Absolute Isotope Ratios of Carbon Dioxide – A Feasibility Study
– Electronic Supplementary Information (ESI)

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1 Gravimetric Mixture

This section is a brief summary of the gravimetric mixture approach, we discuss a generic system of N_{is} isotopes. In the case of a system of N_{iso} isotopes, N_{iso} starting materials – each enriched in one different of the N_{iso} isotopes – are needed. For a system with N_{iso} different isotopes, there are $(N_{iso}-1)$ isotope ratios $R_{i/1}$, where 1 is the reference isotope, and therefore, there are also $(N_{iso}-1)$ K-factors. In the case of an isotopologue system like carbon dioxide, the starting materials must be enriched in on of the isotopologues. With N_{iso} starting materials, there are in total $(n_{iso} \times (n_{iso}-1))/2$ different binary blends prepared from the starting materials, see figure 1, where all possible combinations are shown for carbon dioxide having twelve isotopologues (not considering the unstable isotopes). The starting materials are represented as squares, and the blends are represented as circles. The bars in the circles and squares indicate the amount-of-substance fraction of each isotopologue. The preparation of the binary mixtures is done under gravimetric control and in such a way that the resulting ratio of the two major isotopes/isotopologues is close to unity. For example, if material A is enriched in the first isotope and material B is enriched in the second isotope, the resulting blend AB should have a ratio $R_{2/1}$ close to 1. It has been shown that the ratios of the two major isotopes in the binary blends (AB to AX) can be expressed as linear combinations of the corresponding ratios of the two parent materials[1]. By setting up this kind of equation for at least $(n_{iso}-1)$ binary mixtures, a system of linear equations is obtained. By taking into account the relation between the absolute isotope ratios R and measured ion intensity ratios R^m, see equation 1, the $(n_{iso}-1)$ K-factors are introduced into this system of linear equations. This system can be solved for the wanted K-factors for any number of isotopes in a non-iterative way by using the so-called Gaussian elimination[2], and also the uncertainty associated with the K-factors can be calculated by solving the system several thousand times during a Monte Carlo simulation[3]. A generic expression of such equations is given in equation 2. The quantities appearing in equation 2 are as follows: K_j correcting the jth intensity ratio, M_j being the molar mass of the jth species, $R^m_{A,i}$ being the ith measured intensity ratio in material A, $R^m_{Y,i}$ being analogously defined, $R^m_{AY,i}$ being the ith measured intensity ratio in blend AY, m_{AY} being the mass of material A used to prepare AY and finally m_{YA} is the mass of material Y used for preparing blend AY. It has also been shown that it is not necessary to prepare all possible binary blends and that there is, in terms of the lowest achievable uncertainty associated with the K-factors, a best choice of blends and measured ratios. The lowest uncertainty can be achieved by using all the blends that contain material A, which has a very high amount-of-substance fraction of the most abundant isotope (higher than its natural abundance). In the case of carbon dioxide, $x\left({}^{12}C^{16}O_2\right)$ of material A would be very high and blends AB to AG must be prepared, see figure S 1, if we consider the ideal case where all the twelve isotopologues can be resolved and detected and starting materials A to G exist.

$$R_{i/1} = \frac{n_i}{n_1} = K_{i/1} \times R^m_{i/1} = K_{i/1} \times \frac{I_i}{I_1} \tag{1}$$

$$0 = \sum_{j=1}^{N_{iso}} \left[K_j \times M_j \times \left(\frac{R^m_{A,i}}{m_{AY} \times \left(R^m_{AY,j} - R^m_{A,j} \right)} - \frac{R^m_{Y,i}}{m_{YA} \times \left(R^m_{Y,j} - R^m_{AY,j} \right)} \right) \right] \tag{2}$$

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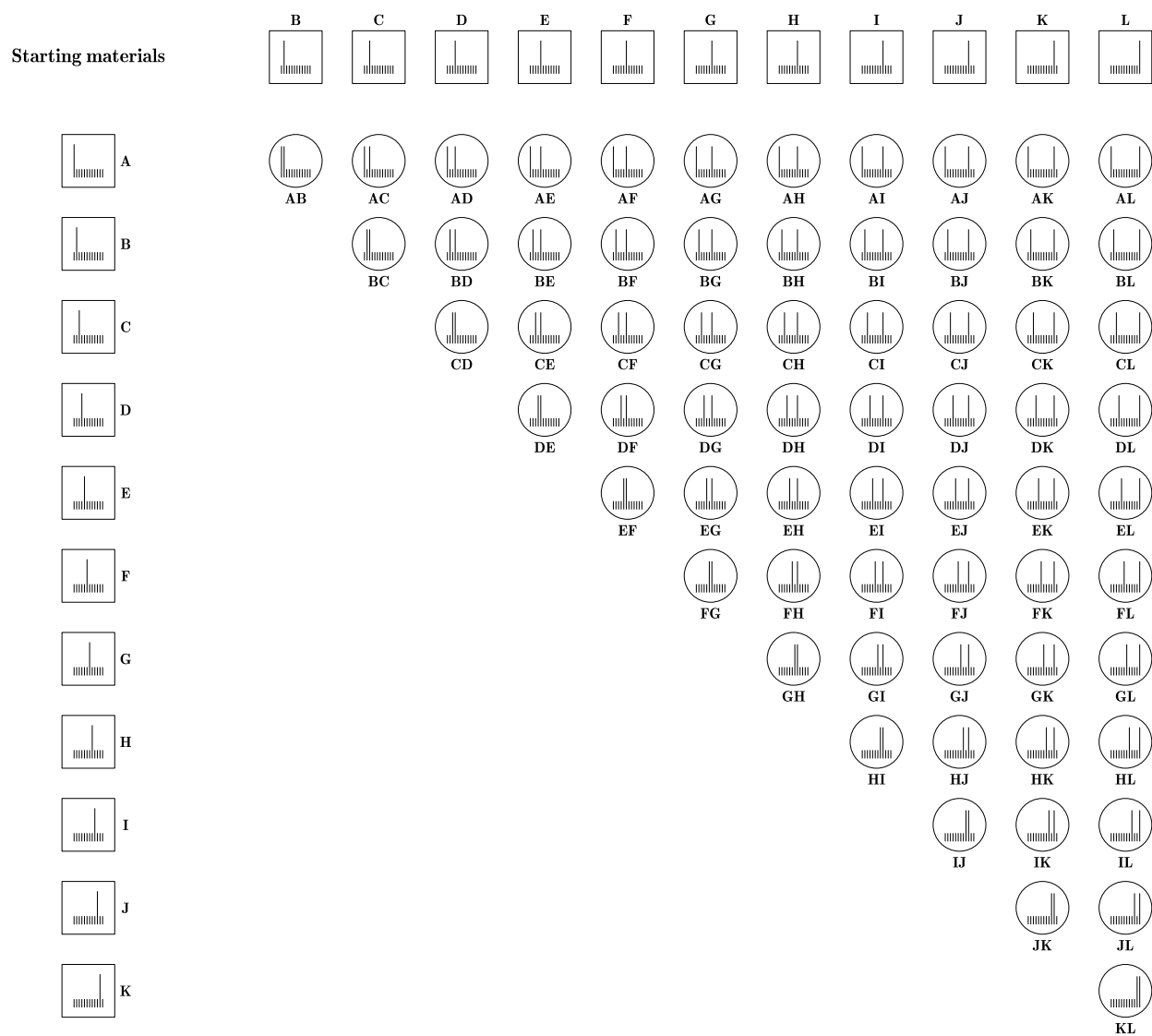
Fig. S 1 All 66 different binary mixtures that can be prepared from the twelve different starting materials A to K. The starting materials are represented as squares, and blends are represented as circles. The amount-of-substance fraction of each isotopologue is indicated with the bars in the squares and the circles, respectively.

