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Reply

Definite Change Since the Formation of the Earth. Reply to Kleber, A. Comment on "Koutsoyiannis, D. Net Isotopic Signature of Atmospheric CO_2 Sources and Sinks: No Change Since the Little Ice Age. *Sci* 2024, 6, 17"

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Careful inspection of the title and graphical abstract of the original paper [1] would have eased the concerns expressed by Kleber [2] in his Comment. The title of the original paper clarifies that it examines the period since the Little Ice Age, and during this period no change was found in the net isotopic signature of atmospheric CO_2 sources and sinks. Obviously, this result should not and cannot be extended to longer periods such as the last glacial cycle, brought up by the Commentator, or to even longer periods. Definitely, there has been change ever since the formation of the Earth [3], and there always will be in the future. And even the last glacial cycle alone helps us to see this change. I will refer to it in more detail below.

A closer look at the graphical abstract of the original paper [1], reproduced as Figure 1 in this Reply, would have alleviated the Commentator's concern in the Comment [2] about my

> *mistake [. . .] to assume or pretend that an increase in photosynthesis should lead to a* ***decrease*** *in δ^{13}C, whereas the exact opposite is the case.* [my emphasis]

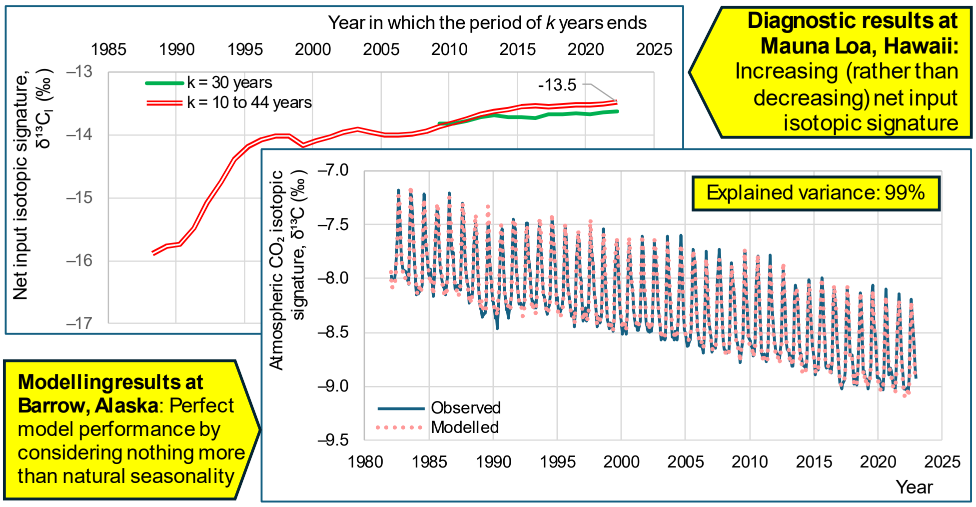

Figure 1. Reproduction of the graphical abstract in [1].

Actually, I do not assume or pretend anything. I analyse data. The data show an overyear decrease in δ^{13}C in the atmosphere—which obviously could not be attributed to the rise of photosynthesis. I clearly state the opposite of what the Commentator regards as my "mistake" [1] (p. 10, top):

Citation: Koutsoyiannis, D. Definite Change Since the Formation of the Earth. Reply to Kleber, A. Comment on "Koutsoyiannis, D. Net Isotopic Signature of Atmospheric CO_2 Sources and Sinks: No Change Since the Little Ice Age. *Sci* 2014, *6*, 17". *Sci* **2024**, *6*, 63. https://doi.org/10.3390/sci6040063

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> *In particular, photosynthesis removes CO_2 from the atmosphere and the fractionation that characterises it results in an* ***increase*** *in $\delta^{13}C$ in the atmosphere, during the months it occurs*. [my emphasis]

The graphical abstract shows an increase in the $\delta^{13}C$ input signature ($\delta^{13}C_I$) of the atmosphere at Mauna Loa. Those accepting the mainstream idea that human emissions are responsible for the changes seen in the isotopic synthesis of atmospheric CO_2 would expect the opposite behaviour. The observed behaviour of $\delta^{13}C_I$ contradicts the mainstream idea and could perhaps be linked to the increased photosynthesis due to the Earth's greening [4–7], even though this is very difficult to infer based on the analyses in my paper [1]. What is certain is that the increase in $\delta^{13}C_I$ could not be caused by the overstated increasing human CO_2 emissions.

Furthermore, the lower panel of the graphical abstract should have replaced all the Commentator's descriptions of seasonality. The original paper [1] describes the related processes correctly (i.e., that $\delta^{13}C$ increases in spring and summer, when plants absorb CO_2, selectively capturing the lighter isotope, and decreases in autumn and winter, when plants and soils release CO_2 depleted in ^{13}C). Moreover, it proceeds to an impressively accurate quantification of the processes as suggested by the agreement between observations and model results, which is seen in Figure 1; notice that the explained variance is 99%.

