Final Response to Reviewer #1
MS No.: amt-2014-151

We thank the Reviewer#1 for helpful and constructive comments.
Our responses (in blue) follow each comment given by Reviewer#1 in the Supplement.

General opinion:

My main point is that it has not been shown in the manuscript that their d17O is actually on VSMOW scale. A large portion of past work on d17O of terrestrial materials (CO2, rocks and minerals) has not been reported on VSMOW scale for d17O (see Pack & Herwartz, EPSL, 2014). This makes usage of D17O for complex applications (involving water, air components, etc.; e.g. Pack et al., GCA, 2013) impossible (when using data from different labs). Exceptions are high-precision studies on water samples that report d17O on VSMOW scale. If the authors cannot give their d17O on VSMOW scale, it should be noted. For the purpose they developed their technique small systematic offsets in d17O are not relevant.

Also, the definition and meaning of D17O is not clear in the manuscript and deserves clarification (see my comments on PDF). The D17O is simply a better illustration for small deviations in d17O from a linear/curved relation in d17O vs. d18O diagrams. It is not a measured value; the D17O should not be reported relative to VSMOW. VSMOW is a point and D17O is a deviation from a line; hence there is no D17O(VSMOW).

We agree that VSMOW alone is not sufficient to define ^{17}O excess values, but we disagree that this means $\Delta(^{17}\mathrm{O})$ should not be reported "relative to VSMOW". While it is true that VSMOW is just one point along the reference mass-dependent fractionation line, it is clearly a point that defines the line, together with the slope of the line. So, in principle, one should define $\Delta(^{17}\mathrm{O})$ as $\Delta(^{17}\mathrm{O}, \mathrm{VSMOW}, \lambda)$, but since $\delta(^{17}\mathrm{O})$ and $\delta(^{18}\mathrm{O})$ are on the VSMOW scale, we would submit that it makes sense to say that the resulting ^{17}O excess is also on a VSMOW scale (on the understanding of being used in accordance with the functional relationship and coefficient of its definition.)

Supplement:

1. P6824, line 6:

I do not like the term "excess" not. It was used in the past in order to distinguish between "normal" (i.e. no excess) and "anomalous" (i.e. with positive or negative excess) materials. High precision measurements have shown that there is no such "normal" material, neither in rocks not in meteoric waters. Water samples show variations from an average line with slope 0.528 that are outside the uncertainty and hence all "anomalous".
I prefer simply saying: "The D17O is derived from ...".

Excess is a neutral term that refers to a mathematical definition of a physical quantity as relative or absolute difference between two values. The word excess is therefore entirely appropriate, according to the definition of the corresponding quantity. We do not interpret anon-zero ^{17}O excess as being "anomalous" (in whatever way), although some authors in the past may have (erroneously) done so. Rather, triple isotope excess values should be seen primarily as convenient mathematical definitions used to ease communication. While writing $\Delta(^{17}\mathrm{O})$ alone is fine, pronouncing it requires auxiliary constructs such as "capital delta" to refer to in spoken language, which is why we prefer the term ^{17}O excess. The latter term has been in use for at least 15 years (Luz and Barkan, 2000).

2. P6824, line 13:

Better: "The standard deviation of D17O is ..."

The sentence: "The standard deviation of the ^{17}O excess analysis is 1.7‰."
Changed to: The standard deviation of $\Delta(^{17}\mathrm{O})$ is 1.7‰.

3. P6824, line 14:

The sentence: "Repeated analyses of an air sample reduce the measurement uncertainty, as expected for the statistical standard error." is trivial and the statement may be omitted.

We agree that "as expected for the statistical standard error" is probably trivial to most readers, but the first part of the sentence introduces the subsequent statements in the abstract and seems entirely appropriate.

4. P6824, line16 and Page 6852, Figure 7

If the SD of a single measurement is 1.7‰, I would expect a SE of 1.7‰/SQRT(270) = 0.1‰. Why 0.2‰ here?

Indeed SE of 0.2 ‰ is reached after about 100 not after 270 measurements. This is also illustrated in Fig. 7. However, the same figure also shows that after more than 100 measurements, the statistical uncertainty is no longer reduced because of limitations in the long-term stability of the measurement system.

5. P6825, line16:

Please point out here, that your d18O is likely well on VSMOW scale, but your d17O is not. It is not because you do not know the d17O of your CeO2 powder on VSMOW scale. Although the uncertainties reported here are large, one should clearly state the scale to which data are reported.

Please see points 8, 9 and 12 for the explanation on VSMOW scale issue.

6. P6825, line23, note about λ:

If I recall correctly, the range is between 0.500 and 0.5305; please check the lower limit.

