Carbon and oxygen isotope geochemistry of Early Neoproterozoic successions on the Kola Peninsula, northwest Russia

JOAKIM SAMUELSSON

The carbon and oxygen isotopic compositions of some Early Neoproterozoic (?early Cryogenian) successions on the Kola Peninsula, northwest Russia (specifically the Sredni and the Rybachi Peninsulas and Kildin Island, Murmansk Coast, and the Chapoma River, Tiersky Coast) have been studied. Organic carbon isotope data were obtained from all investigated rocks, whereas carbonate carbon data, with one exception, were acquired solely from the Kildin Island and the Tiersky Coast. Critical evaluation of the organic carbon preservation showed that approximately two-thirds of the samples contained isotopically altered organic matter. The $\delta^{13}C_{org}$ values regarded as reflecting primary depositional values range between −33.4 and −28.9‰. Various approaches aimed at assessing the signal quality in terms of retention of the primary signal of 13 investigated carbonates indicate that only three carbonates provided a close-to-primary signal. From the Kildinskaya Group on Kildin Island, the least ^{13}C-depleted sample yielded $\delta^{13}C_{carb} = +0.7‰$, a value interpreted to reflect the primary depositional value of seawater at the time of deposition of the group.

Joakim Samuelsson, Institute of Earth Sciences, Micropalaeontology, Norbyvägen 22, S-752 36 Uppsala, Sweden. Present address: Department of Geology and Pedology, Kriegslaan 28158, B-9000 Gent, Belgium

The stable isotope geochemistry of Neoproterozoic rocks, primarily in carbonate successions, has been successfully used both for evaluating secular trends in seawater chemistry and chemostratigraphic correlations (e.g. Knoll et al. 1986, 1995a, 1995b; Fairchild & Spiro 1987; Kaufman et al. 1991, 1993; Derry et al. 1992; Knoll & Walter 1992; Wickham & Peters 1993; Narbonne et al. 1994; Iyer et al. 1995; Kaufman & Knoll 1995). Isotopic chemostratigraphy might also be used in siliciclastic successions by exploiting the organic carbon isotope record, although more precautions have to be taken concerning sample quality and preservation of the primary geochemical signatures (Strauss et al. 1992d; Smith et al. 1994). C-isotopic measurements on Proterozoic organic carbon have been employed either as a supplementary proxy for carbonate carbon isotope values (Knoll et al. 1986) or solely for stratigraphic evaluations (Banerjee et al. 1992; Strauss et al. 1992d, 1992f, 1997).

On the Kola Peninsula, northwestern Russia (Fig. 1), sedimentary rocks of Early Neoproterozoic age are exposed on the northern and southern coasts. In the northern part of the peninsula, an approximately 2 km-thick, shallow-marine, clastic and carbonate succession crops out on the Sredni Peninsula and Kildin Island, and about 4 km of thick, fining-upwards, immature turbiditic sediments occur on the Rybachi Peninsula (Siedlecka et al. 1995a, 1995b; Fig. 1). On the southern coast of the Kola Peninsula (Tiersky Coast; Fig. 1), the Chapoma River cuts through a 250 m-thick succession of shallow-water siliciclastic and carbonate rocks of the Chapoma Formation. Following a study of the palaeobiology and biostratigraphy of the Early Neoproterozoic successions on the Kola Peninsula (Samuelsson 1997), in the present paper stable isotope and other geochemical data are evaluated in order to further constrain the chronostratigraphical age of the successions.

Geological setting and samples

The sedimentary rocks on the Sredni Peninsula, Kildin Island and the Rybachi Peninsula were deposited within and along the margin of the Timanian Aulacogen, one of the Late Proterozoic basins on the Fennoscandian Shield (Siedlecka 1975; Kumpulainen & Nystuen 1985; Vidal & Moczydlowska 1995). Recent detailed descriptions of the geology of Neoproterozoic rocks on the Sredni Peninsula, Kildin Island and the Rybachi Peninsula were published by Siedlecka et al. (1995a, 1995b).

The Sredni-Rybachi Fault Zone (Roberts 1995) separates the Sredni Peninsula from the Rybachi Peninsula, and is thought to be an eastern prolongation of the Trollfjorden-Komagelva Fault Zone. The latter separates the Barents Sea Region from the Tanafjorden-Varangerfjorden Region on the Varanger Peninsula in Finnmark, northeastern Norway.

The sedimentary rocks on the Sredni Peninsula rest unconformably on an Archaean to Palaeoproterozoic crystalline basement. The sedimentary succession on the Sredni is approximately 2000 m thick and divided into two groups, the Kildinskaya and Volokovaya groups. The rocks on Sredni are mainly deltaic, consisting largely of sandy–muddy lithologies (Siedlecka et al. 1995a). The Kildinskaya and Volokovaya Groups are separated by an unconformity with prominent topographic relief. On the Sredni Peninsula, the diagenesis-

grade succession (Rice & Roberts 1995) is subdivided into eight formations.

Kildin Island, situated east of the Sredni/Rybachi Peninsula, is underlain by the Kildinskaya Group, which here is approximately 1300 m thick. The lower part of the Kildinskaya Group on Kildin Island is terrigenous–dolomitic and contains several beds with columnar stromatolites (Lyubtsov et al. 1990; Siedlecka 1995; Siedlecka et al. 1995a). The carbonate rocks represent less than 5% of the entire thickness of the group (Raaben et al. 1995) and are overlain by approximately 1000 m of terrigenous sediments. The succession on Kildin Island is subdivided into seven formations.

The 4000 m-thick sedimentary succession on the Rybachi Peninsula is subdivided into the Bargoutnaya and Einovskaya Groups, and the Skarbeevskaya Formation. Most of the Rybachi Peninsula consists of interbedded grey sandstones, conglomerates and shales, interpreted as a basinal turbidite succession overlain by upper slope deposits (Siedlecka et al. 1995b). The Skarbeevskaya Formation is exposed in the northwestern part of the peninsula and is separated from adjacent rocks by a fault. Rocks on Rybachi are more deformed and cleaved than those on the Sredni Peninsula and Kildin Island, having undergone a stronger, anchizone metamorphism (Roberts 1995; Rice & Roberts 1995).

The Chapoma Formation is intersected by the Chapoma River in the southeastern part of the Kola Peninsula (Lyubtsov et al. 1989; Fig. 1). It consists chiefly of sandstone, siltstone and claystone (Lyubtsov et al. 1989), inferred to have been deposited in a shallow-water environment (Samuelsson 1997). The isotope and geochemical studies are based on samples which were collected from the Kildinskaya and Volokovaya Groups on the Sredni Peninsula and Kildin Island, and the Einovskaya Group and Skarbeevskaya Formation on the Rybachi Peninsula, as well as from the Chapoma Formation along the Chapoma River (Fig. 1, Appendix).

Biostratigraphic record and age estimation

The pioneering biostratigraphic work of Timofeev (1969) showed from recovered microfossil assemblages that the age of the investigated rock units is Late Proterozoic (i.e. Late Riphean and Vendian). Samuelsson (1997) supported the formerly inferred Early Neoproterozoic, pre-Varangerian age for the investigated units (see also Siedlecka 1975, 1995; Chumakov & Semikhatov 1981; Vidal & Siedlecka 1983; Lyubtsov et al. 1989), providing a biostratigraphic correlation based on microfossils. Further biostratigraphic support comes from stromatolitic assemblages of the Kildinskaya Group on Kildin Island that are considered to be typical of Late Riphean R3 forms (Raaben et al. 1995).

The micropalaeontological studies yielded taxonomically sparse assemblages of isolated and clustered sphaeromorphic acritarchs and filamentous tubular microfossils (Timofeev 1969; Lyubtsov et al. 1989; Samuelsson 1997). In common with Early Neoproterozoic records world-wide, microfossils of the genus *Leiosphaeridia* greatly outnumber the other recovered taxa. Age-diagnostic taxa include *Lophosphaeridium laufeldii* (Vidal) Samuelsson, *Satka colonialica* Jankauskas, *Simia annulare* (Timofeev) Mikhailova, *Tasmanites rifejicus* Jankauskas, *Trachysphaeridium laminaritum* Timofeev, *Valeria lophostriata* Jankauskas and *Vandalosphaeridium ?varangeri* Vidal (Samuelsson 1997). The suggestion was that the presence of these taxa indicated a Late Riphean age for the Kildinskaya and Einovskaya Groups and the Chapoma Formation (Samuelsson 1997). Together with lithostratigraphic data obtained by Siedlecka et al. (1995a), a Terminal Riphean (R4) age was inferred for the Volokovaya Group on the Sredni Peninsula. The tectonically distinct Skarbeevskaya Formation on the Rybachi was considered to be comparable to parts of the Bargoutnaya Group (Rice & Roberts 1995), but the age of this formation could not be determined on the basis of its microfossil contents.

