

Interactive comment on “Carbonate chemistry in sediment pore waters of the Rhône River delta driven by early diagenesis (NW Mediterranean)” by Jens Rassmann et al.

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We thank the reviewer for his helpful and constructive comments. In the following document, we answer the questions one by one. Modifications that have been done in to the manuscript are written between quotation marks in *italics*.

Referee: Unfortunately, the discussion of the results is too general and poorly focused. Overall I think much more could be done with the data. Much of the data interpretation is too speculative or is simply based on comparisons with what other workers have seen in these (and other) sediments. In many places the text reads more like a data report interspersed with comments about similarities between these results and results from other studies. The things that are new and exciting and different about this work,

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as compared to these other studies, are not clearly presented.

Answer: In the reviewed version, we focus more on the new findings of our work. For this area, we present the first data set containing at once pore water concentrations of DIC, TA and microprofiles of oxygen and pH in order to deal with carbonate dissolution/precipitation in these delta sediments. But as diagenetic processes are very complex, we were not able to measure all parameters. For this reason, sometimes we have no other choice than to rely on literature data and hypothesis. Concerning the importance of the presented work, the following sentences have been added to the abstract (line 29):

"The large production of pore water alkalinity characterizes these sediments as an alkalinity source to the water column which may increase the CO₂ buffering capacity of these coastal waters. Estuarine sediments should receive more attention in future estimations of global carbon fluxes. "

To differentiate our work from previous studies, we added a couple of lines in the introduction (line 94):

"Previous studies in this region often focused on organic matter mineralization pathways measurements in the oxic sediment layers and analysis of particulate carbon (Lansard et al., 2008; Cathalot et al., 2010) or could not provide simultaneous DIC and TA pore water measurements (Pastor et al., 2011a). These studies did not provide information on TA production and fluxes at the SWI. Accordingly, we designed a study to investigate the interaction of mineralization processes on porewater pH and the fate of solid calcium carbonates. For that purpose, we used a combination of in situ oxygen and pH microelectrode measurements and pore water analysis of DIC, TA, SO₄²⁻ and Ca²⁺ concentrations to examine various diagenetic pathways on different vertical scales."

Referee: Questions about whether sediments such as these are alkalinity sources is an important one, and the authors note this in places in the text. While they do have

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some discussions of their results with such considerations in mind, the discussions are rather disjointed. At a bare minimum, Fig. 5 shows that all of these sediments are a source of alkalinity to the water column, although this simple observation seemed (at least to me) to get lost in the overall discussion. I would urge the authors to re-structure the paper so that this general topic is much more clearly examined with their data. In my opinion, this will make this paper one that people will want to read (and should read).

Answer: Indeed this question is very important and we modified the text to focus the article more in this direction. To better introduce this question, we added in the introduction (line 44) ... :

"Anaerobic reactions also lead to production of total alkalinity (TA) that increases the CO₂ buffer capacity of seawater (Thomas et al., 2009). Variations in DIC and TA affect the partial pressure of CO₂ (pCO₂) in seawater and ultimately the CO₂ exchange with the atmosphere (Emerson and Hedges, 2008). By increasing the CO₂ buffer capacity of seawater, the release of TA from anaerobic sediments into the water column could account for a majority of the CO₂ uptake in shelf regions and deliver as much TA to the oceans as is derived from rivers (Thomas et al., 2009). Due to high dynamics, spatial heterogeneity and complex biogeochemical mechanisms, estimations of TA fluxes from the sediments are affected by high uncertainties (Krummins et al., 2013)."

... and discussed more explicitly in new paragraph between lines 325 and 326:

"In the Rhône River delta sediments, OM mineralization leads to DIC production, and under anoxic conditions, also to TA production. Our results demonstrate strong DIC and TA pore water gradients in the anoxic layer of the sediments indicating high anaerobic respiration rates. As a result, DIC and TA diffuse towards the SWI. No oxic reaction consumes DIC except potential carbonate precipitation. Our results indicate that more DIC is produced in the sediments than consumed by precipitation of CaCO₃. This means, that OM mineralization in the sediments leads to strong DIC fluxes from the

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sediments into the water column. For TA, the situation is more complicated, as oxidation of reduced species can consume as much TA as has been produced to reduce these species (Table 2). In a 1D system, where no precipitation occurs and no reduced species can be exported, 100 % of the anaerobic TA would be consumed in the oxic layer.

