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Comment

## ***Interactive comment on “Dissolved iron (II) in the Baltic Sea surface water and implications for cyanobacterial bloom development” by E. Breitbarth et al.***

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**Overview** This work reports on a series of repeat occupations of stations in the Baltic during the summer cyanobacterial blooms that occur in the Baltic. The authors undertook measurements of Fe species in the water column along with the key oxidants (H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>) of Fe(II) and information on the nutrients and relevant biological communities present at the time. This paper clearly has an interesting dataset and examines a topic of intense interest to both biogeochemists and modellers, most notably the redox cycling of iron and its effect on iron speciation and bioavailability. However problems with numeracy reduce the impact of the paper at present as the Fe(II) oxida-

Full Screen / Esc

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Discussion Paper



tion calculations are applied incorrectly and other calculations regarding Fe fluxes into the surface waters are not made. I applaud the authors for taking on such a study but strongly suggest that they revise their manuscript along the lines of clearly identifying candidate processes for the supply and cycling of iron in the surface waters and backing this up with numerical estimates of the fluxes, turnover/residence times etc. A fairly extensive list of suggestions and corrections is provided for the authors to help them achieve this revision.

### General Comments

**Fe(II) Oxidation Rates:** The absence of measured oxidation rates and the reliance on inorganic rates from lab experiments (Gonzalez-Davila et al., 2005; King and Farlow, 2000; Millero and Sotolongo, 1989; Millero et al., 1987; Millero et al., 1995; Santana-Casiano et al., 2000; Santana-Casiano et al., 2004; Santana-Casiano et al., 2006) is a pity as the oxidation rates are easy enough to do when the samples are measured for Fe(II). Indeed for my own work we routinely measure the Fe(II) oxidation rate and use it as one of a set of criteria for confirming the validity of the data (Croot et al., 2008; Croot et al., 2007). Such data also helps to argue for the existence of organic complexation of Fe(II) though it must be pointed out that when the chelators are present in low concentration most of the Fe(II) produced may also still be oxidized and these processes are difficult to separate (Croot et al., 2007). However the main problem with this paper at present, as the authors also have noted via their correction, is that the estimated Fe(II) oxidation rates have been calculated incorrectly and this whole part of the work needs to be examined carefully particularly as the revised version of the manuscript must highlight the fact that it H<sub>2</sub>O<sub>2</sub> that controls Fe(II) oxidation rates and not O<sub>2</sub> as is stated presently.

**Differences between DGT and FIA for Fe(II):** The differences between the two analysis systems for Fe(II) in anoxic waters is interesting but also raises questions about the sample handling and the steps to which the authors took to keep O<sub>2</sub> from their samples. Below in the specific comments I outline a possible analytical reason for the low Fe(II)

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observed by the FIA but this is untested and sample handling remains a critical issue that authors must address. In my own work I now take samples for Fe(II) from GO-FLOs or Niskins using the same technique as workers sampling for dissolved gases such as O<sub>2</sub> (Grasshoff et al., 1999) to avoid any O<sub>2</sub> artifacts in determining concentrations and oxidation rates for sub-oxic samples, and this seems to work well in combination with a N<sub>2</sub> atmosphere for the headspace and sampling within an hour. Sampling via syringe would have to be very carefully done anyway but if the syringe material is rapidly O<sub>2</sub> permeable and they are left too long in the open air this may also cause problems. I think what is required here is a more detailed examination of methodology as the speciation argument used currently by the authors does not appear to hold based on our understanding of the Fe(II) speciation in anoxic waters (Landing and Westerlund, 1988).

