Reply to comments on manuscript https://doi.org/10.5194/cp-2023-58

Reviewer's comments (RC) are marked in black, authors' responses (AC) are marked in blue.

Reviewer 1: Thomas Algeo

General response:

This study is well-executed overall. I have only minor comments, which are given in the annotated PDF that I am returning. I will thank the authors for making appropriate modifications to the manuscript per these comments.

We thank Thomas Algeo for his kind words and the thorough read-through of the manuscript. Our responses to the comments in the annotated PDF are given below point-by-point.

Kind regards,

The authors.

Individual comment response:

Line 12: "Upper" --note; Use of time terminology ("early/late") versus rock-time terminology ("lower/upper")—"Early" and "Late" are used in reference to geologic time, e.g., "basin subsidence during the Late Cretaceous" or "a negative d13C trend through the Late Cretaceous (time)". "Lower" and "Upper" are used in reference to rock units or constituents of rock units, e.g., "an Upper Cretaceous limestone", an "Upper Cretaceous ammonite fossil", or "a negative d13C trend through the Upper Cretaceous (strata)". With regard to capitalization of these terms ("early/late" and "lower/upper"), they should be capitalized for formally defined units and not capitalized if used in an informal or general sense. "lowermost" and "uppermost" are always informal and are never capitalized.

We thank the reviewer for pointing out this rather obvious mistake. We propose to check the manuscript throughout for similar errors and correct them. The International Subcommission on Devonian Stratigraphy (SDS) has decided by formal voting to subdivide the Famennian into four stages, the youngest of which was named as uppermost Famennian. Since the substages have not yet been formalized, e.g. by ICS approval, they are not yet capitalized. However, there will be a formal Uppermost Famennian in the future.

Line 30: "buildup" (single word).

This will be corrected.

Line 33: interesting hypothesis; see my comments in Discussion section.

Thank you; see our response to the comments in the Discussion section.

Line 62: The results of the Lu et al. (2021) study need to be more thoroughly considered, as the findings were similar to those of the present study.

We propose to consider this paper in more detail in the Discussion section.

Fig. 5b: subscript.

This will be corrected.

Fig. 5 "periodicity" must have units of time; you may mean "wavelength" here.

We will change "periodicity" to "wavelength" wherever it is necessary in the text and figures.

Fig. 6a: subscript.

This will be corrected.

Fig. 6c: significance in power spectra is often too casually evaluated; see Smith (2023, PPP).

This is true, and we agree that this is a problem within the field of cyclostratigraphy. We do not use the significance levels as an argument in favour of our cyclostratigraphic interpretation (in fact, they are not in favour of this interpretation), but rather focus on the fit of the amplitude modulations, the agreement with the lithological changes, and the similarities to other floating timescales for the Kellwasser interval. The significance levels are included because this is common practice in cyclostratigraphic studies, and not mentioning them at all might rightfully cause suspicion.

This nuance is, however, not expressed in the manuscript. We propose to include 1-2 sentences that explains our inclusion of the significance levels, and subsequent non-utilisation of them. A proposed addition is given below (in italics):

Line 335: These are not all significant at the 90% confidence level (Fig. 6c-e). *Moreover, the 90-95% CL boundary that is widely applied in cyclostratigraphy does not suffice to rule out false positives, according to rigorous statistical analysis (Vaughan et al. 2011, Smith 2020, Weedon 2022, Smith 2023). We therefore rely on other lines of evidence to support our cyclostratigraphic interpretation.*

These other lines of evidence are expanded on in the rest of this section in the current version of the manuscript (amplitude modulation fit, correspondence with lithology, TimeOpt results, agreement with previous cyclostratigraphic studies).

References:

Vaughan et al. ,2011, https://doi.org/10.1029/2011PA002195

Smith, 2020, https://doi.org/10.21701/bolgeomin.131.2.005

Weedon, 2022, https://doi.org/10.1016/j.earscirev.2022.104261

Smith, 2023, https://doi.org/10.1016/j.palaeo.2023.111744

Fig. 6c-e: units? cm^-1 ?

This was indeed missing from the figure. We thank the reviewer for pointing it out and will amend the relevant panels.

Fig. 7b: subscript.

This will be corrected.

Line 567: plus: Algeo et al. 1995 GSA Today.

This is indeed a key citation that we missed. We will include it.

