

# Measurement of changes in atmospheric Ar/N<sub>2</sub> ratio using a rapid-switching, single-capillary mass spectrometer system

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(Manuscript received 8 May 2003; in final form 13 April 2004)

## ABSTRACT

The atmospheric Ar/N<sub>2</sub> ratio is expected to undergo very slight variations due to exchanges of Ar and N<sub>2</sub> across the air–sea interface, driven by ocean solubility changes. Observations of these variations may provide useful constraints on large-scale fluxes of heat across the air–sea interface. A mass spectrometer system is described that incorporates a magnet with a wide exit face, allowing a large mass spread, and incorporates an inlet with rapid (5 s) switching of sources gases through a single capillary, thus achieving high precision in the comparison of sample and reference gases. The system allows simultaneous measurement of Ar/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> ratios. The system achieves a short-term precision in Ar/N<sub>2</sub> of 10 per meg for a 10 s integration, which can be averaged to achieve an internal precision of a few per meg in the comparison of reference gases. Results for Ar/N<sub>2</sub> are reported from flask samples collected from nine stations in a north-to-south global network over about a 1 yr period. The imprecision on an individual flask, as estimated from replicate agreement, is ±11 per meg. This imprecision is dominated by real variability between samples at the time of analysis. Seasonal cycles are marginally resolved at the extra-tropical stations with amplitudes of 5 to 15 per meg. Annual-mean values are constant between stations to within ±5 per meg. The results are compared with a numerical simulation of the cycles and gradients in Ar/N<sub>2</sub> based on the TM2 tracer transport model in combination with air–sea Ar and N<sub>2</sub> fluxes derived from climatological air–sea heat fluxes. The possibility is suggested that Ar/N<sub>2</sub> ratios may be detectably enriched near the ground by gravimetric or thermal fractionation under conditions of strong surface inversions.

## 1. Introduction

The oceans play a major role in global climate through their ability to absorb and release heat. Every year, the oceans transport around 60 ZJ (1 zetajoule = 10<sup>21</sup> J) from lower to higher latitudes in each hemisphere, thus moderating the climate differences between equator to poles; and each spring and summer the oceans at middle and high latitudes absorb around 150 ZJ and return an equivalent amount of heat to the atmosphere in the autumn and winter, thus reducing the temperature contrast between summer and winter (Peixoto and Oort, 1992). The oceans are also believed to be slowing the atmospheric response to increasing greenhouse gases by absorbing around 10 ZJ globally each year (Levitus et al., 2000, 2001). The magnitude of these heat flows, however, is still subject to considerable uncertainty, and the variations in these flows from year to year are not easily measured,

which reduces our ability to make reliable climate forecasts on various timescales.

The need for improved determinations of air–sea heat flux has fuelled the development of new measurement methods, such as technologies for expanding the coverage of ocean temperature measurements (Gille, 2002), and methods based on acoustic tomography (Munk and Wunsch, 1979; Baggeroer et al., 1998) and satellite altimetry (Cabanes et al., 2001). This need has also stimulated interest in developing a method based on measuring changes in atmospheric composition, specifically the relative abundances of N<sub>2</sub> and the inert gases Xe, Kr, Ar, Ne and He in the atmosphere. These gases are sufficiently unreactive that the total burden of each gas in the combined ocean/atmosphere system is constant to a very high level. The partitioning of these gases between the ocean and the atmosphere is, however, sensitive to ocean temperature, via the temperature dependence of the solubility (Craig and Wiens, 1996). Warmer water tends to hold less gas than colder water, so heating of the oceans results in a net release of gas to the atmosphere, while cooling causes a net uptake. This temperature effect is more pronounced for the

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heavier of these gases, which have Bunsen solubilities that are larger and more strongly dependent on temperature. The ratio of the heavy to light gases in the atmosphere (Xe/Ar, Kr/N<sub>2</sub>, Ar/N<sub>2</sub>, etc.) should therefore increase in response to ocean warming and decrease in response to ocean cooling. The effect of water temperature on the dissolved gas abundances has been exploited in palaeoclimate studies (e.g. Stute et al., 1995) but the reciprocal effect on atmospheric abundances remains largely unexplored.

Hydrographic surveys (Craig et al., 1967; Hamme and Emerson, 2002) and time-series studies (Spitzer and Jenkins, 1989; Schudlich and Emerson, 1996) confirm that most of variability in dissolved N<sub>2</sub> and the heavier inert gases is explained by the temperature dependence of the solubility. Solubility control is expected based on the relevant timescales: dissolved gases within the ocean mixed layer equilibrate with the atmosphere on a typical timescale of days to a few weeks, which is shorter than the typical timescale of months for the mixed layer to undergo substantial temperature changes. For a gas to remain near solubility equilibrium in spite of warming and cooling, it is a requirement that the air–sea fluxes of these gases be governed, to a first approximation, by (Keeling et al., 1993):

$$F_i = P_i(-dS_i/dT)Q/C_p \quad (1)$$

where  $F_i$  (mol m<sup>-2</sup> yr<sup>-1</sup>) is the net flux (positive into the air) of gas species  $i$ ,  $P_i$  (atm) is the partial pressure of species  $i$  in air,  $dS_i/dT$  (mol m<sup>-3</sup> atm<sup>-1</sup> °C<sup>-1</sup>) is the temperature derivative of the Bunsen solubility,  $Q$  (J m<sup>-2</sup> yr<sup>-1</sup>) is the net heat flux into the water (sum of latent heat, sensible heat, long-wave and short-wave components) and  $C_p$  is the heat capacity of seawater (J m<sup>-3</sup> °C<sup>-1</sup>).

In Table 1, we have estimated via eq. (1) the change in the total atmospheric burden of N<sub>2</sub> and the inert gases for a heat input to the ocean of 100 ZJ. The change is larger for heat input into colder

water, because the solubility derivatives ( $-dS_i/dT$ ) are larger at low temperatures. From Table 1, an input of 100 ZJ into a 10 °C ocean water mass which maintains solubility equilibrium would release enough Kr, Ar and N<sub>2</sub> to increase the total atmospheric burden of these gases by 0.00104%, 0.00043% and 0.00017% respectively. If the excess were mixed uniformly throughout the entire atmosphere, this would increase in the Kr/N<sub>2</sub> ratio by 0.00104% – 0.00017% = 0.00087% and the Ar/N<sub>2</sub> ratio by 0.00043% – 0.00017% = 0.00026%. It is customary to express such small changes in “per meg” units, for example:

$$\delta(\text{Ar}/\text{N}_2) \text{ (per meg)} = \left( \frac{(\text{Ar}/\text{N}_2)_{\text{sample}}}{(\text{Ar}/\text{N}_2)_{\text{reference}}} - 1 \right) \times 10^6 \quad (2)$$

so that a change of 0.00026% is expressed as 2.6 per meg.

Changes in relative atmospheric inert gas abundances are expected both globally and locally. At a given location, the atmospheric inert gas abundances will depend on the magnitude of air–sea heat exchanges, kinetic barriers to air–sea gas exchange and rates of atmospheric mixing. The largest expected changes are quasi-regular seasonal cycles at middle and high latitude tied to the seasonal cycle of ocean heat storage. Based on model simulations using different heat flux and heat storage climatologies (Samuels and Cox, 1987; Gibson et al., 1997) and several atmospheric transport models (Heimann, 1995; Tans et al., 1989), and assuming the validity of eq. (1), we estimate that the atmospheric Ar/N<sub>2</sub> ratio should exhibit seasonal variations at sea level in middle and high latitudes of the order of 10 to 20 per meg. The cycles are expected to be superimposed on a global long-term increase of around 3 per meg per decade due to global warming, and superimposed on gradients with latitude of a few per meg (in the annual mean) due to ocean circulation and associated transport of heat and dissolved gases.

This paper reports progress in a programme at the Scripps Institution of Oceanography to measure changes in the atmospheric Ar/N<sub>2</sub> ratio. The Ar/N<sub>2</sub> ratio has the advantage that both gases are relatively abundant in air, allowing the use of small (~several litres) air samples. Although ratios involving the heavier gases (e.g. Kr/N<sub>2</sub> and Xe/N<sub>2</sub>) would be more sensitive to heat exchanges, their measurement (e.g. via isotope dilution mass spectrometry) would require much larger samples and additional processing to concentrate the inert gas prior to analysis. We have focused on Ar/N<sub>2</sub> primarily because the measurement is feasible using flasks already being collected for interferometric O<sub>2</sub>/N<sub>2</sub> measurements at Scripps (Keeling et al., 1998).

Our study parallels that of Battle et al. (2003), which was the first study to document significant variations in the Ar/N<sub>2</sub> ratio of the atmosphere. The study of Battle et al. (2003) presented data over a 3-yr period from six stations distributed globally and demonstrated that the Ar/N<sub>2</sub> ratio indeed varies seasonally, with roughly the magnitude expected based on seasonal air–sea heat exchanges. The Battle et al. (2003) study further illustrates the usefulness of such data for constraining coupled models of the ocean/atmosphere system. The study also shows the need

Table 1. Effect of ocean warming at different temperatures on global atmospheric composition

		Relative change in atmospheric burden <sup>b</sup> , (dP <sub>i</sub> /P <sub>i</sub> ) × 10 <sup>6</sup> , per 100 ZJ of ocean warming		
		0 °C	10 °C	20 °C
	Mole fraction in dry air <sup>a</sup>			
He	5.24 × 10 <sup>-6</sup>	0.23	0.14	0.10
Ne	18.2 × 10 <sup>-6</sup>	0.54	0.40	0.33
N <sub>2</sub>	0.0781	2.66	1.75	1.22
Ar	0.00934	6.56	4.31	2.99
Kr	1.14 × 10 <sup>-6</sup>	16.40	10.43	6.95
Xe	0.087 × 10 <sup>-6</sup>	40.27	23.73	14.80

<sup>a</sup>Glueckauf (1951).

<sup>b</sup>Computed from eq. (1) based on the total mass of dry air of 5.124 × 10<sup>21</sup> g (Trenberth, 1981), a mean molecular weight of dry air of 28.97 g mol<sup>-1</sup>, and solubility data compiled in Ozima and Podosek (1983) for a salinity of 35 practical salinity units (PSU).

for improving measurement precision and eliminating sampling biases, which limit the usefulness of the existing data.

Our approach, like that of Battle et al. (2003), involves using a multicollector mass spectrometer for whole-air analysis, as pioneered by Bender et al. (1994) for  $O_2/N_2$  measurements. We apply this approach using a wide-sector mass spectrometer that allows for simultaneous measurement of  $O_2/N_2$ ,  $CO_2/N_2$  and  $Ar/N_2$  ratios. The mass spectrometer incorporates an inlet system in which sample and reference gases are switched upstream of a single inlet capillary. Leuenberger et al. (2000) recently described a system that bears some similarity to that described here. Our approach differs from that of Leuenberger et al. (2000) principally in allowing for higher beam strengths and more rapid sample/reference switching, thus further increasing precision.