Iron solubility and particle dynamics: In the manuscript it is stated several times that Fe(III) is rapidly removed from the water column through particle formation and this is based on studies from the open ocean. I think the authors need to re examine this paradigm in light of two key observations: (1) The lower salinity encountered in the estuary that is the Baltic Sea is typically lower than the usual salinity range where particle/colloidal coagulation and removal of humics is seen (Boyle et al., 1977; Hunter et al., 1997; Hunter and Leonard, 1988; Mayer, 1982; Sholkovitz, 1978; Sholkovitz et al., 1978). (2) The presence of large surface slicks is a common feature associated with cyanobacteria blooms in the Baltic and the resulting organic carbon and TEP must provide a significant pool of ligands in the particle and colloidal size ranges for maintaining iron in suspension (not soluble). Thus I believe the Baltic data in the present manuscript needs to highlight more the differences between the Baltic and the Open Ocean while presently it uses the paradigms of the Open Ocean to interpret a very different system.

Precision and uncertainties – Throughout the manuscript data are quoted to what is apparently a high precision (2 or 3 decimal places) but not uncertainties or error es-

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timates are provided. In several places in the manuscript it is clear that there must have been a considerable amount of variability in the data and so the absence of information on this hampers the interpretation of the data in its correct sense. This is particular important when it comes to interpreting the figures where almost no error bars are provided.

Units – for biogeochemical studies it is always preferred (read: required) to have chemical quantities in the units that chemists use: moles. This makes comparing mole ratios much simpler and thus I would strongly suggest that the authors use mol L<sup>-1</sup> for their O<sub>2</sub> and H<sub>2</sub>S data in figures 3-5. I would also point out that the data in Figure 11 appears to have calculated incorrectly for O<sub>2</sub> as the figure indicates an O<sub>2</sub> concentration of ~600 umol L<sup>-1</sup> while for water at 0°C and zero salinity the equilibrium value is only 457 umol L<sup>-1</sup> (Millero, 1986. Solubility of oxygen in seawater. UNESCO Tech. Pap. Mar. Sci. 50).

Iron sources: There is a lot of discussion in this manuscript about where the iron is coming from but no numerical estimates are made. Given that the authors have the water column data and that there is data available on typical rainfall Fe concentrations (e.g. Fe(II) in rain: (Falkowska et al., 2008)) it would be a major help here if they examined the potential fluxes of iron into the surface layers from below and from above so that some of their statements in the manuscript were backed up with more evidence. This would also allow then an estimate of the residence time for iron in Baltic surface waters which could be compared to estimates from other regions (Croot et al., 2004a; Jickells, 1995; Jickells, 1999; Lohan and Bruland, 2008)

Baltic studies: There are also a number of other studies specific to the Baltic that should be included in the discussion of the present work as they have direct relevance to key aspects. Recently papers have been published on the iron nutrition of cyanobacteria in the Baltic (Schubert et al., 2008), also a highly relevant study, which includes samples from Gotland deep, on Fe bioavailability via reporter genes in a cyanobacteria (Boyanapalli et al., 2007), and similarly papers on the detection of siderophores in the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Baltic (Kosakowska, 2000; Kosakowska et al., 1999). As Cu complexation is invoked by the authors as a source of Fe(II) ligands the earlier work on this in the Baltic should be included (Kremling et al., 1981), as well as some other papers of relevance concerning trace metal redox and particle flux studies in the Baltic (Dyrssen and Kremling, 1990; Neretin et al., 2003; Pohl et al., 2004; Pohl et al., 2006).

### Specific Comments

P3804 Abstract. I find a lot of the statements in the abstract are not so easily found in the main body of the manuscript nor in the conclusions themselves and also the whole abstract needs to be rewritten in light of the changes to the manuscript with regard to the oxidation rates of Fe(II).

P 3804, Line 24. . . .in many different vital biological processes.

P3805, Line 3. This sentence needs to be reworded as it clumsily constructed at present. The readers, and authors, are no doubt aware of the work on coastal Californian studies which show clearly iron limitation in coastal waters (Bruland et al., 2001; Firme et al., 2003; Hutchins et al., 1998) so this needs to be recognised at this point in the introduction.

