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Ice-core Records and Ozone Depletion—Potential for a Proxy Ozone Record

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Figure 1. University of Kansas radar mounted on a sled.

Figure 2. Twin Otter aircraft with antenna mounts for Kansas radar.

the bottom echoes (at depths of roughly 1.1 kilometers), and also the internal layers. The "A scope" displays allowed estimates of the roughness at the ice/bedrock interface.

Plans for the 1988 field season are to conduct application-oriented measurements at the Siple Coast Upstream B (USB). Measurements will be made of a 35-by-8 kilometer area from a Twin Otter aircraft, supplemented by sled measurements.

A method has been devised for comparing the shape of the bottom echo with that of a simulated pulse whose shape depends on the roughness parameters: standard deviation of height and autocorrelation function of height. With this method, we made roughness estimates for some of the bottom surface in the Downstream B area.

We have developed a two-dimensional, matched-filter method for removing the hyperbolas characteristic of point-target echoes from the bottom of the ice sheet. This method replaces a hyperbola with a single image point at the location of the scatterer. With such a method, the shape of the bottom may be more readily interpreted, and weak target echoes are not covered up by strong hyperbolic echoes from nearby targets.

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Ice-core records and ozone depletion—Potential for a proxy ozone record

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Time-series of the ionic composition in polar ice cores can provide detailed direct and proxy records of seasonal to millenial scale fluctuations in climate, atmospheric chemistry, and volcanic activity. Even though problems of species-source links and air/snow fractionation have not all been entirely resolved, the fact remains that ice cores currently hold the best hope of retrieving detailed paleoatmospheric records. While direct links between the chemistry in ice cores and the ozone depletion phenomenon cannot be guaranteed, ice-core records provide the only means by which signals related to the ozone cycle can be produced for pre-measurement periods or for unmonitored sites. We propose that measurements of nitrate and/or chloride in polar snow/ice samples may provide proxy records of ozone depletion because of the role these species play in the ozone cycle (e.g., see summary review by Schoeberl and Krueger 1986). Heterogeneous chemical reactions in the antarctic atmosphere involving catalyzing agents such as chlorine monoxide, bromine monoxide, and/or nitrogen oxides are known to be effective in reducing ozone concentrations through their effect on the general reaction: oxygen plus ozone forms $2O_2$ (e.g., McElroy et al. 1986a). Removal of nitrogen oxides by condensation from polar stratospheric clouds (e.g., Toon et al. 1986; McElroy et al. 1986b; Crutzen and Arnold 1986) triggered particularly by cooling in the stratosphere helps set the stage for more efficient removal of ozone by reactions with chlorine monoxide and bromine monoxide (e.g., McElroy et al. 1986a). These reactions may result in increased concentrations of nitrate and chloride in polar snow/ice cores.

An ozone proxy pilot study. In 1984, we conducted a detailed glaciochemical program that included collecting a 201-meter core, collecting snowpit-samples, and taking surface-snow samples at a site 500 kilometers from the South Pole, in the Dominion Range (85°15'S 166°10'E, mean elevation, 2,700 meters above sea level). (See figure 1.) This site lies along the contact between the Transantarctic Mountains and the east antarctic ice sheet and provides an excellent site for monitoring the interaction of coastal and inland air masses. This site is

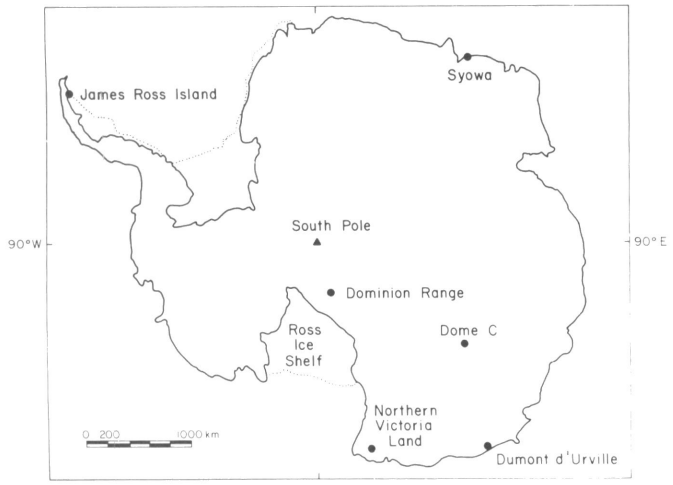

Figure 1. Location map.

also located within the area affected by the austral spring "ozone hole." The low mean annual temperature, −38.8°C, and relatively low accumulation rate (approximately equivalent to 4 centimeters of water) make the site ideal for the recovery of relatively long-period, undisturbed paleoatmospheric records. We established the dating for the core by counting annual maxima in chloride, nitrate, and sodium as well as by using lead-210, and total beta-activity measurements. Unfortunately, the upper 18 meters (AD 1984–1910) of the core were lost, due to melting, while being transported from McMurdo Station, Antarctica, to Port Hueneme, California. Fortunately, a 6-meter (3-centimeter sample interval) snowpit is available to fill in the detail for the period AD 1984–1910.