Here we describe our method in some detail and describe tests we have performed to assess the system performance. We also describe results for  $Ar/N_2$  from flasks collected from stations in a global North–South network over roughly a 1-yr period.

## 2. Methods

### 2.1. Mass spectrometer system

We used a Micromass IsoPrime mass spectrometer, which is configured with eight collectors (Table 2) that can be integrated simultaneously, thus allowing three distinct elemental ratios ( $Ar/N_2$ ,  $O_2/N_2$ ,  $CO_2/N_2$ ) and four distinct isotopic ratios ( $^{15}N$ - $^{14}N$ ,  $^{15}N$ - $^{14}N$ ,  $^{15}N$ - $^{14}N$ ,  $^{15}N$ - $^{14}N$ ,  $^{18}O$ - $^{16}O$ ,  $^{16}O$ - $^{16}O$ ,  $^{36}Ar$ / $^{40}Ar$ ) to be measured simultaneously in an air sample. Our focus here is exclusively on the elemental ratios, with particular emphasis on  $Ar/N_2$ . The IsoPrime employs an asymmetric analyser geometry with an effective radius of 108 mm. The wide exit face of the electromagnet enables a mass spread of 62% to be utilized on the focal plane of the instrument, allowing the simultaneous measurement of masses 28 to 44, as shown in Fig. 1. The analyser housing employs an open design in which the source, flight-tube and detector elements are incorporated into a single rectangular vacuum vessel, thus providing mechanical rigidity as well as

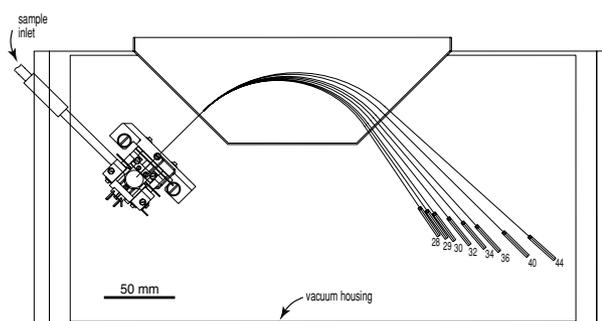


Fig. 1. IsoPrime ion optics.

an unrestricted flight tube permitting the wide mass spread. The open design of the flight tube also allows for efficient evacuation by a single turbomolecular pump, which reduces the instrumental non-linearity. An electron impact source is used, fitted with a thoriated iridium filament for sensitivity. The collector array is composed of deep Faraday cups. Each collector has a slit width designed so that, in normal use, the beam from each monitored mass falls entirely within the collector.

The native control software for the IsoPrime, called “MassLynx”, controls all aspects of instrument tuning, operation and data acquisition. The highly specific nature of the data processing requirements of this application has driven the development of an additional suite of software written in the LabView programming language. This LabView software controls MassLynx via a number of ActiveX and COM interfaces. The interfacing involves the LabView program sending commands to MassLynx at 10 min intervals, and retrieving the collector signals in nearly real time with 100 ms resolution. The LabView software further processes the collector signals to compute “initial” delta values (described below) at 10 s intervals, which in turn are displayed graphically and stored in output files.

The measurement of isotope or elemental ratios via mass spectrometry typically requires switching between sample and reference gases in order to cancel instrument drift. With traditional inlet systems, however, the rate at which gases can be switched—and thus the degree to which instrument drift can be cancelled—is limited by the need to allow the ion source to recover from pressure transients caused by switching. This typically limits the switching rate to 15 s or longer. Measurement precision may also be degraded by imbalances between sample and reference gas pressure, which can lead to biases due to non-linear source effects (Bender et al., 1994; Leuenberger et al., 2000).

Here we overcome these limitations by employing the custom inlet system shown in Fig. 2. This system employs the standard Micromass changeover valve, operated here with inlet flows of 10 to 20 sccm and outlet pressures of  $\sim 0.4$  atm. The output of one side of the changeover valve is directed to a “T”, which allows a small fraction of the flow ( $\sim 0.01$  STP  $ml\ min^{-1}$ ) to be delivered via a crimped stainless steel capillary into the mass spectrometer source. The remainder of the gas delivered through this exhaust

Table 2. Mass spectrometer detector configuration

Collector ( $M/Z$ )	Feedback resistance ( $G\Omega$ )	Typical ion current (nA)	Typical amplifier voltage (V)
28	0.1	37	3.7
29	20	0.27	5.4
30	1 <sup>a</sup>	0.15	1.5
32	0.5	8.6	4.3
34	200	0.036	7.2
36	2 <sup>a</sup>	0.059	0.12
40	5	0.78	3.6
44	200	0.028	5.6

<sup>a</sup>Resistance sized for isotope dilution studies.

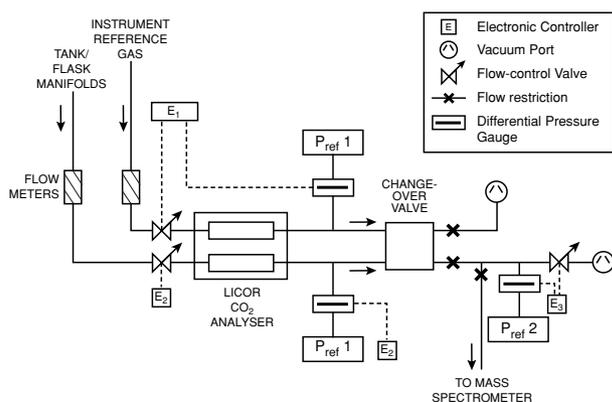


Fig 2. Mass spectrometer inlet system.

port is wasted to a vacuum pump. The output of the other side of the changeover valve is similarly wasted to the same vacuum pump. The pressures and flows upstream of the changeover valve are equalized via active electronic pressure control and by adjusting flow restrictions (manual flow control valve and crimps), thus effectively reducing the pressure fluctuations downstream of the changeover valve caused by switching. Small residual fluctuations at the capillary inlet are further suppressed via an additional stage of active pressure control downstream of the changeover valve. A Licor non-dispersive infrared (NDIR) CO<sub>2</sub> analyser, which also takes advantage of the pressure-control scheme, is incorporated upstream of the changeover valve. The NDIR provides a measure of CO<sub>2</sub> concentration that is largely redundant to that based on the  $M/Z = 44$  and  $M/Z = 28$  ion currents. One input port of the changeover valve is connected to a fixed instrument reference gas, which also serves as reference gas for the NDIR analyser. The other input port allows the introduction of samples and reference gases as described further below.

An example of the mass spectrometer output is shown in Fig. 3. Here the changeover valve is switching at 5 s intervals, alternately allowing the instrument reference gas versus sample gas into the mass spectrometer. These two gases have well-resolved differences in CO<sub>2</sub> concentration (44/28) and in O<sub>2</sub>/N<sub>2</sub> ratio (32/28) but not in Ar/N<sub>2</sub> ratio (40/28). The timescale for replacing one gas with the next is seen most clearly from the 44/28 ratio signal: there is a  $\sim 1$  s delay between the switch and the initial arrival of new gas, and an additional  $\sim 1$  s is required for the exchange of gases to progress to 90% completion. There is no indication of any pressure transients in the replacement of one gas with the next.

With the 5 s switching scheme, the concentration difference between the sample and instrument reference gas can be determined with 10 s resolution. We denote this difference, which we compute based on the raw ratio signals (see Fig. 3) with the symbol  $\delta_i$  ( $i$  for “instrument”). Under typical conditions,  $\delta_i$  is determined every 10 s to a precision of 10 per meg ( $1\sigma$ ) in the 40/28 ratio, 4 per meg in the 32/28 ratio and 60 per meg in the

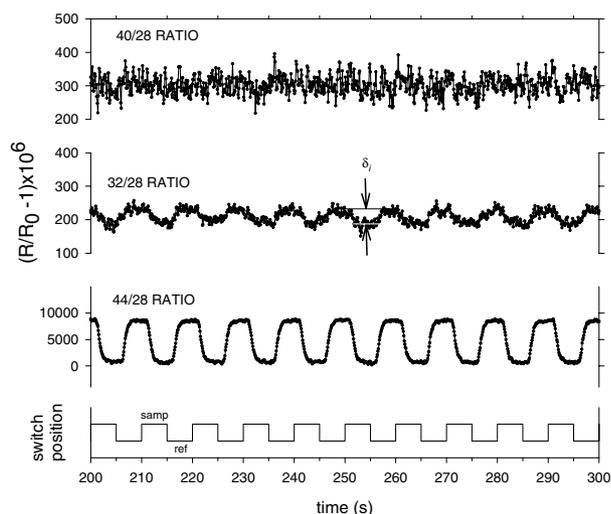


Fig 3. Sample data from mass spectrometer system at 0.1 s resolution. Shown is the ratio ( $R$ ) of two collector currents (e.g.  $M/Z = 40$  versus  $M/Z = 28$ ) expressed as parts per million deviation from an initial ratio. During this sequence, sample and instrument reference gases are being switched at regular 5 s intervals. The quantity  $\delta_i$  is computed according to  $\delta_i = (R_{\text{samp}}/R_{\text{ref}} - 1) \times 10^6$ , where  $R_{\text{ref}}$  is based on the average of the leading and trailing reference gas segments. The initial ratio  $R_0$  is used here for plotting purposes only.

44/28 ratio. Based on sensitivity tests with known CO<sub>2</sub> additions, described below, the 44/28 precision corresponds to 0.03  $\mu\text{mol mol}^{-1}$  in the CO<sub>2</sub> mole fraction.