2   Calculating R_{47}^{m}

R_{47}^{m} was derived from the isotope ratios R_{13}, R_{17} and R_{18}, according to equation 3.

$$R_{47}^{\mathrm{m}} = 2 \times R_{18} \times R_{17} + 2 \times R_{18} \times R_{13} + R_{17} \times R_{13}^2 \tag{3}$$

The isotope ratios were derived by solving equation 4, the so-called Santrock algorithm[4]. For λ and K, the values recommended by Brand[5] ($\lambda = 0.528$, $K = 0.01022461$) were chosen. It should be pointed out that K is not a K-factor and should not be confused with them, but we did not change its symbol as it is well established in the literature. K is defined as $K = R_{17,\mathrm{VPDB}}/R_{18,\mathrm{VPDB}}^{\lambda}$ and, therefore, describes the oxygen isotope composition of VPDB-CO_2. Since $\lambda \neq 0.5$, equation 4 cannot be solved for R_{18} analytically and must be solved iteratively. In the ESI, we present a code which calculates the isotope ratios and their associated uncertainties. To solve equation 4, the so-called *regula falsi*[6] is implemented.

$$0 = -3 \times K^2 \times R_{18}^{2 \times \lambda} + 2 \times K \times R_{45}^{\mathrm{m}} \times R_{18}^{\lambda} + 2 \times R_{18} - R_{46}^{\mathrm{m}} \tag{4}$$

For the calculation of the uncertainties associated with the isotope ratios, we made the following considerations. The standard uncertainty associated with R_{46}^{m} can be calculated according to the guide titled 'Evaluation of measurement data - Guide to the expression of uncertainty in measurement' (GUM)[7] as shown in equation 5. Since $u_{\mathrm{c}}^2(R_{45}^{\mathrm{m}})$ and $u_{\mathrm{c}}^2(R_{46}^{\mathrm{m}})$ are known from the extrapolation, this equation can be solved for the known $u_{\mathrm{c}}^2(R_{18})$. The needed partial derivatives occurring in equation 5 are given in equations 6a and 6b.

$$u_{\mathrm{c}}^2(R_{46}^{\mathrm{m}}) = \left(\frac{\partial R_{46}^{\mathrm{m}}}{\partial R_{45}^{\mathrm{m}}}\right)^2 \times u_{\mathrm{c}}^2(R_{18}) + \left(\frac{\partial R_{46}^{\mathrm{m}}}{\partial R_{45}^{\mathrm{m}}}\right)^2 \times u_{\mathrm{c}}^2(R_{45}^{\mathrm{m}}) \tag{5}$$

$$\frac{\partial R_{46}^{\mathrm{m}}}{\partial R_{18}} = 2 \times K \times R_{18}^{(\lambda-1)} \times R_{45}^{\mathrm{m}} \times \lambda - 6 \times K^2 \times R_{18}^{(2 \times \lambda-1)} \times \lambda + 2 \tag{6a}$$

$$\frac{\partial R_{46}^{\mathrm{m}}}{\partial R_{45}^{\mathrm{m}}} = 2 \times K \times R_{18}^{\lambda} \tag{6b}$$

Inserting these partial derivatives and solving for $u_{\mathrm{c}}(R_{18})$ obtains:

$$u_{\mathrm{c}}(R_{18}) = \sqrt{\frac{u_{\mathrm{c}}^2(R_{46}) - \left(2 \times K \times R_{18}^{\lambda}\right)^2 \times u_{\mathrm{c}}^2(R_{45})}{\left(\left(2 \times K \times R_{18}^{(\lambda-1)} \times R_{45} - 6 \times K^2 \times R_{18}^{(2 \times \lambda-1)}\right) \times \lambda + 2\right)^2}} \tag{7}$$

Since R_{18} has been determined iteratively, the found value of R_{18} may differ from the true value, due to machine precision and rounding errors. In order to take this difference into account within the uncertainty budget, the found value of R_{18} is inserted into equation 4, and the deviation from zero (ε) is calculated. This deviation from zero is another uncertainty source and can be considered by equation 8.

$$u_{\mathrm{total}}(R_{18}) = \sqrt{u_{\mathrm{c}}^2(R_{18}) + \varepsilon^2} \tag{8}$$

After calculating R_{18} and $u_{\mathrm{total}}(R_{18})$, also R_{13}, R_{17} and their associated uncertainties can be calculated using the following equations.

$$R_{17} = K \times R_{18}^{\lambda} \tag{9a}$$

$$u_c(R_{17}) = K \times \lambda \times R_{18}^{\lambda-1} \times u_{\mathrm{total}}(R_{18}) \tag{9b}$$

$$R_{13} = R_{45}^{\mathrm{m}} - 2 \times R_{17} \tag{10a}$$

$$u_{\mathrm{c}}(R_{13}) = \sqrt{u_{\mathrm{c}}^2(R_{45}^{\mathrm{m}}) + 4 \times u_{\mathrm{c}}^2(R_{17})} \tag{10b}$$

Combining all the given equations, the uncertainty associated with R_{47} can finally be calculated using:

$$\begin{aligned} u_{\mathrm{c}}(R_{47}) = \big[&\left(4 \times R_{17}^2 + 8 \times R_{13} \times R_{17} + 4 \times R_{13}^2\right) \times u_{\mathrm{total}}^2(R_{18}) + \\ &\left(4 \times R_{18}^2 + 8 \times R_{13} \times R_{17} \times R_{18} + 4 \times R_{13}^2 \times R_{17}^2\right) \times u_{\mathrm{c}}^2(R_{17}) + \\ &\left(4 \times R_{18}^2 + 4 \times R_{17}^2 \times R_{18} + R_{17}^4\right) \times u_{\mathrm{c}}^2(R_{13}) \big]^{0.5} \end{aligned} \tag{11}$$

3 Calculation of theoretical ratios

For the calculation of the theoretical ratios ratios of blend AB ($R_{45,AB}^{neq}$, $R_{45,AB}^{neq}$, $R_{45,AB}^{eq}$, $R_{46,AB}^{eq}$), the following equations are necessary. In table S 1, all quantities occurring in the following equations are defined.