Krumins et al., (2013) reported that the effective TA flux from the sediments into the water column is far less important than the anaerobic TA production due to the TA loss in the oxic layer. Unfortunately, the resolution of the DIC and TA pore water profiles in this current study does not give precise information about the gradients in the oxic layer. Thus, we can only speculate about the oxic TA consumption in this region and related TA fluxes across the SWI. According to (Pastor et al., 2011a), 97 % of the reduced species precipitate in the anoxic sediments in the Rhône prodelta. Therefore, the majority of the produced TA is likely released into the water column which can counterbalance the effects of the DIC fluxes and increase the CO₂ buffer capacity of the overlaying waters."

and rephrased from line 455 to the end :

"As the alkalinity fluxes produced by anaerobic processes are high and likely not much reduced by reoxidation of reduced species in the oxic layer due to iron sulfide precipitation, net TA fluxes of the same order of magnitude than DIC fluxes are likely to occur. Therefore, the alkalinity build up in the anoxic zone could diffuse across the oxic sediment layer and contribute to buffer bottom waters and increase CO₂ storage capacity of these waters. The large precipitation of calcium carbonate in the proximal zone may have implications for the CO₂ source potential from the sediment. Indeed, calcium carbonate precipitation generates CO₂ (R2b) which can then be exported to the water column. In addition, calcium carbonate precipitation consumes TA. However, the order of magnitude of the TA consumption by carbonate precipitation in these sediments is below the quantity of TA produced by sulfate reduction. Without this TA flux, the pCO₂ of the bottom waters in the prodelta of the Rhone would likely be much higher than

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observed."

In order to make sure if these sediments are important alkalinity sources or if the majority of the anaerobically produced TA is consumed in the oxic sediment layer, we carried out in situ flux measurements together with Martial Taillefert and Eryn Eitel in September 2015. The data which are still being processed will be published in a separate paper.

Referee: Before final publication the manuscript will need to be carefully copy-edited by a native or fluent English-speaker. There are many places where there are grammatical errors, awkward syntax, and curious phrasings.

Answer: The manuscript was copy-edited by a native English-speaker (Patrick Lacey, LSCE)

Referee: One last general comment. When I read lines 91-94 and the sentence starting at the end of line 124 ("The sea floor in this region : : :) I had the sense that these sediments have some degree of similarity to those of other large river deltas like, e.g., the Amazon (see, for example, Aller's 1998 Marine Chemistry paper cited here). In contrast, much of the discussion of the data in the text takes a very traditional, steady-state "Froelich et al."-type approach (see, for example, section 2.7 and much of section 4.1). To me, this approach seems to contradict the text on lines 91-94 and 124, and I think that some clarification is needed.

Answer: Indeed, this environment is very dynamic, but very different from the Amazon delta due to the lack of tidal mixing and strong permanent currents. The prodelta of the Rhône is dominated by very high accumulation rates due to flood depositions and resuspension events during winter storms can remove several centimeters of sediment. Despite this fact, molecular diffusion is the dominant transport process and we find the same general tendencies from cruise to cruise.

We added a sentence to the description of the sampling site to point at the particularity

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of this environment at line 92 and rephrased:

"The "predominance" of sediment accumulation over other dynamic processes and the absence of tidal mixing and dominant marine currents differentiate the prodelta of the Rhône differs from other deltaic environments like the Amazon, where the surface sediments are constantly reworked (Aller et al., 1998). "

To discuss different transport mechanisms, we added at the end of the section 4.1 (line 387) :

"Finding this clear succession of reactions is interesting, particularly the pH profiles that look classical in the aerobic sediment layers sampled from this complex and dynamics system. As OPDs measure only a couple of mm, molecular diffusion is by far the dominant transport process (Peclet number $\ll 1$ on a scale of the OPD). The microstructure of these sediments is restored very fast after disturbances like resuspension events (Toussaint et al., 2014). Furthermore, the comparison with previous studies shows, that despite the high sediment dynamics in this region, the general biogeochemical tendencies are maintained throughout time."

and added a new reference: Toussaint F., Rabouille, C., Cathalot, C., Bombled, B., Abchiche, A., Aouji, O., Buchholtz, G., Clemenson, A., Geyskens, N., Répécaud, M., Pairaud, I., Verney, R. and Tisnérat-Laborde, N.: A new device to follow temporal variations of oxygen demand in deltaic sediments: the LSCE benthic station, *Limnol. Oceanogr.: Methods*, 12, 729-741, 2014

Referee: Specific Comments (line numbers in parentheses) (215) I never realized there were 12 parameters of the carbonate system. Is this a typo or am I missing something?

