As an example of the utility of the diffusion equation model for estimating ages, we applied Eq. 8 to two sets of scarp morphology data from Utah (5). The data consist of measurements of  $\theta$ ,  $\alpha$ , and d for each of several profiles measured along the length of the scarps. Both time  $\tau$  and diffusion or rate coefficient c in Eq. 8 are unknown. The rate coefficient must in some way be estimated or determined in order to solve for time. In rare cases of independently dated scarps, the rate coefficient can be calculated directly from Eq. 8.

The Bonneville shoreline is a widespread wave-cut scarp in Utah (5), whose abandonment is radiocarbon-dated at about 15,000 years ago (13). The Bonneville shoreline probably had a rounded initial profile with a midslope near the angle of repose. The time to reach the initial angle for the diffusion equation model was probably a small fraction of the scarp age. Using 15,000 years and the calculated  $c\tau$  value of  $13.5 \pm 5.9$  (Fig. 2A) gives an estimate for c of 9.0  $\times$  10<sup>-4</sup> m<sup>2</sup>/year.

The Drum Mountains scarps are a set of single-event fault scarps near former Lake Bonneville that are younger than the Bonneville shoreline (5). The scarps have a calculated  $c\tau$  value of 4.3 ± 1.8 (Fig. 2B). The c value of 9.0  $\times$  10<sup>-4</sup> m<sup>2</sup>/ year calculated for the Bonneville shoreline yields an age of about 4800 years for the Drum Mountains scarps. To this age must be added the time required to remove the free face from the scarps, probably a few hundred years.

The diffusion equation model has potential for estimating the ages of many scarps. The most serious limitation at present is difficulty in estimating rate coefficient c.

> STEVEN M. COLMAN KEN WATSON

U.S. Geological Survey, Denver Federal Center, Denver, Colorado 80225

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## Anthropogenic Chlorofluoromethanes in the **Greenland and Norwegian Seas**

Abstract. The concentrations of two industrially produced chlorofluoromethanes,  $CCl_3F(F-11)$  and  $CCl_2F_2(F-12)$ , have been measured in the water column and in the marine atmosphere of the Greenland and Norwegian seas. Measurable concentrations of these two chlorofluoromethanes have penetrated to the deep basins of both of these regions, and the general characteristics of their vertical distributions are similar to those of the bomb-produced radioisotopes injected into the atmosphere on a similar time scale. The data have been fitted to a time-dependent box model based on deep convective mixing in the Greenland Sea and lateral exchange between the deep basins. The model calculations for the two chlorofluoromethanes in the Greenland Sea give similar results, with a time scale for deep convection of about 40 years. The time scale for lateral mixing between the deep Greenland Sea and the deep Norwegian Sea is estimated to be 20 to 30 years, although the agreement between the calculations for the two chlorofluoromethanes is limited by analytical uncertainties at the low concentrations found in the deep Norwegian Sea and by uncertainties in the model assumptions.

The potential value of dissolved atmospheric CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> as conservative time-dependent tracers of ocean circulation and mixing has been recognized for some years (1). These compounds are extremely stable in the troposphere and in natural waters, they have no natural sources, and their histories of release to the atmosphere are fairly well known (2). Because of their importance in stratospheric chlorine chemistry and in the modulation of the earth's  $O_3$  layer (3), the global atmospheric distributions of these gases are closely monitored. Unlike the transient increases in tritium and radiocarbon resulting from atmospheric nuclear-weapons testing, which are now being used as oceanic tracers on a similar decadal time scale, the atmospheric distributions of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> are not strongly dependent on latitude, and their surface-water concentrations can be expected to come into relatively rapid solubility equilibrium with the atmosphere (4). The presence of two separate chlorofluoromethanes (CFM's) with different rates of increase in the atmosphere provides an additional time-dependent constraint on models of subsurface circulation and mixing.

Until recently, the development of oceanic CFM measurements has been limited by analytical difficulties. Although the early measurements of Hahne

et al. (5) and Hammer et al. (6) established the general vertical distributions of these tracers, these measurements were significantly affected by sample contamination and limited analytical precision. Recent measurements by Gammon and his co-workers in the North Pacific (7) and North Atlantic (8) have demonstrated that these difficulties can be largely overcome. The measurements we report here were made with the use of a modified version of their technique.