$$R_{45,bk}^{neq} = \frac{(x_{44,X} \times n_X \times R_{45,pi} + x_{44,pj} \times n_Y \times R_{45,Y})}{(x_{44,X} \times n_X + x_{44,Y} \times n_Y)} \tag{12}$$

$$x_{44,X} = x_X(^{12}C) \times x_X(^{16}O) \times x_X(^{16}O) \tag{13}$$

$$n_X = m_X / M_X \tag{14}$$

$$\begin{aligned} M_X = & M(^{12}C) \times x_X(^{12}C) + M(^{13}C) \times x_X(^{13}C) + \\ & 2 \times (M(^{16}O) \times x_X(^{16}O) + M(^{17}O) \times x_X(^{17}O) + M(^{18}O) \times x_X(^{18}O)) \end{aligned} \tag{15}$$

$$R_{45,X} = \frac{x_X(^{13}C)}{1 - x_X(^{13}C)} + 2 \times \frac{x_X(^{17}O)}{1 - x_X(^{17}O) - x_X(^{18}O)} \tag{16}$$

$$R_{46,bk}^{neq} = \frac{(x_{44,X} \times n_X \times R_{46,pi} + x_{44,pj} \times n_{pj} \times R_{46,pj})}{(x_{44,pi} \times n_X + x_{44,pj} \times n_{pj})} \tag{17}$$

$$\begin{aligned} R_{46,pi} = & 2 \times \frac{x_X(^{13}C)}{1 - x_X(^{13}C)} \times \frac{x_X(^{17}O)}{1 - x_X(^{17}O) - x_X(^{18}O)} + \\ & 2 \times \frac{x_X(^{12}C)}{1 - x_X(^{13}C)} \times \left(\frac{x_X(^{17}O)}{1 - x_X(^{17}O) - x_X(^{18}O)} \right)^2 \\ & + 2 \times \frac{x_X(^{13}C)}{1 - x_X(^{13}C)} \times \frac{x_X(^{16}O)}{1 - x_X(^{17}O) - x_X(^{18}O)} \times \frac{x_X(^{18}O)}{1 - x_X(^{17}O) - x_X(^{18}O)} \end{aligned} \tag{18}$$

$$R_{45,bk}^{eq} = x_{bk}(^{13}C) + 2 \times x_{bk}(^{17}O) \tag{19}$$

$$x_{bk}(^{13}C) = \frac{(x_X(^{12}C) \times n_X \times R_{13,pi} + x_{pj}(^{12}C) \times n_{pj} \times R_{13,pj})}{(x_X(^{12}C) \times n_X + x_{pj}(^{12}C) \times n_{pj})} \tag{20}$$

$$R_{13,pi} = \frac{x_X(^{13}C)}{1 - x_X(^{13}C)} \tag{21}$$

$$x_{bk}(^{17}O) = \frac{(x_X(^{16}O) \times n_X \times R_{17,pi} + x_{pj}(^{16}O) \times n_{pj} \times R_{17,pj})}{(x_X(^{16}O) \times n_X + x_{pj}(^{16}O) \times n_{pj})} \tag{22}$$

$$R_{17,pi} = \frac{x_X(^{17}O)}{1 - x_X(^{17}O) - x_X(^{18}O)} \tag{23}$$

$$\begin{aligned} R_{46,bk}^{eq} = & 2 \times x_{bk}(^{13}C) \times x_{bk}(^{16}O) \times x_{bk}(^{17}O) + x_{bk}(^{12}C) \times x_{bk}(^{17}O)^2 + \\ & 2 \times x_{bk}(^{12}C) \times x_{bk}(^{17}O) \times x_{bk}(^{18}O) \end{aligned} \tag{24}$$

$$R_{18,pi} = \frac{x_X(^{18}O)}{1 - x_X(^{17}O) - x_X(^{18}O)} \tag{25}$$

Table S 1 Definition of all quantities appearing in the above equations, in order of appearance.

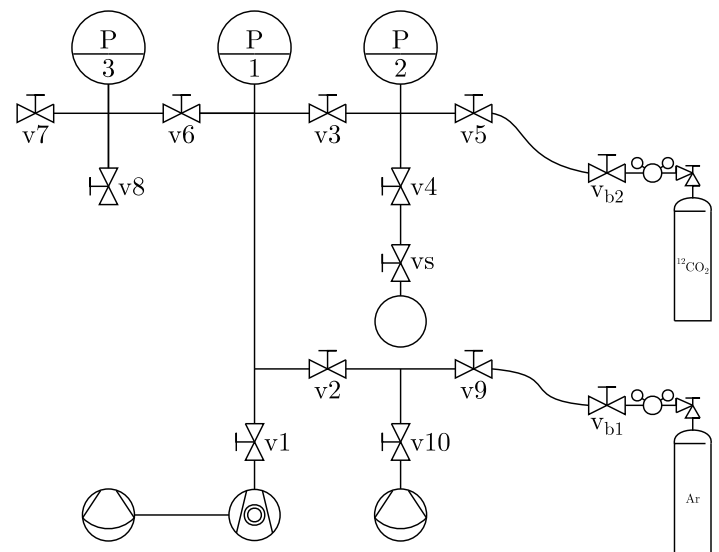| quantity	definition
$R_{q,\mathrm{b}k}^{\mathrm{neq}}$	isotopologue ratio $q/44$, $q \in \{45,46\}$ of blend bk, without assuming a statistical isotope distribution
n_X	amount of substance of parent material X
$x_{44,X}$	amount-of-substance fraction of $^{12}\mathrm{C}^{16}\mathrm{O}_2$ in parent material X
m_X	mass of parent material X
M_X	molar mass of parent material X
$M(q)$	molar mass of qth isotope, $q \in \{^{12}\mathrm{C},^{13}\mathrm{C},^{16}\mathrm{O},^{17}\mathrm{O},^{18}\mathrm{O}\}$
$x_X(q)$	amount-of-substance fraction of $q^{\prime}ext{th}$ isotope, $q \in \{^{12}\mathrm{C},^{13}\mathrm{C},^{16}\mathrm{O},^{17}\mathrm{O},^{18}\mathrm{O}\}$ in parent material X
$R_{q,X}^{\mathrm{neq}}$	isotopologue ratio $q/44$, $q \in \{45,46\}$ of parent material X, without statistical isotope distribution
$x_{\mathrm{b}k}(q)$	amount-of-substance fraction of qth isotope, $q \in \{^{12}\mathrm{C},^{13}\mathrm{C},^{16}\mathrm{O},^{17}\mathrm{O},^{18}\mathrm{O}\}$ in blend bk
$R_{q,\mathrm{b}k}^{\mathrm{eq}}$	isotopologue ratio $q/44$, $q \in \{45,46\}$ of blend bk, with assuming a statistical isotope distribution