## 2.2. Instrument noise spectrum

While the 5 s switching sequence effectively cancels detector drift on timescales longer than  $\sim 10$  s, considerable noise remains on shorter timescales. Could faster switching rates reduce this noise? To assess this question we introduce a steady stream of air from a high-pressure cylinder into the mass spectrometer without switching at all. We then process the collector signals as if switching had occurred, to compute differences  $\delta_i$  between consecutive segments. We carry out this processing for variable (hypothetical) switching period as well as for variable “dead time”, i.e. the time window over which the signals are discarded to allow for stabilization after the switch (also known as “idle time”). From these data, we compute the standard error in  $\delta_i$  over a 20 min interval. This we compute according to  $\sigma_i/(N)^2$ , where  $N$  is the number of (hypothetical) reference–sample–reference jogs of one polarity that fit into 20 min and where  $\sigma_i = [(\sum (\delta_i)^2)/N]^2$ . The summation is carried over the  $N$  jogs, and  $\delta_i$  for each jog is computed by averaging the 0.1 s mass spectrometer output over the sample and reference segments and interpolating between reference segments, as per Fig. 3. (Note that because the ensemble mean is known to be zero *a priori*, the observed mean value of  $\delta_i$  is not subtracted in the expression for

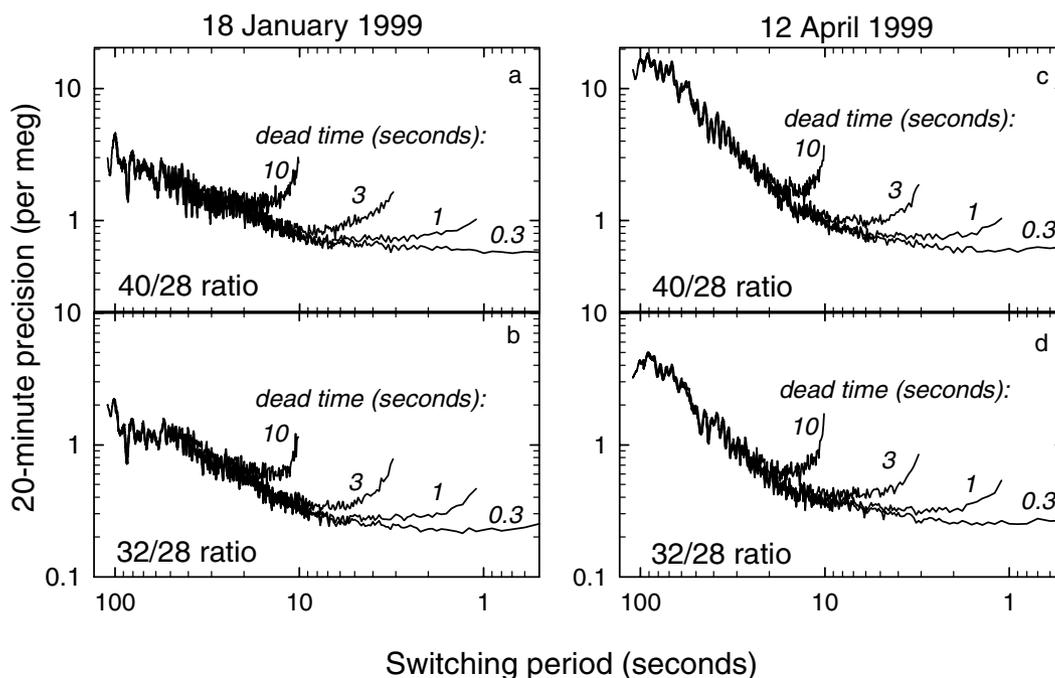


Fig. 4. Precision of the mass spectrometer for a hypothetical 20 min sample–reference integration as a function of switching rates between sample and reference gas (see text). The results shown are based on a 20 min segment of raw (0.1 s) data, during which a single gas was introduced into the mass spectrometer without switching the changeover valve.

$\sigma_i$ , and  $N$  is used in the denominator, rather than  $N - 1$ .) This analysis, carried out for variable switching periods, is roughly equivalent to computing the noise power spectrum.

The results, shown in Fig. 4, show several interesting features. Focusing on the results with a short dead time of 0.3 s, we see that the standard error improves as the switching rate is increased, consistent with the improved cancellation of instrument drift and consistent with the mass spectrometer having a red noise spectrum at low frequencies. At high switching rates, however, the standard error becomes independent of switching rate, consistent with a white spectrum at high frequencies. In this limit, the performance is limited by the shot noise or Poisson counting statistics from the ion currents. As the figure shows, however, achieving this limit requires having a short dead time. With longer dead times, the precision degrades if the switching is too rapid, as a large fraction of the data is then being discarded. For a dead time of 10 s, the optimum switching period is around 20 s, corresponding to retaining half the data. For a dead time of 1 s, the optimum switching period is around 5 s, with a very broad optimum that is close to the shot-noise limit.

Comparing results for the two dates in Fig. 4, we see that the performance at slower switching rates can vary from day to day, presumably as a result of changes in instrument tuning, filament conditions or external environmental parameters. At higher switching rates, however, the performance is anchored near the statistical limit. Comparing results for the different ion ratios, we find that the optimum switching rate (for a given

dead time) is slightly faster for 32/28 than for 40/28, consistent with the former having higher beam strength, smaller shot noise and hence a larger relative contribution from red or “flicker” noise.

Our standard operating conditions, with actual gases being switched, employs a switching rate of 5 s and allows for  $\sim 2$  s of dead time, after a 1 s delay. According to Fig. 4, we would expect the performance under these conditions to be within a factor of two of the statistical limit. Our results comparing two gases confirm this expectation, showing that little additional noise is introduced by the switching of the valve itself and implying that only a rather modest improvement in performance would be achieved by faster switching, by itself. Further noise reduction could potentially be achieved, however, by a combination of faster switching and increasing the beam strengths.

### 2.3. Gas handling

For a number of years, the  $O_2$  laboratory at Scripps has employed a system for analysing flask samples for  $O_2/N_2$  ratios and  $CO_2$  concentrations using a custom interferometer and a Siemens Ultramat 3 NDIR  $CO_2$  analyser. This system, described in detail in Keeling et al. (1998), is calibrated using reference gases derived from high-pressure cylinders, which are introduced via a manifold upstream of both analysers.

We have now interfaced the mass spectrometer in such a way that it is fed by the same calibration gases. This was done using a

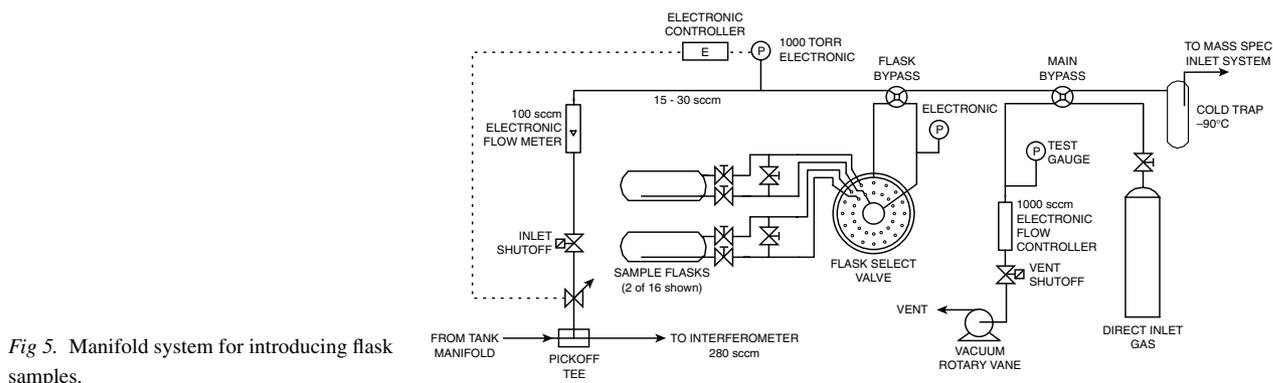


Fig 5. Manifold system for introducing flask samples.

pickoff “T” upstream of the NDIR and interferometric analyser, which allows calibration gases to be compared in parallel on both systems. The T operates at the regulator delivery pressure of around 10 psig (pounds per square inch gauge). To minimize the potential for thermal fractionation at the T, we employ a concentric design suggested by M. Bender, in which the pick-off flow is derived from a smaller bore tubing that is aligned axially within the larger bore of the main (bypass) flow. Temperature gradients are further reduced by embedding the T in a machined brass block that, in turn, is embedded in insulation. It is possible that the T may still fractionate due to orifice effects, but we expect that such fractionation would be constant with time, and thus have the effect of inducing a constant offset between the Ar/N<sub>2</sub> ratios reported on tanks versus flasks. We have not tried to correct our data for any such effect at this time.

Downstream of the pick-off T, we have introduced a new manifold system for mass spectrometric analysis of flask samples, as shown in Fig. 5. This system incorporates (1) a multiport rotary valve (Valco Instruments, Inc.) for introducing flasks, (2) a vacuum system for purging and evacuating flask lines, (3) a “direct inlet gas” for maintaining stable operating conditions in the mass spectrometer during preparations for flask analysis and (4) active pressure control for matching the reference gas delivery pressure to that in individual flasks, thereby minimizing pressure changes when flask air is introduced. Although the manifold has 16 positions, only four positions are used for our normal 5 l flasks due to space constraints. The manifold system incorporates a thermal enclosure surrounding the flasks and the nearby bypass valves. The manifold includes magnetic stirrers for mixing the air in the 5 l flasks during analysis. The motor units for driving the magnets are located outside the thermal enclosure, with only a rotating shaft penetrating the enclosure.

The set-up allows flasks to be analysed either in a “purge” mode, in which both the inlet and outlet ports of the flasks are opened and the flask air is diluted with tank air during analysis, or alternately in a “sniff” mode, in which only the outlet port of the flask is connected and the flask pressure decreases during analysis. The latter mode was used for all results presented here. In this mode, two lines are connected to each flask at a single

specially designed ball and socket joint, to allow purging of all lines up to this joint prior to analysis.

The preparation sequence starts by inserting stir-bars into the flasks and connecting the flasks at this ball joint. We then purge the connections with dry air, first at a flow rate of around 200 ml min<sup>-1</sup> and then at the nominal analysis flow of 15 ml min<sup>-1</sup>, while monitoring the mass spectrometer and CO<sub>2</sub> analyser output to ensure complete removal of room air or diagnose leaks. At completion of the purge, each flask position is then evacuated for 1 min and the sample loop is isolated at the flask bypass valve. The manual purge valve is then closed and the flask stopcock opened, resulting in backfill of the loop with sample. After a short equilibration time, the pressure of the flask is recorded and the flask select valve is advanced to the next flask position, where the procedure is repeated. Unused ports are capped off and treated as if they contained flasks to reduce cross-port contamination during switching. Once this preparation sequence has been completed for all flasks, the thermally insulated enclosure, which houses all flasks, is then sealed, the stir-bars are activated and 30 min is allowed to elapse before proceeding. During this time, working gas flow is maintained into the mass spectrometer via the flask bypass valve.

At the start of each analysis, the flask select valve moves to a mounted position (still isolated via the flask bypass valve) and the working gas pressure is adjusted with an active pressure controller to agree with the flask pressure determined earlier. The working gas is analysed at this pressure to establish a leading baseline, whereupon the flask bypass valve is switched to introduce flask air, effectively stopping the working gas flow through the bypass valve. (Working gas flow is maintained, however, into the interferometer, via the other branch of the T.) The analysis continues for 10 min at which point the flask pressure will have dropped nominally by ~31 mbar. The bypass valve is switched to reintroduce working gas, thus establishing a trailing baseline.

Our air samples are collected in 5 l glass flasks equipped with Viton O-rings which are flushed in the field with a freeze-dried air stream. At stations near sea level, the pressure in the flasks is maintained just above ambient barometric pressure via an open exhaust line. At the high-elevation stations (Mauna Loa, South

Pole) the pressure is maintained near  $\sim 1$  atm via a back-pressure regulator located near the outlet of the exhaust line, separated from the flasks by several metres of tubing. The air is dried to a dew point between  $-45$  and  $-80$  °C, depending on the station. Flasks are typically collected in triplicate, either serially in time or simultaneously as a serially flushed string of three, depending on the sampling station. At all stations other than Kumukahi, flasks are sampled indoors, in order to minimize thermal gradients, with the intake line extending to a nearby high point or tower outside. At Kumukahi, the flasks are collected outdoors under a portable shade, to reduce solar heating. Starting in the summer of 2001, we began analysing two of three replicates on the mass spectrometer system in sniff mode prior to analysis on the interferometer system. The third flask was analysed only on the interferometer system. This approach provides a measurement of Ar/N<sub>2</sub> ratios and redundant measurements of CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> on two out of three flask replicates.

