Antarctic Total Ozone in 1958

Paul A. Newman

The Antarctic ozone hole results from catalytic destruction of ozone by chlorine radicals. The hole develops in August, reaches its full depth in early October, and is gone by early December of each year. Extremely low total ozone measurements were made at the Antarctic Dumont d'Urville station in 1958. These measurements were derived from spectrographic plates of the blue sky, the moon, and two stars. These Dumont plate data are inconsistent with 1958 Dobson spectrophotometer ozone measurements, inconsistent with present-day Antarctic observations, and inconsistent with meteorological and theoretical information. There is no credible evidence for an ozone hole in 1958.

The Antarctic ozone hole, a region of massive ozone loss, has been annually appearing since the 1970s. The hole begins to develop each August and culminates by early October, subsequently disappearing by early December. October column ozone amounts are now at least 50% lower than values seen in the 1970s.

The ozone hole was discovered by Farman *et al.* (*1*) using Dobson spectrophotometer data from Halley Bay (76°S, 27°W) (*2*). Farman *et al.* found that spring total ozone had decreased from values higher than 300 Dobson units (DU) in the late 1950s and early 1960s to values near 200 DU in the early 1980s. Their results were confirmed with both Total Ozone Mapping Spectrometer (TOMS) satellite data (*3*) and ozone data from other Antarctica sites (*4*). Antarctic total ozone values in 1993 were below 100 DU (*5*). Recent Antarctic experiments have demonstrated that the ozone hole results from the increased stratospheric chlorine and bromine concentrations, combined with the peculiar meteorology of the Southern Hemisphere winter (*6, 7*).

A spring ozone minimum over Antarctica is a natural phenomenon, which was first noted in the 1960s (*8*). This ozone minimum results from normal winter Antarctic circulation patterns (9) and is not an ozone hole. The ozone hole is defined as the large ozone loss that further reduces this minimum from normal values of about 300 DU. During the late-spring vortex breakdown, this minimum feature increases as ozone is resupplied to the Antarctic region by the circulation pattern. Generally, the vortex remains centered near the pole over the course of the winter and moves into the Western Hemisphere toward South America during the breakdown (*10*).

Rigaud and Leroy (*11*) suggested that ozone values were low in 1958, well before significant chlorofluorocarbon (CFC) emissions. They based their interpretation on values derived from spectrographic plates taken at Dumont d'Urville (66.7°S, 140°E). The ultraviolet (UV) light sources for the plates were weak, consisting of the blue sky, the moon, and two stars. Data from these plates were originally not used because the data were obtained from the star observations and showed "unusual variability and inconsistency" (*12*). In addition, the original data catalog noted (*13*):

> All the instruments were intercompared. But the differences between the results obtained with different instruments were apparently much larger than results with different Dobson instruments. . . . Owing to large and at times surprisingly abnormal values found at some of these places, and at Dumont d'Urville, Elbruz and Elmas, it is suggested that the individual days' data of these places should be scrutinized before using them for any critical work.

Rigaud and Leroy (*11*) reexamined the original plates with a microdensitometer and noted that the data were in good agreement with the original values determined from those plates. They found ozone levels as low as 120 DU on 18 October 1958 and 110 DU on 8 September 1958. In addition, they found extremely low total ozone in the fall, with measurements down to 150 DU on 17 April and 110 DU on 16 July 1958 (*14*).

These Dumont 1958 observations call into question ozone hole observations and ozone loss theory. If an ozone hole existed in 1958, then there was some natural loss mechanism that destroyed enormous quantities of stratospheric ozone. However, the 1958 Dumont d'Urville plate spectrographic observations are inconsistent with Dobson spectrophotometer observations from other Antarctic sites and with current observations, and a more logical explanation of the anomalously low 1958 Dumont data is a large instrumental bias.

Antarctic total ozone data for 1958 are available for (i) plate spectrographic observations from Dumont d'Urville and (ii) Dobson spectrophotometer observations from Halley Bay, Little America, Argentine Island, and Macquarie Island (Fig. 1). Ozone measurements made from spectrographic plates are subject to numerous serious problems. The UV light sources must be strong, the UV response of the plates must be carefully understood, the plates must be carefully developed, and the operators must be extremely cautious. On the other hand, Dobson spectrophotometers were designed to be highly accurate instruments (an error of less than 1%) that could be used by nonprofessionals on a routine observational basis.

