

Michał GRUSZCZYŃSKI and Krzysztof MAŁKOWSKI

Institute of Paleobiology
Polish Academy of Sciences
Żwirki i Wigury 93
02-089 Warszawa, POLAND

Stable isotopic records of the Kapp Starostin Formation (Permian), Spitsbergen

ABSTRACT: Stable isotopes ^{18}O and ^{13}C record of the Kapp Starostin Formation (Late Permian) is presented. The interdependence of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope time series is applied for calculating paleotemperatures in the depositional basin of the Kapp Starostin Formation. The obtained results indicate overall cooling from c. 25° — 10°C , and confirm some paleogeographical and paleoclimatical inferences.

Key words: Arctic, Spitsbergen, Late Permian, stable isotopes O and C, paleotemperatures.

Introduction

Previous geological (Birkenmajer 1964, 1977) and paleoecological (Małkowski and Hoffman 1979) investigations of the Permian sedimentary strata of Spitsbergen have allowed for a reconstruction of depositional environments and facies development in the Late Permian sea in this area. The Upper Permian Kapp Starostin Formation (Cutbill and Challinor 1965, Burov *et al.* 1965, Forbes *et al.* 1958, Szaniawski and Małkowski 1979) is representative of a shallow open shelf (Fig. 1).

The depositional history of this formation included three distinct episodes of tectonism, which caused local regressions allowing for a chronostratigraphic correlation between different geological sections of the Kapp Starostin Formation (Małkowski 1982). The formation consists mainly of cherts and carbonates associated with terrigenous rocks (Siedlecka 1970). A number of facies, each of them with its characteristic fossil assemblage, have been distinguished among the carbonate and terrigenous rocks (Małkowski and Hoffman 1979). A sequence of these facies and a parallel trend toward

impoverishment of the fossil assemblages is observed in particular geological sections (Fig. 2), presumably due to a fundamental change in paleogeography (Fig. 3) and the associated change in climate, from warm subtropical to cool temperate conditions (Małkowski *in press*).

The present study has been undertaken in order to evaluate this climatic change during the sedimentation of the Kapp Starostin Formation also by stable isotope analyses, which might help to assess its extent in more quantitative terms. Several analyses of this kind have been performed on Permian strata in various geographic areas (Magaritz and Schulze 1980, Rao and Green 1982, Magaritz *et al.* 1983, Clemmensen *et al.* 1985, Holser *et al.* 1986) and provide a context for our study.

Materials and methods

For the purpose of stable isotope analyses, we took 12 samples covering roughly the geographic and stratigraphic extent of the Kapp Starostin Formation (Fig. 1—2). From each particular stratigraphic horizons (Małkowski 1982) couple of samples were taken, thus permitting us to test for consistency among isochronous samples. In order to ensure compatibility of the geochemical results, we largely restricted the sampling to the low magnesium calcite (LMC) in productacean brachiopod shells, while the associated rock was sampled only for comparative purposes; this supplementary sample set included rocks with micritic and sparitic matrix as well as diagenetic sparite.

Previous geochemical studies on brachiopod shells indicate that, in contrast to skeletal remains of foraminifers, corals, and echinoderms (*see* Weber 1968, Weber and Woodhead 1970, Woodruff *et al.* 1980, Swart 1983, Veizer 1983), both LMC of the brachiopod shell and its isotopic composition essentially are not subject to diagenetic alterations (Lowenstam 1961, Brand and Veizer 1980, 1981; Brand 1981a, b; Al-Aasm and Veizer 1982, Popp *et al.* 1986, Veizer *et al.* 1986). Various brachiopod families rather insignificantly fractionate oxygen and carbon isotopes, and their shells are close in isotopic composition to the seawater (Veizer *et al.* 1986). Stable isotope analyses of samples derived from a single fossil brachiopod family are therefore likely to reflect well the isotopic composition of seawater in the geological past (Hudson 1977). Carbonate rocks, by contrast, undergo during diagenesis serious alterations which may also affect the original isotopic composition (Veizer 1977a, b; Dickson and Coleman 1980, Wagner and Matthews 1982).

The present investigation deals only with a small number of samples and is merely a pilot study intended to identify the most interesting stratigraphic intervals and problems for further, more detailed analysis.

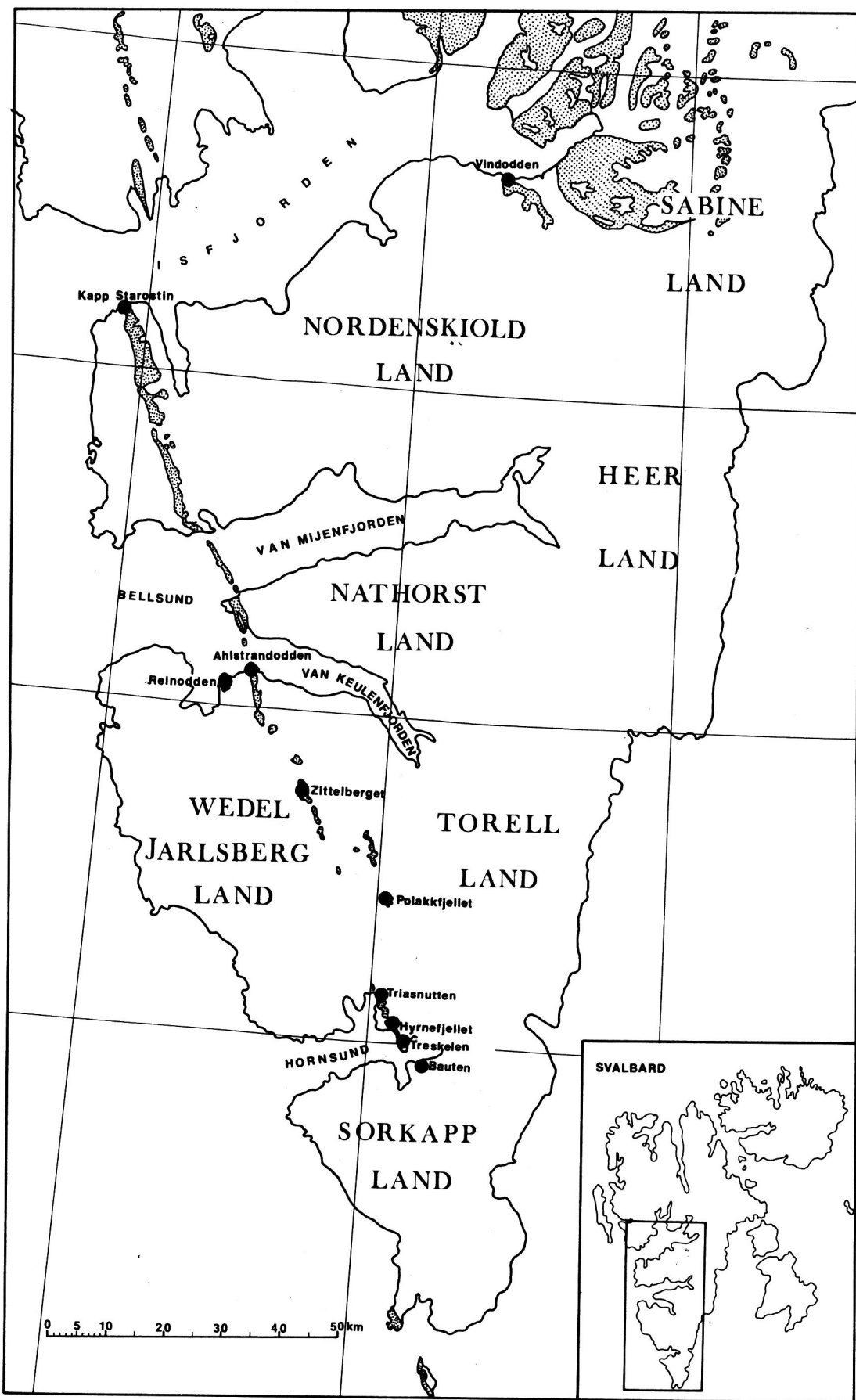


Fig. 1. Geographic extent of the Kapp Starostin Formation deposits (stippled).

