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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 in *italics*.

All minor comments of Reviewer 2 were taken into account.

Referee: Rassmann and collaborators present a very nice dataset of sediment properties in the Rhône river delta. Based on direct (microelectrodes) measurements of pH and O2 and on pore-water analyses of DIC, TA, Ca2+ and SO42- along a gradient from the river mouth to the open Mediterranean Sea (3 domains considered), this

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manuscript aims to describe and understand the main diagenetic reactions that control these sediment properties and the impact of the sediment on the bottom water carbonate chemistry. I would recommend publication of this manuscript following the proposed minor modifications and an extensive copy-edition by a native speaker.

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

Referee: Table 2 and Section 2.7 should not be presented in the Material and Methods section but more likely in the Discussion.

Answer: We moved Section 2.7 to the beginning of the discussion and rephrased it.

Referee: I do not believe CO2 dissolution should be presented as a diagenetic reaction. Table 2 should be made much clearer and for instance updated by: 1) providing the full name of the presented reactions, 2) dividing into 3 parts with reactions occurring in the presence of oxygen (oxic mineralization and reoxidation of reduced species), in the anoxic section (anaerobic mineralization and precipitation of reduced species), and both: CaCO3 dissolution or precipitation. Reaction R2, it is not clear whether you present CaCO3 dissolution or precipitation or both. I would consider 2 lines, one for precipitation, and one for dissolution as their effects on TA, DIC, pH and Omega are opposite. Finally, I would move this reaction to the end of the table (see above).

Answer: We sub-divided Table 2 into the 3 suggested categories and split reaction 2 into two lines for dissolution and precipitation.

Referee: Why don't you show nitrate reduction? This can be in some cases an important pathway.

Answer: Waters of the Northwest Mediterranean Sea show low nitrate concentrations. Only a minor part of OM is mineralized by this pathway in the study area. Nevertheless, denitrification has been added to the reaction table. To justify not to discuss nitrate reduction in this area, we cite (Pastor, L., Cathalot, C., Deflandre, B., Viollier,

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E., Soetaert, K., Meysmann, F.J.R., Ulses, C., Metzger, E. and Rabouille, C.: Modeling biogeochemical processes in sediments from the Rhône River prodelta area (NW Mediterranean Sea), Biogeosciences, 8, 1351-1366, 2011a.) at line 387:

"In contrast to other nearshore environments, nitrate reduction has been shown to account only for 2-5 % of OM mineralization in the sediments of the prodelta of the Rhône whereas other anaerobic mineralization processes account for 30-40 % in the distal domain and up to 90 % in the proximal domain (Pastor et al., 2011a). Nitrate reduction produces less TA than DIC (TA/DIC ratio = 0.8/1) and thus lowers Ω*."*

Referee: All reactions should be presented considering the same amount of OM mineralized (in some cases you have 1 or 2 moles of CH2O mineralized).

Answer: The stoichiometric coefficients in table 2 have been adjusted to 1 mol of CH_2O.

Referee: Figure 6 should be updated. First, you don't show the same Y-axis scale than on Figure 5, why is that? and furthermore, this scale in not the same between the 3 domains in this Figure 7.

Answer: We adjusted the scale on all figures to 40 cm depth.

Referee:I am a bit surprised by the very high heterogeneity that you found between stations in the Proximal domain and believe there are a number of mistakes to correct. For instance, you have DIC and TA data for station Z' until 30cm while you calculate pH up to 25. For station A', you seem to have DIC/TA data down to 25 cm and you calculate pH data down to 35 cm or more. Please check.

Answer: In effect, the area is highly heterogeneous, differences of 10 mmol/L in DIC or TA pore water concentrations at a same station in a certain depth are definitely possible. We checked the figures for consistency. Indeed, some data points had disappeared on the graphs and were re-introduced.

Referee: Furthermore, I have calculated pH for station Z at the last sampled depth (between 20 and 25 cm) considering TA of 48 and DIC of 50 mmol/L, I end up with a

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pH of 7.18, far from the 7.8 shown in Figure 6. Again, this should be carefully checked.

Answer: We use CO2SYS with the thermodynamic constants from (Lueker, T. J., Dickson, A. G., Keeling, C. D.: Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2 : validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium, Mar. Chem., 70, 105-119, 2000.) with TP = 0.1 μmol kg^{-1} and TSi = 6.4 μmol kg^{-1} (Denis, L., Grenz, C.: Spatial variability in oxygen and nutrient fluxes at the sediment-water interface on the continental shelf in the Gulf of Lions (NW Mediterranean), Oceanologica Acta, 26, 373-389, 2003) and making the hypothesis that theses values are constant with depth (in lack of better data). Furthermore, we use the bottom water salinity of 37.5 and the in situ temperature of 16.0 °C. The water depth at this station is 18 m. The analysis has been done at a temperature of 25 °C.

