

Interactive comment on “Oxygen isotopic signature of CO₂ from combustion processes” by M. Schumacher et al.

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General comments: Schumacher et al. present a thorough laboratory study of oxygen isotope fractionation during combustion processes, focussing on the product CO₂. They found that the fuel isotope composition has virtual no influence, but also that the product CO₂ does not simply acquire the isotopic composition of the O₂ supporting the combustion reaction, as is often assumed. Isotope fractionation effects occur that depend on a number of parameters, e.g. structure and surface/volume ratio of the fuel, water content, etc., some of which were investigated in the present study. The authors give a full account of their method and results including a very thorough discussion.

As already pointed out in the conclusions, the full value of the study will only become apparent when measurements of actual combustion processes in the field are made.

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However, it is noteworthy that models of local and regional pollution processes would be incomplete if they did not account, at least to some extent, for the effects measured here.

One of the main points of the paper is that the isotopic composition of the produced CO₂ has little to do with that of the fuel oxygen. At the moment, this is just discussed in the text, but it may be better to present this also in a figure or several figures. For example, this figure could show $\delta^{18}\text{O}$ of the fuel on the x-axis and $\delta^{18}\text{O}$ of the derived CO₂ on the y-axis. Similar for $\delta^{13}\text{C}$. A dual-isotope plot like Figures 3 and 4 is another possibility, but really this would mean incorporating the fuel isotope composition into these already rather overloaded figures.

Unfortunately, the manuscript suffers from awkward and sometimes almost unintelligible sentences. I have given some examples below. Please use clear and simple English and make concise and accurate statements, see also <http://www.atmospheric-chemistry-and-physics.net/submission/index.html>. The introduction and methods sections are not too affected by this, but results and discussion section are difficult to read, which makes the paper unsuitable for ACP in its current form.

Specific comments: In the following I refer to page x, line y as "x/y".

18994/15: What do you mean by "fractionation effects" and "differentiation"? The relative ¹⁸O/¹⁶O isotope ratio difference between CO₂ product and fuel oxygen?

18995/26: Isotopologues are not isotope ratios.

18998/15: $\ln(1+\epsilon) \propto 1/T$ with ϵ being the isotope effect. The isotope effect is *not* $\propto 1/T$, even though for small values of ϵ , $\epsilon \approx \ln(1+\epsilon)$.

18999/3: This is not a chemical equation and a straight arrow should not be used. Please either balance the reaction or use a wavy arrow or something else to indicate that this is not a reaction equation. Consider including H₂O as an explicit reaction product.

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18999/16-25: The definitions "emission factor", "combustion efficiency" and "combustion factor" should also be given as a mathematical equation, e.g. emission factor = $m(\text{product } 1) / \text{Sum}(\text{all products})$. This would also clarify whether these quantities refer to mass, molar or other other ratios.

19001/4: Simplify to "This hypothesis was tested by comparing the isotopic composition of CO₂ produced from dry and wetted material."

19001/7: Simplify to "Two waters of distinct isotopic composition, one from the Atlantic Ocean [...]" Was this sample distilled or could there have been a salt effect?

19002/9: Previous studies have reported oxygen isotope exchange with quartz. Please comment on whether your results may be affected by this.

19004/6: How were the results normalised? Using which reference materials?

19011/6: Replace "inherent oxygen" by "fuel oxygen", also at other places throughout the manuscript.

19011/15+16: Please round to one decimal.

19011/18: Simplify to "We assessed the contribution of fuel oxygen to the $\delta^{18}\text{O}$ in CO₂ by a two end-member mixing model comprising fuel oxygen and cylinder O₂ with a $\delta^{18}\text{O}$ value of 27.2 ‰). The expected $\delta^{18}\text{O}$ value for stoichiometric combustion of cellulose is 29.3 ‰[rounded] but the measured value is only 13.0 ‰." I suggest to avoid giving isotope ratio differences in ‰, to avoid the need to clarify whether this is merely the arithmetic difference or the properly calculated isotope ratio difference (cf. e.g. Mook (2000)). Unfortunately, I cannot reconcile the value of 29.3 ‰with the average isotopic composition of cellulose of 32.23 ‰given in Table 2". The reaction equation is $\text{C}_6\text{H}_{10}\text{O}_5 + 6 \text{O}_2 \rightarrow 6 \text{CO}_2 + 5 \text{H}_2\text{O}$. The $\delta^{18}\text{O}$ value should therefore be $(5 \cdot 32.23 \text{ ‰} + 12 \cdot 27.2 \text{ ‰}) = 28.7 \text{ ‰}$, shouldn't it? Please verify your other calculations as well.

19015/5: Correct and simplify to "Thus, the results from combustion experiments per-

formed with either natural air or pure oxygen cannot be compared directly." "Humidity and temperature also influence the combustion process. Water vapour from fuel or humid air may cool the combustion gases and affect chemical reactions between reactants and products, for example, through isotope exchange with condensing water."

