

## 8. Nitrous Oxide and Halocarbons Group

### 8.1. CONTINUING PROGRAMS

#### 8.1.1. SAMPLES

GMCC scientists have been analyzing flask samples for nitrous oxide ( $N_2O$ ), and halocarbons CFC-12 ( $CCl_2F_2$ ) and CFC-11 ( $CCl_3F$ ) since 1977 at the GMCC baseline observatories and NWR. During 1987, air samples pressurized to about 8 psig were collected in a pair of 0.3-L Summa treated stainless steel cylinders each week at BRW, NWR, MLO, and SMO. Station personnel at SPO collected a pair of flask samples each week only during the Antarctic summer (November-January). These air samples were shipped back to Boulder for analysis by EC-GC.

Figure 8.1 shows plots of the average concentration from a flask pair versus time for  $N_2O$ , CFC-12, and CFC-11 at BRW, NWR, MLO, SMO, and SPO. Table 8.1 lists monthly concentration means for NOAA/GMCC flask pairs as mole fraction in dry air for  $N_2O$ , CFC-12, and CFC-11 collected from NOAA/GMCC baseline stations and NWR. Estimated secular trends and  $\pm 2$  standard deviations at the 95% confidence level are also presented. Flask data are not included for May 1984 to February 1985, because the ECD response during this time was not linear. Figure 8.2 shows the strong latitudinal dependence, higher in the northern hemisphere than the southern hemisphere, and the accumulation rates of CFC-12 and CFC-11 from plots of the yearly mean concentration versus latitude since 1977. More information on experimental design and techniques used in data selection are described in *Thompson et al.* [1985].

Since 1983, a manually operated Shimadzu Mini-2 GC at SPO measured  $N_2O$ , CFC-12, and CFC-11 in situ twice a week. The monthly mean concentrations of  $N_2O$ , CFC-12, and CFC-11 from the in situ GC were compared with monthly means from

flask samples and are shown in the bottom panel of Figure 8.1. The ECD on this GC became contaminated by February 1987, and analyses were stopped until a new detector arrived during the midwinter air drop in June 1987. The results from the flasks and in situ GC at SPO were so sporadic that it was decided to upgrade the existing in situ GC in early 1988. The upgraded GC system will include unattended, automated analyses, increased frequency of atmospheric sampling to once every 3 hours, and the additional sampling of new compounds, methyl chloroform ( $CH_3CCl_3$ ) and carbon tetrachloride ( $CCl_4$ ). An IBM PC clone computer will be used to store chromatographic information from two HP integrators, and to send this information back to Boulder via satellite each week for rapid analysis of data and for diagnosis of potential problems. These improvements may help resolve the question concerning the effects of vertical transport on the ozone hole. More technical information on GMCC's SPO  $N_2O$  and halocarbon measurements can be found in *Robinson et al.* [1988] and *Elkins et al.* [1988].

The calibration scales for GMCC's atmospheric measurements of CFC-12 and CFC-11 have been based since 1977 on the OGC scale of R. Rasmussen [*Rasmussen and Lovelock*, 1983]. NOAA primary calibration tank no. T3072, which was used exclusively from 1977 until 1985 when it was expended, was calibrated last in 1983. The current primary calibration tank no. T3088 was compared almost every 6 months between 1977 and 1985 with tank no. T3072 and replaced it in 1985. Because of concerns about the stability of CFC-12 and CFC-11 in the new tank, it was calibrated at OGC in December 1987. Drift was found to be about  $-4.5$  ppt  $yr^{-1}$  for CFC-12 and negligible for CFC-11 during its 2 years of use. It was assumed that, before 1987, the drift of T3088 was identical to the drift of tank no. T3072, having drift rates of about  $-1.5$  ppt  $yr^{-1}$  for CFC-11 and  $+5$  ppt  $yr^{-1}$  for CFC-12. The new drift corrections

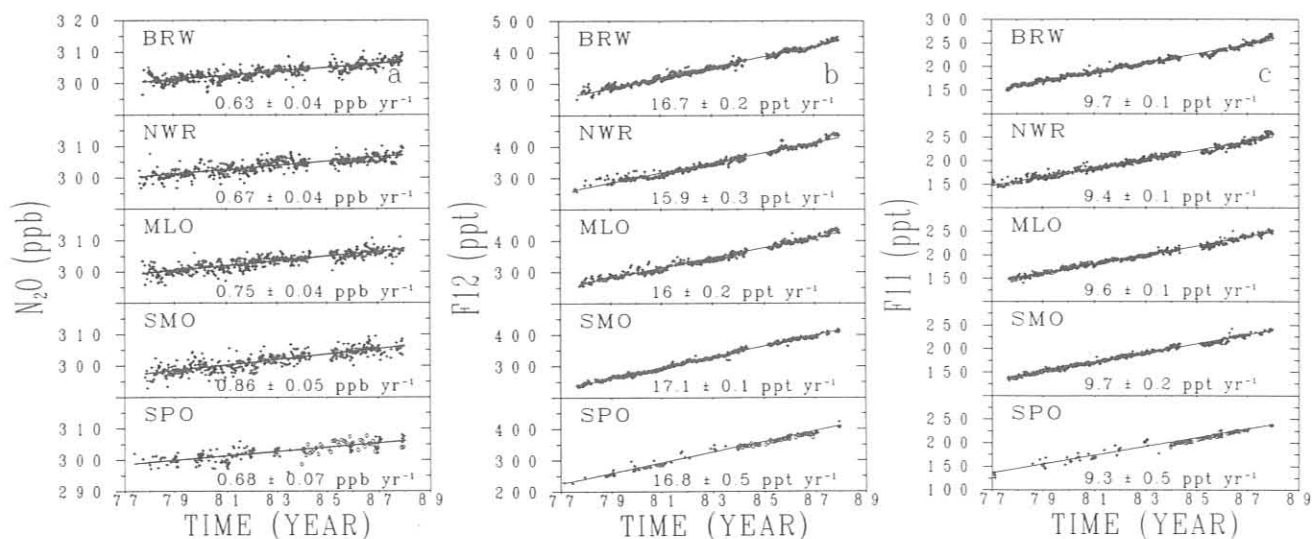


Fig. 8.1. Average concentration of (a)  $N_2O$ , (b) CFC-12, and (c) CFC-11 from measurements of paired flask samples versus time at BRW, NWR, MLO, SMO, and SPO. The trends and  $\pm 2$  s.d. errors are shown. The bottom panel (SPO) in each plot also shows the monthly means (o) from a manually operated GC.