P3805, Line 5. The idea that over 99% of iron is organically complexed applies to situations where there is an excess of iron ligands – in coastal regions this may not be the case as has been observed in Swedish fjords (Croot and Johansson, 2000) and in the Mississippi river plume (Powell and Wilson-Finelli, 2003) where a large amount of colloidal iron may be present.

P3805, Line 19. This sentence needs to be reworded to clearly state the main oxidants are H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> and that temperature and pH have a strong effect on the rates of oxidation by those two reactive oxygen species.

P3805, Line 23. The photoreduction of inorganic iron depends on the concentration relative to the organic iron there are other papers that have invoked only the inorganic

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

reduction of colloidal iron (Johnson et al., 1994) for open ocean redox cycling. See also Croot et al. (2001) for a comparison of potential Fe(II) formation rates in seawater as their Table 1 summarizes these processes nicely.

P3805, line 23. No mention is made of the other possible sources of Fe(II) in seawater via reduction by cellular processes induced by uptake systems (Maldonado and Price, 2001; Shaked et al., 2002; Shaked et al., 2004) or non-photochemical cellular superoxide production (Garg et al., 2007b; Kustka et al., 2005; Rose et al., 2005).

P3806, Line 6. Riparian (from the Latin riparius, from ripa ‘bank’) refers to being on the banks beside a stream or river, so using the term for Baltic countries seems inappropriate as the Baltic, despite being relatively fresh, is not a river. The term should be replaced with something more appropriate.

P3806, Line 7. Replace more and more with increasing.

P3806, Line 15. What are the N and P terms here? Is it Total N and P or simply nitrate and phosphate? It is important to be clear what this is throughout the manuscript.

P3807, Line 2. The two cited references (Kuma et al., 1995; Kuma et al., 1992) are for photoreduction and not for the process stated in the sentence (Fe(II) release from anoxic sediments). The authors should replace the present citations with something more appropriate.

P3807, Line 13. (Incorrect word usage) Replace precluding with preceding.

P3808, Line 8. As mentioned above there are studies from the Mississippi delta (Powell and Wilson-Finelli, 2003).

P3808, Line 20. . . .period of time with limited exchange. . .

P3809, Line 13. How was the addition of oxygen avoided in the sampling for Fe(II)?

Syringes gas tight no bubbles. . . .take samples as for dissolved O<sub>2</sub> Filtration would seem to be difficult to do without introducing oxygen. Similarly when sampling in the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

rain (high H<sub>2</sub>O<sub>2</sub> and Fe(II)), was the sampling protected from contamination by rain-water? P3810, Line 3. . . .with the reagent luminol (5-amino. . . .

P3811, Line 2. Define GD here – it is defined on pg 3815 but it needs to be defined the first time it is used.

P3811, Line 24. The analyses would be hard to do on frozen samples and how do you re-thaw a sample? As this implies it was thawed before. So please reword the sentence to simply state that analysis was performed on thawed aliquots of samples that were at the time of collection.

P3813, Line 15. Measurements of seawater pH are complicated by liquid junction potentials, and the use of NBS/NIST buffers may not be appropriate here, the authors are referred to the works of Millero on this subject (Millero, 1986; Millero et al., 1993).

P3813, Line 24-25. The charges are missing from the measured nutrients (NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) and should be reinstated.

P3813, Line 18. . . .Lugol's iodine (I<sub>2</sub> and KI) ...

P3815, Line 11. . . .more distance. . .

P3815, Line 18. GD and LD should both be defined earlier in the manuscript – see above comments.

P3816, Line 19. Replace changing with variable.

P3816, Line 20. Replace altered with alternating.

P3817, Line 20-21. I note the author's correction regarding this section and also point out that  $t_{\frac{1}{2}}$  should always be in units of time and not reciprocal time as was in the original manuscript. How even with the author's correction I still have some problems with this section as the oxidation times appear to be too long given the data in the paper (e.g. 14°C water at pH 8.0 saturated with O<sub>2</sub> has a half-life of 6 minutes) . As suggested above in the general comments this whole section needs to be re-examined

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



more carefully. The switch between O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> as being the primary oxidant of Fe(II) as a function of temperature has been discussed previously (Croot and Laan, 2002).

