

THE CHEMICAL STRATIGRAPHY OF POLAR ICE SHEETS— A METHOD OF DATING ICE CORES

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ABSTRACT. Studies of the chemical stratigraphy in the snow near Vostok station, which is near the centre of the East Antarctic ice sheet, show that sodium exhibits annual concentration differences of up to a factor of ten. Similar work on the 952 m Vostok ice core enabled accumulation rates along selected parts of the core to be determined. This in turn enables the core to be dated. The accumulation rate in this central region of the East Antarctic ice sheet for the last 50 000 years has been determined and is presented. An interesting result is that the accumulation rate during the last glacial period is only half that in post-glacial times. Results from the bottom of the core provide some evidence of a past surge in the East Antarctic ice sheet.

RÉSUMÉ. *La stratigraphie chimique des calottes polaires — une méthode de datation des carottes de glace.* Les études de la stratigraphie chimique de la neige près de la station Vostok qui est voisine du centre de la calotte glaciaire de l'Est Antarctique montrent que le sodium présente des variations annuelles de concentration pouvant aller jusqu'à un facteur 10. Un travail analogue sur la carotte de glace 952 m à Vostok permet de déterminer les taux d'accumulation en des points choisis de la carotte. Ceci permet en retour de dater l'échantillon. Le taux d'accumulation dans cette région centrale de la calotte Est Antarctique au cours des 50 000 dernières années a été déterminé et est présenté. Un résultat intéressant est que le taux d'accumulation au cours de la dernière période glaciaire est seulement la moitié de celui de l'époque post glaciaire. Les résultats issus du fond de la carotte montrent quelques traces d'une crue passée dans la calotte glaciaire de l'Est Antarctique.

ZUSAMMENFASSUNG. *Die chemische Stratigraphie polarer Eisschilder — eine Methode zur Datierung von Kernen.* Studien über die chemische Stratigraphie im Schnee bei der Vostok-Station, die nahe dem Zentrum des ostantarktischen Eisschildes liegt, zeigen, dass Natrium während eines Jahres Unterschiede in der Konzentration bis zum Faktor 10 aufweist. Ähnliche Untersuchungen an dem 952 m langen Eisbohrkern von Vostok gestatten die Bestimmung von Akkumulationsraten an ausgewählten Teilen des Kerns. Daraus wiederum ergibt sich eine Datierung des Kerns. Die Akkumulationsrate in diesem Zentralbereich des ostantarktischen Eisschildes wurde für die letzten 50 000 Jahre bestimmt. Ein interessantes Ergebnis ist darin zu sehen, dass die Akkumulationsrate während der letzten Eiszeit nur halb so gross war wie in der Postglazialzeit. Ergebnisse vom Unterteil des Kernes geben Hinweise auf einen Ausbruch des ostantarktischen Eisschildes in der Vergangenheit.

INTRODUCTION

The ice sheets of Greenland and Antarctica contain extremely long and detailed palaeoclimatic and palaeoenvironmental records. These ice sheets can be cored and already much valuable information on past climate has been obtained from studies of, for example, the $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios and the dust content of the water in the ice sheet. Perhaps the greatest problem in developing the full potential of the palaeoclimatic information contained in the ice sheets is the difficulty of dating the ice, particularly that from deep in the ice sheets. This paper describes a study of the chemical stratigraphy of polar ice cores and shows how such information can be used as a dating method and as a source of palaeoclimatic information.

There have been three principal approaches to the dating of ice cores based on:

1. *Glacial theory.* It is possible to calculate the age of the ice from the glaciological theory of the flow of ice in an ice sheet. This method has been used extensively (see for example, Johnson and others (1972)) but can have problems if the underlying terrain does not have a simple geometry and assumptions have to be made as to how the accumulation rate has changed with time.
2. *Radiometric measurements.* The decay of radioactive isotopes such as ^{210}Pb and ^{14}C initially present in the ice can be used for dating the core. This method is most useful for the upper more recent layers of an ice sheet, and is clearly limited by the half life of the radioactive isotope measured. The technique requires large quantities of ice and is technically very difficult. There is little immediate prospect of dating ice beyond 40 000 years.