TABLE 8.1. Continued

	N <sub>2</sub> O					CFC12					CFC11				
	BRW	NWR	MLO	SMO	SPO	BRW	NWR	MLO	SMO	SPO	BRW	NWR	MLO	SMO	SPO
FEB 85	305.4	---	306.8	303.0	---	389.3	---	377.3	369.8	---	225.3	---	220.9	211.4	---
MAR 85	306.1	305.4	305.4	304.4	---	387.8	380.0	379.5	368.0	---	224.5	218.8	219.1	209.4	---
APR 85	306.6	306.0	305.7	305.5	---	389.7	379.9	375.4	369.4	---	227.8	219.2	217.2	210.7	---
MAY 85	307.5	307.2	305.4	304.7	---	392.5	384.8	382.4	373.0	---	225.5	222.0	220.3	210.9	---
JUN 85	306.3	305.0	306.0	306.8	---	394.6	385.0	390.5	373.5	---	222.4	219.5	220.6	208.8	---
JUL 85	303.7	306.5	304.6	304.9	---	388.1	386.1	382.7	375.7	---	222.0	218.4	217.4	210.4	---
AUG 85	304.4	305.7	304.4	305.4	---	393.4	393.4	384.5	373.7	---	227.5	221.0	219.0	211.0	---
SEP 85	305.0	306.0	305.9	304.4	---	400.8	406.6	396.0	379.8	---	227.9	230.6	222.4	214.4	---
OCT 85	305.4	306.0	306.4	305.8	---	404.0	401.6	398.6	381.5	---	233.4	229.6	226.7	215.1	---
NOV 85	305.7	306.7	306.7	304.7	304.4	406.8	403.7	392.3	375.6	375.1	235.7	230.3	224.9	214.3	214.6
DEC 85	305.3	305.8	306.7	305.9	305.1	408.3	397.1	398.3	383.6	377.6	236.1	229.0	231.1	218.0	220.9
JAN 86	305.5	306.1	306.5	303.8	306.4	407.0	396.7	395.1	383.9	381.0	236.8	228.3	223.5	217.2	---
FEB 86	305.8	306.2	305.8	306.4	---	408.4	396.1	400.0	388.8	---	236.6	226.3	227.2	216.2	---
MAR 86	305.9	306.1	307.2	305.5	---	409.6	398.4	398.4	386.6	---	233.9	227.2	228.4	218.6	---
APR 86	306.7	306.6	306.4	306.0	---	410.7	397.2	400.2	387.1	---	244.6	231.9	234.0	225.7	---
MAY 86	307.5	306.4	306.4	305.4	---	407.7	404.2	399.5	387.7	---	238.5	234.2	232.6	234.0	---
JUN 86	307.7	306.3	306.7	307.1	---	407.8	404.5	401.1	393.5	---	238.4	234.8	235.4	226.1	---
JUL 86	308.3	307.5	307.9	306.5	---	406.7	400.3	397.2	388.9	---	237.9	231.7	234.1	225.6	---
AUG 86	307.6	306.6	307.4	307.9	---	404.3	405.5	402.1	391.7	---	240.4	237.0	232.4	226.6	---
SEP 86	306.3	306.4	307.4	306.9	---	406.4	399.2	403.1	392.6	---	240.5	233.9	239.4	228.9	---
OCT 86	306.4	306.9	308.6	306.3	---	413.7	406.3	412.1	392.4	---	248.9	240.7	240.4	227.4	---
NOV 86	306.7	306.8	307.7	307.9	305.9	415.5	405.2	409.7	390.8	385.3	246.5	243.8	240.2	225.7	227.1
DEC 86	305.9	306.9	307.1	306.3	304.9	419.4	406.8	409.8	394.1	387.3	250.5	239.9	239.9	229.9	---
JAN 87	307.3	307.7	307.2	305.7	307.3	417.0	409.0	410.5	396.0	390.5	248.9	240.3	239.4	229.6	228.2
FEB 87	307.8	306.7	306.6	304.7	---	417.5	406.7	401.9	398.4	---	249.8	243.5	---	236.4	---
MAR 87	308.0	308.0	307.6	305.3	---	424.9	418.9	421.5	404.5	---	250.2	243.9	243.3	---	---
APR 87	307.2	307.3	305.2	303.9	---	422.6	418.3	412.6	408.1	---	253.3	242.8	---	235.0	---
MAY 87	309.1	307.5	307.5	---	---	430.9	---	---	---	---	253.9	247.4	---	---	---
JUN 87	308.1	307.5	307.0	301.5	---	429.1	433.0	423.1	400.5	---	253.1	249.7	244.9	232.0	---
JUL 87	307.3	305.5	305.6	304.2	---	434.4	432.3	422.2	408.0	---	255.1	248.8	242.2	232.9	---
AUG 87	307.7	307.0	307.2	---	---	433.1	429.2	426.5	---	---	256.5	251.1	246.2	---	---
SEP 87	308.3	305.3	305.5	304.9	---	439.5	438.4	435.8	---	---	259.0	254.5	249.8	239.2	---
OCT 87	308.4	307.9	307.2	304.8	---	443.5	441.3	435.9	409.1	---	262.7	260.8	254.5	236.5	---
NOV 87	307.7	308.4	308.4	304.8	307.6	444.1	439.0	436.0	413.0	407.8	265.5	258.3	252.7	239.9	238.1
DEC 87	309.4	310.1	307.7	305.2	307.2	444.9	438.9	429.0	413.5	410.9	265.9	260.0	248.5	241.1	237.4

Data presented for 1986-1987 are subject to change, pending final calibrations. See text for discussion of calibrations and gaps in data.