Radiometric age determinations are few and poorly constrained. The most recent dates obtained for the lower Kildinskaya Group, 1050 to 619 Ma, were obtained by K/Ar age determinations on glauconite, indicating a Late Riphean age (Siedlecka et al. 1995a). Detrital illites in the Volokovaya Group were dated by Rb/Sr and yielded ages in excess of 800 Ma (Gorokhov et al. 1995). Whole-rock age determinations on shales from the Einovskaya Group on the Rybachi were cited by Timofeev (1969), who reported a K/Ar age of 887 Ma without, however, providing any analytical data. No absolute ages have yet been reported either for the Chapoma Formation on the Tiersky Coast or for the Skarbeevskaya Formation on the Rybachi Peninsula.

Despite poorly constrained radiometric ages, the relative age of the studied successions has been assessed, mainly by lithostratigraphical and biostratigraphical correlations (Siedlecka 1995; Samuelsson 1997). Biochronological correlations with the Barents Sea Group of the Barents Sea Region and the Vadsø Group of the Tanafjorden-Varangerfjorden Region in northern Norway are of special interest. Whole-rock isotope dating on shale samples from the Kongsfjord Formation of the Barents Sea Group yielded a Rb/Sr age of 810 ± 19 Ma (Siedlecka & Roberts 1992), whereas the Klubbnasen Formation of the lower Vadsø Group yielded a comparable age of 807 ± 19 Ma (Sturt et al. 1975). Lithostratigraphically, the Kongsfjord Formation is comparable to the inferred turbiditic successions on the Rybachi (Siedlecka et al. 1995b), whereas the Vadsø Group has been biochronologically correlated with the Kildinskaya Group (Siedlecka 1975, 1995; Vidal 1981; Vidal & Siedlecka 1983; Siedlecka et al. 1995a; Samuelsson 1997). Hence, if these correlations are correct, the isotopic dates from the Murmansk Coast can be bound to the early Cryogenian interval, ca. 850–730 Ma (Cowie et al. 1989; Kaufman & Knoll 1995).
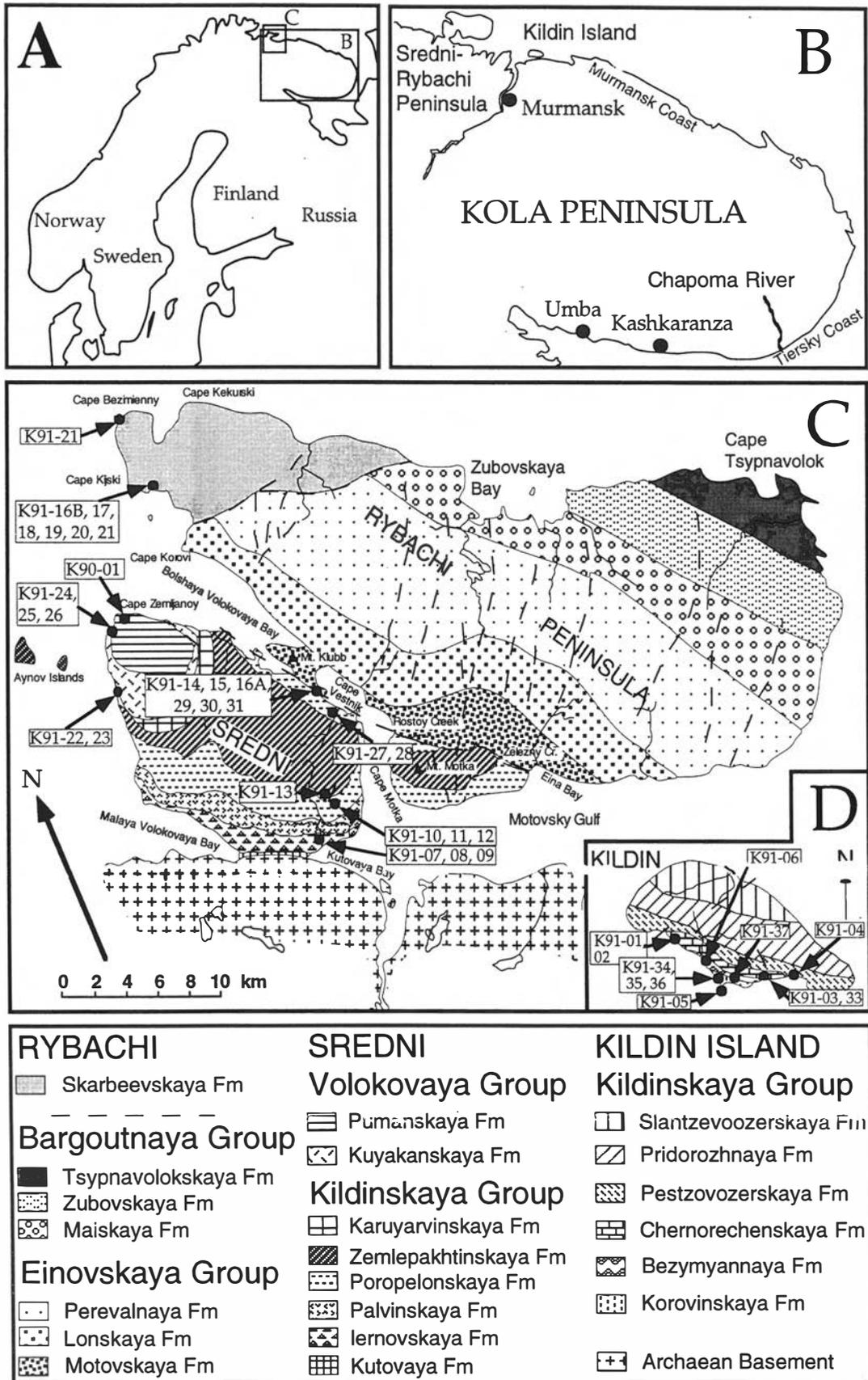
Fig. 1. A. Location of Kola Peninsula in relation to northern Europe. The boxes B and C on the map show where the detailed map-areas are geographically situated. B. Locations of the Sredni/Rybachi Peninsula, Kildin Island, Murmansk Coast and the Chapoma River, Tiersky Coast, Kola Peninsula. C. Geological map of the Sredni/Rybachi Peninsula showing sampling localities. D. Geological map of Kildin Island; scale is the same as in C. Maps C and D are modified from Siedlecka (1995) with permission.

In summary, the available biostratigraphic, lithostratigraphic and radiometric evidence suggest a Neoproterozoic, pre-Varangerian age for the investigated rock units.

Analytical methods

Prior to the geochemical analyses all samples were crushed to smaller pieces and subsequently etched in a mixture of 10% HCl and 20% HF in order to eliminate possible organic contaminants, and then ground to a fine powder. Sixty-three samples were analyzed for their carbonate and organic carbon content in a LECO analyzer (Strauss et al. 1992a). Samples with a carbonate content >2% were selected for whole-rock carbonate isotopic analysis. Nearly all samples were analysed for their organic carbon isotopic composition.

A number of organic-rich samples (with TOC $\geqslant 0.1$ mgC/g) were selected for kerogen isolation and elemental analysis. In addition to treatment with hot concentrated HCl, the kerogen fraction was further isolated by treatment with diluted HF to remove silicate minerals. The residue was then washed with deionized water until neutrality (pH ≈ 7) was obtained. Subsequently, the isolated kerogens were dried and ground to a fine powder. Kerogen powders were then investigated for their elemental abundance of C, H and N in a Carlo Erba elemental analyser. The other 36 samples with TOC $\leqslant$ 0.1 mgC/g were repeatedly treated with concentrated HCl to remove carbonate minerals. Both the isolated kerogen and the low TOC sample powders were then mixed with CuO and sealed in evacuated quartz tubes for combustion at 550°C for 12 hours. The CO_2 formed by combustion was cryogenically purified and the isotopic compositions were determined by conventional mass spectrometric techniques.