3. *Stratigraphic techniques.* If some annual difference can be detected in the ice core, then at any section of the core the accumulation per year can be determined. If the curve of accumulation with respect to time is integrated, a plot of depth in core versus age can be determined. Different types of stratigraphy have been exploited:
- (a) *Isotope stratigraphy* exploits the fact that the winter precipitation is isotopically more depleted in ^{18}O and ^2H than the summer precipitation, so that annual layers can be seen. This approach appears to be limited to an age of *c.*20 000 years, beyond which time molecular diffusion tends to obliterate the annual layers. Further, this technique is applicable only in regions where sufficient summer precipitation survives. At Vostok in the centre of the East Antarctic ice sheet, for example, there is little precipitation in summer and much of this is lost by evaporation. This is unfortunate since it is the East Antarctic ice sheet, because of its low accumulation rate (*c.*2.5 g cm⁻² H₂O/year) and great thickness (*c.*4 000 m), which should produce cores covering the greatest time span.
 - (b) *Microparticle stratigraphy.* It has been found by Marshall (1959) that the concentration of microparticles in ice sheets may have an annual pattern and this can be used to determine the yearly accumulation rate (see for example, Thompson (1977)). This technique exploits Coulter-type counters, developed initially in microbiology, which require reasonably large samples. For this reason the technique is only applicable to ice cores from regions of moderately high accumulation rates. However, it does not suffer from the diffusion limitations of isotope stratigraphy.
 - (c) *Chemical stratigraphy.* This paper describes a chemical stratigraphy technique which is most applicable where the isotope techniques tend to fail—where there is high summer evaporation as on the East Antarctic ice sheet.

GEOCHEMISTRY OF POLAR ICE SHEETS

The work described in the paper was carried out at Vostok station (lat. 78° 30' S., long. 107° E.) in the summer of 1977–78. Vostok is at the centre of the East Antarctic ice sheet at an altitude of 3 500 m; the mean temperature is -57° C. It was part of a long-term project to study the geochemistry of Antarctic snow with the hope of contributing to the field of atmospheric chemistry in general and to gain a better understanding of Antarctic processes. Earlier work (Wilson and House, 1965) had shown that marine salts can reach points as remote from the ocean as the South Pole.

EXPERIMENTAL METHODS TO STUDY CHEMICAL STRATIGRAPHY

Snow samples were scraped from the surface under study using a carefully cleaned metal spirit level. All manipulations were carried out using plastic gloves. The area scraped was about 500 cm² and every effort was made to ensure that the surface was kept horizontal. Each sample was placed in a carefully cleaned plastic cup and allowed to melt. The resultant water was analysed in the flame photometer as described below.

Because of the extremely low concentrations of salts in snow falling in the central parts of the polar ice sheets, the most suitable material to analyse for was sodium (Na⁺) and, once the apparatus was set up, this analysis could be done on very small quantities (fraction of a cm³) of melted snow or ice in a few seconds. The principle of the analytical technique, which is called flame emission photometry, is to inject the water sample into a flame where the sodium atoms are excited and, on dropping to the ground state, emit light quanta of characteristic wavelength (the sodium-D line). The amount of light emitted depends (at low concentrations

linearly dependent) on the sodium concentrations. Commercially available flame photometers are not sufficiently sensitive for measurements of sodium concentrations found in the central parts of the East Antarctic ice sheet (as low as 0.5 ppb Na⁺), and for the work described in this paper the signal from the photocell had to be amplified electronically before measurement on the galvanometer of the instrument used (in the present case an Eel). Sodium emits at its characteristic wavelength most efficiently in low-temperature flames, and for this work bottled liquefied petroleum gas (mostly propane and butane) air flames were used. The most serious problem, however, in carrying out the analysis for sodium at such low concentrations is the background light emitted from dust particles drifting into the flame. This problem could presumably be eliminated by working in a specially built dust-free room, but in our case we carried out our analysis on the polar plateau itself, where, because of the altitude, the distance from the ocean, and general lack of bare ground and human activity, there were very few salt or dust particles in the air; so few, in fact, that measurements could be made between individual particles drifting into the flame. There were some periods, however, even at Vostok, when the abundance of aerosol particles in the air made measurements very difficult. This may possibly be due to snow particles evaporating to windward of the measuring site.