Line 574: I do not see any papers of Retallack or Schobben cited, so how do they figure in the development of this hypothesis?

We included the wrong Pisarzowska and Racki here; the 2012 Chemical Geology paper instead of the 2020 Stratigraphy & Timescales chapter. This will be corrected.

The term 'Retallack/Racki—Schobben hypothesis' was introduced by Pisarzowska and Racki (2020), which is what the citation should have been. This study bases the hypothesis on Retallack and Huang

(2011), Racki (2020), and Schobben et al. (2019). For completeness, and to give credit where it is due, we should have cited all three papers that the hypothesis draws from. We will include all three in the amended manuscript.

References:

Retallack and Huang 2011, https://doi.org/10.1016/j.palaeo.2010.10.040

Schobben et al. 2019, https://doi.org/10.2138/gselements.15.5.331

Racki 2020, https://doi.org/10.1130/2020.2544(01)

Pisarzowska and Racki 2020, https://doi.org/10.1016/bs.sats.2020.08.001

Line 588: this was addressed in detail in: Algeo, T.J., Scheckler, S.E. and Maynard, J.B., 2001. Effects of the Middle to Late Devonian spread of vascular land plants on weathering regimes, marine biotas, and global climate. In Plants invade the land: evolutionary and environmental perspectives (pp. 213-236). Columbia University Press.

We thank the reviewer for providing an additional reference; we will read through it and incorporate it in the discussion.

Line 598: maybe, but it seems unlikely without some additional factors related to land plant spread and resulting nutrient flux changes.

We agree that it is unlikely, but would like to keep the possibility open, especially when short-lived events and thin black shales are concerned. As noted on line 590, the development of vascular and rooted land-plants may have likely played at least a long-term role in priming the system and making anoxia more likely. See also Percival et al. (2020). We propose to include this citation in this discussion.

Reference:

Percival et al. 2020, https://doi.org/10.1016/j.gloplacha.2019.103070

Line 603: I beg to differ on this point: Racki's work offers very little evidence for volcanc influence; it is almost entirely a speculative compilation of diverse records. to call this "well-documented evidence for widespread volcanism" is a big stretch.

We stated that, based on Racki and other's work, there is certainly some evidence from different continents for volcanic activity around the F-F boundary, and we stand behind this point. We do agree, however, that there are issues with the dating of the LIPs and their temporal relation to the Kellwasser Crisis, as well as the absence of mercury enrichments in some sections, and the question whether volcanism, if present, was actually a causal factor. However, we feel that a hypothesis that is as prevalent as this one should at least be addressed. We propose to present the widespread volcanism hypothesis in a more nuanced way. A paragraph is proposed below:

Such a combination of orbital forcing and volcanism has been proposed for Mesozoic OAEs (Batenburg et al., 2016; Ait-Itto et al., 2023). Given the growing body of work indicating an influence on the timing of the Kellwasser Crisis, it is possible that the Kellwasser Crisis was another of these perfect storms (De Vleeschouwer et al., 2017; Da Silva et al., 2020; Ma et al., 2022; this study). Large-scale volcanic events have been radioisotopically dated to around the age of the Kellwasser Crisis (Courtillot et al., 2010; Ricci et al., 2013; Polyansky et al., 2017; Percival et al., 2018; Ernst et al., 2020), and mercury enrichments around the Frasnian-Famennian boundary have been interpreted to show a precise temporal and causal relationship between the two (Racki, 2020, and references therein). This is especially true for the mid-European study area, where widespread ash layers have been shown to be temporary close to the Kellwasser horizons (Winter, 2015). However, this link has been questioned due to the lack of mercury peaks at some records, particularly in North America (e.g., Zhang et al., 2021;

Zhao et al., 2022; Zheng et al., 2023; Pippenger et al., 2023), and unlike the Mesozoic warming events, the Kellwasser Crisis is more notably marked by climate cooling (Joachimski and Buggisch, 2002; Balter et al., 2008, Huang et al., 2018). Thus, the Kellwasser Crisis may also have represented a solely astronomically forced event, or even a different kind of 'perfect storm' that combined a favourable orbital configuration with another (non-volcanic) factor.

