

sidered on zoogeographic grounds to mark the separation of the Atlantic-Caribbean and Indo-Pacific faunal provinces (32). On the basis of the chronology of the section, this level has an age of about 3.8 Ma, in good agreement with the previously estimated minimum age of 3.6 Ma (32).

The Blake Plateau section, then, is a record of both tectonic and climatic events as they have affected the North Atlantic circulation. The results in general support the generally although not universally held view that the planetary circulation should be invigorated during times of glacial climate (33). But instead of short-term (10^3 to 10^4 years) glacial-interglacial fluctuations, such as those of the late Pleistocene on which this concept is based, the Blake Plateau section seems to be a response to climatic trends extending over a period of 10^5 to 10^6 years that can perhaps be characterized as fluctuations between long-term relatively glacial and relatively nonglacial modes of circulation.

ANSIS G. KANEPS

3211 Cadencia Street,
Carlsbad, California 92008

References and Notes

1. B. A. Warren and G. H. Volkmann, *J. Mar. Res.* **26**, 110 (1968); L. V. Worthington, *Johns Hopkins Oceanogr. Stud.* **6** (1976).
2. W. A. Berggren and C. D. Hollister, *Am. Assoc. Pet. Geol. Spec. Publ.* **20** (1974), p. 126.
3. A. Agassiz, *Bull. Mus. Comp. Zool. Harv. Coll.* **14**, 314 (1888).
4. R. M. Pratt and B. C. Heezen, *Deep-Sea Res.* **11**, 721 (1964).
5. JOIDES, *Science* **150**, 709 (1965).
6. D. B. Ericson, M. Ewing, G. Wollin, B. C. Heezen, *Geol. Soc. Am. Bull.* **72**, 193 (1961).
7. D. S. Gorsline, *J. Geol.* **71**, 422 (1963).
8. B. C. Heezen, C. D. Hollister, W. F. Ruddiman, *Science* **152**, 502 (1966).
9. C. Emiliani, S. Gartner, B. Lidz, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **11**, 1 (1972).
10. The sediments carry extremely weak magnetic remanence; demagnetization in various field strengths failed to produce any internally consistent pattern of magnetic inclinations or reversals.
11. D. B. Ericson and G. Wollin, *Science* **162**, 1227 (1968); M. Briskin and W. A. Berggren, in *Late Neogene Epoch Boundaries*, T. Saito and L. H. Burckle, Eds. (Micropaleontology Press, New York, 1975), p. 167.
12. J. D. Phillips, W. A. Berggren, A. Bertels, D. Wall, *Earth Planet. Sci. Lett.* **4**, 118 (1968); W. A. Berggren, *G. Geol.* **35**, 291 (1968).
13. J. D. Hays, T. Saito, N. D. Opdyke, L. H. Burckle, *Geol. Soc. Am. Bull.* **80**, 1481 (1969).
14. T. Saito, L. H. Burckle, J. D. Hays, in *Late Neogene Epoch Boundaries*, T. Saito and L. H. Burckle, Eds. (Micropaleontology Press, New York, 1975), p. 226.
15. F. Rögl and H. M. Bolli, *Init. Rep. Deep Sea Drill. Proj.* **15**, 553 (1973).
16. D. B. Ericson, M. Ewing, G. Wollin, *Science* **139**, 727 (1963).
17. J. P. Kennett and N. D. Watkins, *Geol. Soc. Am. Bull.* **85**, 1385 (1974).
18. D. Bukry and M. N. Bramlette, *Tulane Stud. Geol.* **6**, 149 (1968). In their original description of *C. rugosus*, Bukry and Bramlette noted its occurrence from 161 to 210 cm in core V3-153, equivalent to zones 8 and 9 of the present study. Bukry (personal communication, 1976) has examined samples from zones 3 through 7 of core V26-145 without finding *C. rugosus*.
19. S. Gartner, *Geol. Soc. Am. Bull.* **84**, 2021 (1973).
20. W. H. Blow, in *Proceedings of the First International Conference on Planktonic Microfossils*, P. Brönnimann and H. H. Renz, Eds. (Brill, Leiden, 1969), p. 199.

