

Carbon isotope variations in the Upper Carboniferous – Permian Mallek Mountain Group, eastern North Greenland

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Isotope data from Late Palaeozoic limestones of the Wandel Sea Basin in eastern North Greenland show a variation of $\delta^{13}\text{C}$ from 0.0 ‰ to 5.7 ‰ vs PDB. Carbonates depleted in ^{13}C occur in the basal part of lower Moscovian, upper Moscovian and middle Gzhelian transgressive sequences. ^{13}C enriched limestones occur later in the cycles. The most ^{13}C enriched limestones occur in the youngest (late Early Permian-early Late Permian) part of the sequence in Amdrup Land. The isotopic data is believed to represent changes in the global carbon cycle. Thus ^{13}C enriched carbonates correlate to periods of burial of organic carbon mostly as coal, while ^{13}C depleted carbonates formed as the result of erosion and oxidation of organic carbon during sea-level low stands.

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Introduction

Chemical events, especially those with isotopic signatures, are being increasingly recognized in the marine record (Holser 1984). Carbon isotope ratios in marine rocks have been shown to vary in response to geological events on several time scales. In the Pleistocene from glacial to interglacial time $\delta^{13}\text{C}$ increased sharply within several thousands of years (Shackleton 1977). Episodes of organic rich sedimentary deposition in the deep sea show high $\delta^{13}\text{C}$ values for periods of several million years over all the oceans, e.g. in the Miocene (Berger & Vincent 1986). Very sharp drops of $\delta^{13}\text{C}$ are associated with mass extinction events e.g. at Permian-Triassic (Holser et al. 1986) and Frasnian-Famennian (Playford et al. 1984) boundaries. By analogy periods of intensive deposition of coal and coaly sediments might also be expected to show significant increase of marine dissolved carbonate $\delta^{13}\text{C}$ values. Coaly sediments may be substantially preserved during transgressions, but mostly eroded during regressions. Therefore during an era of coaly deposition, a transgression, should be characterized by rising in $\delta^{13}\text{C}$ values in marine carbonate rocks, followed by a regression with a sharp de-

crease in ^{13}C . We will present evidence of large variations in $\delta^{13}\text{C}$ values in the Upper Palaeozoic sequence of North Greenland and relate them to large scale changes in sea-level.

Regional setting

The Late Palaeozoic sedimentation in the Wandel Sea Basin post-dates the Caledonian orogeny in Northeast Greenland and the Ellesmerian orogenesis in northern Greenland (Håkansson et al. 1981, Higgins et al. 1985, Hurst et al. 1985). Deposition of the Late Carboniferous to mid-Permian Mallek Mountain Group sediments was related to the structural development of two rift basins formed along the north and east coast of Greenland (figs 1, 2) (Stemmerik & Håkansson in press).

The Mallek Mountain Group includes shelf carbonates, clastics and minor evaporites. Two major fining-upwards cycles of Late Carboniferous age are followed by widespread limestone deposition in the Early Permian. Major transgressions are recorded in the lower Moscovian, upper Moscovian, and middle Gzhelian part of the sequence (fig. 3). Deposition took place in