4 Gas mixing device

For preparing binary, mixtures a gas mixing device was set up at PTB. The device is built from CF flanges (DN 16 CF). The device is depicted in figure S 2 and a schematic description is also given. The gas mixing device is equipped with a turbo pumping station, consisting of a HiPace 80 and MVP 015-2, both from Pfeiffer Vacuum GmbH, Asslar Germany. With this set up a pressure of roughly 1×10^{-7} mbar can be reached. The pressure in the piping is measured with a Pirani/cold cathode gauge from Pfeiffer (part number PT R26 252) and the gas pressure for filling the process is measured with a capacitance gauges also from Pfeiffer (PT R24 602). The gas mixing device is equipped with a second membrane pump (Pfeiffer, PK T05 065), which can be used to evacuate the piping to roughly 1×10^{-1} mbar, this by-pass pump is very convenient for evacuating the piping without rebooting the turbo pump. Additionally, the system is equipped with an argon flush unit (valve v9), the hole piping can be flush with argon (purity $0.999\,990\,\mathrm{L\,L^{-1}}$). The symmetrical set-up allows to prepare binary mixtures and avoid cross contaminations. The valves v1 and v2 are inline valves (Pfeiffer, DVC 016 SX), v3 to v8 are all metal angle valves (Pfeiffer, UVH 016 CU) and v9 and v10 are diaphragm valves (VACOM GmbH, Großlöbichau, Germany, part number 15DVM-16KF-VV-A). The hole mixing device has been heated before each filling using heating taps, $T \approx 60\,°\mathrm{C}$, for roughly 12 h. The actual mixing procedure is summarized in figure S 3.
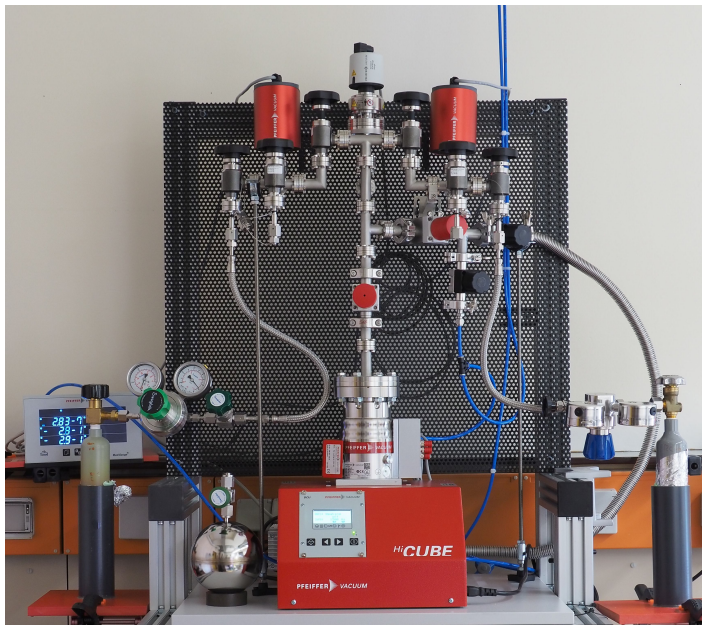
(a) Photography of gas mixing device at PTB.　　(b) Rrepresentation of gas mixing device at PTB.

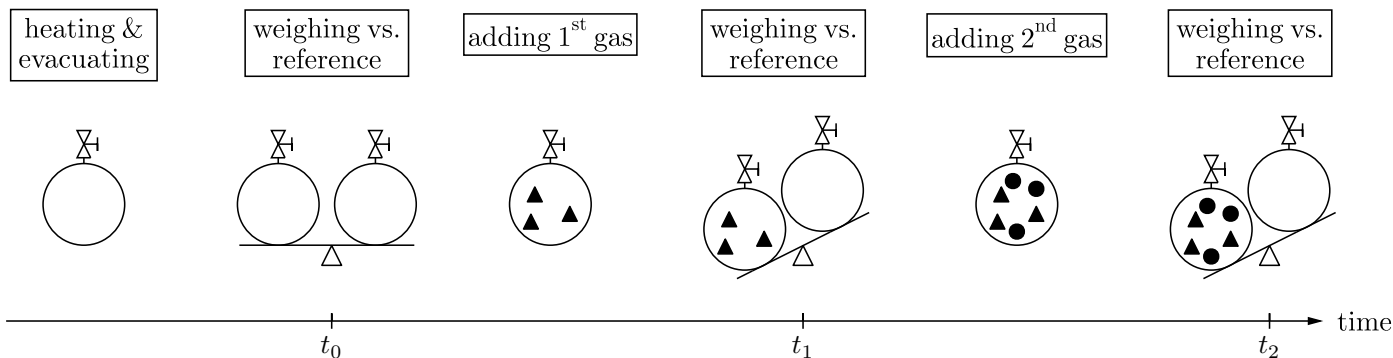**Fig. S 2** Photography and schematic representation of gas mixing device at PTB.

Fig. S 3 Schematic representation of the preparation of the binary blends. Please note that the weighing here is depicted using a double pan balance, whereas in this study, a single pan balance was used. At times t_0, t_1 and t_2, the target sphere is weighed against the same evacuated reference sphere.

5 Measurement of natural CO_2

As mentioned the main text, we also measured CO_2 with a natural isotopic composition ($\delta_{VPDB}{}^{13}C = (-17.526 \pm 0.016)\ ‰$ and $\delta_{VPDB\text{-}CO_2}{}^{18}O = (-10.118 \pm 0.019)\ ‰$, with $k=1$ in both cases). Previous to the measurement we heated the gas, which was filled into one of our gas spheres. The heating temperature ϑ was roughly $1800\,°C$ and the gas was heated for $30\,min$. The logarithm of R_{45}^m (top) and R_{46}^m (bottom) over time are shown in figure S 4.
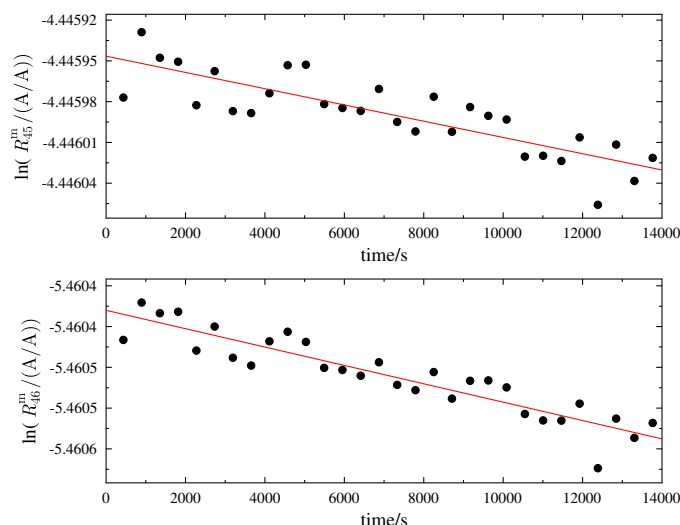

Fig. S 4 Logarithm of R_{45}^m (top) and R_{46}^m (bottom) over time. The red lines indicate linear regression fits. Previous to the measurement the gas has been heated for $30\,min$ at $1800\,°C$.

6 ISL code for deriving time zero t_0

For extrapolating to time zero t_0, the starting time (when the corresponding valve opens and the gas flows from the bellows into the ionization chamber) needs to be defined. The following code is written Isodat Script Language (ISL) and therefore only works on Thermo Fisher gas mass spectrometers (e.g. MAT253). This script opens valve v15 (see figure 5) and records the time. The time is logged into a txt file. Before the valve is opened, Isodat will ask where this file should be saved. The script must be run as a prescript and works on Isodat 3.0, it has not been tested on any other version of Isodat. By change '`_Set("Dual Inlet System/Valve 15",1)`' in line 25 to '`_Set("Dual Inlet System/Valve 25",1)`' the right bellows can be used. After the valve has been opened and an idle time of $10\,s$ the measurement starts normally. The idle time allows the gas flow to settle and can be adjusted if necessary.
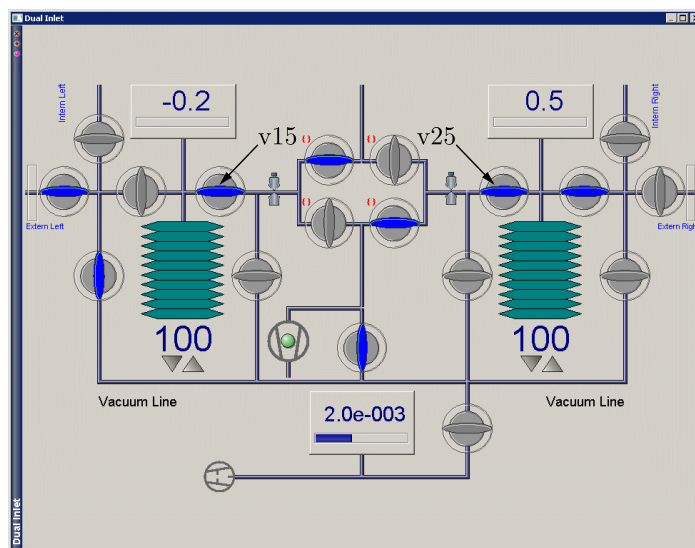
Fig. S 5 Dual inlet system of a MAT 253 from Thermo Fisher, Bremen, Germany. v15 and v25 connect the corresponding gas reservoir with the changeover valve system. For extrapolating to time t_0 the absolute time when the corresponding valve is opened is needed.