P3818, Line 4. Sentence construction is clumsy and needs to be reworded.

P3818, Line 6. I assume the authors mean tens (10 m) and not tenths (0.1 m) of metres.

P3819, (Yao and Millero, 1995) (Von Gunten and Schneider, 1991)

P3819, Line 10. Is there any reason for the big differences in H<sub>2</sub>O<sub>2</sub> concentrations between GD and LD?

P3819, Line 13. The H<sub>2</sub>O<sub>2</sub> maxima at 100 m does seem completely anomalous, was it raining at the time of sampling?

P3820, Line 14. Any indications what causes the increase in total iron? Identifying the source of the iron increase would be a useful step to understanding the changes seen during this time.

P3820, Line 26. What are the error estimates in these measurements? As the values quoted seem amazingly precise for such measurements and it would be of interest if the differences seen are statistically significant.

P3821, Line 1. If L increases then Fe' has to decrease if the dissolved iron remains the same and K is constant so this is not so surprising and I would omit the term anti-correlates then and reword the sentence accordingly.

P3821, Line 1. The term “excess ligand concentrations” I find confusing as it is not defined in the text and appears to be simply the total ligand concentration minus the dissolved Fe concentration (FeL). For an iron saturated system such as this appears to be, the dissolved iron level is controlled by the total ligand concentration and thus the excess ligand number is meaningless once error estimates are applied. I would suggest that this term not be used in the present manuscript.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)



P3821, Line 12. The difference between the DGT and FIA measurements for Fe(II) are interesting and raise a number of questions regarding the sampling techniques (see general comment above).

P3822, Line 3. What is meant here by the term up-concentration factor? The sentence seems to be lacking a subject and so needs to be reworded.

P3822, Line 4. Not exactly sure what is being stated here, is it that for the controls and the enrichments experiments the H<sub>2</sub>O<sub>2</sub> concentrations did not significantly change with time? As that is not what is observed in Fig 11 in which it appears that those fractions all increase with time as one might expect for the sunlit part of the day. The H<sub>2</sub>O<sub>2</sub> levels in all the treatments is very high at the last time point and considerably much higher than what was observed in the field data which brings into question the effectiveness of the neutral density screening used. Bottle factors can enhance the observed rates considerably (Leifer, 1988) but in the present case it would be useful to have some discussion on the disparity between the field and incubation data.

P3822, Line 9. I would be wary of any Fe(II) measurements when the H<sub>2</sub>O<sub>2</sub> concentration is over 1  $\mu$ M as the half-life could be significantly less than the analysis time and the data thus extremely variable. I note that no errors are reported here or in the supporting figure, is such data available?

P3823, Line 19. These method actually detect the O<sub>2</sub>- that is produced by the oxidation of Fe(II) at the reaction pH (10.15) and thus any chemical reactions that either oxidize or complex Fe(II) or react with O<sub>2</sub>- could potentially alter the observed signal. The authors suggestion of Fe(II) only being detected by their method is problematic given that most speciation estimates for Fe(II) in anoxic environments suggest that Fe(II) in solution is present mostly as the free aquo ion (Landing and Westerlund, 1988) unless the sulfide concentration is greater than 10  $\mu$ M. So it is clear that the authors need to do the equilibrium calculations to validate their assumptions regarding the detection of iron species for their analytical system.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

P3823, Line 19. What evidence is there that the FIA method does not measure Fe sulfides? I could find no reference to this in any of the citations mentioned here. I would suggest however a simple explanation based on the FIA system used in this study. The method as described in Croot and Laan (2002) uses sample injection, by where a loop of sample is injected into the reagent stream which is always flowing to the detector. When the sample has no O<sub>2</sub> in it all the O<sub>2</sub>- generated from the oxidation of Fe(II) has to come from the reagent stream but the O<sub>2</sub> there will also be consumed by reaction with the S-2 resulting in a reduced apparent Fe(II) signal compared to samples which contain some O<sub>2</sub>. In this case then samples should be calibrated using standard additions in order to correctly determine the Fe(II) concentration.