While the complete interpretation of the full AD 1984 to approximately 1050 BC composite snowpit/ice core record will be dealt with in future papers, examination of the general trends in the time-series of nitrate ion and chlorine ion (figure 2) reveals the following:

- a marked increase in nitrate ions is apparent as of approximately AD 700,
- the period AD 1984–1910 (6-meter snowpit) is characterized by higher nitrate-ion values than any other period of similar duration in the record, and
- the chlorine-ion record shows only minor variations.

In an attempt to explain the trend in nitrate ionization, the potential sources of this species to the Dominion Range site need to be examined. These sources include:

- nitrogen fixation by lightning at tropical and/or mid-latitude sites (Legrand and Delmas 1986);
- volcanic activity;
- ionization via solar related phenomena (Zeller and Parker 1981);
- production via thermonuclear detonations (Holdsworth 1986);
- anthropogenic, and
- temperature controls on condensation.

Some of these sources do not appear to be important in explaining the observed trend in nitrate ionization. For example, no evidence exists for trends in either lighting and/or volcanic source nitrate that match the observed record. Trends in nitrate ionization attributed to fluctuations in solar activity (e.g., Parker, Zeller, and Gow 1982) are controversial (Risbo, Clausen, and Rasmussen 1981; Herron 1982; Legrand and Delmas 1984, 1986) and do not explain the trend in the Dominion Range record. Thermonuclear sources are thought to have been sig-

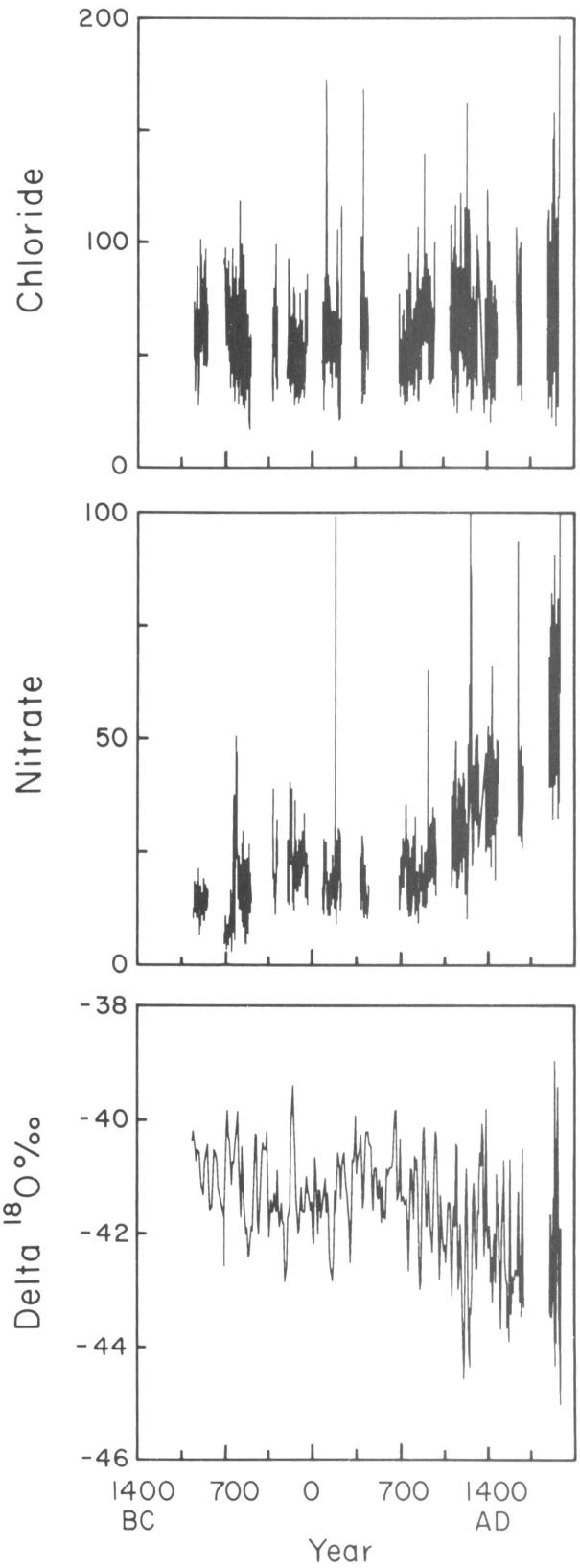

Figure 2. Dominion Range nitrate (in micrograms per kilogram), chloride (in micrograms per kilogram), and delta oxygen-18 (in parts per thousand, ‰) time series for the period AD 1984 to approximately 1050 BC.

nificant from the 1950s to 1970s due to extensive atmospheric testing (Holdsworth 1986), however, for other periods the source is probably negligible.

