

Stable isotope study through the Permian-Triassic boundary in East Greenland

LARS CLEMMENSEN, W. T. HOLSER & D. WINTER



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A survey of stable isotope ratios in sediments spanning the Permian-Triassic boundary in East Greenland shows Upper Permian evaporites to have $\delta^{34}\text{S} = +10.6 \pm 1.6\%$ and limestones to have $\delta^{13}\text{C}_{\text{carb}} = +4.5 \pm 0.4\%$, in conformity with similar values from probable correlative formations in Europe and North America. Most values of both isotopes in Triassic formations are lower and scattered, apparently reflecting varying inputs of non-marine waters including the oxidative erosion of isotopically light sulfur. This transition in the East Greenland section has obscured any clear detection of chemical events recorded elsewhere: a drop in marine $\delta^{13}\text{C}_{\text{carb}}$ near the Permian-Triassic boundary, and a sharp rise in $\delta^{34}\text{S}_{\text{st}}$ in latest Scythian time.

L. B. Clemmensen, *Institute of General Geology, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark*, W. Holser, *University of Oregon, Eugene, OR 97403, USA*, D. Winter, *Department of Geology, University of California, Los Angeles, CA 90024, USA, March 16th, 1984*.

Introduction

Although the general forms of the isotope age curves through Phanerozoic time of sulfur isotopes ($\delta^{34}\text{S}_{\text{st}}$) in marine evaporites (Claypool, Holser, Kaplan, Sakai & Zak 1980) and of carbon isotopes in marine limestones (Veizer, Holser & Wilgus 1981; Lindh, Saltzman, Sloan, Mattes & Holser 1981) have been described, the details of short-term changes in these curves are as yet little known (Holser 1977; Scholle & Arthur 1980). In particular, possible isotope shifts associated with the Paleozoic-Mesozoic era boundary have been investigated for carbon only in the western USA (Wilgus 1981), and additionally for sulfur in northwestern Europe (Claypool et al. 1980). Inasmuch as East Greenland exposes one of the classic sections spanning this interval, we have made a reconnaissance of possible isotope variations using samples from the collections of the Geological Survey of Greenland. This area was of particular interest because of the completeness of the section, its distance from sections previously studied, and because of its correlation with the Zechstein sections of northwestern Europe.

Palaeogeography, stratigraphy, and sampling

The section in East Greenland (fig. 1) lies alongside the seaway that fed the basins of north-western Europe with Arctic marine waters throughout the Permian, possibly continuing into the Griesbachian (Callomon, Donovan & Trümpy 1972). Later in Triassic times any connection of the Arctic to Europe via East Greenland is problematic (Callomon et al. 1972; Warrington 1970). Much of the Triassic in East Greenland is a red-bed sequence with palaeontological and sedimentological evidence of continental origin (Clemmensen 1978, 1980), so the Arctic marine source may not have reached there. However, in other basins some evaporites and limestones have been found to be dominantly of marine derivation even though enclosed in red beds. Consequently we have analysed the whole East Greenland section without *a priori* decision as to whether their chemical components were of marine or continental origin.

The stratigraphic relations and lithology of formations and members sampled in the Upper Permian and the Triassic of East Greenland are out-