21. P. Brönnimann and J. Resig, *Init. Rep. Deep Sea Drill. Proj.* **7**, 1235 (1971); D. G. Jenkins and W. N. Orr, *ibid.* **9**, 1059 (1972); A. G. Kaneps, *ibid.* **16**, 713 (1973).
22. T. Saito, *Geology* **4**, 305 (1976).
23. W. E. Benson, R. E. Sheridan, P. Enos, T. Freeman, F. Gradstein, I. O. Murdmaa, L. Pastouret, R. R. Schmidt, D. H. Stuermer, F. M. Weaver, P. Worstell, *Geotimes* **21** (No. 2), 23 (1976).
24. P. J. Fox, B. C. Heezen, A. M. Harian, *Nature (London)* **220**, 470 (1968).
25. A. Lowrie, Jr., and B. C. Heezen, *Science* **157**, 1552 (1967).
26. M. G. Rutten and H. Wensink, *21st Int. Geol. Congr. Part 4* (1960), p. 62.
27. R. J. Curry, *Science* **154**, 770 (1966).
28. I. McDougall and J. J. Stipp, *Nature (London)* **219**, 51 (1968).
29. W. A. Berggren, *Init. Rep. Deep Sea Drill. Proj.* **12**, 953 (1972); N. J. Shackleton and N. D. Opdyke, *Nature (London)* **270**, 216 (1977).

30. D. E. Hayes and L. A. Frakes, *Init. Rep. Deep Sea Drill. Proj.* **28**, 919 (1975).
31. L. D. Keigwin, Jr., *Micropaleontology* **22**, 419 (1976).
32. A. G. Kaneps, thesis, Columbia University (1970).
33. D. A. Johnson, *Geol. Soc. Am. Bull.* **83**, 3121 (1972).
34. Supported through National Science Foundation grants GA-1193, GA-558, and GA-10635 and Office of Naval Research grant N00014-67-A-0108-0004. I thank C. Adelseck for reviewing this manuscript and for helpful comments, and J. D. Hays and U. von Rad for reviewing an earlier version. I am indebted to the late M. Ewing for providing ship time and to the scientists and crews of R.V. *Conrad*, cruise 11, and R.V. *Vema*, cruise 26, who successfully carried out the coring operations.

9 June 1978; revised 8 January 1979

Dynamic Chemical Equilibrium in a Polar Desert Pond: A Sensitive Index of Meteorological Cycles

Abstract. *The dramatic variation in the composition of a brine pond in Antarctica is a seasonal phenomenon. The phase relations of salts in solution are such that hydrologic conditions and temperature determine composition during the austral summer. Temperature is the primary determinant of composition during the winter.*

Don Juan Pond is situated in a closed basin in the ice-free region (1) of southern Victoria Land, between the East Antarctic Ice Cap and the Ross Sea. The pond, discovered in 1961 (2), has attracted considerable attention because of its extraordinary, highly variable chemistry and because it remains unfrozen for

most of the year in a region where the mean annual air temperature is approximately -18°C . Salinities ranging from 200,000 to almost 400,000 parts per million (ppm) have been reported, and 90 percent of the salt is calcium chloride (3, 4). The mineral antarctite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), discovered in 1965 (5), is peculiar to the Don Juan basin. Geophysical studies (6) preliminary to the Dry Valley Drilling Project (DVDP) (7) indicated that rock units underlying the basin are highly saline and perennially unfrozen, suggesting the presence of a reservoir of liquid groundwater. Drilling revealed that unfrozen water with a salinity of almost 200,000 ppm and a temperature of about -16°C is present to a depth of at least 75 m; the basin is, in fact, the site of the only known Antarctic occurrence of groundwater discharge from a confined aquifer (8).

During the austral summer of 1975 to 1976, two of us studied the mass balance of the pond as part of a research program begun in 1973 (9). The study included (i) bathymetric mapping, (ii) continuous measurement of fluid levels in the pond and DVDP borehole number 13, (iii) continuous measurement of air temperature, (iv) pan measurement of pond water evaporation rates, and (v) sampling of waters for chemical analysis. We can now demonstrate that the peculiar chemical behavior of Don Juan Pond is controlled by both hydrologic factors and temperature.