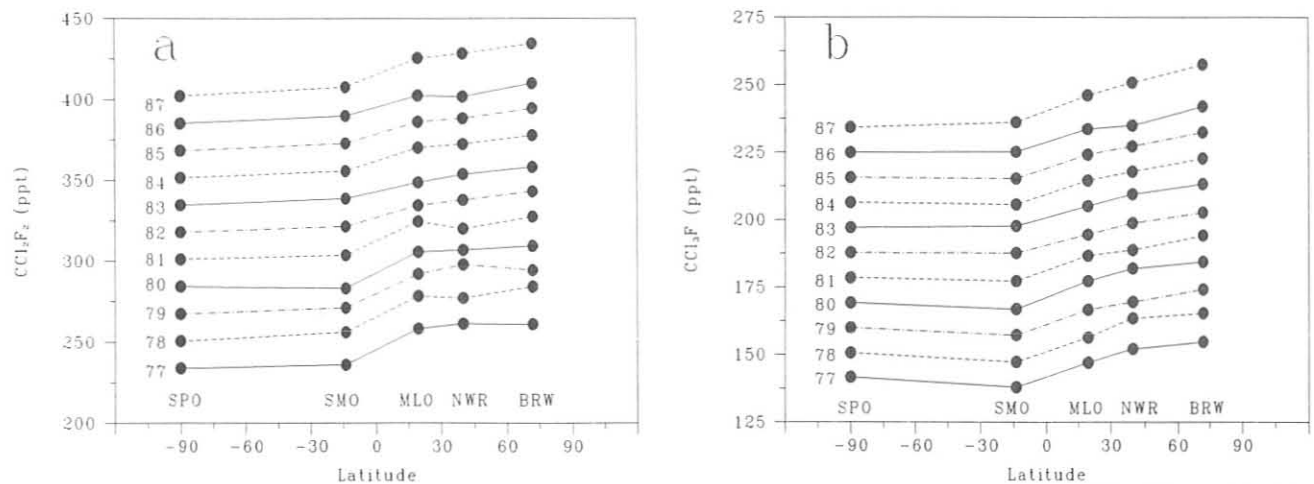


Fig. 8.2. Latitudinal dependence of yearly means for (a) CFC-12 and (b) CFC-11 concentrations at BRW, NWR, MLO, SMO, and SPO for 1977-1987. Yearly means for years 1977, 1984, and 1985 were calculated from the coefficients of the linear least-squares fit in Figure 8.1.

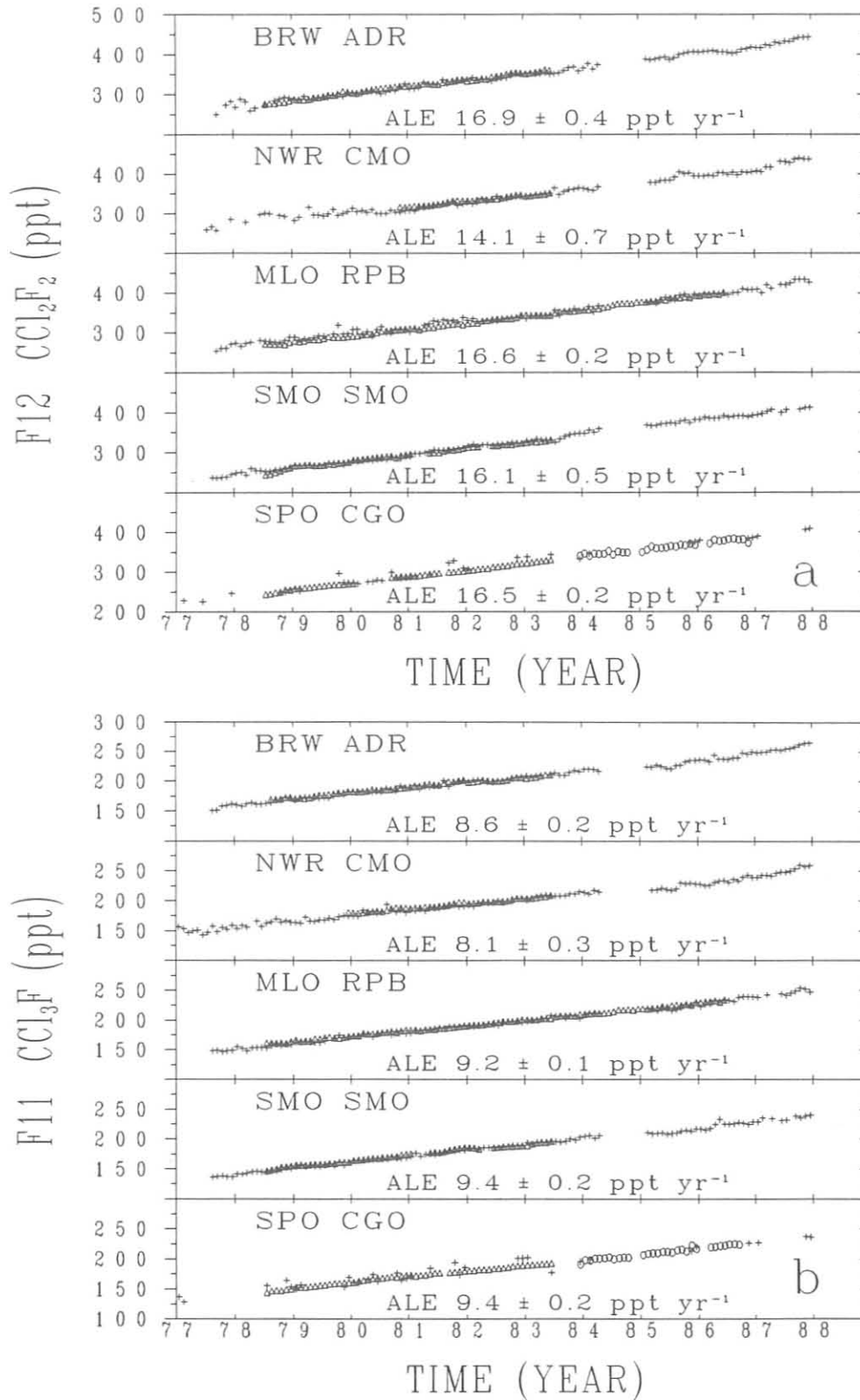


Fig. 8.3. Monthly mean concentrations for (a) CFC-12 and (b) CFC-11 from the NOAA/GMCC flask (+) and the ALE/GAGE ( $\Delta$ ) networks. The SPO plots also show monthly means (o) from the GMCC in situ GC. The ALE/GAGE data were from *Cunnold et al.* [1986], and some additional preliminary data for RPB were provided by P. Simmonds. The trends and  $\pm 2$  s.d. errors are shown for the ALE/GAGE data.

to tank no. T3088 had the effect of reducing the concentration values of CFC-12 and CFC-11 in the last 3 years, yielding for CFC-12 and CFC-11 about a 1 and a 0.6 ppt yr<sup>-1</sup> lower growth rate, respectively, than reported in *Schnell and Rosson* [1987].

