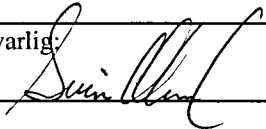


NGU Rapport 96.086

**Carbonate rocks of Karelia: geochemistry
and carbon-oxygen isotope systematics in the
Jatulian stratotype and potential for
magnesite deposits.**

Rapport nr.: 96.086		ISSN 0800-3416	Gradering: Open
Tittel: Carbonate rocks of Karelia: geochemistry and carbon-oxygen isotope systematics in the Jatulian stratotype and potential for magnesite deposits.			
Forfatter: Melezhik, V., Fallick, A., Medvedev, P. & Makarikhin, V.		Oppdragsgiver: NGU	
Fylke: Karelia		Kommune: Petrozavodsk	
Kartblad (M=1:250.000) unknown		Kartbladnr. og -navn (M=1:50.000) unknown	
Forekomstens navn og koordinater: Onega magnesite 35° 25' 00 "E, 62° 14' 29" N		Sidetall: 61	Pris: 153,-
Feltarbeid utført: September 1995		Rapportdato: 06.06.96	Prosjektnr.: 67.6421.02
		Ansvarlig: 	
Sammendrag: Closely spaced samples (73 in number) of shallow water, red, stromatolitic dolomite and magnesite from the Palaeoproterozoic (1980±27 Ma as a minimum age) Tulomozerskaya Formation in a distal portion of the Onega palaeobasin, Russian Karelia, have been analysed for $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$, trace and major elements. The 800 m-thick terrigenous-carbonate succession is interpreted to be formed in lacustrine evaporitic settings prograding to sabkha, and then to marine environment. The carbonate rocks (essentially stromatolitic dolostones with minor magnesites), despite their depositional settings, exhibit throughout isotopically heavy carbon. The $\delta^{13}\text{C}$ values range from +5.7 to +17.2‰ (mean +9.9±2.3‰) and $\delta^{18}\text{O}$ from +18.6 to +26.0‰ (mean +22±1.6‰). The $\delta^{13}\text{C}$ records show a substantial downward increase from +8‰ up to +17.2‰ while the $\delta^{18}\text{O}$ values display no systematic variations. Dolostones were precipitated from the diagenetic pore-water which was apparently isotopically similar to the basinal water. Magnesite occurs in a number of 1 to 2 m-thick layers and formed as a secondary phase during early diagenesis under evaporitic conditions. The magnesite mineralisation is considered to be similar to the Coorong type (playa lake) and based on that evaluated as sub-economic. None of the recent environments developed under normal conditions can provide a model which may result in the formation of large amount of carbonates with $\delta^{13}\text{C}$ falling between +5 and +17‰ such as the case for the Tulomozerskaya dolostones. Diagenetic and evaporative models, as well as a model of restricted basin with high bioproduction, are not applicable as they are in conflict with existing data. The rise of $\delta^{13}\text{C}$ in the Onega palaeobasin must have generated in a global or semi-global scale as indicated by its continuity across the Fennoscandian Shield through Scotland and Canada. The excess Corg deposition which must have caused the $\delta^{13}\text{C}$ anomaly, took place in an area external to the Onega palaeobasin. The tectonic model by Des Marais (Des Marais et al. 1992; Des Marais 1994), the stratified ocean as proposed by Keith (1992), and a model of stromatolitic basin (Shark Bay model) have been discussed as possible mechanisms leading to the rise in $\delta^{13}\text{C}$ in the carbonate formation studied.			
Emneord: Industrimineraler	Magnesitt	Isotop	
Geologisk undersøkelse	Prekambrium		

CONTENTS

1	INTRODUCTION.....	5
2	INDUSTRIAL DEMANDS AND SCIENTIFIC PROBLEM.....	5
3	GEOLOGICAL BACKGROUND.....	7
4	LITHOSTRATIGRAPHY AND PALAEOENVIRONMENTS OF THE TULOZOZERSKAYA FORMATION.....	11
5	RESULTS.....	16
6	EVALUATION OF DIAGENESIS.....	23
7	INTERPRETATION OF ^{13}C ENRICHMENT.....	24
	7.1 <i>Diagenetic model</i>	25
	7.2 Model of evaporitic basin.....	26
	7.3 Model of restricted basin with high bioproduction.....	30
	7.4 Tectonic model (Des Marais model).....	34
	7.5 Model of oceanic anoxic event.....	35
	7.6 Model of stromatolite basin (Shark Bay model).....	36
8	ORIGIN OF Mg-RICH CARBONATES.....	41
9	CONCLUSIONS.....	43
	REFERENCES.....	46

FIGURES

Fig. 1:	Geographical and geological position of the studied area.....	6
Fig. 2:	Geological map of the northern Onega Lake area.....	8
Fig. 3:	Lithostratigraphical subdivisions of the northern Onega Lake area and position of studied drill holes.....	9
Fig. 4:	Lithostratigraphical subdivisions of the Tulomozerskaya Formation in the northern Onega Lake area...	13
Fig. 5:	Lithostratigraphy and variations of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and MgO/CaO-ratio in the section studied in drill hole 4699.....	14
Fig. 6:	Lithostratigraphy and variations of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and MgO/CaO-ratio in the section studied in	

drill hole 5177.....	15
Fig. 7: Plot of Sr values with depth in core 4699 and 5177. The Tulomozerskaya Formation, the northern Onega Lake area.....	18
Fig. 8: MgO/CaO-Sr (a) and MnO-Sr (b) cross-plots for carbonate rocks of the Tulomozerskaya Formation.....	19
Fig. 9: The $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ values (per mille) and MgO/CaO-ratio of carbonate rocks as a function of depth for the Tulomozerskaya Formation, the northern Onega Lake area.....	20
Fig. 10: Histogram of $\delta^{13}\text{C}$ values of carbonate rocks and stromatolites from the Tulomozerskaya Formation.....	21
Fig. 11: Carbon and oxygen isotopes versus MgO/CaO-ratio, Sr and Mn for carbonate rocks of the Tulomozerskaya Formation, the northern Onega Lake area.....	22
Fig. 12: The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot (a) and $\delta^{13}\text{C}$ versus depth (b) for Forth carbonates - North Sea (data from Watson et al. 1995).....	27
Fig. 13: The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot for Ca- and Mg-carbonates of some typical recent evaporitic environments, and for Tulomozerskaya Formation.....	29
Fig. 14: The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot for carbonates of some typical 'open' and 'closed' recent lakes, and for Tulomozerskaya Formation.....	31
Fig. 15: The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot (a) and $\delta^{13}\text{C}$ versus depth (b) for the Lake of Kivu carbonates.....	33
Fig. 16: The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot for carbonates of some typical recent and ancient stromatolites, and for carbonates of the Tulomozerskaya Formation.....	37
Fig. 17: Histogram of $\delta^{13}\text{C}$ values of carbonates from stromatolites of Shark Bay.....	39
Fig. 18: The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot for stromatolitic and shell carbonates of Shark Bay (unpublished data from Pokrovsky & Krylov).....	40

APPENDICES

- Appendix 1. Chemical composition of carbonate rocks, drill hole 5177 from Onega area, Karelia.
- Appendix 2. Chemical composition of carbonate rocks, drill hole 4699 from Onega area, Karelia.

1 INTRODUCTION

This report represents the preliminary results of lithological and geochemical investigation of ca. 2 billion-year-old carbonate formations of the Onega Lake area, Russian Karelia (Fig. 1). This has been a one-year research project initiated by the Kola Mineral Resources Project (67.6421.02) and carried out by the Geological Survey of Norway (NGU) jointly with the Scottish Universities Research & Reactor Centre (SURRC) (Glasgow, Scotland), Institute of Geology (IG) of the Russian Academy of Sciences (Petrozavodsk, Karelia) and the Karelian Exploration Expedition (KE) (Petrozavodsk, Karelia). The main objectives of the research project have been as follows: (i) potential for magnesite deposits; (ii) detailed chemostratigraphical subdivision of carbonate formations; (iii) stable isotope systematics. The first objective was commissioned by Norsk Hydro, the second was of primary interest for KE. The third goal was of mutual interest for the NGU, SURRC and IG. The field work was financially supported by Norsk Hydro. The carbon and oxygen isotope analyses were performed at SURRC supported by the Consortium of Scottish Universities. XRF main and trace element analyses were obtained at NGU and financially supported by the Kola Mineral Resource Project.

The field work was carried out by V. Melezhik (NGU) and P. Medvedev (IG). KE provided the drillcore material. The stable isotope analyses were made possible by A. Fallick (SURRC).

