Tellus (1987), *39B*, 96–99

Measurement of the N_2O correction for $^{13}C/^{12}C$ ratios of atmospheric CO_2 by removal of N_2O

By WILLEM G. MOOK and JAAP JONGSMA, *Isotope Physics Laboratory, University of Groningen, Westersingel 34, 9718 CM Groningen, The Netherlands*

(Manuscript received April 21; in final form August 21, 1986)

ABSTRACT

Measured $^{13}\delta$ and $^{18}\delta$ values of atmospheric CO_2 extracted from air samples by condensation in liquid nitrogen have to be corrected for the presence of N_2O which interferes with the mass spectrometric analysis. The theoretically-derived correction anticipated previously is now confirmed by measurements after complete removal of N_2O.

1. Introduction

Carbon dioxide is easy to extract from air samples cryogenically. The disadvantage of this method is that N_2O is also condensed in the liquid nitrogen trap. However, the alternative procedure, CO_2 absorption in an alkaline solution, ruins the $^{18}O/^{16}O$ ratio by exchange with water, while large isotope fractionation occurs if the CO_2 extraction from the air sample is incomplete. N_2O has isotopic masses equal to those of CO_2, and consequently causes a discrepancy between measured and true 45/44 and 46/44 ratios in the mass spectrum (Craig and Keeling, 1963).

According to Weiss (1981) and Weiss et al. (1981), the N_2O/CO_2 ratio was $(0.89 \pm 0.01) \times 10^{-3}$ by January 1, 1978, decreasing by about 0.2% per year, due to a CO_2 increase in excess of the N_2O increase.

Taking this number, the resulting calculated effects on $^{13}\delta$ and $^{18}\delta$ are 0.31‰ and 0.44‰, respectively, making the measured values too negative. However, Mook and Van der Hoek (1983) observed that the mass-44 ion production efficiency in the ion source is 0.73 times smaller for N_2O than for CO_2. Therefore, they concluded that the corrections should rather be +0.23‰ and 0.33‰. These values were confirmed by measurements made on artificial $CO_2 + N_2O$ mixtures. They did not manage, however, to confirm these correction values by analysing actual atmospheric CO_2 samples before and after removal of N_2O. It now turns out that their procedure of removing N_2O by passing the samples once through copper pellets at 650°C was not sufficiently efficient. Moreover, they did not check the efficiency by an independent method. This has now been performed by measuring the relative ratio of the mass-30 peak involving $^{12}C^{18}O^+$ and $^{14}N^{16}O^+$ ions to the mass-44 peak (Moore, 1974). An efficient procedure for N_2O removal was found in circulating the sample during a certain period of time through hot copper by the action of a small circulation pump.

2. Experimental procedure

The system used for N_2O removal is shown schematically in Fig. 1. After isotopic analysis and measurement of the mass-30 and mass-44 peaks, 1–2 ml of CO_2 sample containing N_2O ($\sim$1‰) is circulated for 15 min through copper pellets at 650°C, after which CO_2 is frozen and N_2 pumped off. Below 600°C, the reducing action of copper turned out to be less efficient. Again, the isotopic composition is determined as well as the mass-30/mass-44 peak ratio. The $^{18}O/^{16}O$ ratio is destroyed by this procedure and is therefore no longer meaningful. The results of a series of atmospheric CO_2 samples, part of our

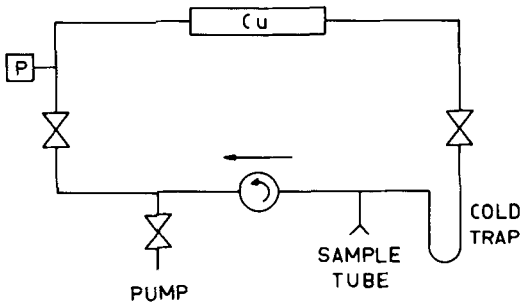

Fig. 1. Vacuum line for complete removal of N_2O from air-CO_2 samples (P = pressure gauge). An amount of 1–2 ml of sample is circulated by a small pump through copper (0.5 × 4 mm pieces of wire) at 650°C for 15 min after which CO_2 is condensed in the cold trap and N_2 pumped off. Length of Cu filling = 150 mm, tube diameter = 8 mm.

CO_2 project with Dr. C. D. Keeling, are shown in Table 1. The mass ratio 30/44 has to be corrected for the presence of $^{12}C^{18}O^+$ fragments in the mass spectrum of pure CO_2.

