

## ***Interactive comment on “The stable isotopic signature of biologically produced molecular hydrogen (H<sub>2</sub>)” by S. Walter et al.***

**Anonymous Referee #2**

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Measurement of atmospheric DH in H<sub>2</sub> is challenging, especially when the abundance of DH is so small. The authors here present some new measurements indicating the extreme isotopic depletion from H<sub>2</sub> derived from certain biological sources. While reasonable, and probably correct, I am concerned about the accuracy of the measurements. In particular, I find it difficult to imagine one can use a gas tight syringe for transporting and injecting molecular hydrogen. In the old days, there was concern of H<sub>2</sub> diffusing through glass in mass spectrometric systems (e.g., Craig). In fact, it was a result of these technical problems that people largely stopped studying H<sub>2</sub> after the 1960's. There was a flurry of papers in the old JGR volumes, and then nothing. Of course, there have been huge advances in isotopic analysis of trace gases, but I still find H<sub>2</sub> to be a tricky one to handle. Without proven, reliable, reproducible results from calibration gas mixtures, I am not sure how much of a difference there is between

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dD=-600 and dD=-700 per mil.

My first thought regarding the measurements is that it is largely consistent with theoretical studies; the differences are, relative to uncertainties in the calibration of H<sub>2</sub> (at least as presented here), small.

One of the goals of using a calibration gas is to be able to intercompare with other laboratories. Unfortunately, this is not possible, for such depleted DH values, with the 'calibration' used here.

It would be nice if the authors provided more detail to show that the calibration of H<sub>2</sub> is robust. It is a difficult thing to do. Another option is to perhaps revisit the level of uncertainty associated with the reference gas and include that in the overall reported error.

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Interactive comment on Biogeosciences Discuss., 8, 12521, 2011.