2 INDUSTRIAL DEMANDS AND SCIENTIFIC PROBLEM

Scattered dolostone-hosted magnesite mineralisation has been found in a number of localities in the vicinity of Onega Lake in relation with the Tulomozerskaya Formation, the Jatulian informal lithostratigraphical unit (Aksenov et al. 1975; Melezhik et al. 1981; Akhmedov et al. 1993; Melezhik 1993). Since 1993 Jatulian carbonate formations are considered to have good potential for sedimentary-diagenetic magnesite ores (Melezhik, 1993). The Onega Lake area has the thickest and most extensively developed carbonate formations of Jatulian age and therefore it has been considered to present a possibility for magnesite exploration. The work carried out and reported here has shown a negative rather than positive result.

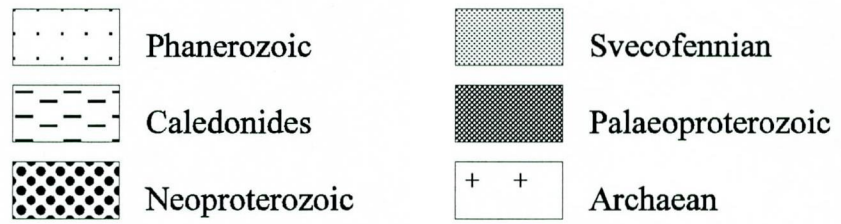
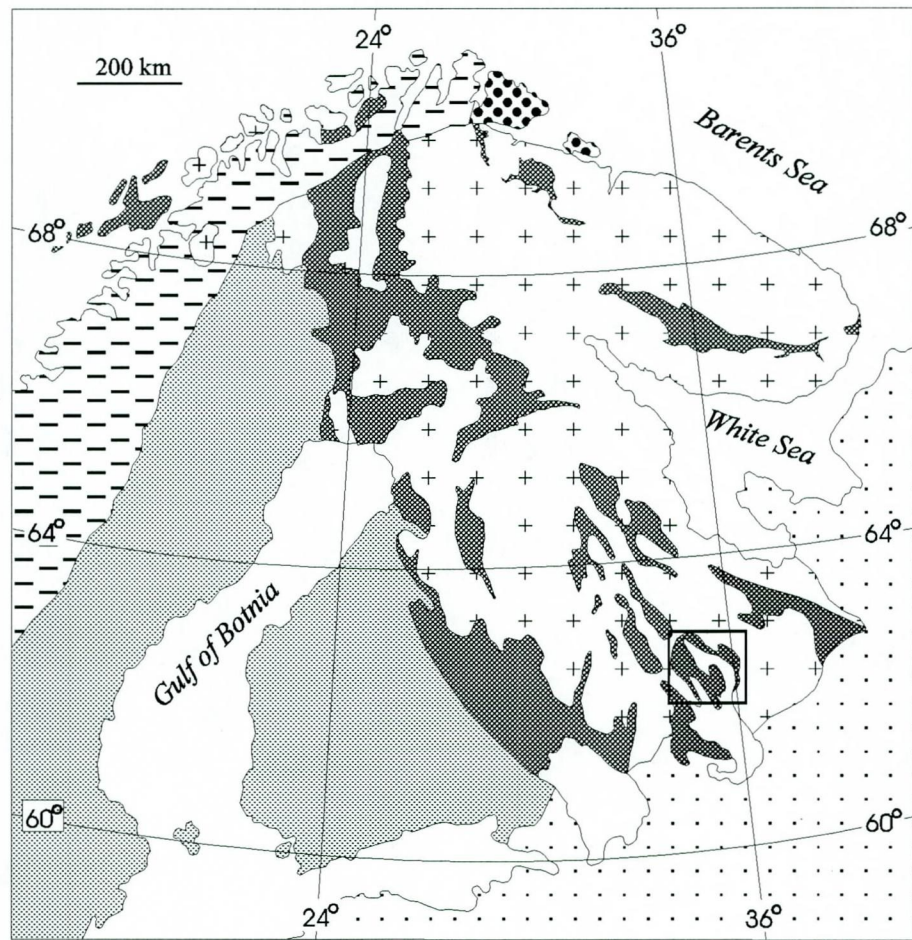


Fig. 1. Geographical and geological location of the study area.

The Onega Lake area (Fig. 1) is an excellent example of a Palaeoproterozoic carbonate platform. The 2,300 m-thick carbonate-shungite* succession has been intensively drilled with the purpose of establishing and describing the Palaeoproterozoic stratotype section of the Russian Federation. In this connection the detailed litho- and chemostratigraphical subdivision as well as palaeontological study of the succession has become one of the main items of research.

Since Yudovich et al. (1991) reported isotopically heavy carbonates from in the Tulomozerskaya successions of Karelia, the Onega Lake area has been the main target for investigation of the Jatulian 'heavy phenomenon' (Karhu 1993; Tikhomirova & Makarikhin 1993; Akhmedov et al. 1993). The Jatulian carbonate formations (2.33-2.06 Ga-old) with isotopically heavy carbon were deposited over an area of more than 10,000 km². The Onega Lake palaeobasin appears to be one of the largest and most important provinces for the study for the early Palaeoproterozoic positive excursion of $\delta^{13}\text{C}$ originally described by Schidlowski et al. (1976) in Zimbabwe as the 'Lomagundi event'. The Onega Lake area occupies an exceptional position in the Precambrian high $\delta^{13}\text{C}$ records, as reported in the literature, because the ¹³C -rich carbonates in this province have a very low metamorphic grade and are both extensively and thickly developed. These features give the area a high priority for the investigation of 'isotopically heavy phenomenon' which is related to a fundamental problem of the lithostratigraphy, global carbon cycle, biological evolution and oxygenation of the hydrosphere-atmosphere system in Precambrian.

3 GEOLOGICAL BACKGROUND

The Tulomozerskaya succession is one of the formations of the Palaeoproterozoic platformal sequence which is preserved as a synform exposed on the northern side of the Lake Onega as well as on its islands and peninsulas (Fig. 2). The Onega synform consists of a number of smaller NW-SE trending and dipping SE synclines and anticlines. The Palaeoproterozoic

* Shungite is a mineral comprising partly crystallised, reduced, free carbon (a form between amorphous carbon and graphite). The mineral was discovered a 100 years ago in Karelia, near the tiny village of Shunga from which its name originated. Later, all rocks (chert, dolostone, limestone, siltstone, tuff) containing more than 50% of the mineral shungite have been termed a 'shungite'.