A prepared $N_2O + CO_2$ mixture with a volumetrically determined N_2O/CO_2 ratio serves to calculate the N_2O/CO_2 ratio of the samples, according to

$$(N_2O/CO_2)_s = \frac{(30/44)_s - (30/44)_{CO_2}}{(30/44)_{std} - (30/44)_{CO_2}} (N_2O/CO_2)_{std}, \quad (1)$$

where the subscripts s, std and CO_2 refer to the samples, the calibrated standard gas, and pure CO_2, respectively. Table 1 shows that the measured N_2O/CO_2 ratios are close to those

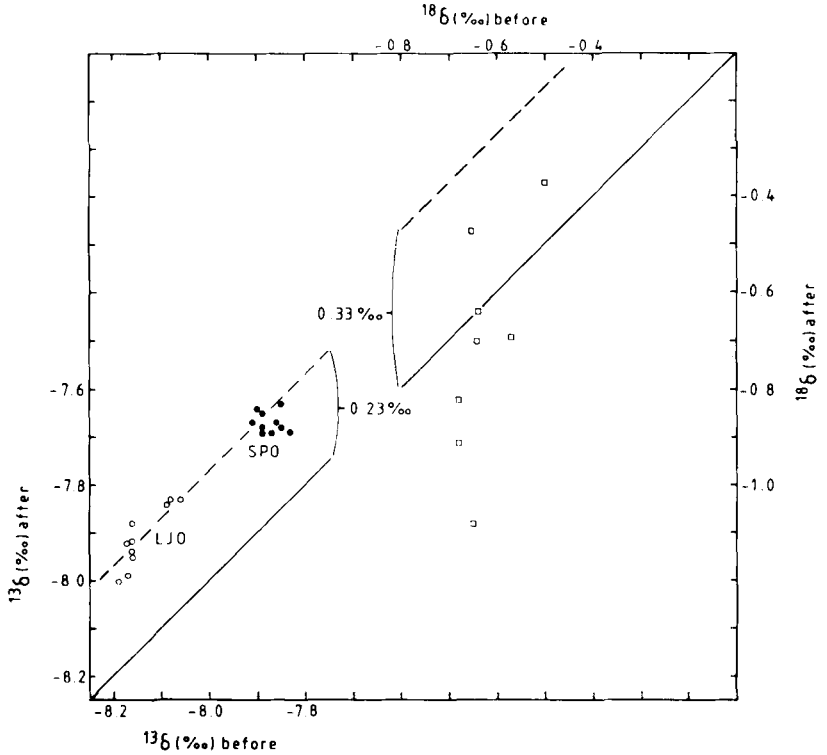

Fig. 2. Comparison of $^{13}\delta$ values (lower left-hand scales) and $^{18}\delta$ values (upper right-hand scales) of atmospheric CO_2 cryogenically extracted from air samples, before and after removal of N_2O. Series of samples from the Scripps Institution of Oceanography (LJO) and the South Pole (SPO) were provided by C. D. Keeling. The dashed lines indicate the theoretical N_2O corrections of +0.23‰ for ^{13}C and +0.33‰ for ^{18}O. The latter values are obviously destroyed by the hot copper treatment.

Table 1. *$^{13}\delta$ and $^{18}\delta$ values (in ‰) versus PDB and mass-30/mass-44 ion beam ratios of atmospheric CO_2 samples from LJO (Scripps Institution of Oceanography) and SPO (South Pole) before and after removal of N_2O*

