

# Applications of stable isotope analysis to atmospheric trace gas budgets

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**Abstract.** Stable isotope analysis has become established as a useful method for tracing the budgets of atmospheric trace gases and even atmospheric oxygen. Several new developments are briefly discussed in a systematic way to give a practical guide to the scope of recent work. Emphasis is on applications and not on instrumental developments. Processes and reactions are less considered than applications to resolve trace gas budgets. Several new developments are promising and applications hitherto not considered to be possible may allow new uses.

## 1 Introduction

This synopsis presents applications of stable isotope analyses in atmospheric chemistry to supply information for non-isotope-experts to more readily understand scope and potential. It is meant to be a practical guide for elucidating a specialized set of methods as applied to atmospheric chemistry. The importance of the biosphere including soils for atmospheric processes means that the methods also apply to certain biogeochemical issues. The set of isotope methods and applications is rapidly becoming more complex. In many cases the development was driven by isotope experts looking at atmospheric applications. However, stable isotope analyses will most likely grow in the number of applications originating in atmospheric chemistry. Here the judgement about usefulness will be made quickly. In this paper the emphasis is on how trace gas budgets can be resolved. In many papers on this theme, statements like “constraining trace gas budgets” are tabled, but in many cases there is a long way to go. At the best, budget calculations can be constrained. There also is a need for clarity, certainly considering some confusion that existed considering subtle effects that were discovered. Altogether, there are many fascinating new developments.

It is well known that the subtle stable isotope variations in natural systems on Earth provide a wealth of information. In particular in palaeo-climatology one wonders what we would have known about past temperatures not having had stable isotope information. It is like Radiocarbon dating that about 50 years ago started to overthrow some of the often ingenious guesswork of estimating ages of the successive civilizations in the old continent. What were the temperatures 20,000 years ago? The  $^{18}\text{O}/^{16}\text{O}$  ratio of oxygen in water molecules in polar ice or of oxygen in carbonates deposited on the ocean floor that long ago is the source of quantitative information. With lower polar temperatures less  $^{18}\text{O}$  in accumulated ice. When marine life produces shells, small and big alike, remarkably, the carbonate is in a temperature-dependent non-biological isotopic equilibrium with the local ocean water. What about applications in the atmosphere?

Applications in atmospheric chemistry and biogeochemistry are generally of quantitative nature and several fundamental new insights have been obtained. When dealing with atmospheric processes, emissions of trace gases, their transport, mixing and in the end their removal, are considered. Not forgotten should be that also aerosol are subjected to isotope analyses. Anyway, considering the sources of trace gases we have the isotopic composition depending on

biological, chemical and physical processes. For instance methane has a range of isotopically distinct sources. Next, methane emitted from these sources is transported and mixed throughout the atmosphere. At the same time, methane is broken down by mainly the hydroxyl radical (OH), and the mixture from the different sources is gradually modified. What is left over gets heavier. Figure 1 shows an example for carbon monoxide, CO. Note that the advantage of isotope studies is that one approaches the cycle of a trace gas at the process level. A totally different approach is based on concentration measurements in particular satellite based observations. Here processes cannot be studied that well. Compared to concentration measurements only, one has a direct coupling to the actual process. These processes, for instance those of the sources processes themselves can be studied further using the isotopic tracers.

Progress in this field has been enormous. Measurements have become exceedingly precise, down to 0.005‰. Thus for instance variations in the ~1.1% natural abundance of  $^{13}\text{C}$  as small as 5 ppm are detectable. Measurements are now mostly based on GC techniques, i.e. in a flow of carrier gas (helium), and not on transfer under vacuum in a dual viscous inlet system. This has meant smaller samples and more analysed at the same time. Before systematically visiting the various trace gases from an isotopic point of view we introduce and comment on essential concepts. In this article we must be brief and thus cannot do justice to all isotope work on all gases. Mostly recent work is quoted and analytical info is omitted. Recent reviews are [1–3].

## 2 Basic concepts

The rare isotopes of the lighter elements (here H,C,N,O,S) are of low abundance. That means that isotopic composition does NOT affect processes. Only for chlorine, where  $^{37}\text{Cl}$  happens to be ~25% with the abundant isotope  $^{35}\text{Cl}$  being ~75%, can changes in isotopic composition really change the bulk behaviour. In all other cases, isotopes are mere tracers. It also means that doubly substituted molecules are very rare. For  $\text{H}_2$ , DD would statistically be only  $\sim(0.015\%)^2$  abundant. Later we will see that deviations from this statistical distribution may be interesting (clumped isotope analysis).

Isotope effects are small. Only for hydrogen do large effects (say 50%) occur. Here the reason is that the 2 isotopes Deuterium (D) and Protium (simply H) have large relative mass differences. The isotope ratio is expressed relative to a standard, for instance ocean water for  $^{18}\text{O}$  and D present in water samples. The delta notation is used which gives the per mil relative deviation. Delta values are not additive quantities.

The isotope ratios are on the basis of atomic ratios. This is immediately clear when we look at the example hydrogen. It is easy to see that the ratio HD/ $\text{H}_2$  is twice the D/H ratio. Here we add that measurements are based mostly on stable isotope ratio mass spectrometry which in this case means comparing a beam of HD<sup>+</sup> ions (mass 3) with the main beam of  $\text{H}_2^+$  (mass 2) ions. Also laser based methods exist for D,  $^{13}\text{C}$  and  $^{18}\text{O}$ . The D/H ratio of atmospheric water vapour can even be measured using remote sensing from outside the atmosphere.

Because stable isotope effects are small, their measurement (necessarily mostly) by stable isotope ratio mass spectrometry has always been tedious and elaborate. A breakthrough has been the development of continuous flow IRMS. Here the gas to be analysed is analysed like a GC effluent, where the isotope ratio mass spectrometer has been “degraded” to a mere detector. Thus the needed high precision and accuracy have been achieved for small amounts of analyte gas carried in a flow of helium. This has revolutionized IRMS applications (compound specific isotope analysis), also in atmospheric applications. Note that nearly always the trace gas is transformed into a gas suitable for isotope analysis. Thus oxidation, reduction, and pyrolysis are used. To give an example, the D/H ratio of  $\text{CH}_4$  is determined by converting  $\text{CH}_4$  to  $\text{H}_2$  by pyrolysis. The high temperatures needed make this rather difficult, but direct measurement of  $\text{CH}_4$  gives for mass 17 (M/Z) information about  $^{13}\text{C}$  and D together. The variations in the rare D isotope cannot be resolved this way readily.