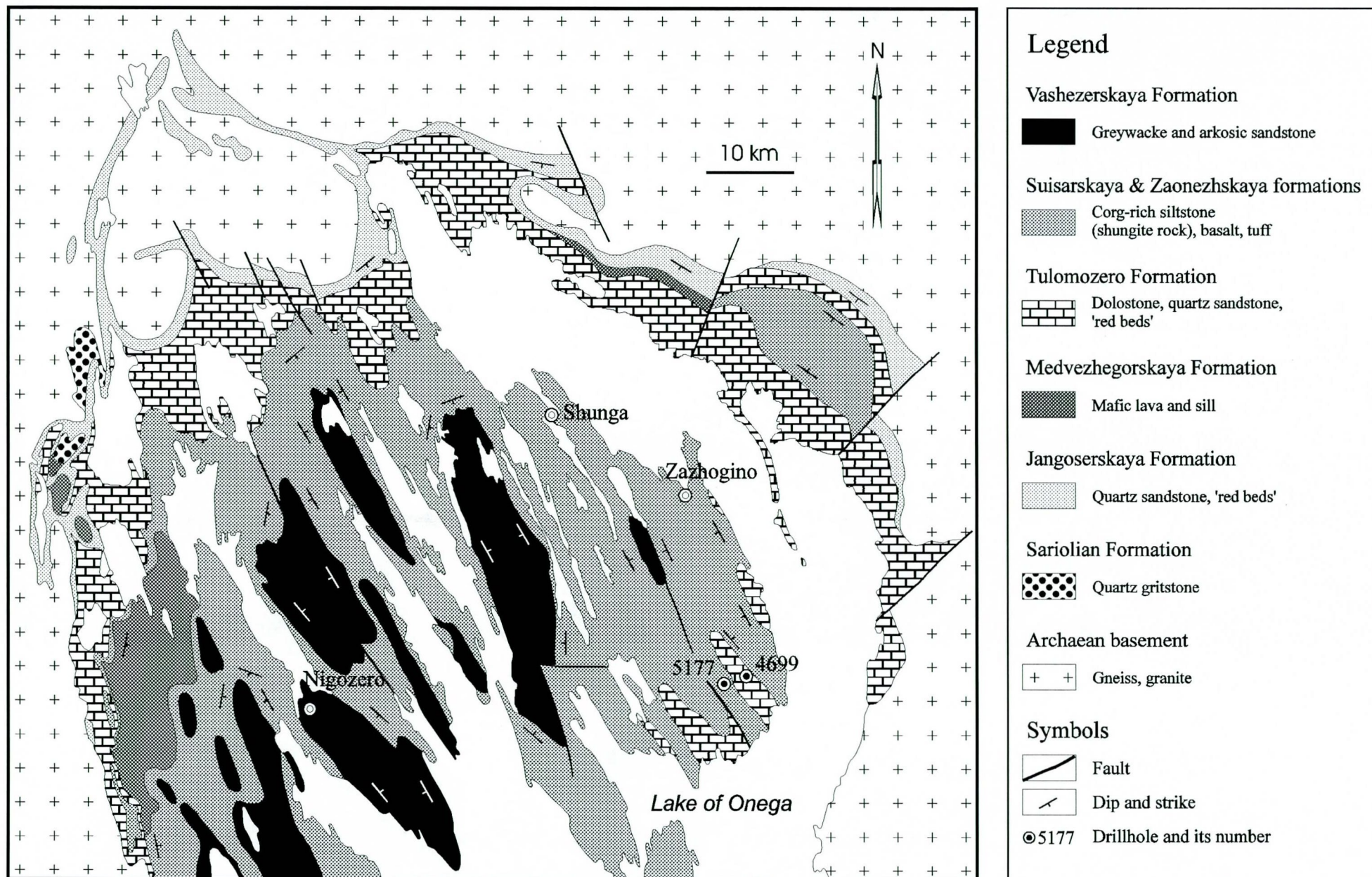


Fig. 2. Geological map of the northern Onega Lake area (simplified from Akhmedov et al. 1993)

LITHOSTRATIGRAPHIC UNIT		THICKNESS	PALAEOFACIES	
			MARGINAL	DISTAL
Vepsi	Shokshihskaya	1000		
	Petrozavodskaya	450		
Kalevi (Livvi)	Vashezerskaya	190		
Ludikovi	Suisarskaya	400		
	Zaonezhskaya	1500	<p>5177 800.7 m</p> <p>4699 806 m</p>	
Jatuli	Tulomozerskaya	800		
	Medvezhegorskaya	70		
	Yangozerskaya	50		
Sarioli	Pal'ozerskaya	400		
Sumi	Kumsinskaya	300		

Fig. 3. Lithostratigraphical subdivisions of the northern Onega Lake area and positions of the studied drill holes.

sequence of the N. Onega Lake area includes seven formations (Fig. 3), namely the Pal'ozerskaya, Jangozerskaya, Medvezhegorskaya, Tulomozerskaya, Zaonezhskaya, Suisarskaya and Vashezerskaya formations (Sokolov 1987). The Palaeoproterozoic rocks, with the Pal'ozerskaya basal polymict conglomerates, unconformably overlie the Archaean substratum. The Jangozerskaya, Medvezhegorskaya and Tulomozerskaya formations altogether are known as the Jatulian Group (Sokolov 1970). Originally 'Jatuli' was introduced by Sederholm (1899) and Eskola (1919), and later was widely used by Väyrynen (1933), Kratz (1963), Sokolov (1970) and Negruzta (1984). At present Jatuli has been defined as an informal lithostratigraphical unit of the Palaeoproterozoic successions of the Fennoscandian Shield (Sokolov 1980; Laajoki 1986). The stratotype section of Jatuli has been described by Russian geologists in the Onega Lake area, Russian Karelia. In the stratotype area (e.g. Sokolov 1987) the Jatulian succession begins with the 50-120 m thick Jangozersakaya Formation, which rests either conformably on the Sariolian conglomerates or unconformably on weathered Archaean gnesses and granites. The Jangozersakaya strata comprises predominantly oxidised red terrigenous sediments characterised by cross-bedding and desiccation cracks and subordinate calcareous siltstones. These rocks are conformably overlain by the 70 m thick Medvezhegorskaya Formation. This formation consists of mafic lava with subordinate cross-bedded quartz sandstones, gritstones and 'red beds'. The Tulomozerskaya Formation conformably overlies the Medvezhegorskaya succession. The formation comprises an 800 m package of red, thinly-bedded micritic and intraclastic dolostones as well as stratiform, domal and columnar stromatolites, variegated quartz sandstones and siltstones. Sandstones, siltstones and intraclastic dolostones are characterised by cross-bedding, ripple marks, desiccation cracks, scour surfaces, and channels. The carbonate rocks are marked by numerous stylolitic seams.

The three Jatulian formations are unconformably overlain by organic carbon-rich siltstones and mudstones (shungite rocks) with subordinate dolostones of the 1,500 m thick Zaonezhskaya Formation. This is followed by the Suisarskaya Formation, 400 m thick succession of basalts intercalated with numerous gabbro sills. A gabbro intrusion from the upper part of the Suisarskaya Formation has given a Sm-Nd mineral isochron age of 1980 ± 27 Ma (Pukhtel' et al. 1992). The Palaeoproterozoic succession ends with the 190 m-thick Vashezerskaya Formation comprising greywacke and arkosic sandstones.

4 LITHOSTRATIGRAPHY AND PALAEOENVIRONMENTS OF THE TULOMOZERSKAYA FORMATION

Carbonate samples analysed in this study were obtained from the Tulomozerskaya Formation. Only drill core material has been investigated. The samples were collected from drill holes 5177 (35° 25' 00" E, 62° 14' 29" N) and 4699 (35° 28' 00" E, 62° 14' 30" N) made by the Karelian Geological Expedition. These drill holes intersect an 800 m thick succession (Fig. 3) located in a distal part of the Onega palaeobasin (Fig. 2). A published description of this succession is only available in Russian (e.g. Satzuk et al. 1988; Akhmedov et al. 1993). Therefore, because lithostratigraphical data are critical to our geochemical interpretations, we will provide a sedimentological and stratigraphical summary.

As based on the lithology and mineralogical composition the Tulomozerskaya Formation has been divided into a number of 'piles' (Akhmedov et al. 1993) which we have renamed here as 'members' (Fig. 4) in accordance with the International Stratigraphic Code (ISSC, 1976). Furthermore some members, for instance, such as the Magnesite-Dolomite and Stromatolite-Dolomite are confusing because stromatolites are characteristic features of all the members and magnesite, as we discuss below, has been found throughout the succession. Therefore we have joined these two members with the Phosphate-Dolomite Member and given them the common term Member B. For practical reasons and for consistency we have here substituted letters for other names, starting with an 'A' for the lowermost Limestone-Dolomite-Mudstone Member (Fig. 4). The whole succession, consisting of the eight lithostratigraphical members (A-H), can be also divided (correlated) in the six units with the distinctive groups of stromatolites, onkolithes and microfossils (Fig. 4).

The lowermost Member A is a ca. 250 m thick succession of micritic dolostones and dolomitic stylo-brecias with subordinate layers of quartz sandstone and pink finely-laminated siltstones (Fig. 5). The whole succession was deposited in a shallow-water lacustrine environment.

Member B (90 m) consists predominantly of dolostones (Fig. 6). It begins with the 1 to 2 m thick magnesite band which is followed by beige crystalline sandy dolostones up to 20-30 m

thick. These are followed by a 20-40 m thick succession of yellow, pink and beige fine- to coarse-grained dolostones separated by two intervals of grey fine-grained dolostones and magnesites containing subaqueous shrinkage cracks. The latter have been also interpreted as the stromatolite *Lukanoa*. The upper part of Member B, a 17-26 m thick unit, is pink micritic dolostones, dolarenites, dolorudites with one shaley interval. The micritic dolostones are sporadically marked by the dolomite pseudomorphs after small crystals of gypsum. The carbonate rocks are richly stromatolitic, containing spectacular developments of *Nucleophyton*, *Carelozoon*, *Sundosia* and *Parallelelophyton*. The large oncoids *Osagia* are also abundant (Makarikhin and Kononova, 1983). Member B has been interpreted as either a coastal lake or an entirely marginal marine, sabkha-like environment (e.g. Akhmedov et al. 1993).

Member C, 105 m thick, is largely red finely laminated, hummocky cross-stratified mudstones intercalated with subordinate purple micritic dolostones, dolomitic marls, and grey crystalline dolostones. The marls contain abundant dolomite pseudomorphs after gypsum and desiccation cracks. The carbonate rocks of this unit is richly stromatolitic, containing various developments of *Omachtenia* and *Colleniella*, as well as *Carelozoon* and *Stratisfera*. The Member C sediments have been interpreted to have formed in an evaporative subtidal environment (e.g. Akhmedov et al. 1993).