Sample collections and analyses were carried out aboard C.S.S. Hudson expedition 82-001 to the Greenland and Norwegian seas during February through April 1982. The major objectives of this expedition were to observe possible deep convection during times of maximum surface density and to study wintertime physical and chemical properties in this important region of deep water formation. The locations of stations at which CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> measurements were made are shown in Fig. 1. We discuss here the results of our CCl<sub>3</sub>F and  $CCl_2F_2$  measurements at station 60  $(74^{\circ}N, 1^{\circ}W)$  and at station 88  $(70^{\circ}N, 1^{\circ}N)$ 11°E), located in the deep basins of the Greenland and Norwegian seas, respectively.

Concentrations of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> were measured in seawater and in air samples by shipboard electron-capture



gas chromatography (9). Seawater samples were collected in Niskin bottles and were carefully isolated in 100-ml glass syringes to avoid contact with shipboard air, which contained high concentrations of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub>. Measured seawater volumes of  $\sim 30$  ml were injected into a stripping chamber, where the dissolved CFM's were purged with a stream of purified N<sub>2</sub> and were collected on a low-temperature trap for subsequent injection into the gas chromatograph. Samples were usually analyzed within a few hours of collection. Measured volumes of clean ambient' air ( $\sim 3$  ml), drawn from a continuously pumped outdoor sampling line and dried with magnesium perchlorate, were analyzed by injection into the same low-temperature trapping system.

Contamination blanks in the system were monitored at regular intervals, and instrument sensitivity and nonlinearity were calibrated by frequent analyses of compressed gas standards in various aliquot sizes. These synthetic air standards were prepared in our laboratory by volumetric dilution to contain mole fractions of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> near their present atmospheric values. The precision of the seawater measurements, as given by the mean standard deviation for replicate samples, is  $\sim 0.02$  pmole/kg (1 pmole =  $10^{-12}$  mole) for both CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub>, and systematic sampling and handling errors are estimated to be of the same order. The relative standard deviation of the atmospheric measurements, based on replicate analyses, is  $\sim 1$  percent for CCl<sub>3</sub>F and  $\sim 0.4$  percent for  $CCl_2F_2$ . Overall systematic calibration errors are estimated to be  $\sim 2$  percent for both gases.

The measured concentration profiles of dissolved  $CCl_3F$  and  $CCl_2F_2$  in the Greenland and Norwegian seas are plotted in Fig. 2. The profiles of both CFM's show progressively lower concentrations

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with increasing depth, reflecting the greater isolation of deeper waters from air-sea exchange. For comparison, profiles of the potential density parameter  $\sigma_2$  (10) at these stations are also plotted in Fig. 2. At depths below 1500 m in both basins, the concentrations of both CFM's are remarkably uniform, with significantly lower concentrations in the deep Norwegian Sea than in the deep Greenland Sea. The vertical structures of these profiles are similar to those for bomb-produced tritium and radiocarbon in these regions (5, 11). Although the 1976 Norwegian Sea CFM measurements of Hahne et al. (5) cannot be compared directly with our 1982 measurements, the general shapes of the profiles defined by their least-contaminated samples are similar to ours.

Fig. 1. Station locations of

C.S.S. Hudson expedition 82-

001 at which measurements of

CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> were made.

Our clean-air CFM measurements at stations 60 and 88 show uniform mixing ratios, with average dry-air mole fractions of 194  $\times$   $10^{-12}$  for CCl\_3F and 343  $\times~10^{-12}$  for  $CCl_2F_2.$  These values are in good agreement with the March 1982 average mixing ratios of  $200 \times 10^{-12}$  for CCl<sub>3</sub>F and  $338 \times 10^{-12}$  for CCl<sub>2</sub>F<sub>2</sub> reported by the Atmospheric Lifetime Experiment program for their nearest monitoring station at Adrigole, Ireland (52°N,  $10^{\circ}W$  (12), especially in view of the fact that their calibration is completely independent of ours. Unfortunately, we are prevented from assessing the degree of atmospheric equilibrium in our surfacewater measurements by the lack of accurate seawater solubility data for CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> over the necessary ranges of temperature and salinity (13).