Answer: Sorry, there are 9 parameters, the mistake has been corrected.

Referee: (225) Here and on line 291 they talk about good agreement between measured and calculated pH values. It might be good to show this, and/or present some

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additional information like, e.g., the slope and r^2 value of a scatter plot of the two pH's.

Answer:We added at line 292 : *"A linear relationship of the pH data measured with microelectrodes against calculated pH by CO2SYS shows a correlation with a slope of 1.01 +/- 0.02 and an $r^2 = 0.7483$ (graph not shown)."*

We compared the pH values calculated from DIC and TA data with microelectrode data. As the porewaters represent an integration of a certain sediment zone, the average signal of the microelectrodes for the same zone was used. The size of the influenced zone was calculated following: Seeberg-Elverfeldt, J., Schlüter, M., Feseker, T., Kölling, M.: Rhizon sampling of porewaters near the sediment-water interface of aquatic systems; *Limnology and Oceanography: Methods*, 3, 361-371, 2005

Because we already include 10 figures, we did not include a figure showing the correlation. In this answer, the correlation is shown on figure 1.

Referee: (251) I would probably be good to list here what atmospheric pCO_2 was at the time of sampling.

Answer:We added at line 251:

"During the sampling period, the Integrated Carbon Observation System (ICOS) station at Manosque (l'Observatoire de Haute Provence, <https://icos-atc.lsce.ipsl.fr/?q=OHP>) measured a pCO_2 of 410 ppm. At most stations, pCO_2 was oversaturated compared to the atmosphere, with the lowest values calculated close to the river mouth at stations A and Z and the highest values calculated in the bottom waters at the shelf stations."

Referee: (265) The way the pH data is plotted makes it hard to see things like differences in inflection points for different regions. It might be helpful to break Fig. 4 up into 3 panels like Figs. 5 and 6. It might also be useful to similarly sub-divide Fig. 2 (O_2 profiles) into 3 panels.

Answer:Figure 2 and Figure 4 were sub-divided into 3 panels.

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Referee: (286) Are these slopes statistically different in the three different regions? If not I would not report them separately but would simply list an overall slope for all of the sediments.

Answer:We changed the corresponding sentence at line 286 into:

"The DIC and TA pore water profiles are well correlated in each core and the concentrations show a linear correlation with a slope of 1.01 and an $r^2 = 0.9982$ (130 data points)."

Referee: (317 -) Plotting sulfate concentrations and carbonate saturation state for each region on the same panels is very confusing. I would recommend separating them.

Answer:The figure in question was subdivided into two figures showing sulfate profiles and saturation states separately.

Referee: (405-) I would think that all of the things discussed here (organic matter oxidation state, carbonate precipitation, AOM) would affect the magnitude of the slope of a DIC/Sulfate plot, and not the scatter around the best-fit line. I'm also surprised that the slope is 2 despite all of these factors. Maybe they act (somehow) in such a way as to cancel each other out?

Answer:We changed the representation of the results into a ΔDIC vs ΔSO_4^{2-} plot that has a slope of 1.65. Taking into account the difference of the diffusion speed in sediments of these two species, we come close to a ratio of 2. Indeed, this is very surprising and we think that the processes in question cancel each other out. We rephrased the corresponding section in the discussion at line 400 to 409:

"To estimate the actual $\Delta\text{DIC}/\Delta\text{SO}_4^{2-}$ ratio due to diagenetic processes, the slope of the correlation between produced DIC (ΔDIC) and consumed sulfates (ΔSO_4^{2-}) in the pore waters (Fig 10) has to be corrected for molecular diffusion following the equation proposed by Berner (1980). Accordingly, we used the diffusion coefficients determined by Li and Gregory (1973). Below 10 cm depth, the observed diffusion corrected

