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Interactive comment on "Isotopic evidence for biogenic molecular hydrogen production in the Atlantic Ocean" *by* S. Walter et al.

S. Walter et al.

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Dear referee, thanks for your comments. Please find our reply in-line. Kind regards, S. Walter

Major Comments: Page 16440-42, Section 2.4.3, diss. H2 measurements: Since the extraction method is new and presented for the first time, I would like to see a discussion about the overall measurement errors of both the diss H2 conc. and its isotope signature in seawater. Reply: The following discussion has been included in the manuscript: A new method has been presented to extract H2 from surface waters for isotopic determination. Before discussing the measurement results, we will give an overview of the possible main errors and their effects. To show the effect of the errors

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on the measurements, we will present error factors, thus how much the final data differ by shifting the respective parameter by 1 % and also the absolute assumed error. For the extraction method several error sources could be identified: the determination of pressure, especially in the sampling vessel before adding the make–up gas and during extraction, the temperature of air and water, respectively the difference between them when the sample is extracted from the headspace, and the volume of the set–up and the sample. The determination of pressure in the sampling vessel would be one issue of further improvement, because the error caused by pressure deviations for the total pressure after adding the make–up gas is about a factor of 0.7 for concentrations and 0.2 for the isotopic values. The error based on temperature of air, water and sample is negligible due to high–precision measurements and the short handling time between water sampling and headspace extraction. The error for the volume parameter for the set–up is negligible due to the high volume, the precise determination of the glass vessel volume by weighing, and the calculation of the tubing volume. The main error source is the water volume of the sample, which counts by a factor of 5.9 for the concentration, but with negligible effect on the isotopic values. Although the relative error factor is quite high the absolute value is assumed to be around 0.5% due to the sample size, which has also been weighed at the home lab. The H2 measurement procedure is the same as for atmospheric samples and possible errors are described in the respective sessions or related literature. However, the error caused by the determination of the dry mole fraction itself seems to have the main input by a factor of 5.3 for concentration and 4.6 for the isotopic values of dissolved H2. Errors of the determination of the isotopic value are much less significant and count by a factor of 0.2. Taking measurement and handling errors during the extraction as well as errors in the determination of the dry mole fraction into account, we assume a robust standard deviation of $\pm$6.9 % for the dissolved H2 mole fractions and $\pm$4.7 % for the isotopic values by calculating the root of the sum of the squared uncertainties. As shown in Table 4 we also tested the effect of equilibrium isotopic fractionation and kinetic isotopic fractionation. The effect is less than 0.2%. Therefore, recommendations for the extraction

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method are to additionally measure parameters such as the initial pressure in the glass vessel and to ensure a precise determination of the sample volume. Besides this we recommend high–precision IRMS measurements and to consider multiple sampling for better statistics on the data. Absolute error assumptions: Δ T air–sea: 0.3% Pressure sensor: 0.5% Temperature air: 0.01°C Temperature water: 0.01°C V vessel: 0.5% V tubing: 10% IRMS measurements: 1%

p.16441, Eq.(6): H2 solubility in seawater is also depending on the salinity, thus, I am wondering why the 'salt effect' is not considered in Eq.6. Reply: The actual salinity has been taken into account in the concentration calculations.

p.16441, l. 16; Eq.(7); p.16449, l.6: The extraction efficiency is given as 92%. Is this a mean value? The extraction efficiency according to Eq.(7) is depending on the Ostwald solubility coefficient which, in turn, depends on the temperature. Was the temperature always the same? Please give details. Reply: the mean value is 92.12 ($\pm$0.013)%. Due to the very low variation we mentioned just one value without decimal places. We included this to the manuscript for completeness.

p.16441, l.16: Please cite a reference for the Ostwald coefficient. Reply: we included a reference for the Ostwald coefficient.

p.16448, l.13-15: '. . . possibilities for improvements ...' are mentioned. However, what does that mean for the analytical error of the presented data? Or in other words are they just by chance in agreement with the literature data? Reply: The possible improvements include a better monitoring of additional data such as temperature and pressure in the vessel itself, this was not possible yet. As already mentioned in chapter 2.3, the temperature dependence of the H2 solubility is quite low with less than 0.3% per K, and also the used pressure sensors (Omega, PAAR21R) work within a low error range of 0.5% or even below. In combination with the high extraction efficiency and the standardized sampling procedure over the two cruises, we are convinced that the presented data sets are comparable and not just by chance in agreement with the

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literature data. Please see the discussion about possible error sources above.

Table 4: I was surprised to see a positive (i.e. excess) H2 concentration differences resulting in undersaturations of 0.35 and 0.94. That does not seem to be logical at all: How can a concentration excess of H2 result in a H2 undersaturation? Please explain. Reply: We gave the supersaturation factor, but changed this to saturation in % as also suggested by referee #2 to avoid misunderstandings.

Discussion of oceanic sources of H2 (see Section 3.3.1; Table4; Figure7): It is obvious that the majority of H2 data pool associated with the low temperatures has been measured in the coastal upwelling system off Mauritania. Upwelled waters off Mauritania, however, are originating from water depths down to 150-200m (i.e. upper oxygen minimum zone, OMZ). Thus, it is not that surprising to see a different H2 signature because in OMZ waters there might different sources/sinks at work: E.g., the interplay between H2 production (i.e. by N2 fixation at depth) and associated H2 oxidizing bacteria (which live at oxic/anoxic interfaces in particles and sediments). Reply: We showed in Walter et al. 2012, that bacteria and algae species with quite different H2 pathways (C. saccharolyticus, A. brasiliensis, E. coli, C. acetobutylicum and C. reinhardtii) produce H2 with similar, highly depleted isotopic signatures of around –700 ‰.The tested species included a N2-fixer as well as fermentative bacteria and also a limnic green algea. As mentioned (Chen et al. 2015) an isotopic enrichment causing a shift of almost 400‰ just by removal of H2 is unlikely due to unrealistic large fractions needed to be removed. Although OMZ waters and borders are known as microbial very active areas and we therefor cannot exclude such high turn–over rates completely, we assume another source responsible for the differing isotopic signature. As suggested in Walter et al. 2013, photochemical degradation of VOCs could play a role. The up–welling areas are quite productive and could indirectly emit pre-cursors of H2. Unfortunately, up to now there are no data available about the isotopic signature of photochemically produced H2 in surface waters. The value given for atmospheric photochemically produced H2 is around +100 to +200‰ and would fit to this hypothesis.

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Moerover, I am not really convinced by the argument against a H2 sink (see p.16451, lines 1-5) since the observed undersaturations point towards a net H2 sink (sink > source) they can, therefore, not result from a single source (see p.16451, l.17-20). Reply: We changed from reporting the supersaturation factor to the saturation to avoid misunderstandings.

Technical Comments: Mauretania should read Mauritania, please check spelling throughout the manuscript. Reply: spelling has been checked and corrected

Table 4: Xh and Da are mentioned in the table caption, but do not appear in the header of the table: I guess that Xm and Dm should read Xh and Da (or the other way round). Reply: this has been corrected

p.16439/40; Figures 4 and 5: Please remove the CO data when they are not essential for the discussion of the H2 data Reply: The CO data are indeed not essential for this publication, but CO data are used to model H2 emissions caused by N2 fixation. We therefore prefer to keep them in as general information, although we do not discuss them in detail.

Suppl. Material: There are citations in the text of the Supplement, but there is no list of references. Please add list with full references. Reply: we added the reference list.

Interactive comment on Biogeosciences Discuss., 12, 16431, 2015.