Listing S 1 ISL source code of function to extrapolate to time t_0 and calculate the responding ratios and their associated uncertainties.

```
1  //==================================================================
2  //                          Date 20-11-18
3
4  include "lib\stdisl.isl"
5  include "lib\instrument.isl"
6  include "lib\DualInlet_lib.isl"
7  main()
8  {
9   call InitScript();
10
11  //defining txt file for writing starting time
12  string csFileName;
13  string date;
14  bool bDoStore =FALSE;
15  bool bOk=FALSE;
16  date=_GetDate();
17
18  //the file location may needs to be adjusted
19  csFileName="C:\Thermo\Isodat NT\Global\User\Dual Inlet
20  System\Results\starting-time-t0";
21  csFileName += date;
22  bDoStore=_FileSelect(FALSE,"*.txt",csFileName);
23
24  //Opening Valve 15
25  string t0 = _GetTime();
26  _UserInfo(t0,0,00);
27  Set("Dual Inlet System/Valve 15",1);
28
29  //delay of 10 sec for gas flow to settle
30  _Delay(10000);
31  if (bDoStore)
32   {
33    bOk=_Write(csFileName, "Start time","Start time %",t0);
34   }
35  }
36  //==================================================================
```

7 VBA code for extrapolation to t_0

In this section a VBA code (Visual Basics for Applications) for EXCEL® is presented. This code allows to perform the linear extrapolation of $\ln(R_{45}^m)$ and $\ln(R_{46}^m)$ to time zero. The input for this function are three ranges: The time, the logarithm of R_{45}^m and R_{46}^m. The function returns $R_{45,0}^m$ and its associated uncertainty ($k = 2$!) and $R_{46,0}^m$ and its associated uncertainty ($k = 2$!). Additionally, the isotope ratios R_{13}, R_{17} and R_{18} derived from the extrapolated values of $R_{45,0}^m$ and $R_{46,0}^m$. Also the expanded uncertainties of the isotope ratios are returned, $k = 2$. For the calculation of R_{18} the SSH algorithm[4] (named after Santrock, Studley and Hayes) is solved using the so-called *regula falsi*, the VBA codes of both are also given here. Please note that for the SSH algorithm it is necessary to choose K and λ. If necessary, the values of these two quantities

can be changed by the user. The values used in our codes were taken from Brand et al[5].

Listing S 2 VBA source code of function to extrapolate to time t_0 and calculate the responding ratios and their associated uncertainties.

```vba
1  Public Function co2_all_in_one(lnR45 As Range, lnR46 As Range, rel_time As Range) As Variant()
2
3      Dim K As Variant
4      Dim lambda As Variant
5      Dim R45_0 As Variant
6      Dim R46_0 As Variant
7      Dim R18_rf As Variant
8      Dim delta As Variant
9      Dim R_17 As Variant
10     Dim R_13 As Variant
11     Dim z() As Variant
12     Dim y() As Variant
13     Dim ur_45 As Variant
14     Dim ur_46 As Variant
15     Dim ur_18 As Variant
16     Dim ur_17 As Variant
17     Dim ur_13 As Variant
18     Dim results() As Variant
19     ReDim results(1 To 5, 1 To 3)
20
21     lambda = 0.528
22     K = 0.01022461
23
24     z() = WorksheetFunction.LinEst(lnR45, rel_time, 1, 1)
25     y() = WorksheetFunction.LinEst(lnR46, rel_time, 1, 1)
26
27     R45_0 = Exp(z(1, 2))
28
29     R46_0 = Exp(y(1, 2))
30
31     uR_45 = Exp(z(1, 2)) * z(2, 2)
32
33     uR_46 = Exp(y(1, 2)) * y(2, 2)
34
35     R18_rf = regula_falsi_R18(R45_0, R46_0)
36
37     delta = ssh(R45_0, R46_0, R18_rf)
38
39     uR_18 = ur18(R18_rf, R45_0, R46_0, ur_45, ur_46, delta)
40
41     R_17 = K * R18_rf ^ lambda
42
43     R_13 = R45_0 - 2 * r_17
44
45     uR_17 = K * uR_18 * R18_rf ^ (lambda - 1) * lambda
46
47     uR_13 = (uR_45 ^ 2 + 4 * K ^ 2 * lambda ^ 2 * R18_rf ^ (2 * lambda - 2) _
48             * uR_18 ^ 2) ^ 0.5
49
50     results(1,1)= "R_{45,0}"
51     results(2,1)= "R_{46,0}"
52     results(3,1)= "R_{13}"
53     results(4,1)="R_{17}"
54     results(5,1)="R_{18}"
55     results(1, 2) = R45_0
56     results(1, 3) = uR_45 * 2
57     results(2, 2) = R46_0
58     results(2, 3) = uR_46 * 2
59     results(3, 2) = R_13
60     results(3, 3) = uR_13 * 2
61     results(4, 2) = R_17
62     results(4, 3) = uR_17 * 2
63     results(5, 2) = R18_rf
64     results(5, 3) = uR_18 * 2
65
66     co2_all_in_one = results()
67
68  End Function
```

Listing S 3 VBA source code of *regula falsi* to calculate to R_{18}.

```vba
1  Function regula_falsi_R18(r_45 As Variant, r_46 As Variant) As Variant
2
3      Dim a As Variant
4      Dim b As Variant
5      Dim z As Variant
6      Dim counter As Integer
7      Dim fa As Variant
8      Dim fb As Variant
9      Dim fz As Variant
10
11     a = 100
12     b = 0
13
14     lambda = 0.528
15     K = 0.01022461
16
17     fa = ssh(r_45, r_46, a)
18     fb = ssh(r_45, r_46, b)
19
20     z = a - (b - a) / (fb - fa) * fa
21     fz = ssh(r_45, r_46, z)
22
23     While Abs(fz) <> 0
24
25         If (Sgn(fa) = Sgn(fz)) Then
26             a = z
27             b = b
28             Debug.Print ("Sgn(fa) = Sgn(fz)")
29         ElseIf (Sgn(fb) = Sgn(fz)) Then
30             b = z
31             a = a
32         Else
33             Debug.Print ("Warning, fa and fb have the same sign!")
34         End If
35
36         z = a - ((b - a) / (fb - fa)) * fa
37         fz = ssh(r_45, r_46, z)
38         fa = ssh(r_45, r_46, a)
39         fb = ssh(r_45, r_46, b)
40         counter = counter + 1
41
42         If counter > 10000 Then
43             fz = 0
44         End If
45
46     Wend
47
48     regula_falsi_R18 = z
49
50  End Function
```

Listing S 4 VBA source code of the SSH alogrithm.

```vba
1  Function ssh(r_45 As Variant, r_46 As Variant, r_18 As Variant) As Variant
2
3      Dim K As Variant
4      Dim lambda As Variant
5
6      lambda = 0.5278
7      K = 0.01022461
8
9      ssh = -r_46 - 3 * K ^ 2 * r_18 ^ (2 * lambda) + 2 * K * r_45 * r_18 ^lambda _ + 2 * r_18
10
11 End Function
```