Figure 8.3 shows monthly mean concentrations of CFC-12 and CFC-11 from the in situ GCs of the ALE/GAGE network, [Cunnold *et al.*, 1986] and the monthly means from GMCC's halocarbon flask network. Stations of comparable latitude from each network are plotted together. For example, CFC-11 and CFC-12 data from the RPB station of the ALE/GAGE network, which is partly supported by NOAA, at 13°N, 59°W in the North Atlantic Ocean is plotted with data from MLO. P. Simmonds from RPB has graciously provided further data, which are currently provisional and subject to change from mid-1985 to mid-1987. The comparison in growth rates for CFC-12 and CFC-11 between the two networks is very good at most locations, and excellent where the two networks share the same site at SMO.

The calibration scale used for GMCC's atmospheric N<sub>2</sub>O measurements is the NBS SRM scale, prepared using gravimetric techniques [Zielinski *et al.*, 1986]. On average, this scale is 1 ppb lower than the gravimetric and dynamic dilution scale of *Komhyr et al.* [1988] and 1 ppb higher than the manometric scale of *Weiss et al.* [1981], and is acceptably within the experimental uncertainties of other techniques. The NBS N<sub>2</sub>O scale is about 3 ppb lower than the Rasmussen scale currently used by the ALE/GAGE network.

#### 8.1.2. RITS CONTINUOUS GAS CHROMATOGRAPH SYSTEMS AT GMCC BASELINE STATIONS

The new RITS automated GC and data processing system was installed at MLO in June. This system joined others that were installed at SMO in June 1986 and at BRW in October 1986. Additions in 1987 to the systems included a separate backflush EC-GC for measuring N<sub>2</sub>O without any interference from CO<sub>2</sub>, a Supelco SP2100 column to separate CFC-113 from CFC-11, two calibration standards instead of one, and specially treated aluminum cylinders to enhance the stability of halocarbons in standards. The system consists of an HP model no. 5890 GC, a Shimadzu model no. GC-8AIE GC, two Nelson Analytical interfaces, an HP9816 computer, an HP9133 15-megabyte hard disk drive, and a printer. The system measures air concentrations of N<sub>2</sub>O, CFC-12, CFC-11, CH<sub>3</sub>CCl<sub>3</sub>, and CCl<sub>4</sub> every 3 hours. Figure 8.4 shows a comparison of flask samples with daily means from the in situ RITS GC for CFC-12 at BRW and SMO. The growth rate of CFC-12 in 1987 from BRW flask pairs appears to have increased from its average rate by about 8 ppt yr<sup>-1</sup>, and this increase is also apparent from the in situ GC results at BRW. The reason for the increase is unknown and is being investigated for both real and experimental causes. Figure 8.5 shows results from the new back-flush N<sub>2</sub>O GC at BRW and SMO. The N<sub>2</sub>O concentration values from the flask pairs that include a correction for CO<sub>2</sub> and H<sub>2</sub>O interference appear to be 1 to 2 ppb higher than those measurements from the in situ back flush GC's at the stations. This implies that our correction for the N<sub>2</sub>O values from the flask pairs may need further refinement. Owing to regulator contamination problems,

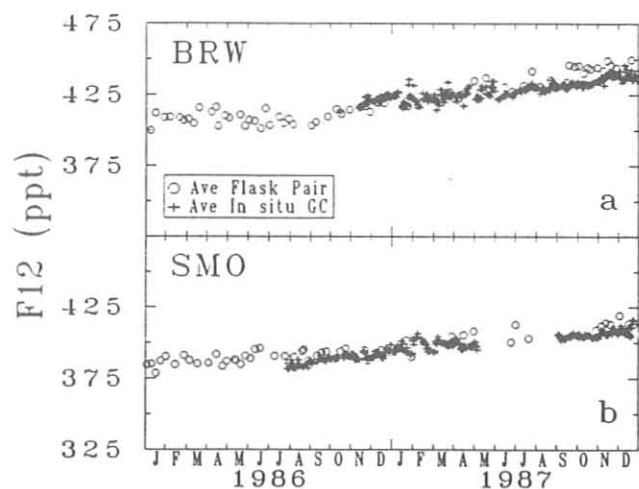


Fig. 8.4. CFC-12 concentrations from flask pair samples (o) and daily means from the in situ RITS GCs (+) versus time at (a) BRW and (b) SMO.

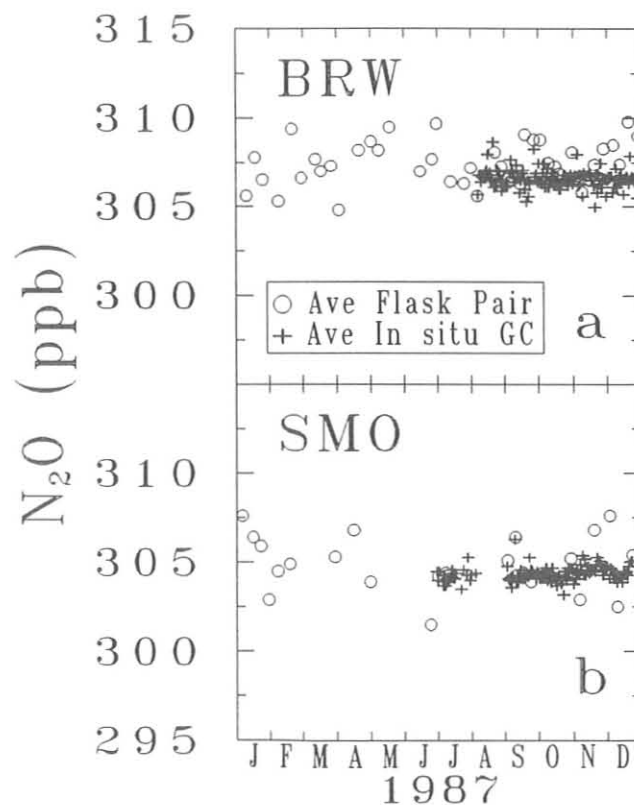


Fig. 8.5. N<sub>2</sub>O concentrations from flask pair samples (o) and daily means from the in situ RITS GCs (+) (using Porapak Q in backflush mode) versus time at (a) BRW and (b) SMO.