From whole-rock carbonates, CO_2 was liberated for isotope analysis through phosphorylation with enriched H_3PO_4 for 12 hours (Wachter & Hayes 1985). Carbon and oxygen isotope results are reported in the standard delta notation as standard normalized per mil difference from the Peedee belemnite (PDB) standard. Reproducibility, as determined by replicate analyses, was generally better than ± 0.6 per mil units for the organic carbon and ± 0.3 per mil units for the carbonate carbon.

In order to evaluate the degree of alteration of carbonate samples, additional analytical techniques were applied. The first step was to gold-plate and examine all polished carbonate thin sectioned samples in a cathodoluminescence (CL) microscope. The CL microscope used in this investigation was a hot-cathode CL device HC1-LM (Neuser 1995). A minimum of two CL-micrographs were taken of each sample. Subsequently, on thick sections representing the polished counterparts to the CL-examined thin sections, two to three microsamples were prepared from zones showing different levels of luminescence. Where possible, microsamples were isolated from zones composed of non-luminescent microspar or

dolomicrospar and highly luminescent portions of the sample for succeeding isotopic analysis. In some cases, an intermediate luminescent portion was also analysed. The sub-sampling was done using a Medenbach microdrilling device (described in Förtsch et al. 1992) mounted on a regular petrographic microscope. The sub-samples were then analyzed for carbon and oxygen isotopes applying the same method as for the whole-rock isotope examination.

Carbonate samples were further analysed for their elemental concentrations (Ca, Mg, Sr, Fe, Mn) using atomic absorption spectroscopy following HCl-dissolution in order to assess the degree of alteration associated with meteoric diagenesis (Veizer 1983; Popp et al. 1986). Elemental abundances were corrected for the insoluble residue.

Results

Abundances for total organic carbon (TOC) in the investigated Kola Peninsula samples were highly variable, ranging from only trace amounts to 5.83 mgC/g sample (Table 1). Average values of 1.07 mgC/g sample for shales ($n = 34$) and 0.29 mgC/g sample for carbonates ($n = 7$) from the Murmansk Coast, and 1.15 mgC/g sample for shales ($n = 13$) and 0.86 mgC/g sample for carbonates ($n = 7$) from the Tiersky Coast, are comparable to the averages for late Proterozoic shales (2.30 mgC/g) and carbonates (0.30 mgC/g) given by Strauss et al. (1992b). Organic carbon isotopic compositions range from -41.2 to $-22.3‰$, with an average $\delta^{13}C_{org} = -30.8‰$ ($n = 58$; Table 1). The mean H/C value for analysed kerogens from the Kola Peninsula is 0.52 ($n = 23$), with values ranging between 0.15 and 1.03 (Table 2). These values are comparable to previously reported H/C values from Proterozoic successions elsewhere (Strauss et al. 1992b). Note that two of the kerogen samples (K91-11 and K91-30) did not yield any H/C value, as no hydrogen was detected in the analysis of these kerogens. The ash content of the investigated kerogens was very high, with an average value of 72.9% ($n = 26$; Table 2). The thermal alteration index values (TAI) of the present samples have been presented previously (Samuelsson 1997). On the Sredni Peninsula, Kildin Island and the Tiersky Coast, the TAI values vary between $2+$ and $4-$, whereas on the Rybachi Peninsula they vary between 3 and 5. The TAI values in the lower range ($2+$ to 3) correspond to a catagenesis stage of thermal maturation with burial temperatures around 100°C, whereas the higher values ($4-$ to 5) are equivalent to a metagenesis stage with burial temperatures around 200°C (Strauss et al. 1992d).

Twelve of the present samples, seven from the Kildinskaya Group on Kildin Island and five from the Chapoma Formation on the Tiersky Coast, are carbonates, and were measured for whole-rock carbonate carbon isotope values. A single calcareous conglomerate

Table 1. Oxygen and organic and inorganic carbon isotope and other geochemical data from the Kola Peninsula. The $\delta^{13}C_{org}$ values (in bold) are regarded as better preserved (see main text). Abbreviations: %Carb = % carbonate; WR = whole rock; k = organic carbon isotope analysis performed on isolated kerogen; TOC = Total Organic Carbon; TAI = Thermal Alteration Index; KK = Kildinskaya Group on Kildin Island; KS = Kildinskaya Group on the Sredni Peninsula; V = Volokovaya Group; EIN = Einovskaya Group; IER = Iernovskaya Formation; KOR = Korovinskaya Formation; BEZ = Bezymyannaya Formation; CHE = Chernorechenskaya Formation; PES = Pestsovozerskaya Formation; POR = Poropelonskaya Formation; ZEM = Zemlepakhtinskaya Formation; KAR = Karuyarvinskaya Formation; KUY = Kuyakanskaya Formation; PUM = Pumanskaya Formation; MOT = Motovskaya Formation; SKA = Skarbeevskaya Formation; CHA = Chapoma Formation.

Sample	Group	From	Lithology	%Carb	$\delta^{13}C_{WR}$ (‰, PDB)	$\delta^{18}O_{WR}$ (‰, PDB)	TOC (mgC/g)	TAI		$\delta^{13}C_{org}$ (‰, PDB)
K91-05	KK	IER	mudstone	0			0.05	3+		−28.2
K91-34	KK	KOR	limestone	83.2	−2.8	−13.6	0.51			−28.9
K91-35	KK	KOR	dol limestone	94.3	−1.1	−9.0	0.56			n.d.
K91-36	KK	KOR	calc dolomite	90.5	−2.4	−8.4	trace			−29.0
K91-06	KK	BEZ	calc dolomite	74.4	−0.4	−8.4	trace			−25.0
K91-37	KK	BEZ	calc dolomite	88.8	−0.2	−8.2	0.47			−22.3
K91-01	KK	CHE	shale	0			2.88	3+	k	**−31.1**
K91-02	KK	CHE	limestone	64.6	−0.7	−9.6	0.04			−25.7
K91-03	KK	CHE	shale	0			0.69	3+		−28.3
K91-33	KK	CHE	limestone	92.6	−0.1	−9.4	0.07			−34.5
K91-04	KK	PES	shale	0			1.06	4−	k	−28.9
K91-07	KS	IER	mudstone	0			1.33	3	k	−31.6
K91-08	KS	IER	mudstone	0			0.96	3+		−31.1
K91-09	KS	IER	shale	0			5.83	4−	k	**−31.1**
K91-10	KS	POR	shale	0			0.77	3		−30.7
K91-11	KS	POR	shale	0			1.05	3+	k	−41.2
K91-12	KS	POR	shale	0			1.15	3+	k	**−33.4**
K91-14	KS	POR	mudstone	0			0.64	4−		−29.7
K91-15	KS	POR	mudstone	0			0.72	3+		−30.4
K91-16A	KS	POR	mudstone	0			0.40	3+		−30.0
K91-27	KS	POR	mudstone	0			0.66	3+		−29.8
K91-29	KS	POR	mudstone	0			1.05	4−	k	**−30.8**
K91-30	KS	POR	phosphates	0			0.47	4−	k	n.d.
K91-30′	KS	POR	mudstone	0			1.11		k	**−31.1**
K91-28	KS	POR	mudstone	0			0.85	3+		−30.2
K91-13congl	KS	ZEM	congl calc dolom	32.1	−13.3	−6.0	0.08			−28.1
K91-13phosp	KS	ZEM	phosph congl	0			0.30			n.d.
K91-22	KS	KAR	micaeous shale	0			2.05	3+	k	**−31.4**
K91-23	KS	KAR	micaeous shale	0			2.36	4−	k	**−31.6**
K91-24congl	V	KUY	conglomerate	0			0.05			−31.5
K91-24phosp	V	KUY	phosph clasts	0.2			0.36			−31.9
K91-24shale	V	KUY	shale	0			0.09			−24.4
K91-25	V	KUY	phosph pebbles	0.2			0.17			−30.0
K90-01A	V	KUY	phosphates	0.1			0.26			−27.0
K90-01B	V	KUY	phosph congl	0			0.42			−27.2
K91-26	V	PUM	mudstone	0			1.26	4−	k	**−39.9**
K91-31	EIN	MOT	mudstone	0			1.39	5	k	**−37.9**
K91-16B		SKA	mudstone	0			1.60	5	k	−34.6
K91-17		SKA	phosph congl	0			0.49			−31.7
K91-18		SKA	mudstone	0			0.80		k	−31.3
K91-19		SKA	mudstone	0			0.99		k	−32.8
K91-20		SKA	mudstone	0.3			1.00		k	**−31.9**
K91-21		SKA	phosphates	0			1.34	5	k	−31.4
K92-01		CHA	mudstone	0.2			0.03	3		−30.3
K92-02		CHA	shale	0.5			2.76	3−	k	**−40.4**
K92-03		CHA	shale	0.5			0.71	3+	k	−35.6
K92-04		CHA	shale	0.5			0.64	3+	k	−37.4
K92-05		CHA	limestone	33.6	−5.5	−8.8	0.14			−26.4
K92-06		CHA	shale	0			0.49	3+	k	−38.2
K92-07		CHA	carbonate	0.7			1.12			**−32.9**
K92-08		CHA	dol limestone	33.4	−4.4	−5.0	4.05		k	**−34.1**
K92-09		CHA	strom limestone	63.5	−4.3	−6.9	0.29	3+		−31.2
K92-10		CHA	mudstone	0.3			0.54	3+		−29.5
K92-11		CHA	shale	0.4			0.28	3+		−27.9
K92-12		CHA	shale	0.1			0.29	3+		n.d.
K92-13		CHA	limestone	39.5	−6.4	−6.1	0.07			−23.7
K92-14		CHA	limestone	32.5	−6.3	−7.3	0.12			−27.4
K92-15		CHA	carbonate	1.1			0.21			−24.9
K92-16		CHA	shale	0.2			0.47	3+		n.d.
K92-17		CHA	shale	0			0.30	3+		−26.1
K92-18		CHA	shale	0			3.30	4−	k	**−29.7**
K92-19		CHA	shale	0			2.48		k	**−29.6**
K92-20		CHA	phosphates	0			2.61	3+	k	**−30.6**

