black Sea surface layer.

Page 6277, line 5 ff: I don't understand: river input with N:P>80 dominating and across-pycnocline transport of phosphate (no nitrate in deeper waters) inhibited favors N2-fixation?

Page 6277 ff (4.2): I found the entire discussion on "timescales of chloro- and pheopigment synthesis" (who synthesises pheopigments anyway?) very difficult to follow....and the text does nothing to assess the controlling parameters and instead again offers a lot of assumptions and possible explanations.....I hope that other reviews may provide a more informed assessments of the contents. What does the last sentence before the Conclusions want to say?

Page 6278, line 8 ff: Pigments as monolayers? Mayer (1994) does not deal with pigments.....

Interactive comment on Biogeosciences Discuss., 7, 6265, 2010.