the data for CH<sub>3</sub>CCl<sub>3</sub> and CCl<sub>4</sub> are very noisy. Changes will be made in 1988 to correct the contamination problems.

### 8.1.3. LOW ELECTRON ATTACHMENT POTENTIAL SPECIES

Considerable progress was made towards our goal in measuring the low electron attachment potential species (LEAPS). LEAPS are atmospheric gases which have a low response on an ECD either due to their low atmospheric concentration levels or their lack of sensitivity on the ECD. A literature review was completed on possible approaches for measuring the four gases: halons 1211 (CBrClF) and 1301 (CBrF<sub>3</sub>), and halocarbons CFC-22 (CHClF<sub>2</sub>) and CFC-113 (CCl<sub>2</sub>F-CClF<sub>2</sub>). Decisions were made by GMCC scientists concerning sample collection, concentration, and analysis, and the gas chromatograph and columns were chosen. The initial approach will involve preconcentrating samples onto tubes packed with adsorbent. The ultimate choice of collection temperature and adsorbent will depend on the results of ensuing tests. The tubes can then be brought to Boulder for analysis. The gases adsorbed to the tube packing will be thermally transferred to a cryogenic focusing trap, injected onto a wide-bore capillary column, and measured by temperature-programmed EC-GC. Pressurized Summa-treated stainless steel flasks also will be collected at baseline observatories and NWR, and shipped to Boulder for analysis by cryogenic focusing and capillary EC-GC.

It is planned to compare a number of columns, including the new PLOT columns, for their ability to separate these gases. These columns should be able to separate all of the gases without interference from oxygen. However, CFC-22 may require carrier-gas doping. If two columns are needed, the LEAPS GC is equipped with two independent channels for separate analyses. It also is apparent that it will be possible to obtain measurements of CFC-113 from the packed SP2100 columns on RITS station GCs. The problems that have been identified with the current CFC-113 analyses are contamination by the gas regulators and preparation of a long-lived standard. An investigation of possible solutions to these and other problems has begun, and it is anticipated that the first measurements of LEAPS gases will occur in 1988.

### 8.1.4. GRAVIMETRIC STANDARDS

A gravimetric standards laboratory was completed at Boulder in 1987, and a CIRES research assistant was hired to prepare gravimetric standards. A custom Voland double-pan analytical balance, which is capable of weighing 10 kg cylinders (0.9 m tall by 0.3 m wide) to  $\pm 1$  mg, was installed. For liquid phase halocarbons, like CFC-11, CFC-113, CH<sub>3</sub>CCl<sub>3</sub>, and CCl<sub>4</sub>, a microbalance capable of weighing 4 g of a liquid in a glass tube to precisions of  $\pm 0.1$   $\mu$ g was also set up. Gravimetric standards of N<sub>2</sub>O were compared against the OGC scale and the SIO scale, and the results were discussed at the end of section 8.1.1. Gravimetric standards of CFC-12 and CFC-11 were compared against the OGC scale. The results were in good agreement with the NOAA scales for CFC-12 and CFC-11 from gravimetric standards, and were found to be about 1 and 4% lower than the OGC scale, respectively. NOAA/GMCC will continue to report CFC-12 and CFC-11 values on the OGC scale until these small disagreements are resolved. Gravimetric

standards for CH<sub>3</sub>CCl<sub>3</sub>, and CCl<sub>4</sub> were prepared, and the NOAA scale for these gases will be compared in the future to other international standards.

## 8.2. SPECIAL PROJECTS

### 8.2.1. SOVIET-AMERICAN GAS AND AEROSOL EXPERIMENT

#### Objectives

The N<sub>2</sub>O and Halocarbons group took the lead for GMCC's effort in SAGA II, a joint US/USSR research cruise that occurred from April to August 1987. This expedition involved the measurement of atmospheric and dissolved trace gases in and over the west Pacific and east Indian Oceans, and was conducted in conjunction with the Carbon Cycle group of GMCC, NOAA/PMEL, OGC, SIO, University of Washington, Washington State University, and University of Hawaii. The gases measured by GMCC were N<sub>2</sub>O in the atmosphere, surface waters, and at depth, and CFC-11, CFC-12, CO<sub>2</sub>, and CH<sub>4</sub> in the atmosphere and surface waters. Flask samples were also collected for subsequent analysis of CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and perhaps the LEAPS gases as well.

The cruise track is shown in Figure 8.6. GMCC scientists began the cruise at Hilo, Hawaii, sailed up to the Kamchatka Peninsula, down to Wellington, New Zealand, around Australia into the Indian Ocean, up to Singapore, and back to Hilo.