Member D (60 m) is dominated by massively bedded and cross-stratified intraclastic dolostones with desiccation cracks and dolomite pseudomorphs after gypsum. The uppermost part is represented by red fine-grained dolostones and pisoid dolostones. Three layers of crystalline magnesite occur in the middle and uppermost part of the member. The large columnar stromatolite, up to 0.5 m diameter, and various developments of *Omachtenia*, as well as *Colonnella* are very abundant. One prominent stromatolitic marker, *Omachtenia kintsiensia*, anchors lithostratigraphic correlation of this member throughout the Karelian region (Medvedev et al. 1990). The succession was apparently deposited in a lagoonal environment.

Member E is a 110 m thick succession of predominantly pink platy cross-stratified quartz sandstones with carbonate matrix. The sandstones are rich in hematite. Ripple marks and desiccation cracks are well developed. From two to three thin intervals of dolostones occur in

		Akhmedov et al. 1993	This study	Makarikhin & Medvedev in Akhmedov et al. 1993		
Tulomozerskaya Fm.	'Red Bed'-Dolomite Member		zn ₁ H	20*	Layers with <i>Calevia ruokanensis</i>	
	Oncolite-Dolomite Member		G	30	Layers with <i>Butinella</i>	
			F	25		
	Dolomite-Mudstone Member		E	110		
	Heamatite-Sandstone Member					
	Pisolith-Dolomite Member		D	60		Layers with <i>Omachtenia kintsiensis</i>
	Siltstone Member		C	105		
	Stromatolite-Dolomite Member		B	90	Layers with <i>Sundosia</i>	
	Magnesite-Dolomite Member				Layers with <i>Nuclephyton</i>	
	Phosphate-Dolomite Member					
Limestone-Dolomite-Mudstone Member		A	250	Layers with <i>Lukanoa</i>		

Fig. 4. Lithostratigraphical subdivisions of the Tulomozerskaya Formation in the northern Onega Lake area.

* The thickness is shown in metres as measured in drill hole 4699 (Member A) and 5177 (Members B-H). zn₁ is the Zaonezhskaya Formation.

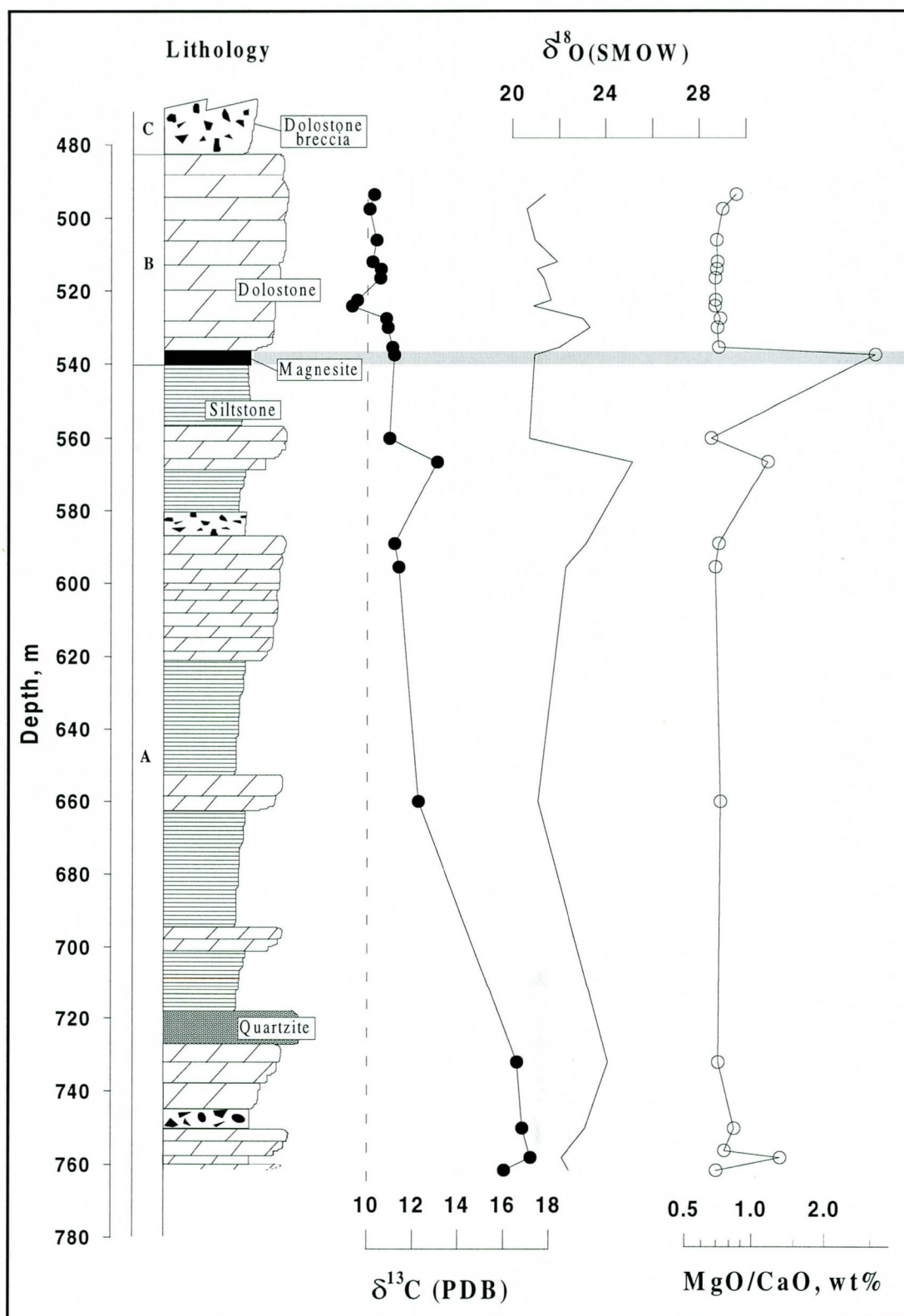


Fig. 5. Lithostratigraphy and variations of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and MgO/CaO-ratio in the section studied in drill hole 4699.