For the data point cited:
Z(18 cm): TA = 46.215 $\pm$ 0.474 μmol kg^{-1}, DIC = 45.440 $\pm$ 0.190 μmol kg^{-1} leads to pH= 7.636 $\pm$ 0.059
Z(22 cm): TA = 49.189 $\pm$ 0.504 μmol kg^{-1}, DIC = 47.363 $\pm$ 0.129 μmol kg^{-1} leads to pH= 7.801 $\pm$ 0.048 and
Z(26 cm): TA = 44.514 $\pm$ 0.484 μmol kg^{-1}, DIC= 44.506 $\pm$ 0.051 μmol kg^{-1} leads to pH=7.492 $\pm$ 0.051

If the discrepancies of your and our calculations persist, we should do a more detailed comparison of our methods with a whole dataset.

Referee: L284-287: You should present the determination coefficients and the corresponding slopes for each domain separately.

Answer: As the slopes were not significantly different, we followed the suggestion of Reviewer 1 and reported the overall slope 1.01 with r^2 = 0.9982.

Referee: L291: I would really like to see a more detailed comparison between mea-

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sured and calculated pH.

Answer: As already posted in the answer to Reviewer 1:

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 visible on Figure 1.

Referee: Section 3.4. Why all stations are not shown for Ca2+ (D, A' and Z' missing), why 3 datasets for A ?

Answer: We do not have any data for stations D and Z'. In fact, there has been a confusion at station A: the data sets are from A and A' and a longer core at station A that has been removed in the reviewed version of the paper.

Referee:L43: This is not correct, following your Table 2, aerobic mineralization does not produce TA.

Answer: We rephrased:

"Aerobic and anaerobic reaction pathways contribute to the production of dissolved inorganic carbon (DIC), which creates acidification of the bottom waters. Anaerobic reactions lead as well to production of total alkalinity (TA)"

Referee: L152: I don' understand what is "the slope of the pH variation", please

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rephrase.

Answer: We rephrased:

"The calibration of the pH electrodes was carried out using NBS buffers, thus allowing the estimation of the slope of the electrode signal in fonction of pH variation at onboard temperature. The slope was then recalculated at in situ temperature and the electrode signal variation was transformed into pH changes. "

Referee: L156: .. "using this BW value the micro electrode measured pH variations", please rephrase

Answer: We rephrased:

"The pH of bottom waters was determined using the spectrophotometric method with m-cresol purple following Clayton and Byrne, (1993) and Dickson et al., (2007). Pore water pH on the total proton scale (pHt) was recalculated using the signal of the micro-electrode adjusted to this BW value."

Referee: L162: surface of 109 cm, this is not a surface.

Answer: The surface of the head of the moving unit of the lander, where the electrodes are mounted measures 109 cm^2.

Referee:L171: according to Broecker and Peng (1974) L180 to 191: please precise how many replicates were measured for each parameter (pH, O2, DIC and TA)

Answer: *"All bottom water concentrations were measured as triplicates. Small sample volumes in pore waters only allowed for replicates for the DIC, SO_4^{2-} and Ca^{2+} analysis."*

Referee: L299: (Fig. 5) L313: $>$ 95% calcite + $>$5 % Mg-calcite do not leave much room for aragonite: : :.

Answer: Yes, indeed, we did not detect any aragonite in this area. The drainage basin

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of the Rhône River is characterized by old carbonates and the calcifying organisms on site (foraminifers) produce calcite tests. There are no corals in this area.

In lack of better material, the aragonite standard used for the calibration of the X-ray analysis is natural coral powder, characterized to have less than 2 % of Ca content. (Kindler, P., Reyss, J.-L., Cazala, C., Plagnes V.: Discovery of a composite reefal terrace of middle and late Pleisocene age in Great Inagua Island, Bahamas. Implications for regional tectonics and sea-level history, Sedimentary Geology, 194, 141-147, 2007). It's diffraction analysis gives the following diffractogramme (Figure 2) with the clearly visible principal Ar peak at 2θ = 26.297° and its secondary peak at 27.298° (both slightly shifted from the theoretical value) .

A typical diffractogramme of Rhone delta sediments looks like Figure 3 (Station Z). We recognize clearly the principal calcite peak at 2θ = 29.468° with a little deformation at the right indicating the presence of magnesian calcite. The position of the aragonite peak is covered by the base of another peak at 2θ = 26.674°. These diffractogrammes do not allow a better deconvolution of the peaks and we have an uncertainty about the material used to calibrate our DRX measurements. So the presence of aragonite cannot be completely excluded, but is unlikely.