The input of anthropogenically derived nitrate to the Dominion Range site cannot be assessed in any straight-forward manner at this time. In southern Greenland, however, a twofold increase in nitrate since AD 1955 and a threefold increase in sulfate since AD 1900 has been documented and attributed to anthropogenic activity (Mayewski et al. 1986). It has been assumed that because the vast majority of fossil fuels are consumed in the Northern Hemisphere that Antarctica has not been affected by anthropogenically derived nitrate or sulfate (Wolff and Peel 1985). Notably there is no increase in sulfate in the Dominion Range record throughout the period of nitrate increase although other sources of sulfate could potentially mask an anthropogenic signal. To estimate the significance of the anthropogenic source of nitrate ions to the Antarctic, we can draw upon a knowledge of documented trends in nitrous oxide and lead. Pearman et al. (1986) using polar ice core data propose an approximately 8 percent increase in nitrous oxide due to fossil-fuel combustion since AD 1600 which is similar to nitrous oxide emission data model calculations made by Hao et al. (1987) for the period AD 1860 to present. Boutron and Patterson (1987) have recently argued that 80 percent of the lead found in the antarctic troposphere is anthropogenic and that lead levels have risen fivefold since the Holocene. Through the last 200 years, Greenland lead values have risen approximately 200 times (Murozumi, Chow, and Patterson 1969; Ng and Patterson 1981). If we use the ratio Greenland-lead-increase to antarctic-lead-increase (200:5) as a rough approximation of the differences expected in anthropogenic effect between the two hemispheres and assume that the same general relationship holds for nitrate, we would expect approximately a 2.5 percent increase due to anthropogenic activity for nitrate in Antarctica. Neither analogy explains the approximate twofold increase in nitrate since the early 1800s that is observed in the Dominion Range record. It should be noted, however, also that neither analogy provides definitive evidence of the increased flux of nitrate to the Antarctic due to anthropogenic sources because of differences in transport style (lead analogy) and atmospheric residence time (nitrous oxide analogy) compared to nitrate.

As noted by Toon et al. (1986) and Hamill, Toon, and Turco (1986), polar stratospheric clouds which form at temperatures of approximately 190°K could be composed of as much as 50 percent nitric acid/water. Therefore, recent cooling of the stratosphere such as that observed over Syowa Station for the period AD 1974–1985 (Chubachi 1986) could possibly have resulted in increased condensation of nitric acid in polar stratospheric clouds. Hofman et al. (1988) and Parrish et al. (1988) note that during the period of ozone depletion, and within the geographic area affected by the depletion, lower stratospheric air appears to be transported downward. Thus, fallout of the condensed nitric acid from polar stratospheric clouds may, in fact, be occurring directly onto the antarctic ice sheet particularly at latitudes as high as 85°S where the tropopause may be fairly close to the surface of the ice sheet.

Examination of the Dominion Range oxygen isotope record (figure 2) reveals a trend toward more negative values starting at approximately the same time as the beginning of the increase in nitrate ionization. If the nitrate ionization trend we observe reflects the rate of condensation of nitric acid in polar stratospheric clouds and the trend in nitrate is controlled by cooling in the stratosphere, the oxygen isotope signal measured in our core could be linked to condensation temperatures in the stratosphere.

Sources for chloride ion to the antarctic include: volcanic activity, marine input, and fallout of hydrogen chloride from polar stratospheric clouds (e.g., Toon et al. 1986). The relatively weak trend in the chloride record does not necessarily allow the differentiation of all of these sources. Volcanic inputs are usually seen as discrete signals as opposed to trends. The other two sources could produce trends in the record depending upon, respectively, changes in the circulation intensity of marine air masses and changes in temperature and overall composition of associated polar stratospheric clouds. Notably odd nitrogen is expected to be removed more efficiently than chlorine gases from polar stratospheric clouds (Wofsy et al. 1988) and, therefore, the trend in chloride may not be expected to be as dramatic as that in nitrate.