Nonetheless, I am grateful to the Commentator as his Comment allows me to make further clarifications and explain additional issues, which were not included in the paper.

The Comment's scope can be inferred from the quotation above, related to what the Commentator (mistakenly) regards as my "mistake", i.e., "to assume or pretend" something that is the "exact opposite" of reality. In addition, the Comment's scope is indicated in the following quotation from it [2]:

> *So, when organic matter, such as fossil fuels, is burned, its isotopes mix with those in the atmosphere and $\delta^{13}C$ is modified.*

This aligns with what I called the *generally accepted hypothesis*, which, however, as also asserted in [1], may reflect the ideological dogma of blaming everything on human actions. In [1], I have provided many quotations from the literature that support the fact that, indeed, this is the generally accepted hypothesis, and it is pointless to repeat them here or add more.

There are two main issues with the generally accepted hypothesis: (a) the focus on fossil fuel burning, even though it constitutes only 4% of the CO_2 inflow to the atmosphere, with the remaining 96% being caused by natural processes, and (b) the emphasis on the inflow part, while, in fact, the change in $\delta^{13}C$ is the combined result of inputs and outputs.

On the first issue, Figure 1 in [1], reproduced from Graven et al. [8], shows that, while the isotope ^{13}C is generally depleted in fossil fuels, this is also the case in the biosphere. Here, I provide in Figure 2 more detailed information based on the ranges of $\delta^{13}C$ values given by Trumbore and Druffel [9].

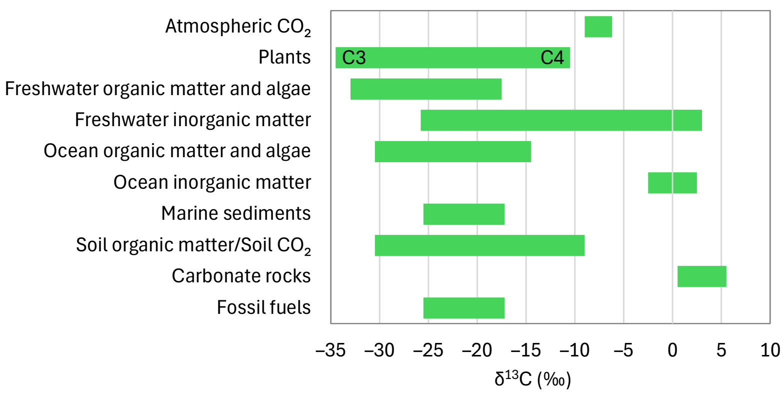

Figure 2. Ranges of $\delta^{13}C$ values for common carbon reservoirs. (Adapted from Trumbore and Druffel [9], after grouping similar categories).

It is readily seen in Figure 2 that C3 plants (e.g., evergreen trees, deciduous trees, and weedy plants) have much lower δ^{13}C values than fossil fuels. Lower values than in fossil fuels also appear in freshwater and ocean organic matter and algae, and in soil organic matter and soil CO_2. When the C3 plants (or other organisms with a low δ^{13}C content) respire, they emit to the atmosphere a low δ^{13}C content. Hence, the atmospheric δ^{13}C content is decreased. It is, therefore, absurd to suggest that it is the emissions from burning fossil fuels, which amount to only 4%, that are causing the atmospheric δ^{13}C value to fall.

Fractionation in photosynthesis has the opposite effect. As both the original paper [1] and the Comment [2] correctly state, the result of photosynthesis alone would be an increase in atmospheric δ^{13}C value. But we have both inputs and outputs of CO_2 in the atmosphere. As thoroughly studied in [1], it is this combined action of the processes producing both inflows and outflows of CO_2 that determines the overall behaviour. In particular, it has been shown theoretically (Section 3 in [1]) that (a) the overannual behaviour of δ^{13}C changes depends on the seasonal one, (b) if the input signature of δ^{13}C were equal to the output signature, then that on the annual scale would be exactly the same, of the order of −25‰, and (c) the fact that the overannual input signature is much larger, i.e., about −13‰, entails a lower signature of the δ^{13}C output (say, −28‰; see Figure 4, left, in [1]) during the season of the year that the absorption dominates. Here is the role of photosynthesis, which indeed increases the seasonal value of −25‰ to the annual value of about −13‰. These theoretical considerations are confirmed by data analyses, as seen in Table 3 in [1].