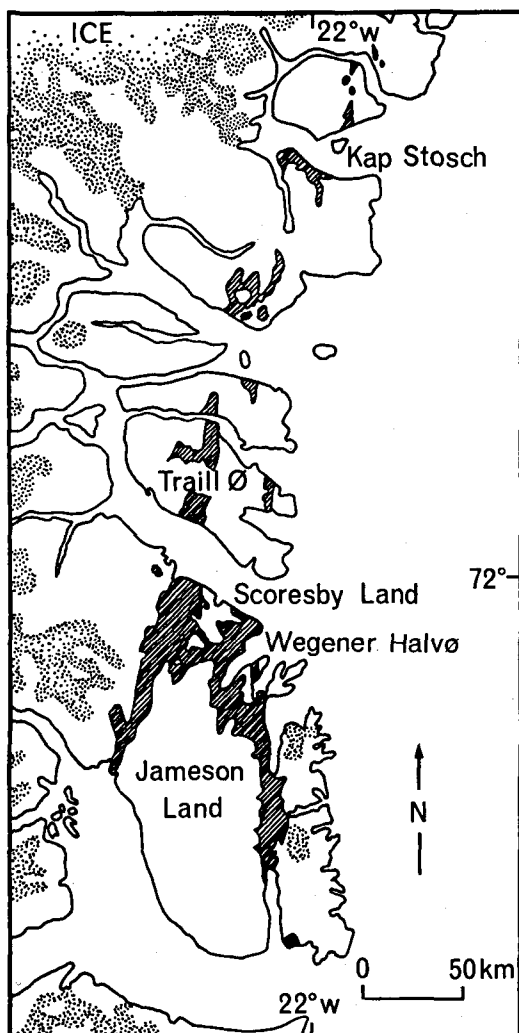


Fig. 1. The distribution of Upper Permian and Triassic sedimentary rocks in central East Greenland.

lined in table 1 (Birkelund & Perch-Nielsen 1976; Clemmensen 1980; Grasmück & Trümpy 1969; Maync 1942, 1961; Perch-Nielsen, Birkenmajer, Birkelund & Aellen 1974). The Upper Permian Foldvik Creek Formation (Birkelund & Perch-Nielsen 1976) consists mainly of a number of shallow marine facies associations, one of which is characterised by finely laminated gypsum (Surluk, Piasecki, Rolle, Stemmerik, Thomsen & Wrang, in press). The overlying Lower Scythian Wordie Creek Formation is composed of shallow marine sandstones and siltstones, which only

rarely are gypsum-bearing. During Scythian time the depositional regime apparently shifted rather abruptly to one that was dominantly continental: the Upper Scythian (?) to Lower Rhaetian (?) Pingo Dal, Gipsdalen and Fleming Fjord Formations were deposited mainly in environments described as alluvial fan, fluvial, aeolian, sabkha and lacustrine (Clemmensen 1978, 1980). Gypsum occurs as centimeter-sized nodules, millimeter to centimeter thin veins, massive layers (up to *ca.* 30 cm) and sand-sized particles (often forming cross-bedding) in the Kolledalen, Solfaldsdal and Kap Seaforth Members of the Gipsdalen Formation. Rock salt pseudomorphs are common in the Kap Seaforth Member, but also occur rarely in the overlying Edderfugledal Member (Table 1). Palaeontological affinities are mainly with the Zechstein to the south in the Late Permian, and with Arctic Canada in the Scythian; in the rest of Triassic time fossils are sparse and mainly non-marine. A mixture of Permian and Triassic faunas in the basal part of the Wordie Creek Formation, and its apparent conformity with the underlying Foldvik Creek Formation, has led to controversial assertions that deposition was continuous across the era boundary, but mainly on sedimentological grounds current opinion favours a hiatus during the Latest Permian (Teichert & Kummel 1973; Flügel 1973). That determination is supported by a local erosional unconformity at the base of the Lower Triassic (Birkenmajer 1977). Thus although the Foldvik Creek Formation seems to be correlated with the Zechstein Series, which is the latest Permian represented in northern Europe, the correlation of the Zechstein itself is vague (e.g. Visscher 1973) in relation to both the type section and the best documented Permian sections in central Asia, and latest Permian may be absent in both western Europe and eastern Greenland. The Foldvik Creek Formation has only one major evaporite unit, and there is no information as to which of the four to six evaporite cycles of the Zechstein it may be correlative.

The samples analysed are listed in Tables 2 and 3, and include most of the evaporitic and limestone horizons from the gypsum facies of the Upper Permian (mainly Kazanian; Piasecki, pers. comm. 1984) Foldvik Creek Formation through the Ladinian (?) Kap Seaforth Member of the Gipsdalen Formation.