Listing S 5 VBA function for calculating $u_c(R_{18})$.

```vba
1  Function ur18(r_18 As Variant, r_45 As Variant, r_46 As Variant, ur_45 _
2              As Variant, ur_46 As Variant, epsilon As Variant) As Variant
3
4
5      Dim lambda As Variant
6      Dim K As Variant
7
8      lambda = 0.528
9      K = 0.01022461
10
11     ur18 = ((ur_46 ^ 2 - (2 * K * r_18 ^ lambda) ^ 2 * ur_45 ^ 2) / _
12             (2 * K * r_18 ^ (lambda - 1) * r_45 * lambda - 6 * K ^ 2 * r_18 ^ (2 * _ lambda - 1) * lambda + 2) ^ 2 + epsilon ^ 2) ^ 0.5
13
14 End Function
```

8 Alternative equations

In main text of this publication, it has been shown how a system of non-linear equation based on the ratios R_{45}, R_{46} and R_{47} can be set-up and solved for the absolute ratios and the K-factors. Depending on the isotopic composition of the starting materials it is also possible to measure other intensity ratios and consequently for calculating the absolute isotope ratios and the K-factors a different set of equations is needed. The solving routine is the same and must be adapted accordingly. Please note that three ion intensity ratios must be measured, so that enough information is available and the system of equations can be solved. Equations 26a to 26e describe the measured ion intensity ratios of the two parent materials and the binary blend, y stands for A, B or AB.

$$0 = K_{45} \times R_{45,y}^{m} - (R_{13,,y} + 2 \times R_{17,y}) \tag{26a}$$

$$0 = K_{46} \times R_{46,y}^{m} - (2 \times R_{18,y} + 2 \times R_{17,y} \times R_{13,y} + R_{17,y}^{2}) \tag{26b}$$

$$0 = K_{47} \times R_{47,y}^{m} - (2 \times R_{18,y} \times R_{17,y} + 2 \times R_{18,y} \times R_{13,y} + R_{17,y}^{2} \times R_{13,y}) \tag{26c}$$

$$0 = K_{48} \times R_{48,y}^{m} - (2 \times R_{13,y} + R_{18,y}^{2}) \tag{26d}$$

$$0 = K_{49} \times R_{49,y}^{m} - (R_{13,y} \times R_{18,y}^{2}) \tag{26e}$$

In order to reduce the number of unknowns, the absolute isotope ratios of the binary blend AB must be expressed as linear combinations of the corresponding ratios of the two parent materials. This is shown in equations 27a to 27c.

$$R_{13,AB} = \frac{(n_A \times x_{12,A} \times R_{13,A} + n_B \times x_{12,B} \times R_{13,B})}{(n_A \times x_{12,A} + n_B \times x_{12,B})} \tag{27a}$$

$$R_{17,AB} = \frac{(n_A \times x_{16,A} \times R_{17,A} + n_B \times x_{16,B} \times R_{17,B})}{(n_A \times x_{16,A} + n_B \times x_{16,B})} \tag{27b}$$

$$R_{18,AB} = \frac{(n_A \times x_{16,A} \times R_{18,A} + n_B \times x_{16,B} \times R_{18,B})}{(n_A \times x_{16,A} + n_B \times x_{16,B})} \tag{27c}$$

The amounts of substance can be expressed as:

$$n_y = m_y / M_y \tag{28}$$

Whereas y stands for A or B. The molar mass of the corresponding material can be expressed as:

$$M_y = M(^{12}C) \times x_y(^{12}C) + M(^{13}C) \times x_y(^{13}C) + \\ 2 \times (M(^{16}O) \times x_y(^{16}O) + M(^{17}O) \times x_y(^{17}O) + M(^{18}O) \times x_y(^{18}O)) \tag{29}$$

The occurring amount-of-substance fractions must be expressed in terms of the isotope ratios:

$$x_{12,y} = 1 / (1 + R_{13,y}) \tag{30a}$$

$$x_{13,y} = R_{13,y} / (1 + R_{13,y}) \tag{30b}$$

$$x_{16,y} = 1 / (1 + R_{17,y} + R_{18,y}) \tag{30c}$$

$$x_{17,y} = R_{17,y} / (1 + R_{17,y} + R_{18,y}) \tag{30d}$$

$$x_{18,y} = R_{18,y} / (1 + R_{17,y} + R_{18,y}) \tag{30e}$$

Taking all these relations into account equations like the ones already shown in the main text can be set-up. In the second Mathematica notebook ('equation-system.nb') accompanying this publication all possible initial equations are give.

9 Supplement to the Simulation

In the main text, we described a simulation, where we calculated the absolute isotope ratios, the K-factors, and all associated uncertainties of the two parent materials via a Monte Carlo simulation. The input is listed in Table S2. The results of our code are the density probability functions (PDF) of the above listed quantities, see figure S6. From those PDFs the best estimates and the uncertainties associated with them are derived. The PDFs are assumed to be normal distributions, therefore the uncertainty u is σ and the best estimate is μ. The number of Monte Carlo trials was to 1×10^5.

Table S 2 Input of the second simulation with made-up numbers of the two parent materials (A', B') and the binary blend AB'. Note that the uncertainties ($k = 1$) (of the measured ratios and the masses), on the other hand, stem from real measurements in order to assess the performance of the method. The isotopologue ratios were calculated from the isotope ratios and transformed into the intensity ratios by dividing them with the corresponding K-factors, which are also given in table .
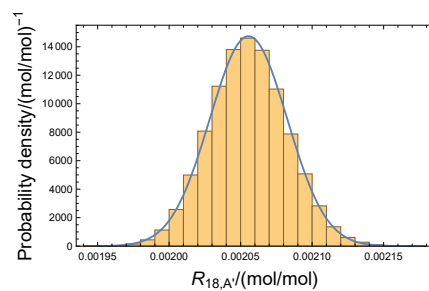
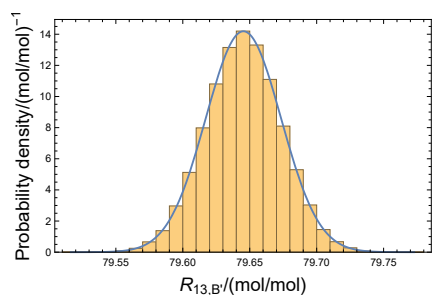|	A'	B'	AB'
$R_{45,y}^{\mathrm{m}}/(\mathrm{A\,A^{-1}})$	0.012 148 8(14)	83.5958(60)	1.040 411(10)
$R_{46,y}^{\mathrm{m}}/(\mathrm{A\,A^{-1}})$	0.004 961 380(74)	1.948 05(40)	0.030 691 8(31)
$R_{47,y}^{\mathrm{m}}/(\mathrm{A\,A^{-1}})$	0.000 057 939(12)	2.740 52(90)	0.019 227 1(40)
m_x/g	0.994 70(19)	1.0023(19)	–
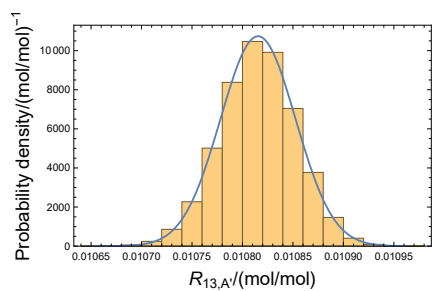
(a) PDF and histogram of $R_{13A'}$.
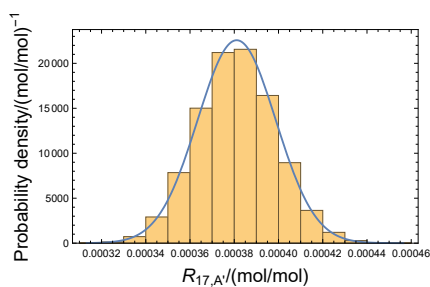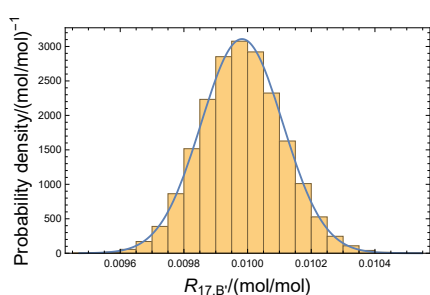