Kaiser (2008) argues that the limit for θ (λ under steady state conditions) is generally expected to vary between 0.501 and 0.531. The lower limit (θ_{min} = 0.501) was calculated using Eq.(21) from Young et al. (2002) taking into account exact nuclide masses. $\theta_{min} = 0.5$ when integer nuclide masses are used in the calculation.
The upper limit of $\lambda(\theta_{max})$ corresponds to equilibrium isotope fractionation at high temperatures (Matsuhisa et al., 1978; 2002) $\theta_{max} = 0.5305$.

In our article, we refer to the lambda range with three decimal places, hence the range 0.501 to 0.531.

7. P6826, line 9:

Here, the different techniques should be described in more detail. Barkan & Luz (2012) do NOT convert CO2 into O2, but equilibrate CO2 with water and then analyze the water (by reacting water to O2). Other techniques acrually convert CO2 to O2 (direct fluorination) or equilibrate CO2 with O2, etc.

One possibility to determine $\delta^{17}O$ is by measuring the 33/32 ion current ratio of O_2 originated from CO_2. Following this approach several methods have been developed: Bhattacharya and Thiemens (1989) converted CO_2 to O_2 by reacting it with BrF_5; Brenninkmeijer and Röckmann (1998) used conversion of CO_2 into CH_4 and H_2O by reaction with H_2; in a second step they fluorinated the H_2O with F_2 to produce O_2 and HF; Barkan and Luz (2012) equilibrated CO_2 with H_2O and used water fluorination to produce O_2. These methods are labor-intensive and time consuming, but can be very precise because the ^{13}C interference is effectively removed.

8. P6831, line 15

Where has the d17O of the reference CO2 been analyzed? Is that a calculated d17O value, assuming that the CO2 is "normal"? If so, please inidcate that and note that the d17O reported throughout the manuscript is not on VSMOW scale. It is not crucial for the purpose of this study, but crucial for other studies that may want to use the data from this study.

For our measurements we use two working reference gases: reference CO_2 ($RefCO_2$) and reference oxygen ($RefO_2$). The isotope values for the laboratory standards are: $\delta^{13}C(RefCO_2)$ = -34.84 ‰ vs. VPDB, $\delta^{18}O(RefCO_2)$ = 5.20 ‰ vs. VSMOW, $\delta^{17}O(RefO_2)$ = 9.33 ‰ vs. VSMOW and $\delta^{18}O(RefO_2)$ = 19.00 ‰ vs. VSMOW. The isotope values of $RefCO_2$ were measured at the Department of Earth Science of Utrecht University, The Netherlands, relative to the calcite reference material NBS-19 ($\delta^{18}O$ = 28.65 ‰ vs. VSMOW; $\delta^{13}C$ = 1.95 ‰ vs. VPDB). The carbonate was reacted at 70 °C and the oxygen isotopic composition of the $RefCO_2$ was calculated using an acid fractionation factor α (CO_2-calcite) = 1.00871 (Kim et al., 2007).

The isotope values of $RefO_2$ were measured in Grenoble (Joël Savarino group, Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France). The calibration of the O_2 gas can be traced back to the original SMOW of H. Craig via the laboratories in Grenoble and UCSD (J. Savarino and M. Thiemens). Due to multiple transfers of the scale between gas-bottles there may be a small systematic offset to VSMOW scale, however, this is not relevant for the data presented here (see point 9).

9. P6832, line18

What is the isotopic composition (d17O, d18O) of the O2 used? What is the composition of the CeO2 that has equilibrated with that O2. If bottle O2 has been used, the authors must be aware that they transfer an "anomaly" from the O2 to the CeO2 and hence equilibrate the CO2 with something "anomalous". Again, this will result in d17O values that are not on VSMOW scale. Not important for this work, but it must be outlined in the manuscript.

The isotopic composition of O_2 used for oxygenation is given in paragraph 2.1.6. It is important to underline that CeO_2 is being oxygenated with O_2 of non-mass dependently fractionated O_2 and hence the "anomaly" of O_2 is further transferred to PostCO_2 of each gas measured. Because of that we cannot calculate delta values of the sample air directly on VSMOW scale. Instead, we use measurements of Reference air, measured before and after the sample, to calculate delta values of the sample air relative to the average of reference air. Since both (reference air and sample air) were equilibrated with virtually the same CeO_2 the "anomaly" cancels out (see Eq. 7 – 9).

10. P6834, line 24 and P6835, line 1

It is fine to report D17O relative to a line with slope of 0.528 and zero intercept. For clarity, it should NOT be stated that this is (the only) mass dependent relationship between d17O and d18O (see Pack & Herwartz, 2014, on that topic). Instead it is an (arbitrarily) chosen slope of the reference line. That is, as such, fine.