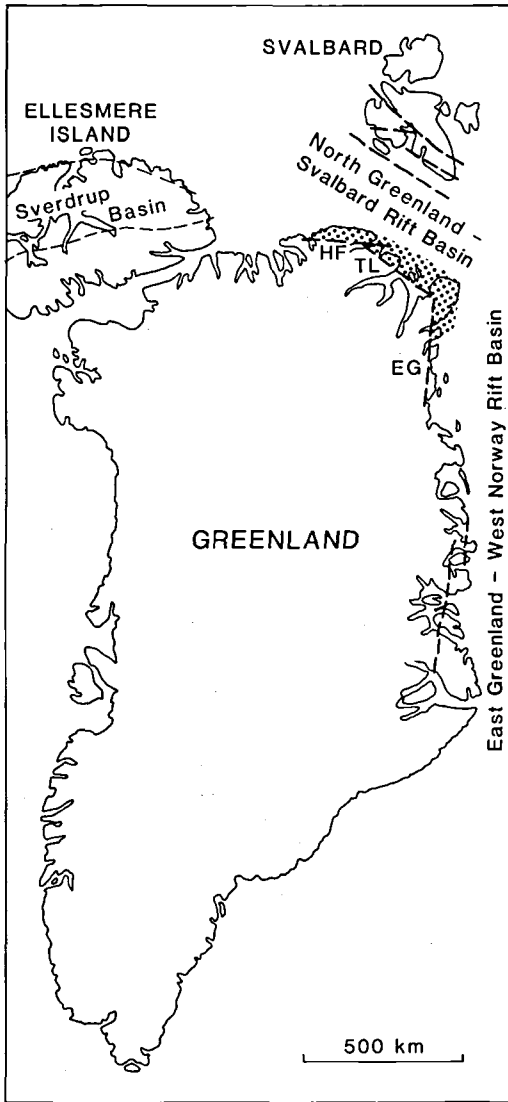


Fig. 1. General pre-drift configuration of Greenland, Ellesmere Island and Svalbard. The stippled area indicates the known extent of the Upper Palaeozoic basins. HF = Harder Fjord Fault Zone, TL = Trolle Land Fault Zone, EG = East Greenland Fault Zone.

partly isolated fault controlled basins making detailed lithological correlation between nearby areas difficult during the Late Carboniferous (Håkansson & Stemmerik 1984, Stemmerik & Håkansson in press). The gross pattern seen in the Wandel Sea Basin is, however, similar to that described from Svalbard (Steel & Worsley 1984) and the Sverdrup Basin (Davies & Nassichuk in press) implying that the depositional history to some degree was related to global changes in

sea-level and the general northwards drift of the continents (Steel & Worsley 1984). The similarity reached its climax in the Early Permian when carbonate platforms developed along the margins of the entire Arctic Basin.

Stable isotope measurements have been carried out during this study on samples from three sections (figs 2, 3). The sections in Amdrup Land and Holm Land include sediments of Late Carboniferous to mid-Permian age (fig. 3). The Carboniferous to earliest Permian part of the sections is well dated on the basis of fusulinids and is easily correlatable to the Russian (and American) stages, although the precise boundary between the *Wedekidellina* and the *Triticites* zone is unknown (fig. 3) (Stemmerik & Håkansson in press). The upper part of the Amdrup Land section yielded a rich brachiopod fauna (Dunbar 1962) which can be correlated to that found in the lower part of the Kapp Starostin Formation in Svalbard (Nakamura et al. 1987). This indicates a latest Early Permian or eventually an early Late Permian age for the upper part of the Mallebuk Mountain Group in this area.

The lower part of the section in Peary Land is dated by fusulinids (fig. 3) (Petryk 1977, Stemmerik & Håkansson in press). The upper part of the Mallebuk Mountain Group is poorly dated in

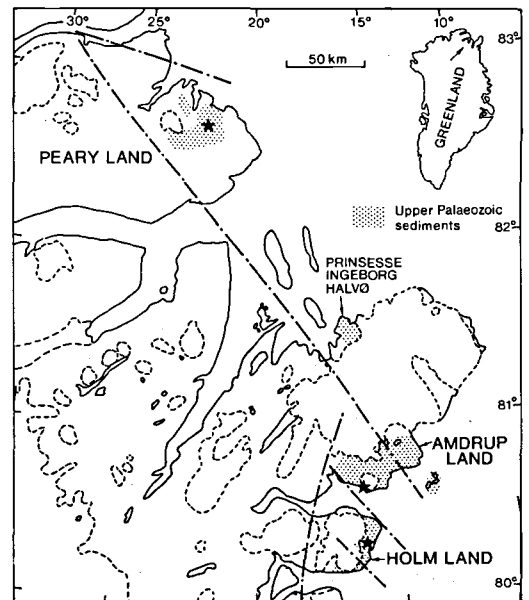


Fig. 2. Map of eastern North Greenland showing distribution of Upper Palaeozoic sediments and major structural elements. Location of analysed sections marked by asterix.