	Before N_2O removal				After N_2O removal				Correction	
Sample	$^{13}\delta$	$^{18}\delta$	30/44 ($\times 10^{-6}$)	N_2O/CO_2 (ppm)[1]	$^{13}\delta$	$^{18}\delta$	30/44 ($\times 10^{-6}$)	N_2O/CO_2 (ppm)	$\Delta^{13}\delta$ calc.[2]	$\Delta^{13}\delta$ obs.[3]
K85-205	−8.09	−0.68	315	909	−7.84	−0.82	156		0.227	0.25
K85-206	−8.06	−0.65	299	818	−7.83	−0.47	156		0.205	0.23
K85-208	−8.08	−0.65	312	892	−7.83	−1.08	157		0.223	0.25
K85-209	−8.19	−0.64	310	881	−8.00	−0.64	155		0.220	0.19
K85-210	−8.16	−0.68	308	869	−7.95	−0.91	156		0.217	0.21
K85-211	−8.16	−0.57	307	864	−7.94	−0.69	153		0.216	0.22
K85-212	−8.16	−0.50	307	864	−7.88	−0.37	155		0.216	0.28
K85-214	−8.16	−0.64	307	864	−7.92	−0.70	152		0.216	0.24
K85-215	−8.17	−0.63	304	847	−7.99	+1.33	194*	222	0.156*	0.18*
K85-216	−8.17	−0.70	306	858	−7.92	−2.78	199*	250	0.152*	0.25*
Calibr.			290	767						
Average K85 series from LJO							155		0.218 ±0.002	0.234 ±0.010
K86-172	−7.96	+0.51	326	909	−7.75	−0.19	168		0.228	0.21
K86-173	−7.92	+0.56	326	909	−7.75	−0.60	166		0.228	0.17
K86-174	−7.98	+0.53	328	920	−7.71	+0.10	167		0.230	0.27
K86-175	−7.94	+0.51	329	926	−7.69	−0.54	167		0.232	0.25
K86-176	−7.97	+0.55	331	937	−7.73	−1.11	163		0.235	0.24
K86-177	−7.95	+0.58	330	932	−7.74	−0.16	163		0.233	0.21
K86-178	−7.91	+0.40	331	937	−7.74	−1.11	165		0.235	0.17
K86-179	−7.92	+0.49	329	926	−7.73	+0.42	166		0.232	0.19
K86-180	−7.96	+0.55	329	926	−7.70	−0.08	167		0.232	0.26
K86-181	−7.95	+0.56	330	932	−7.75	+0.23	166		0.233	0.20
Calibr.			301	767						
Average K86 series from SPO							166		0.232 ±0.001	0.217 ±0.011

[1] From eq. (1).
[2] From eq. (2).
[3] By subtracting columns 2 and 6.
* Cu furnace ineffective; values deleted from average.
The mass-44 beam currents were adjusted to 4×10^{-9} A. The volumetrically prepared calibration sample has a N_2O/CO_2 ratio of 767 ppm.

reported by Weiss et al. (1981). These ratios refer to ρ in the general equation of Mook and Van der Hoek (1983):

$$\Delta^{13}\delta = (343 \pm 6)\rho E,$$
$$\Delta^{18}\delta = (497 \pm 6)\rho E, \quad (2)$$

used to calculate the required N_2O correction. E is the mass-44 ion yield ratio from equal inlet pressures of N_2O and CO_2, which for our instruments (VG micromass 903 and VG SIRA 9) is 0.73. Observed $^{13}\delta$ values of 2 series of samples before and after removal of N_2O are shown in Fig. 2. The calculated corrections are given in Table 1, together with the observed shift in $^{13}\delta$ by removal of N_2O (last column). Obviously the $^{18}\delta$ values, shown for the LJO series, are seriously affected by the hot copper treatment. The agreement between observed and theoretical $^{13}\delta$ shift is very good, from which we conclude that it is

justified to correct all $^{13}\delta$ as well as $^{18}\delta$ values on atmospheric CO_2 by:

$$\Lambda^{13}\delta = +0.23‰, \qquad \Lambda^{18}\delta = +0.33‰, \tag{3}$$

on any instrument, provided the 44-ion yield ratio of N_2O and CO_2 is about 0.7. This number was also observed by Siegenthaler (pers. comm.) and by Francey (pers. comm.). It is obvious that only variations in the N_2O/CO_2 ratio exceeding 5%, related to seasonal, latitudinal or secular changes, affect the N_2O correction significantly (more than 0.01‰). In continental air samples with much higher CO_2 concentrations, the correction may therefore deviate from the numbers in eq. (3).

REFERENCES

Craig, H. and Keeling, C. D. 1963. The effects of atmospheric N_2O on the measured isotopic composition of atmospheric CO_2. *Geochim. Cosmochim. Acta 27*, 549–551.

Mook, W. G. and Van der Hoek, S. 1983. The N_2O correction in the carbon and oxygen isotopic analysis of atmospheric CO_2. *Isot. Geosci. 1*, 237–242.

Moore, H. 1974. Isotopic measurement of atmospheric nitrogen compounds. *Tellus 26*, 169–174.

Weiss, R. F. 1981. The temporal and spatial distribution of tropospheric nitrous oxide. *J. Geophys. Res. 86*, 7185–7195.

Weiss, R. F., Keeling, C. D. and Craig, H. 1981. The determination of tropospheric nitrous oxide. *J. Geophys. Res. 86*, 7197–7202.