Proper nomenclature is needed. For instance  $^{13}\text{C}$  is the rare stable isotope of carbon, with  $^{12}\text{C}$  being the main, or abundant isotope. Atmospheric methane gas has a 47‰ lower  $^{13}\text{C}/^{12}\text{C}$  ratio than ocean carbonate (official standard material was V-PDB, now NBS-19). It is said to be

depleted in  $^{13}\text{C}$ . Isotope fractionation in the bacterial processes forming  $\text{CH}_4$  favours formation of  $^{12}\text{CH}_4$  over  $^{13}\text{CH}_4$ . These molecules are two isotopologues of methane. Isotopomers are like isomers.

Essential are the processes that modify isotope ratios. The main distinction in types of isotope fractionation is that between equilibrium and kinetic isotope effects. Equilibrium isotope effects in chemical reactions are easier to calculate than kinetic effects. Spectroscopic data reveal bond strength parameters and can be used to calculate the partitioning ratios. Physical processes are generally simpler to calculate, for instance the kinetic isotope effects for  $^{18}\text{O}$ ,  $^{17}\text{O}$  and D in the diffusion of water vapour in air. Chemical reaction, photolysis, diffusion, phase transition, all induce isotope effects.

Nearly all isotope effects are mass dependent. This sounds trivial, then what else would drive different behaviour of stable isotopes but their mass? Electron spin effects underlie certain isotope fractionation processes (e.g. spin forbidden transitions). However, mostly it is merely mass. If an element happens to possess at least 3 stable isotopes, one can verify mass dependence directly because the fractionation for a mass difference of 2 units must be double that for a mass difference of 1 unit. Thus the change in enrichment or depletion for  $^{18}\text{O}$  is twice that for  $^{17}\text{O}$ .

If this rule is broken, and it is severely violated for ozone ( $\text{O}_3$ ), one speaks of Mass Independent Fractionation (MIF). In fact the enrichment in ozone is for  $^{17}\text{O}$  almost the same as for  $^{18}\text{O}$ , which remained a big mystery for years. This one to one relationship was called MIF. But it is not exactly 1.0. Does mass play some role, and is it not totally mass independent? The expression MAF (Mass Anomalous Fractionation) has been coined, with the remark that it perhaps better should not be used. Also MAD (Mass Anomalous Fractionation) has been proposed. Here we advise to use the expression MIF when the fractionation clearly deviates from the expected mass dependence. Ozone is a clear case. Molecules that “inherit” MIF from ozone, for instance  $\text{NO}_2$  because it is formed from  $\text{O}_3 + \text{NO}$ , can be said to exhibit MIF.

Some confusion existed at times when this slope of nominally 0.5 for  $^{17}\text{O}$  fractionation relative to that for  $^{18}\text{O}$  was not well known, or the processes causing fractionation were not well identified. At times one was not always sure whether deviations between measured  $^{17}\text{O}/^{16}\text{O}$  ratios and the ratios expected on the basis of the  $^{18}\text{O}/^{16}\text{O}$  ratio were due to MIF, or just due to different slopes [4]. For small differences one has to be careful to attribute an anomaly to MIF. In other words deviations do not imply that an unusual fractionation process is at work.

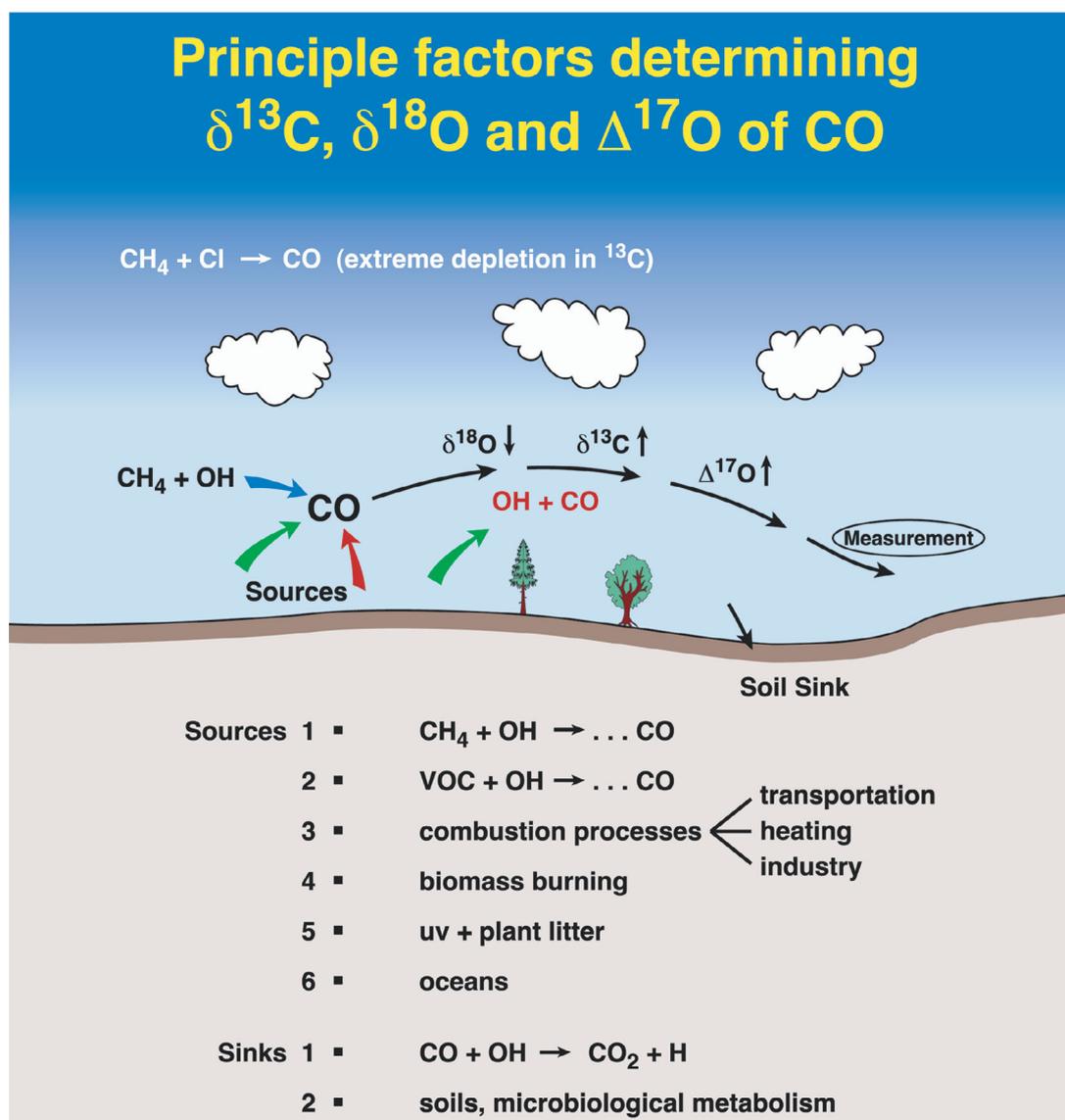
Since then different slopes have been measured accurately and these agree with the values calculated for mass dependence. The following slopes have been determined for selected processes with enormous precisions: Waters [5] 0.528, Diffusion of water vapor [6] 0.5184, respiration [7] 0.518, minerals [8] 0.5247.