References:

Ait-Itto et al., 2023, https://doi.org/10.1016/j.cretres.2023.105618

Batenburg et al., 2016, https://doi.org/ 10.5194/cp-12-1995-2016

Balter et al., 2008, https://doi.org/10.1130/G24989A.1

Courtillot et al., 2010, https://doi.org/10.1016/j.epsl.2010.09.045

Da Silva et al., 2020, https://doi.org/10.1038/s41598-020-69097-6

De Vleeschouwer et al., 2017, https://doi.org/10.1038/s41467-017-02407-1

Ernst et al., 2020, https://doi.org/10.1016/j.gloplacha.2019.103097

Huang et al., 2018, https://doi.org/10.1016/j.epsl.2018.05.016

Joachimski and Buggisch, 2002, https://doi.org/10.1130/0091-7613(2002)030<0711:CAOSIC>2.0.CO;2

Ma et al., 2022, https://doi.org/10.1016/j.gloplacha.2022.103874

Percival et al., 2018, https://doi.org/10.1038/s41598-018-27847-7

Percival et al., 2020, https://doi.org/10.1016/j.gloplacha.2019.103070

Pippenger et al., 2023, https://doi.org/10.1016/j.palaeo.2023.111751

Polyansky et al., 2017, https://doi.org/10.1016/j.lithos.2017.02.020

Racki, 2020, https://doi.org/10.1016/j.gloplacha.2020.103174

Ricci et al., 2013, https://doi.org/10.1016/j.palaeo.2013.06.020

Winter, 2015, http://doi.org/10.1127/1860-1804/2015/0092

Liu et al., 2021, https://doi.org/10.1016/j.palaeo.2021.110502

Zhao et al., 2022, https://doi.org/10.1016/j.epsl.2022.117412

Zheng et al., 2023, https://doi.org/10.1016/j.epsl.2023.118175

Line 604: add Lu et al. 2021 EPSL

This reference will be added.

Line 649: "mL"

This will be corrected.

Line 649: subscripts

This will be corrected.

Reviewer 2: Damien Pas

General response:

The submitted paper by Wichern et al. 2023 entitled "Astronomically-paced climate and carbon-cycle feedbacks in the leadup to the Late Devonian Kellwasser Crisis" present research focusing on the mechanism triggering the Kellwasser Crisis based on a section from the Rhenohercynian Massif in Germany.

Overall, the manuscript is of excellent quality and provides interesting hypotheses to increase our understanding of causal mechanisms that have triggered the Kellwasser crisis. The method is clear, the manuscript in its whole is well-written, and a large number of references are used to support their findings. The quality of the figures is excellent.

My major comments are here below, and the minors are in the pdf.

The authors examined 144 carbon isotopes within a 12-meter section, meaning they had approximately one sample for every 8 cm. Assuming an average sedimentation rate of 1.2 centimeters per thousand years (ky), this implies there is one carbon isotope sample available every 6.6 ky. This sampling rate should enable the authors to effectively distinguish between short- and long-term orbital eccentricities, and obliquity.

When considering the paper by De Vleeschouwer et al. (2017) and the emphasis those authors placed on the significance of obliquity in driving the late Devonian Kellwasser events, it is somewhat surprising that the authors did not provide a more detailed explanation for their decision not to utilize delta 13C. Their stated reason is that "at Winsenberg, delta 13C displays limited variability outside of the Kellwasser intervals, which hinders its applicability in confirming or refuting the presence of an obliquity peak just before the UKW."

It is worth noting that power within the obliquity band has been observed in each of the six sections studied in De Vleeschouwer et al. (2017), including the Sinsin section, which is relatively close to the Winsenberg site. Hence, I believe it is valuable for the authors to offer insights into the reasons behind the limited variability in delta 13C at Winsenberg and explore potential underlying mechanisms. Indeed, it is important to discuss what could make the Winsenberg section, a site responding differently to obliquity than usually observed in the literature.

Subsequently, the authors mentioned, "there is a lack of obliquity-related power in Winsenberg, this is not surprising considering that these sediments were deposited in a paleotropical region where precession effects are dominant." While I concur with this statement, as it aligns with established theory, it raises an important question. Given the presence of obliquity-related power in most of the sections examined in De Vleeschouwer et al. (2017), which are all situated near the tropics and where teleconnections appear to play a substantial role in transferring power from higher to lower latitudes, it becomes essential to understand why obliquity-related power is absent in the Winsenberg section. This aspect requires further clarification.