Flasks are typically analysed against the gas delivered from a working tank (WT), and the working tank is analysed on a daily basis against a series of secondary reference gases, or “secondaries” (A and B). A typical sequence is shown in Fig. 6.

Reference gases are pumped at Scripps and dried to the level of  $\sim 2 \mu\text{mol mol}^{-1}$  H<sub>2</sub>O or better using a molecular sieve. During usage, all reference and working tanks are laid on their side and placed in an insulated enclosure. Within the enclosure, the end-to-end (horizontal) temperature gradients of the tanks is typically of order  $\sim 0.02$  °C. The tank regulators are located outside the enclosure and connected to the cylinder head valves via 1/16 in O.D. nickel lines (see Keeling et al. (1998) for further details).

#### 2.4. Calibration

We compute changes in Ar/N<sub>2</sub> from the mass spectrometer raw signals in several steps, with the net effect being a transformation

of the form

$$\delta(\text{Ar}/\text{N}_2) = a\delta_i(40/28) + b\delta_i(32/28) + c\delta_i(44/28) + d \quad (3)$$

where  $a$  accounts for the combined influence of the intrinsic sensitivity of the mass spectrometer (i.e. non-linearity) and incomplete sample/reference replacement during switching (“cross-over contamination”),  $b$  and  $c$  account for interferences due to isobaric effects or ion–molecule chemistry, and  $d$  accounts for variations in the composition of the instrument reference gas, working gas and the additional reference gases.

Coefficients  $a$ ,  $b$  and  $c$  were established in August 2001 by recording the mass spectrometer response as a function of known changes in gas composition. The gas composition was altered by bleeding variable amounts of a prepared gas mixture into a reference gas stream and analysing the resulting mixture. The prepared gas mixture consisted either of (1) pure CO<sub>2</sub>, (2) a gravimetric mixture of O<sub>2</sub> and CO<sub>2</sub> or (3) a gravimetric mixture of Ar and CO<sub>2</sub>. The relative proportions of the reference gas and the prepared gas were determined by measuring changes in CO<sub>2</sub> mole fraction on a well-calibrated CO<sub>2</sub> system (Keeling et al., 1998). The addition of pure CO<sub>2</sub> allowed the coefficient  $c$  to be measured. Coefficients  $a$  and  $b$  were computed based on results for the other two gas mixtures, after subtracting the influence of CO<sub>2</sub> on the beam ratios. These tests showed that  $b = 0$  to within uncertainties, that  $c$  is consistent with a weak isobaric interference on mass 28 due to CO<sup>+</sup>, and that  $a$  is consistent with a cross-over contamination effect of several per cent and an intrinsic non-linearity of less than 2%.

Variations in  $a$  and  $c$  relative to August 2001 are determined based on a span normalization factor, derived based on the apparent changes of a tank prepared with relatively large differences in Ar/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub>.

Coefficient  $d$  is established based on a hierarchical scheme of reference gas comparisons. Briefly, the  $\delta_i(40/28)$  values for flasks

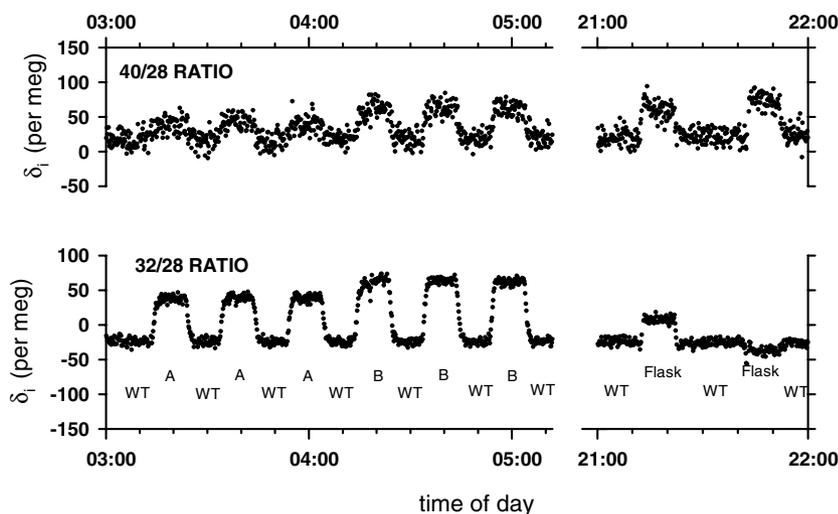


Fig 6. Sample data from the mass spectrometer system at 10 s resolution, expressed as  $\delta_i$  (see Fig. 2). The sequence shows the changing value of the difference between the sample and the instrument reference gas as the sample side alternately receives gas from various tanks (WT, A, B) or flasks.

samples are subtracted from the  $\delta_i(40/28)$  values of the working gas (WT) and the resulting difference is added to an assigned value for the working gas. The working gas assignment is made on a daily basis, based on comparison with the “secondaries” (see Fig. 6, segments A and B). The results are then adjusted for sensitivity and interference effects (coefficients  $a$ ,  $b$  and  $c$  in eq. 3) and a time-varying additive adjustment is made (via  $d$ ) to maintain constancy in the  $\delta$  values of a suite of primary reference gases, or “primaries”. The primaries are analysed using essentially the same procedures and algorithms as flask samples. The procedure assumes that the primaries are stable over the long term. Unlike the common practice for reporting isotopic ratios, the zero value of the  $\delta(\text{Ar}/\text{N}_2)$  scale does not necessarily correspond to the concentration of an actual reference material. The redundancy inherent in this approach is advantageous in producing a scale with long-term stability. We have used the same approach for maintaining an  $\delta(\text{O}_2/\text{N}_2)$  scale in our laboratory (see Keeling et al. (1998) for additional details).

Working gases typically last several months and are replaced when their pressure drops to about 800 kPa, while the secondaries typically last a year or more and are replaced when their pressures drop to about 3300 kPa. Procedures for replacing these gases in a self-consistent manner are described in Keeling et al. (1998). Primaries are used sparingly in order to last decades without significant depletion.

### 3. Performance tests

#### 3.1. Thermal fractionation

In the course of conducting tests of the performance of our system, we have found that a ubiquitous challenge is the need to minimize thermal fractionation of samples and reference gases. To aid in subsequent discussions, we digress briefly here to present estimates of the relevant thermal fractionation factors for O<sub>2</sub>/N<sub>2</sub> and Ar/N<sub>2</sub> in air. Table 3 summarizes literature estimates of the

thermal diffusion factor  $\alpha$ , thermal diffusion sensitivity  $\Omega$  and diffusivity  $D$  for Ar and O<sub>2</sub> in air.  $\Omega$  is computed according to  $(\alpha/T) \times 10^6$  (per meg °C<sup>-1</sup>), where  $T$  is the temperature in kelvin (Severinghaus et al., 2001). Table 3 also summarizes estimates of the ratio of  $\alpha D$  for Ar/N<sub>2</sub> versus  $\alpha D$  for O<sub>2</sub>/N<sub>2</sub> both from the literature and as recently measured in our laboratory.

The thermal diffusion factor  $\alpha$  and sensitivity  $\Omega$  are measures of the steady-state concentration gradient that is induced by a temperature gradient in the absence of bulk flow. In contrast, the product  $\alpha D$ , is a measure of the fractionating flux under transport-limited conditions, as is commonly the case in the presence of bulk flow. We expect that under most conditions relevant to our laboratory and field operations, any thermal fractionation will scale more nearly in proportion to  $\alpha D$  rather than to  $\alpha$ .

We have measured the ratio  $\alpha D$  for Ar/N<sub>2</sub> versus  $\alpha D$  for O<sub>2</sub>/N<sub>2</sub> (i.e.  $(\alpha D)_{\text{Ar}/\text{N}_2}/(\alpha D)_{\text{O}_2/\text{N}_2}$ ) by dividing a flowing gas stream at a T junction while slightly heating one branch of the T and measuring differences in Ar/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> between the two branches of the T directly on the mass spectrometer. We found that the differences in Ar/N<sub>2</sub> between the branches of the T were highly correlated to differences in O<sub>2</sub>/N<sub>2</sub>, and we interpret the slope of the correlation plot as measuring  $(\alpha D)_{\text{Ar}/\text{N}_2}/(\alpha D)_{\text{O}_2/\text{N}_2}$ . The experiment was carried at pressures of 1 atm and 120 atm, the latter being characteristic of pressures in high-pressure gas cylinders. The results, presented in Table 3, clearly establish that the ratio  $(\alpha D)_{\text{Ar}/\text{N}_2}/(\alpha D)_{\text{O}_2/\text{N}_2}$  is pressure dependent, with lower values at higher pressures.

#### 3.2. Tank stability

A useful measure of the performance of our analysis system is provided by the daily value of the working gas, which is determined each day that flasks or reference gases are analysed. A composite history of eight working gases is shown in Fig. 7a. The working gas Ar/N<sub>2</sub> ratios fluctuate on a day-to-day basis by  $\sim \pm 2$  per meg, which is about twice the value expected based on

Table 3. Thermal diffusion factors for Ar/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> in air

Description	Magnitude	References <sup>a</sup>
$\alpha_T$ for Ar/N <sub>2</sub> at 1 atm, 20 °C	0.071	(1)
$\alpha_T$ for Ar/N <sub>2</sub> at 1 atm, 27 °C	0.074	(2)
$\alpha_T$ for O <sub>2</sub> /N <sub>2</sub> at 1 atm, 20 °C	0.018	(1)
$\Omega$ for Ar/N <sub>2</sub> at 1 atm, 20 °C	242 per meg °C <sup>-1</sup>	(1)
$\Omega$ for O <sub>2</sub> /N <sub>2</sub> at 1 atm, 20 °C	61 per meg °C <sup>-1</sup>	(1)
$D$ for Ar in air at 1 atm, 20 °C	0.19 cm <sup>3</sup> s <sup>-1</sup>	(3)
$D$ for O <sub>2</sub> in air at 1 atm, 20 °C	0.20 cm <sup>3</sup> s <sup>-1</sup>	(3)
$(\alpha_T D)_{\text{Ar}/\text{N}_2}/(\alpha_T D)_{\text{O}_2/\text{N}_2}$ in air at 1 atm, 20 °C	4.15	(1), (3)
$(\alpha_T D)_{\text{Ar}/\text{N}_2}/(\alpha_T D)_{\text{O}_2/\text{N}_2}$ in air at 1 atm, 20 °C	3.77 ± 0.04	This work
$(\alpha_T D)_{\text{Ar}/\text{N}_2}/(\alpha_T D)_{\text{O}_2/\text{N}_2}$ in air at 120 atm, 20 °C	2.17 ± 0.02	This work

<sup>a</sup>(1) Grew and Ibbs (1952, p. 130); (2) eq. (5) in Trengove and Dunlop (1982) using an Ar mole fraction of  $x_1 = 0.01$ ; (3) formula of Fuller, as described in Reid et al. (1987, p. 587).