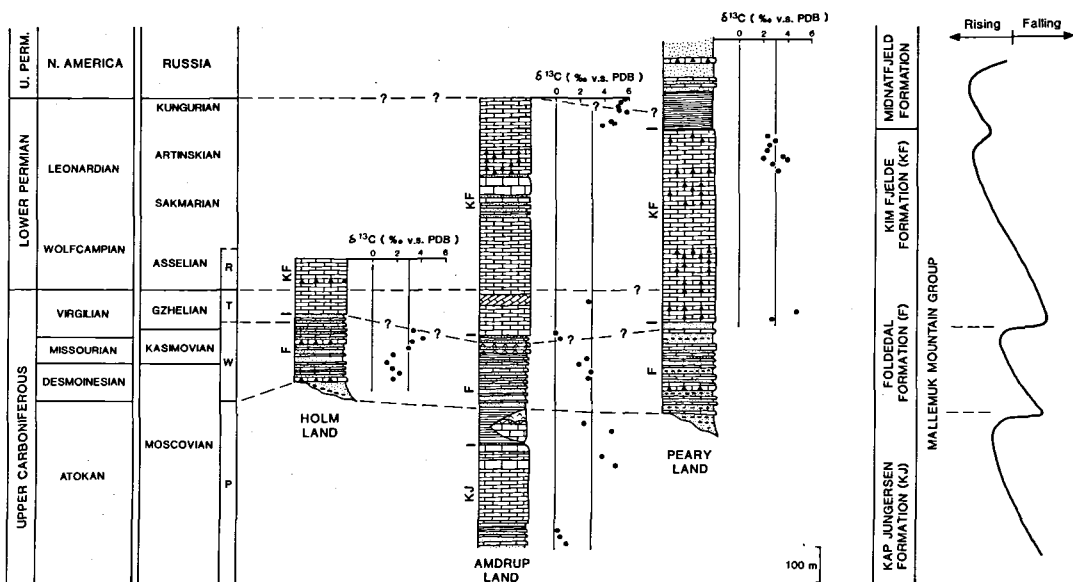


Fig. 3. Stratigraphic variation of $\delta^{13}\text{C}$ in the northern Holm Land, southern Amdrup Land, and Peary Land sections. The dotted lines are proposed biostratigraphic correlation based on fusulinids. P = zone of Profusulinella, W = zone of Wedekidellina, T = zone of Triticites, and R = zone of Rugosofusulina. KJ = Kap Jungersen Formation, F = Foldedal Formation, and KF = Kim Fjelde Formation. Lithology and stratigraphy based on Håkansson & Stemmerik (1984) and Stemmerik & Håkansson (in press). The sea-level curve to the right shows a generalized trend of the regional changes in sea-level based on Stemmerik & Worsley (in prep.).

this area. The overlying Midnattfjeld Formation yielded fossils of late Early Permian and Late Permian age (Håkansson 1979) suggesting an early Permian age for the youngest part of the Mallebuk Mountain Group in Peary Land. This means that the top part of the Mallebuk Mountain Group in Peary Land is slightly older than in Amdrup Land (fig. 3) (Håkansson & Stemmerik 1984, Stemmerik & Håkansson in press).

Analytic Methods

All analyses were performed on whole rock samples of shallow marine biogenic limestones and dolomites. An aliquot of the powder was analysed by standard X-ray diffraction procedure to detect the content of dolomite. Weighted percent dolomite/(dolomite + calcite) was calculated using the area under the peaks ($\text{Cu-K } 2\theta = 30.8^\circ$ and 29.5°) and the formula of Weber & Smith (1961).

The carbon and oxygen isotopes in carbonate minerals were measured using the conventional phosphoric acid method (McCrea 1950). For samples containing more than 50% dolomite we used the procedure described by Magaritz & Ka-

fri (1981), measuring only the dolomitic component. The CO_2 gas was analysed in a Varian M250 Mass spectrometer and results are given using the “ δ ” notation relative to the PDB standard (Table 1). The isotope values were calibrated using NBS 19 Calcite standard ($\delta^{18}\text{O} = -2.20\text{‰}$, $\delta^{13}\text{C} = 1.96\text{‰}$).

Reproducibility of duplicate samples is better than 0.1 ‰ for $\delta^{13}\text{C}$ and 0.15 ‰ for $\delta^{18}\text{O}$.

The problems using whole rock analyses in isotopic work have been discussed by Beauchamp et al. (1987). The rocks analysed in the present study are dominantly unaltered shallow-water limestones in the sense of Beauchamp et al. (1987). However, aragonitic components in wackestones and packstones have been replaced by sparry calcite. The dolomite is microcrystalline to finely crystalline preserving the original texture of the sediment. In limestone and dolomite, changes in the carbon isotopic value vary with time by a different amount from the changes in oxygen isotopic value. This behaviour can be understood by considering the material balance of the whole diagenetic system (i.e. sediment plus pore water). It has been shown (Magaritz 1983) that there are only few carbon ions in solution in such a system. So, in order for there to be a small

Table 1. Carbon and oxygen isotopic ratios, and dolomite percentages of the analysed carbonate samples.