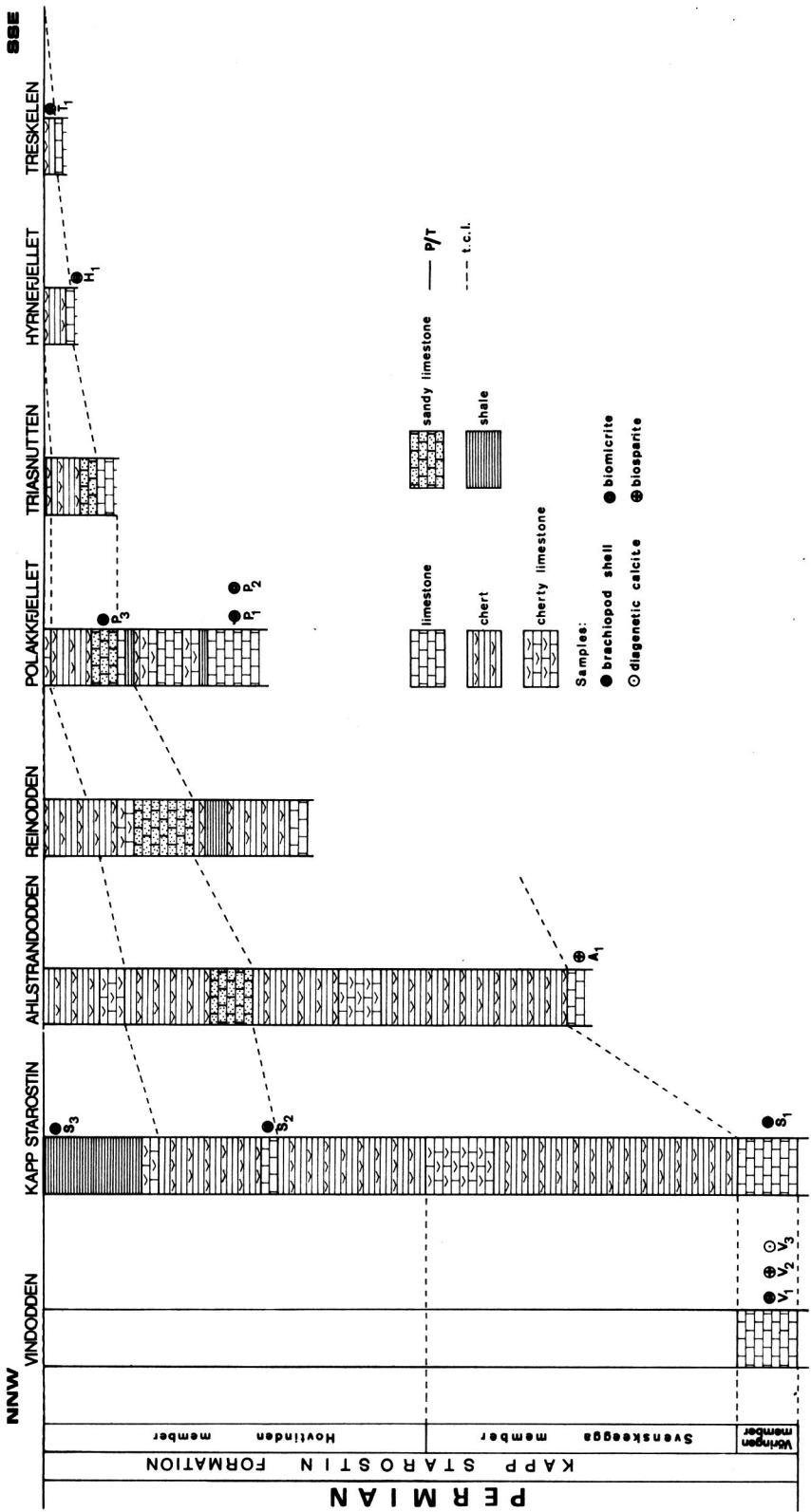


Fig. 2. Stratigraphic columns of the Kapp Starostin Formation deposits in selected localities, with sampled horizons, time correlation lines (t.c.l.), Permian-Triassic boundary — P/T.

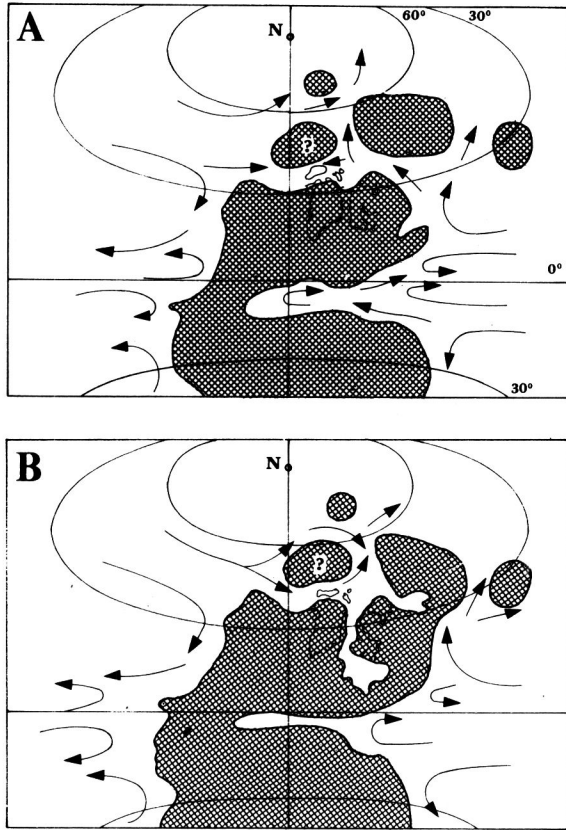


Fig. 3. Paleogeographical position maps of northern Pangea before (A) and after (B) the Kapp Starostin Formation deposition time equivalent. Compilation based partly on Harland (1973, with question mark on his hypothetical plate) and Scotese *et al.* (1979)

The measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in our samples were made by Dr. S. Hałas and his colleagues from the Laboratory of Nuclear Physics of the Maria Curie-Skłodowska University, Lublin.

Results

The analytic results (Table 1) are presented in the context of the stratigraphic position of the samples, thus constituting time series of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during the Late Permian in the investigated area (Fig. 4). The curves are based on the brachiopod LMC measurements. Generally, measurements on the rock matrix primarily reflect the extent of diagenetic alterations toward more negative values (Hudson 1977). The distinct shift in $\delta^{18}\text{O}$ expresses the successive stages of burial diagenesis (Bathrust

1980), when carbonate rocks undergo a graduate change in isotopic composition due to pore water influences (Dickson and Coleman 1980). The absence of a significant shift in $\delta^{13}\text{C}$ from the rock matrix relative to the brachiopod samples indicates only negligible effects of the meteoric water (Allan and Matthews 1977, *see also* Hudson 1977). Our sample set is too small to allow for statistical evaluation of the reliability of particular measurements.