The objectives were (1) to test a highly precise technique for measuring N<sub>2</sub>O under rigorous operating conditions, (2) to test a new, automated, headspace sampler for measuring dissolved N<sub>2</sub>O, (3) to compare the latitudinal, atmospheric gradients with those indicated from our station sampling network, (4) to detect any sharp interhemispheric gradients of N<sub>2</sub>O, CFC-11, CFC-12, CO<sub>2</sub>, or CH<sub>4</sub> near the equator, (5) to evaluate the fluxes of these gases from the sea surface to the atmosphere along this transect,

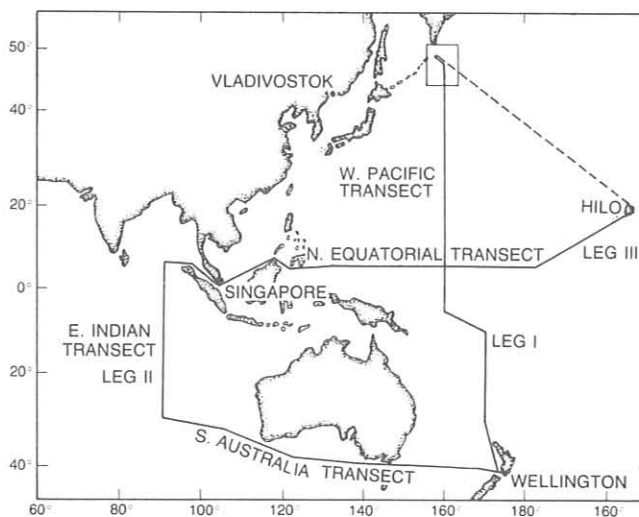


Fig. 8.6. Cruise track of the SAGA II experiment during April-July 1987 aboard the Soviet research vessel *Akademik Korolev*. The dashed line shows the shake-down leg.

(6) to observe any signals that may be associated with the recent ENSO event, and (7) to compare our atmospheric measurements with those from other shipboard investigators and from some of the ALE/GAGE network stations.

### Results

More than 2000 measurements were made each for  $N_2O$ , CFC-11, and CFC-12 in the air and surface water and more than 600 measurements of  $N_2O$  at depth. The precision of the  $N_2O$  backflush technique, discussed by Zielinski *et al.* [1986], remained at less than  $\pm 0.2\%$  for air samples; atmospheric CFC-12 and CFC-11 were measured with precisions of  $\pm 0.3\%$  and  $\pm 0.5\%$ . Relative error was less than  $\pm 1\%$  for the equilibrated surface water and less than 2% for the automated headspace sampler. Substantial  $CO_2$  and  $CH_4$  data were obtained for most of the first leg, but the Weiss dual-catalyst FID GC never fully recovered from a breakdown near the equator.

Figure 8.7 shows the atmospheric, the surface water, and the difference between air and surface water concentrations for  $N_2O$ , CFC-12, and CFC-11 versus distance traveled. The average atmospheric  $N_2O$  concentration in the northern hemisphere was about 0.97 ppb higher than that for the southern hemisphere. This is essentially equivalent to results from our station network and very close to results reported by Weiss [1981]. Except for some apparently seasonal cooling effects in

the middle-Southern latitudes, the surface waters were supersaturated with  $N_2O$ , with an overall mean of 2.5%. This is consistent with the concept of the ocean as a source of  $N_2O$ , but it is the lowest value reported to date. Although the area of coverage may have contributed in part to this lower value, the suppression of equatorial upwelling in the west Pacific in association with the 1987 ENSO event may have played a part as well. There may have been other ENSO effects, but they are more difficult to ascertain. The overall effect may have been significant, in that the mean surface concentration of  $N_2O$  did not differ significantly from that reported by Weiss [1978], in spite of an atmospheric increase of nearly 5 ppb during the past decade.

Although the equilibrator measurements of surface CFC-12 and CFC-11 required some filtering, owing to contamination by the ship, it is clear that seasonal warming and cooling predominated in determining surface saturations. The atmospheric profiles of CFC-12 and CFC-11 were virtually identical, underscoring their value as inert tracers. Small supersaturations (averaging between 4 and 6% above atmospheric levels) of CFC-12 and CFC-11 were found in the surface waters of the north Pacific ocean. On average, the oceans represent a small sink for the atmospheric CFCs; however, small supersaturations and undersaturations of dissolved CFCs can result due to the fact that the rate of thermal warming between the surface waters and the atmosphere is faster than the rate of gas exchange