RESULTS AND DISCUSSION OF CHEMICAL STRATIGRAPHY

Representative results are given in Figure 1 from two areas from the surface of the "polygon strain site" 2 km north of Vostok station (near stake No. 26 and stake No. 46) and from c.3 m below the pre-human-era snow surface in the Vostok station snow mine. It can be seen that the Na⁺ concentration in the snow samples varies considerably as one moves down

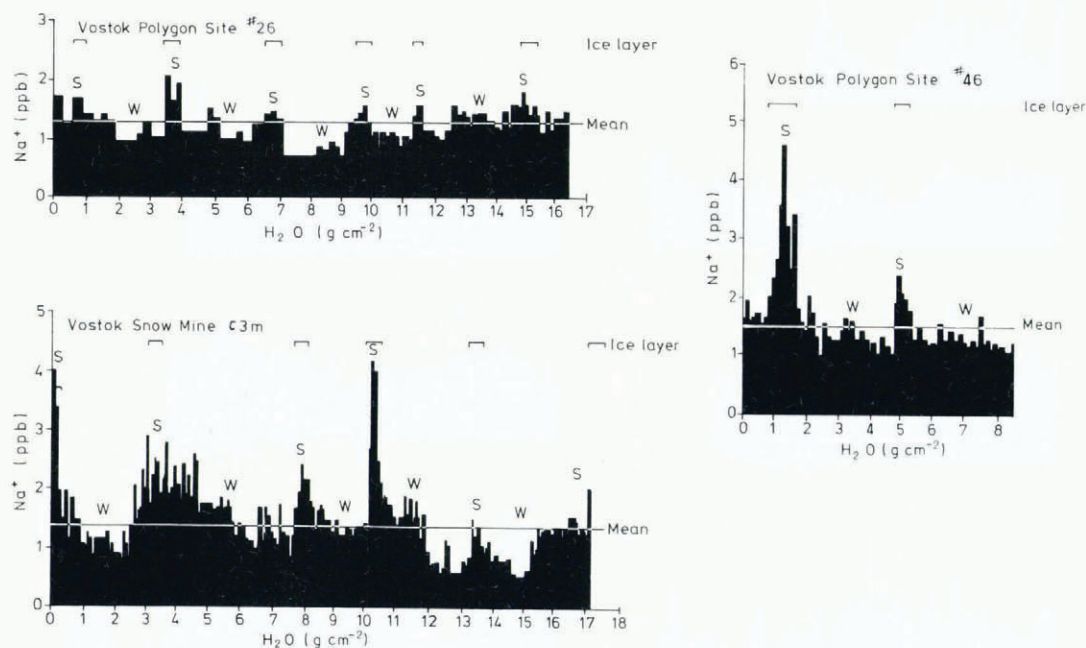


Fig. 1. The chemical stratigraphy of the surface snow at a selection of near-surface sites near the centre of the East Antarctic ice sheet (Vostok). Two of the sites are from the polygon strain array 2 km north of Vostok station, near stake No. 26 and stake No. 46. One is from the Vostok snow mine about 3 m below the pre-human-era snow surface at Vostok station itself. Note the enhanced Na⁺ levels of the summer surfaces. Note also the effect of sampling interval and the effect of (presumably) non-horizontal stratigraphy. S summer; W winter.

the profile with the high values corresponding to the "ice layers" which are more "sugary" and are believed to represent the summer surface. It is proposed that the higher sodium concentrations found in the summer surfaces are the result of greater loss of water by sublimation during the summer period. If the original snow surface had not been horizontal—which would frequently be the case—then samples would be obtained from more than one stratigraphic layer and this would tend to lower the summer peaks. Again, if thicker samples are taken, this problem becomes more serious. Note in Figure 1 that the summer-to-winter difference depends on the sampling interval and on the actual position in the section—due presumably to non-horizontal stratigraphy. At all the sampling sites shown in Figure 1 the "summer ice layers" were still visible and are marked on the diagram.

The results on the surface samples were sufficiently encouraging for the authors, with the kind co-operation of the Soviet Antarctic Programme, to attempt work on the 952 m Vostok core.

Contamination is a very serious problem at such low values of Na^+ (probably the lowest values of Na^+ ever determined in a natural system). However, using a carefully cleaned tool-steel blade and removing the outside of the core until acceptable values of Na^+ were obtained, ice samples were shaved from sections of the core. The results are given in Figure 2.