GGU No.	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	% dol
196130	4.40	-8.9	0
196138	2.75	-6.9	0
196201	3.65	-7.8	0
196204	2.88	-8.3	0
196218	3.97	-5.5	0
196220	2.26	-9.3	0
196222	2.55	-7.7	56
196224	3.01	-6.8	0
196228	2.31	-6.9	0
220655	0.30	-8.6	0
220656	0.36	-8.1	0
220658	0.90	-8.2	0
221346	2.84	-0.2	100
221348	3.05	-0.9	100
221349	2.05	-1.3	95
221351	2.63	+0.7	95
221363	3.86	-2.9	0
221364	4.87	-5.5	0
221365	4.61	-6.8	0
221366	5.94	-5.2	0
221367	5.25	-5.6	0
221368	5.24	-5.1	0
221370	5.35	-5.4	0
221371	5.66	-7.6	0
221374	4.90	-1.8	100
221375	3.86	-1.9	100
221377	4.68	-1.7	93
221378	2.29	-5.3	88
221382	2.18	-2.2	56
221384	0.02	-8.0	27
221386	2.79	-5.6	0
221392	1.91	-9.2	0
221393	2.41	-5.9	60
221394	1.87	-7.3	0
221395	1.27	-9.1	0
221396	1.97	-6.8	0
221397	3.19	-7.8	0
221398	3.43	-7.0	0
221399	-0.45	-7.5	0
221400	3.50	-6.8	51

shift in $\delta^{13}\text{C}$ in the solid phase, at least 1500 times the pore volume of solution must pass through the system. The same change in $\delta^{18}\text{O}$ can happen if only 5 times the pore volume of solution passes through. Since these values are minima (they assume that exchange occurs with every atom in the fluid), the actual amounts of fluid needed to affect a change in the $\delta^{13}\text{C}$ values are likely to be even larger.

This model is supported by evidence from carbonate cements, which are formed entirely during diagenesis. Allan & Matthews (1977, 1982) explained the marine range of $\delta^{13}\text{C}$ values in the meteoric waters in these cements as the result of repeated cycles of dissolution and precipitation. Thus the value of $\delta^{13}\text{C}$ in the pore water gradually

approached that in the marine carbonate. Dickson & Coleman (1980) found a similar marine range of $\delta^{13}\text{C}$ and proposed that the main source of carbon in pore solution is dissolution of marine carbonates. Thus it is believed that diagenesis has had negligible effect on the C-isotope composition, and the measured values represent primary differences.