The propagation of transient tracers into the Greenland and Norwegian seas has been modeled for bomb-produced tritium and radiocarbon by Peterson and Rooth (14). Based on an analysis of the temperature and salinity characteristics of this region, they assumed as a first approximation that mixing or convection between surface and deep waters occurs only in the Greenland Sea and that the tracer composition of the deep Norwegian Sea is dominated by lateral exchange with the deep Greenland Sea. The mean compositions of these basins were represented by a two-box model, with variations in surface-water input concentrations estimated from the transient behavior of the atmospheric source.

Our measured distributions of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> have been fitted to a similar model. We have assumed that the deep water masses of the two basins, as defined by uniform CFM concentrations and  $\sigma_2$  profiles, are confined to depths below ~ 1500 m and are of roughly equal volume. The time-dependent conservative behaviors of the CFM's in this twobox model are thus given by the following derivatives:

$$\frac{dC_G}{dt} = \mu_1(C_S - C_G) + \mu_2(C_N - C_G)$$
$$\frac{dC_N}{dt} = \mu_2(C_G - C_N)$$

in which  $C_S$ ,  $C_G$ , and  $C_N$  are, respectively, the CFM concentrations as a function of time *t* in convecting Greenland Sea surface water, Greenland Sea deep water, and Norwegian Sea deep water;  $\mu_1$  is the exchange coefficient between surface and deep water in the Greenland Sea; and  $\mu_2$  is the lateral exchange coefficient between the deep waters of the Greenland and Norwegian seas.

We have assumed that the concentrations of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> in Greenland Sea surface waters which undergo deep convection are proportional to their atmospheric mixing ratios and that their wintertime 1982 concentrations can be estimated from our surface-water measurements at station 60. In our model calculations we have used winter 1982  $C_{\rm S}$  values of 4.43 pmole/kg for CCl<sub>3</sub>F and 1.74 pmole/kg for  $CCl_2F_2$ , which are about 3 percent lower than the station 60 surface-water values after correction for the estimated effect on gas solubility (15) of small differences in potential temperature and salinity as compared to Greenland Sea deep water. The temporal trends of the Northern Hemisphere CFM mixing ratios for the period since 1976 have been taken from direct measurements (12, 16). For the period 1933 to 1976, we have integrated annual CFM release figures (17), assuming tropospheric residence times of 50 years for CCl<sub>3</sub>F and 90 years for CCl<sub>2</sub>F<sub>2</sub>, and have normalized these results to match the direct measurements in 1976. The timedependent source function  $C_{\rm S}$  for each CFM has been calculated by again nor-

malizing these atmospheric mixing ratios to our 1982  $C_{\rm S}$  values and is therefore independent of the calibration scales used to measure the atmospheric trends.

The model was integrated numerically, and the values of  $\mu_1$  and  $\mu_2$  were determined by successive approximation to match the average measured 1982 deep water concentrations of 0.76 pmole of CCl<sub>3</sub>F per kilogram and 0.31 pmole of  $CCl_2F_2$  per kilogram in the Greenland Sea and 0.16 pmole of CCl<sub>3</sub>F per kilogram and 0.15 pmole of CCl<sub>2</sub>F<sub>2</sub> per kilogram in the Norwegian Sea. We carried out the calculations independently for the two CFM's, assuming zero initial concentrations in both basins. Because the relative rate of increase of the CCl<sub>3</sub>F source function is about 40 percent greater than that of the  $CCl_2F_2$  source function, the two CFM's provide a redundant check on the validity of the model. For CCl<sub>3</sub>F the model yields the exchange times  $1/\mu_1 = 42 \pm 3$  years for the renewal of Greenland Sea deep water by surface exchange and  $1/\mu_2 = 28 \pm 5$ years for lateral exchange between the deep Greenland Sea and the deep Norwegian Sea. The comparable results for  $CCl_2F_2$  are  $1/\mu_1 = 35 \pm 5$  years and  $1/\mu_2 = 10 \pm 4$  years. The quoted error limits show the effects of analytical precision on the calculations and do not include systematic effects or errors in the model assumptions.