Many geochemical studies on large stratigraphic intervals (Degens and Epstein 1962, Keith and Weber 1964, Veizer and Hoefs 1976, Veizer 1983) indicate that measurements on roughly coeval samples generally do not differ by more than 2‰, even though these studies cover carbonates which are likely to be at various diagenetic stages. We assume therefore that our empirical $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves, based entirely on a single brachiopod family, are highly reliable (Veizer *et al.* 1986, Popp *et al.* 1986) and the potential error is unlikely to exceed 1‰.

Our samples come from various facies of the Late Permian basin, different in their biotic and abiotic characteristics (Małkowski and Hoffman 1979) as well as in land proximity. Thus, they may have been differentially affected by freshwater influx from land (Craig 1953, Degens 1969). The effects of this factor on our results can hardly be accounted for without a through sedimentological analysis, but the observations on isotopic variations in the skeletons of living invertebrates (Magaritz and Heller

Table 1
Results of oxygen and carbon isotopic analyses from the Kapp Starostin Formation samples

Sample	^{13}C	^{18}O
V ₁	4.23	-4.11
V ₂	1.60	-7.49
V ₃	1.71	-12.08
S ₁	3.84	-6.59
A ₁	3.88	-7.28
P ₁	3.86	-4.46
P ₂	3.36	-5.64
S ₂	4.97	-5.69
P ₃	6.64	-7.13
H ₁	6.04	-6.18
T ₁	1.05	-10.05
S ₃	-1.42	-11.47

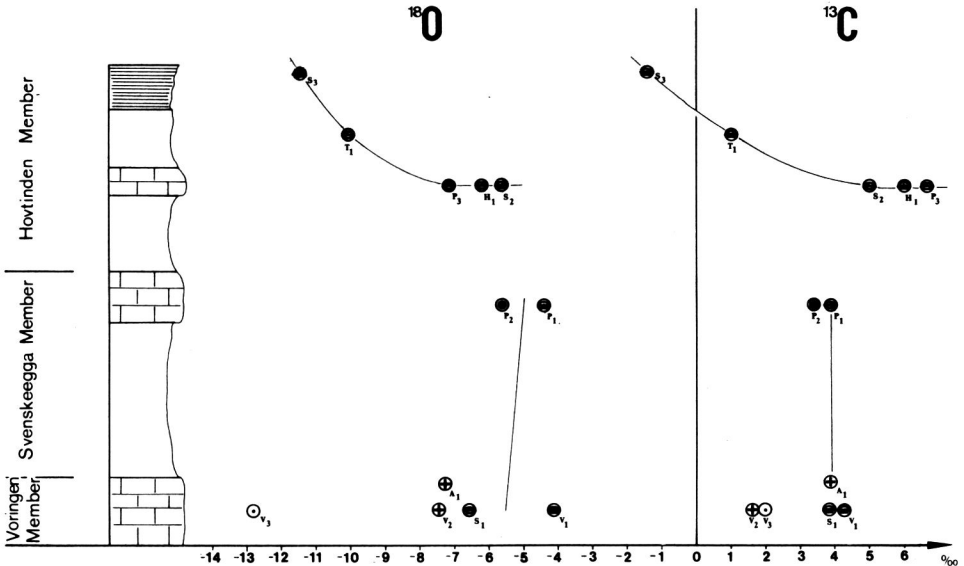


Fig. 4. Time series of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ during Permian

1983) suggest that these effects are likely to be less than the measurement error. Therefore, in the Kapp Starostin Formation, these effects are neglected.

Our $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ time series (Fig. 4) are clearly bipartite, with a zone too crudely sampled to be interpreted in the middle. The isotopic composition is roughly constant in the lower part of the sampled stratigraphic interval ($\delta^{18}\text{O}$ may slightly increase up the section), but both the curves shift dramatically toward lower values in the upper part. The inflection of the curves cannot be here considered because any interpretation of its geometry would require many more sample points than we have had at our disposal. This problem will be the subject of our future study.

The observed shift in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ indicates a substantial change in oxygen and carbon flux through the investigated paleochemical system (Garrels and McKenzie 1971), which must have also affected the paleoecological conditions in the basin (Fischer 1984a, b; Schidlowski and Eichman 1977).

In fact, a macroscopic study of the litho- and biofacies in the Kapp Starostin Formation suggests a significant change in its uppermost part. Therefore, we studied also over 200 petrographic thin sections, covering the entire formation but with a focus on the stratigraphic intervals sampled for stable isotope analysis (Pls. 1–2).

Discussion

After the initial enthusiasm for paleotemperature reconstruction from $\delta^{18}\text{O}$ changes (Urey *et al.* 1951, Epstein *et al.* 1953, Emiliani 1955,

Craig 1965, Shackleton and Opdyke 1973, Shackleton and Kennett 1975), a certain crisis developed in this field due to difficulties with accounting for local or regional changes in seawater isotopic composition (Hudson 1977, Veizer 1983) and with estimating the global changes in $\delta^{18}\text{O}$ through geological time (*cf.* Degens and Epstein 1962, Keith and Weber 1964, Veizer and Hoefs 1976). Nevertheless, several authors continue to determine paleotemperatures in Phanerozoic rocks on the basis of their oxygen isotopic composition. Such paleotemperatures generally are overestimated (Hudson 1977), sometimes reaching even 100°C (Dorman 1968), and they are often explained by nonactualistic conditions in the ocean in the geological past (Brumsack 1980, Brand 1981b, 1982, Popp *et al.* 1986); this is also the case with the Permian (Rao and Green 1982, Veizer *et al.* 1986). Given, however, the obvious continuity in the history of life on Earth and the known temperature tolerances of plants and animals (*cf.* Knauth and Epstein 1976), we are forced to conclude that ocean water temperatures could not dramatically differ from those prevailing today. We are therefore compelled to assume that oxygen isotope measurements of paleotemperatures for older, particularly Paleozoic, rocks are systematically biased because many authors did not consider a possibility of change in the global oxygen cycle in the exogenous system (Lerman 1979). A quantitative change in this cycle, however, must have also affected the oxygen isotope fractionation (Veizer and Hoefs 1976).

The oxygen and carbon isotope curves obtained for the Kapp Starostin Formation cover a time interval (Kazanian-Tatarian) on the scale of 10^6 – 10^7 years. Stable isotope studies on younger sedimentary rocks, Cretaceous through Recent, demonstrate patterns of change on a variety of time scales — from seasonal to hundreds of thousands of years (Mörner and Karlen 1984). Seasonal changes are particularly well reflected by planktic foraminifers (Shackleton 1977, Kroopnick *et al.* 1977); benthic studies generally refer to greater time scales. On the geological time scale, as in our study, all these smaller scale changes are overwhelmed by very general trends of seawater isotopic composition through time.

The oxygen and carbon isotope time series obtained for the Kapp Starostin Formation are remarkably congruent (Fig. 4). This suggests their mutual interdependence, which is in fact well known from the Pleistocene (Shackleton and Pisias 1985) and well justified by theoretical models on the global scale (Berner *et al.* 1983, Kump and Garrels 1986). We have therefore undertaken to employ this interdependence for calculating paleotemperatures in the depositional basin of the Kapp Starostin Formation.