Table 1
Upper Permian and Triassic stratigraphy of East Greenland

Stage	Formation	Member	Lithology (<i>evaporites in italics</i>)
Norian		Ørsted Dal	125-250 m; fluvial conglomerates and sandstones; non-marine trace fossils; marine limestones at top.
Carnian(?)	Fleming Fjord	Malmros Klint	30-225 m; lacustrine fine sandstones and siltstones; non-marine trace fossils.
		Edderfugledal	40-130 m; lacustrine dolostones, stromatolites, sandstones and siltstones; rare <i>rock salt pseudomorphs</i> ; non-marine trace fossils.
Ladinian(?)		Kap Seaforth	20-160 m; lacustrine sandstones, siltstones, and <i>gypsum</i> ; common <i>rock salt pseudomorphs</i> .
Anisian(?)	Gipsdalen	Solfaldsdal/ Kolledalen	50-165 m; aeolian, fluvial and lacustrine sandstones and siltstones with <i>gypsum</i> ; non-marine trace fossils; intercalation of marine limestones (0-35 m)
		Klitdal/ Paradigmabjerg/ Rødstaken	70-700 m; fluvial conglomerates, arkose and sandstones; non-marine trace fossils; locally beds of limestone at top with marine microfossils.
	Scythian Gries- bach- ian Dinerian	Wordie Creek	[8 faunal zones] 70-700 m; marine sandstones, siltstones and shales; minor <i>gypsum</i> .
Kazanian - Tatarian		Foldvik Creek	[5 facies associations] 50-300 m; marine limestones, shales, sandstones and <i>gypsum</i> ; fluvial conglomerates at base.

Analytical methods

For sulfur isotope analysis, gypsum was picked from hand samples. All samples were crushed to 42 mesh, dissolved in 6N HCl and filtered with Millipore filters (0.45 μm). The solutions were precipitated with 10% BaCl₂ and allowed to stand overnight; precipitated BaSO₄ was filtered, washed, and dried. SO₂ for the mass spectrometer was prepared by firing the BaSO₄ with organic-free quartz powder, and the purified gases were analysed on a Nuclide RMS 6-60 Mass Spectrometer against Canyon Diablo SO₂.

For carbon isotope analysis pure limestones, for the most part micritic, were crushed and sieved to 42-100 mesh, reacted with hypochlorite overnight to remove organic carbon, and centrifuged with distilled water until neutral. About 10 mg of dried sample was reacted under vacuum with 100% H₃PO₄ at 25C for 24 hours. The CO₂ evolved was purified and analysed on a Finnigan MAT 250 mass spectrometer.

Analytical results are expressed in the customary per-mil deviation (δ) relative to standards of

Canyon Diablo troilite for sulphur and Pee Dee Belemnite for carbon. Precision of the isotope analysis is $\pm 0.1\%$ for C and O, and $\pm 0.3\%$ for S.

Results and discussion

The results are tabulated in tables 2 and 3, and summarized in fig. 2.

The sulfur isotope analyses fall into two rather distinct groups: the Upper Permian and Scythian samples with $\delta^{34}\text{S} = +10.6$ to 13.5‰, and the overlying later Triassic samples with $\delta^{34}\text{S} = -0.2$ to +8.2‰. As expected, the values from the Upper Permian Foldvik Creek Formation are consistent with the very large number of previous determinations on marine Upper Permian evaporites, in both the Zechstein Series throughout western Europe and the Ochoan Series of the USA, with $\delta^{34}\text{S} = +11 \pm 1.5\%$ (Claypool et al. 1980). The determination of $\delta^{34}\text{S} = +13.5\%$ for the single Scythian sample also mimics the slight rise in the earliest Triassic previously found in

Table 2. Isotope analyses of Triassic rocks from East Greenland.
(For locations see Perch-Nielsen *et al.* 1974; Clemmensen 1980).