An evaluation of whether only one station could have detected a hole in 1958 can be made on the basis of recent hole observations. Because the ozone hole is both generally centered on the pole and large (an average horizontal diameter of about 5600 km), it should be observable at more than one station. The size of the hole is limited by the polar vortex, with the hole and the vortex being roughly colocated with one another. This colocation results from the well-mixed nature of the interior of the polar vortex, such that localized ozone losses are mixed across the vortex interior (*15*). Because of the mixing, these localized inner-vortex losses will quickly distribute inside the vortex, and because the vortex is so large, the loss will be observable at more than one station. For the case of 23 September 1992, Halley, Little America, and Argentine Island would have observed the ozone hole, while Dumont and Macquarie would not.

The stations operating in 1958 were well situated for observation of the ozone hole. As a test, I interpolated daily TOMS data (September through October, 1984 to 1992, 549 days of data) to the station locations and used an objectively determined cutoff value (240 DU) to determine if the station was inside the hole. The hole was observed by one or more stations 97% of the time. The hole was observed at Halley on 93% of the days (Little America, 66%; Argentine Island, 52%; and Dumont, 8%). The hole is observed by only one of the stations 18% of the time (14% for Halley, 3% for Little America, 1% for Argentine Island, and 0.2% for Dumont). On the basis of the recent TOMS ozone hole data, it is unlikely that Dumont would be the only station to observe the ozone hole.

The Dumont plate data are substantially lower than Dobson data from Little America, Halley Bay, Argentine Island, and Macquarie Island. Dumont plate total ozone was 140 DU on 6 October 1958, whereas observations at Little America showed 322 DU on 5 October and 304 DU on 7 October. Little America detected a minimum of 293 DU (9 October) and a maximum of 407 DU (20 October), a 114-DU increase. On the other hand, Dumont had a minimum of 120 DU (18 October)

Atmospheric Chemistry and Dynamics Branch, NASA Goddard Space Flight Center, Code 916, Greenbelt, MD 20771, USA.

and a maximum of 420 DU (9 October), a 300-DU decrease. All of the Dobson station observations are inconsistent with the plate Dumont data.

Vertical profiles of ozone from Argentine Island in 1958 do not show large losses in the 12 to 22 km region, in good agreement with the Dobson data (*17*). During 1958, eight Umkehr vertical profiles of ozone were obtained at Argentine Island. These Umkehr profiles agree with the Dobson data and show an ozone peak in the layer from 125 to 64 hectopascals (1 hPa = 100 Pa). Recent ozone profiles inside the ozone hole (1985 to 1992) show substantial reductions of this peak value to near zero (*18*). The 1958 ozone profiles show no evidence for losses.

The 1958 Halley data are in good agreement with recent observations of total ozone by TOMS, whereas Dumont plate data are too low. As a check on the representativeness of the 1958 data, I compared the Halley data and the Dumont plate data to climatologies developed from the 1978–1992 TOMS data. The 1958 Halley data generally track the 1978–1992 TOMS overpass data (Fig. 2A). Exceptions occur during spring and summer, when the Halley data is higher than the TOMS values. This is expected, because the TOMS climatology is derived from the recent period when the ozone hole was well developed. In contrast, the Dumont plate data are consistently lower than both the satellite overpass climatology and Macquarie Dobson data (Fig. 2B). Of the 90 days of 1958 Dumont measurements, 59 days were record low measurements when compared to the TOMS overpass data. In particular, Dumont plate data are inconsistent with the TOMS climatology during the fall (February to May). Dumont plate observations show 135 DU on 13 May 1958, whereas the record low value observed by TOMS during April and May is 190 DU (2 April 1989). Of the nine measurements made at Dumont during April and May 1958, four are below the record low 190-DU TOMS overpass observation.

Extreme variability of the Dumont plate data suggests that these data are not self-consistent (Fig. 2B). As an example of this day-to-day variability, total ozone jumps 130 DU from 17 to 18 April 1958. The TOMS overpass climatology shows day-to-day total ozone changes that are usually less than 50 DU. The largest single-day total ozone change in the TOMS Dumont overpass data during fall was 74 DU (5 to 6 April 1990). The large 1987 spring excursions result from the passage of the ozone hole edge (see Fig. 1). The Macquarie Dobson data also show relatively small variability. The 1958 Dumont plate data are lower and more variable than both the TOMS overpass data and the 1958 Dobson station data.