Because of the high rate of carbon cycling in nature (Campbell 1977), $\delta^{13}\text{C}$ time series reflects changes in the global carbon cycle, especially when it is correlated with $\delta^{34}\text{S}$ time series (Veizer *et al.* 1980, Kump and Garrels 1986). The Upper Permian is the best known case of $\delta^{13}\text{C}$

and $\delta^{34}\text{S}$ intercorrelation (Holser 1984), and our $\delta^{18}\text{O}$ curve almost perfectly conforms to $\delta^{13}\text{C}$ curve. We assume therefore that our empirical isotope composition curves represent a single geochemical process involving both carbon and oxygen. It then follows from Kump and Garrels's (1986) model of geochemical relationships between carbon, oxygen, and sulphur that we must here deal with a global process of change from a period of sulphate and organic matter burial in the sediments to a period of sulphide deposition and organic matter decay in the ocean — according to the reaction:



The causes of such a change are to be thought in perturbations of the global carbon dioxide cycle (Arthur 1982, Kennett 1983, Miller and Fairbanks 1985, Andersen and Malahoff 1977). What is important for our studies on the Upper Permian is that organic matter (CH_2O) decay in the ocean causes a negative shift in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Brumsack 1980, Brand 1981b, Hoefs 1973).

In each particular sample, $\delta^{18}\text{O}$ depends not only on the oxygen isotope composition of water in the world ocean but also on the local conditions: temperature and the possible influence of isotopically light fresh-water influx from land (Veizer and Fritz 1976). The latter factor seems to us negligible in the case of the Kapp Starostin Formation, as there is no independent paleontological or sedimentological evidence for any freshwater influx. Generally, significant freshwater influx occurs on the time scale of 10^3 — 10^5 years and hence should appear on the geological time scale as rapid fluctuations in $\delta^{18}\text{O}$ independent of the associated $\delta^{13}\text{C}$ curve (Allan and Matthews 1982); such fluctuations, however, are invisible in our data. We assume therefore that our empirical $\delta^{18}\text{O}$ curve is the net result of only two factors: global changes in oxygen isotope composition of seawater and local changes in water temperature. If not for the local changes in temperature, our $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves should therefore be fully congruent, depending solely on the global system.

The differences between the actual values of $\delta^{18}\text{O}$ and the values obtained assuming perfect congruence between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ curves (Fig. 5) can then be interpreted as local paleotemperature corrections on the global oxygen isotope curve in the Late Permian ocean. Provided that water temperature at the starting point of our time series — the base of the Kapp Starostin Formation — can be estimated on independent evidence, these corrections allow for quantitative reconstruction of the local temperature curve. The small number of measurements and lack of samples in the middle of the section, however, permit us merely to assess the general, long-term trend in temperature, which may be represented by linear approximation.

The oldest rocks in the Kapp Starostin Formation (Forbes *et al.* 1958,

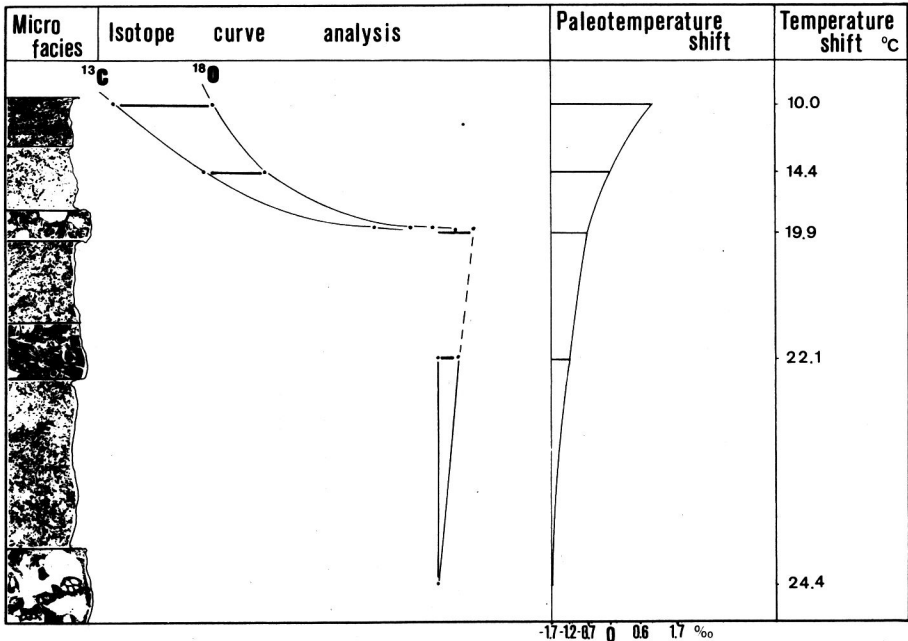


Fig. 5. Isotope curve analysis and inferred paleotemperature calculations.

Siedlecka 1970) constitute the Vöringen Member (Fig. 2). Because of their high-diversity biofacies defined by thick-shelled brachiopods, crinoids, bryozoans, and algal mats (*cf.* Małkowski and Hoffman 1979), and of their proximity to evaporates (Nysaether 1977), these rocks are here interpreted as deposited in a warm subtropical epicontinental sea (*see* Fig. 3 for the paleogeographic position). Water temperature at the time of their deposition can therefore be assumed to approximate $25 \pm 5^\circ\text{C}$. Following from this figure and from our estimated paleotemperature corrections on the $\delta^{18}\text{O}$ curve, water temperatures can be calculated for the successive stratigraphic intervals (Fig. 5). The obtained figures indicate overall cooling by some 15°C . With the profound paleogeographic change that took place during the sedimentation of Kapp Starostin Formation (*cf.* Fig. 3) taken into account, they thus fall well within the range predicted by the actualistic thinking on paleoceanographic changes. We consider this consistency as a corroboration of our line of argument.

The largest drop in paleotemperature occurs in the upper part of the Hovtinden Member and amounts to 10°C . Such a cooling should be reflected also in the paleontological record. Facies analysis indeed confirms this conclusion. Macroscopically, there are changes in size and abundance of solitary tetracorals, as well as a change in composition and impoverishment of brachiopod and bryozoan assemblages (Małkowski *in press*). Thin section analysis clearly shows a decline in size and abundance of bioclasts and a transition

from predominantly authigenic to terrigenous sediments (Pls. 1—2, Fig. 5). At least a part of these changes in the record may be related to climatic cooling (Davis 1977, Schopf 1980).

General remarks

Several authors present the results of their stable isotope analyses in the form of covariation scattergrams of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (e.g., Rao and Green 1982, Veizer *et al.* 1986, Popp *et al.* 1986). They thus discard a possibility of isotope time series reconstruction and analysis. We demonstrate in this paper the potential of such time series for paleotemperature reconstruction. Covariation scattergrams, by contrast, present clouds of measurement points and thus suggest very wide margins of error and low reliability of the procedure (*cf.* Rao and Green 1982).