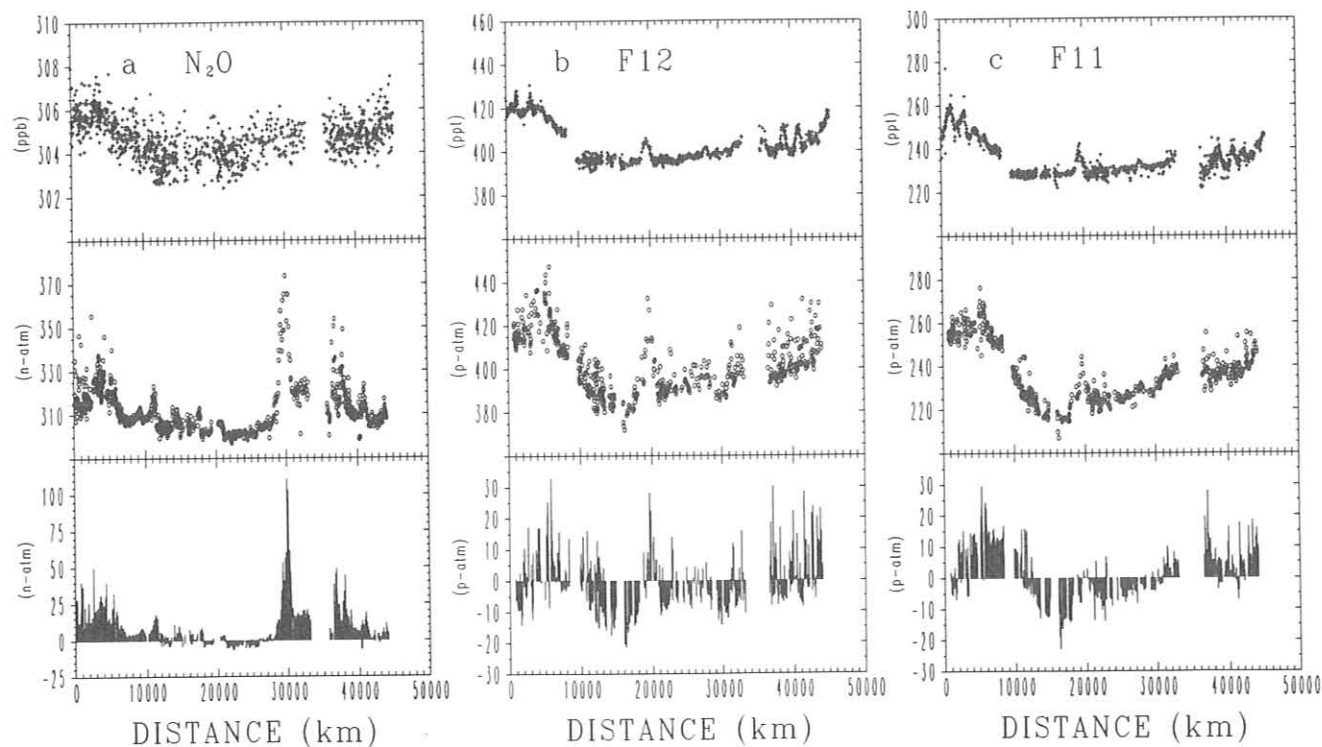


Fig. 8.7. Atmospheric concentrations (top panel), surface water concentrations (middle panel), and the saturation anomaly (bottom panel) for (a)  $N_2O$ , (b) CFC-12, and (c) CFC-11 versus distance traveled. The distance ranges for various sections were the following: Hilo to Kamchatka (0-4921 km), Leg I (4921-14770 km), Leg II (14785-33172 km), and Leg III (35706-45471 km).

between the atmosphere and surface waters. Along the west Pacific meridian, both gases decreased at a rate of  $0.35 \text{ ppt deg}^{-1}$  latitude in the northern hemisphere and remained virtually constant in the southern hemisphere. These gradients, as well as the absolute values shown in Figure 8.8, also corresponded well with results from the GMCC station network and measurements from other investigators. The CGO CFC-12 and CFC-11 provisional data were provided by P. Fraser of CSIRO, and the Khalil and Rasmussen CFC-12 and CFC-11 data were from the cooperative programs section 10.2 of this report.

As shown by others [Yoshinari, 1976; Elkins *et al.*, 1978],  $\text{N}_2\text{O}$  at depth from the SAGA II cruise correlated negatively with dissolved  $\text{O}_2$  and positively with  $\text{NO}_3^-$ . Figure 8.9 shows

dissolved  $\text{N}_2\text{O}$  and  $\text{O}_2$ , and  $\text{NO}_3^-$  concentrations over the Kuril Trench. The data from the headspace sampler were very consistent, giving us the most widespread data set of subsurface  $\text{N}_2\text{O}$  to date. The highest  $\text{N}_2\text{O}$  concentrations were in the intermediate waters of the northern hemisphere in both the west Pacific and east Indian Oceans. Waters bearing higher  $\text{N}_2\text{O}$  were found in the high northern latitudes, near the equator, and near other regions where surface currents diverge, including the ocean boundaries. Dissolved  $\text{N}_2\text{O}$  in waters of the southern hemisphere was much lower than that in the north, giving generally uneventful profiles. A strong temperature relation, similar to that discovered by Elkins *et al.* [1978], was found between the amount of dissolved  $\text{N}_2\text{O}$  produced ( $\Delta\text{N}_2\text{O}$ ) and the