Going into more and more detail, one started to consider where in a molecule the isotopic substitution has taken place. The best example is nitrous oxide,  $\text{N}_2\text{O}$ . Being structurally  $\text{NNO}$ , a  $^{15}\text{N}$  atom can be in position one or position two [9]. These two isotopomers are these days routinely measured and give valuable additional information for the complex cycle of  $\text{N}_2\text{O}$ .

Going even further, recently one has started to seriously address with careful measurements questions like “is the  $^{18}\text{O}$  content of  $^{13}\text{CO}_2$  is the same as that of  $^{12}\text{CO}_2$ ?” This is now called “Clumped Isotope Analysis” (CIA [10]). Thereto, in a mass spectrometer, not merely the common masses 44, 45 and 46 are to be measured, but also mass 47. This is only one example. The question is how to use deviations from non-stochastic (statistical) distributions of isotopes.

Not discussed here is the fairly extensive work on D and  $^{18}\text{O}$  in  $\text{H}_2\text{O}$ . Traditional use was for hydrological applications. Presently, also using measurements by sensors on satellites, work focuses on climate aspects and transport of  $\text{H}_2\text{O}$  into the stratosphere. Amazing discoveries and applications have been made by Luz, Barkan and co-workers [11]. A range of subtle mass dependent effects have been studied, giving the traditional MD fractionation effects a new lease on life. The interested reader is referred to their extensive, accurate, often amazing work on processes of diffusion, evaporation and plant physiological processes.

After having outlined the essentials of isotope effects, the straightforward way to introduce and briefly discuss atmospheric applications is to visit the trace gases for which isotope analyses



**Fig. 1.** Schematic to illustrate the use of isotopic information to study the atmospheric cycle and budgets of trace gases, here CO. Fractionation processes “inside” the sources determine the “source signature”. This can be complex reactions, for instance the oxidation processes of isoprene. Not all fractionation processes inside this source of CO are known, but characteristic values are expected, which may depend however on temperature and levels of NO<sub>x</sub>. Also CO from biomass burning has isotopic compositions depending on a host of processes. As indicated CH<sub>4</sub> + Cl produces CO strongly depleted in <sup>13</sup>C (by about - 80‰). This provides an excellent method to check for the importance of this reaction in the marine boundary layer as it has already been identified in the stratosphere (during ozone hole conditions). The mix of CO from the different sources is modified by the kinetic fractionation in reaction with mainly OH, and to complicate the issue, fresh CO is added continuously from CH<sub>4</sub> oxidation and the other sources. Few air masses remain isolated. Here the help of modellers is really needed to figure out the complex interplay. Also source studies are needed for many such applications as illustrated here.

are being done, or will be done in the near future. Some effects are rather complex, yet can be fascinating.

Finally it is noted that correction factors in mass spectrometry have received much attention [12,13] in view of the ever smaller effects studied.

## Hydrogen, mass 2, H<sub>2</sub>, HD

Atmospheric hydrogen has a lifetime of  $\sim 1.4$  year and a concentration of 0.5 ppmv. It is produced in the atmosphere mainly by the photolysis of formaldehyde (HCHO) which itself is an incompletely oxidized intermediate compound. Hydrogen also is emitted by surface sources, namely fossil fuel combustion, biomass burning, nitrogen fixation and oceans. It is removed by hydrogen atom extraction in  $\text{OH} + \text{H}_2$ , but rather slowly. This photochemical sink can be directly calculated because we know OH and the reaction rate constant. However, the removal by soils is complex. Sources are likewise hard to estimate.

An increase in H<sub>2</sub>, may lead to an increase of this gas in the stratosphere, where it is oxidized to water. Increased water in the stratosphere is undesirable because of cloud formation with various bad consequences (ozone loss on polar stratospheric cloud ice particles). This is of potential concern as H<sub>2</sub> has been considered as an energy carrier in the future. The idea that car engines using H<sub>2</sub> would mainly emit H<sub>2</sub>O (not the greenhouse gas CO<sub>2</sub>) has appealed to politicians (cars “running” on water) and some funding has been made available for research.

Hydrogen does not decrease with altitude crossing from the troposphere into the stratosphere. This strange effect is mainly caused while H<sub>2</sub> is still formed from CH<sub>4</sub> oxidation in the stratosphere, but the effective soil sink is missing here. Thus a weaker source, but concomitantly a much weaker sink. Also strange is the strong D enrichment in the stratosphere which was modelled by Mar et al. [14] after measurements had revealed this effect. The entire process tracing isotopic composition of H<sub>2</sub> produced via HCHO starting with CH<sub>4</sub> is complex.

Rhee et al. [15] used D/H measurements of tropospheric H<sub>2</sub> collected by aircraft to calculate the overall D enrichment. This enrichment is a linear combination of the small enrichment caused by fractionation in the large soil sink ( $\sim 88$  Tg/yr), and the large fractionation by the smaller photochemical sink  $\text{H}_2 + \text{OH}$  ( $\sim 19$  Tg/yr). Because the abundance of OH and the large fractionation (0.58) are known, and because the soil fractionation (only 0.943) is known, the soil sink strength can be calculated. This is a clear example of the use of stable isotopes for trace gas budgets.

It is expected that more isotope measurements of atmospheric H<sub>2</sub> and sources of H<sub>2</sub> will be conducted in the near future for the purpose of better understanding its budget. As Rhee [15] pointed out, global warming increases the soil sink strength, which has to be monitored. Here isotope analyses can truly help to distinguish between changes in sources and sinks.