Table 2. Abundances of C, H and N and associated elemental ratios and ash content for analyzed kerogen.

Sample	N(%)	C(%)	H(%)	H/C	Ash(%)
K91-01	1.29	60.9	1.97	0.39	35.8
K91-04	0.11	4.92	n.d.	n.d.	<95.0
K91-07	0.40	23.0	1.02	0.53	75.6
K91-09	0.57	38.5	1.86	0.58	59.1
K91-11	0.13	9.55	0	n.d.	90.3
K91-12	0.50	31.1	0.84	0.32	67.3
K91-16B	0.16	24.4	0.38	0.19	75.0
K91-18	0	8.08	0.20	0.29	91.7
K91-19	0.25	27.0	0.35	0.15	72.4
K91-20	0.08	13.0	0.83	0.76	86.1
K91-21	0.09	21.8	0.82	0.45	77.3
K91-22	1.17	49.9	1.55	0.37	47.3
K91-23	1.10	46.5	1.72	0.44	50.6
K91-26	0.11	21.4	1.18	0.66	77.3
K91-29	0.56	25.7	0.99	0.46	72.7
K91-30	0	2.47	0	n.d.	97.5
K91-30'	0.54	26.2	0.85	0.39	72.4
K91-31	0	16.0	0.90	0.68	83.1
K92-02	0.14	12.1	0.52	0.51	87.3
K92-03	0.39	26.1	1.23	0.56	72.3
K92-04	0.10	10.4	0.62	0.71	88.8
K92-06	0.16	16.6	0.75	0.54	82.4
K92-08	0.40	16.7	0.75	0.54	82.1
K92-18	0.72	58.2	4.99	1.03	36.1
K92-19	0.60	38.8	2.85	0.88	57.8
K92-20	0.67	35.2	1.85	0.63	62.3

from the Kildinskaya Group on Sredni was also analysed (Table 1). The whole-rock isotopic abundances varied widely, $\delta^{13}C_{carb}$ between -13.3 and $-0.1‰$, and corresponding whole-rock $\delta^{18}O$ between -13.6 and $-5.1‰$ (Table 1). The amount of carbonate in the samples studied here ranged from 0.1 to 94.3%, with the majority of the samples containing very little or no carbonate at all (Table 1). Element abundances (Ca, Mg, Sr, Fe, Mn) of the Kola Peninsula carbonates vary extensively: Ca between 14.6 and 39.0%, Mg between 0.497 and 11.4%, Sr between 25 and 265 ppm, Fe between 0.118 and 7.06% and Mn between 0.117 and 1.41% (Table 3). The $\delta^{13}C_{part}$ for sub-sampled carbonates ranges between -12.2 and $+0.7‰$, comparable to corresponding whole-rock values (Table 4; Fig. 6). The $\delta^{18}O_{part}$ values vary between -15.1 and $-0.9‰$, a greater range than for corresponding whole-rock values (Table 4).

Table 3. Element abundances (Ca, Mg, Sr, Fe, Mn) for the Kola carbonates.

Sample	Ca %	Mg %	Sr ppm	Fe %	Mn %	Mn/Sr	Mg/Ca
K91-34	33.9	2.52	140	1.73	0.514	37	0.074
K91-35	22.1	10.1	41	2.92	0.298	73	0.458
K91-36	20.9	10.5	25	4.33	0.324	128	0.504
K91-06	21.6	11.2	32	2.40	0.402	128	0.519
K91-37	20.6	11.4	33	2.57	0.414	126	0.551
K91-02	37.2	0.497	249		1.39	56	0.013
K91-33	38.2	0.924	144	0.118	0.117	8	0.024
K91-13congl	14.6	7.97	109	4.65	1.41	129	0.547
K92-05	32.7	0.796	177	1.33	1.00	57	0.024
K92-08	21.2	4.46	193	7.06	0.272	14	0.210
K92-09	39.0	1.35	265	1.77	0.373	14	0.035
K92-13	27.9	1.90	187	2.93	0.451	24	0.068
K92-14	28.8	1.26	218	2.32	0.510	23	0.044

Cathodoluminescence examination of carbonate-thin sections yielded somewhat variable, but generally orange-red, brightly luminescent images.

Preservation of organic matter

In general, carbon preserved as sedimentary organic matter is a mixture of detrital carbon derived from various sources. In the Proterozoic, these sources would have included dissolved organic compounds, particulate organic matter and whole cells or larger cellular aggregates (Hayes et al. 1983). Organic carbon derived from different sources has different isotopic signatures (Schidlowski et al. 1983). However, the isotopic value of sedimentary organic carbon is strongly affected by post-depositional processes that cause severe alteration or even complete loss of primary signals. The aim of the present work is to try to recognize primary temporal rather than alteration trends of the sedimentary organic matter. It is therefore necessary to evaluate the state of preservation of the C_{org} prior to a discussion of the significance of the $\delta^{13}C_{org}$ values obtained.

Two essentially different processes account for the modification and subsequent isotopic alteration of sedimentary organic matter, biological reworking and thermal maturation. Biological reworking within the sediment has the potential to impose an additional fractionation of the primary value, whereas thermal alteration ultimately results in ^{13}C-enriched organic matter (Hayes et al. 1983; Strauss et al. 1992e). A reliable way of assessing the degree of thermal alteration is by comparing the colour of preserved sedimentary organic matter to a known standard.

The colour of preserved kerogen seen in strew slides can range from pale yellow to black depending on the extent to which it has been thermally modified. In order to quantify the kerogen colours, a thermal alteration index (TAI) has been introduced (Pearson 1984). The obtained TAI values (Table 1) are indicative of burial temperatures between 100 and 200°C. The higher temperatures correspond to a metagenesis stage of thermal alteration. Isotopic shifts in kerogen during low-temperature diagenesis and catagenesis are usually minor, but once metagenesis and metamorphism begin, substantial displacements in the original C-isotopic composition of the C_{org} are possible (Strauss et al. 1992c).

Isolated kerogens were analysed for their elemental composition (C, H, N) as a reliable way to assess their preservation (Hayes et al. 1983; Strauss et al. 1992c). In particular, the H/C value is meaningful as it approaches zero for extensively thermally altered organic matter. Recently deposited organic matter, depending on its source, has an H/C ratio approaching 2 (Strauss et al. 1992c). A low H/C ratio (<0.2) suggests loss of ^{12}C-rich portions from the kerogen that results in significant isotopic shifts towards higher $\delta^{13}C_{org}$ values, obliterating any primary biogeochemical signal (Strauss et al. 1992c).