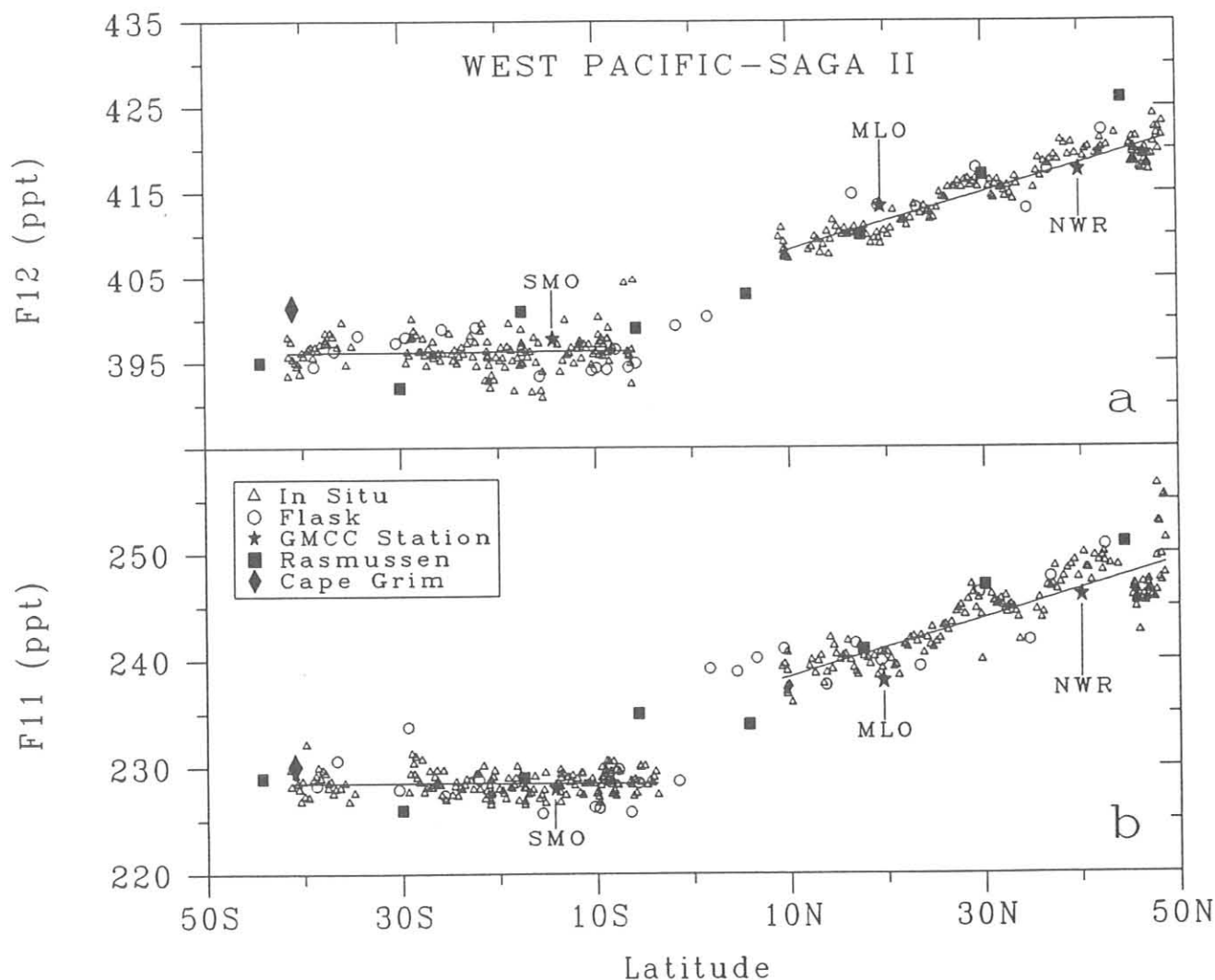


Fig. 8.8. Latitudinal dependence of (a) CFC-12 and (b) CFC-11 during Leg I of SAGA II from in situ GMCC GC (triangles) and GMCC flask analysis in Boulder (circles). Measurements are compared with SAGA II averages from the data presented in section 10.2 of this report (squares), GMCC stations (stars), and preliminary data from the CGO (diamonds) (P. Fraser, private communication).



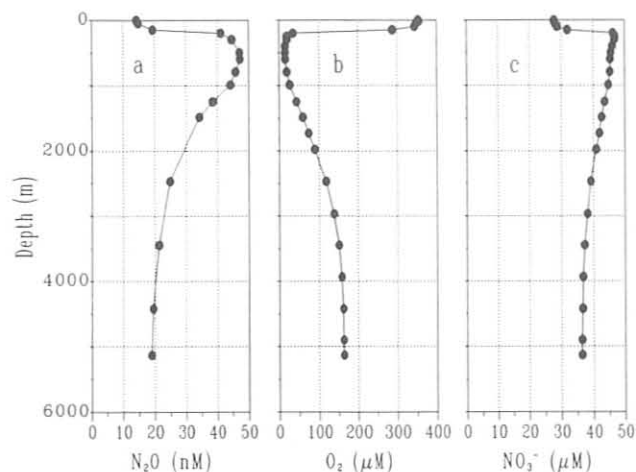


Fig. 8.9. Dissolved (a)  $\text{N}_2\text{O}$  and (b)  $\text{O}_2$ , and (c)  $\text{NO}_3^-$  concentrations versus depth over the Kuril Trench during the SAGA II experiment.

amount of dissolved oxygen consumed (AOU). It is apparent from these data that warmer water promotes a more rapid, subsurface production, which is consistent with laboratory studies of  $\text{N}_2\text{O}$  microbial production (Figure 8.10).

### 8.2.2. FT-IR SPECTROMETER ARCHIVE PROJECT

A Nicolet FT-IR spectrometer was moved from NBS in Gaithersburg, Md., and installed in Boulder in RL-2. This instrument will be used to archive IR solar spectra for future analysis of compounds not currently analyzed by GMCC. Methods of analysis will be checked by comparing column densities determined by the FT-IR spectrometer against Dobson ozone measurements and other trace species measured by GMCC. The instrument was put to its first test on analyzing a flask sample for high levels of  $\text{CO}_2$  from inside the second boat pit of Khufu's pyramid in Egypt (see section 4.2). Figure 8.11

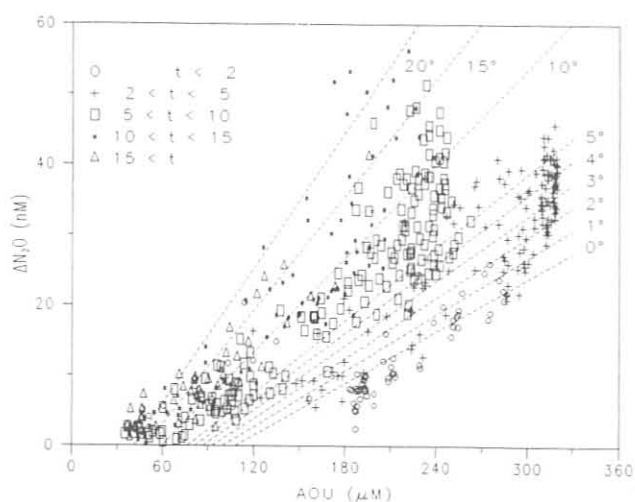


Fig. 8.10.  $\Delta\text{N}_2\text{O}$  versus AOU (or dissolved oxygen consumed) as a function of temperature  $t$  for all SAGA II data for AOU > 35  $\mu\text{M}$ . The equation,  $\Delta\text{N}_2\text{O} = -13.3 + (0.124 + 0.0094t) \text{ AOU}$ , was determined by a nonlinear, least-squares fit.

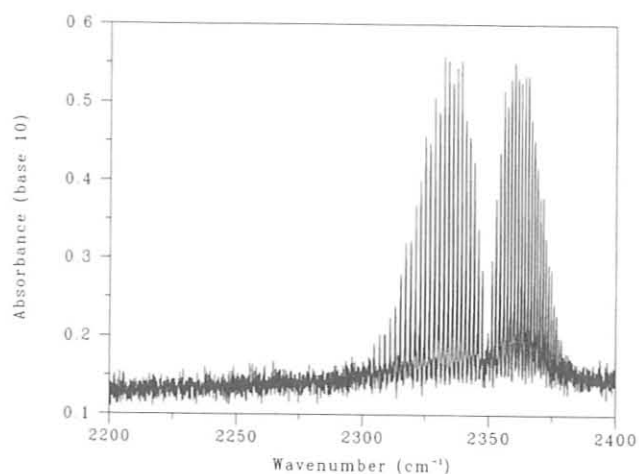


Fig. 8.11. FT-IR spectrum of the  $\nu_3$  band of  $\text{CO}_2$  from a sample, SIS, that was taken in a tomb from Khufu's pyramid. The resolution of the FT-IR spectrometer was  $0.06 \text{ cm}^{-1}$  and the  $\text{CO}_2$  concentration was measured at 745 ppm.

shows a spectrum of the  $\nu_3$  band of  $\text{CO}_2$  in a 10-cm-long cell with KBr windows at 500-mm-Hg pressure. The measured concentration was 745 ppm compared with the Weiss dual-catalyst FID GC analysis of  $750 \pm 7$  ppm (95% confidence level).

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