## Methane, mass 16, CH<sub>4</sub>, <sup>13</sup>CH<sub>4</sub> and CDH<sub>3</sub>

Methane has a lifetime of  $\sim 9$  years and a concentration of  $\sim 1.75$  ppmv. It is emitted by surface sources, namely wetlands, rice paddies, ruminants (all because of anaerobic bacterial processes) and fossil fuel related sources (e.g. coal mining) and combustion and biomass burning. Sources are manifold and difficult to quantify. It is mainly removed by  $\text{OH} + \text{CH}_4$ .  $\text{Cl} + \text{CH}_4$  is a minor sink, that needs further quantification.

The increase in CH<sub>4</sub> harbours 3 concerns. 1) It is a greenhouse gas with an impact comparable to that of CO<sub>2</sub>. 2) It acts like a “Trojan Horse” that upon entering the stratosphere delivers, by oxidation, H<sub>2</sub>O in the stratosphere. More moisture here leads to changes in temperatures and ice cloud formation causing ozone losses. 3) It is throughout the atmosphere the main reaction partner of OH (the atmosphere’s natural powerful bleaching agent). It burdens this oxidative capacity. If we can better control the emissions of this gas, humankind would book another tangible progress in abating global change.

Important is the history of CH<sub>4</sub> variations in the Earth’s atmosphere in relation to past climate changes. These variations can be measured in air extracted for ice core sections. This information from the past is so valuable that isotopic analysis of CH<sub>4</sub> is mandatory. Thus studying the present isotopic composition of all sources implies that we can better unravel the past, including possible changes in climate triggered or driven by methane [16].

CH<sub>4</sub> transported into the stratosphere is there gradually oxidized away by OH, O(<sup>1</sup>D) and Cl. All three H abstracting reactions have different fractionation constants. Models show a good agreement with data for <sup>13</sup>C changes. In the troposphere only OH is important. New Zealand

researchers have reported that they have seen evidence for the reaction with Cl, which induces a large KIE. However this needs further confirmation. There are too few D measurements for atmospheric CH<sub>4</sub> a problem that needs to be addressed. The link with OH is of importance because a change in OH would change <sup>13</sup>C and D in CH<sub>4</sub>. Conversely, these may allow conclusions about variations in OH. Most applications try to use <sup>13</sup>C and D to better estimate the many sources of CH<sub>4</sub>. It is expected that isotope analysis of atmospheric CH<sub>4</sub> will be continued, although some programs were terminated.

### **Carbon monoxide, CO, mass 28, <sup>13</sup>CO, C<sup>17</sup>O, C<sup>18</sup>O, <sup>13</sup>C<sup>18</sup>O**

CO has a lifetime of weeks to months depending on latitude and season. Therefore temporal and spatial variations are large being between 35 (Antarctic summer) and 200 ppbv (Arctic winter). The turnover of CO at ~2600 Tg per year is larger than that of CH<sub>4</sub>. Sources are fossil and biofuel fuel combustion, biomass burning, forest and savanna fires. Large inter-annual variations occur (e.g. during El Niño years with more biomass burning). CO also is produced in the atmosphere in the photochemical oxidation of CH<sub>4</sub> and other hydrocarbons. About 5% of CO is removed by soils, with CO + OH being the main sink. This pressure dependent reaction has been extensively studied, but is not yet fully understood.

An increase in CO does burden the OH based oxidative capacity of the atmosphere. However, it seems that the CO increase has been less vigorous in recent years. Fuel efficiency, catalytic converters, increased use of methane play a role here. This is good news because CH<sub>4</sub> may be removed faster when CO emission decrease. The diatomic molecule CO itself has no significant greenhouse properties.

The multiple sources, the OH sink, the large turnover, the large variability all render CO isotope analysis useful. If future work shows that CO remains trapped in ice cores without being slowly modified or contaminated, there are exciting possibilities to reconstruct aspects of past atmospheric chemistry. The carbon KIE for CO + OH is small. However  $\delta^{13}\text{C}(\text{CO})$  varies between -31 and -25‰. Low values occur at the end of summer, when CO values are low and the relative fraction of CH<sub>4</sub> derived CO peaks. Given that the KIE in CH<sub>4</sub> + OH is ~ -5‰ and that  $\delta^{13}\text{C}(\text{CH}_4) = -47\text{‰}$ , CH<sub>4</sub> derived CO is with -52‰ well below that of organic matter. This explains the large seasonal cycle in <sup>13</sup>C.

The seasonal cycle for <sup>18</sup>O also is large, but here the KIE is the main driving mechanism. Interestingly in CO + OH, C<sup>18</sup>O reacts almost 10 times per thousand faster. The further away from sources, the more depleted the remaining CO becomes. In autumn  $\delta^{18}\text{O}$  has reached its lowest values. Not known is however  $\delta^{18}\text{O}$  of CO from CH<sub>4</sub> oxidation. In view of the complex calculations needed, laboratory experiments are advisable [17].

May the inverse isotope effect for C<sup>18</sup>O be surprising, the behavior of <sup>17</sup>O in relation to <sup>18</sup>O is a true mystery. Atmospheric measurements show that C<sup>17</sup>O behaves more normal in that it has a weak KIE, and not inverse. Laboratory experiments of this reaction have shown that the common mass dependence is violated.

It is expected that isotope analyses of atmospheric CO will continue to be made in greater detail (including  $\Delta^{17}\text{O}$ ). Clumped isotope analyses of CO have been reported by Eiler's group. The prospect to apply all these isotope analyses to ice cores and firn air are good, and such would mean doing true palaeo atmospheric chemistry. The history of biomass burning and the oxidative capacity may be reconstructed to some degree. There is no other such information.

### **Formaldehyde, HCHO, mass 30, HCDO, H<sup>13</sup>CHO, HCH<sup>18</sup>O**

Formaldehyde survives in the atmosphere for less than a day (not considering the extreme of polar nights). Its concentration in background air is very low (pptv) yet variability is large. Fire and combustion produce formaldehyde (incomplete combustion). The main source by far is the photochemical oxidation of CH<sub>4</sub>, but also other reduced compounds produce formaldehyde upon oxidation. Formaldehyde is photolyzed in sunlight to give either H<sub>2</sub> and CO, or H and

HCO. In the latter case no H<sub>2</sub> formation takes place. The other main sink for HCHO is reaction with OH.