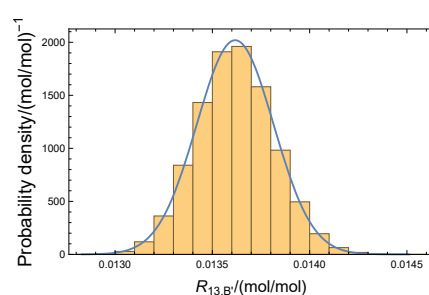**(b)** PDF and histogram of $R_{17A'}$.

(c) PDF and histogram of $R_{18A'}$.

(d) PDF and histogram of $R_{13B'}$.

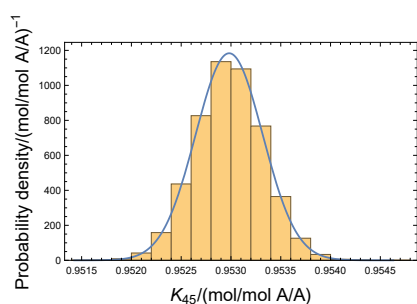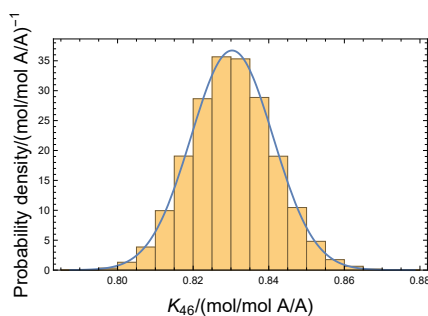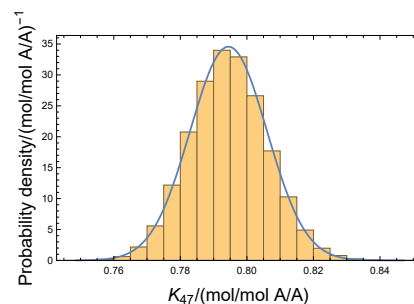**(e)** PDF and histogram of $R_{17B'}$.

(f) PDF and histogram of $R_{18B'}$.

(g) PDF and histogram of K_{45}.

(h) PDF and histogram of K_{46}.

(i) PDF and histogram of K_{47}.

Fig. S 6 Probability density functions (blue lines, Gaussian functions) and histograms obtained by Monte Carlo simulation. The number of Monte Carlo trials was set to 1×10^5.

10 Code for solving the system of non-linear equations

In the main text it is described how K-factors for CO_2 can be calculated when the isotopic equilibrium is considered. Since we presented a Mathematica file to solve the non-linear equation system, we also like to share the code for all other users who do not use Mathematica but like to implement our code in a different way. Please note, the system of non-linear equations is not directly shown in the code, since they are excessively long. The non-linear equation system, the equations for calculating the initial guesses, and the function for generating normally distributed deviates were imported from the file titled 'equations-r45-r46-r47.m'. Therefore, these two files must be saved in the same directory. The functions in this file are all given in the main text. The data evaluation is also imported from a file ('data-evaluation.m', see listing 7). This file must also be saved in the same directory.

Listing S 6 Mathematica code for solving the system of non-linear equations.

```
 1  SetDirectory[NotebookDirectory[]];
 2  Import["equations-r45-r46-r47.m"];
 3  Import["data-evaluation.m"];
 4  (***********************************************)
 5  (* input *)
 6
 7  (* nr is the number of Monte Carlo trials *)
 8      nr = 1000000;
 9
10  (* Atomic mass of the five stable isotopes *)
11      M12C = 12;
12      muM13C = 13.00335483521;
13      muM16O = 15.9949146196;
14      muM17O = 16.9991317566;
15      muM18O = 17.9991596128;
16
17  (* uncertainties (k=1) associated with the atomic mass of the five \
18  stable isotopes *)
19      uM13C = 2.3*^-10;
20      uM16O = 1.7*^-10;
21      uM17O = 7*^-10;
22      uM18O = 7*^-10;
23
24  (* masses of the parent materials A and B  *)
25      mumA = 0.9947;
26      mumB = 1.0023;
27
28  (* uncertainties (k=1) associated with the masses of the parent \
29  materials A and B *)
30      umA = 1.9*^-4;
31      umB = 1.9*^-4;
32
33  (* measured ion intensities of material A *)
34      mur45A = 0.0121488105002256;
35      mur46A = 0.00496138026894439;
36      mur47A = 0.0000579385118709506;
37
38  (* uncertainties (k=1) associated with the measured ion intensities of \
39  material A *)
40      ur45A = 0.00000139711320752594;
41      ur46A = 0.0000000744207040341659;
42      ur47A = 0.0000000121670874928996;
43
44  (* measured ion intensities of material B *)
45      mur45B = 83.5957511985939;
46      mur46B = 1.94805231823881;
47      mur47B = 2.74051699405287;
48
49  (* uncertainties (k=1) associated with the measured ion intensities of \
50  material B *)
51      ur45B = 0.006018894;
52      ur46B = 0.00038961;
53      ur47B = 0.000904371;
54
55  (* measured ion intensities of blend AB *)
56      mur45AB = 1.04041111720587;
57      mur46AB = 0.0306918329606498;
58      mur47AB = 0.0192271177872782;
59
60  (* uncertainties (k=1) associated with the measured ion intensities of \
61  material AB *)
62      ur45AB = 0.0000100919878368969;
63      ur46AB = 0.00000306918329606498;
64      ur47AB = 0.00000403769473532842;
65  (* *********************************************** *)
66
67  (* list for storing the results and later data evaluation *)
68      listK45 = Table[Null, nr];
69      listK46 = Table[Null, nr];
70      listK47 = Table[Null, nr];
71      listR13A = Table[Null, nr];
72      listR17A = Table[Null, nr];
73      listR18A = Table[Null, nr];
74      listR13B = Table[Null, nr];
75      listR17B = Table[Null, nr];
76      listR18B = Table[Null, nr];
77  (***********************************************)
```