For deep convective mixing in the Greenland Sea, the model calculations based on the two CFM's give similar results, with an average  $1/\mu_1$  exchange time of  $\sim 40$  years. This value is somewhat greater than the exchange time of  $\sim$  30 years calculated by Peterson and Rooth (14) on the basis of the 1973 tritium and radiocarbon measurements. However, the upper boundary of the Greenland Sea deep water in their calculations was placed at a depth of 500 m as compared to our value of 1500 m. Their model thus includes a shallower portion of the water column which is marked by higher tracer concentrations and is therefore subject to more rapid vertical exchange. We have repeated our CFM model calculations, using the same depth intervals as those used by Peterson and Rooth, and have obtained  $1/\mu_1$  values of 34 years for CCl<sub>3</sub>F and 29 years for  $CCl_2F_2$ , which are in good agreement with their results.

For lateral exchange between the deep Greenland Sea and the deep Norwegian Sea, the model calculations based on the two CFM's are in poor agreement, with the value of  $1/\mu_2$  based on CCl<sub>3</sub>F being about three times greater than the value based on  $CCl_2F_2$ . These calculated ex-

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CFM (p ole/kg) 0 CCI 2 F2 CCl<sub>2</sub>F<sub>2</sub> CCI3F CCIaF ŝ σ  $\sigma_{i}$ Depth 2 з 36.5 37.0 37.5 37.0 37.5 36.5  $\sigma_{\alpha}$ 

Fig. 2. Concentration profiles of  $CCl_3F$  and  $CCl_2F_2$  (a) at station 60 in the Greenland Sea (18 March 1982) and (b) at station 88 in the Norwegian Sea (26 March 1982). Replicate measurements are shown as separate points. Vertical density structures at these stations are shown in terms of profiles of the potential density parameter  $\sigma_2$  (10).

change rates are subject to larger errors because of the greater influence on more isolated water masses of uncertainties in the earlier atmospheric release histories and because of the analytical difficulties associated with accurately measuring the extremely low concentrations found in the deep Norwegian Sea. The latter is especially true for the measurement of CCl<sub>2</sub>F<sub>2</sub>, which has a lower solubility and is therefore more vulnerable to contamination by the admixture of small amounts of air. This problem was compounded aboard C.S.S. Hudson by exceptionally high levels of CCl<sub>2</sub>F<sub>2</sub> contamination in shipboard air. Contamination of this type would lead to an erroneously low value of  $1/\mu_2$ , which is consistent with the discrepancy we observe. Although somewhat greater than our estimated levels of contamination, we cannot exclude the possibility of CCl<sub>2</sub>F<sub>2</sub> sampling or handling blanks on the order of 0.05 pmole/kg, which would bring the model calculations for the two CFM's into agreement. We have therefore placed greater weight on the CCl<sub>3</sub>F measurements in estimating  $1/\mu_2$  to be on the order of 20 to 30 years.

By comparison, Peterson and Rooth have estimated  $1/\mu_2$  to be at least 100 years. Their estimate was based on 1973 measurements showing essentially no tritium or bomb-produced radiocarbon in the deep Norwegian Sea (11). However, these data are not supported by the 1976 measurements of Hahne et al. (5) or the 1981 measurements of Lee and Peterson (18), showing significant tritium concentrations in Norwegian Sea deep water which are roughly consistent with the lower  $1/\mu_2$  values calculated from our CFM data. The data thus demonstrate a major vulnerability in these models, which may incorrectly include the assumption that deep water formation and mixing in this region may be regarded as steady-state processes.

> J. L. BULLISTER R. F. WEISS

Scripps Institution of Oceanography, University of California, San Diego, La Jolla 92093

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5 October 1982; revised 17 January 1983.