P3823, Line 27. No evidence is presented here to show that this method can not measure in anoxic waters and the rationale for the low Fe(II) measurements found in this work suggested above may be plausible. Which suggests that the problems found in the current work may simply be in the calibration methods, or in the handling and storage of the samples before analysis. So I do not think at present this statement that this FIA method does not work in anoxic environments is valid and should be amended.

P3824, Line 9. How realistic is advective transport of Fe(II) from sediments? At this depth how far away are the nearest sediments and are they anoxic? While anoxic sediments could be a source of both phosphate and Fe(II) (Golterman, 2001; Lohan and Bruland, 2008; Morse and Luther III, 1999) more information is needed to support this potential pathway.

P3824, Line 19. The authors should also be aware of other work on phytoplankton production of superoxide (Garg et al., 2007a; Kim et al., 2000; Kim et al., 2004; Marshall et al., 2005a; Marshall et al., 2005b; Tanaka et al., 1994), including cyanobacteria (Rose et al., 2005). However some of the works I have cited here must be examined carefully as they involved ultra-sonicating samples (Beckett and Hua, 2001; Hua and Hoffmann, 1997; Kanthale et al., 2008) which produces superoxide and was apparently erroneously attributed to the phytoplankton.

P3824, Line 16. More recent direct evidence including a diel cycle was found during the EIFeX experiment in the Southern Ocean (Croot et al., 2008).

P3824, Line 20. The genome for *Nodularia spumigena* CCY9414 (<https://research.venterinstitute.org/moore/SingleOrganism.do?speciesTag=N9414>) has apparently been sequenced, so I suggest the authors examine this genome to see if such uptake mechanisms are present.

P3825, Line 2. Replace anti-correlates with inversely related.

P3825, Line 6. I think the term closely resembles is a misnomer here as while the numbers are similar this could be said for other log K's determined for a wide range of iron organic complexes, so this does not constitute strong proof that these are river derived fulvics.

P3826, Line 6. It should be stated clearly here if the authors are suggesting that these are marine, or river, derived humic and fulvic acids. If they are of Riverine origin then some attempt needs to be made to show how they can be present in surface Baltic waters at these concentrations.

P3826, Line 9. Do they need to be siderophores? It seems that the mucus produced by cyanobacterial colonies could also be iron complexing to some extent and in the absence of strong evidence of iron limitation (Geiss et al., 2001) it seems speculative to suggest it is siderophores.

P3826, Line 26. This citation seems out of place as the sentence refers to photoreduction of iron-ligand complexes and the cited paper is on inorganic colloids. It seems more appropriate to replace this citation with a more relevant one (e.g. from the recent work of Barbeau or Rijkenberg).

P3827, Line 2. In blooms such as these a major sink for the Fe will be on the surfaces of the algae themselves and this may explain the increase in total iron and the decrease in dissolved iron.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive  
Comment

P3827, Line 15. A more appropriate citation here that deals directly with this issue is the work of Rijkenberg (2006). The cited Abele-Oeschger (1997) paper is for a tidal flat and does not concern the photoreduction of Fe complexes.

P3827, Line 15. This section needs to be re-evaluated given the authors problems with calculating the oxidation rates of Fe(II) by H<sub>2</sub>O<sub>2</sub> and their underestimation of the role it plays in oxidizing Fe(II).

P3827, Line 21. Before looking for another mechanism to produce H<sub>2</sub>O<sub>2</sub> the authors should examine more critically the role of mixing as this is the normal process by which H<sub>2</sub>O<sub>2</sub> is supplied to waters below the euphotic zone.