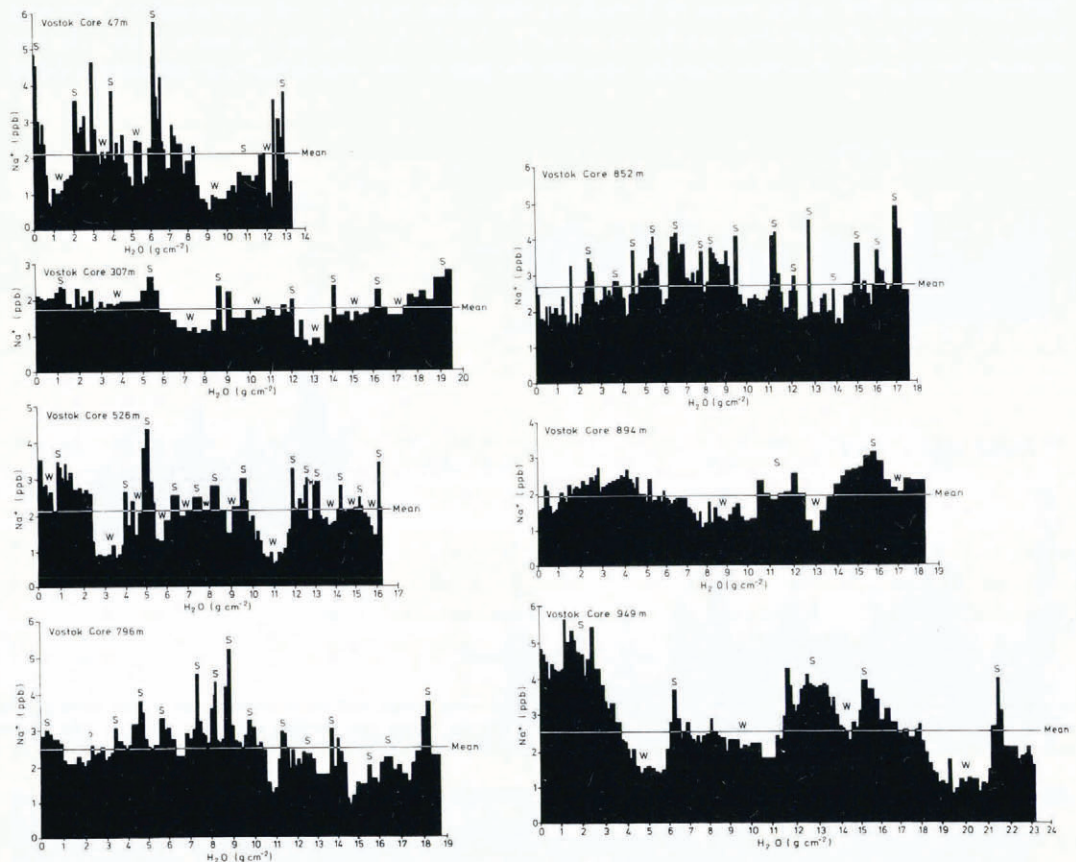


Fig. 2. Chemical stratigraphy of samples of the 952 m Vostok ice core. S summer; W winter.

DISCUSSION

It might be thought that problems of sastrugi, drift, and lack of horizontal surfaces may render this technique difficult to implement, but it must be remembered that the aim is to determine the accumulation rate in g/cm² year (or cm accumulation/year) and, as long as the surface sampled is sufficiently horizontal to enable annual changes to be detected, this is all that is required. Parts of the core which were difficult to interpret due to the core intercepting the sides of sastrugi can be neglected—see for example 894 m, 1–8 cm. Drift can be seen in that a section of the core will have exactly the same chemical composition but be more concentrated than expected for fresh snow—see for example Figure 2, 307 m, 4.0–5.0 cm. The data show that little of the accumulation at Vostok can be attributed to drift. The only problem, also shared by other methods based on stratigraphy, would occur if there were times in the past when large amounts of the surface were eroded and removed from the site by wind. The present surface is so hard that the possibility does not seem likely. It should also be borne in mind that this was only a preliminary investigation carried out to assess the feasibility of the technique, and that it would be possible to make measurements on many more sections of core and do much longer runs at each depth to refine the data on the actual accumulation rate at each depth. It would even be possible to build a special machine and, if necessary, process the whole core.