Low total ozone temporal variability in summer and fall (Fig. 2B) results from weak dynamical activity associated with the normal summer-fall circulation. The easterly winds in the stratosphere inhibit propagation of synoptic and planetary waves into the stratosphere; hence, from January until May, dynamically driven variability is small. The standard deviation of the TOMS overpass data for this period is 30 DU (mean value of 323 DU). In contrast, the 1958 Dumont plate data have a standard deviation of 68 DU (mean value of 230 DU). De Muer (*14*) estimated the instrumental error as 30 DU, using the Halley data to calculate monthly mean variability. Using the same technique with the TOMS overpass data, I estimate an instrumental error of 61 DU ($\sqrt{68^2 - 30^2}$), with a mean difference of 93 DU.

Rapid recovery of total ozone in the spring occurs during the polar vortex breakdown. The 1987 TOMS overpass data show large total ozone excursions as the polar vortex passed over Dumont. Because the vortex usually moves from the Western Hemisphere across Antarctica, the breakdown is first evident at stations such as Dumont and is last evident at stations such as Halley. In essence, the high ozone values in the southern Indian and Pacific oceans (Fig. 1) push across Antarctica, while the vortex weakens and moves into the South Atlantic. The overpass observation of 420 DU on 9 October 1987 resulted when the ozone hole moved toward the pole. The ozone increase at Dumont (Fig. 2B) is virtually complete by late October, whereas the ozone increase at Halley (Fig. 2A) is not complete until late November.

The 1958 breakdown dates at the stations are consistent with one another and are consistent with the TOMS overpass climatology. As was noted by Rigaud and Leroy (*11*), the Dumont plate data showed recovery between 8 and 21 October. The recovery is also apparent in the Little America data (ozone values increased from 293 DU to 405 DU between 9 and 22 October) and Halley Bay data (total ozone increased to values over 400 DU by late November). The timing of the 1958 ozone recovery agrees with recent observations by TOMS overpass climatology data. The ozone recovery occurs first at Dumont and Little America during October and then occurs at both Argentine Island and Halley in November, consistent with recent observations of the breakdown.

The extremely low Dumont plate values before and after breakdown suggest that these Dumont values have a large negative bias. Before the breakdown, the stations are inside the polar vortex and reflect the minimum ozone values over Antarctica (300 DU at Argentine Island, 301 DU at Halley, 314 DU at Little America, and 155 DU from the Dumont plate data). After the breakdown during December, the TOMS overpass data have a mean value of 360 DU, whereas the Dumont data have a mean value of 252 DU. The consistency of the Argentine, Halley, and Little America data before the breakdown suggests that the Dumont plate data are biased low by at least 100 DU.

The low ozone values have been suggested to be caused by (i) displacement of the

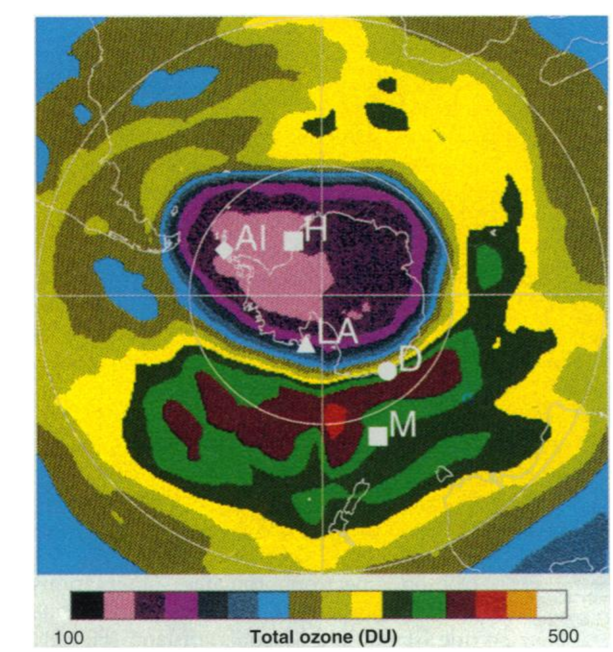

Fig. 1. Total ozone false color image of TOMS data for 23 September 1993. Station locations: Dumont d'Urville (D), Little America (LA), Argentine Island (AI), Halley Bay (H), and Macquarie Island (M). The lowest total ozone value on this date was 126 DU and the area of the ozone hole was 24 million kilometers square.

polar vortex toward Dumont and away from Halley, (ii) higher solar elevation at Dumont, and (iii) a volcanic eruption that enhanced aerosol levels in the stratosphere.

