Biogeosciences Discuss.,
doi:10.5194/bg-2016-106-RC1, 2016

Biogeosciences Discussions

Interactive comment on "Clumped isotopes in near surface atmospheric CO_2 over land, coast and ocean in Taiwan and its vicinity" *by* Amzad H. Laskar and Mao-Chang Liang

Anonymous Referee #3

Received and published: 4 May 2016

This manuscript reports new measurements of clumped isotope compositions of atmospheric CO2 collected from different environments and settings. Studies of clumped isotope composition of atmospheric CO2 were among the first applications of clumped isotope methods, but have received less attention in recent years compared to other applications. It's great to see another focused study on this subject. The dataset presented in this study is quite extensive, and mostly confirms the major findings from previous studies. However, the conclusion the authors draw regarding the effect of photosynthesis on the clumped isotope composition of CO2 differs significantly from previous studies, and could potentially open many research opportunities. Overall, this manuscript improves our understanding of the various controls on the clumped isotope

composition of atmospheric CO2, and can help future efforts to better constrain the atmospheric CO2 budgets. I have several specific comments about this manuscript, as detailed below, and would recommend these issues be addressed prior to publication.

Major comments:

1. Separation of N2O from CO2. A GC column was used to separate N2O from CO2 in this study. The authors showed a reasonable separation of the two in Fig. S2, but didn't mention the exact CO2 trapping time in their experiments. It's possible the CO2 yield was compromised in order to achieve the optimal separation of N2O. The authors need to provide more details and discuss how the compromised yield and/or residual N2O might affect their clumped isotope data.

2. Photosynthesis effect. In their greenhouse experiments, the authors observed that the clumped isotope compositions of CO2 were higher than what expected from thermodynamic equilibrium when photosynthesis was active. This finding is very intriguing and differs from what observed in previous studies (e.g. Eiler and Schauble 2004), where the clumped isotope compositions of CO2 residual to photosynthesis were shown to generally decrease.

a. Given the importance of this finding, I think the authors need to provide D48 and D49 data of their measurements to show that the elevated D47 values were not related to any contamination issues. More generally, the authors are encouraged to include all their raw clumped isotope measurement data in the electronic supplementary material of their manuscript, which is becoming a convention in the clumped isotope community.

b. The authors need to expand their discussion about the clumped isotope effects associated with photosynthesis they observed, especially in relation to the findings in Eiler and Schauble (2004), and explore ways to reconcile the findings from the two studies.

c. The authors did a nice job estimating the carbon and oxygen isotope fractionations

associated with photosynthesis in their greenhouse experiments. But their discussion about the clumped isotope effect is mostly qualitative. The authors might want to construct a simple (semi-)quantitative model to simulate the evolution of the concentration and isotopic composition of CO2 in their greenhouse experiments. Such a model might enable them to quantitatively estimate the clumped isotope effects associated with photosynthesis, which would be an important contribution of this study.

Minor comments:

1. Line 440: the authors neglected the daytime respiration when estimating the isotope effects associated with photosynthesis. They need to provide evidence to support this approach.

2. In section 4.1, the authors estimated the rates of respiration, photosynthesis, and CO2-water exchange in their greenhouse experiments, in the unit of molecules cm-2 s-1. But it's not entirely clear how those values were derived. More details are needed.

Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-106, 2016.