Table 4. Carbon and oxygen values from sub-sampled carbonates together with whole-rock isotope data and $\Delta\delta$ of C_{org}/C_{carb} pairs for the sub-sampled portions. Abbreviations: WR = whole rock; CL = cathodoluminescence; NL = non-luminescent portion; LL = least luminescent portion; ML = medium luminescent portion; HL = highly luminescent portion.

Sample	Category	$\delta^{13}C_{WR}$ (‰, PDB)	$\delta^{18}O_{WR}$ (‰, PDB)	$\delta^{13}C_{PART}$ (‰, PDB)	$\delta^{18}O_{PART}$ (‰, PDB)	$\Delta\delta$ (for sub-sampled value)
K91-02	WR	−0.7	−9.6	n.d.	n.d.	25.0 (WR)
K91-06-I	no CL	−0.4	−8.4	−0.6	−8.3	24.5
K91-06-II	no CL			−0.1	−7.5	25.0
K91-13-I	LL	−13.2	−6.0	−6.5	−6.3	21.6
K91-13-II	HL			−12.2	−5.6	15.9
K91-33-I	ML	−0.1	−9.4	0.7	−6.8	35.2
K91-33-II	ML			0.4	−7.7	34.9
K91-34-I	HL	−2.8	−13.6	−3.4	−15.0	25.4
K91-34-II	HL			−3.7	−15.1	25.2
K91-35-I	HL	−1.1	−9.0	−1.4	−9.4	
K91-35-II	ML			−1.3	−9.4	
K91-36-I	NL	−2.4	−8.4	−2.8	−9.0	26.2
K91-36-II	NL			−2.5	−8.6	26.5
K91-37-I	ML	−0.2	−8.2	−0.6	−8.6	21.7
K91-37-II	ML			0.4	−7.4	22.5
K92-05-II	HL	−5.5	−8.8	−5.4	−8.4	21.0
K92-08-I	ML	−4.4	−5.0	−4.0	−5.8	30.1
K92-08-II	ML			−3.6	−4.8	30.5
K92-08-III	ML			−3.7	−5.1	30.4
K92-09-I	LL	−4.3	−6.9	−2.8	−0.9	28.4
K92-09-II	HL			−5.1	−10.9	26.1
K92-09-III	HL			−4.4	−6.5	26.8
K92-13-II	HL	−6.4	−6.1	−6.5	−6.3	17.2
K92-14-I	HL	−6.3	−7.3			21.1 (WR)

In Fig. 2, the $\delta^{13}C_{org}$ values of analyzed kerogens are plotted against corresponding H/C ratios. Two values have H/C < 0.2 (Table 2; Fig. 2).

Kerogen samples rich in ash (the amount of mineral matter present in the kerogen residue after combustion) might yield systematic analytical errors. This error arises because samples rich in inorganic material usually carry excess hydrogen, in the form of water of hydration, bound to the inorganic contaminants, thus shifting the H/C ratios to higher values (Hayes et al. 1983). Taking this into consideration, Des Marais et al. (1992), in their discussion of the Proterozoic organic carbon isotopic record, considered only those kerogens with an ash content less than 25%. The ash content of the samples from the Kola Peninsula is much higher than 25%; however, there is no correlation between high ash content and high H/C values within th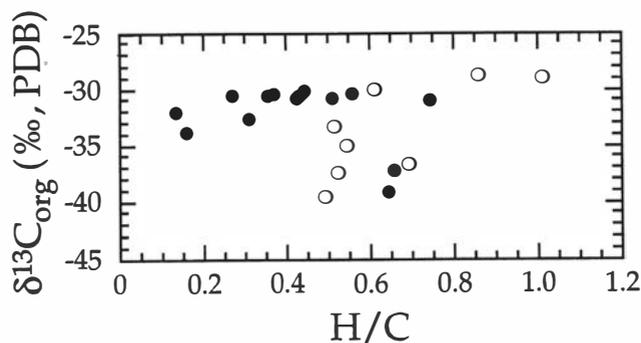is suite of samples (Fig. 3). There-fore, it can be concluded that the H/C values obtained from the Kola Peninsula samples not are systematically in error because of their high ash content.

Judging from the colour and the H/C values of the investigated samples, the sedimentary organic matter from the Kola Peninsula has undoubtedly been altered. In this report, the least altered kerogen samples are considered to have TAI < 4− and H/C > 0.2. These $\delta^{13}C_{org}$ values are marked in bold in Table 1.

Isotopic composition of organic carbon

Hayes et al. (1983) demonstrated that the $\delta^{13}C_{org}$ of a given unit tends to increase as concentrations of C_{org}
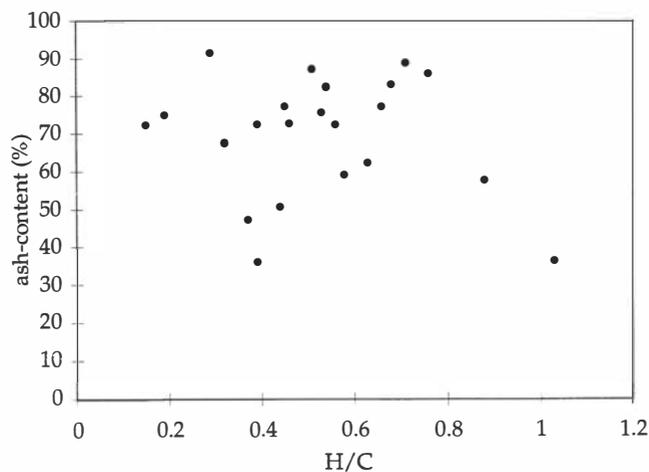

Fig. 2. Plot of the H/C ratios and corresponding $\delta^{13}C_{org}$ values for isolated kerogens. The filled circles denote values obtained from samples taken from strata on the Sredni/Rybachi Peninsula and Kildin Island; open circles for samples from the Tiersky Coast. (See main text for discussion.)

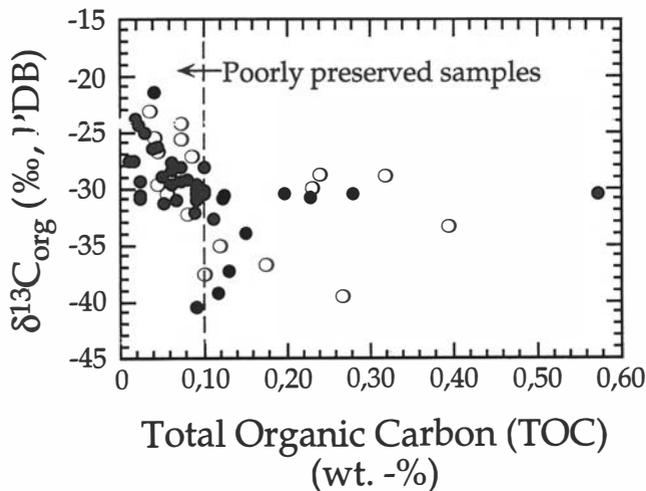*Fig. 3.* Plot of the H/C ratios and corresponding ash content for *all* isolated kerogens. (See main text for discussion.)

Fig. 4. Plot of Total Organic Carbon (TOC) and $\delta^{13}C_{org}$ for *all* organic carbon values. Filled circles = samples from the Sredni/the Rybachi Peninsula and Kildin Island; open circles = samples from the Tiersky Coast.

decline. The cross plot in Fig. 4 is consistent with their observation. In addition, samples having low TOC are likely to be affected by contamination with recent organic matter, commonly resulting in $\delta^{13}C_{org}$ approaching values of modern terrestrial C_{org}, −23 to −25‰ (Narbonne et al. 1994). Five of the low TOC samples from the Kola Peninsula have values that lie within this lower critical interval (Table 1). Following previous practice, only those samples with TOC > 1 mgC/g are given further consideration (Hayes et al. 1983; Kaufman & Knoll 1995).