Please also cite Barkan & Luz (2012) that confirm that the slope defined by CO2 in equilibrium with water has a slope of 0.523. That is the slope for a singly physical equilibration reaction. Therefore, the Hofmann et al. and Barkan et al. observation is, by not means, in contradiction with the choice of a slope of a reference line of 0.528. It is incorrect, however, to assume that a slope of 0.528 is something like a universal "equilibrium fractionation" slope (see Pack & Herwartz, 2014).

The D17O may be reported relative to a line (defined by slope AND intercept) that is appropriate for the scientific application. There is NO thing such as a terrestrial fractionation line, however. If the authors want to report their data relative to the water line; they should also consider the intercept of that line (0.033‰). On the other hand, more complicated studies will have to consider number lines, each having a slope and an intercept. Therefore, Pack & Herwartz, 2014, decided to (arbitrarily) chose the high-T equilibrium approximation for the definition of D17O (with zero intercept). This line has, at least, some physical meaning as the high-T approximation of the equilibrium slope applies to all equilibrium pairs.

The D17O was introduced ONLY TO BETTER DISPLAY small variations in d17O and d18O from some linear/curved trends. It is not a measured value (such as d18O and d17O). Therefore, no need for a consensus on how to best define D17O is necessary.

The manuscript should be clarified in this point.

λ describes the mass-dependent relationship between the three oxygen isotopes. The theoretical range for many mass-dependent fractionation processes is $0.501 < \lambda < 0.531$ (but values outside this range may be attained even for mass-dependent fractionation where $^{18}\alpha$ fractionation factor straddles the value of 1). Kaiser (2008) has adopted $\lambda = 0.528$ for mass dependently fractionated CO_2 samples, as have Assonov and Brenninkmeijer (2003) for their ^{17}O-correction algorithm. However Hofmann et al. (2012) have shown that for CO_2-water equilibration $\lambda = 0.522 \pm 0.002$. This value was supported by Barkan & Luz (2012) who found $\lambda = 0.5229 \pm 0.0001$ for the same process. However, as pointed out by Kaiser (2008), Δ^{17}O is not a measured quantity and may be reported relative to an arbitrarily chosen mass-dependent fractionation line. In the absence of an international recommendation with respect to the preferred definition, any definition should be treated on an equal footing to any other. Comparing data between laboratories always requires recalculation of Δ^{17}O from measured quantities, i.e. δ^{18}O and δ^{17}O, and with different λ. For results shown in this paper we define $\lambda \equiv 0.528$ because it has often been used in the past for CO_2 triple isotope studies.

11. P6836, line 8

Details about the procedure have to be given here. How did Boering get the d17O(VSMOW) for the CO2? Did they fluorinate CO2 and compare their value relative to O2 liberated from VSMOW?

The description on P6836, line 8 extended to:

The CO_2 in the reference air was calibrated vs. international standards at UC Berkeley (group of K. Boering). Three samples of 20 µmol CO_2 each, were extracted cryogenically from the reference air at IMAU laboratory, flame sealed in glass ampules and shipped to UC Berkeley. The method of Assonov and Brenninkmeijer (2001) was applied for the isotope ratio measurements of CO_2. Detailed description of the procedure can be found in the Appendix of Wiegel et al., (2013). At UC Berkeley the samples from Utrecht were measured against the secondary laboratory standard, which, in turn, was calibrated against the three NIST CO_2 reference materials RM8562, RM8563 and RM8564. The $\delta(^{17}O)$ value of the UC Berkeley lab standard is not known, but calculated from its $\delta(^{18}O)$ with respect to VMSOW assuming $\lambda = 0.528$ and $\Delta(^{17}O) = (0 \pm 0.5)$ ‰ (Wiegel et al., 2013). The measurements at UC Berkeley resulted in the following isotope deltas for CO_2 in Utrecht reference air: $\delta^{13}C(RefAir/VPDB) = (8.25 \pm 0.10)$ ‰; $\delta^{17}O(RefAir/VSMOW) = (16.95 \pm 0.40)$ ‰; $\delta^{18}O(RefAir/VSMOW) = (32.74 \pm 0.08)$ ‰ and $\Delta^{17}O = -(0.2 \pm 0.5)$ ‰. The uncertainty in brackets corresponds to the average of three samples measured.

12. Page 6838, line 14

How would your results (on VSMOW scale) change if your CeO2 is "anomalous" (as it is likely the case because you conditioned with anomalous O2; see bottle O2 data in Pack et al., 2007 [their d17O data are not on VSMOW scale either; see Pack & Herwartz, 2014]).

