Reviewer 2

The manuscript by Saiz et al. describes a series of experimental burns in Australia in which they measured the isotopic composition of pyrogenic carbon emitted and de- posited after the fire. The authors show that relative to the isotopic composition of the carbon in the original fuels, the composition of pyrogenic carbon is more depleted, which is consistent with products from trees and shrubs ending up preferentially in this recalcitrant carbon pool. It is also more consistent with C4 grass biomass combusting more efficiently. Pyrogenic carbon emissions from fires (including savanna fires) are highly uncertain and poorly constrained by measurements. Hence, this study presents and exciting opportunity to look directly at the production and isotopic composition of pyrogenic carbon from savanna fires. Measuring fire-derived PyC is particularly challenging and this study presents an innovative approach, which is an important contribution to our capabilities of directly measuring PyC from savanna fires. While the study address issues that are of great importance for the field, hence contributing to our knowledge and understanding of PyC production and composition during savanna fires, there are a couple of aspects of the methods and results that are not very clearly explained in the current version of the manuscript. Overall the introduction is comprehensive, well balanced and provides a clear motivation for the study in terms of implications for the carbon cycle, interpretation of the origin of soil carbon pools using isotopes, and aerosols. The methods look to be state-of-the-art and are described in a robust way. The methods and results are logically presented, although as described below, some additional information would be helpful to the reader. In the discussion, the size of the impact of the isotopic disequilibrium presented by the authors here is likely to be an upper bound because some of the depleted pyrogenic carbon would be expected to decompose in subsequent years, lowering the instantaneous effect measured immediately after fire. Over all the paper presents new observations collected in a careful and quantitative manner that are relevant for fields of paleoecology and studies of atmospheric composition. In this context, the paper is likely to be relevant and of interest to readers of Biogeosciences. In the opinion of this reviewer, the paper may be suited for publication after consideration of the comments below.

...Specific comments

Our comments are in bold

The authors may wish to provide more motivation for isolating a HyPyC component of the pyrogenic carbon and description of their approach for measuring HyPyC. While the difference between the HyPyC and PyC pools is based on the chemical definition, the implications and meaning of this distinction are not very clear.
We have used the last paragraph of the introduction to further stress the importance of not just focusing on total PyC but in its most recalcitrant component as well (HyPyC).

In the results section 3.1. (Production of PyC during savanna burning) – PyC is only mentioned once, whereas the rest of the text is focused on HyPyC.

This section is now expanded a bit more and makes use of the concept of combustion completeness as suggested by the reviewer later on. Now the contribution of PyC is also better balanced in the first section of the discussion (4.1), as we have discussed our results in light of previous studies.

When the SIDE effects are discussed though, the authors note that the significance of SIDE during burning is more pronounced when considering the PyC produced by the fires than when considering the HyPyC component alone. What mechanisms contributing to this difference?

Indeed, the significance of SIDE is more pronounced when the PyC pool is considered as a whole. In section 3.2 we include the statistics for both the proximal and distal fluxes. For the distal fraction the difference between SIDE of PyC vs HyPyC is not significant ($p=0.25$), while it is significant for the proximal fraction ($p<0.01$). In the discussion section (4.3) we argue that the observed patterns highlight the importance of SIDE for the more labile or semi-labile components of the PyC flux, into which C4-derived PyC may be preferentially partitioned. Whereas the significance of SIDE is less pronounced in the more stable pool of PyC flux, into which C3-derived PyC may be preferentially partitioned. This is thus, the mechanism that may account for the PyC-HyPyC differences.

Another aspect discussed in the paper is the partitioning of PyC and HyPyC into distal and proximal fluxes, based on particles size separation of greater (distal flux) and smaller (proximal flux) than 125 micrometers. More information on why 125-micrometer threshold is used as the separation point between the two size fractions is needed.

Section 2.2.2 in M&M, contains a statement justifying our choice, further supported with two references. The text reads: 'This mesh size was chosen to conform to standard dimensions used to differentiate between micro- and macro-charcoal in palynological studies, e.g. Blackford (2000); Haberle (2005)'.

Blackford, J.: Charcoal fragments in surface samples following a fire and the implications for interpretation of subfossil charcoal data, Palaeogeography, palaeoclimatology, palaeoecology, 164, 33-42, 2000.

Haberle, S.: A 23,000-yr pollen record from Lake Euramoo, Wet Tropics of NE Queensland, Australia, Quaternary Research, 64, 343-356, 2005.

The authors conclude the manuscripts by discussing the implications of this study for the 13C composition and interpretation of soil organic carbon (SOC). However, the concept and importance of SOC and its isotopic composition are barely mentioned in the rest of the paper – one sentence in the abstract and one in the introduction. The SOC topic needs further emphasis, and it is more suitable to move this section to the discussion rather than the conclusions.

We agree that some reorganization of the paper, as well as some emphasis on these points, makes this a stronger contribution. We moved the discussion of implications for SOC to a section in the discussion. We then

made the conclusions section a simple summary of the main points of the paper.