Despite its importance, there are comparatively few formaldehyde concentration measurements. Moreover, measuring the isotopic composition of atmospheric HCHO is a true analytical challenge [18]. HCHO derived from CH<sub>4</sub> oxidation should be strongly depleted in <sup>13</sup>C and D. This will give a useful source signal. Also the sink reactions give information. Laboratory experiments concerning isotope fractionation caused by photolysis [19,20], and reaction with OH, Cl, Br, and NO<sub>3</sub> radicals [21] have been carried out. Normal and inverse isotope effects were observed. This is of interest in the fundamental theoretical work of understanding isotope effects. A practical application is in understanding the isotopic composition of H<sub>2</sub> in the troposphere and stratosphere [14].

It is expected that few, if any, larger sets of the isotopic composition of atmospheric HCHO will become available due to the great analytical difficulty. Optical (*in situ*) measurements would have a better chance.

### Ethane, mass 30, C<sub>2</sub>H<sub>6</sub>, <sup>13</sup>CCH<sub>6</sub>, C<sub>2</sub>DH<sub>5</sub> (and other hydrocarbons)

Hydrocarbons form a family of mostly anthropogenic trace gases having short lifetimes (ethane is comparable to CO) and serving as tracers for chemistry and transport. Their concentrations are below 0.5 ppb, their lifetimes are short to very short (e.g. C<sub>5</sub>H<sub>12</sub>), and their impact on chemistry small. Nevertheless their cycles should be understood. As tracers that are continuously oxidized at differing rates they allow estimates of the photochemical ages of air masses, and in some cases they give information of whether Cl or Br played a role or not. Isoprene, which is emitted in large quantities by vegetation is of importance to atmospheric chemistry. It reacts with O<sub>3</sub> and OH, but only few <sup>13</sup>C studies are known.

Anticipating their use as tracers, the group of Rudolph [22] has carried out many laboratory studies on the kinetic isotope effects of hydrocarbons. Applications have been made using <sup>13</sup>C by Yoshida [23] and his group. The budgets of these gases over the ocean have been studied. Reactions with OH and Cl can be studied when one considers an air mass as an isolated unit from which a hydrocarbon disappears.

The inherent useful aspect of stable isotope is that, unlike the traditional use of a set of different hydrocarbons, only one hydrocarbon has to be considered on its own. This means that one has eliminated uncertainties concerning a change in the emission ratios within the set hydrocarbons. The concept “chemical clock” has been introduced. The isotope ratio changes are for a single species. Surprisingly, as Rudolph [24] showed, small fractionation factors are more useful than large fractionation factors. We refer to the original paper for an explanation. This aspect is not intuitive. On the other hand, large isotope effects show clear signals, and it is hoped that there will be more D/H hydrocarbon studies despite their greater analytical difficulty.

### Oxygen, O<sub>2</sub>, mass 32, <sup>18</sup>OO, <sup>17</sup>OO

There is a long standing interest in atmospheric molecular oxygen. Its lifetime is ~10<sup>3</sup> years, being produced by photosynthetic plants and consumed by respiration, burning and combustion. The <sup>18</sup>O(O<sub>2</sub>) enrichment of 23.5‰ (V-SMOW) is named the Dole effect. Its cause lies mainly in respiration that discriminates “consumption” of <sup>18</sup>OO by ~20‰. Understanding the isotopic composition of O<sub>2</sub> requires global models incorporation the biosphere [25].

Presently a discussion is taking place about the strange effect that O<sub>2</sub> has a small deficiency of <sup>17</sup>O. To discover this effect one obviously needs oxygen from a different source that is “normal”. Air O<sub>2</sub> is “Mass Independent” fractionated. How is it possible that such a large reservoir is isotopically “corrupted”? The reason is that a very small fraction of O<sub>2</sub> is continuously being converted to O<sub>3</sub>, which has about the same enrichment in <sup>17</sup>O as <sup>18</sup>O (see O<sub>3</sub>). In the stratosphere a fraction of O<sub>3</sub> is photolysed in a way to that produces energetic O atoms (O(<sup>1</sup>D)) that can react with CO<sub>2</sub> to CO<sub>3</sub> and back to CO<sub>2</sub> and O. In this the <sup>17</sup>O excess is

transferred to some degree to  $\text{CO}_2$ . This in turn exchanges O isotopes with  $\text{H}_2\text{O}$  (leaf, soil and ocean water mainly), which constitutes a huge reservoir [26,27]. In effect, an excess of  $^{17}\text{O}$  is taken from the large  $\text{O}_2$  reservoir and deposited in the very large  $\text{H}_2\text{O}$  reservoir, thus depleting air  $\text{O}_2$  in  $^{17}\text{O}$ . There is a discussion whether this photochemical effect is the only source of the  $^{17}\text{O}$  depletion and the interested reader must carefully consult the various papers on this complex issue.

### **Nitrous oxide, $\text{N}_2\text{O}$ , mass 44, $^{15}\text{NNO}$ , $\text{N}^{15}\text{NO}$ , $\text{NN}^{17}\text{O}$ , $\text{NN}^{18}\text{O}$**

$\text{N}_2\text{O}$  has a lifetime of roughly 100 years and a concentration of presently  $\sim 320$  ppbv, tendency rising. Given the long lifetime it has a very weak seasonal cycle, and the same obviously applies to isotopic changes. Sources are oceans and soils and to a lesser degree combustion processes. Its sink is in the stratosphere, where it decreases with altitude. It undergoes 2 processes here, one is photolysis to  $\text{NO}$  and  $\text{O}$ , or  $\text{N}_2$  and  $\text{O}$ , the other is reaction with  $\text{O}(^1\text{D})$  to 2  $\text{NO}$  molecules. All  $\text{N}_2\text{O}$  produced at the surface of the planet must be “digested” through these reaction channels taking place in harsh photochemical environment of the stratosphere.

The concern about the increase in  $\text{N}_2\text{O}$  due to land use changes and the use of fertilizers is twofold. It is a long lived greenhouse gas. Second, the production of  $\text{NO}$  in the stratosphere affects ozone levels there.