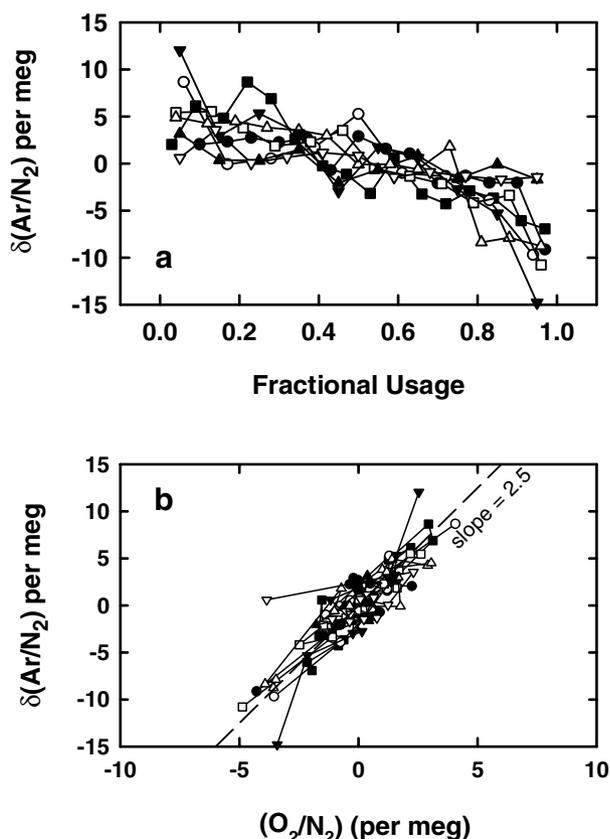


Fig 7. (a) Working gas concentrations of  $\delta(\text{Ar}/\text{N}_2)$  as a function of the (approximate) fractional tank usage. For each tank the mean value of  $\delta(\text{Ar}/\text{N}_2)$  was subtracted to allow the curves to be overlaid. Zero usage corresponds to approximately the fill pressure of  $\sim 14\,000$  kPa (2100 psig) while full usage (1.0) corresponds to a residual pressure of approximately  $\sim 800$  kPa (120 psig). (b) Scatter plot of  $\delta(\text{Ar}/\text{N}_2)$  versus  $\delta(\text{O}_2/\text{N}_2)$  for the same working tanks as (a).

the imprecision in  $\delta_i$ , indicating that some day-to-day variability results from imperfect gas handling. Superimposed on these fluctuations is a downward trend in Ar/N<sub>2</sub> that is detectable in most tanks. The change from first to last analysis on a given working gas ranges from  $-2$  to  $-27$  per meg, with an average of  $-13$  per meg. The drift seems to accelerate near the point the tank is used up and is possibly also faster for some tanks at the very onset of usage. Discarding the first and last analyses, the drift ranges from 0 to  $-12$  per meg, with an average of  $-7$  per meg. The working gas drift must be a consequence of gas usage, because it is assessed relative to the secondaries, which differ from the working tank only in being depleted less rapidly.

As shown in Fig. 7b, the WT variations in Ar/N<sub>2</sub> are well correlated with variations in O<sub>2</sub>/N<sub>2</sub> at a ratio of around 2.5:1. This small effect in WT O<sub>2</sub>/N<sub>2</sub> ratios was not noticed previously (Keeling et al., 1998), and came to our attention only in light of the more obvious changes in Ar/N<sub>2</sub>. The effect may have become more pronounced after our laboratory moved to a new

building in 1999. We believe the effect is likely caused by thermal fractionation in the tanks, as the ratio of 2.5 is close to the ratio of 2.17 which we measured for  $(\alpha D)_{\text{Ar}/\text{N}_2}/(\alpha D)_{\text{O}_2/\text{N}_2}$  at a typical tank pressure of 120 atm.

The same depletion effect may influence our secondaries, although at a much slower rate due to their more limited usage. A typical shift of around  $-5$  per meg in Ar/N<sub>2</sub> and  $-2$  per meg in O<sub>2</sub>/N<sub>2</sub> in the secondaries would be expected over their lifetime, considering the tanks are used only over a limited intermediate pressure range. We have not yet been able to verify this predicted drift, due to the short time span of the Ar/N<sub>2</sub> measurements. In principle, such drift should be detectable via the comparisons with the primary reference gases, which are depleted even less rapidly.

### 3.3. Pressure-induced thermal fractionation

In the course of the initial testing of the flask manifold system, shown previously in Fig. 5, some difficulty was encountered in generating stable Ar/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> ratios from air delivered from flasks in sniff mode. The Ar/N<sub>2</sub> ratios would drift downwards by as much as 20 per meg within the 10 min analysis period. We have traced this effect to thermal diffusion within the flasks in response to pressure-induced temperature changes. As the flask pressure drops during analysis, the air in the flask cools by adiabatic expansion, with the maximum cooling occurring near the centre of the flask and the minimum occurring near the walls, due to the thermal buffering of the glass. The air exiting the flask is thus exposed to a thermal gradient which will deplete the Ar/N<sub>2</sub> ratio of the air exiting the flask relative to the average composition in the flask. Scale analysis suggests it should be possible to fractionate Ar/N<sub>2</sub> at the centre of the flask by the order of 100 per meg relative to the walls, given the pressure drop ( $\sim 3\%$ ), the thermal diffusion sensitivity of Ar/N<sub>2</sub> ( $\sim 250$  per meg  $^\circ\text{C}^{-1}$ ), the diffusivity of Ar in air at  $20^\circ\text{C}$  ( $\sim 0.19$  cm<sup>2</sup> s<sup>-1</sup>), the flask radius ( $\sim 15$  cm) and the timescale for our flask analyses ( $\sim 10$  min).

To better quantify this pressure-induced fractionation effect, we conducted tests in order to isolate the effect of dropping pressure on the composition of the air delivered from a flask. A flask was mounted on the manifold, the insulated enclosure was sealed and the flask was purged with working gas until a stable baseline was achieved on the mass spectrometer. The inlet stopcock of the flask was then closed (using a manual shaft that penetrated the insulation), while the outlet stopcock was left open, and the response of the mass spectrometer signal was noted as the flask pressure dropped. The test was done at our typical analysis flow rate of  $15$  ml min<sup>-1</sup> with an initial flask pressure of 1 atm. This test was repeated four times, and a representative result is shown in Fig. 8. Within a few minutes of closing the stopcock, the Ar/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> ratios decreased, achieving lower quasi-stable baselines within about 5 min. The baseline shift was highly reproducible. The baseline shift in Ar/N<sub>2</sub> ratio averaged

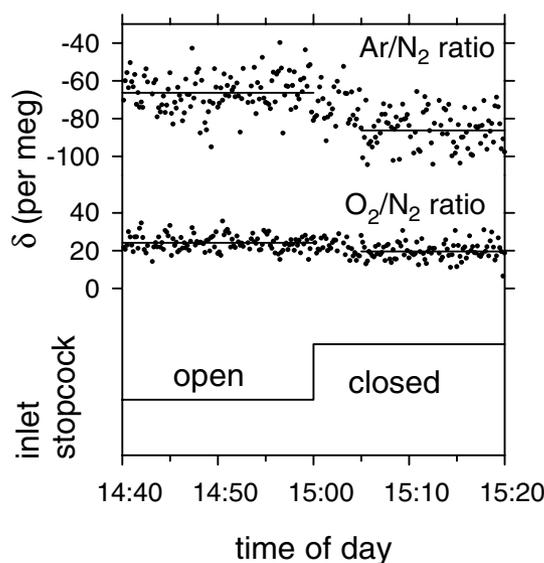


Fig 8. Mass spectrometer signals for Ar/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> ratios (reported as  $\delta_i$ ) of the air delivered from a 5 l flask during controlled testing. Initially, both inlet and outlet stopcocks of the flask are open, and the flask is purged with air of constant composition at a constant pressure. The inlet stopcock is then closed. This stops the inlet flow while leaving the exit flow unchanged (due to active control). The change in composition after stopping the inlet flow is attributed to thermal fractionation driven by pressure-induced cooling within the flask (see text). Points are 10 s values of  $\delta_i$ . Lines are time averages over the corresponding segments.

$-17 \pm 3$  per meg, while the baseline shift in O<sub>2</sub>/N<sub>2</sub> averaged  $-4.5 \pm 0.4$  per meg. The ratio  $(17 \pm 3)/(4.5 \pm 0.4) = 3.8 \pm 0.18$  is consistent with the ratio of 3.77 which we measure for  $(\alpha D)_{\text{Ar}/\text{N}_2}/(\alpha D)_{\text{O}_2/\text{N}_2}$  at 1 atm pressure, thus pointing to thermal diffusion as the ultimate cause. We were able to reduce the effect by  $\sim 20\%$  by stirring the air continuously in the flask with a magnetically driven stir-bar (as is done for our normal flask analyses). The stirring was insufficient to eliminate the effect, presumably because it induced regular circular motion without greatly enhancing the mixing between the centre of the flask and the walls.

In a second test, we were able to demonstrate that the baseline shift is due to the pressure drop in the flask, rather than in the gas lines downstream of the flask. In this test, the flow was directed through the “flask select” valve and through the flask bypass valve, but the flask itself was closed. The pressure set point on the electronic pressure controller was then reduced at a steady rate mimicking the pressure drop for the flask run. This test produced no detectable baseline shift.

The pressure-induced thermal fractionation effect is also evident in analysis of actual flask samples. In Fig. 9, we have combined 520 separate flask analysis peaks by bin-averaging the time-varying concentrations during analysis to produce a single high-precision peak. The peak is characterized by a plateau in which the Ar/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> ratios are quite stable, on average.

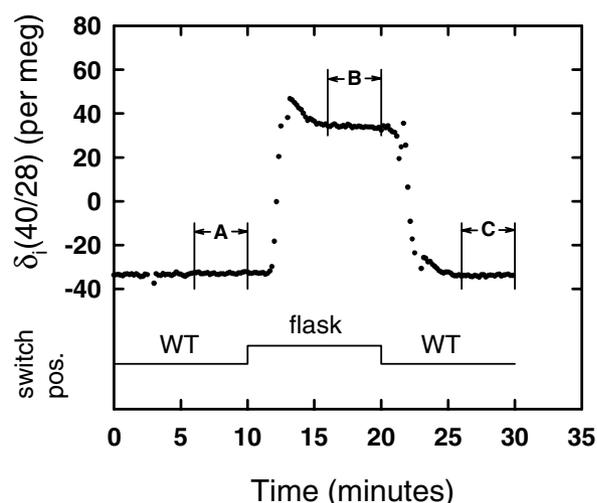


Fig 9. Mass-spectrometer signals for Ar/N<sub>2</sub> ratio, reported as  $\delta_i(40/28)$ , immediately before, after, and during a flask analysis. The data shown are derived by bin-averaging 520 separate flask analyses.