The paleotemperature assumed in this study for the Vöringen Member and thus fixing the entire paleotemperature curve equals the value obtained on the assumption that $\delta^{18}\text{O}$ deviation from the modern standard (SMOW) — which is generally accepted as the basis for paleotemperature calculations (Craig 1965, Shackleton and Kennett 1975) — is identical with $\delta^{13}\text{C}$ deviation in the same sample. One might apply this assumption also to the base of the upper portion of our empirical curve, that is, to the carbonate facies of the Hovtinden Member. We prefer our simple linear approximation because of uncertainty concerning the quantitative geochemical links between carbon and oxygen balances at either stratigraphic level.

Our results seem to corroborate the validity of our method; they thus point to an interesting perspective on paleoceanographic and paleobiologic studies on stable isotope ratios. Highly promising are also studies on chronostratigraphic correlation of stable isotope shifts (*cf.* Magaritz *et al.* 1983, Holser *et al.* 1986), especially in $\delta^{13}\text{C}$, because of their potentially global nature. The rapid negative shift in $\delta^{13}\text{C}$ observed in our data seems to offer a correlation marker for the uppermost Permian strata (Holser *et al.* 1986).

Paleotemperature analysis can only be reliably extended far back in the Phanerozoic after the global curve of $\delta^{18}\text{O}$ through geological time will have been constructed, with precision and reliability at least equating those of $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ curves (*cf.* Claypool *et al.* 1980, Veizer *et al.* 1980, Hoefs 1982). Nevertheless, paleotemperature estimate error will even then be on the order of at least a few centigrades.

Perhaps the most interesting results on the operation of the global exogenic system (including the entire biosphere) in geological time will come from interpretation of the global $\delta^{13}\text{C}$ curve, especially when taken in conjunction with other stable isotope curves and geological and paleoecological

observations (Fischer 1984a, Holser 1984). The complexity of this system allows thus far only for its preliminary characteristics (Fischer 1984b, Degens *et al.* 1986), working hypotheses (Hsü 1986, Kasting *et al.* 1986), and general computer models intended to represent at least a part of the known interactions (Berner *et al.* 1983, Kump and Garrels 1986).

It is nevertheless possible to quantitatively estimate the geochemical phenomena underlying stable isotope curves (Spitzzy and Degens 1985), and hence to evaluate rival hypotheses with respect to their explanatory potential. For example, the observations of $\delta^{13}\text{C}$ beyond 4‰, encountered both in our study and also in other areas (Holser *et al.* 1986), and the consequent shift to negative values seem to demand a huge input of isotopically light carbon to the Permian ocean as an explanation; however, the amount of carbon involved must have considerably exceeded the total standing crop of land ecosystems of the time (Tiffney 1985).

We believe that the only acceptable process that could causally explain such a dramatic change in carbon isotope composition of the world ocean is a change in flux between the main reservoirs of organic carbon (Lerman 1979, Kump and Garrels 1986), such as organic carbon buried in sedimentary rocks and/or fossil fuels which can be mobilized by global megatectonics (Pollack 1982, Brass *et al.* 1982).

Acknowledgements. We are very grateful to Associate Professor Józef Kaźmierczak and Dr. Antoni Hoffman for their helpful remarks to the text and merit of the article.

References

- AL-AASM I. S. and VEIZER J. 1982. Chemical stabilization of low-Mg calcite: an example of brachiopods. — *J. Sedim. Petrol.*, 52: 1101—1109.
- ALLAN J. R. and MATTHEWS R. K. 1977. Carbon and oxygen isotopes as diagenetic tools: surface and subsurface data, Barbados, West Indies. — *Geology*, 5: 16—20.
- ALLAN J. R. and MATTHEWS R. K. 1982. Isotope signatures associated with early meteoric diagenesis. — *Sedimentology*, 29: 979—817.
- ANDERSEN N. R. and MALAHOFF A. 1977. The fate of fossil fuel CO₂ in the oceans. — Plenum Press, New York and London, 749 pp.
- ARTHUR M. A. 1982. The carbon cycle—controls on atmospheric CO₂ and climate in the geologic past. — *In: Climate in Earth history*. National Academy Press, Washington, D.C., 55—67.
- BERNER R. A., LASAGA A. C. and GARRELS R. M. 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. — *Am. Jour. Sci.*, 283: 641—683.
- BATHURST R. G. C. 1980. Lithification of carbonate sediments. — *Sci. Prog.*, 66: 451—471.
- BIRKENMAJER K. 1964. Devonian, Carboniferous and Permian formations of Hornsund, Vestspitsbergen. — *Studia Geol. Pol.*, 11: 47—123.
- BIRKENMAJER K. 1977. Triassic sedimentary formations of Hornsund area, Spitsbergen. — *Studia Geol. Pol.*, 44: 7—43.

- BRAND U. 1981a. Mineralogy and chemistry of the Lower Pennsylvanian Kendrick Fauna, eastern Kentucky. — *Chem. Geol.*, 32: 1—16.
- BRAND U. 1981b. Mineralogy and chemistry of the Lower Pennsylvanian Kendrick Fauna, eastern Kentucky, 2. Stable isotopes. — *Chem. Geol.*, 32: 17—28.
- BRAND U. 1982. The oxygen and carbon isotope composition of Carboniferous fossil components: sea water effects. — *Sedimentology*, 29: 139—147.
- BRAND U. and VEIZER J. 1980. Chemical diagenesis of a multicomponent carbonate system — 1: Trace elements. — *J. Sedim. Petrol.*, 50: 1219—1236.
- BRAND U. and VEIZER J. 1981. Chemical diagenesis of a multicomponent carbonate system — 2: Stable isotopes. — *J. Sedim. Petrol.*, 51: 987—997.
- BRASS G. B., SALTZMAN E., SLOAN II J. L., SOUTHAM J. R., HAY W. W., HOLSER W. T. and PETERSON W. H. Ocean circulation, plate tectonics, and climate. — *In*: Climate in Earth history. National Academy Press, Washington D.C., 83—89.
- BRUMSACK H. J. 1980. Geochemistry of Cretaceous black shales from the Atlantic Ocean (DSDP Legs 11, 14, 36 and 41). — *Chem. Geol.*, 31: 1—25.
- BUROV Yu. P., GAVRILOV B. P., KLUBOV B. A., PAVLOV A. V. and USTRITSKY V. I. 1965. Novye dannye o verhneperskikh otloscheniah Spitsbergena. — *In*: V. N. Sokolov (ed.), *Materialy po geologii Spitsbergena*. NIIGA, Leningrad, 11—126.
- CAMPBELL I. M. 1977. Energy and the atmosphere. — John Wiley and Sons Ltd. London, New York, Sydney, Toronto, 398 pp.
- CLAYPOOL G. E., HOLSER W. T., KAPLAN I. R., SAKAI H. and ZAK I. 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. — *Chem. Geol.*, 28: 199—260.
- CLEMENSEN L. B., HOLSER W. T. and WINTER D. 1985. Stable isotope study through the Permian-Triassic boundary in East Greenland. — *Bull. Geol. Soc. Denmark*, 33: 253—260.
- CRAIG H. 1953. The geochemistry of the stable carbon isotopes. — *Geochim. Cosmochim. Acta*, 3: 53—93.
- CRAIG H. 1965. The measurement of oxygen isotope paleotemperatures. — *In*: E. Tongiorgi (ed.), *Stable isotopes in oceanographic studies and paleotemperatures*. Consiglio Nazionale Ricerch, Lab. Geol. Nucleare, Pisa, 161—182.
- CUTBILL J. L. and CHALLINOR A. 1965. Revision of the stratigraphical scheme for the Carboniferous and Permian rocks of Spitsbergen and Bjørnøya. — *Geol. Mag.*, 102: 418—439.
- DAVIS R. A. 1977. Principles of oceanography — Addison-Wesley Publishing Company, 505 pp.
- DEGENS E. T. 1969. Biogeochemistry of stable carbon isotopes. — *In*: G. Eglinton and M. T. J. Murphy (eds.), *Organic geochemistry*, Springer — Verlag, Berlin, Heidelberg, New York, 304—329.
- DEGENS E. T. and EPSTEIN S. 1962. Relationship between O^{18}/O^{16} ratios in coexisting carbonates, cherts, and diatomites. — *Bull. Am. Assoc. Petrol. Geol.*, 46: 534—542.
- DEGENS E. T., KAZMIERCZAK J. and ITTEKKOT V. 1986. Biomineralization and the carbon isotope record. — *TMPM Tschermaks Min. Petr. Mitt.*, 35: 117—126.
- DICKSON J. A. D. and COLEMAN M. L. 1980. Changes in carbon and oxygen isotope composition during limestone diagenesis. — *Sedimentology*, 27: 107—118.
- DORMAN F. H. 1968. Some Australian oxygen isotope temperatures and a theory for a 30-million-year world-temperature cycle. — *J. Geol.*, 76: 297—313.
- EMILIANI C. 1955. Pleistocene temperatures. — *J. Geol.* 63: 538—578.
- EPSTEIN S., BUCHSBAUM R., LOWENSTAM H. A. and UREY H. C. 1953. Revised carbonate water isotopic temperature scale. — *Geol. Soc. Am. Bull.*, 64: 1315—1326.
- FISCHER A. G. 1984a. The two Phanerozoic supercycles. — *In*: W. A. Berggren and J.