There has been enormous progress in stable isotope studies of  $\text{N}_2\text{O}$ , covering source process (which are very complex), lab studies, and many atmospheric measurements in the stratosphere and troposphere. As a result, the budget of  $\text{N}_2\text{O}$  has indeed become very much better known. Known are today, the  $^{15}\text{N}$  isotopic composition for both positions in the molecule (2 isotopomers), the  $^{18}\text{O}$  composition, and a small degree of MIF. In the latter case it is difficult to discern the true cause for a small excess in  $^{17}\text{O}$ . Is it due to unknown sources in the atmosphere involving  $\text{O}_3$ , or due to source processes?

Like mentioned for  $\text{O}_2$ , the proper selection of a reference for  $^{17}\text{O}$  deviations (that is the proper  $\delta^{17}\text{O} - \delta^{18}\text{O}$  relationship for the relevant range of values) is important. The use of a MDF value of 0.528 (waters) will lead to apparently reduced  $\Delta^{17}\text{O}$  values compared to using commercial  $\text{N}_2\text{O}$  gases.

### **Carbon dioxide, $\text{CO}_2$ , mass 44, $^{13}\text{CO}_2$ , $\text{C}^{17}\text{OO}$ , $\text{C}^{18}\text{OO}$ , $^{13}\text{C}^{18}\text{OO}$**

This gas needs little introduction. Its main feature are the huge natural fluxes on which the unabated man made flux is superimposed. Isotope measurements have been carried out for over 5 decades, and have helped to better understand its budget. The enrichment in  $^{18}\text{O}$  and MIF that take place in the stratosphere are well understood, although fundamental work on the exchange processes involving the short lived  $\text{CO}_3$  complex continue [28].  $^{18}\text{O}$  in tropospheric  $\text{CO}_2$  is an extremely useful indicator reflecting the exchange with water in plants, soils and oceans. Changes in temperature (via the fractionation constant), in relative humidity (via the kinetic isotope effect in evaporation) and in the hydrological cycle affect  $^{18}\text{O}$  in a complex but distinct manner.  $^{13}\text{C}$  is nearly always well correlated with the inverse concentration, reflecting photosynthesis, respiration and fossil fuel related emissions. Large data sets for  $\text{CO}_2$  concentration and  $^{13}\text{C}$  and  $^{18}\text{O}$  as being established by NOAA-ESRL will indeed help to “constrain” the  $\text{CO}_2$  budget and to follow effects of man’s impact on nature.

New possibilities are based on the “clumped isotope analysis” mentioned before. Affek et al. [29] have analysed mass 47 abundances in  $\text{CO}_2$  extracted from urban air, car exhaust, and human breath. At high temperatures, thermodynamic equilibrium exists, other processes show deviations that although being small (sub per mil), may be useful.

### **Nitrogen oxides (NO), ( $\text{NO}_2$ ), nitrate**

The importance of  $\text{NO}$ , which is emitted by soils, and produced by lightning, biomass burning, and forest fires is enormous.  $\text{NO}$  governs the recycling of radicals that keep upright the oxidative

capacity of the atmosphere. When NO increases the chemistry speeds up. Given the presence of reduced gases (CO, hydrocarbons) it leads to the formation of photo chemical smog, and atmospheric chemists seem to divide the atmosphere in two regimes of low NO<sub>x</sub> (ozone loss) and high NO<sub>x</sub> (ozone producing).

Clearly, isotope studies of NO would be valuable to understand its complex chemistry. This is however, at the time being, not possible. NO concentrations are very low, and the gas reacts immediately with O<sub>3</sub>. Only sunlight forms back NO. Both NO and NO<sub>2</sub> measurements are difficult, not to mention isotope analyses. The interesting aspect is the reaction with O<sub>3</sub>, which transfers the MIF signal from O<sub>3</sub> to NO<sub>2</sub> and NO [30].

However, there is great progress in analysing nitrates, the end product of the oxidation processes. Nitrates can be collected as aerosol material on filters and are successfully subjected to <sup>17</sup>O, <sup>18</sup>O and <sup>15</sup>N analyses. Insofar nitrates do not exchange O atoms with water the signal is retained. This implies the interesting possibility to study the NO-nitrate cycle in the polar regions in the past using ice core analyses.

### **Ozone, O<sub>3</sub>, mass 48, <sup>17</sup>OO<sub>2</sub>, <sup>18</sup>OO<sub>2</sub>, O<sup>18</sup>OO, and many more**

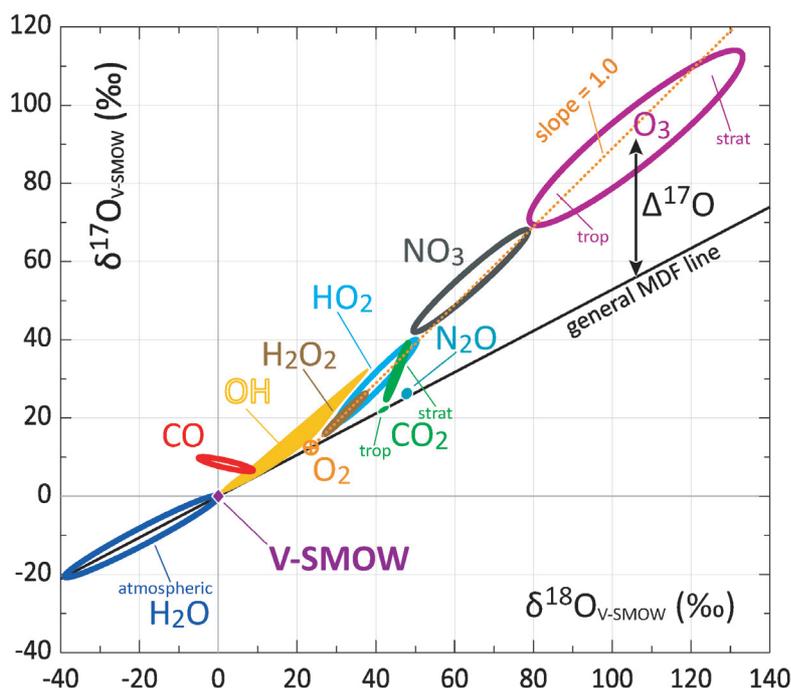
Ozone needs little introduction as its roles as a shield against UV radiation, as a greenhouse gas, as a precursor of OH, and as pollutant (photochemical smog) are widely documented. It is the most monitored and thoroughly studied atmospheric trace gas next to CO<sub>2</sub>. Ozone is formed by the Chapman cycle in the stratosphere and everywhere continuously photolysed at a high rate and formed back by O reacting with O<sub>2</sub>. This process causes a large enrichment in <sup>18</sup>O and the surprisingly almost equal enrichment in <sup>17</sup>O (MIF). This anomaly propagates through many reactions, as outlined in Figure 2. Tropospheric O<sub>3</sub> arises from import from the stratosphere while the photolysis of NO<sub>2</sub> to NO and O is the sole *in situ* source. Temperature and pressure differences are the causes for differences in isotopic composition between tropospheric and stratospheric O<sub>3</sub>.