In line 350, the authors make a statement that is not accurate. In Figure 2 of De Vleeschouwer et al. (2017), obliquity power is evident in Iowa H32, CG1, and Sinsin tuned magnetic susceptibility records. Therefore, I wonder why the authors do not detect obliquity-related power in the Winsenberg section, neither in detrital records (TiO_2/Al_2O_3) nor in delta 13C, especially considering their excellent sampling resolution. Addressing this question will help to understand the issue raised in the previous comment.

All in all, I believe the manuscript is a good contribution for CP but the points raised above need to be addressed.

Best regards,

Damien Pas

The authors thank Damien Pas for his extended review and kind words. We agree that the absence of obliquity has not been given the attention it deserves, considering that it is rather complex and suspect for all the reasons outlined by the reviewer above. We will amend the statement on line 350 following the reviewer's correct point that there is an obliquity signal in the Sinsin MS record, although it is rather weak compared to precession.

The reviewer's insight led us to re-investigate potential obliquity signals, for which we are very grateful as an oversight was discovered. It turns out that one of the proxies used, K_2O/Al_2O_3, does contain a clear signal in the obliquity band, as illustrated below (Fig. Xc). The other two proxies do not show a clear signal in the obliquity band (Fig. Xa-b), although bandpass filtering obliquity (0.025-0.035) reveals a weak signal that is similar to the stronger K_2O/Al_2O_3 signal (Fig. Xd-f).