The flux of pond water occurs by four distinct mechanisms, of which at least three are highly sensitive to meteorological

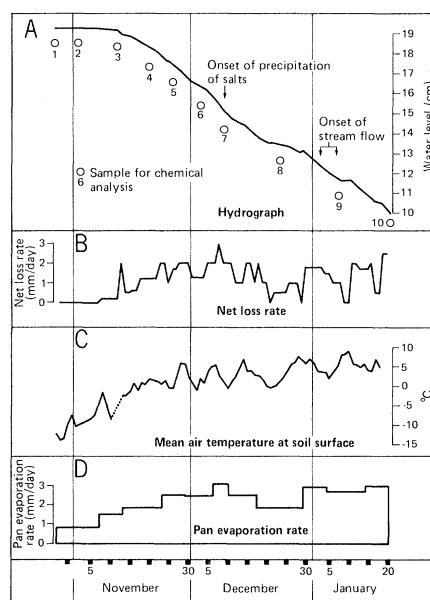


Fig. 1. (A) Hydrograph of Don Juan Pond, 27 October 1975 to 20 January 1976. (○) Date of sample for chemical analysis; samples are numbered sequentially. Precipitation of salts was first observed on 9 December; stream-flow began between 3 and 6 January. (B) Net loss rate. (C) Mean air temperature at the soil surface 100 m southwest of the pond. (D) Average of evaporation rates in two pans containing pond water, one at the southwest and the other at the northeast edge of the pond.

logical conditions. Water is lost only through evaporation or sublimation; the striking correlation between variations in net loss rate and variations in mean air temperature at the soil surface reveals the dependence of evaporation rate on weather (Fig. 1). Both in magnitude and in seasonal variation, the evaporation rates we report are similar to ice ablation rates measured elsewhere in Wright Valley. Long-term studies at Lake Vanda recorded mean ablation rates in excess of 2.0 mm/day during midsummer (November through January) and on the order of 0.25 to 0.5 mm/day during the winter (April through September) (10). Short-term studies gave midsummer rates ranging from 1.9 to 3.5 mm/day (11). If winter ablation rates at the pond and Lake Vanda are the same, at least 16,000 m³ of water is lost from the pond annually.

Water enters the pond from three sources. During the period of record, one light snowfall (< 1 cm of snow) occurred, with no effect apparent in the hy-

drograph. Mean annual precipitation in the Dry Valley Region is between 5 and 10 g/cm², suggesting that precipitation accounts for 15 to 30 percent (2400 to 4800 m³) of the annual budget of the pond. In late December and January, there is melting in the active layer of ice-cemented permafrost lying west of the pond; the resulting flows of unconfined groundwater form small freshwater (< 500 ppm of dissolved solids) streams having highly erratic discharges. This streamflow effected a flattening of the hydrograph during two short intervals in January; total volume of flow was about 1500 m³. Confined, saline groundwater discharged to the pond at a rate of more than 25 m³/day (9100 m³/year) during the period of the hydrograph. This deep groundwater flux is most clearly evidenced between 27 October and 12 November; in spite of evaporation exceeding 0.5 mm/day, net loss from the pond was negligible.

These data indicate that between January 1975 and January 1976, the pond lost

two to three times its greatest measured volume (8000 m³) without going dry. Under current climatic conditions, this precarious equilibrium is maintained by the two groundwater fluxes; if either should cease, the pond would be dry within a year. Indeed, at the third DVDP Seminar (Tokyo, 5 to 10 June 1978), P. N. Webb reported that the pond did not exist in the summer of 1957 to 1958, and T. Torii reported that in 1977 to 1978 the pond was at its smallest volume since 1961. That the pond has persisted since 1961 suggests that at least 200,000 m³ of groundwater has discharged to the basin.

The chemistry of the pond is highly sensitive to fluid balance and to temperature. We show this sensitivity by using a trilinear phase diagram (Fig. 2C) constructed with laboratory data (12). The diagram is of a type unconventional for aqueous systems, both because it includes water as a component and because it is drawn for a range of temperatures. As is customary, the composition of the fluid phase is indicated by the three scales bordering the diagram; the fields of stability of solid phases are separated by heavy lines and designated by the patterns keyed in Fig. 2B. At any particular fluid composition, the temperature determines whether the appropriate mineral or minerals are stable. For example, ice would not be stable (that is, it would dissolve) in a solution having 21 parts per hundred (pph) of CaCl₂ and 0 pph of NaCl at temperatures above -20°C; however, such a solution would "precipitate" ice if the temperature were lowered to -20°C or less. Precipitation of ice would have the effects on the fluid phase of decreasing the concentration (causing dilution) of H₂O, increasing the concentration of CaCl₂, and lowering the freezing point; these effects would be seen in the phase diagram as a leftward displacement, a shift away from the H₂O vertex of the component triangle.