This plateau, however, is preceded by a “hump” (before segment B) during which the O<sub>2</sub>/N<sub>2</sub> and Ar/N<sub>2</sub> ratios are both elevated. By comparing peaks from flasks with different concentrations (not shown), we have verified that the hump is anchored relative to the flask plateau and hence represents altered flask air rather than an altered residue of the working gas (or a mixture of the two). A synchronous hump of the same sign is seen in O<sub>2</sub>/N<sub>2</sub> with a magnitude around 3.5 times smaller. A similar hump in Ar/N<sub>2</sub> is seen on the second working gas segment (before segment C), although this feature is less well correlated to changes in O<sub>2</sub>/N<sub>2</sub>. This second hump is almost certainly influenced by the stopping and restarting of the WT flow in the lines upstream of the flask, and thus has a different origin from the hump preceding segment B.

All the evidence points to the hump preceding segment B as resulting from the same phenomenon as was isolated in our tests above. In other words, segment B represents flask air that has been thermally fractionated due to pressure-induced cooling, while the hump preceding segment B represents flask air that has been less fractionated. To compute flask concentrations, we rely only on the data within the stable segments (A, B, C) in Fig. 9. We therefore expect that our flask results are likely biased low by  $\sim 14$  per meg in Ar/N<sub>2</sub> (i.e. 80% of 17 per meg) relative to the initial concentration in the flasks. The flask results presented below have not been corrected for this bias.

### 3.4. Flask replicate agreement

Another useful measure of performance is the level of agreement between replicate flasks collected at the same place and time. Following Keeling et al. (1998), we compute differences between each flask and the replicate mean, and scale these residuals by a factor of  $(N/(N - 1))^{1/2}$ , where  $N$  is the number of replicates.

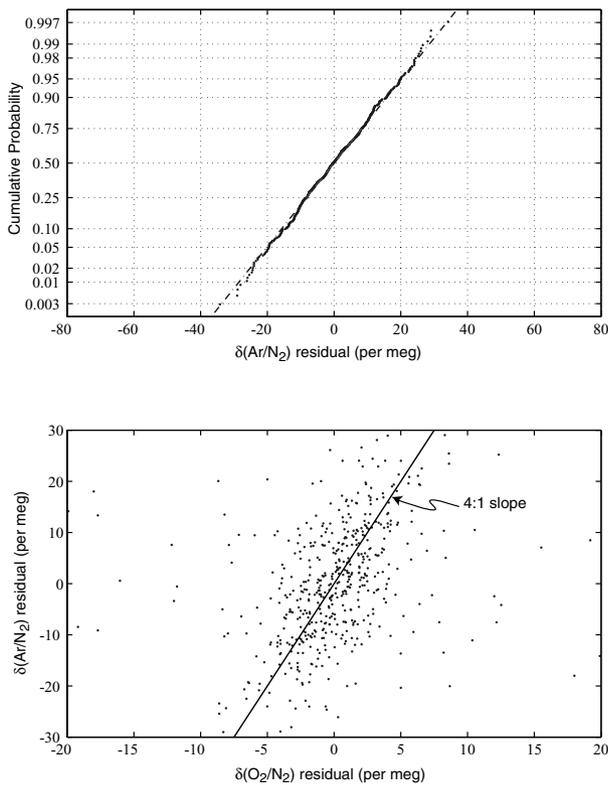


Fig 10. Top panel: normal probability plot of  $\text{Ar}/\text{N}_2$  residuals relative to replicate average. Bottom panel: residuals in  $\text{Ar}/\text{N}_2$  versus residuals in  $\text{O}_2/\text{N}_2$ . Residuals have been scaled according to  $[N/(N-1)]^{1/2}$ , where  $N$  is the number of replicates (see text).

This scaling is used so that the standard deviation of the residuals is equal to that of the hypothetical parent distribution with an infinite number of replicates, and thus represents the imprecision that should be assigned to an individual flask measurement. A normal probability plot of scaled residuals for  $\text{Ar}/\text{N}_2$  is shown in Fig. 10a, which indicates that the residuals follow a normal distribution to a very good approximation. This plot is based on 520 flasks collected at our nine sampling stations. The implied  $\sigma$  on an individual flask is  $\pm 11$  per meg in  $\text{Ar}/\text{N}_2$ . In subsequent discussions, we refer to this  $\sigma$  based on residuals from replicate mean as the “uncorrelated error”  $\sigma_{\text{uncorr}}$  to distinguish it from error which is shared by all members of a set of replicates. This latter we refer to as “correlated error”  $\sigma_{\text{corr}}$ . The residuals in  $\text{Ar}/\text{N}_2$  among flask replicates are correlated with corresponding residuals in  $\text{O}_2/\text{N}_2$  as shown in Fig. 10b. Roughly 31% of the variability in  $\text{Ar}/\text{N}_2$  is explained by variability in  $\text{O}_2/\text{N}_2$  and vice versa. Most of the data cluster around a line with a slope of around 4:1 ( $\text{Ar}/\text{N}_2:\text{O}_2/\text{N}_2$ ), which is consistent with the ratio expected from thermal fractionation at 1 atm pressure.

### 3.5. Flask storage tests

Finally, we conducted a limited test of the long-term stability of  $\text{Ar}/\text{N}_2$  ratios in our flasks. The test involved purging the contents

of several flasks plumbed in series at a flow of  $1 \text{ STP } 1 \text{ min}^{-1}$  with air derived from a particular high-pressure cylinder. The output of the final flask was vented to the room through a long section of tubing, to establish a pressure near 1 atm in the flasks while avoiding the introduction of room air. The flasks stopcocks were then closed and the flasks were stored at ambient pressure in our normal shipping boxes. Two of these flasks were analysed 98 days after the initial purge date, and three were analysed 363 days after the purge date. The purge tank was also analysed before and repeatedly after the date of fill, which established its concentration at the time of fill to around  $\pm 5$  per meg. The observed  $\text{Ar}/\text{N}_2$  ratios in the five flasks were all within a range of  $\pm 15$  per meg of the tank concentration. There was no clear evidence of systematic drift in flask concentrations over time. By itself, this test probably sets an upper bound to any drift in our flasks of  $\sim 15$  per meg in  $\text{Ar}/\text{N}_2$  per year. Note that the flasks used for these storage tests, like the flasks collected for our programme at field stations, were prepared with an internal pressure near 1 atm, which minimizes effects due to differential permeation of  $\text{Ar}$  and  $\text{N}_2$  through the O-ring seals on the stopcocks.

Although we would have liked to conduct more sensitive storage tests, we have been hampered in this goal by difficulties in preparing flasks with sufficiently reproducible  $\text{Ar}/\text{N}_2$  ratios with the above procedures. On 14 separate dates, we purged sets of flasks (typically four in number) using the same approach as for the storage test, and then analysed the flasks within a few days of preparation. The analysed  $\text{Ar}/\text{N}_2$  ratios of these flasks were 9 per meg higher than the purge tank on average, with a standard deviation of  $\pm 19$  per meg. The deviations were not random. Flasks purged at the same time tended to cluster together with standard deviations relative to the replicate mean of around 8 per meg. Much of the overall flask variability was therefore evidently caused by changes in the  $\text{Ar}/\text{N}_2$  ratio of the purge gas stream. Different purge flows, ranging from 0.5 to  $4 \text{ STP } 1 \text{ min}^{-1}$  were used on different dates. The highest  $\text{Ar}/\text{N}_2$  ratios were obtained under the highest flows, while lower flows tended to correlate with lower  $\text{Ar}/\text{N}_2$ , although the variability was higher at lower flows. After the first few sets, we modified the purge set-up to insulate the purged flasks from fluctuations in room temperature. This had no noticeable effect on the mean or variability of the  $\text{Ar}/\text{N}_2$  content of the flasks. The deviations in  $\text{Ar}/\text{N}_2$  from the purge gas were correlated with the deviations in  $\text{O}_2/\text{N}_2$  with a slope of around 2:1 ( $\delta(\text{Ar}/\text{N}_2):\delta(\text{O}_2/\text{N}_2)$ ), consistent with the ratio expected from thermal fractionation within high-pressure cylinders.

## 4. Modelled $\text{Ar}/\text{N}_2$ variations

Before discussing flask results, we describe a numerical model used to simulate variations in atmospheric  $\text{Ar}/\text{N}_2$  which is useful for comparing against the data. The model is based on the TM2 atmospheric tracer transport model (Heimann, 1995), with air-sea  $\text{N}_2$  and  $\text{Ar}$  fluxes as a lower boundary condition.

The air–sea N<sub>2</sub> flux was computed via eq. (1) on a monthly basis over the ice-free ocean surface. The solubility derivatives needed in eq. (1) were based on the Weiss (1970) solubility relation evaluated at the annual-mean sea-surface temperature (SST) at each grid point, and were treated as spatially variable but constant with time. The annual-mean SSTs and the ice mask were derived from the Shea et al. (1992) climatology. The heat fluxes needed in eq. (1) were treated as separate annual-mean and monthly anomaly components. The annual-mean component was based on the climatology of da Silva et al. (1994), while the monthly anomalies were based on the European Centre for Medium-Range Weather Forecasting (ECMWF) monthly heat flux climatology (Gibson et al., 1997). The air–sea Ar flux was computed by multiplying the molar N<sub>2</sub> flux by a constant scale factor of 0.0295. According to the solubility relations of Weiss (1970), this factor should vary slightly with temperature, but the variations are too small to be significant. The model was run for a total of 4 yr, using only the final model year for comparison with observations.

From the favourable data/model comparison presented in Battle et al. (2003), we are encouraged to believe that this model provides a reasonable “first guess” for the mean annual cycle of atmospheric Ar/N<sub>2</sub> ratio, with a probable phasing error of the order of 1 month. Although we cannot be as confident in the predicted annual-mean Ar/N<sub>2</sub> values, the model still should be useful for establishing the plausible rough magnitude of annual-mean gradients.

## 5. Flask results

### 5.1. Station data

Results for Ar/N<sub>2</sub> from flasks collected at an array of nine stations are presented in Fig. 11 as summarized in Tables 4 and 5. The data are collapsed into a single year since the data do not resolve any meaningful long-term trends.

Also shown in Fig. 11 are the model simulations of the expected seasonal variations in Ar/N<sub>2</sub>. The model output for the grid points corresponding to the flask sampling stations were fitted to a function consisting of a constant (annual-mean value) plus an annual cycle (consisting of the fundamental plus three harmonics). To facilitate graphical comparison of the model and observations, we adjust the model predictions at each station by an additive constant to minimize the residuals between the model and the individual flask concentrations in a least-squares sense. The annual-mean value of the adjusted model is therefore effectively a measure of the observed, rather than modelled, annual-mean Ar/N<sub>2</sub> at each station. These adjusted annual means are summarized in Table 5 along with the annual-mean concentrations originally predicted by the model.