Plots of nitrate and chloride from the 6-meter snowpit record compared to mean ozone concentrations (figure 3) measured at South Pole (Komhyr, Grass, and Leonard 1986) and Syowa Station (Sekiguchi 1986) for the same time periods reveal interesting similarities in trend. We stress here *only* the general correspondence between trends in nitrate and chlorine ionization and annual minima in ozone concentrations since the Dominion Range is located 500 kilometers north of the closest ozone minitoring site, South Pole. Differences in ozone concentration and hence relationship to nitrate and/or chloride for any one time period could differ significantly from site to site due to distance from the center of the polar vortex (e.g., McCormick and Larsen 1986). Is the general relationship in figure 3 coincidence or causality? We suggest that there is significant potential for future study.

Further confirmation that there may be an association between nitrate precipitated onto the antarctic ice sheet and the ozone cycle comes from the geographic distribution of relatively recent nitrate values. The increase inland observed along the Dumont d'Urville-Dome C traverse (Legrand and Delmas 1985) and the relatively low concentrations measured from coastal sites [e.g., mean 16 micrograms per kilogram on James Ross Island (Aristarain, Delmas, and Briat 1982); mean 40 micrograms per kilogram on the Ross Ice Shelf (Herron 1982) and mean 42 micrograms per kilogram in northern Victoria Land (Allen et al. 1985)] compared to inland sites [e.g., range 65–130 micrograms per kilogram at South Pole (Legrand and Delmas 1984) and range 35–265 micrograms per kilogram from the Dominion Range (this study)] all tend to suggest that nitrate has a source which first enters the interior portions of Antarctica. Recent work which indicates that stratospheric air descends during periods of ozone depletion (Hofman et al. 1988; Parrish et al. 1988) coupled with the knowledge that the annual maximum in nitrate is an austral spring phenomenon further substantiates the link between increases in nitrate in the ice sheet and ozone depletion at 12–20 kilometer altitude.

Toward a more perfect ozone proxy record. While the Dominion Range record discussed in this paper is suitable as a pilot study it cannot provide the quality of record needed to firmly demonstrate and develop a proxy record of ozone depletion. However, South Pole provides an optimal site for such a study because:

- it is within the ozone hole;
- records of mean monthly total ozone are available that extend back to the period prior to the dramatic depletion (Komhyr et al. 1986);
- atmospheric column temperatures are available to compare with oxygen isotope measurements from snow/ice cores;