P3827, Line 23. Again the Abele-Oeschger (1997) paper is for a tidal flat and is not related to sub euphotic zone H<sub>2</sub>O<sub>2</sub> production, other references for this process are easily suggested (Croot et al., 2004b; Obernosterer et al., 2001; Palenik and Morel, 1988; Yuan and Shiller, 2001; Yuan and Shiller, 2005; Yuan and Shiller, 2004).

P3827, Line 27. The Fan (2008) paper is a modelling paper and thus while it cites experimental work with these processes in it, it is in itself not an example of this. Omit or replace this citation with a more appropriate one.

P3828, Line 6. All aquatic organisms, particularly phototrophs, must be able to eliminate H<sub>2</sub>O<sub>2</sub> from their systems via catalase or peroxidase activity. The authors are reminded that the data in figure 11 is the result of both production and consumption terms and that the high production seen in the absence of plankton indicates that consumption rates must be very high. Additionally any organisms that inhabits near surface environments must be capable of dealing with high concentrations of H<sub>2</sub>O<sub>2</sub> due to the combination of its rapid photochemical production and high cellular permeability (similar to H<sub>2</sub>O). So I strongly disagree with the statement that these organisms do not specifically consume H<sub>2</sub>O<sub>2</sub> and urge the authors to rethink this section.

P3828, Line 16. The Rijkenberg et al. (2008) diatom culture study shows only weak

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

evidence for increasing Fe(II) in the system as if you look carefully enough it is clear that the experimental treatments are below the Fe(II) levels of their abiotic experiment (control) and thus one could make the conclusion that there was no enhancement of the Fe(II) pool relative to the abiotic control (Compare their figure 5 to figure 3 and 4). Instead Rijkenberg et al. focused on the temporal changes seen in the samples with diatoms, the critical point is however, and it applies to the current paper also, is did the cycling of Fe(II) increase? If the measured Fe(II) is low but the production and oxidation rates fast then the bioavailability of the iron may be enhanced relative to a high Fe(II) concentration that is strongly complexed and oxidizes slowly or not at all. Another facet to this is that any Fe(II) produced is more likely to be oxidized by O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> than be complexed by a low concentration ligand (Croot et al., 2007).

P3828, Line 20. As stated early this O<sub>2</sub> concentration seem anomalously high even for productive Baltic waters and the value should be rechecked.

P3828, Line 22. Given the correction regarding the miscalculation of H<sub>2</sub>O<sub>2</sub> rates this section needs to be rewritten.

P3829, Line 2. I find the term rain deposition a little jarring as what else does rain do but fall? It certainly deposits metals and other substances and this could be termed wet deposition. Simply rainfall would suffice here I think.

P3829, Line 3. Replace imply with infer.

P3829, Line 11. Half-lives are in s or min not s<sup>-1</sup> or min<sup>-1</sup>. Also these numbers do not agree with each other are they for O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> oxidation?

P3829, Line 14. The section referred to here (4.2) precedes this section (4.3.3) so the past tense would be more appropriate here assuming the manuscript is intended to be read in a linear fashion.

P3830, Line 22. The authors need to check their assumptions here regarding the iron speciation in sulfidic waters as it appears that Fe(II) is the predominant dissolved

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species under these conditions (see above).

P3831, Line 14. Significant contribution it seems more likely it is an oversupplied and thus not a limiting nutrient for these species given the reported demand and supply terms.

P3831, Line 17. initiates

P3832, Line 5. What about simple vertical diffusion? The iron gradient is certainly in the right direction to supply iron to surface waters, some calculations on this would be helpful before the conclusions section in order to support the statements here.

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6, C309–C329, 2009

Interactive  
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Full Screen / Esc

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Interactive Discussion

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6, C309–C329, 2009

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Full Screen / Esc

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Interactive Discussion

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C329

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