- Van Couvering (eds.), *Catastrophes and Earth history: the new uniformitarianism*. Princeton University Press, Princeton, 129—150.
- FISCHER A. G. 1984b. Biological innovations and the sedimentary record. — In: H. D. Holland and A. F. Trendall (eds.), *Patterns of change in Earth evolution*. Dahlem Konferenzen 1984, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 145—157.
- FORBES C. L., HARLAND W. B. and HUGHES N. F. 1958. Palaeontological evidence for the age of the Carboniferous and Permian rocks of Central Vestspitsbergen. — *Geol. Mag.*, 95: 465—490.
- GARRELS R. M. and MCKENZIE F. T. 1971. *Evolution of sedimentary rocks*. — Norton New York, 397 pp.
- HARLAND W. B. 1973. Tectonic evolution of the Barents Shelf and related plates. — In: *Arctic Geology*. Am. Ass. Petrol. Geol. Mem., 19: 599—608.
- HOEFS J. 1973. *Stable isotope geochemistry*. — Springer-Verlag, Berlin, Heidelberg, New York, 140 pp.
- HOEFS J. 1982. Isotope geochemistry of carbon. — In: H. L. Schmidt, H. Førstel and K. Heinzinger (eds.), *Stable isotopes*. Elsevier, Amsterdam-Oxford-New York, 103—113.
- HOLSER W. T. 1984. Gradual and abrupt shift in ocean chemistry during Phanerozoic time. — In: H. D. Holland and A. Trendall (eds.), *Patterns of change in Earth evolution*. Dahlem Konferenzen 1984, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 123—143.
- HOLSER W. T., MAGARITZ M. and CLARK D. L. 1986. Carbon — isotope stratigraphic correlations in the Late Permian. — *Am. Jour. Sci.*, 286: 390—402.
- HSÜ K. J. 1986. Environmental changes in times of biotic crisis. — In: D. M. Raup and D. Jablonski (eds.), *Patterns and processes in the history of life*. Dahlem Konferenzen 1985. Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, 297—312.
- HUDSON J. D. 1977. Stable isotopes and limestone lithification. — *J. Geol. Soc. London*, 133: 637—660.
- KASTING J. E., RICHARDSON S. M., POLLACK J. B. and TOON O. B. 1986. A hybrid model of the CO₂ geochemical cycle and its application to large impact events. — *Am. Jour. Sci.*, 286: 361—389.
- KEITH M. L. and WEBER J. N. 1964. Carbon and oxygen isotopic composition of selected limestones and fossils. — *Geochim. Cosmochim. Acta*, 28: 1787—1916.
- KENNETT J. P. 1983. Paleooceanography: global ocean evolution. — *Rev. Geophys. Space Phys.*, 21: 1258—1274.
- KNAUTH L. P. and EPSTEIN S. 1976. Hydrogen and oxygen ratios in nodular and bedded cherts. — *Geochim. Cosmochim. Acta*, 40: 1095—1108.
- KROOPNICK P. M., MARGOLIS S. V. and WONG C. S. 1977. $\delta^{13}\text{C}$ variations in marine carbonate sediments as indicators of the CO₂ balance between the atmosphere and oceans. — In: N. R. Andersen and A. Malahoff (eds.), *The fate of fossil fuel CO₂ in the oceans*. Plenum Press, London, New York, 295—322.
- KUMP L. R. and GARRELS R. M. 1986. Modeling atmospheric O₂ in the global sedimentary redox cycle. — *Am. Jour. Sci.*, 286: 337—360.
- LERMAN A. 1979. *Geochemical processes water and sediment environments*. — John Wiley & Sons, New York, Chichester, Brisbane, Toronto, 481 pp.
- LOWENSTAM H. A. 1961. Mineralogy, ¹⁸O/¹⁶O ratios, and strontium and magnesium contents of Recent and fossil brachiopods and their bearing on the history of the oceans. — *J. Geol.*, 69: 241—260.
- MAGARITZ M. and SCHULZE K. H. 1980. Carbon isotope anomaly of the Permian period. — In: H. Füchtbauer and T. M. Peryt (eds.), *The Zechstein Basin of Europe*, *Contrib. Sedimentology*, 9: 269—277.
- MAGARITZ M., ANDERSON R. Y., HOLSER W. I., SALTZMAN E. S. and GRABER