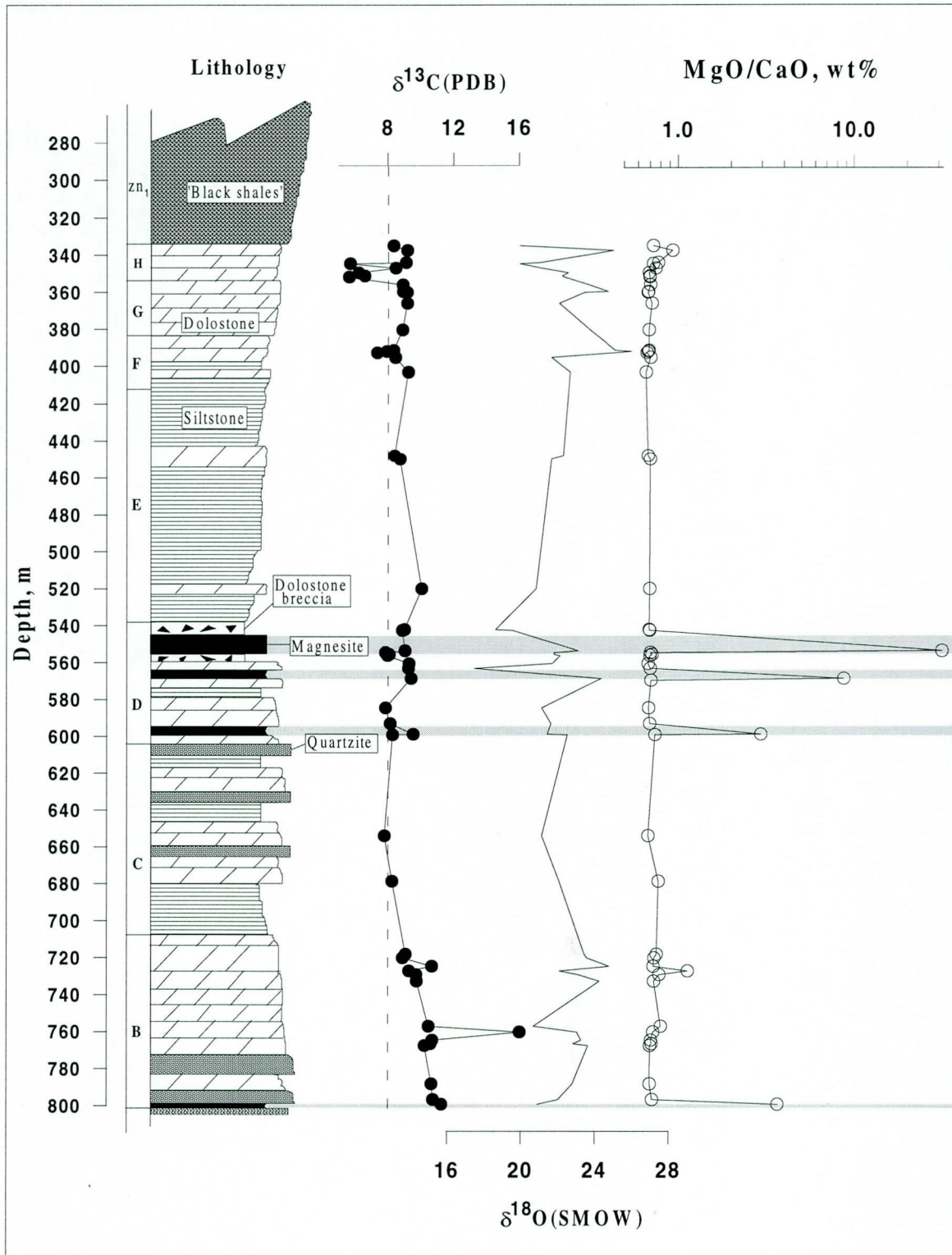


Fig. 5. Lithostratigraphy and variations of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and MgO/CaO-ratio in the section studied in drill hole 5177.

the lower and upper part of the member. They contain abundant *Palia*, *Carelozoon* and *Colleniela*. A number of thin layers of grey siltstones are sporadically developed throughout the succession and contain in places dolomite pseudomorphs after halite. The sedimentological features match with a coastal lake, evaporitic environment.

Member F (25 m) consists of siltstones, sandstones, dolostones and widely developed dolerudites. The dolostones with *Butinella* may be occasionally observed.

Member G is a 30 m thick unit of hummocky laminated dolostones interbedded with dolerudites. The member ends with a number of layers of oncolite (*Radiolites*) dolostones intercalated with developments of *Calevia*, *Stratifera* and various *Butinella*. A remarkable stromatolitic marker, *Butinella*, anchors the lithostratigraphic correlation of this member within the Onega palaeobasin (Makarikhin et al. 1994).

The uppermost Member H, a 20 m thick unit of brown to red fine-grained finely laminated dolostones and dolomitic marls with *Djulmekella* and *Galevia*, unconformably overlies Member G. The 'red beds' gradationally pass through variegated siltstones to 'black shales' of the Zaonezhskaya Formation. The Member H dolostones and marls are considered to be deposited in a marine environment.

5 RESULTS

The 50 samples were collected from drill hole 5177 and 21 samples from drill hole 4699. One sample from each second metre was taken in those cases where the thickness of a carbonate band exceeded 40 m. Each metre of carbonate bands with thickness less than 40 m was sampled. The whole sample collection was analysed for the oxygen and carbon isotopes as well as for major and trace elements (Appendix 1 and 2). The major and trace element analyses were performed at NGU using a Philips PW 1480 x-ray spectrometer. The carbon and oxygen isotopic composition was measured at SURRC using standard techniques.

The overall bulk rock chemical composition of Tulomozerskaya carbonates approximates a sandy dolostone (Appendix 1 and 2). Five thin layers of magnesite or magnesite-bearing dolostones have been detected in the whole succession. The first layer (MgO/CaO=3.1) is found in the uppermost portion of Member A, and the second (MgO/CaO=3.4) is located at the base of Member B (Fig. 5). The three other layers are in the middle and upper part of Member D. They show that MgO/CaO ratios increase upwards the stratigraphy from 3.0 to 31.4 (Fig. 6). Limestones per se. have not been observed among the collected samples. If magnesite bearing layers are excluded the overall range of MgO/CaO ratio is 0.66-1.32 with an average value of 0.74 ± 0.11 .

The Sr content displays a considerable variation with a range from <5 to 491 ppm (Fig. 7). The average Sr values for the Member A-E carbonates (199, 138, 77, 130 and 129 ppm respectively) are essentially higher than the average figures for the carbonates of the three uppermost Members, F, G, and H (26, 54 and 64 ppm respectively). Depletion in Sr does not expose any covariation with manganese content (Fig. 8a). Scatter of Sr content in dolostones is also independent of the MgO/CaO ratio, though the magnesite bearing dolostones show depletion in Sr as the MgO/CaO ratio increases (Fig. 8b).

The available O/C isotope measurements (Appendix 1 and 2) are summarised in Figs. 9-11. The spread of isotope values in the available data set is about 17.5-26.0‰ (22.3 ± 1.6 ‰) for oxygen, and 5.6-17.2‰ (9.9 ± 2.3 ‰) for carbon (Fig. 9). A histogram of the carbon isotope data reveals two maxima of $\delta^{13}\text{C}$ at 9.4 ± 1.4 ‰ and 16.5 ± 0.8 ‰ (Fig. 10). The first maximum represents 93% of the samples studied. The four samples from the second population are dolostones highly enriched in ^{13}C which are located in the lowermost part of the succession (Member A), and one sample derived from the Member B (Fig. 9). The carbon isotope values demonstrate an erratic decrease upwards in the stratigraphy from +17.2‰ in the lowermost part of Member A down to +8.0‰ in Member C (Fig. 9). Higher up in the succession overall, the observed values $\delta^{13}\text{C}$ values of Members D-H are less variable and fall within the range 7.3-10.1‰. The only exception from this pattern is the four samples from the lower portion of Member H carbonates with $\delta^{13}\text{C}$ of 5.6-6.6‰. Oxygen isotope composition is less variable and exhibits no systematic variation related to the stratigraphy (Fig. 9).