	$\delta^{13}\text{C}_{\text{carb}}$, ‰	$\delta^{18}\text{O}_{\text{carb}}$, ‰	$\delta^{34}\text{S}_{\text{sft}}$, ‰
<i>Ladinian</i> (?)			
229777 Gypsum, pink, sand-size and massive; Kap Seaforth Member of Gipsdalen Formation, Jameson Land, Triaselv.			- 0.2
181206 Sandstone, with 3-mm concordant layer of sand-sized gypsum; formation as above, Scoresby Land, Sporfjeld.			+ 6.1
181230 Shale, brownish gray, with 1-cm lenses of white gypsum; formation as above, Jameson Land, Malmros Klint.			+ 5.4
229738 Gypsum, medium brown to white; formation and locality as above.			+ 5.2
<i>Anisian</i> (?)			
229734 Limestone, medium gray, well-bedded, coquina of microfossils, a few thin spar veins; Gråklint Beds of Solfaldsdal Member of Gipsdalen Formation, Jameson Land, Solfaldsdal.	- 8.49	- 2.28	
229732 Limestone, dark gray, thin-bedded, with 1-cm coquina band; formation and location as above.	- 1.85	- 9.95	
229733 Limestone, medium gray, well-bedded; <i>Myalina</i> coquina; formation and location as above.	+ 0.69	- 9.76	
181310 Gypsum, massive, pink; Kolledalen Member of Gipsdalen Formation, Scoresby Land, Kolledalen.			+ 6.1
181211 Gypsum sand, pink; formation and locality as above.			+ 8.2
<i>Scythian, Lower Griesbachian</i>			
229793 Limestone, light gray, sandy, wave-bedded with 2-cm brachiopod mold; <i>P. rosenkrantzi</i> Zone, Ødepas Member, Wordie Creek Formation, 200 m above base of member, Traill Ø, Svinhufvuds Bjerge.	+ 1.48	- 8.01	
229800 Limestone, pale brown, stromatolitic bioherm facies; zone and position as above, 100 m above base of member, locality as above.	+ 1.92	- 8.10	
95558 Gypsum, pink nodules in gray dirty gypsum; upper non-fossiliferous part of <i>Glyptophiceras martini</i> Zone, Wordie Creek Formation, Kap Stosch, River II.			+ 13.5

samples from both Germany (summarized in Claypool *et al.* 1980) and the Western Interior, USA (Wilgus 1981).

Most of the Anisian-Ladinian sulfates are lighter than any marine sulfate of any age previously analysed, and in particular they are much lighter than the range of $\delta^{34}\text{S} = +15$ to $+23\%$ previously found for marine evaporites of this age. Low values of $\delta^{34}\text{S}$ are expected in non-marine evaporites that are fed by streams having a mixture of sulfate from older evaporites ($\delta^{34}\text{S} =$

$+20 \pm 10\%$) and oxidized sulfide from shales ($\delta^{34}\text{S} = -17 \pm 10\%$) or igneous rocks ($\delta^{34}\text{S} = +1 \pm 2\%$), although only a few non-marine evaporites have been analysed for isotopes previously (Permian Rotliegend, Holser 1977; Permian Kupferschiefer, Marowsky 1969; Triassic Keuper, Taylor 1983; Eocene of the Paris Basin, Boch, Marcé & Mégnien 1974; Pleistocene Searles Lake, Holser & Kaplan 1966). The Gipsdalen Formation is of generally non-marine aspect, except for a thin intercalation of marine

Table 3. Isotope analyses of Permian rocks from East Greenland.

	$\delta^{13}\text{C}_{\text{carb}}$, ‰	$\delta^{18}\text{O}_{\text{carb}}$, ‰	$\delta^{34}\text{S}_{\text{sft}}$, ‰
<i>Kazanian - Tatarian (Zechstein)</i>			
234953 Limestone, medium brown, poorly bedded, with many well-preserved macrofossils; some thin span veins (not analysed); Martinia Limestone Member, Foldvik Creek Formation, Wegener Halvø.	- 5.27	- 7.42	
269159 Limestone, pale yellowish brown, massive, fossil fragments, non-reef facies; Limestone-Dolomite Member, Foldvik Creek Formation, Jameson Land, Schuchert Dal.	+ 5.28	- 9.16	
269145 Limestone, as above.	+ 4.94	- 8.33	
234908 Limestone, brownish gray, fine grained, reef facies; Limestone-Dolomite Member, Wegener Halvø.	+ 4.22	- 12.49	
234903 Limestone, light gray, fine grained, reef facies; Limestone-Dolomite Member, Wegener Halvø.	+ 4.36	- 10.31	
234902 Limestone, greenish gray, coarsely fossiliferous, reef facies; formation and location as above.	+ 4.51	- 10.68	
234901 Limestone, brownish green, coarsely fossiliferous, reef facies; formation and location as above.	+ 4.18	- 11.33	
269191 Limestone, medium brown, stromatolitic; uncertain member of Foldvik Creek Formation, Jameson Land, Schuchert Dal.	+ 5.10	- 5.00	
111199 Gypsum, white, massive; Gypsum Member, Foldvik Creek Formation, Scoresby Land, Werner Bjerge.			+ 12.2
111159 Gypsum, white, massive; formation as above; Scoresby Land, Werner Bjerge, Malmbjergj.			+ 11.6
269125 Gypsum, white, massive; formation as above, Jameson Land, Schuchert Dal.			+ 9.3
269219 As above.			+ 9.1