- J. 1983. Isotope shifts in the Late Permian of the Delevare Basin, Texas, precisely timed by varved sediments. — *Earth Planet. Sci. Letters*, 66: 11—124.
- MAGARITZ M. and HELLER J. 1983. Annual cycle of $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ isotope ratios in landsnail shells. — *Chem. Geol.*, 41: 243—256.
- MAŁKOWSKI K. 1982. Development and stratigraphy of the Kapp Starostin Formation (Permian) of Spitsbergen. — *Palaeont. Pol.* 43: 69—81.
- MAŁKOWSKI K. Paleocology of Productacea (Brachiopoda) from the Permian Kapp Starostin Formation, Spitsbergen. — *Pol. Polar Res.*, 9. 1988.
- MAŁKOWSKI K. and HOFFMAN A. 1979. Semi-quantitative facies model for the Kapp Starostin Formation (Permian), Vestspitsbergen. — *Acta Palaeont. Pol.*, 24: 217—230.
- MILLER K. G. and FAIRBANKS R. G. 1985. Oligocene to Miocene carbon isotope cycles and abyssal circulation changes. — *In*: E. T. Sundquist and W. S. Broecker (eds.), *The carbon cycle and atmospheric CO₂: natural variations Archean to Present*. Amer. Geophys. Union, Geophys. Monograph 32, Washington, D.C., 469—486.
- MÖRNER N.-A. and KARLÉN W. 1984. Climatic changes on a yearly to millennial basis. — D. Reidel Publishing Company, Dordrecht, Boston, Lancaster, 667 pp.
- NYSAETHER E. 1977. Investigations on the Carboniferous and Permian stratigraphy of the Torell Land area, Spitsbergen. — *Norsk Polarinst. Arbok* 1976, 21—41.
- POLLACK J. B. 1982. Solar, astronomical, and atmospheric effects on climate. — *In*: *Climate in Earth history*. National Academy Press, Washington, D.C., 68—76.
- POPP B. N., ANDERSON T. E. and SANDBERG P. A. 1986. Textural, elemental, and isotopic variations among constituents in Middle Devonian Limestones, North America. — *J. Sedim. Petrol.*, 56: 715—727.
- RAO C. P. and GREEN D. C. 1982. Oxygen and carbon isotopes of Permian cold-water carbonates, Tasmania, Australia. — *J. Sedim. Petrol.*, 52: 1111—1126.
- SCHIDLOWSKI M. and EICHMAN R. 1977. Evolution of the terrestrial oxygen budget. — *In*: C. Ponnamperna (ed.), *Chemical evolution of the Early Precambrian*. Academic Press Inc., New York, San Francisco, London, 87—99.
- SCHOPF T. J. M. 1980. Paleooceanography. — Harvard University Press, Cambridge, London, 341 pp.
- SCOTESE Ch. R., BAMBACH R. K., BARTON C., VAN DER VOO R. and ZIEGLER A. M. 1979. Paleozoic base maps. — *J. Geol.*, 87: 217—277.
- SIEDLECKA A. 1970. Investigations of Permian cherts and associated rocks in southern Spitsbergen. Parts I and II. — *Norsk Polarinst. Skr.*, 147: 86 pp.
- SHACKLETON N. J. 1977. Carbon — 13 in *Uvigerina*: tropical rainforest history and the equatorial Pacific carbonate dissolution cycles. — *In*: N. R. Andersen and A. Malahoff (eds.), *The fate of fossil fuel CO₂ in the oceans*. Plenum Press, London, New York, 401—427.
- SHACKLETON N. J. and OPDYKE N. D. 1973. Oxygen isotope and paleomagnetic stratigraphy of equatorial Pacific core V-28-238: oxygen isotope temperatures and ice volumes on a 10^5 year and 10^6 year scale. — *Quat. Res.*, 3: 39—55.
- SHACKLETON N. J. and KENNETT J. P. 1975. Paleotemperature history of the Cenozoic and the initiation of Antarctic glaciation: oxygen and carbon isotope analyses in DSDP sites 277, 279 and 281. — *In*: J. P. Kennett and R. E. Houtz (eds.), *Initial reports of the Deep-Sea Drilling Project, 29*, U.S. Gov. Printing Office, Washington, 29, 743—755.
- SHACKLETON N. J. and PISIAS N. G. 1985. Atmospheric carbon dioxide, orbital forcing, and climate. — *In*: E. T. Sundquist and W. S. Broecker (eds.), *The carbon cycle and atmospheric CO₂: natural variations Archean to present*. Amer. Geophys. Union, Geophys. Monograph 32, Washington, D.C., 303—317.

- SPITZY A. and DEGENS E. T. 1985. Modeling stable isotope fluctuations through geologic time. — *Mitt. Geol.-Paläont. Inst. Univ. Hamburg*, 59: 155—166.
- SWART P. K. 1983. Carbon and oxygen fractionation in scleractinian corals: a review. — *Earth-Sci. Rev.*, 19: 51—80.
- SZANIAWSKI H. and MAŁKOWSKI K. 1979. Conodonts from the Kapp Starostin Formation (Permian) of Spitsbergen. — *Acta Palaeont. Pol.*, 24: 231—264.
- TIFFNEY B. H. 1985. Geological factors and the evolution of plants. — *In*: B. H. Tiffney (ed.), *Geological factors and the evolution of plants*. Yale University Press, New Haven and London, 1—10.
- UREY H. C., LOWENSTAM H. A., EPSTEIN S. and MCKINNEY C. R. 1951. Measurement of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark, and southeastern United States. — *Bull. Geol. Soc. Am.*, 62: 399—416.
- VEIZER J. 1977a. Diagenesis of pre-Quaternary carbonates as indicated by tracer studies. — *J. Sedim. Petrol.*, 47: 565—581.
- VEIZER J. 1977b. Geochemistry of lithographic limestones and dark marls from the Jurassic of Southern Germany. — *N. Jb. Geol. Paläont. Abh.*, 153: 129—146.
- VEIZER J. 1983. Trace elements and isotopes in sedimentary carbonates. *In*: R. J. Reeder (ed.), *Carbonates: mineralogy and chemistry*. *Rev. Mineralogy*, 11, Min. Soc. Amer., Book Cratters Inc., Chelsea, 265—300.
- VEIZER J. and FRITZ P. 1976. Possible control of post-depositional alternation in oxygen paleotemperature determination. — *Earth Planet. Sci. Letters*, 33: 255—260.
- VEIZER J. and HOEFS J. 1976. The nature of $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ secular trends in sedimentary rocks. — *Geochim. Cosmochim. Acta*, 40: 1387—1395.
- VEIZER J., HOLSER W. T. and WILGUS C. K. 1980. Correlation of $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$ secular variations. — *Geochim. Cosmochim. Acta*, 44: 579—587.
- VEIZER, FRITZ P. and JONES B. 1986. Geochemistry of brachiopods: oxygen and carbon isotopic records of Paleozoic ocean. — *Geochim. Cosmochim. Acta*, 50: 1679—1696.
- WAGNER P. D. and MATTHEWS R. K. 1982. Porosity preservation in the Upper Smackover (Jurassic) Carbonate Grainstone, Walker Creek Field, Arkansas: Response of paleophreatic lenses to burial processes. — *J. Sedim. Petrol.*, 52: 3—18.
- WEBER J. N. 1968. Fractionation of the stable isotopes of carbon and oxygen in calcareous invertebrates: the Asteroidea, Ophiuroidea and Crinoidea. — *Geochim. Cosmochim. Acta*, 32: 33—70.
- WEBER J. N. and WOODHEAD P. M. J. 1970. Carbon and oxygen isotope fractionation in the skeletal carbonate of reef-building corals. — *Chem. Geol.*, 6: 93—117.
- WOODRUFF F., SAVIN S.M. and DOUGLAS R. G. 1980. Biological fractionation of oxygen and carbon isotopes by recent benthic foraminifera. — *Marine Micropaleont.*, 5: 3—11.

Received March 25, 1987

Revised and accepted April 2, 1987

Streszczenie

Badania stosunków izotopów stałych $^{18}\text{O}/^{16}\text{O}$ i $^{13}\text{C}/^{12}\text{C}$ (tab. 1) w osadach formacji Kapp Starostin (fig. 1—2) zostały zastosowane do oceny zmian paleotemperatur w permskim morzu Spitsbergenu.