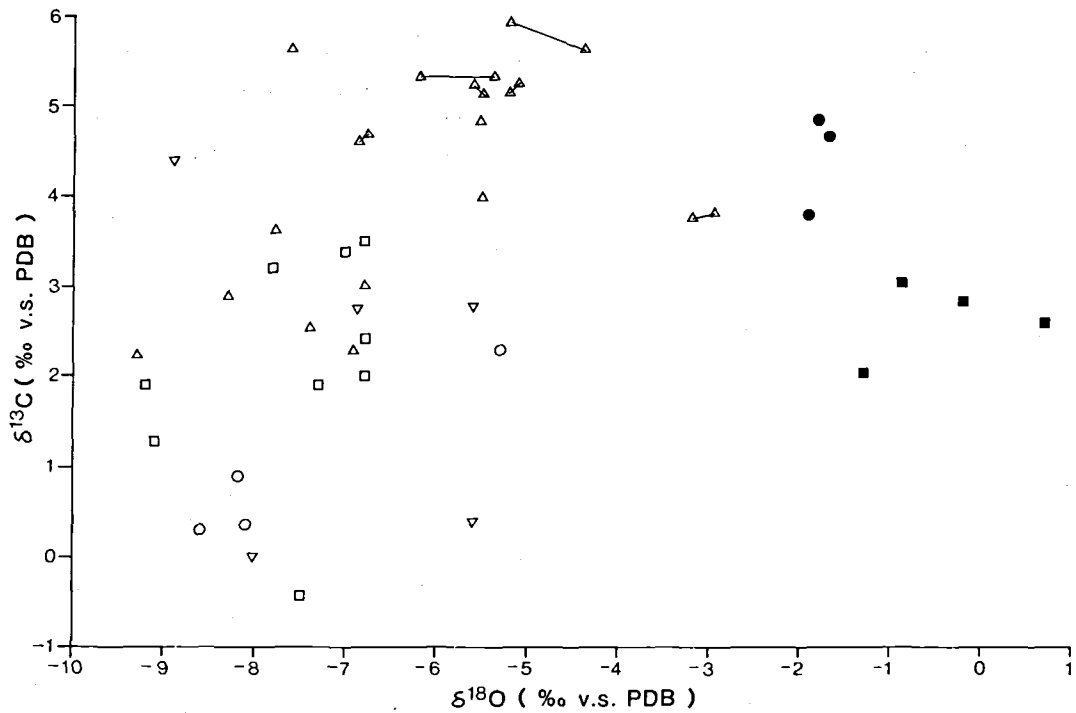
Results

Carbon isotope values vary from almost 0 ‰ to +5.7 ‰ in the Upper Carboniferous to Lower Permian limestones of the Wandel Sea Basin (fig. 3). Though not sampled in detail one can detect a trend of the $\delta^{13}\text{C}$ values which apparently correlates to the depositional pattern (fig. 3). $\delta^{13}\text{C}$ values are low (+0.3 to +0.9 ‰) in the basal part of the lower Moscovian Kap Jungersen Formation becoming much enriched in ^{13}C (2.3 to 4.9 ‰) in the upper part. The upper Moscovian – mid Gzhelian Foldedal Formation was analysed in two sections 30 km apart. The carbonates have low $\delta^{13}\text{C}$ values at the base (1.3–2.4 ‰) and higher values 2.0 to 3.5 ‰ near the top (fig. 3). The topmost limestone bed in the Foldedal Formation marking the beginning of a regional transgression has a $\delta^{13}\text{C}$ value of 0.4 ‰ dropping to 0.0 ‰ at the base of the Gzhelian-Permian Kim Fjelde Formation (fig. 3). The $\delta^{13}\text{C}$ values increase to 2.8–4.4 ‰ higher in the sequence (fig. 3). Further enrichment from 3.8 ‰ to values above 5 ‰ is recorded in the topmost part of the formation in Amdrup Land.

$\delta^{18}\text{O}$ values show ^{18}O depletion in most calcitic samples with values in the range -3.0 to -9.3 ‰. These values, unlike the $\delta^{13}\text{C}$ values, indicate post-depositional alteration of marine values, commonly found in ancient limestones (Magaritz 1975). $\delta^{18}\text{O}$ values of dolomite samples are more enriched in ^{18}O (+0.7 to -1.9 ‰) (fig. 4).

Discussion

Although the sampling is not of great detail, a general picture of $\delta^{13}\text{C}$ variation in the early Moscovian to Kungurian or earliest Late Permian can be obtained. At least three carbon isotope cycles (from ^{13}C depleted to ^{13}C enriched carbonate)



CALCITE DOLOMITE

△		Lower Permian - ? lower Upper Permian
▽		upper Gzhelian
□	■	upper Moscovian - lower Gzhelian
○	●	lower Moscovian

Fig. 4. Carbon and oxygen isotope composition of the investigated Late Palaeozoic limestones and dolomites.

were detected. A similar pattern was detected in a section through Upper Carboniferous of the Pedregosa Basin, New Mexico (Holser & Magaritz unpubl. data). There, $\delta^{13}\text{C}$ values varied from more negative values at the base of the Atokan, Desmoinesian and Missourian transgressive sequences to more ^{13}C enriched values higher in each of the sequences. The similarity of the general carbon isotope pattern between the North Greenland and SW USA sections may support a model which relates the fluctuation of $\delta^{13}\text{C}$ values to changes in sea-level caused by the frequent glaciations occurring during the Upper Palaeozoic. At the beginning of a transgression $\delta^{13}\text{C}$ values are low, becoming enriched in ^{13}C towards the peak of the transgression. The reason for this sea-level dependent change in the oceanic $\delta^{13}\text{C}$ is

suggested to be erosion and oxidation of the organic carbon stored on the shelves and near coastal regions during sea-level low stands and increased accumulation of organic carbon during sea-level high stand. The model of $\delta^{13}\text{C}$ increase in marine carbonate with transgressive phases of deglaciation was discussed in relation to the Upper Pleistocene (Shackleton 1977, Broecker & Takahashi 1984). The place where the organic carbon was stored during the late Pleistocene is not yet known, but may be in the rain forest or on the extended shelf, whereas in the late Palaeozoic it probably was stored as coal. Two different types of C_{org} storage exist: a) Biomass accumulation (e.g. tropical forest) as part of the ecological system which has capacity to store only a limited amount of biomass but is capable to change the