limestone (the Gråklint Beds; Clemmensen 1980). Stauber (1942) and Perch-Nielsen et al. (1974) supposed that the gypsum depositum was lagoonal. An analysis of sedimentary features by Clemmensen (1978) concluded that the gypsum was deposited in dune and inland sabkhas, and our sulfur isotope data confirm such a non-marine regime of deposition. Clemmensen (1978) also speculated that while some of the evaporite may have been wind-blown "cyclic" marine salt (which would also have contributed sulfate), the major source was erosion of Permian gypsum exposed in the western borderlands of the basin. The sulfur isotope data indicate, however, that sulfide, presumably from the weathering of shales, was a major component of the source sulfur.

Unfortunately none of the *marine* evaporites in East Greenland are young enough to record the very high $\delta^{34}\text{S}$ of the Röt Event (Holser 1977).

The high values of $\delta^{13}\text{C} = +4.2$ to 5.3‰ from limestones in the Limestone-Dolomite Member of the Foldvik Creek Formation are in excellent agreement with similarly high $\delta^{13}\text{C}$ previously described in detailed sections above the base of the Zechstein Series in northwestern Europe (Margaritz & Schulze 1980; Margaritz & Turner 1982), the Ochoan Series of the western USA (Margaritz, Anderson, Holser, Saltzman & Garber 1983), and the Bellerophon Formation of the Dolomite-Carnic Alps (Holser & Margaritz 1984), and the Changxing Formation of southern China (Chen, Shao, Huo & Yao 1984).

