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## ***Interactive comment on “Peat decomposition records in three pristine ombrotrophic bogs in southern Patagonia” by T. Broder et al.***

### **Anonymous Referee #2**

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This paper is an interesting contribution to an apparently rich body of literature on chemical and physical properties in Patagonian and/or ombrotrophic bogs. Using so many complementary tools to study the chemistry and degree of decomposition of the peat is a neat approach that does not seem well explored in the literature and is of great global importance as peat stores a great deal of carbon which is sensitive to decomposition. Although I do think that all of this great information should be published, I don't really think that this paper is quite ready for the reasons numbered below. It is my suggestion that this paper just describe the degree of decomposition rather than trying to attribute decomposition to paleoclimatic events or other physical and chemical properties (such as ash content, sea spray input, non-quantitative observations of soil moisture), unless a more rigorous approach is taken (see point 4 below). It feels too far reaching right now. My other major sticking point is that humification is never defined

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and when I read humification, I have to assume that someone means an increase in aromaticity. But, some evidence in your manuscript indicates that this is not what you mean. For example, your relationships between decreasing C/N and increasing humification index (see point 1). There are also a few methodological things I am worried up that I would like explained before this moves through (see points 3, 5, and 6). It's also just a very data rich study which is great, but it's hard to read because the message is getting lost (see point 2 for specifics). Given that the methodological questions that I have in points 3,5, and 6 can be cleared up and assuming that either a more rigorous approach is taken to explain the controls on decomposition or the authors choose to simply put forth observations about soil chemistry, then this paper should be able to move into publication.

1. I think that the way that you have presented your FTIR data is really quite accessible. Using these ratios of various functional groups to polysaccharides has given you a neat way to interpret the data. On page 10549 around line 25 you list all of the functional groups that you are looking at, but none of these are cited. I am not as familiar with peat literature, but I am sure those citations are out there. There has been extensive work done on the application of FTIR to soils, and the confirmation of each of these regions in soils, so these should be cited. Also, when you introduce your ratios, it might be nice to include a table re-describing what each of those ratios is; for example, 1630/1090 is aromatic C=C or C=O of amides/polysaccharides. From a quick literature search, I see that there is a rich history of using the term “humification index” to describe the fraction of non-humic material to total humic and fulvic acids extracted using NaOH (Gigliotti et al. 1999) or to quantify molecular complexity and condensation (Kalbitz et al. 2003). My concern with use of the term humification in this manuscript is that there has been a shift from the traditional view that the oldest compounds in the soil are highly aromatic as a result of the condensation of quinones (Kononova 1961) to the concept that the oldest compounds in soils are chemically labile molecules (carbohydrates, long chain fatty acids, amino acids) that they are protected from degradation by the mineral matrix (see literature by Plante, AF; Paul, EA; Miltner; von Lustov; Kogel-Knaber). I guess I

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would just like to see a definition of humification in your text to better understand how you are interpreting humification and decomposition.

2. I feel that the “take-home message” of the paper is a bit jumbled and mostly it is because you have a vast amount of data to discuss. Mostly, I have gotten confused about whether the discussions of ash and isotopes are included as paleoclimatic indicators of decomposition or whether you are trying to attribute some chemical characteristic to decomposition. At first, it seems that you measured the C and N isotopes to assess a degree of decomposition. To introduce this concept, more discussion about how microbial processes fractionate C and N would aid in the interpretation. But then when you discuss the results, it seems that there was no clear trend with decomposition and the isotopes. So, then you use them as indicators of age. It’s just not clear what angle you are taking. Perhaps if they aren’t important indicators of decomposition, you could just say that and then discuss them as indicators of age. Your message here is just not clear. The same tends to be true for the ash- sometimes you use it to date the profile and sometimes you are discussing the impact of the ash itself on decomposition. These should be separated. Perhaps all of the paleoclimate information should go together.

3. On page 10555, lines 5-8, you seem to be trying to attribute the low HI to sea spray input. But, there is also a vegetation difference between your sites. How can you know that it’s not just the vegetation that has affected the 1630/1090 input (and residual in the peat)? I see that the site you are referring to is Sphagnum dominated and that Sphagnum has the highest C/N of any of your plant samples. Perhaps vegetation is more of a control on HI/ decomposability than sea spray input. But, you haven’t tested for this.

4. Continuing with my concern of your attempts to attribute decomposition to environmental factors (sea spray input, precipitation, vegetation; see 10560 lines 24+ and 10556 lines 7-8), it doesn’t seem that these assumptions are validated very rigorously. Perhaps you could use some statistical tool (i.e. multiple linear regression) to deter-

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mine what factors of the many that you measure control decomposition at each site. If this is beyond the scope of your intentions with this paper, then you should omit sweeping statements about controls on decomposition and just describe the chemical characteristics with depth. This is still novel and interesting.

5. How long was the extracted and filtered pore water stored before analysis? At what temperature was it stored?

6. You admit that the mineral interference makes interpretation of your FTIR spectra near the ash impossible. But, how do you know that you did not have a large interference from ash in the non-ash layers. For example, you did not observe an ash layer in Sky I. How do you know it just not all mixed together? Did you ash your samples to see if it was all organic material?

7. Comments on tables and figures: a. In table 3, is there a standard error that should be reported for these vegetation samples? b. In table 4, you might consider including an average peat accumulation that can be referred to with text on page 10559. c. Figure 3- you never stated anywhere that you weren't investigating between 2000 and 4000 cm<sup>-1</sup>. d. Figure 4, the delta 13C trends between the DOM and solid are different between the Sky samples and the PBr2. Do you know why? Also, the Skyll peat is enriched in 15N at the surface while the other two samples are not. Do you know why? You don't discuss this in the paper.

## References

Gigliotti, G., D. Businelli, and P. L. Giusquiani. 1999. Composition changes of soil humus after massive application of urban waste compost: a comparison between FT-IR spectroscopy and humification parameters. *Nutrient Cycling in Agroecosystems* 55:23-28. Kalbitz, K., J. Schmerwitz, D. Schwesig, and E. Matzner. 2003. Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* 113:273-291. Kononova, M. M. 1961. *Soil organic matter, its nature, its role in soil formation and in soil fertility*. Pergamon Press, Oxford.

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