19015/11: Correct and simplify to "The combustion process is influenced by the fuel and the environmental conditions."

19015/15: Delete the superfluous phrase "in a more or less pronounced way".

19016/4: It is too simplistic to state that above 600 °C, CO is converted to CO₂. At higher temperatures, the Boudouard equilibrium $C + CO_2 \rightleftharpoons 2 CO$ is shifted to the product side.

19016/12: Please justify this assumption.

19017/8: What are the burning conditions "insufficient" for?

19017/9: "bunch of other products" - please avoid colloquial language.

19018/6: This is the arithmetic difference. In isotopic terms, the relative isotope ratio difference is $(24.90\text{‰} - 12.64\text{‰}) / (1.01264) = 12.12\text{‰}$.

19020/20: Please back up your observation of a "continuously ongoing enrichment of ¹⁸O in atmospheric O₂" with references. However, I have doubts that the <0.1 change in atmospheric O₂ since the pre-industrial is reflected by an observable change of its isotopic composition. Also, O₂ is produced by photosynthesis without isotope effect and therefore virtually in equilibrium with water over a timescale of about 1000 years.

Table 1: What are the "estimated contributions of the oxygen sources"? And what is their order, e.g., in the degassing phase is "structure material" or "ambient air" the most important O source. It would be helpful if a quantitative value for the estimated contribution could be included in the table or, if it's just a qualitative statement, then this should be explained. What is meant by "formation dependencies"? Formation of

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what? And why are there so many gaps in this column? "Thermal converted" should be "thermally converted". Also, a reaction process is missing for "cellular water" in the open flame phase. Finally, the "progression of the decomposition front" should be indicated by an arrow.

Table 2: It is good to have this information in a table, but it seems that the three values for each sample could be presented more concisely as (average \pm standard deviation). Please also note my comment above that the information in this table may better/also be presented as a figure.

Figure 1: Please indicate the position of the valves.

Figure 2: What is the scientific reason for using 7 different types of arrows? What does the use of a box as opposed to an ellipse mean? Also, several of the boxes show significant overlap, e.g. "sources" really belongs to "fuel material", "burning behaviour" belongs to "combustion process". I suggest that this figure be simplified such as that there are only three boxes: 1. reactants - isotopic composition of a) fuel oxygen, b) atmospheric oxygen, c) water oxygen in fuel; 2. combustion process - isotopic fractionation influenced by environmental conditions, fuel composition and structure, temperature; 3. products - isotopic composition of a) CO₂, b) H₂O, c) CO, d) other side products. The headings of each box should appear in the same position (top) of the box - at the moment they are sometimes at the top, sometimes at the bottom right, sometimes at the bottom left. If possible, please increase the font size further - it is still quite small.

Figure 3: This figure is overloaded with information and difficult to follow. Please add a legend that explains the symbols. Use colour instead of shades of grey to distinguish the symbols - you may want to use different colour intensities so that the symbols are also distinguishable when the paper is printed in black white. Perhaps also link up identical symbols with lines to make guide the reader through the figure. What do the dotted boxes mean? What is the O₂ source for these combustion products? What

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does the circle symbol mean? Replace "are indicating" by "indicate" [but this may be obsolete once an adequate legend is put in place.]

Figure 4: Please add a legend explaining symbols. Use colour. Why are circles/dotted boxes only used in Figure 3, but not here? Replace "are indicating" by "indicate".

Technical corrections: "respectively" is not equivalent to German "beziehungsweise". The word is used correctly in 18995/3, but on 7 other occasions throughout the paper the word has been used incorrectly at the beginning of a subordinate clause.

"in the order of" should be "on the order of" or "of the order of" - 4 occasions

The sentence order is muddled at many places throughout the manuscript, especially in section 3 (Results and discussion). In English, a subject must precede the verb. Also, the position of adverbs/adverbial clauses is often wrong. For example, the sentence on 19013/6, has to be "In addition to the parameters described so far, the atmosphere modulates the environmental conditions through changes in wind, humidity and temperature as well as additional reactants." Besides removing the grammatical errors, this sentence could be improved by a subsequent sentence explaining what "additional reactants" are. Often, the use of a comma would make your text clearer, e.g. after 19013/10 "To investigate the influence of the oxygen availability, [...]".

The past participle of "to grind" is "ground", not "grinded" - several occasions throughout the manuscript.

18995/5: "global carbon cycle" should not have major initials.

18996/12: Add comma after "in addition" and delete "the" before independent.

18998/3: Please round to -17.0 ‰.

19001/7: Replace "welled" by "soaked".

19003/13: "The air flowed through Dekabon tubing ..."

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19008/18: "The internal scaffolding determines the mechanic stability".

19008/19: "The shape of the object also influences the burning conditions from ignition to ultimate collapse."

19010/16: "anaerobic"

19015/18: Word order wrong - should be "Two factors mainly influence the combustion process: [...]"

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 18993, 2008.

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