The Commentator's most important epistemological point is that "*hypotheses cannot be proven. They can, however, be falsified*". This reflects Popper's (1935) [10,11] falsifiability principle, whose usefulness is beyond doubt when examining deterministic systems. However, there are several caveats in it, when examining macroscopic systems approached through stochastics, the involvement of which is necessary when analysing data. Popper himself was aware of this, as he wrote [11] (p. 133):

> *Although probability statements play such a vitally important role in empirical science, they turn out to be in principle impervious to strict falsification.*

Hence, in complex systems, deduction usually becomes impossible and we must resort to induction. In induction, affirmative results about a hypothesis are not unimportant or negligible. They contribute to weak propositions that the hypothesis "becomes more plausible" (see Jaynes [12]). At the same time, as admitted by Popper, strict falsification may become impossible.

After these clarifications, we may discuss the Commentator's "falsification" attempt. The attempt is based on Eggleston et al.'s [13] δ^{13}C atmospheric record. This is primarily based on the Talos Dome deep ice core (72°49′ S, 159°11′ E, length of core: 1620 m) and goes back 155,000 years before present. This record, plotted in Figure 1 of the original source (Eggleston et al. [13]), has been reproduced in Figure 1 of the Comment [2] and is also reproduced in Figure 3 of this Reply.

As "before present" by convention means "before 1950" [14], while the modern instrumental δ^{13}C records began in 1978 (or later at the South Pole; see Figure 1), we may highlight the fact that there is no overlap between this paleoclimatic record and the instrumental data. The modelling part in [1] was based on instrumental data, and therefore it could only cover the period after 1978. In contrast, in the paleoclimatic record used in [1], there is some overlap with the instrumental record, indicating the compatibility of the two (see Figure 15 in [1]).

Notably, Figure 1 in Eggleston et al. [13] also contains plots of [CO_2] as well as of additional isotopes, including δD and δ^{18}O. None of those were reproduced or discussed in the Comment, even though, arguably, to make an inference at least one more variable is necessary to provide a basis for comparison. Here, I choose the additional dataset to be the most relevant, i.e., the [CO_2] record, which is a compilation from four Antarctic ice cores. This is also plotted in Figure 3 of this Reply.

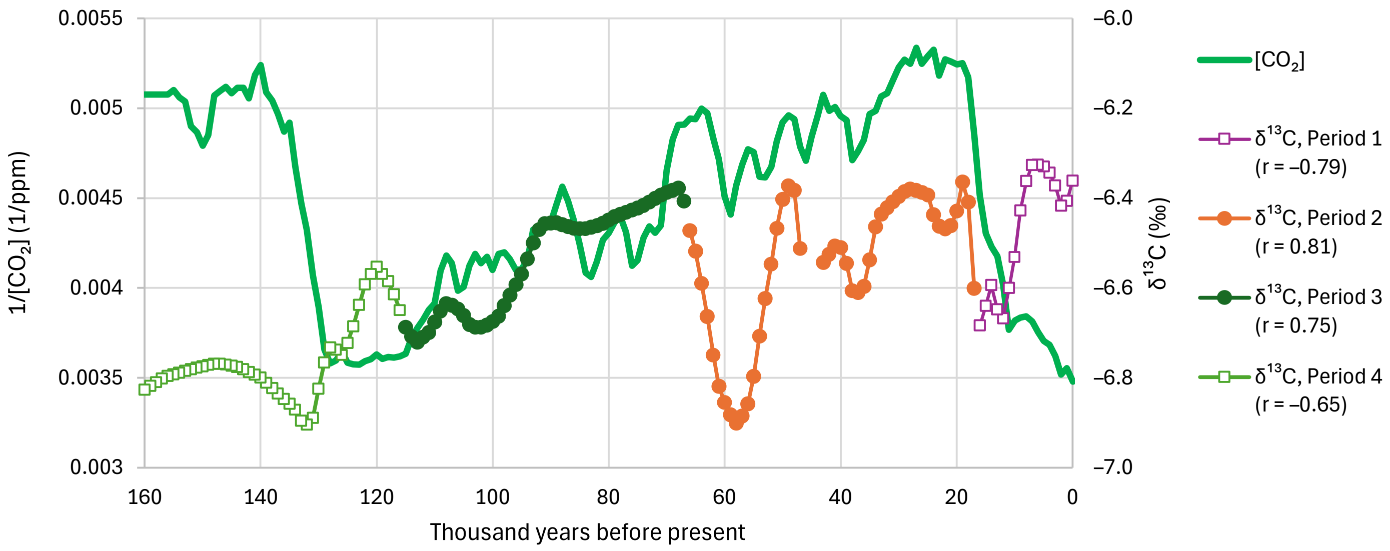

Figure 3. Time series of [CO_2] and $\delta^{13}C$ reproduced from Eggleston et al. [13] after digitisation of their Figure 1. Notice that the time axis is reversed if compared to those in [2,13], so that the time's arrow is directed from left to right, according to the standard convention. The [CO_2] plot was constructed from the digitised data points, after smoothing by taking the average of all points within an interval of 1000 years. The $\delta^{13}C$ curve was made after digitising the Monte Carlo cubic spline average given in [13]. The latter curve is partitioned into four segments, with the breakpoints being found after numerical optimisation, so that the sum of squared cross-correlation coefficients with $1/[CO_2]$ is at maximum. The attained cross-correlation coefficients per segment are shown in the legend.