Figure 1 is complicated and includes 5 panels and a table. It would be easier for the reader if the lat/lon information and site information were contained in a separate stand-alone table. This would also give the authors an opportunity to write out the full site names for all the sites, some of which are not provided in the text. It would also allow the reader to more easily see the pictures of the individual sites, which are now relatively small. It would also be helpful if the map of the study area is bigger with more clearly defined vegetation cover (maybe overlay vegetation cover layer on top of the image of Northern Australia).
We have split former Figure 1 into two new figures (Fig. 1 and Fig. 2) and a new table (Table 1) according to his/her suggestions. We did attempt to overlay a reputable land cover map on new Figure 1, but as a result of the non-unified nomenclature used in vegetation classification in different tropical/subptropical systems (i.e Australia, Africa and South America), we felt that rather than helping the reader to extract more information, it was actually making things more difficult. In any case, a combination of Figure 1, 2 and Table 1, should provide sufficient information for a good comprehension of our work.

In the calculations and modeling, why assume mean isotope values from the literature for C4 grass biomass? Why not use C4 grass values measured from the individual field sites?
We used two methods to estimate the isotopic composition of total biomass, one based on assumptions from the literature, and the other based on measured values (see text). The two approaches generally agree (see response to reviewer 1 comments). We have added some text to address as similar comment in response to reviewer 1.

How robust is the SIDE effect computed in Figure 5d as a function of grass biomass with respect to these assumed values?
Because there is good agreement between the two methods of estimating d^{13}C of biomass, we feel the analysis in the newly named Figure 6d is robust, and includes an analysis of errors associated with these estimates.

In the fire carbon cycle literature, combustion completeness (the amount of fuels consumed relative to their starting abundance) is used as a measure to analyze emission factors and other processes. The authors may wish to add a sentence or two about these results to the first paragraph of the results, and perhaps add a column for it to Table 1.
We have added the concept of combustion completeness in the first paragraph of the results, and have provided the median [range] for all fires. In our study, this measure is reciprocal to that of production of PyC relative to TCE, which is already shown in newly named Table 2.

The hypothesis that biomass from C3 vegetation is preferentially integrated into the pyrogenic fraction, contributing the observed disequilibria is an interesting

one. Is it contradicted by the individual site results from MIT grassland sites that also show a strong disequilibrium effect, yet from the site pictures, no trees or shrubs appear to be influencing the composition for the grassland sites at this location?

MIT sites were mainly composed of an axylale stratum (grass and herbs) as the newly named Table 2 shows (99.8-97.5 % grass biomass). However, it was still possible to observe some shrubs/small trees in isolated spots at the landscape level. We also noticed the occurrence of sparse *Acacia sp.* seedlings underneath the grass stratum that would likely be combusted in subsequent fires.

For the mass balance d13C estimate, please clarify it is really the isotopic composition of CO2 and other trace gases (CO, CH4, etc) which may add up to 3-5% or more of the total combusted loss.

We have added this clarification in the methods section.

Page 15166. The estimate of the global disequilibrium from pyrogenic fractionation (0.75 Pg C per mil) is really an upper bound, in the opinion of this reviewer, because it does not take into decomposition of some or most of the depleted PYC material in the months and years after fire. This has to be a lot, because the pre-fire HyPyC is less than half the post-fire HyPyC on average from Table 1, the FRT is ~ 2 years, and it's difficult to imagine erosion is a dominant pathway at these relatively flat and dry sites.

We have added this clarification in the text.

Minor comments:
Page 15158: Line 15 –Define TOC – acronym is used for the first time.
The acronym is now defined.

Page 151159: Line 3-4 – The authors mentioned they weighted samples pre- and post-drying to determine fuel moisture. It would be interesting to know the results, whether or not the moisture was high/low/variable, and if it could have any possible effects on the PyC production.

Regrettably, we were only able to retrieve fresh biomass weights for about half of the experimental burns. Therefore, we could not assess the potential effect of fuel moisture on PyC production in a robust manner. The experiments for which we could accurately calculate fuel moisture contents showed that they were all consistently low (<12% on a dry basis) showing very small variability among them. This result is hardly surprising as fires were purposely chosen to occur on days with no prior recorded rainfall for at least two weeks and at times coincident with maximum daily temperatures. Besides, fires took place late in the dry season, which in these ecosystems is characterized by the presence of senesced vegetation.

There is a typo or mis-formed sentence on page 15159 between lines 20 and 25 "evaporator remove the liquid"

We have corrected this. The text now reads: 'the soot retrieved after cleaning the structure with the water/methanol solution was placed in a rotary evaporator to remove the liquid phase'.

Page 15160 : Line7 – Write out Mo – molybdenum is used for the first time. Section 4.3.
The entire molybdenum word is now used.

Page 15165 Line 18-19: "Values consistent with relative 13C depletion of PyC in savanna fires" – citations?
The work by Krull et al. (2003) is now cited.

General comment - please consider including SIDE values in Table 2
We considered this, but these are relatively simple subtraction calculations. To minimize complexity of the table, we leave these calculations to the reader.