stored volume over very short periods of time, and b) Burial storage of biomass (e.g. coal) where the biomass potential stored is much greater and the time involved much longer. One can suggest that the Upper Pleistocene carbon isotope shift relates to type 'a' storage while the much more significant shifts in the Upper Palaeozoic relate to type 'b' storage. This may explain the enrichment recorded in the uppermost part of the Amdrup Land section where $\delta^{13}\text{C}$ values range between 4 ‰ and 6 ‰ (fig. 3). These values are comparable to values recorded in the Upper Permian of East Greenland (Clemmensen et al. 1985, Magaritz & Stemmerik unpublished data) and in other Upper Permian sequences of Northern and Southern Europe and Southeast USA (Holser et al. 1986) supporting a suggested late Early Permian to early Late Permian age of this part of the sequence.

Beauchamp et al. (1987) recorded rather uniform and high $\delta^{13}\text{C}$ values from Late Palaeozoic limestones in the Sverdrup Basin in Arctic Canada contrasting the cyclic pattern found in North Greenland. The $\delta^{13}\text{C}$ values recorded from the Sverdrup Basin (Beauchamp et al. 1987) are similar to the ^{13}C enriched values found in the Upper Carboniferous and topmost Permian parts of the sections in Greenland. Lower Permian values in contrast are enriched ca. 2 ‰ in the Sverdrup Basin.

Beauchamp et al. (1987) proposed a model for the Sverdrup Basin values involving ^{13}C enrichment due to local storage of organic carbon and deposition of evaporites in an enclosed basin. Limited water exchange with the ocean and limited exchange with the atmosphere due to proposed low atmospheric pressure was suggested as a mechanism keeping the Sverdrup Basin in isotopic unbalance to the ocean (Beauchamp et al. 1987). The high $\delta^{13}\text{C}$ values recorded in the Upper Carboniferous sequences of the Sverdrup and Wandel Sea Basins compared to elsewhere (e.g. Veizer et al. 1980, Brand 1981) imply interconnection of the two basins as previously suggested on basis of stratigraphic similarities (e.g. Steel & Worsley 1984, Davies & Nassichuk in press, Stemmerik & Håkansson in press). The absence of a cyclic pattern of $\delta^{13}\text{C}$ in the Sverdrup Basin comparable to that described from the Wandel Sea Basin may be explained in two ways: 1) The narrow intervals yielding depleted ^{13}C in North

Greenland have not been analysed in the study of Beauchamp et al. (1987), or 2) The semi-enclosure of the Sverdrup Basin prevented the transgressive sea from reaching the basin until a very late stage of the transgression. The dissolved inorganic carbon in the sea-water then will be considerably less depleted in ^{13}C and mixing with ^{13}C enriched water from the deeper parts of the basin probably will make the differences in $\delta^{13}\text{C}$ values between limestones of different cycles too small to be recorded.

Conclusions

Carbon isotope studies of Late Palaeozoic limestones in the Wandel Sea Basin show a cyclic pattern of ^{13}C with time. Low values of $\delta^{13}\text{C}$ (0.0 ‰ – 1.0 ‰) are confined to the basal transgressive stages of three major fining-upwards cycles each corresponding to a formation within the Mallemuk Mountain Group. Later in each of the transgressive cycles carbonates are enriched in ^{13}C having $\delta^{13}\text{C}$ values in the range 2–4.5 ‰.

The high values found in the Sverdrup Basin and the Wandel Sea Basin suggest that the two basins were connected during the Late Palaeozoic and somehow had only limited water exchange to the ocean.

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Dansk sammendrag

Isotopundersøgelser af Sen Palæozoiske kalksten fra Wandel Sea Basin i det østlige Nordgrønland viser en variation i $\delta^{13}\text{C}$ fra 0.0 ‰ til 5.7 ‰ relativt til PDB. Kalksten fattige på ^{13}C forekommer i den nederste del af transgressive sekvenser, mens kalksten rige på ^{13}C forekommer under maksimal transgression.

Det er postuleret, at isotopskiftene skyldes skift i det globale kulstofkredsløb, således at kalksten rige på ^{13}C dannes i perioder, hvor der er stor ophobning af organisk kulstof i form af kul. Kalksten fattige på ^{13}C dannes i perioder, hvor havniveau

er lavt og det ophobede kulstof derfor bliver eroderet og oxideret.

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