Four different localities on the Kola Peninsula were investigated for stable isotope geochemistry. From the Kildin Island, two well-preserved C_{org}-isotopic values of shales from the Kildinskaya Group yielded $\delta^{13}C_{org} = $ −31.4‰ and −28.9‰ respectively. On the Sredni Peninsula, well-preserved C_{org} isotopic values from the Kildinskaya Group range between −33.4 and −31.1‰, and from the Volokovaya Group a single well-preserved kerogen sample yielded $\delta^{13}C_{org} = $ −39.9‰. From the Rybachi Peninsula, only one sample, K91-20 from the Skarbeevskaya Formation, yielded a C_{org}-isotopic signal regarded as primary ($\delta^{13}C_{org} = $ −31.9‰). On the Tiersky Coast, the investigated Chapoma Formation yielded six well-preserved $\delta^{13}C_{org}$ values, ranging between −40.4 and −29.6‰ (Table 1).

Two of the well-preserved samples yielded $\delta^{13}C_{org}$ values of −39.9‰ (K91-26) and −40.4‰ (K92-02) respectively. A variety of post-depositional reactions, including methanotrophy and sulphide- or ammonia-oxidation resulted in a biomass depleted in ^{13}C (Irwin et al. 1977; Strauss & Beukes 1996). Accumulation of isotopically light biomass as a result of bacterial reworking of sedimentary organic matter in the total organic carbon might thus explain the low $\delta^{13}C_{org}$ values observed herein. These low $\delta^{13}C_{org}$ values cannot be regarded as characteristic of primary values typical for organic matter which was formed in the surface waters.

Secular variations of organic carbon

Carbon-isotope values obtained from C_{org} have been utilized for chemostratigraphic correlations in the Proterozoic (see e.g. Knoll et al. 1986; Strauss et al. 1997), and several studies show covariation of the C-isotopic curve for both C_{org} and C_{carb} in well-preserved successions (e.g. Knoll et al. 1986; Narbonne et al. 1994). Previously reported secular C_{org}-isotopic variations in Late Proterozoic sections are few, but suggest $\delta^{13}C_{org}$ values of shales in the interval from −30.6 to −22.2‰ and of carbonates in the interval from −30.4 to −22.2‰ (Strauss et al. 1992e). Organic carbon in whole-rock samples from several different Proterozoic localities world-wide has previously been reported (Strauss & Moore 1992). Their report shows that for shale samples with TOC > 1 mgC/g, $\delta^{13}C_{org}$ values range from −32.2 to −25.1‰ for the time-interval 700–900 Ma. More systematic studies on Early Neoproterozoic C_{org}-isotopic values were carried out by Knoll et al. (1986, 1995b). Broadly time-equivalent successions to those on the Kola Peninsula that were investigated for their C_{org} isotopes by Knoll et al. included the Veteranen and Akademikerbreen Groups, Spitsbergen, Svalbard; the Franklinsundet, Celsiusberget and Lower and Middle Roaldtoppen Groups in Nordaustlandet, Svalbard (Knoll et al. 1986); and the Turukhansk Uplift in northwestern Siberia (Knoll et al. 1995b). The $\delta^{13}C_{org}$ values from Svalbard range between −33.1 and −11.4‰ (Knoll et al. 1986; Strauss & Moore 1992). The most ^{13}C-enriched of the Svalbard values are certainly from diagenetically altered samples. In the Turukhansk Uplift, the $\delta^{13}C_{org}$ values plot in a much more narrow interval between −30.8 and −27.0‰ (Knoll et al. 1995b).

In comparison with C_{org}-isotopic data from contemporary early Cryogenian successions discussed above, the isotopic values obtained from the best-preserved sedimentary organic matter from the Kola Peninsula yielded values in agreement with these data.

Assessment of carbonate diagenesis

Whole-rock analyses of Proterozoic limestones and dolostones are commonly comparable to depositional isotopic compositions (Narbonne et al. 1994 and references therein). However, in certain cases, substantial post-depositional isotopic shifts arise, and samples should therefore be evaluated for possible alteration (Zempolich et al. 1988; Fairchild et al. 1990; Narbonne et al. 1994). Recently, several papers have dealt with the general theoretical background to evaluating the signal quality obtained from carbonates (e.g. Marshall 1992; Narbonne et al. 1994; Kaufman & Knoll 1995).

The C-isotopic composition of a non-metamorphosed carbonate can be modified by re-equilibration with fluids of different isotopic composition during neomorphism or recrystallization, or by the addition of isotopically distinct carbonate to the rock (Kaufman & Knoll 1995).

Neomorphism or recrystallization might alter C-isotopic values if accompanied by adequate permeability and access to meteoric waters (Fairchild et al. 1990). In comparison to calcite, dolomite is enriched in ^{13}C by about 2‰ (Sheppard & Schwarcz 1970). The oxygen isotope fractionation observed between Holocene calcite and dolomite ranges between 2 and 4‰ (Land 1980; McKenzie 1984). However, several studies have shown that most Proterozoic dolomites are isotopically indistinguishable from associated limestones and could equally well preserve a primary signal (Tucker 1983; Knoll et al. 1986; Fairchild et al. 1991).

Either ^{13}C enrichment or depletion occurs where secondary carbonates are precipitated in response to organic matter degradation by bacteria in organic-rich sediments (Irwin et al. 1977). A number of other processes that ultimately result in alteration or destruction of the primary C-isotopic signal exist, but for Proterozoic carbonates these are of limited importance (Kaufman & Knoll 1995).

The element concentrations of Ca, Mn, Sr, Fe, and Mg are important for understanding the degree of post-depositional alteration, as the abundances of these elements are typically modified by formation waters. The Mn/Sr ratio has proved to be especially useful for evaluating sample quality (Veizer 1983; Popp et al. 1986; Derry et al. 1992; Kaufman et al. 1992, 1993). This is because under the influence of meteoric fluids, Sr is expelled from carbonates, while Mn and Fe are incorporated (Hayes et al. 1989 and references therein). Kaufman & Knoll (1995) observed that both limestones and dolostones with Mn/Sr < 10 commonly retain near-primary $\delta^{13}C_{carb}$ values.

Oxygen-isotopic compositions are sensitive indicators of diagenesis, as meteoric or hydrothermal water alteration commonly results in depletion of ^{18}O or both ^{18}O and ^{13}C in carbonates (Fairchild et al. 1990). Because the primary O-isotopic composition of Neoproterozoic carbonate is understood to have ranged between -5 and 0‰, Kaufman & Knoll (1995) proposed that δ^{18}O of the carbonates with values less than -5‰ represent some degree of O-isotopic alteration, and they regarded samples with values below -10‰ as unacceptably altered.

Another way of recognizing diagenetic effects and concomitant isotopic shifts in C_{carb} is to study the difference between the isotopic compositions of C_{carb} and C_{org} pairs. Precipitation of carbonate in seawater and generation of organic matter by photosynthetic organisms in the same water tend to maintain a constant isotopic difference between C_{carb} and C_{org}, but diagenetic processes commonly alter the isotopic composition in either C_{carb} or C_{org}. The magnitudes and the directions of the isotopic shifts are controlled by several unrelated factors (Knoll et al. 1986; Narbonne et al. 1994). In examining thick Neoproterozoic successions in Svalbard and East Greenland, Knoll et al. (1986) concluded that the isotopic fractionation between C_{carb} and C_{org}, defined as $\Delta\delta = \delta^{13}C_{carb} - \delta^{13}C_{org}$, yields $\Delta\delta = 28.5 \pm 2$‰ for this time interval. A slightly greater $\Delta\delta$ value of 33 ± 2‰ appears to be representative for Vendian sediments (Kaufman & Knoll 1995).

It is necessary to sub-sample in detail because of heterogeneities in isotopic and elemental composition between various carbonate phases in whole-rock samples (Hudson 1977; Kaufman et al. 1991). The first step in sub-sampling is commonly cathodoluminescence examination (Narbonne et al. 1994; Kaufman & Knoll 1995). In sedimentary carbonates, luminescence is activated by Mn^{2+} concentrations of approximately 100 ppm and quenched by Fe^{2+} concentrations greater than 10,000 ppm (Hemming et al. 1989), although Savard et al. (1995) recently showed that other factors may also influence cathodoluminescence.