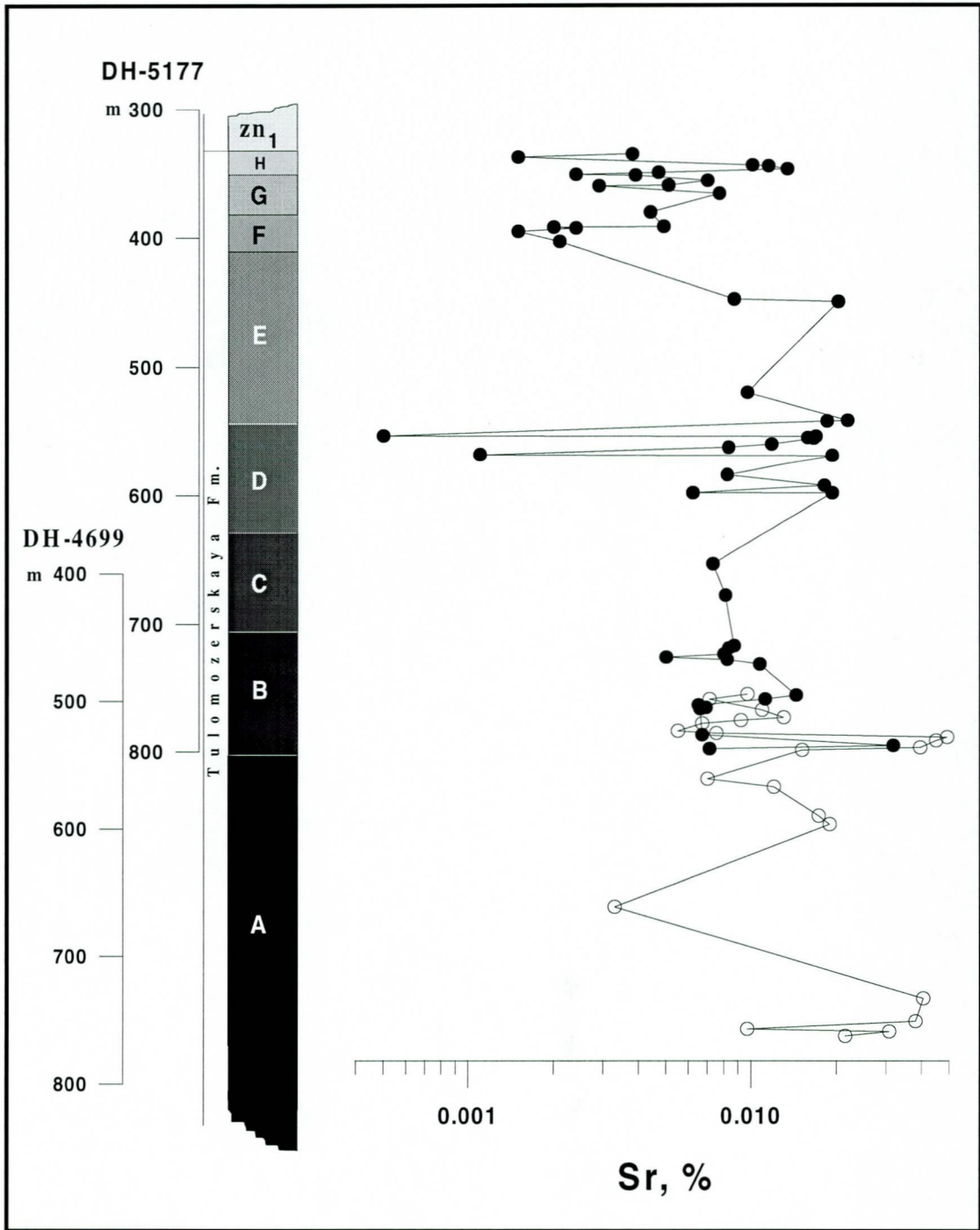


Fig. 7. Plot of Sr values with depth in core 4699 and 5177. Tulomozerskaya Formation, northern Onega Lake area.

A-H are members of the Tulomozerskaya Formation, Zn_1 is the Zaonezhskaya Formation.

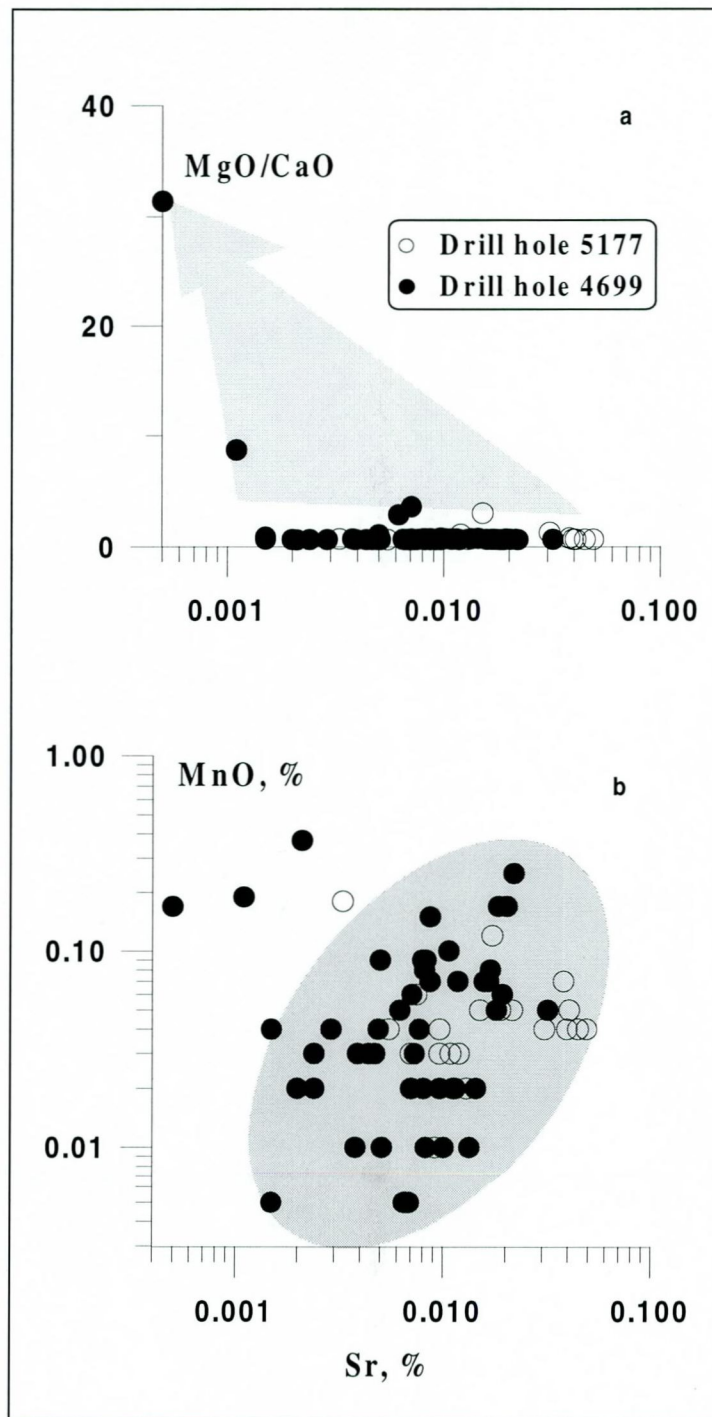


Fig. 8. MgO/CaO-Sr (a) and MnO-Sr (b) cross-plots for carbonate rocks and stromatolites of the Tulomozerskaya Formation.

Note that only two magnesite samples are relatively depleted in Sr, and that MnO and Sr show positive covariation.

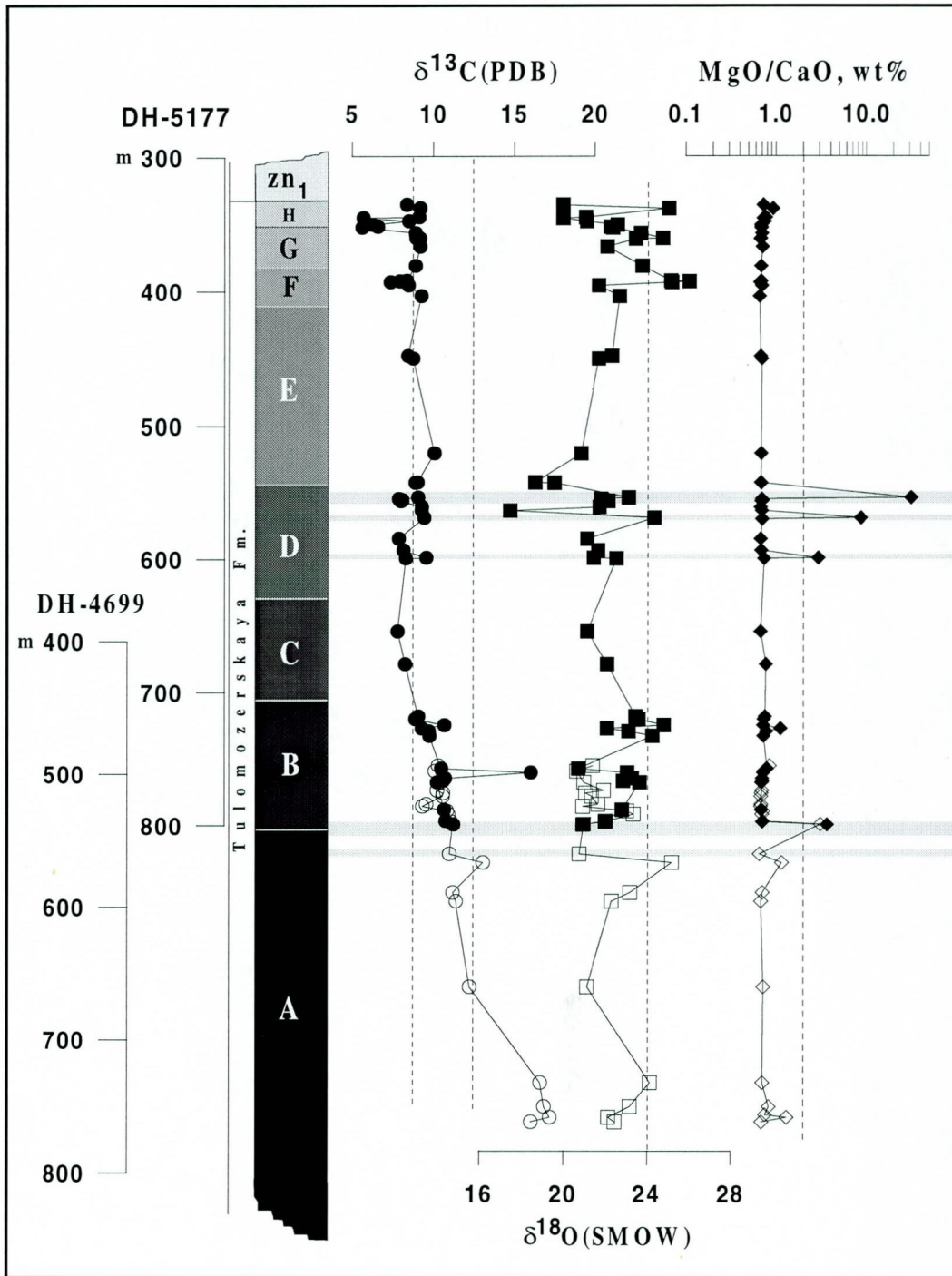


Fig. 9. The $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ values (per mille) and MgO/CaO-ratio of carbonate rocks as a function of depth for the Tulomozerskaya Formation, the northern Onega Lake area. Magnesite-rich layers are shown by shaded bars. Note magnesite-rich layers appear in Member A, B and D. The $\delta^{13}\text{C}$ values increase erratically with depth, while $\delta^{18}\text{O}$ values show no systematic variations.