Chemical analyses of ten fluid samples taken between 27 October and 20 January at a single location in Don Juan Pond are plotted in the phase diagram as a numbered sequence (Fig. 2D). The date of each sample is indicated in Fig. 1A, allowing comparison of the hydrology, temperature, and chemistry of the pond. Analyses of 21 samples of groundwater taken on the same dates at various depths in borehole 13 are plotted as a solid bar labeled GW in Fig. 2D. During the 86 days of record the composition of the pond varied markedly, passing across the stability fields of all four minerals. In fact, six stages of development, five of which are directly evidenced in the phase diagram, may be identified. These

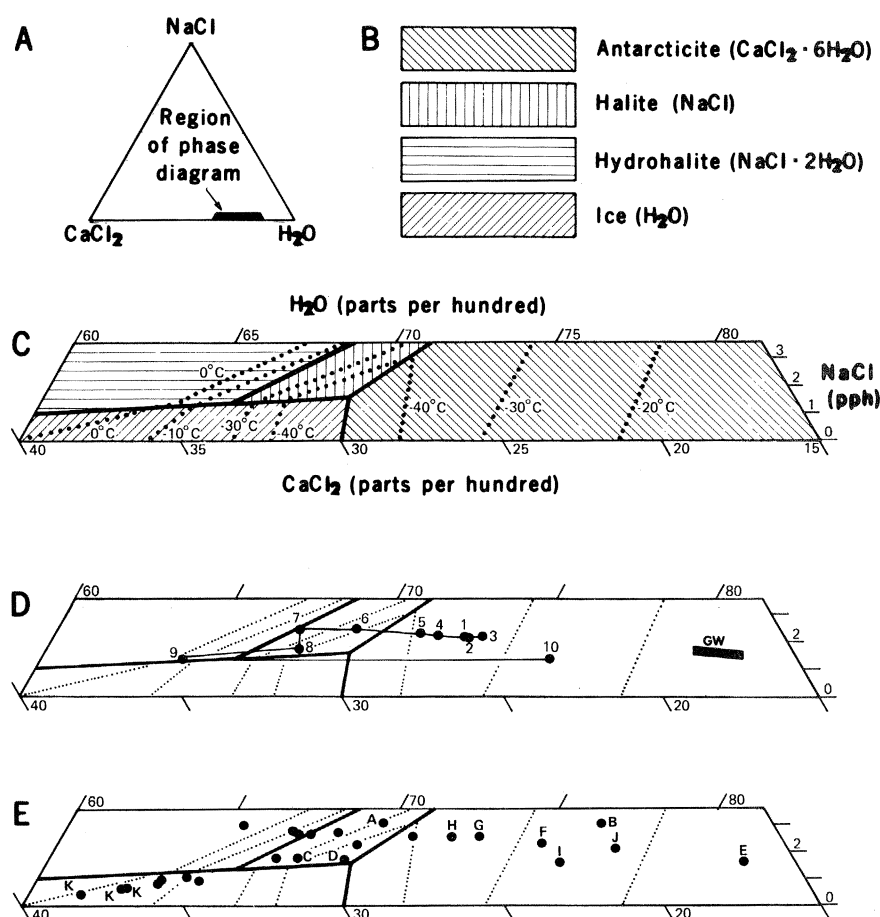


Fig. 2 (A) Component triangle showing region (shaded) of phase diagram. (B) Key for (C), identifying minerals (solid phases) occurring in region of phase diagram. (C) Phase diagram. Phase boundaries are heavy lines separating patterned areas; isotherms, in degrees Celsius, are dotted lines, and all but the 0°C isotherm are of negative temperatures. (D) Phase diagram of (C) with our pond water (●) and groundwater (GW) analyses plotted; pond analyses are connected by a solid line and numbered in sequence, the numbers correspond to those in Fig. 1A. Phase boundaries are heavy lines; isotherms are dotted lines. (E) Phase diagram with previous pond water analyses plotted (●); lettered analyses are explained in the text.

stages, and their relation to hydrology and temperature of the pond, are discussed below.

Stage 1 (samples 1 through 3): stasis in chemical composition, or perhaps a very slight dilution of CaCl_2 and concentration of H_2O . Loss of H_2O from the pond by evaporation was approximately balanced by discharge of deep groundwater.