Referee: Many grammatical and formatting errors in the Discussion.

Answer: Grammatical and formatting errors have been corrected.

Referee: All figures starting from Figure 2: Average OPD for each domain should be shown on these plots.

Answer: The vertical scale on figures 2 and 4 is in mm whereas the vertical scale on the following figures is given in cm. The average OPD for each domain is situated between the sediment water interface and the first scale trait, so it would be invisible on these figures.

Referee: Figure 2 legend: in situ in italics Figure 3 legend: what do the vertical error

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bars correspond to? Please add.

Answer: We added in the legend of the figure:

"Error bars are standard deviations between the diffusive fluxes calculated from the 5 single oxygen profiles measured at each station."

Referee: Figures 5 and 7: I would use the same x-axis scale for all 3 domains

Answer: We decided not to use the same concentration scale because the gradients are very different. Adjusting the scale for all figures would hide the form of the profiles in the prodelta and distal domain. To alert the reader about difference between the three concentration scales, we added to the figure caption:

"For better visibility of the profiles in each domain, the scale of the concentrations has been individually adjusted for each domain."

Referee:and for Figure 7 separate SO42- and Omega, consider using 2 figures. On Figure 7, please note that the legend box hides the axis, which should be avoided.

Answer: The figure has been split into individual figures for sulfate concentrations and calcium carbonate saturation states.

Referee: Figure 6 and 7, and legends: what do the horizontal error bars correspond to? Please add.

Answer: We added to the caption of figure 6:

"The error bars are estimations of the error propagation from the measured data in the calculation."

Answer:and to the caption of figure 7:

"The error bars represent the uncertainties of the ICP-AES measurement."

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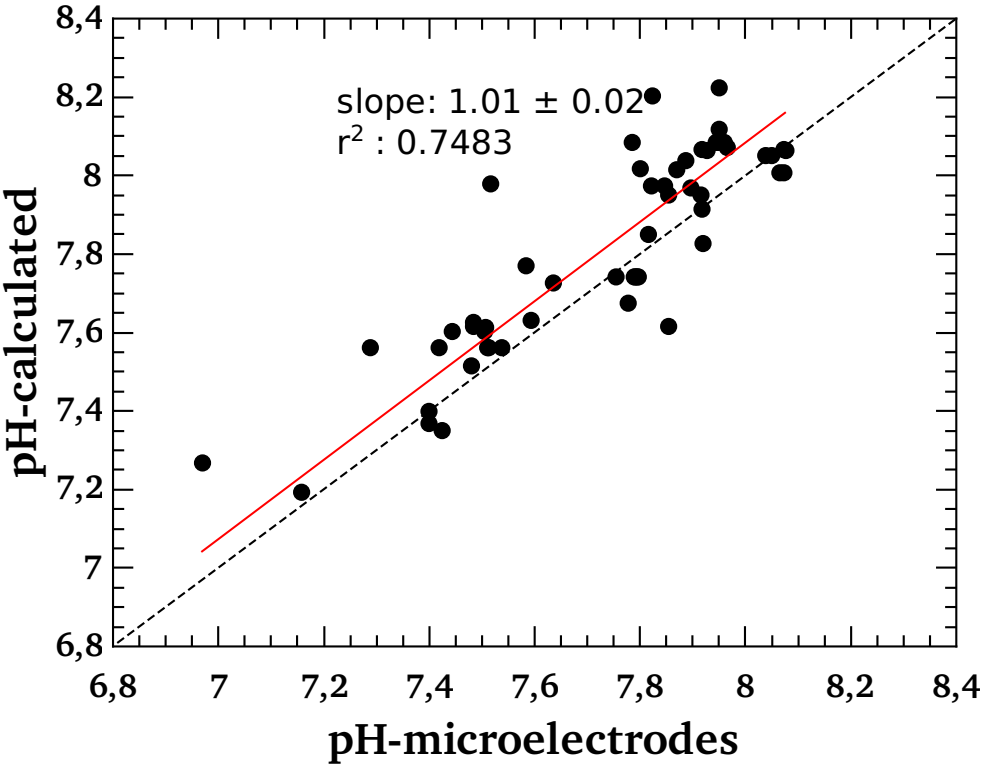

Fig. 1.