The behavior of the 1958 total ozone values suggests that the vortex was not displaced away from Halley. Rigaud and Leroy (*11*) claimed that the polar vortex was displaced toward Dumont on the basis of 200- and 300-hPa charts (*19*). Most of the mass of ozone at Antarctic latitudes is not located in the 200- to 300-hPa layer, but higher aloft in the 100- to 50-hPa layer (*18*). October 50-hPa geopotential heights, temperatures, and winds are comparable to present day observations and show the vortex pushed away from Dumont toward the pole, more closely located near Halley. Further, the November ozone recovery at Halley is evidence that Halley was inside the polar vortex during October, not outside the vortex as suggested in (*11*).

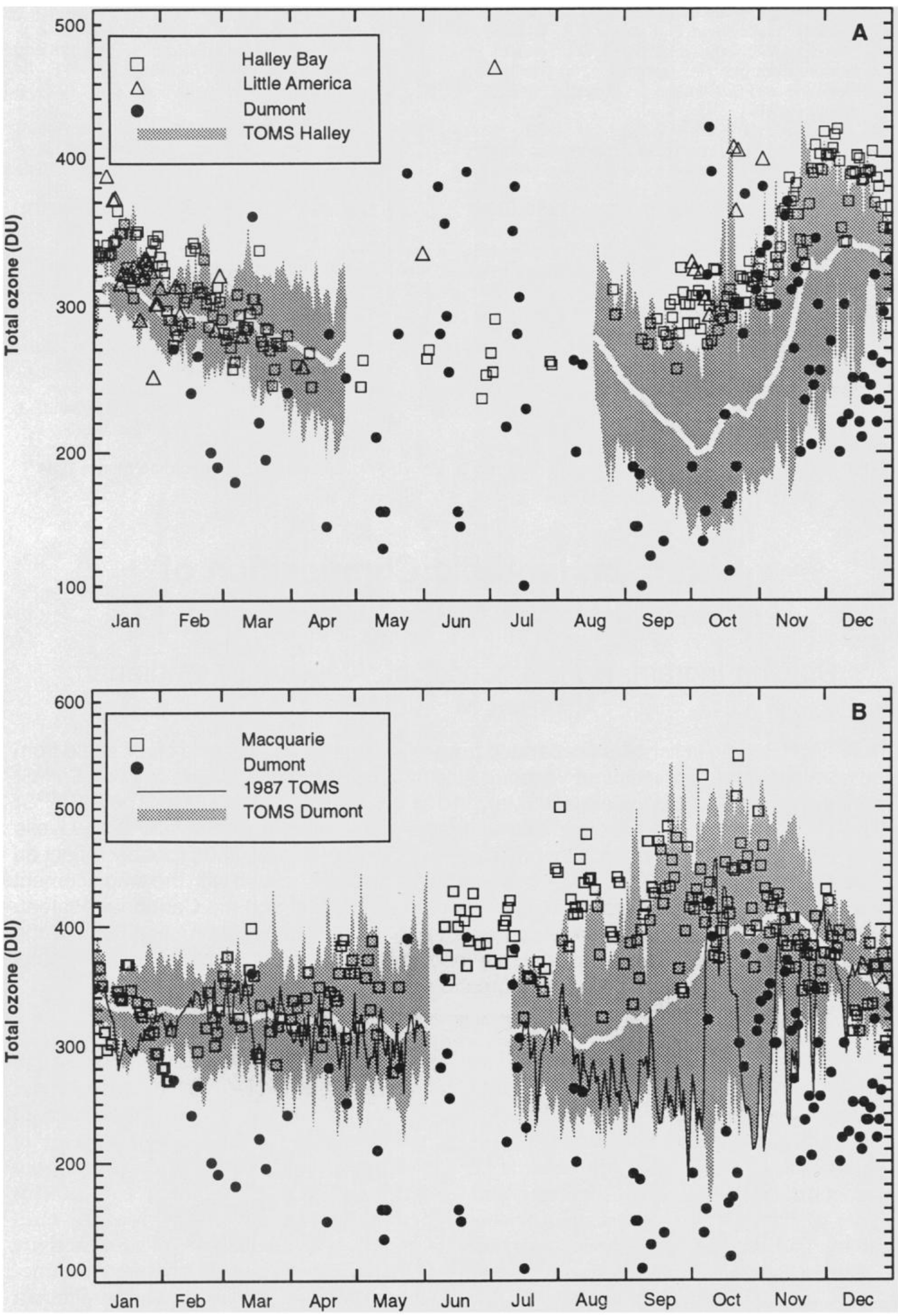

Fig. 2. Time series of total ozone. Comparison of values from Dumont d'Urville (●) with those from (**A**) Halley Bay (□) and Little America (△) and (**B**) Macquarie Island (□). The TOMS climatology (shaded values) was developed from satellite overpasses of (A) Halley Bay and (B) Dumont between November 1978 and January 1992. The grey shading represents the range of data (minimum and maximum values) for each day over the 13 years, and the thick white line is the average total ozone value at each site.

Temperature data from October 1958 also indicate that the Dumont plate data are in error. It has been widely recognized that stratospheric temperatures are highly correlated with total ozone (*20*). Temperatures in 1958 were −35°, −58.4°, and −64.8°C at Dumont, Little America, and Halley, respectively (*19*). October total ozone at Halley was lower than that at Little America, in agreement with these temperatures. However, the Dumont data show the opposite behavior, with high temperatures associated with low ozone (*21*). The 1958 Dumont plate data do not show the ozone-temperature correlation.

Wind patterns for 1958 also suggest a discrepancy between the Little America data and the Dumont plate data. Dumont was upstream of Little America in 1958 at 50 hPa (as would be expected from the strong cyclonic flow field during October) (*19*). With this wind pattern, any massive local loss of ozone above Dumont should be observable downstream at Little America within 1 to 2 days. Further, the normal eastward propagating planetary wave pattern would move any ozone low over Little America within 1 to 2 days (*22*). However, low total ozone was not observed at Little America.