Stage 2 (samples 3 through 7): concentration of CaCl_2 and NaCl and dilution of H_2O . Evaporative loss of H_2O far exceeded replacement by groundwater, causing concentration of salts dissolved in the pond.

Stage 3 (samples 7 and 8): precipitation (dilution) of NaCl . The precipitation evidenced in the diagram was detected in two other ways. We first observed white isometric crystals at the sampling site on the date of sample 7; additional salt precipitated between samples 7 and 8. We also calculated the mass of each ion dissolved in the entire pond on the date of each sample; the mass of dissolved NaCl decreased between samples 7 and 8. Although precipitation took place in the field of hydrohalite (13), the mean temperature was near 0°C . This suggests either that hydrohalite precipitated metastably or that the phase boundaries or isotherms, or both, are incorrectly placed. As in stages 4 and 5, continued net loss of H_2O by evaporation effected precipitation by forcing the composition of the pond into a region of salt stability or metastability.

Stage 4 (samples 8 and 9): continued precipitation of NaCl , concentration of CaCl_2 , and dilution of H_2O . Precipitation was also detected visually and by mass balance calculations. Evaporation again far exceeded inflow.

Stage 5 (sample 9): precipitation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Precipitation is not directly apparent in the diagram but is suggested by the position of the analysis, near the 0°C isotherm on the boundary of the antarcticite stability field. We first saw poorly crystallized salts similar in appearance to antarcticite on the date of sample 9; the mass of dissolved CaCl_2 decreased slightly between samples 6 and 9.

Stage 6 (samples 9 and 10): concentration of H_2O , slight concentration of NaCl , and dilution of CaCl_2 . The late season inflow of fresh stream water caused dilution of dissolved CaCl_2 ; all of the antarcticite and some of the NaCl precipitated earlier were seen to have redissolved. As the sampling site was situated near the mouth of a stream in order to detect the first effects of streamflow, sample 10 was not representative of the entire pond on 20 January. It is probable

that sample 9 was also diluted in CaCl_2 by fresh stream water.

By contrast with the chemistry of the pond, that of the deep groundwater was temporally invariant. The small variation shown was a function only of depth in borehole 13, the deepest samples being the most saline. Although the geologic history of the salts in the Don Juan basin remains problematic, the position of these analyses suggests that groundwater is the proximate origin of salts in the pond. Once the groundwater discharges, the polar desert climate effects a net loss of water, causing a concentration of the salts.

Although we took no samples during winter, our phase diagram allows prediction of the winter composition of the pond. The midwinter air temperature in Wright Valley is about -50°C ; at this temperature, the fluid phase would be in equilibrium with the precipitates antarcticite, hydrohalite, and ice. Sublimation would remove water from the ice-covered pond without changing the composition of the fluid phase. The path of compositional evolution effected by the transition from summer to winter temperatures would be a function of the composition at the end of the summer.

Earlier chemical analyses (2–4) gave the impression that the composition of the pond varied dramatically from year to year. In most years, however, only a single sample was taken. When the apparently diverse yearly analyses are assembled in the context of the phase diagram (Fig. 2E), they fall into a pattern much like the one we observed in the course of a single austral summer. In fact, the few published analyses of samples taken during a single summer show stages of development like those we observed. Analyses A and B (7 January and 15 January 1971) and C and D (18 December 1975 and 5 January 1976) indicate a freshwater influx like that during our stage 6; analyses E through H (1 November 1974 through 9 January 1975) indicate a net loss of water like that during our stage 2. Analyses I (April 1974) and J (July 1974) are of the only winter samples known to us; the surface of the pond was frozen during sampling (14) and ice was probably included in the samples, in which case they would not represent equilibrium winter compositions of the liquid phase. Analyses K are also of particular interest; Torii and co-workers (4, 5) found antarcticite when the samples were collected.

The demonstrated sensitivity of Don Juan Pond to meteorological conditions, together with its persistence in a climate marked by severe seasonal variations,

suggests that the chemistry of the pond exhibits a recurring, seasonal pattern of development. The dramatic variations in composition reported previously reflect the season when the pond was sampled.