Some of the Kola Peninsula carbonates are partially or completely dolomitized as shown by high concentrations of Mg and the Mg/Ca ratios (Table 3). The dolomites have elevated Mn/Sr ratios and the limestones tend to have comparably lower Mn/Sr. In comparison to other Proterozoic carbonates, e.g. those from the Shaler Group, the Upper Tindir Group and the Windermere Supergroup, northwestern Canada (Asmerom et al. 1991; Kaufman et al. 1992; Narbonne et al. 1994), the Kola carbonates generally show Mn/Sr values several orders of magnitude higher than those from the units mentioned above. Furthermore, in the present sample population, only a single sample, K91-33, has Mn/Sr < 10 (Table 3). Variable carbonate contents between 32.1 and 94.3% are indicative of the presence of siliciclastic material. CL analyses revealed a more or less homogeneous bright orange-red luminescence suggesting an advanced degree of diagenetic alteration. This observation is corroborated by increased abundances of Fe and Mn. In other words, the elemental abundances within these samples indicate substantial diagenetic alteration.

Oxygen isotope values for whole-rock Kola carbonate samples are much lower than the proposed critical $\delta^{18}O < -5$‰, and with two sole exceptions the same observation also applies to the δ^{18}O values obtained from the sub-sampled portions (Table 4). The O-isotopic values are thus corroborating the conclusion above that the carbonates have been diagenetically altered. Fig. 5 shows cross-plots of δ^{18}O vs. the concentrations of Sr and Mn respectively, further supporting this interpretation. The cross-plot of δ^{18}O and the corresponding $\delta^{13}C_{carb}$ in Fig. 6 shows that the $\delta^{13}C_{carb}$ values vary with decreasing δ^{18}O values. A positive correlation between $\delta^{13}C_{carb}$ and δ^{18}O is typical of carbonates altered by meteoric fluids (Veizer 1983; Derry et al. 1992; Marshall 1992). Note that the $\delta^{13}C_{carb}$ values obtained from the Chapoma Formation are more depleted (with ca. 2 per mil units) than those from the Murmansk Coast, one possible explanation being that the Chapoma Formation was deposited in a shallow-water environment where sediments are generally exposed to meteoric waters before reaching mineralogical stability (Marshall 1992). The sub-sampled C- and O-isotopic values have also
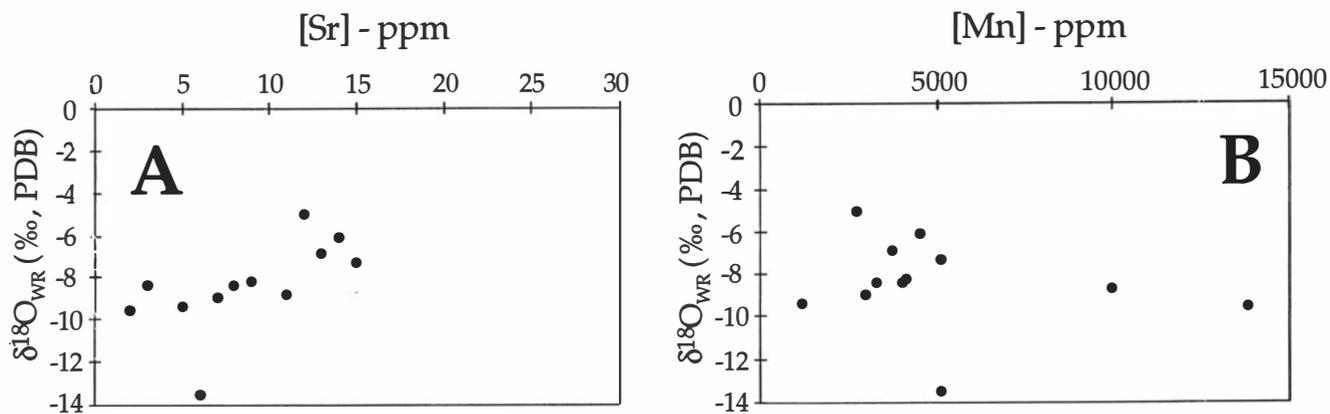
Fig. 5. Plots of Sr and Mn vs. $\delta^{18}O$ values of all analyzed whole-rock carbonates.

been plotted in Fig. 6. The figure clearly shows that the sub-sampled values are generally both less ^{13}C-depleted and display a greater range of variability than corresponding whole-rock values.

Samples with low $\Delta\delta$ values are common among the present carbonates (Table 4). The average $\Delta\delta$ for whole rock samples is 24.6 ± 9.8‰ ($n = 7$) for samples from the Murmansk Coast, and 23.5 ± 6.2‰ for samples from the Tiersky Coast, indicating that the effects of organic diagenesis are of major importance for the carbonate samples investigated herein. Using the $\Delta\delta = 28.5 \pm 2$‰, as discussed above, carbonate samples with $\Delta\delta < 26.5$‰ are herein regarded as altered.

All tests performed to evaluate the state of diagenesis of the Kola Peninsula carbonates have yielded the same result, namely that these rocks have been subject to severe diagenetic alteration. Of the 13 investigated carbonates, only a single sample, K91-33 from the Kildin-skaya Group on Kildin Island, can be regarded as providing a close-to-primary signal. Even if somewhat more generous criteria are employed for the present samples (Mn/Sr = 73, $\delta^{18}O > -10$‰ and $\Delta\delta > 26.5$), only two additional samples, K92-08 and K92-09 from the Chapoma Formation, Tiersky Coast, can be added. The conclusion must therefore be that with only one or possibly three exceptions, the present carbonate samples are too severely altered to be of any direct use for chemostratigraphy. Bearing this in mind, it is still interesting to compare the present C_{carb}-isotopic data to earlier presented data sets for the Cryogenian time frame.

Isotopic composition of carbonate carbon

Highly variable $\delta^{13}C_{carb}$ values characterize the early Cryogenian where periods of deposition of ^{13}C-enriched carbonates were followed by intervals of ^{13}C-depleted seawater and associated carbonate deposition (Kaufman & Knoll 1995). Times of deposition of ^{13}C-depleted carbonates appear to have occurred directly after the Neoproterozoic glaciations (Kaufman et al. 1993; Nar-

bonne et al. 1994). To date, a limited number of early Cryogenian successions have been investigated for stable isotope geochemistry, as discussed previously. These successions generally show the same pattern of $\delta^{13}C_{carb}$ variations. Values range between -5.8 and $+5.4$‰ in the Veteranen and lower Akademikerbreen Groups, Spitsbergen, and equivalents in Nordaustlandet and East Greenland (Knoll et al. 1986); between -3.3 and $+2.8$‰ in the Atar Group, Mauretania (Fairchild et al. 1990); from -3.9 to $+8.9$‰ in the Otavi Group, Namibia (Kaufman et al. 1991); between -5.0 and -3.1‰ in the Pocatello Formation, Idaho (Smith et al. 1994); and from -2.7 to $+4.6$‰ in the Turukhansk Uplift, Siberia (Knoll et al. 1995b). These isotopic ranges are comparable to those obtained from the Early Neoproterozoic carbonates of the Kola Peninsula around a whole rock average of -1.5 ± 1.4‰ ($n = 7$) for the samples from the Murmansk Coast (excluding the conglomerate sample) and a whole rock average of -5.4 ± 1.0‰ ($n = 5$) for samples from the Tiersky Coast (Fig. 7).