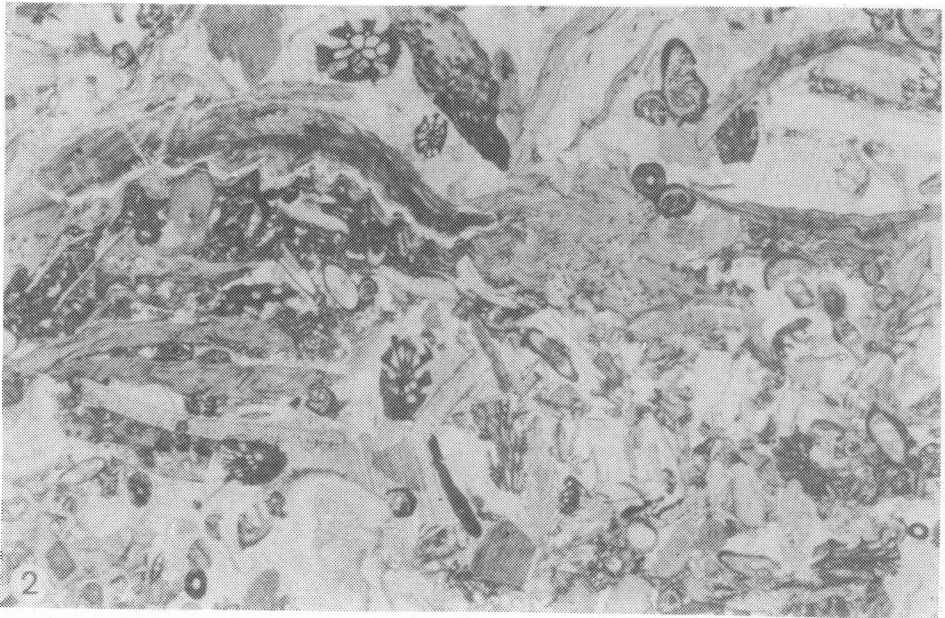
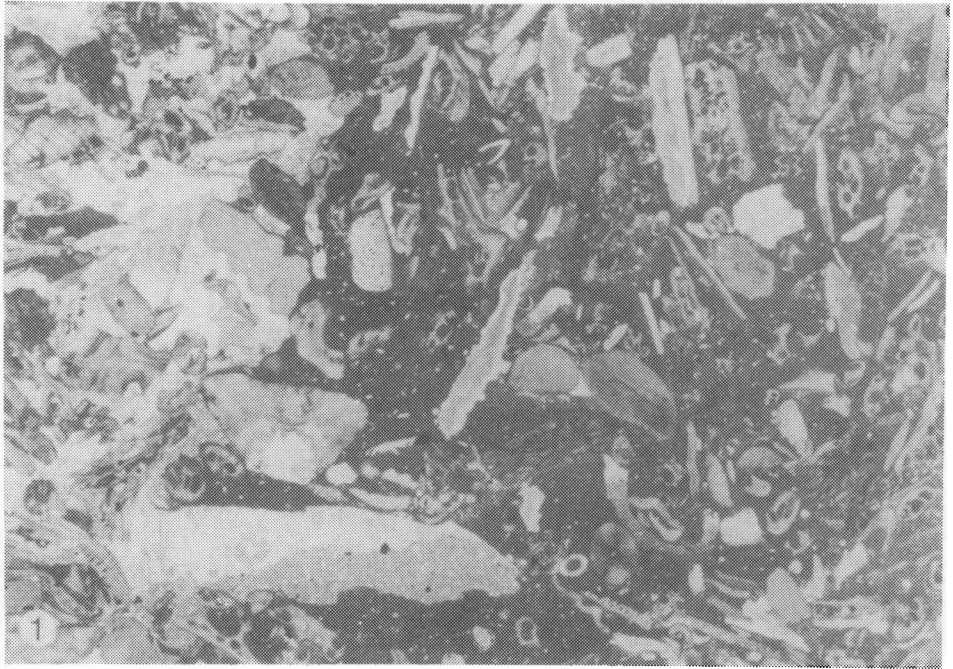
Analiza facjalna i pozycja paleogeograficzna badanego obszaru, przed i po okresie sedy-

mentacji osadów formacji Kapp Starostin (fig. 3), prowadzą do wniosku o stopniowym ochładzaniu się klimatu w tym czasie.

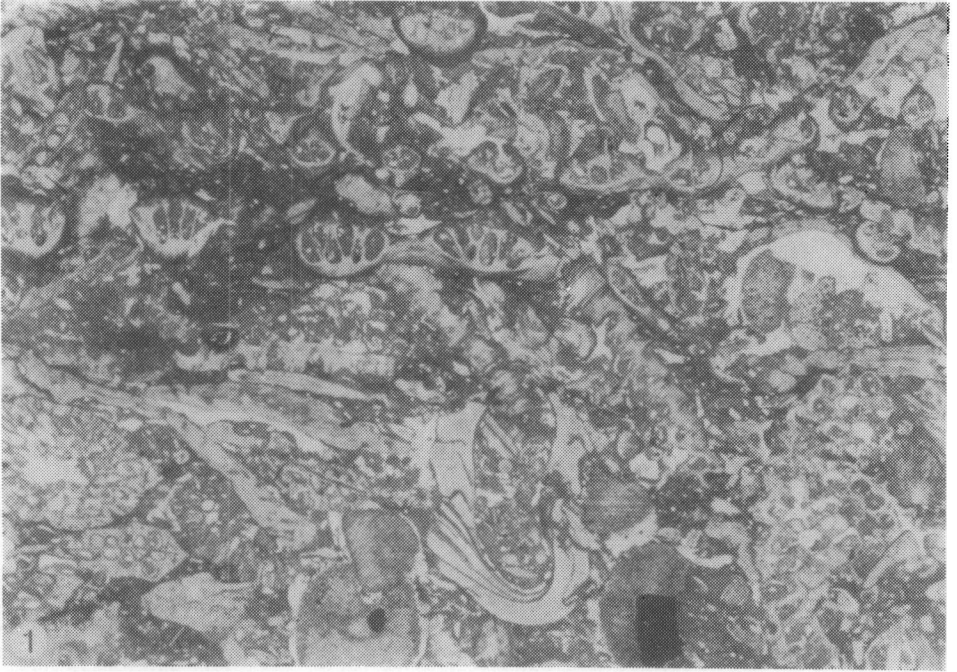
Dla określenia metodą Urey'a paleotemperatur odpowiadających uzyskanym pomiarom izotopowym (fig. 4), przyjęto wartości globalnego stosunku $^{18}\text{O}/^{16}\text{O}$ na podstawie współzależności zmian $\delta^{18}\text{O}$ i $\delta^{13}\text{C}$ w czasie późnego permu. W wyniku uzyskano gradient permskich temperatur w zakresie od 25°C do 10°C (por. fig. 5).

Zarejestrowane zmiany paleoklimatyczne mają swoje odbicie w mikrofacjalnym zapisie paleontologicznym (pl. 1—2).

Praca została wykonana w ramach problemu CPBP 03.03. B.8.



Biointramicrite (1) and coquinite (2), with brachiopod, crinoid and bryozoan skeletal fragments. Both sections of S_1 horizon. (Vöringen Member)



Coquinite (1) with brachiopod, crinoid and bryozoan skeletal fragments. Section of S₂ horizon. (Hovtinden Member)

Siliciclastic-cherty-muddy aleurite (2—3), with some brachiopod skeletal fragments and sponge spicules. Both sections of T₁ horizon. (Hovtinden Member)