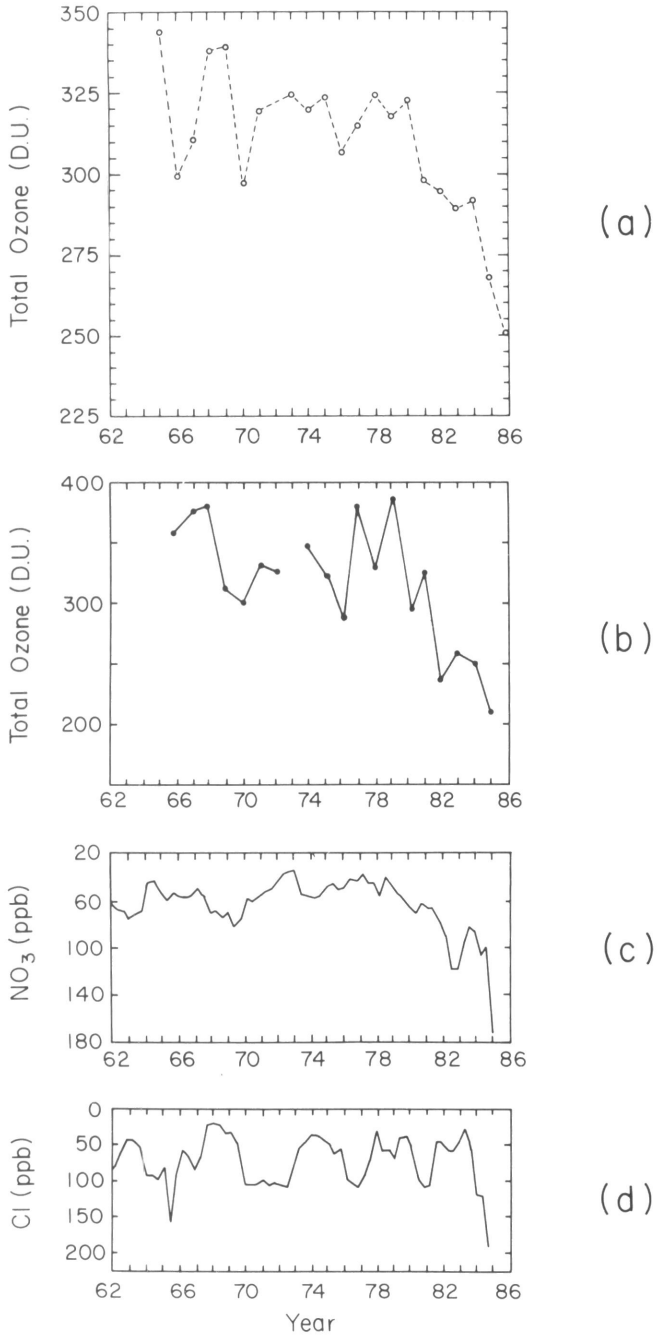

Figure 3. (a) South Pole mean October to February total ozone values (Komhyr et al. 1986), (b) Syowa Station October monthly total ozone (Sekiguchi 1986), (c) Dominion Range springtime (annual maxima) in nitrate, and (d) Dominion Range springtime (annual maxima) in chloride. (ppb denotes parts per billion.)

- mean annual temperatures (approximately −59°C) assure preservation of the chemical record;
- stratigraphic markers such as oxygen isotopes, total beta-activity, and stratigraphy have been demonstrated to provide excellent chronological control over periods of decades; and
- accumulation rates of approximately 0.26 centimeters per year snow equivalent are low enough to allow the collection of decadal records from snowpits and shallow cores with resolution on the order of 10–15 samples per year. We suggest that nitrate and chloride measurements from South Pole would be extremely valuable for establishing the validity of any proxy relationship with ozone depletion.

Some nitrate measurements have been conducted at South Pole by Zeller and Parker (1981), Parker et al. (1982), and Legrand and Delmas (1984). These studies while all extremely valuable do not provide the appropriate data necessary to test for a proxy ozone record since the studies were developed for other purposes. The time-series of nitrate from these earlier studies are either too low in resolution, are not substantiated by companion measurements, and/or the measurements cover too short a time period.

During the 1988–1989 austral summer we plan to sample a 6–10-meter snowpit covering several decades from a site 10–40 kilometers from South Pole to examine this issue further. This site is close enough to South Pole so that the results can be directly compared with the South Pole records of ozone but far enough away so that local contamination is minimized (Mayewski et al. 1987). Potentially this record could provide details concerning the onset and temporal characteristics of ozone depletion. Such future studies could dramatically expand our spatial and temporal understanding of this problem.

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Detailed glaciochemical investigations in southern Victoria Land, Antarctica—A proxy climate record

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Advances in climate prediction depend on a knowledge of historical climatic sequences ranging in scale from decades to millennia. Proxy data produced by pollen, sediment, tree rings, glacier fluctuations, and ice and snow cores are valuable in the construction of climatic sequences when direct observations of the atmosphere are either spatially or temporally lacking. Links between proxy data and the atmosphere generate the most confidence when actual components of climate are preserved in the proxy medium.

The best preserved data pertaining to former climate is found in the time-series available from snow and ice cores retrieved from appropriately chosen glaciers. Records from polar and high-altitude, low- to middle-latitude glaciers have proven valuable in obtaining time series relatable to climatic change for time periods of 10 to 100,000 years. Analysis of the physical and chemical components of ice and snow such as: stratigraphy, stable isotopes, radio-nuclides, and primary anions and cations can all be very effective in determining, on seasonal to multi-year levels, extremely detailed proxy records of climatic change, atmospheric chemistry, and volcanic activity.

The production of climatic change records using time-series retrieved from ice cores has seen minimal application in the Transantarctic Mountains even though glacial geologic studies in this area provide one of the primary bases for understanding the glacial history of Antarctica. Notably while the glacial geologic records provide relatively low-resolution, long-period records, the ice core records could provide an excellent view of an albeit shorter period but with relatively high resolution. Therefore, detailed ice-core records provide the resolution necessary to assess, expand, and utilize the longer, less-detailed glacial geologic records and more importantly allow us to compare in detail the modern environment in Antarctica with the paleoenvironment adding significantly to our understanding of global change.

Three primary ice core sites were chosen for investigation during the 1987–1988 field season: the Royal Society Range, head of Emmanuel Glacier (approximately 78°07′S approximately 161°35′E, approximate elevation 3,000 meters); the Asgaard Range, head of Newall Glacier (approximately 77°37′S approximately 162°30′E, approximate elevation 1,700 meters); and the Convoy Range in the general area of Staten Island Heights/Dotson Ridge (approximately 76°50′S approximately 161°30′E, approximate elevation 1,500 meters).