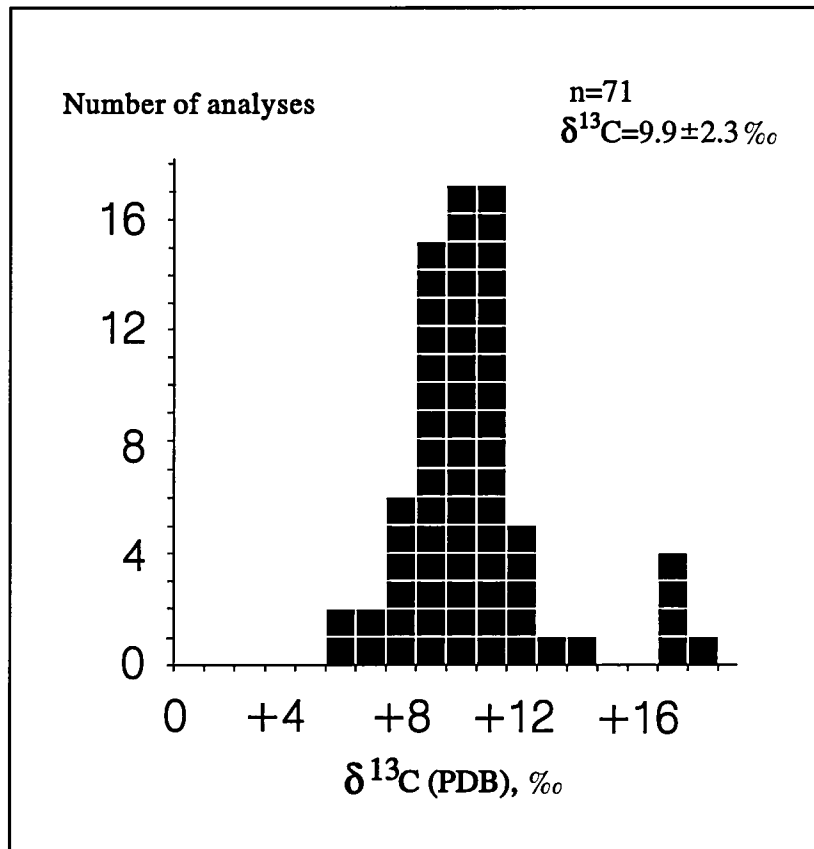


Fig. 10. Histogram of $\delta^{13}\text{C}$ values of carbonate rocks and stromatolites from the Tulomozerskaya Formation.

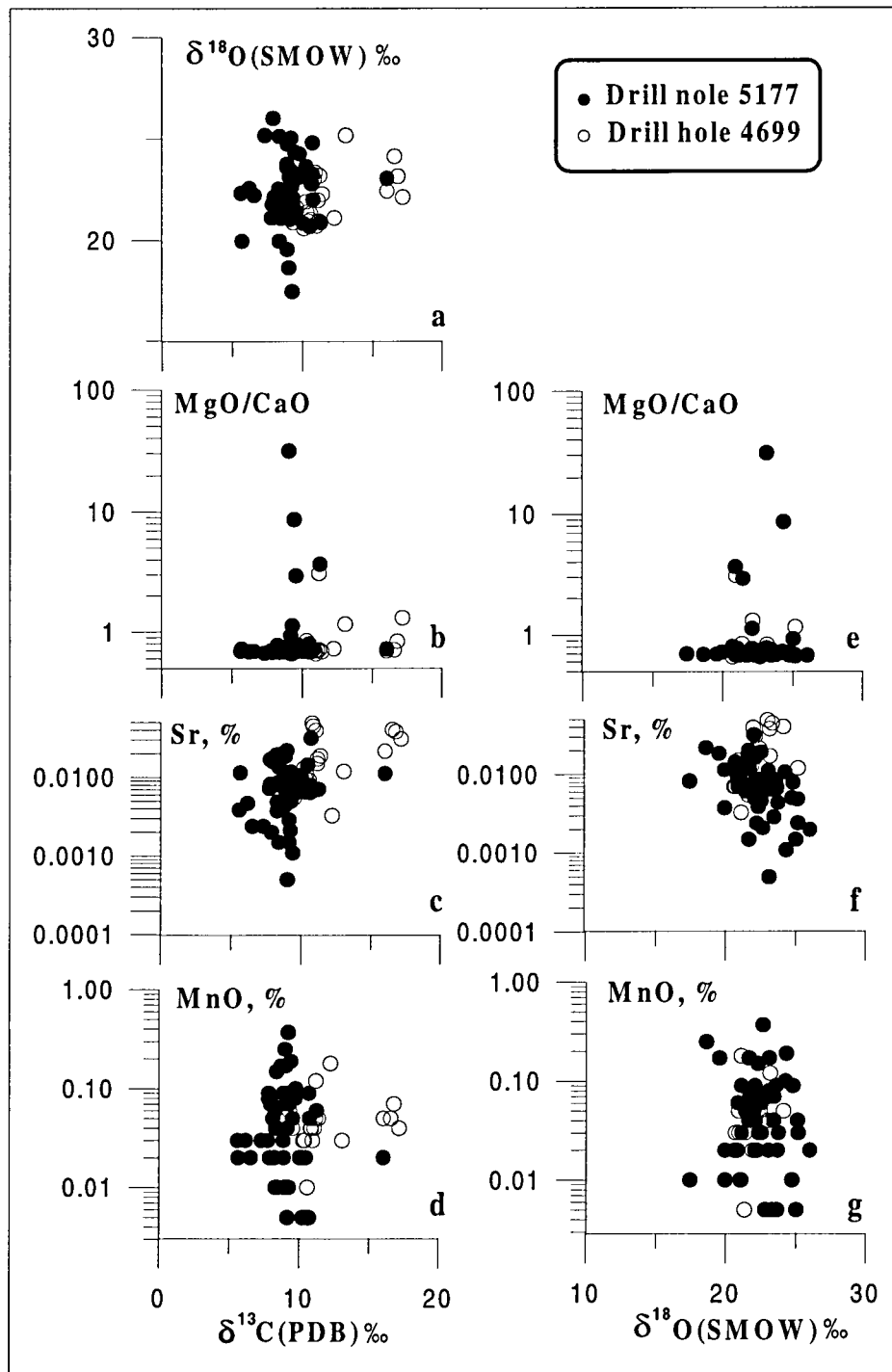


Fig. 11. Carbon and oxygen isotopes versus MgO/CaO-ratio, Sr and MnO for carbonate rocks of the Tulomozerskaya Formation. Note relatively little or no covariance between carbon and oxygen isotopes. Sr and oxygen isotopes show negative covariation.

Cross-plots reveal no reliable covariation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Fig. 11a). No covariations are observed between MgO/CaO ratio and C/O isotopes, as well as between Mn and C/O isotopic values (Fig. 11b, d, e, g). Sr and $\delta^{13}\text{C}$ shows positive covariation (Fig. 11c), although, surprisingly, Sr and $\delta^{18}\text{O}$ expresses negative covariation (Fig. 11f).

6 EVALUATION OF DIAGENESIS

The carbonate sequences of the Tulomozerskaya Formation studied are chemically entirely dolostones apart from five magnesite-bearing samples. Dolomite is generally considered as essentially a diagenetic mineral. Nonetheless, there is growing evidence that precipitation of dolomite in the Precambrian was either coeval with calcite, or that dolomitisation was an early diagenetic phenomenon caused by waters isotopically comparable to that of seawater (e.g. Veizer & Hoefs 1976; Veizer et al. 1992a, b).