A volcanic event can produce three processes that may perturb ozone: (i) a large injection of chlorine (primarily HCl), (ii) a large loading of the stratosphere with aerosols, or (iii) a large modification of the circulation by radiative processes. The only major eruption immediately before 1958 was Bezymianny (56°N, 161°E) on 30 March 1956. Bezymianny had a volcanic explosivity index (VEI) of 5 (in comparison: El Chichon had a VEI of 4 to 5 and Mount Pinatubo had a VEI of 5 to 6) (*23, 24*).

The first process requires a large injection of HCl, well in excess of the injections from El Chichon in 1982 [which increased the global inorganic chlorine burden by about 10% (*25, 26*)] and Pinatubo in 1991 (*27*). Ozone losses would occur by heterogeneous processes on the sulfate aerosols and polar stratospheric clouds (PSCs). However, this scenario seems unrealistic because transport from Bezymianny (56°N) to the South Pole is inefficient (*28*) and any stratospheric injection had over 2 years to settle out. In addition, optical depth measurements did not show large perturbations by volcanic aerosols (*29*), large ozone losses were not identified by other stations, and large ozone losses in subsequent years were not observed (*30*).

In addition to theoretical problems involved with the generation of an ozone hole in October 1958, there is the additional problem of explaining the low Dumont plate measurements in April and May 1958. Heterogeneous reactions on the surfaces of PSCs are necessary for massive losses of ozone, and PSCs form at temperatures below −78°C (*7, 31*). April 1958 temperatures of −60°C are too warm to form PSCs (*19*). It is also possible that chlorine activation may have occurred from the hydrolysis of chlorine nitrate on the sulfate layer. This process requires temperatures below −63°C and a large burden of stratospheric chlorine. Antarctic observations during 1992 indicated elevated levels of OClO beginning in mid-April 1992 as a result of the Pinatubo sulfate layer (*32*). However, although OClO levels were high, ozone levels were near normal. Therefore, even in the presence of both high levels of chlorine and high levels of volcanic aerosols, low ozone at Dumont in April and May 1958 would have been unlikely.