As discussed above, whole-rock isotope values commonly approximate sub-sampled values; this is generally also the case with the Kola Peninsula carbonates (Table 4; Fig. 6). Usually, non- or moderately luminescent portions of the rock yield the least depleted isotopic value of the entire sample (see e.g. Kaufman et al. 1991; Kaufman & Knoll 1995; Knoll et al. 1995a), and this observation is corroborated by the present data. In order to assign a representative value for each sample, the least depleted value from the least luminescent portion of the sub-sampled rock should therefore be chosen (compare Kaufman et al. 1992; Narbonne et al. 1994; Kaufman & Knoll 1995). From the Murmansk Coast, a single limestone sample (K91-33) passed all the screening tests to determine the degree of diagenetic alteration. This sample yielded a representative sub-sampled $\delta^{13}C_{carb} = +0.7$‰ (Table 4). From the Tiersky Coast, two other limestone samples supply a close-to-primary isotopic value, yielding for K92-08 a $\delta^{13}C_{carb} = -3.6$‰ and for K92-09 a $\delta^{13}C_{carb} = -2.8$‰, for the least depleted sub-sampled portions of respective samples (Table 4). In the light of these observations, I suggest that a primary
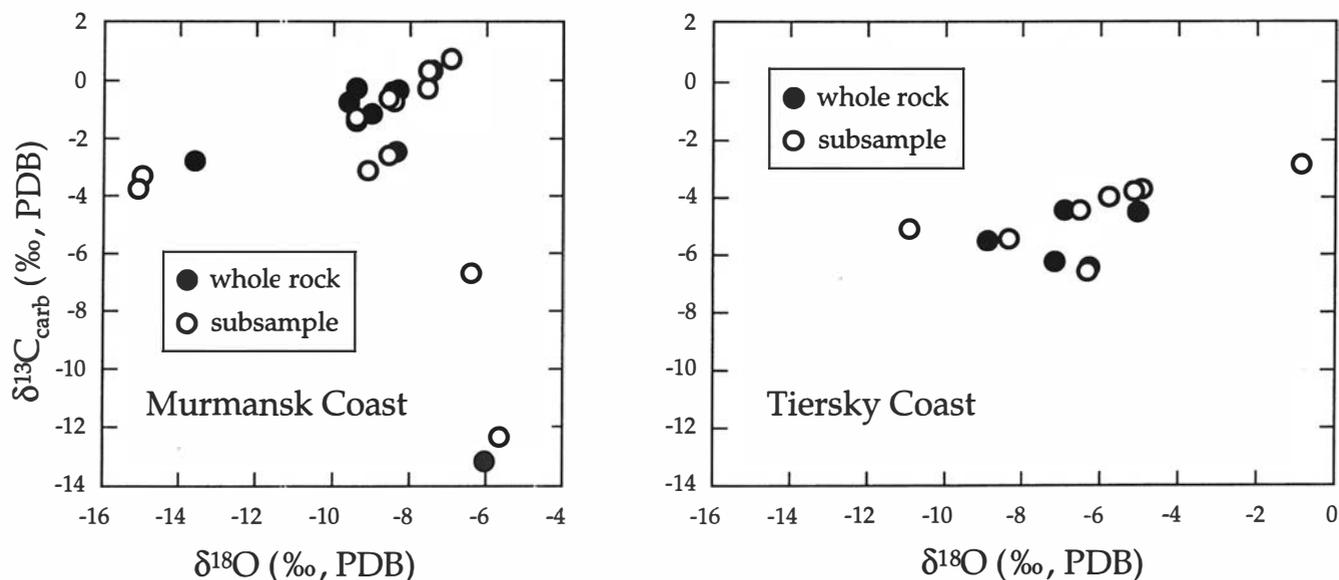
Fig. 6. Plot of $\delta^{18}O$ and $\delta^{13}C_{carb}$ for whole-rock carbonates. Filled circles indicate whole-rock data and open circles sub-sampled data for the Murmansk and Tiersky Coasts, respectively.

$\delta^{13}C_{carb}$ value for the Kildinskaya Group on Kildin Island of +0.7‰ appears to be characteristic of the seawater composition for the time interval of Kildinskaya Group deposition.

Summary and conclusions

The amount of total organic carbon (TOC) within the present samples is comparable to the average for other Neoproterozoic successions, with shales and mudstones displaying the highest values (Strauss et al. 1992b). Several different methods of assessing the quality of the C-isotopic signatures obtained from the preserved organic matter indicate that most of the samples are either poorly preserved or contaminated by recent organic matter. The C_{org}-isotope values regarded as reflecting primary depositional values range between −33.4 and −28.9‰; these values are comparable to values obtained from other Neoproterozoic units.

Fig. 7. Summary of whole-rock carbon isotope data for the samples examined herein (*n* = number of samples).

Thirteen of the present samples are carbonates, and (with a single exception) they all derive from the Kildinskaya Group on Kildin Island and the Chapoma Formation on the Tiersky Coast. Some of the carbonates are dolomitized. Several different approaches to evaluate the C-isotopic signals obtained from all carbonate samples indicate that their isotope signals have been modified by meteoric waters and/or other post-depositional processes. Even when adopting generous limits for the critical parameters in sample evaluation, only three carbonate samples qualify for further stratigraphic consideration. From the Kildinskaya Group on Kildin Island, the least ^{13}C-depleted sub-sampled portion of K91-33 yielded $\delta^{13}C_{carb}$ = +0.7‰. This value reflects the primary depositional value of seawater at the time of deposition of the Kildinskaya Group. From the Chapoma Formation on the Tiersky Coast, the least depleted K92-08 and K92-09 sub-samples yielded $\delta^{13}C_{carb}$ = −3.6‰ and −2.8‰ respectively. These values are in agreement with $\delta^{13}C_{carb}$ values obtained from other early Cryogenian successions in Svalbard and East Greenland, for example.

Unfortunately, very limited information about variations in the sedimentary carbon cycle during the Early Neoproterozoic can be acquired from the predominantly siliciclastic Murmansk and Tiersky Coast successions on the palaeocontinent Baltica. Nevertheless, the information generated herein contributes to the growing body of stable isotope geochemical data for a particularly interesting interval in the Earth's history.
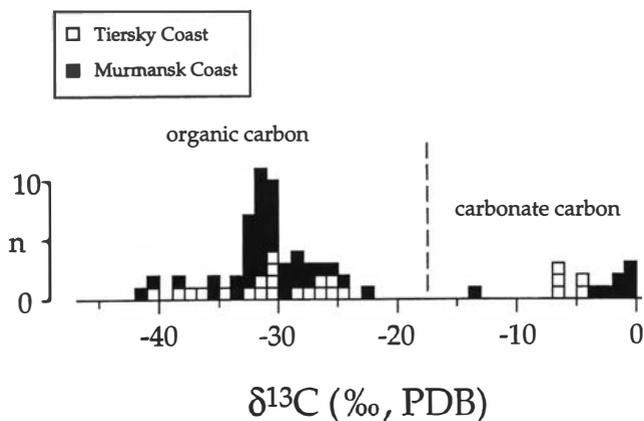
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Appendix

On the Sredni Peninsula, the samples derived from the following formations (geological data are according to Siedlecka et al. 1995a):

1. Three samples from the Iernovskaya Formation. On the Sredni, the Iernovskaya Formation is dominated by sandstones and interbedded mudstones.
2. Eleven samples from the Poropelonskaya Formation. The unit rests with erosional contact on the preceeding Palvinskaya Formation. The Poropelonskaya Formation is predominantly composed of muddy–clayey and sandy shales. Subordinate sandstones also occur.
3. Two samples from the Zemlepakhtinskaya Formation. This formation consists of grey feldspathic sandstones with subordinate beds of silty shales and intraformational conglomerates. It also contains lenses of reworked phosphorites (Negrutsa et al. 1995).
4. Two samples from the Karuyarvinskaya Formation. The unit consists of multi-coloured, fine-grained, terrigenous sediments and laminated dolomites.
5. Six samples from the Kuyakanskaya Formation. The Kuyakanskaya Formation of the Volokovaya Group consists primarily of sandstones and at its base includes a coarse-grained polymict conglomerate. The conglomerate contains clasts of phosphorites, geochemically comparable to phosphorites in the underlying Zemlepakhtinskaya Formation.
6. One sample from the Pumanskaya Formation. The Pumanskaya Formation also belongs to the Volokovaya Group, and consists predominantly of muddy shale with subordinate interbeds of sandstone.

On Kildin Island, the samples derive from Lyubtsov et al. (1990):

1. One sample from the Iernovskaya Formation. In its exposed parts, the formation is characterized by dark-grey muddy shale.
2. Three samples from the Korovinskaya Formation. This formation is represented by 55 m of green-grey muddy sandstone with lenses of glauconitic sandstone and stromatolitic carbonates.
3. Two samples from the Bezymyannaya Formation. Resting conformably on the previous unit, the Bezymyannaya Formation consists predominantly of oncolithic dolomite.
4. Four samples from the Chernorechenskaya Formation. The formation is characterized by red-coloured, very weakly metamorphosed argillaceous rocks, siltstone and limestone. In the middle part of the formation, stromatolitic dolomites are present.
5. One sample from the Pestzovozerskaya Formation. Within this unit, layers of alternating subgreywacke, claystone and muddy sandstone occur.

On the Rybachi Peninsula, the investigated samples derive from geology according to Siedlecka et al. (1995b):

1. One sample from the Motovskaya Formation. This formation is the lowermost unit on the Rybachi and belongs to the Einovskaya Group. It consists mainly of conglomerates and pebbly, coarse-grained sandstones.
2. Six samples from the Skarbeevskaya Formation. The Skarbeevskaya Formation consists mainly of sandstones, mudstones and clayey shales with some carbonates and subordinate conglomerates also present.