13

```
78
79  (*************************************************)
80  (* Monte Carlo trials *)
81  For[i = 1, i <= nr, i++,
82
83      (* generating random deviates *)
84      M13C = muM13C + boxmuller[uM13C, RandomReal[], RandomReal[]];
85      M16O = muM16O + boxmuller[uM16O, RandomReal[], RandomReal[]];
86      M17O = muM17O + boxmuller[uM17O, RandomReal[], RandomReal[]];
87      M18O = muM18O + boxmuller[uM18O, RandomReal[], RandomReal[]];
88      mA = mumA + boxmuller[umA, RandomReal[], RandomReal[]];
89      mB = mumB + boxmuller[umB, RandomReal[], RandomReal[]];
90      r45A = mur45A + boxmuller[ur45A, RandomReal[], RandomReal[]];
91      r46A = mur46A + boxmuller[ur46A, RandomReal[], RandomReal[]];
92      r47A = mur47A + boxmuller[ur47A, RandomReal[], RandomReal[]];
93      r45B = mur45B + boxmuller[ur45B, RandomReal[], RandomReal[]];
94      r46B = mur46B + boxmuller[ur46B, RandomReal[], RandomReal[]];
95      r47B = mur47B + boxmuller[ur47B, RandomReal[], RandomReal[]];
96      r45AB = mur45AB + boxmuller[ur45AB, RandomReal[], RandomReal[]];
97      r46AB = mur46AB + boxmuller[ur46AB, RandomReal[], RandomReal[]];
98      r47AB = mur47AB + boxmuller[ur47AB, RandomReal[], RandomReal[]];
99
100     (*  calculating initial values of material A  *)
101     intR17A = FindRoot[InitalR17[r45A, r46A, r47A, x], {x, 0}];
102     intR17A = x /. intR17A[[1]];
103     intR18A = (r46A - 2*intR17A*r45A + 3*intR17A^2)/2;
104     intR13A = r45A - 2*intR17A;
105
106     (* calculating initial values of material B *)
107     intR17B = FindRoot[InitalR17[r45B, r46B, r47B, x], {x, 0}];
108     intR17B = x /. intR17B[[1]];
109     intR18B = (r46B - 2*intR17B*r45A + 3*intR17B^2)/2;
110     intR13B = r45B - 2*intR17B;
111
112     (* solving the system of non-linear equations *)
113     results =
114     FindRoot[{f1, f2, f3, f4, f5, f6, f7, f8,
115         f9}, {{K45, 1}, {K46, 1}, {K47, 1}, {R13A, intR13A}, {R17A,
116         intR17A}, {R18A, intR18A}, {R13B, intR13B}, {R17B,
117         intR17B}, {R18B, intR18B}}, MaxIterations -> \[Infinity]];
118
119     (* storing results for later data evaluation in lists *)
120     listK45[[i]] = K45 /. results[[1]];
121     listK46[[i]] = K46 /. results[[2]];
122     listK47[[i]] = K47 /. results[[3]];
123     listR13A[[i]] = R13A /. results[[4]];
124     listR17A[[i]] = R17A /. results[[5]];
125     listR18A[[i]] = R18A /. results[[6]];
126     listR13B[[i]] = R13B /. results[[7]];
127     listR17B[[i]] = R17B /. results[[8]];
128     listR18B[[i]] = R18B /. results[[9]];
129  ]
130  (*************************************************)
131
132  (*************************************************)
133  (* data evaluation, calculating of the best estimate and the \
134  associated uncertainty *)
135
136  (* data evaluation for Subscript[R, 13,A] *)
137     dataevaluation[listR13A, "\!\(\*SubscriptBox[
138     StyleBox[\"R\",\nFontSlant->\"Italic\"], \(13, A\)]\)", " mol/mol"];
139     result1 = %;
140
141  (* data evaluation for Subscript[R, 17,A] *)
142     dataevaluation[listR17A, "\!\(\*SubscriptBox[
143     StyleBox[\"R\",\nFontSlant->\"Italic\"], \(17, A\)]\)", " mol/mol"];
144     result2 = %;
145
146  (* data evaluation for Subscript[R, 18,A] *)
147     dataevaluation[listR18A, "\!\(\*SubscriptBox[
148     StyleBox[\"R\",\nFontSlant->\"Italic\"], \(18, A\)]\)", " mol/mol"];
149     result3 = %;
150
151  (* data evaluation for Subscript[R, 13,B] *)
152     dataevaluation[listR13B, "\!\(\*SubscriptBox[
153     StyleBox[\"R\",\nFontSlant->\"Italic\"], \(13, B\)]\)", " mol/mol"];
154     result4 = %;
155
156  (* data evaluation for Subscript[R, 17,B] *)
157     dataevaluation[listR17B, "\!\(\*SubscriptBox[
158     StyleBox[\"R\",\nFontSlant->\"Italic\"], \(17, B\)]\)", " mol/mol"];
159     result5 = %;
160
161  (* data evaluation for Subscript[R, 18,B] *)
162     dataevaluation[listR18B, "\!\(\*SubscriptBox[
163     StyleBox[\"R\",\nFontSlant->\"Italic\"], \(18, B\)]\)", " mol/mol"];
164     result6 = %;
165
166  (* data evaluation for Subscript[K, 45] *)
167     dataevaluation[listK45, "\!\(\*SubscriptBox[
168     StyleBox[\"K\",\nFontSlant->\"Italic\"], \(45\)]\)", " mol/mol/A/A"];
169     result7 = %;
170
171  (* data evaluation for Subscript[K, 47] *)
172     dataevaluation[listK46, "\!\(\*SubscriptBox[
173     StyleBox[\"K\",\nFontSlant->\"Italic\"], \(46\)]\)", " mol/mol/A/A"];
174     result8 = %;
```

```
175
176 (* data evaluation for Subscript[K, 47] *)
177    dataevaluation[listK46, "\!\(\*SubscriptBox[
178    StyleBox[\"K\",\nFontSlant->\"Italic\"], \(47\)]\)", " mol/mol/A/A"];
179    result9 = %;
180
181 (**********************************************)
182
183 (**********************************************)
184 (* printing result file, which contains all best estimates and their \
185 associated uncertainties *)
186
187    filename =
188    "results-file-co2-calculator-" <>
189    DateString[{"Year", "-", "Month", "-", "Day", "-", "Hour", "-",
190      "Minute"}] <> ".txt";
191 nrstring = "Number of Monte Carlo trials was set to " <> ToString[nr];
192 PutAppend[nrstring, result1, result2, result3, result4, result5,
193   result6, result7, result8, result9, filename ];
194 (* ****************************************** *)
```

Listing S 7 Mathematica code the data evaluation.

```
1 dataevaluation[datalist_, name_, unit_] :=
2     (dist = EstimatedDistribution[datalist, NormalDistribution[\[Mu],
3         \[Sigma]]]; mu = dist[[1]]; sigma = dist[[2]]; pdfs = PDF[dist, x];
4
5     ylable = StringJoin["Prpabilitydensity/(", unit,
6       "\!\(\*SuperscriptBox[\(\), \(-1\)]\)"];
7
8     xlable = StringJoin[name, "/(", unit, ")"];
9
10     Print[Show[{Histogram[datalist, Automatic, "PDF",
11         Frame -> {True, True, True, True}, FrameLabel ->
12           {Style[xlable, 16], Style[ylable, 16]}],
13         Plot[pdfs, {x, Min[datalist], Max[datalist]}]}]];
14
15     string = StringJoin["The best estimate of ", ToString[name], " is ",
16       ToString[mu], " ", unit, " "];
17
18      Print["The best estimate of", name,
19      "is ", mu, " and its associated uncertainty is ", sigma, " (",
20      (sigma/mu)*100, " %)."];
21
22     Return[string])
```

Notes and references

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