REFERENCES AND NOTES

1. J. B. Farman *et al., Nature* **315**, 207 (1985).
2. S. Chubachi [in *Atmospheric Ozone: Proceedings of the Quadrennial Ozone Symposium*, C. S. Zerefos and A. Ghazi, Eds. (Kluwer, Norwell, MA, 1985), pp. 243–245] also reported low total ozone at Syowa (69°S, 40°E) for October 1982 [prior to the Farman *et al.* paper (*1*)], but he failed to note that these values were abnormal.
3. R. S. Stolarski *et al., Nature* **322**, 308 (1986).
4. See the Antarctic Ozone special issue [*Geophys. Res. Lett.* 13 (no. 12) (1986)].
5. D. Hofmann, paper presented at the American Geophysical Union fall 1993 meeting, San Francisco, CA, 9 December 1993. Preliminary Meteor-3 TOMS total ozone data on 8 October 1993 showed an ozone value of 85 DU near the South Pole.
6. The Airborne Antarctic Ozone Experiment, the National Ozone Expeditions I and II [*J. Geophys. Res.* **94** (nos. D9 and D14) (1989)], and the Upper Atmosphere Research Satellite [*Geophys. Res. Lett.* **20**, 1215–1330 (1993)].
7. Heterogeneous chemical processes on the surfaces of polar stratospheric clouds enhance the chlorine species that can destroy ozone. These chlorine species catalytically destroy ozone to form the ozone hole [J. G. Anderson, D. W. Toohey, W. H. Brune, *Science* **251**, 39 (1991)].
8. G. Dobson, *Appl. Opt.* **7**, 387 (1968).
9. K. Tung, *Geophys. Res. Lett.* **13**, 1308 (1986).
10. The ozone minimum breakdown is discussed in R. Nagatani, *NOAA Tech. Rep. NWS 40* (1988); D. F. Heath *et al., NASA Ref. Publ. 1098* (1982); A. Krueger *et al., NASA Ref. Publ. 1201* (1988); A. Krueger *et al., NASA Ref. Publ. 1225* (1989); and A. Krueger *et al., NASA Ref. Publ. 1264* (1991).
11. P. Rigaud and B. Leroy, *Ann. Geophys.* **11**, 791 (1990).
12. R. Bojkov, *Geophys. Res. Lett.* **13**, 1236 (1986).
13. International Council of Scientific Unions, *Catalogue of Data in the World Centers, 1957–1958* (Pergamon, New York, 1964), Vol. XXXVI, p. 84.
14. D. De Muer [*Ann. Geophys.* **11**, 795 (1990)] commented on the Rigaud and Leroy (*11*) paper, noting that (i) the Dumont variability was substantially larger than other Antarctic sites (notably Halley Bay), (ii) the lack of a correlation of the Dumont data with meteorological data, (iii) the extremely low values of total ozone in early September, and (iv) the rarity of low ozone values (less than 200 DU) at Dumont during the 1980s.
15. D. Hartmann *et al., J. Geophys. Res.* **94**, 16779 (1989).
16. "Ozone Data for the World, November–December 1971 Supplement, IGY/IGC 1957–1959" (Atmospheric and Environmental Services of Canada, World Meteorological Organization, Downsview, Canada, 1971), vol. 12.
17. J. Farman and R. Hamilton, *Br. Antarct. Surv. Sci. Rep. 90* (1975).
18. *World Meteorological Organization Global Ozone Research and Monitoring Project Rep. 20* (1989); W. Komhyr *et al.*, in *Ozone in the Atmosphere: Proceedings of the Quadrennial Ozone Symposium*, R. Bojkov and P. Fabian, Eds. (Deepak, Hampton, VA, 1990), p. 28; P. McCormick and J. Larsen, *Geophys. Res. Lett.* **13**, 1280 (1989); D. Hofmann and S. Oltmans, *J. Geophys. Res.* **98**, 18555 (1993).
19. J. Alt *et al., IGY Gen. Rep. Ser.* **4**, 1 (1959).
20. G. Dobson *et al.* [*Proc. R. Soc. London Ser. A* **122**, 456 (1928)] first showed the relationship of meteorological observations to total ozone. E. Farkas [*N. Zealand J. Sci.*, 386 (1970)] and P. Newman and W. Randel [*J. Geophys. Res.* **93**, 12585 (1988)] both showed the very tight linear spatial correlation of stratospheric temperatures and total ozone over Antarctica. They found that warm lower stratospheric temperatures were related to high total column ozone, whereas low temperatures were correlated with low ozone. Y. Sekiguchi [*Geophys. Res. Lett.* **13**, 1202 (1986)] used the Syowa station data to show that years with low (high) total ozone in October and November are related to cold (warm) lower stratospheric temperatures.
21. Every year of available meteorological data has shown this tight linear relation of total ozone to lower stratospheric temperatures, which is directly related to the adiabatic compression of air; see K. Tung and H. Yang, *J. Geophys. Res.* **93**, 11123 (1988); (*9*).
22. M. Schoeberl *et al., Geophys. Res. Lett.* **13**, 1217 (1986).
23. G. Bluth *et al., ibid.* **19**, 151 (1992).
24. T. Simkin *et al., Volcanoes of the World: A Regional Directory, Gazetteer, and Chronology of Volcanism During the Last 10,000 Years* (Hutchinson Ross, Stroudsberg, PA, 1981).
25. W. G. Mankin and T. M. Coffey, *Science* **226**, 170 (1984).
26. "Atmospheric Ozone 1985," *World Meteorological Organization Global Ozone Research and Monitoring Project Rep. 16* (1985).
27. W. Mankin *et al., Geophys. Res. Lett.* **19**, 179 (1992).
28. H. Johnston [*J. Geophys. Res.* **94**, 18485 (1989)] showed that there was little transport of ^{14}C from Northern Hemisphere atmospheric nuclear tests to the Southern Hemisphere.
29. M. Sato *et al., J. Geophys. Res.* **98**, 22987 (1993); H. Lamb, *Philos. Trans. R. Soc. London* **266**, 425 (1970).
30. R. Rood, *Geophys. Res. Lett.* **13**, 1244 (1986).
31. M. McCormick *et al., Geophys. Res. Lett.* **17**, 381 (1990).
32. S. Solomon *et al., Nature* **363**, 245 (1993).