Values of $\delta^{13}\text{C}$ in all the younger formations

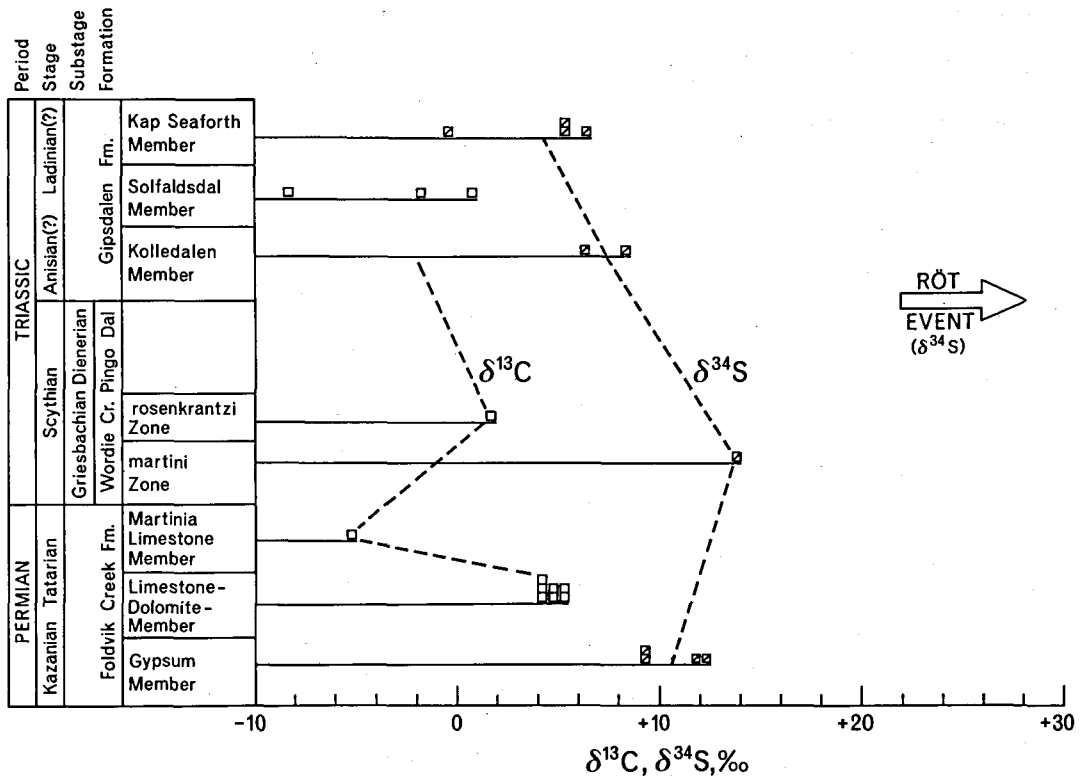


Fig. 2. Variations of stable isotope ratios of carbon and sulfur (per mil relative to PDB and Canyon Diablo, respectively) through the Permian-Triassic interval in East Greenland. The vertical axis is not to time scale; the timing of the Röt Event detected elsewhere is indicated.

sampled are lower, but scattered – while four are within the moderate values of $\delta^{13}\text{C} = 0 \pm 2\%$ expected from limited experience with Triassic marine limestone (Lindh *et al.* 1981; Wilgus 1981), two others are substantially lower and may reflect non-marine contributions (like the $\delta^{34}\text{S}$) or meteoric waters. Certainly all of the limestone measurements for $\delta^{18}\text{O}_{\text{carb}}$ show values so low, -5 to -12% , that the oxygen in the carbonates which exchanges much more easily than the carbon (Magaritz 1983), perhaps exchanged with meteoric waters of the present high-latitude outcrops. Thus while these data from East Greenland affirm the high ^{13}C of marine carbonate found elsewhere in the Upper Permian, neither the timing nor magnitude of a drop into the Early Triassic can be discerned.

Conclusions

In a survey of the Upper Permian through Triassic sediments of East Greenland, $\delta^{34}\text{S}_{\text{sft}} = +10.6 \pm 1.6\%$ in evaporite formations and $\delta^{13}\text{C}_{\text{carb}} = +4.5 \pm 0.4\%$ in limestone formations of Late Permian age confirm similar values previously determined in correlative marine sections in Europe and North America. Triassic values of both isotopes are generally lower and scattered, apparently reflecting varying inputs of non-marine waters in accord with determinations from previous sedimentological studies. Neither a drop in $\delta^{13}\text{C}$ near the Permian-Triassic boundary, nor the sharp rise in $\delta^{34}\text{S}$ in the Early Triassic-Smithian (Röt Event) are evident because of the marine-non-marine transition.

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Dansk Sammendrag

Stabile isotop forhold i sedimenter fra Øvre Perm samt Nedre og Mellem Trias fra det centrale Østgrønland er blevet undersøgt. Evaporitter fra Øvre Perm har $\delta^{34}\text{S} = +10.6 \pm 1.6\%$ og kalksten har $\delta^{13}\text{C}_{\text{carb}} = +4.5 \pm 0.4\%$ i overensstemmelse med de værdier, der kendes fra Øvre Perm sedimenter i Europa og Nordamerika. Sedimenter fra begyndelsen af Nedre Trias har også høje isotopværdier svarende nøje til dem, der kendes fra andre lokaliteter. Derimod har de overliggende Trias sedimenter lave og spredte isotopværdier både for $\delta^{34}\text{S}$ og $\delta^{13}\text{C}_{\text{carb}}$. Disse lave værdier tolkes som resultat af tilførsel af ferskvand samt isotopisk set lette sulfider til sedimentationsbassinet i Mellem Trias. Isotopundersøgelsen af de Permo-Triassiske sedimenter har derfor ikke kunnet vise det normale marine udviklingsmønster, der kendes fra andre lokaliteter og omfatter et fald i $\delta^{13}\text{C}_{\text{carb}}$ nær Perm-Trias grænsen og en pludselig stigning i $\delta^{34}\text{S}_{\text{st}}$ i slutningen af nedre Trias.

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