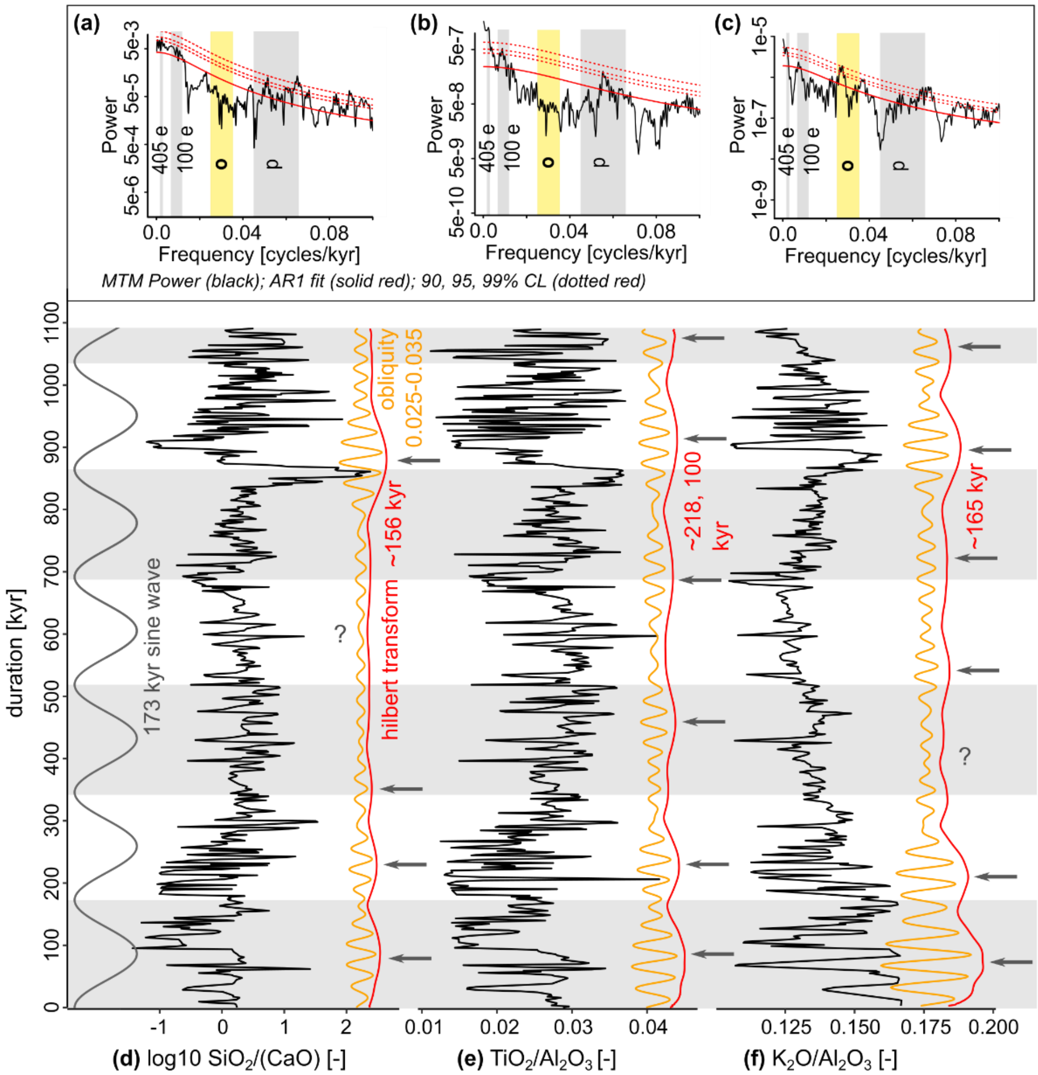

Fig. X Obliquity signals in tuned SiO_2/CaO (a, d), TiO_2/Al_2O_3 (b, e) and K_2O/Al_2O_3 (c, f) records. Panels a-c show the MTM power spectrum (tbw = 2) with the obliquity (o) interval (0.025-0.035) shaded in yellow. Other astronomical parameters (405 kyr eccentricity, 100 kyr eccentricity, precession) are shaded in grey. d-f show the respective proxy record (black), filtered obliquity (orange), and the Hilbert transform of filtered obliquity (red). MTM-inferred periodicities of this Hilbert transform are noted in red. Identified cycles are marked with grey arrows. On the left of panel d), a 173 kyr sine wave is plotted (arbitrary x-axis) and its cycles are marked with white and grey bands.

Moreover, the amplitude modulation (Hilbert transform) of the bandpassed obliquity signal of K_2O/Al_2O_3 has a periodicity of ca. 165 kyr. This is close to the 173 kyr stable amplitude modulation of obliquity and strengthens the argument that this is indeed an obliquity signal. For comparison, a 173 kyr sine wave has been added to the background of Fig. X. The other proxies, SiO_2/CaO and TiO_2/Al_2O_3, show amplitude modulations of slightly different periodicities (156 kyr and 218, 100 kyr, respectively).

We originally missed the K_2O/Al_2O_3 signal due to mislabelling, and did not trust the other signals by themselves due to their weak power in the obliquity band.

We propose to include a paragraph in the manuscript concerning the obliquity signal. This paragraph will discuss 1) the information and figure outlined above; 2) its relation to the hypothesis outlined in De Vleeschouwer et al. (2017); 3) why K_2O/Al_2O_3 might have recorded a stronger obliquity signal than the other proxies, which may be related to the fact that K_2O/Al_2O_3 as a chemical weathering proxy has a more direct link to the global carbon cycle than the other proxies, and 4) why the $\delta^{13}C$ record does not show a clear cyclic signal for most of its length and whether this might be a primary or secondary feature of the record. This latter point may be related to thermal overprinting during late stage diagenesis, something that is widespread in the Rhenish Massif.

We are confident that these amendments will improve the manuscript.

Responses to comments within the annotated PDF are given below.

Kind regards,

The authors.

Individual comment response:

Fig. 1: In the figure nutrient recycling is written but in the caption the focus is on phosphorous recycling. Please be consistent throughout

The capital letter P is used in each panel and I'm not able to find the meaning of this in the caption. Some readers may be less familiar with the topics and wonder what is it.

The authors thank the reviewer for pointing out this inconsistency. ‘P’ indeed stands for phosphorous, but this is not clarified anywhere. We propose to include this in the caption, and to replace ‘nutrient’ with ‘P’ for consistency.

Line 106: This is very interesting but an interpretation that seems to result from your dataset. This section should focus solely on the description of your results!’

This statement is indeed not in the right section. We propose to move it to section 4.2.1 (Lithological variations and rhythmicity within the section).

Figure 3e. No data on iron/pyrite are presented in this log!

This part of the legend key was mistakenly left in from the more extensive log in the appendix. It will be removed.

Line 177: Can you be more specific! It is not so clear to me what have you done here. Did those "data" acquired in through ICP-MS? and how much sample where used for the calibration? Can you elaborate on this.

These data simply consist of the $CaCO_3$ wt% estimate that resulted from weighing the samples before and after the acid digestion, under the assumption that only minimal amounts of other components were digested too. We propose to clarify this in the organic carbon isotope analysis method section.