33. Thanks to G. Labow and E. Hare for supplying the Dobson and Vassey data and to M. Schoeberl, R. Stolarski, J. Gleason, J. Herman, A. Aiken, R. McPeters, J. Miller, B. Mankin, S. Rowland, J. DeLuisi, and G. Bluth for helpful discussion.

24 November 1993; accepted 15 March 1994

Strontium Isotopic Composition of Mid-Cretaceous Seawater

B. Lynn Ingram, Rodolfo Coccioni, Alessandro Montanari, Frank M. Richter

The $^{87}Sr/^{86}Sr$ ratio in fish teeth separated from mid-Cretaceous marl and black shale from the northeastern Apennines and Venetian Alps (Italy) define three periods of low $^{87}Sr/^{86}Sr$ ratio at 121 to 124 million years ago (Ma), 110 to 115 Ma, and 89 to 91 Ma. The $^{87}Sr/^{86}Sr$ excursions correspond to oceanic anoxic events represented by the Livello Selli, Livello 113, Livello Urbino, and Livello Bonarelli black shale marker beds and probably reflect an increase in the low-$^{87}Sr/^{86}Sr$ hydrothermal strontium flux associated with the emplacement of the Ontong-Java and Kerguelen plateaus (120 to 110 Ma) and the Caribbean Plateau (89 to 91 Ma). The modeled flux is consistent with the volumes and eruption rates of the oceanic plateaus but is far smaller than expected from the proposed Cretaceous crustal production rates of 50 to 100 percent greater than modern.

The strontium isotopic composition of seawater exhibits both large and small fluctuations throughout the Phanerozoic; these are attributed to changes in the riverine Sr flux controlled by orogenic uplifting and major glaciations, increased submarine volcanism and sea-floor spreading rates, and overall changes in rock exposures and eustatic sea level (*1–5*). Modeling indicates that major fluctuations are closely tied to continental deformation rates for most of the Phanerozoic except for the period from 300 to 90 Ma (*5*). During part of this period, between 125 and 90 Ma (the mid-Cretaceous), submarine volcanic activity was greater, sea level was higher, thermohaline circulation was markedly different (*6*), and ocean temperatures were warmer than present (*7*). Sedimentary rocks with high amounts of organic carbon, representing so-called "oceanic anoxic events," were deposited during discrete intervals of the mid-Cretaceous (*8–11*).

B. L. Ingram, Department of Geology and Geophysics, University of California, Berkeley, CA 94720, USA.
R. Coccioni, Instituto di Geologia, Via Santa Chiara 27, 61029 Urbino, Italy.
A. Montanari, Osservatorio Geologico di Coldigioco, 62020 Frontale di Apiro (MC), Italy.
F. M. Richter, Department of Geophysical Sciences, University of Chicago, Chicago, IL 60637, USA.