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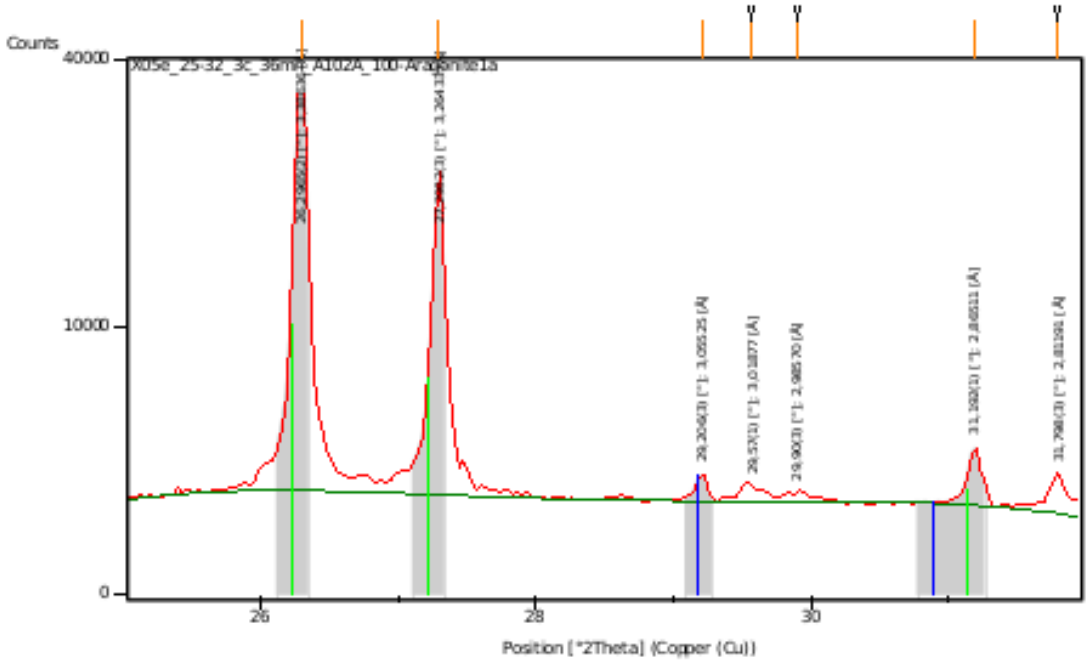

Fig. 2.

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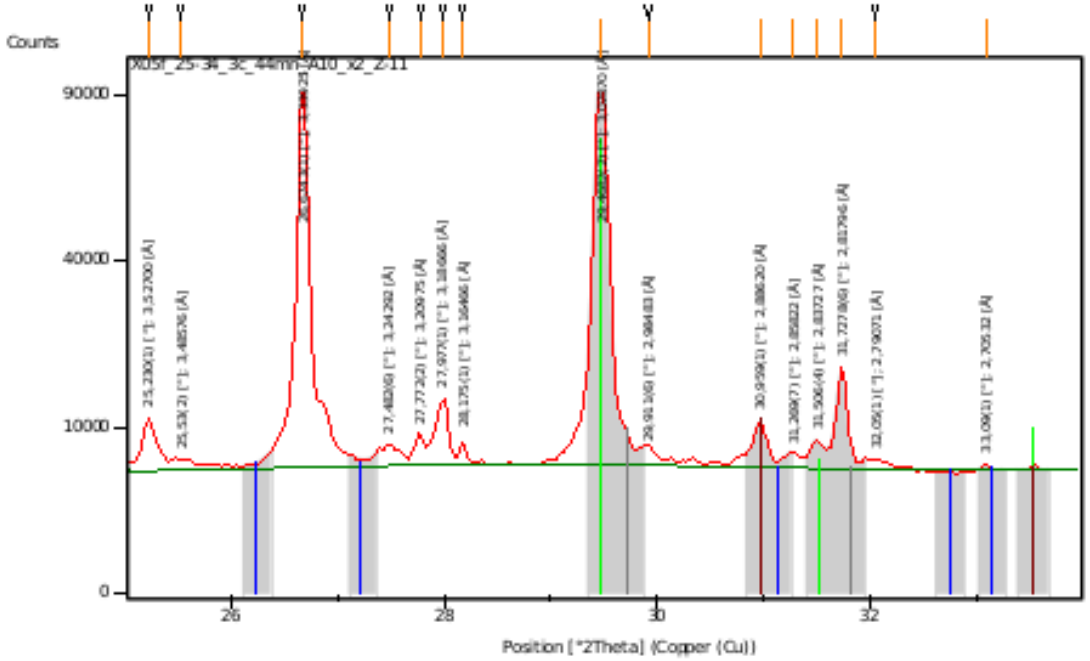

Fig. 3.

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