## Is There Any Chlorine Monoxide in the Stratosphere?

Abstract. A ground-based search for stratospheric chlorine monoxide was carried out during May and October 1981 with an infrared heterodyne spectrometer in the solar absorption mode. Lines due to stratospheric nitric acid and tropospheric carbonyl sulfide were detected at about 0.2 percent absorptance levels, but the expected 0.1 percent lines of chlorine monoxide in this same region were not seen. Stratospheric chlorine monoxide is less abundant by at least a factor of 7 than is indicated by in situ measurements, and the upper limit for the integrated vertical column density of chlorine monoxide is  $2.3 \times 10^{13}$  molecules per square centimeter at the 95 percent confidence level. These results imply that the release of chlorofluorocarbons may be significantly less important for the destruction of stratospheric ozone than is currently thought.

Chlorofluorocarbons are important and widely used industrial chemicals, but current photochemical models of the stratosphere indicate that their release ultimately depletes the  $O_3$  layer (1). Chlorine monoxide (ClO) is thought to be a key tracer of this process, and measurements of its stratospheric abundances are therefore particularly important. Anderson and his colleagues have reported (2) a series of in situ measurements of stratospheric ClO, based on its chemical conversion to chlorine atoms, which are then detected by resonance

Fig. 1. (a) Observed and modeled spectra of the terrestrial atmosphere near the P12<sup>14</sup>CO<sub>2</sub> laser line. The frequency resolution is 25 MHz, and the spectra are displayed as transmittance versus the frequency difference from 856.515 cm<sup>-1</sup>. The modeled spectrum is displaced downward for clarity, and the expected line of <sup>35</sup>ClO (R9.5) is indicated. (b) Observed and modeled spectra centered on the R9.5 ClO line. The frequency resolution in the observed spectrum is 5 MHz, and the modeled spectrum is displayed with infinite resolution. The residual differences between the observations and the modeled spectrum without CIO are shown and are compared with the expected ClO line.



fluorescence. Their results show large variations from flight to flight.

Since direct detection of the ClO electronic resonance bands is not practical. confirmation of the chemical kinetic results has been directed toward detection by rotational and vibrational spectroscopy. Ground-based (3) and balloon-borne (4) measurements of the  $(J = 11/2 \rightarrow 9/2)$ rotational line of <sup>35</sup>ClO at 204.352 GHz have been reported. The balloon-borne detection (5) by infrared vibrational spectroscopy near 12  $\mu$ m is incorrect (6). Precise laboratory spectroscopy shows that the atmospheric line reported by Menzies and his co-workers (5) does not correspond to a transition of ClO; a reexamination of these experimental data (5) does show the presence of a weak absorption line at the correct frequency to be ClO (7).

We report the results of a search for stratospheric ClO, based on the use of a ground-based infrared heterodyne spectrometer. Three vibrational lines were searched for near 12 µm, two from the  $^{2}\pi_{3/2}$  fundamental of  $^{35}Cl^{16}O$  and one from the  $^{2}\pi_{3/2}$  fundamental of  $^{37}$ ClO. These lines should have been detected if currently accepted abundances are correct, yet none was found. We present a detailed comparison of the observed and synthetic atmospheric spectra near 856.515  $\text{cm}^{-1}$ . The upper limit to the stratospheric ClO abundance that we derive is significantly smaller than the abundances obtained from the (independent) chemical kinetic and rotational spectroscopic methods.

Infrared absorption measurements of stratospheric ClO are important (i) because the detection of vibrational absorption lines with the correct frequencies and relative strengths is a necessary condition for the confirmation of ClO and (ii) because quantitative analysis of the line strengths and shapes provides an independent check on the results obtained by other methods. The vibrational fundamental band (v =  $0 \rightarrow 1$ ) of ClO lies near 12 µm, overlapping both a particularly favorable window in the terrestrial atmosphere and the (00°1)-(10°0,  $(02^{\circ}0)_{I}$  band of the  $^{14}C^{16}O_{2}$  laser. The fact that there are close coincidences for lines of ClO (6) with the P8 and P12 transitions of the  ${}^{14}C^{16}O_2$  laser (8) suggests that it might be possible to detect stratospheric ClO by infrared heterodyne spectroscopy (9) using these local oscillator transitions. Furthermore, recent stratospheric infrared spectra (10), taken at 12.8 air masses and at moderately high resolving power, show weak atmospheric absorption lines with only a

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