Line 178: The powder used for delta C org analyses should not contain carbonate as one has to decarbonatize the powder prior the analyze. I suppose the authors meant that they used the CaCO3 values obtained through the Rock-Eval pyrolysis? Can you clarify this !

See the answer above. We were not clear enough in explaining that a (rough) $CaCO_3$ estimate was obtained through acid digestion and we propose to amend this.

Line 183: I would have like to have an introductory sentence explaining the main reasons why you selected these ratios....(e.i., detrital intput, weathering, chemical weathering). Indeed, the explanation comes late in the paragraph.

The authors agree that an introductory sentence would make this section easier to parse. We propose to include one, along the lines of "Three elemental ratios were chosen based on their use as paleoclimatic indicators: SiO_2/CaO for total detrital input, TiO_2/Al_2O_3 for riverine input, and K_2O/Al_2O_3 for chemical weathering".

Line 186: do you mean to be chiefly detrital?

Yes, we thank the reviewer for catching this mistake, it will be corrected.

Line 246: as it is often!

This phrase will be changed to "as has been observed at several records".

Fig. 4h caption: what is less express ? sedimentological features, rhythmicity , etc?

This description refers to the absence of clear bundling in the sedimentology, visually speaking. We propose to explicitly state that the shale bundling is not as clear in this interval as in the preceding interval.

Line 319: Do you have a reference for this statement? ... characteristic braiding pattern...

We propose to include Meyers et al. (2012) as a reference. Here, the term "braiding pattern" is used to refer to the frequency modulation of precession.

Reference:

Meyers et al., 2012, https://doi.org/10.1029/2012PA002286

Line 351: This is not true, see comment the report.

We thank the reviewer for correcting this error, see our general response to the report.

Line 355: A best fit at 1 cm/ky is true for your record! Please be more specific because written like this it seems that it is true for any sedimentary records.

The way TimeOpt was applied here (to our already tuned record) should be true for any record if the inferred tuning is "correct'' (i.e., corroborated by TimeOpt). The record was tuned, then the duration axis was treated as a depth axis and analysed with TimeOpt. If this duration is the same as that inferred by TimeOpt, their correspondence should be one-to-one and the 'sedimentation rate' should be 1. Note that this is not a 'true' sedimentation rate!

For example, applying TimeOpt in this way to an insolation curve that is already plotted against time (while treating the time axis as "depth") will also result in a sedimentation rate of 1 cm/kyr.

What makes this confusing is that the actual inferred sedimentation rate of this record also fluctuates around 1 cm/kyr (Fig. 5e). However; that doesn't change the above approach. If the sedimentological succession had been twice as short, and the sedimentation rate had been twice as high, Fig. 5e would have indicated a sedimentation rate of 2 cm/kyr. However, the inferred duration would have been the same, and thus the outcome of TimeOpt would have been the same.

We hope this clarifies the issue. We propose to re-phrase this section to make it clear what we are actually doing, and to distinguish between the actual and the “synthetic” sedimentation rates, as the confusion might stem from their similarity.

Line 407: The relationship is not so clear to me on the

Part of the sentence is unfortunately missing here. We do not want to make any assumptions on the reviewer’s intent. We will communicate with the reviewer privately to make sure we understand the unclear part better.

Line 407: is most clearly defined

This mistake will be corrected.

Line 541: . ... inferred for, both for the Kellwasser...

This mistake will be corrected.

Line 546: Although with a in capital letter.

The preceding point should actually have been a comma, this will be corrected.

Line 549:

There is an empty comment here that we cannot interpret. We will communicate with the reviewer privately to ensure we did not miss any feedback.

Line 554: This last sentence sounds like a question without question mark? ... can you rephrase it.

We agree that the sentence sounds strange. It will be re-phrased to “This additional mechanism might have been sufficient to enable astronomical forcing to push the climate system past its tipping point and into anoxia”.

Line 561: You may also cite Denayer et al. 2020 (Palaeobiodiversity and palaeoenvironments).

This reference will be added.

Figure C3: Can you precise what is SD in the caption.

We thank the reviewer for pointing this out. “SD = Standard Deviation” will be added to the caption.

Figure D2b: 2 in subscript

This will be corrected.

Figure D2b: Remove s

This will be done, also for the other similar figures (Fig. 5, 6).