H. J. H. HARRIS

K. CARTWRIGHT

Illinois State Geological Survey,
Urbana 61801

T. TORII

Japan Polar Research Association,
Tokyo, Japan

References and Notes

1. This area, known as the Dry Valley Region, has been the object of intensive scientific effort since the International Geophysical Year (1957 to 1958). Bibliographies relevant to the region are available from the Cold Regions Bibliography Project of the U.S. Library of Congress, Washington, D.C. See also the series of volumes *Antarctic Bibliography*, G. T. Thuronyi, Ed., published by the Cold Regions Bibliography Project.
2. G. H. Meyer, M. B. Morrow, O. Wyss, T. E. Berg, J. L. Littlepage, *Science* **138**, 1103 (1962).
3. R. E. Cameron, F. A. Morelli, L. P. Randall, *Antarct. J. U.S.* **7**, 6 (1972); M. G. Mudrey, N. F. Shimp, C. W. Keighin, G. L. Oberts, L. D. McGinnis, *ibid.* **8**, 4 (1973); J. C. F. Tedrow, F. C. Ugolini, H. Janetscheck, *N.Z. J. Sci.* **6**, 150 (1963).
4. T. Torii, N. Yamagata, J. Ossaka, and S. Murata [*Antarc. Rec. (Jpn.)* **58** (1977)] tabulated most of the previously published analyses of Don Juan Pond.
5. T. Torii and J. Ossaka, *Science* **149**, 975 (1965).
6. L. D. McGinnis and T. E. Jensen, *Quat. Res. (N.Y.)* **1**, 3 (1971); L. D. McGinnis, K. Nakao, C. C. Clark, in *Permafrost: The North American Contribution to the Second International Conference* (National Academy of Sciences, Washington, D.C., 1973), p. 136.
7. L. D. McGinnis, T. Torii, P. N. Webb, *Antarct. J. U.S.* **7**, 3 (1972).
8. K. Cartwright, H. Harris, L. R. Follmer, *DVDP Bulletin* **5** (Northern Illinois Univ., DeKalb, 1975), p. 134; K. Cartwright and H. J. H. Harris, *Geol. Soc. Am. Abstr. Programs* (1976), p. 804; H. J. H. Harris and K. Cartwright, in *Third Symposium on Antarctic Geology and Geophysics*, C. Craddock, Ed. (Univ. of Wisconsin Press, Madison, in press).
9. K. Cartwright and H. J. H. Harris, *Antarct. J. U.S.* **11**, 2 (1976).
10. Meteorological and hydrologic records taken in the region since 1958 to 1959 are available, primarily from the Water and Soil Division of the New Zealand Ministry of Works and Development in Christchurch. New Zealand has sponsored an excellent systematic program of measurements since 1969.
11. R. A. Ragotzkie and G. E. Likens, *Limnol. Oceanogr.* **9**, 3 (1964); Y. Yusa, *Contrib. Geophys. Inst. Kyoto Univ. No.* **12** (1972), p. 87.
12. E. W. Washburn, Ed., *International Critical Tables* (National Research Council, Washington, D.C., 1928), vol. 4; W. F. Linke, Ed., *Solubilities, Inorganic and Metal-Organic Compounds*, (Van Nostrand, Princeton, N.J., ed. 4, 1958), vol. 1; S. Z. Makarov and E. F. Shcharkova, *Zh. Neorg. Khim.* **14**, 11 (1969); R. C. Weast, Ed., *Handbook of Chemistry and Physics* (CRC Press, Cleveland, ed. 55, 1974).
13. Only two natural occurrences of hydrohalite have been reported, one in the cold (0°C) bottom waters of Lake Bonney in neighboring Taylor Valley and the other in Siberia [J. R. Craig, R. D. Fortner, B. L. Weand, *Geology* **2**, 8 (1974); J. R. Craig, J. F. Light, B. C. Parker, M. G. Mudrey, Jr., *Antarct. J. U.S.* **10**, 4 (1975)].
14. K. Kato, T. Torii, N. Nakai, *DVDP Bulletin* **8** (National Institute of Polar Research, Tokyo, 1978), p. 30.
15. We thank M. Chapman-Smith, D. Gross, U.S. Naval Air Development Squadron Six, and the people at New Zealand's Vanda Station for their help in Antarctica. Chemical analyses were performed under the direction of R. Ruch, Analytical Chemistry Section, Illinois State Geological Survey. Supported in part by NSF grant OPP 73-05917 AO2.

24 January 1979