Isotope measurements of tropospheric O<sub>3</sub> are hauntingly difficult, because it is so difficult to separate it from air quantitatively. Only 2 experiments are known. Two main aspects about O<sub>3</sub> isotope research are to be mentioned. One is that Mauersberger and his group [31] have carried out the most extensive and precise measurements of ozone formation reactions using all sorts of isotope mixtures. Enormous differences in reaction rate constants have been documented. The other is progress in theoretical studies by Markus and co-workers [32] on explaining the enigmatic enrichment of O<sub>3</sub>. The enrichment of the terminal positions is higher than the overall enrichment. This is of relevance for the transfer of MIF to molecules reacting with O<sub>3</sub>.

### **Methyl chloride, CH<sub>3</sub>Cl, mass 50, <sup>13</sup>CH<sub>3</sub>Cl, CDH<sub>2</sub>Cl, CH<sub>3</sub><sup>37</sup>Cl and many more**

The lifetime of methylchloride is ~1 year. This number is almost as well known as that of methane. The reason is that they share their main sink, namely OH. Methylchloride has a concentration of about 550 pptv. It is emitted by mainly plants, biomass burning, oceans, fungi, salt marshes, coal combustion, wetlands and lesser sources. Special about methylchloride is that it is chiefly produced and consumed in the tropics. This means that it there has a high turnover, and large variability (shorter local lifetime). Tropical values tend to be higher than those at mid and higher latitudes, indicating an excess production there.

There is no special concern about this gas. In the natural atmosphere, devoid of man made halocarbon emissions, methylchloride is the natural supplier of Cl to the stratosphere (where this acts as ozone destructing agent). Obviously, when we consider the uncertainty about the budget of methane (a major greenhouse gas), it is no surprise that the budget of methylchloride is shrouded in uncertainty. Here isotope analyses may certainly help [33]. Interestingly one can study 3 elements in this interesting molecule. However, current research focused on <sup>13</sup>C. A major surprise was that the KIE in CH<sub>3</sub>Cl + OH is large. For CH<sub>4</sub> the KIE is less than 5‰. For CH<sub>3</sub>Cl has been reported to be close to 60‰. It is intuitively unexpected that the abstraction of an H atom from this molecule would be 6% more “difficult” when <sup>13</sup>C replaces <sup>12</sup>C.



**Fig. 2.** This nice diagram (sometimes called a 3 isotope plot for oxygen) shows  $\delta^{17}\text{O}$  relative to  $\delta^{18}\text{O}$  in a simplified form. The proper parameters to be plotted are  $\ln(1 + \delta)$  values. Values indicated are based on atmospheric measurements, and on model results by Sergey Gromov. In the past it has been difficult at times to use isotopic information. Presently however, modelling studies help quantitative applications enormously. The results even show the oxygen isotopic composition of OH, the very short lived natural bleaching agent of the Earth's atmosphere. OH measurements belong to the most difficult measurements, yet, models enable a detailed understanding of the chains of isotopic processes in the atmosphere. Apart from  $\text{H}_2\text{O}$  (physics only), all effects are traceable to mainly chemical effects. The general Mass Dependent Fractionation line has nominal slope 0.5, but for different processes, the actual values have been calculated and measured, often with surprisingly great precision. This has allowed new applications of mass dependent fractionation. Today we much better know the mass dependence than before. If there are deviations, we have – as Weston points out – to see if it due to different mass dependent processes, or to true deviation. For instance the strange behaviour of CO is due to the MIF in the removal reaction  $\text{CO} + \text{OH}$ . Laboratory measurements of this reaction and atmospheric observations leave no doubt about the role of OH. Work is in progress right now by Markus and co-workers to find the theoretical description of the isotope effects in  $\text{CO} + \text{OH}$ . Also Weston works on this tantalizing problem. All other effects shown here may well be due to MIF originating in ozone propagating through the complex reaction schemes. This picture shows that there are many aspects of the oxygen cycle in atmospheric trace gas budgets to be studied.

It is desirable that considerably more isotope studies are devoted to  $\text{CH}_3\text{Cl}$ . For  $\text{CH}_3\text{Br}$ , a close relative of this molecule, several isotope studies have been published. For  $^{13}\text{C}$  studies the gases are combusted to  $\text{CO}_2$ . For D one expects a priori very large effects because only 3 H atoms are present. For D studies, pyrolysis to  $\text{H}_2$  is needed. Cl isotopes can be studied by using this gas directly with a suitable configuration of ion collectors in the mass spectrometer. In fact, Cl isotopes in minerals and groundwater have been studied by converting Cl to  $\text{CH}_3\text{Cl}$  for mass spectrometry.

### Carbonyl sulfide, $\text{COS}$ , mass 60, $^{13}\text{COS}$ , $\text{C}^{17}\text{OS}$ , $\text{CO}^{36}\text{S}$ and many more

COS is a most interesting trace gas, somewhat similar to  $\text{CO}_2$ , but chemically active. It has a lifetime of  $\sim 2$  years and an average concentration of  $\sim 480$  ppbv. COS is mainly produced

by oxidation of oceanic CS<sub>2</sub> and DMS, and other sulphurous compounds natural and anthropogenic. Direct emissions from biomass burning also are relevant. COS is removed by plants, through oxidation by OH and by soils. Like CO<sub>2</sub> it enters stomata upon which a large fraction is irreversibly lost by hydrolysis accelerated by enzymes. The remaining smaller sink is destruction in the stratosphere through its photolysis. This in turn is a major source of ultimately sulphate, which forms a layer of aerosol known as the Junge layer. In the absence of strong volcanic eruptions (like Mt. Pinatubo in 1991) COS and SO<sub>2</sub> entering the stratosphere maintain the Junge layer. The COS budget calculations, which differ strongly between the southern and northern hemisphere, have uncertainties and could benefit from isotope studies.