The observed annual-mean values lie within a range of –6 to +2 per meg, except for the result from the South Pole, which lies at +10 per meg. These annual means are not highly sensi-

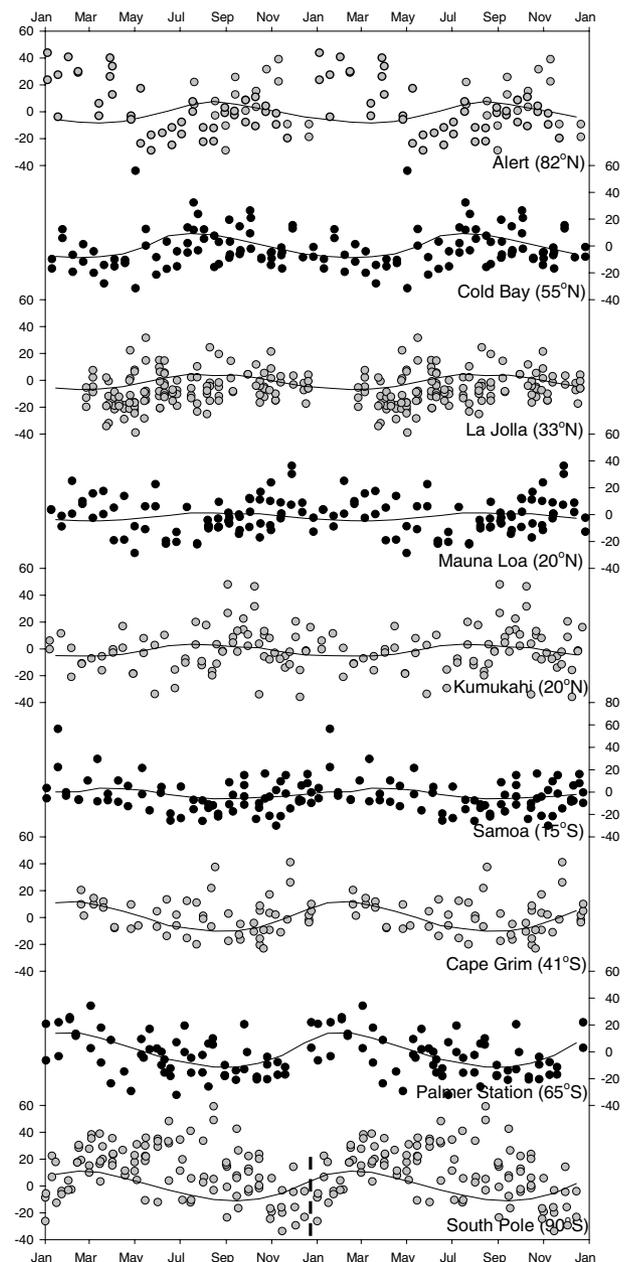


Fig 11. Observed (points) and modelled (curves) variations in the atmospheric Ar/N<sub>2</sub> ratio. The model curves have been adjusted vertically, via an additive constant, to optimally fit the observations at each station. Data have been collapsed into a single year to form a climatology, which is then displayed over 2 yr. For the South Pole, the dashed line separates flasks that “winter-over” (after line) from those that are more promptly return shipped (before line). Station details given in Table 4.

tive to the method of computation. For example, repeating the fitting procedure with no cycle or with a cycle that is doubled in amplitude changes the estimated mean values by only a few per meg. Although the differences in annual-mean values between

Table 4. Sampling stations in the Scripps flask network

Station code	Site	Lat.	Long.	Elevation (m)	Time period
ALT	Alert, Northwest Territories	82°27'N	62°31'W	210	Jul. 2001–Nov. 2002
CBA	Cold Bay, Alaska	55°12'N	162°43'W	25	Jul. 2001–Nov. 2002
LJO	La Jolla, California	32°52'N	117°15'W	20	Jun. 2001–Jun. 2003
MLO	Mauna Loa, Hawaii	19°32'N	155°35'W	3397	Aug. 2001–Dec. 2002
KUM	Kumukahi, Hawaii	19°31'N	154°49'W	40	Jul. 2001–Dec. 2002
SMO	Cape Matatula, American Samoa	14°15'S	170°34'W	42	Aug. 2001–Dec. 2002
CGO	Cape Grim, Tasmania	40°41'S	144°41'E	94	Aug. 2001–Dec. 2002
PSA	Palmer Station Antarctica	64°55'S	64°0'W	10	May 2001–Nov. 2002
SPO	South Pole Station	89°59'S	24°48'W	2810	Jan. 2000–Dec. 2002

Table 5. Ar/N<sub>2</sub> statistics from field stations (per meg)

	ALT	CBA	LJO	MLO	KUM	SMO	CGO	PSA	SPO
Modelled annual mean <sup>a</sup>	−4.7	−3.6	−2.9		−3.1	−1.3	0.0	0.6	0.0
Observed annual-mean <sup>a</sup>	2 ± 3	−2 ± 2	−6 ± 1	0 ± 2	2 ± 2	−4 ± 2	0 ± 3	−3 ± 2	10 ± 2
Modelled seasonality <sup>b</sup>	−13.4	−15.7	−10.3	−5.3	−7.8	6.7	20.1	23.1	19.3
Observed seasonality <sup>c</sup>	19 ± 6	−13 ± 4	−10 ± 3	6 ± 4	−14 ± 6	9 ± 4	8 ± 5	16 ± 6	9 ± 5
Residuals from seasonal model ( $\sigma_{\text{overall}}$ )	±23	±14	±16	±15	±11	±15	±13	±15	±22
Uncorrelated error ( $\sigma_{\text{uncorr}}$ )	±12	±10	±10	±11	±9	±10	±11	±12	±14
Correlated error ( $\sigma_{\text{corr}}$ )	±18	±10	±13	±11	±7	±10	±6	±10	±17
Synoptic variability, estimated upper bound ( $1\sigma$ ) <sup>d</sup>	±2.9	±3.8	±4.6	±2.6	±3.7	±2.7	±2.9	±2.6	±2.6

<sup>a</sup>Difference from value at CGO.

<sup>b</sup>Differences between 3-month averages, Jan/Feb/Mar minus Jul/Aug/Sep.

<sup>c</sup>Differences between 3-month averages, Feb/Mar/Apr minus Aug/Sep/Oct. The observed seasonality is computed 1 month later than modelled seasonality to account for the expected 1-month phasing error of the model.

<sup>d</sup>Calculated from the variability in APO at each station (see text).

stations are statistically robust in some cases, we nevertheless are inclined to view these differences as being mostly the result of systematic sampling errors. Using similar sampling procedures, Battle et al. (2003) reported differences as large as 30 per meg between stations in their network. Although we see no evidence of such large differences in our data averages, it is clear that improvements in methodology will be needed before gradients as small as those expected from the model simulation can be resolved with confidence.

Due to the large scatter and the limited number of samples collected to date, our data are only marginally able to resolve seasonal cycles, although they do provide bounds on the possible magnitude of the cycles. To provide a quantitative model/data comparison, we bin the individual flask measurements into two 3-month seasons, August–October and February–April, and compare the mean concentrations for these periods. These seasons were selected, *a priori*, to coincide roughly with the expected maxima and minima in the Ar/N<sub>2</sub> cycles. We also average the model output over similar 3-month periods, using periods shifted 1 month earlier to account for the expected phasing error. The modelled and observed seasonal differences are

compared in Table 5. The stations with the best-resolved seasonal differences are Cold Bay, La Jolla and Palmer, where seasonal differences of the order of 10 to 20 per meg are evident, in agreement with model predictions. The most notable discrepancy is at Alert, where the data seem to indicate a cycle with opposite phasing from the model. A similar discrepancy may exist at Mauna Loa. At the South Pole, where 3 yr of data are available, a cycle is evident in the data, but shifted several months later than the model predictions. At the remaining stations (Kumukahi, Samoa and Cape Grim), the observed seasonal differences are marginally significant, with a sign and rough magnitude that agrees with the model predictions.

The standard deviation of the residuals in Fig. 11, between observations and the model, are given in Table 5. Depending on the station, these standard deviations, which we denote as  $\sigma_{\text{overall}}$ , range from ±11 to ±23 per meg. These standard deviations are not sensitive to the details of the model. For example, repeating the fitting procedure with no cycle or with a cycle doubled in amplitude changes the resulting standard deviations by typically 20% or less.

## 5.2. Discussion of noise sources

In this section we discuss the possible origins of the overall scatter in our data as reflected in the parameter  $\sigma_{\text{overall}}$ . We start by dividing  $\sigma_{\text{overall}}$  into two contributions according to

$$\sigma_{\text{overall}}^2 = \sigma_{\text{corr}}^2 + \sigma_{\text{uncorr}}^2$$

where  $\sigma_{\text{uncorr}}$  is the  $1\sigma$  error based on flask replicates, as described earlier. This separation, carried out station by station, is summarized in Table 5. It is seen that  $\sigma_{\text{uncorr}}$  and  $\sigma_{\text{corr}}$  are of comparable magnitude and thus make comparable contributions to the overall scatter. There are some notable differences between stations, with ALT and SPO having both larger correlated and uncorrelated errors relative to other stations.

**5.2.1. Uncorrelated errors.** The uncorrelated error  $\sigma_{\text{uncorr}}$  can arise from three potential sources: (1) noise in the mass spectrometer, (2) errors in the daily working gas determinations or (3) random variability in the air recovered from the flasks. The mass spectrometer contributes around  $\pm 3$  per meg, based on the allowed integration time of 4 min on the flask peak and 4 min for each leading and trailing baseline (see Fig. 9) and based on the 10 s imprecision in  $\delta_i$  of  $\pm 10$  per meg. The working gas contributes at most around  $\pm 2$  per meg, based on the results from Fig. 7. Taking the quadrature sum of these two contributions yields only  $\pm 4$  per meg, which is essentially negligible compared with the observed total  $\sigma_{\text{uncorr}}$  of (typically)  $\pm 11$  per meg. We conclude, therefore, that the third source must dominate—in other words, that almost all of the scatter among replicates arises from actual variations in the Ar/N<sub>2</sub> ratios of the air recovered from the flasks.

The variability in the air recovered from flasks could arise either from gas handling in laboratory or in the field. Although we cannot clearly separate these two contributions, a substantial contribution almost certainly arises from laboratory practices. A laboratory imprecision of around  $\pm 8$  per meg would be consistent with the results from baseline tests, described above. Also supporting a laboratory contribution are results we obtained using a different laboratory set-up, which we employed briefly in 1998. Excluding flasks collected from the South Pole, this set-up achieved an uncorrelated imprecision of  $\pm 4$  per meg in Ar/N<sub>2</sub> (based on 77 flasks), which is considerably better than we achieve with our present set-up. In this temporary set-up, which was permanently disassembled when relocating the laboratory in early 1999, flask air was delivered to the mass spectrometer via a pick-off T located directly upstream of the interferometer (see Fig. 1 of Keeling et al., 1998). This allowed higher flows ( $\sim 260$  STP ml min<sup>-1</sup>) to be maintained through the flasks during analysis, while eliminating the pressure drop during analysis, which was possibly advantageous in reducing fractionation in the laboratory.