They would not change. To correct for any CeO_2 isotope "anomaly" we measure Reference air before and after each Sample air. We calculate the δ^{13}C, δ^{18}O and δ^{17}O of the Sample air relative to Reference air (Eq.7). Knowing isotopic composition of Reference air on VSMOW scale we calculate δ values of the sample on VSMOW scale following Eq.8.

All data in the manuscript are reported on the VSMOW scale, besides paragraph 3.3 that shows raw data from IRMS.
For clarification paragraph 3.3 should be read:

The raw-$\delta(^{46}CO_2)$ isotope values of $PreCO_2$ were the following: RefAir = 24.50 ‰; SA1 = 35.40 ‰; SA2 = 36.77 ‰; SA3 = 32.65 ‰ and SA4 = 36.84 ‰ all relative to $RefCO_2$ (1σ = 0.10 ‰). Figure 5 shows $^{46}\delta$ of these four samples and the reference air after isotopic equilibration. In all cases, raw-$\delta^{46}(CO_2)$ is equilibrated to 21.82 ‰ (relative to working reference CO_2, ($RefCO_2$)) with precision of 0.08 ‰,

Also Figure 5 should be changed accordingly, to make it clear that the raw-$\delta^{46}(CO_2)$ in not on the VSMOW scale:

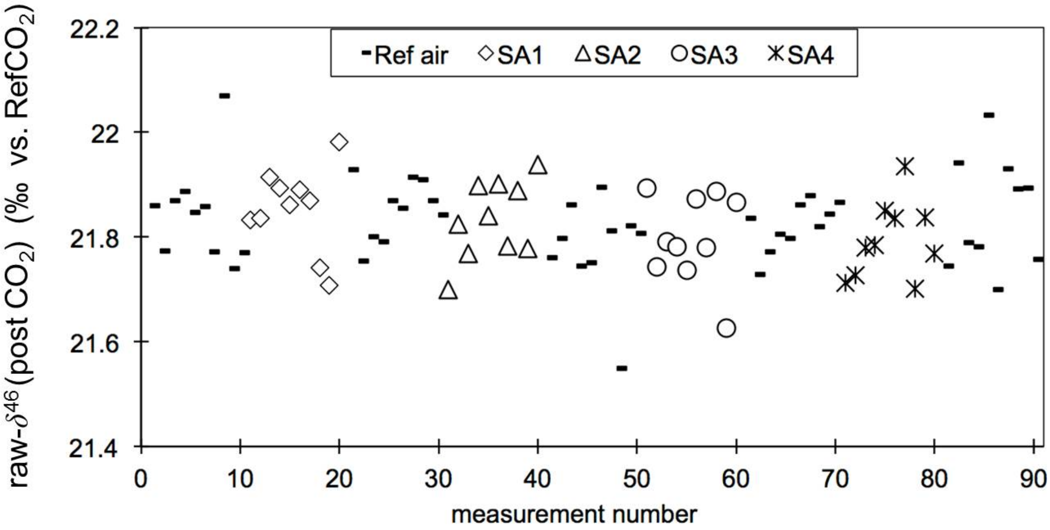

Figure 5. Full and highly efficient oxygen equilibration reaction in the CeO_2 oven represented by isotopically exchanged CO_2 of four diverse atmospheric air samples (SA1-rhombs, SA2-triangles, SA3-circles and SA4-stars) measured against the reference air (stripes). The initial differences in δ^{18}O between the reference air and the air samples were up to 12 ‰ (relative to $RefCO_2$).

13. Page6839, line 4

The D17O is never relative to VSMOW! The d17O is (should be) relative to VSMOW. The D17O is relative to a chosen reference line that may pass through VSMOW. Please clarify.

“The mean value of Δ^{17}O for our RefAir is -0.30 ‰ (vs. VSMOW, λ = 0.528), which reflects…”

14. Page 6851, Figure 6

D17O is not on VSMOW scale; the D17O is simply an illustration of small variations in the d17O - d18O space.

For clarity, the x-axis of Figure 6 should read “Δ^{17}O of Reference air [VSMOW]” to Δ^{17}O(RefAir) (vs. VSMOW, λ = 0.528) “.

15. Page 6852, Figure 7:

The points should not be connected by a spline curve.

We agree.

16. Page 6854, Figure 9

This should not be termed "the" MDF line. It is a MDF line among many (see Pack & Herwartz, 2014). I suggest call it "Reference Line (RL, lambda = 0.528)". This makes the situation clear.

I think that the d17O in this study is not strictly on VSMOW scale. Please clarify throughout the manuscript. Even if it were not on VSMOW scale, the study is good.

For clarity, the axis labels should also be changed from ln^{17}O[‰ vs. VSOMW] to ln(δ + 1) (‰ vs. VSMOW, λ = 0.528) and description of MDF line should be extended from “MDF line” to MDF line (for λ = 0.528).