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$\Delta DIC/\Delta SO_4^{2-}$ ratio equals 1.8 ± 0.02 . The deviation of this measured value, from the theoretical value of 2 can be linked to higher oxidation states of organic matter which increases the SO_4^{2-} requirement for DIC production (in an extreme case, if methane undergoes oxidation, the $\Delta DIC/\Delta SO_4^{2-}$ ratio equals 1), carbonate precipitation lowering DIC concentrations or methanogenesis that increases DIC without consuming SO_4^{2-} (Burdige and Komada, 2011; Antler et al., 2014)."

and further at line 417:

"Despite all these divers reactions that affect the $\Delta DIC/\Delta SO_4^{2-}$ ratio, they are balanced in a way that ΔDIC and ΔSO_4^{2-} correlate well and do not show a deviation in the slope throughout the whole sediment depth investigated (Figure 10). "

Referee: (473) I don't see any direct evidence in the paper that terrestrial organic matter is what is being degraded. It might be, but without evidence to support this I would not be so definitive.

Answer: The sentence in question was rephrased: "*This confirms that the biogeochemistry in the prodelta region is driven by the import and processing of material from the Rhône River (Cathalot et al., 2010, 2013).*"

Furthermore, different studies showed, that the majority of the sediment fraction in the proximal domain is land derived. This fraction decreases in offshore direction. During the DICASE cruise, porewater was sampled for analysis of $\delta^{13}C$ and $\Delta^{14}C$ signatures of porewater DIC in order to evaluate what OM fraction actually undergoes mineralization. The results point in the direction, that land derived material is the DIC source in the pore waters close to the river mouth. An article to publish these results is on its way.

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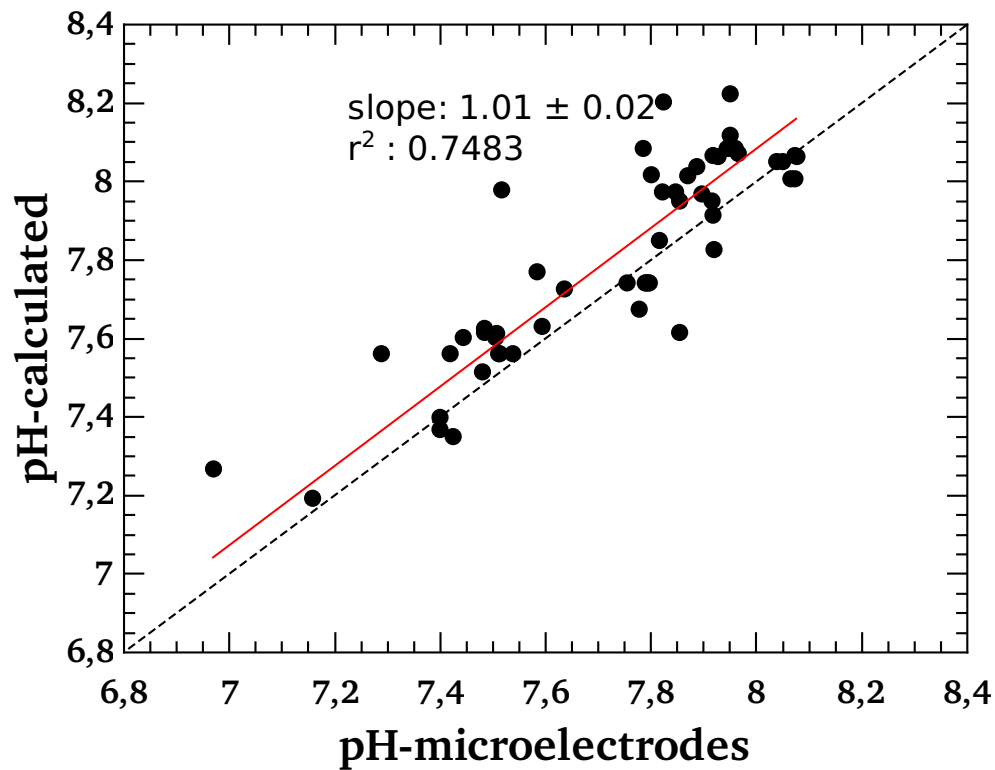


Fig. 1.

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