It is desirable that isotope studies are devoted to COS. Its sink reaction in plant leaves render information about COS particularly useful with regard to CO<sub>2</sub> fluxes. Analytically the main challenge is its separation from CO<sub>2</sub> prior to isotope analysis. COS can be combusted to CO<sub>2</sub> and SO<sub>2</sub> for isotope analyses on the basis of these gases. Direct analysis of COS (mass 60) may be more rewarding, giving information on <sup>13</sup>C, <sup>17</sup>O and <sup>33</sup>S (mass 61), <sup>18</sup>O, <sup>34</sup>S and <sup>33</sup>S + <sup>17</sup>O (mass 62). We leave it to the reader to combine all masses (2 for C, 3 for O and 4 for S) to find its isotopologues, and to see if the system is determined. If ion collectors for 60, 61, 63 and 63 etc. are not sufficient, fragment ion analysis may help to clarify things like was done for N<sub>2</sub>O [9].

### 3 Conclusions

This brief overview explaining the role of trace gases and the scope of isotope analyses should be a compact guide to assess and identify applications. Some promising isotope applications are signalled, which are very much worthwhile to pursue, not only for “constraining” trace gas budgets, but for understanding sink and source processes and may be discovering new effects. Not all gases are mentioned, for instance H<sub>2</sub>O<sub>2</sub>. It is noted that sophisticated modelling of isotope parameters in 3D chemistry-transport models of the atmosphere is increasingly becoming available. This allows quantitative applications, and shows how isotope applications have reached their “adult state”. Finally it is concluded that in particular the important reconstruction of the Earth’s atmosphere past composition, particularly concerning its oxidative state and trace gas levels using the extremely valuable ice core material, warrants detailed studies using isotopic information for the present atmosphere.

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### References

1. C.A.M. Brenninkmeijer, C. Janssen, J. Kaiser, T. Rockmann, T.S. Rhee, S.S. Assonov, *Chem. Rev.* **103**, 5125 (2003)
2. M.S. Johnson, K.L. Feilberg, P. von Hessberg, O.J. Nielsen, *Chem. Soc. Rev.* **31**, 313 (2002)
3. M.H. Thiemens, *Ann. Rev. Earth Planet. Sci.* **34**, 217 (2006)
4. R.E. Weston, *J. Nucl. Sci. Technol.* **43**, 295 (2006)
5. H.A.J. Meijer, W.J. Li, *Isotopes Environ. Health Studies* **34**, 349 (1998)
6. E. Barkan, B. Luz, *Rapid Comm. Mass Spectrom.* **21**, 2999 (2007)
7. B. Luz, E. Barkan, *Geochim. Cosmoch. Acta* **69**, 1099 (2005)
8. M.F. Miller, I.A. Franchi, M.H. Thiemens, T.L. Jackson, A. Brack, G. Kurat, C.T. Pillinger, *Proc. Nation. Acad. Sci. USA* **99**, 10988 (2002)
9. C.A.M. Brenninkmeijer, T. Rockmann T., *Rapid Comm. Mass Spectrom.* **13**, 2028 (1999)
10. J.M. Eiler, *Earth Planet. Sci. Lett.* **262**, 309 (2007)
11. A. Landais, E. Barkan, B. Luz, *Geophys. Res. Lett.* **35** (2008)
12. S.S. Assonov, C.A.M. Brenninkmeijer, *Rapid Comm. Mass Spectrom.* **19**, 627 (2005)
13. J. Kaiser, *Geochim. Cosmochim. Acta* **72**, 1312 (2008)

14. K.A. Mar, M.C. McCarthy, P. Connell, K.A. Boering, *J. Geophys. Res. Atmos.* **112** (2007) doi:10.1029/2006JD007403
15. T.S. Rhee, C.A.M. Brenninkmeijer, T. Rockmann, *Atmos. Chem. Phys.* **6**, 1611 (2006)
16. K.R. Lassey, D.M. Etheridge, D.C. Lowe, A.M. Smith, D.F. Ferretti, *Atmos. Chem. Phys.* **7**, 2119 (2007)
17. R.E. Weston, *J. Phys. Chem. A* **105**, 1656 (2001)
18. A.L. Rice, P.D. Quay, *Anal. Chem.* **78**, 6320 (2006)
19. T.S. Rhee, C.A.M. Brenninkmeijer, T. Rockmann, *Atmos. Chem. Phys.* **8**, 1353 (2008)
20. K.L. Feilberg, M.S. Johnson, A. Bacak, T. Rockmann, C.J. Nielsen, *J. Phys. Chem. A* **111**, 9034 (2007)
21. K.L. Feilberg, M.S. Johnson, C.J. Nielsen, *J. Phys. Chem. A* **108**, 7393 (2004)
22. R. Iannone, R. Koppmann, J. Rudolph, *J. Atmos. Chem.* **58**, 181 (2007)
23. H. Nara, S. Toyoda, N. Yoshida, *J. Atmos. Chem.* **56**, 293 (2007)
24. J. Rudolph, E. Czuba, *Geophys. Res. Lett.* **27**, 3865 (2000)
25. G. Hoffmann, M. Cuntz, C. Weber, P. Ciais, P. Friedlingstein, M. Heimann, J. Jouzel, J. Kaduk, E. Maier-Reimer, U. Seibt, K. Six, *Global Biogeochem. Cycles* **18** (2004) doi:10.1029/2003GB002059
26. B. Luz, E. Barkan, M.L. Bender, M.H. Thiemens, K.A. Boering, *Nature* **400**, 547 (1999)
27. J.R. Lyons, *Geophys. Res. Lett.* **28**, 3231 (2001)
28. K.A. Boering, *Geochim. Cosmochim. Acta* **69**, A444 (2005)
29. H.P. Affek, X.M. Xu, J.M. Eiler, *Geochim. Cosmochim. Acta* **71**, 5033 (2007)
30. J. Savarino, S.K. Bhattacharya, S. Morin, M. Baroni, J.F. Doussin, *J. Chem. Phys.* **128** (2008) doi:10.1063/1.2917581
31. C. Janssen, *J. Geophys. Res. Atmos.* **111** (2006) doi:10.1029/2006JD007768
32. R.A. Marcus, Mass-independent oxygen isotope fractionation in selected systems. Mechanistic considerations in *Advances in Quantum Chemistry: Applications of Theoretical Methods to Atmospheric Science* (2008), pp. 5–19
33. F. Keppler, D.B. Harper, T. Rockmann, R.M. Moore, J.T.G. Hamilton, *Atmos. Chem. Phys.* **5**, 2403 (2005)