Now, the Commentator, based on the single time series of $\delta^{13}C$ and by colouring three parts of the time series plot, makes an inference that "*all three major warming episodes were characterized by increasing $\delta^{13}C$ values*". However, one has to be more careful in making an inference, and, first of all, one has to test whether there is systematic regularity rather than an artificial result due to picking narrow parts of the whole with "desired" behaviours.

Figure 3 allows us to confirm that there is no such systematic regularity. The correlation coefficient between $\delta^{13}C$ and [CO_2] for the entire period is negligible (calculated value of 0.07 for [CO_2] or −0.06 for $1/[CO_2]$). On the other hand, if we partition the entire series into four segments, as is also shown in Figure 3, we may attain correlation coefficients as high as 0.65–0.81, but with alternating signs. In two of the segments, the correlation between $\delta^{13}C$ and $1/[CO_2]$ is negative (or that between $\delta^{13}C$ and [CO_2] positive) and in the other two the opposite is the case. Even considering segments with cross-correlation of the same sign, there is no unique regularity: the linear regression relationships (not plotted to avoid a crowded graph but easily imagined) differ substantially.

Thus, from Figure 3 we can make two relevant observations:

1. There is no systematic regularity that could be exploited, in an inductive framework, for confirmation or falsification of the results found for the study period in [1] (i.e., after the Little Ice Age).
2. The relationship between [CO_2] and $\delta^{13}C$ is hugely varying, including in the sign of the cross-correlation. This reflects the high complexity of the evolution of the biosphere and its interplay with the other components of the climatic system and beyond it.

As already mentioned, the study by Eggleston et al. [13] (and in particular its Figure 1) also contains time series of the isotopic δD and $\delta^{18}O$ values, which are common proxies of temperature (with positive and negative correlation, respectively). It is visually clear in that figure by Eggleston et al. that both these proxies are in impressive correspondence with the time series of CO_2, the reciprocal of which is plotted in Figure 3. This correspondence is actually in full agreement with other studies examining even longer periods in the Late

Quaternary (e.g., 420,000 years in Koutsoyiannis [15], where other proxies from the entire Phanerozoic were also studied).

Hence, the alternating trends (with either the same or opposite sign, depending on the period of study) between $1/[CO_2]$ and $\delta^{13}C$ shown in Figure 3 translate also into alternating trends between temperature and $\delta^{13}C$. Therefore, the following reviewer's statement is untrue:

> *In none of the precedents of the past, nor in the interannual cycles typically determined by the biosphere of the northern hemisphere, is there a correlation in which warming leads to a decrease in $\delta^{13}C$.*

Kleber devotes a part of the Comment [2] to discussing Figure 7 in [1], also providing an adaptation of it, i.e., Figure 2 of [2]. The difference is that the vertical axis of $1/[CO_2]$ in [1] was converted by Kleber to $[CO_2]$. I do not see the point of doing this or of the resulting discussion. It is obvious that a positive correlation between $\delta^{13}C$ and $1/[CO_2]$ would translate into a negative correlation between $\delta^{13}C$ and $[CO_2]$, and that the synchrony of peaks in the former case would translate into the antithesis of peaks in the latter (anticyclical seasonal pattern of $\delta^{13}C$ to use the Commentator's terminology). There is a good reason why I used $1/[CO_2]$ instead of $[CO_2]$ in the plot, which is explained in detail in [1]. Actually, the "invention" of using $1/[CO_2]$ is not mine but Keeling's [16,17] and is more than 60 years old; hence the term "Keeling plot".

Finally, the Commentator remarks that I did not use the ^{14}C isotope in [1]. That is correct, and I clearly stated in the paper that this was beyond its scope, also explaining the reason why its study was excluded. However, in a subsequent article [18], I did study the ^{14}C isotope in a different context and the results are fully consistent with those in [1].

The above considerations and detailed clarifications show that there is nothing in the paper [1] that needs any adaptation. The constancy of the value of about −13‰ in the net input signal of the atmospheric $\delta^{13}C_I$ at an overannual time scale, across the entire globe and throughout the entire period after the Little Ice Age (Table 4 in [1]), supports the conclusion that natural causes drove the changes seen, and a human-caused signature is not discernible.

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Conflicts of Interest: The author declare no conflicts of interest.

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