A substantial contribution to the random variability of the air recovered from flasks probably also arises from flask handling outside our laboratory, either during the sampling, shipping or

storage of flasks. Station-specific effects are implicated at several stations, e.g. Alert, Palmer Station and the South Pole, where the uncorrelated error appears larger than at other stations. Larger uncorrelated error was also noted at the South Pole in flasks analysed with the temporary set-up used in 1999.

As noted earlier, the observed correlation of 4:1 between the Ar/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> residuals (Fig. 10b) is consistent with the ratio expected from thermal diffusion at 1 atm pressure. Thermal diffusion could occur either in the field or the laboratory. For example, in the laboratory, the effect could arise from residual temperature gradients around the flasks during analysis or from flask-to-flask variability in the pressure-induced thermal fractionation, described in Section 3.3. In the field, variable thermal fractionation could occur at the sampling intake, e.g. due to solar heating, or in the flasks themselves, due to non-uniform temperatures during sampling. It should be noted, however, that thermal fractionation is unlikely to be the sole cause of replicate variability because many of the points in Fig. 10b lie well off the 4:1 line. Among the possible complications are oxidation reactions that influence only O<sub>2</sub> and O-ring effects.

**5.2.2. Correlated errors** Turning now to the correlated errors, which are shared by all members of flask replicates, we can conceive of four possible contributions: (1) real atmospheric variability that is not reflected in the smoothed model results, e.g. related to the passage of synoptic weather patterns, (2) other natural atmospheric variability, (3) sampling artefacts and (4) storage effects. We now discuss these possibilities in turn.

An estimate of the contribution from synoptic variability can be formulated based on a scaling argument that makes use of the observed variability in O<sub>2</sub>/N<sub>2</sub> ratio and CO<sub>2</sub> concentration. As described in Stephens et al. (1998), it is possible to combine O<sub>2</sub>/N<sub>2</sub> ratio and CO<sub>2</sub> data to derive the tracer ‘‘APO’’ (‘‘atmospheric potential oxygen’’), that undergoes seasonal cycles and synoptic variability as a consequence primarily of air–sea exchanges of O<sub>2</sub>. The seasonal air–sea fluxes of O<sub>2</sub>, although partially biologically mediated, are largely controlled by ocean heating and cooling (Garcia and Keeling, 2001), and thus should be strongly correlated with air–sea Ar and N<sub>2</sub> fluxes. Given that the surface sources of APO and Ar/N<sub>2</sub> are highly correlated, the synoptic variability in Ar/N<sub>2</sub> must be similar in magnitude to the synoptic variability in APO, when both are expressed as a fraction of the seasonal cycle. Since we have observations of the variability in APO at each of our stations, we can thus easily formulate an estimate of the expected synoptic variability in Ar/N<sub>2</sub> at each station. As summarized in Table 5, the estimates vary between  $\pm 2.5$  and  $\pm 5$  per meg, depending on the station. These estimates assume that the Ar/N<sub>2</sub> cycle at each station has a magnitude equal to 30% of the corresponding APO cycle (with both expressed in per meg units), which is roughly consistent with the Ar/N<sub>2</sub> model predictions in relation to our APO observations and consistent with the results presented in Battle et al. (2003). These estimates of Ar/N<sub>2</sub> variability should probably be treated as upper bounds, since the scatter in our APO data, which

we use as a measure of synoptic variability, may also partly be due to measurement artefacts. In any case, it is clear that synoptic variability makes a negligible contribution to the scatter in our Ar/N<sub>2</sub> data.

While synoptic variability may not be a major contributor to the correlated errors, another source of natural variability perhaps deserves attention. Throughout the free troposphere the separation of air into its constituent components by gravimetric or thermal diffusive separation is overwhelmed by turbulent mixing. However, it is conceivable that a slight separation may occur within stable surface air layers that are capped by strong inversions. In the absence of turbulent motions, Ar/N<sub>2</sub> would fractionate by ~52 per meg per metre of elevation or by ~260 per meg °C<sup>-1</sup> in a thermal gradient (at 0 °C).

Consider, for example, a surface layer 30 m thick with a 5 °C gradient from top to bottom and which maintains a constant composition at the top by turbulent mixing with air above. First, suppose the air within the layer is completely stagnant. The air at the surface will be enriched in Ar/N<sub>2</sub> by 3200 per meg relative to the overlying air, with 60% of the enrichment due to gravimetric fractionation and 40% due to thermal fractionation. At 15 m the enrichment would be half that large, i.e. 1600 per meg, etc. The timescale for approaching this steady state is ~265 days, based on the molecular diffusivity of Ar in air at 0 °C of  $D_{\text{mol}} = 0.16 \text{ cm}^2 \text{ s}^{-1}$  (Reid et al., 1987). Now suppose that the air within the layer is not stagnant, but rather is exchanged with the overlying air on a timescale of 1 day. This corresponds to an effective eddy diffusivity within the layer of around  $D_{\text{eddy}} = 42 \text{ cm}^2 \text{ s}^{-1}$ . In steady state, the enrichment is now 12 per meg at the surface and 6 per meg at 15 m, while the timescale for approaching steady state is ~1 day. The enrichment and the timescale for approaching steady state are both smaller than the stagnant case by a factor of  $D_{\text{mol}}/(D_{\text{eddy}} + D_{\text{mol}})$ . The calculation shows that measurable enrichment may occur within surface layers with depths of the order of 10 m if the exchange times are a long as tens of hours. The calculation does not consider the effects of convergent subsidence flow, which could lead to excess Ar accumulation into even deeper layers.

Most of our samples are collected in daylight in the absence of strong inversions, so are unlikely to be influenced by this sort of mechanism. At Alert and the South Pole Stations, however, strong inversions are present throughout the winter (Kahl et al., 1992; Neff, 1999). The near-surface residence time of air at these sites is not well constrained but is almost certainly of the order of hours or more. It is thus conceivable that measurable near-surface fractionation is occurring. The effects could potentially bias both the mean values and annual cycles at these stations relative to the background troposphere.

Another possible source of correlated error is fractionation at the air intake in the field. Using a continuous field-based O<sub>2</sub>/N<sub>2</sub> system with a sampling rate of 100 STP ml min<sup>-1</sup>, Manning (2001) noted swings of the order of 20 to 30 per meg in O<sub>2</sub>/N<sub>2</sub> over an hourly timescale which he attributed to thermal diffu-

sion at the intake (e.g. related to solar heating), and which therefore were presumably associated with swings in Ar/N<sub>2</sub> that were about four times larger. Manning reduced the effect by removing a glass-wool-filled PVC pipe used as a particle filter from the intake, which reduced the residence time of air in the inlet. A similar effect may influence our flask results, although the magnitude of the effect will be many times smaller due to the much larger sampling flows we employ (2–5 l min<sup>-1</sup>). Thermal diffusion at the intake can presumably be reduced by increasing the sampling flow (e.g. using larger pumps). Shading of the intake from sunlight and restricting sampling to periods of higher winds may also be helpful.

Finally, we must consider the possibility that correlated errors could arise from storage effects. Although we do not expect significant systematic storage effects at most of our stations on the basis of the storage tests reported above, these tests do not rule out substantial problems at the South Pole, where the flasks are stored at the station for as much as 9 months before return shipment. As the station pressure is typically 680 mbar, we might expect our South Pole flasks to be influenced by permeation through the stopcock O-rings to a much greater extent than flasks used in our storage tests. Any such effect, however, would be expected to produce a discontinuity in the South Pole data in late December, since storage times are much greater for flasks after this time of year than before. (The storage times at the South Pole vary depending on the time of year as dictated by the inaccessibility of the station during colder months. The storage times at the station are typically 9 months for samples collected in January, 8 months for samples collected in February, etc., and decreasing to 2 months or less for samples collected between October and December.) Since our results show no obvious discontinuity in late December (see Fig. 11) we conclude that storage effects are unlikely to be a major contributor to the correlated error at the South Pole, although we cannot rule out a small contribution. Storage effects cannot account, for example, for the apparent rise in Ar/N<sub>2</sub> from January to March at the South Pole and the subsequent fall through the remainder of the calendar year.

## 6. Summary

We have described a mass spectrometer system developed to resolve variations in atmospheric Ar/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/N<sub>2</sub> ratios. The system takes advantage of the evolving technology in wide-dispersion mass spectrometers and uses a rapid switching scheme to cancel instrument noise on longer timescales, thus increasing instrument precision. The system allows two flowing gas streams to be compared to a precision of around 10 per meg in Ar/N<sub>2</sub> every 10 s, and also allows simultaneous measurement of CO<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> ratios to very high precision. The Ar/N<sub>2</sub> signals can be meaningfully averaged to compare Ar/N<sub>2</sub> ratios from air delivered from high-pressure cylinders to a precision of a few per meg. These results demonstrate that considerable

progress is being made technologically for measuring changes in the Ar/N<sub>2</sub> ratio of the atmosphere and provide a basis for optimism that such measurements may eventually prove useful for improving estimates of large-scale air–sea heat transport.

The system has been applied to analyse flask samples from a global network of stations. Marginally significant seasonal cycles have been resolved at several stations. The data show surprisingly large scatter, however, which limits their usefulness. This scatter arises mostly from real variations in the Ar/N<sub>2</sub> ratios in the air extracted from the flasks. These variations are evidently caused by gas handling artefacts in both the laboratory and in the field. We see clear evidence of variations that are uncorrelated among sets of flask replicates, and hence may average to zero, as well as errors that, more troublingly, are correlated among sets of flask replicates. In the absence of a clear understanding of these effects, we must assume that these errors have the potential to bias both the seasonal cycles and annual-mean values obtained at different stations. Although similar problems undoubtedly also impact upon O<sub>2</sub>/N<sub>2</sub> measurements made on the same flasks, the effects tend to be smaller for O<sub>2</sub>/N<sub>2</sub> by a factor between 2 and 4.

The mass spectrometer system described here provides a powerful tool for diagnosing fractionation due to its high intrinsic precision, so we are optimistic that substantial improvements in flask handling can be realized in the future. These efforts can also be expected to improve the quality of O<sub>2</sub>/N<sub>2</sub> measurements. Furthermore, a shorter path to making precise atmospheric Ar/N<sub>2</sub> may be possible by using mass spectrometer systems, like that described here, for direct field measurements, bypassing the need for flasks altogether. The ISOPRIME is especially attractive for this purpose, due to its reliability (less than two filaments needed per year of operation) and its low size and weight.

## 7. Acknowledgments

We are indebted to Michael Bender and Mark Battle for useful discussions. This work was supported by the US NSF under grants ATM-94000694, ATM-9601722, ATM-0000923, and the NOAA Office of Global Programs under grant NA77RJ0453A. T. Blaine was supported by a US National Defense Science and Engineering Graduate Fellowship. Much of this work was completed in part while one of us (RK) was hosted at the Max Planck Institute for Biogeochemistry in Jena, Germany. We thank the staff of the NOAA-CMDL program at Mauna Loa, Kumukahi, Samoa and the South Pole, staff of the National Weather Service at Cold Bay, staff of the Cape Grim Station and staff of Palmer Station for collection of air samples.

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