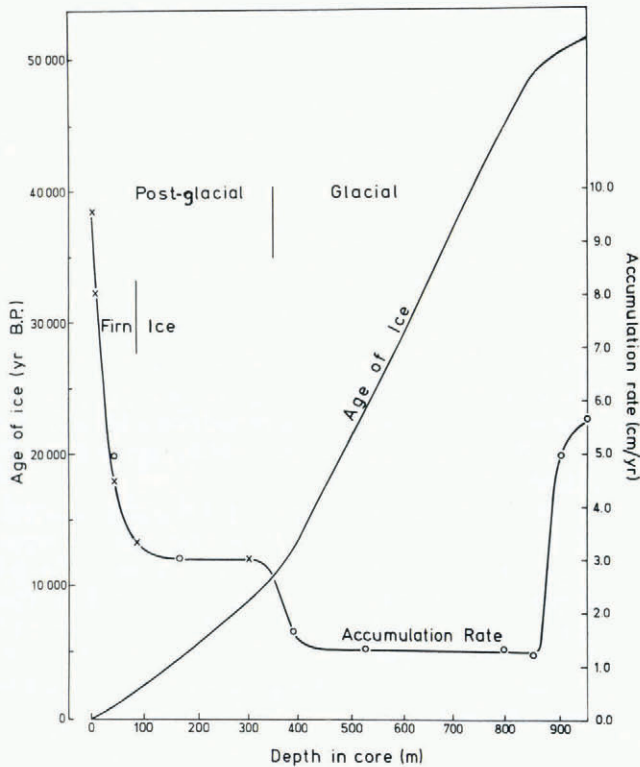


Fig. 3. The accumulation in cm/year plotted as a function of depth in core. Both the data from the work described in this paper and that from Barkov and others (1975) are given. The integral of the accumulation is also plotted to provide age as a function of depth in the core for the Vostok area of the East Antarctic ice sheet. × Data from Barkov and others (1975); ○ Data from this work.

It is interesting to note that even at the lower parts of the core the chemical stratigraphy is still preserved and has not been lost by diffusion, although the accumulation rate was only $1.75 \text{ g/cm}^2 \text{ year}$. This suggests that chemical stratigraphy as a dating method would be applicable to at least 100 000 years and probably to the entire length of a core to bedrock at Vostok ($\approx 4\ 000 \text{ m}$).

The accumulation (in cm/year) is plotted on Figure 3, as well as its integral, which has been plotted as a "depth in core versus age" curve. Barkov and others (1975) measured the accumulation rate to a depth of 391 m using the oxygen-isotope stratigraphy. Their data are also shown plotted on Figure 3 and it can be seen that both techniques give essentially the same results. Barkov and others (1975) could not, however, go to greater depths as they stated that the isotopic stratigraphy was eliminated by molecular diffusion below this level. The accumulation rate in g/cm^2 corrected for thinning is plotted versus time in Figure 4 together

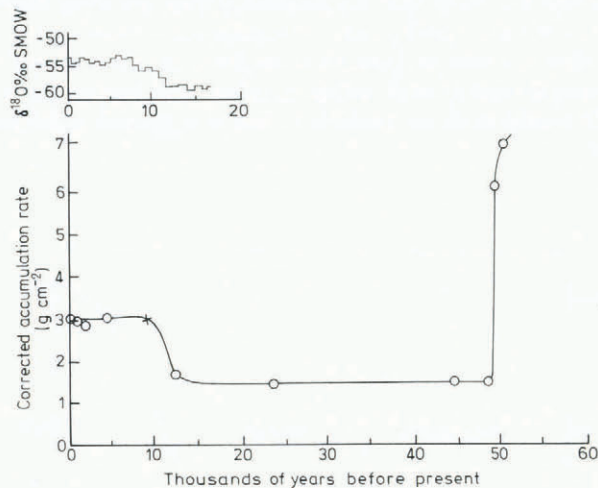


Fig. 4. The accumulation rate in g/cm^2 on the surface of the East Antarctic ice sheet in the Vostok area during the last 50 000 years.

with the isotope data of Barkov and others (1975) (replotted on our time base). It is interesting to note that the accumulation rate drops from 3.0 g/cm^2 to 1.75 g/cm^2 between 10 000 and 13 000 years B.P. at the same time as the isotope composition changes. This resolves a long-standing question as to how the accumulation rate on the Antarctic ice sheet changed between glacial and interglacial times.

Another interesting point to note in Figures 3 and 4 is that the accumulation rate appears to rise sharply toward the very bottom of the core. Prior to 47 000 years ago the East Antarctic ice sheet appeared to be rising rapidly (several centimetres per year). An intriguing possibility is that it was recovering from a surge of the type proposed by Wilson (1964) that had taken place sometime before 51 000 years. Confirmation of this hypothesis and details of such a surge could be obtained from similar studies on core from a deeper drill hole. The total depth of ice at Vostok is of the order of 4 000 m and the scientific potential of a core from a hole to bedrock would be very great indeed.

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