Several geochemical screens for evidence of diagenetic alteration are possible. Hudson (1977) found that oxygen isotopes may be a sensitive indicator of diagenetic alteration. Diagenesis commonly decreases $\delta^{18}\text{O}$ and the effect of diagenesis $\delta^{18}\text{O}$ can be revealed by $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ cross-plot. Fig. 11a shows no reliable correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonate rocks of the Tulomozerskaya Formation and suggests that no visible diagenetic trend can be observed in the studied succession. In fact almost all measured $\delta^{18}\text{O}$ values fall within a range of 17.5-26.0‰ with an average figure of 22.3 ± 1.6 ‰. This is similar to the $\delta^{18}\text{O}$ values reported by Baker & Fallick (1988a, b) from Norway (24‰) and Scotland (22‰). Schidlowski et al. (1976) in reporting a mean $\delta^{18}\text{O}$ of 22.2 ± 1.6 ‰ at Lomagundi commented that such a value was 'fairly normal for sedimentary carbonates of this age'. Veizer et al. (e.g. 1992a, b) have documented the similar 'best preserved' $\delta^{18}\text{O}$ values of 23‰ and 26 ± 2 ‰ for the Archaen to Palaeoproterozoic limestones and dolostones respectively.

Brand and Veizer (1980) reported that Mn and Sr can serve as a tool for calibration of relative diagenetic rank of the studied sequences. An increasing degree of post-depositional alterations leads to Sr depletion and Mn enrichment. The MnO-Sr cross-plot (Fig. 8a) suggests that no clear diagenetic trend can be observed in the studied carbonates except for four samples

enriched in MnO and relatively depleted in Sr. If these four samples are excluded the MnO-Sr cross-plot reveals a positive rather than negative covariation. Overall, the observed MnO and Sr values fall well within the range exhibited by the 'best preserved' carbonate rocks of the similar Early Palaeoproterozoic age reported by Veizer et al. (1992b). The high Sr concentrations of the Tulomozerskaya dolostones, particular those of Member A-E (up to 491 ppm) are very characteristic feature. For dolostones, high Sr concentrations are typical for facies with hypersaline tendencies (e.g. Veizer 1978; Veizer et al. 1978). This may be the reason for the Sr-rich nature of some Member A-E dolostones (Fig. 7). This is consistent with their proposed sabkha to evaporative subtidal environments. The relatively lower Sr concentration in dolostones of the uppermost part of the Tulomozerskaya Formation is also in agreement with their marine origin.

Surprisingly enough the Mn- $\delta^{13}\text{C}$ (Fig. 11d) as well as the MnO- $\delta^{18}\text{O}$ (Fig. 11g) cross-plots of the Tulomozerskaya carbonates do not expose any visible covariation. At the same time covariation between Sr and $\delta^{18}\text{O}$ reveals negative rather than positive tendency (Fig. 11f). The Sr- $\delta^{13}\text{C}$ cross-plot (Fig. 11c) shows a poorly pronounced covariation. However if five samples from the second population, highly enriched in ^{13}C (Fig. 10), are excluded, the cluster of the remaining 93% of the samples displays no covariation. We speculatively suggest that oxygen and carbon isotopic compositions of the Tulomozerskaya dolostones are not principally controlled by diagenetic alteration, and may reflect isotopic parameters of coeval basinal water. This consideration is consistent with the proposition that either dolomite was chemically precipitated or dolomitisation was an early diagenetic phenomenon, caused by waters isotopically comparable to that of coeval basinal water (e.g. Veizer and Hoefs 1976; Veizer et al. 1990).

7 INTERPRETATION OF ^{13}C ENRICHMENT

Carbonate formations rich in ^{13}C were first discovered in the Lomagudi basin (Schidlowski et al. 1976), then reported from the Lofoten-Vesteralen area, N. Norway (Baker & Fallick 1989b), and from Finland (Karhu 1989) and the Onega area, S. Karelia (Yudovich et al. 1990). Recently widespread development of ^{13}C -rich carbonates have been documented, at

around 2.3-2.06 Ga, on the Fennoscandian Shield (Karhu & Melezhik 1992; Karhu 1993; Tikhomirova & Makarikhin 1993; Akhmedov et al. 1993; Pokrovsky & Melezhik 1995; Melezhik and Fallick 1996). As has been discussed earlier, the Fennoscandian Shield represents the largest isotopically anomalous carbonate province yet reported, and the positive $\delta^{13}\text{C}$ excursion (named as the Jatulian phenomenon) together with a series of major global palaeoenvironmental changes seems to be more intensely developed than recorded by the Precambrian/Cambrian transition events (Melezhik & Fallick 1996). However, it is still not clear what kind of mechanism could be attributed to this phenomenon. The Onega palaeobasin exposes an extensive carbonate succession that has been drilled and sampled in great detail. This gives us a chance to test the modelling of certain natural environments in order to explain of the ^{13}C -rich carbonates studied. The Tulomozerskaya carbonate formations are considered in this paper to be a representative example of ^{13}C -rich Jatulian carbonates which were formed on the Fennoscandian Shield at around 2.3-2.06 Ga ago (Karhu 1993; Melezhik & Fallick 1996).

Sedimentary carbonates significantly heavier than average are usually formed in special environments. A restricted volume of isotopically heavy carbonates may be formed during fermentative diagenesis (Irwin et al. 1977). Hot-spring (Friedman 1970), hypersaline (McKenzie 1981; Reitsemá 1980; Stiller et al. 1985) and stromatolite-basin (Shark Bay, Ferguson, Plumb & Walter, in Knoll et al. 1986) environments as well as a closed-lake system' with high bioproduction (e.g. Lake Kivi, Botz et al. 1988) may result in the deposition of relatively larger volume of isotopically heavy carbonates. The known epochs of ^{13}C -rich carbonates of global significance are considered to be assigned to either Oceanic Anoxic Events (e.g. Schidlowski & Junge 1981) or world-wide orogenic episodes (Des Marais 1994), both leading to enhanced deposition of reduced carbon. However, Keith (1982) reported that development of a stagnant stratified ocean has to result in the formation of isotopically light oceanic carbonates.

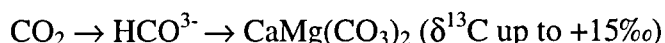
7.1 Diagenetic model

Fermentative diagenesis occurs under anaerobic conditions and starts at depth as soon as sulphate reduction stops (Irwin et al. 1977). The methane generated during this transformation

of buried organic mass results in generation of CH₄ depleted in ¹³C (down to -50 to -70‰) and isotopically heavy CO₂ (δ¹³C=+15‰):



Consequently, isotopically heavy carbon dioxide produced in this process eventually results in δ¹³C-rich carbonate deposition:



CH₄ may be also oxidised to CO₂ which can be introduced to carbonates depleted in ¹³C. Therefore carbonate minerals formed in the course of fermentative diagenesis will show a wide range in δ¹³C though the temperature dependant oxygen isotopes will show very little variation. This can be demonstrated by an example studied by Watson et al. (1995) from Palaeocene and Eocene sandstones having δ¹³C with the overall extent from -31.0 to +12.4‰ (Fig. 12a), and δ¹⁸O values ranging from 17.9 to 22.4‰. A depth-dependant distribution of δ¹³C reveals equal abundances of both extremely heavy and extremely light values at any studied depth interval between 2251m and 2284 m (Fig. 12b).

The studied Tulomozerskaya carbonates are characterised by the entirely different δ¹³C pattern, namely only isotopically heavy values are observed, with variations between +5.5 and +17.2‰ which are coupled with oxygen isotopes falling between 18.6‰ and 26.0‰ (Fig. 9, 11a). Furthermore, the whole carbonate assemblage is a typical 'red bed' association formed under oxidising conditions. There are no signs that the carbonate rocks were subjected to anaerobic, e.g. fermentative, diagenesis. Thus, based on the data discussed above the fermentative diagenetic model cannot be applicable to Tulomozerskaya Formation carbonates.

7.2 *Model of evaporitic basin*

On a basinal scale, enrichment in heavy isotopes can be caused by widespread and persistent evaporitic conditions. Stiller et al (1985) reported extreme ¹³C enrichments in the dissolved inorganic carbon pool (δ_{CO₂}) in evaporitic brines of the Dead Sea. Here, under natural conditions, namely in solar evaporitic ponds, an abiotic effect in evaporating brines resulted in ¹³C enrichments of up to +16.5‰. However it is not clear to what extent ¹³C -rich carbonates may be formed from such evaporating pools. Katz et al. (1977) studying aragonite laminae in deposits from the highly evaporated and saline Lake Lisian, the Pleistocene precursor of the

Dead Sea, found carbonates only moderately enriched in ^{13}C , all values are below +3.5‰. Although an evaporation rate of Lake Lisan was higher than that of the Dead Sea, the evaporating system of the former was not persistent and resulted in highly variable composition

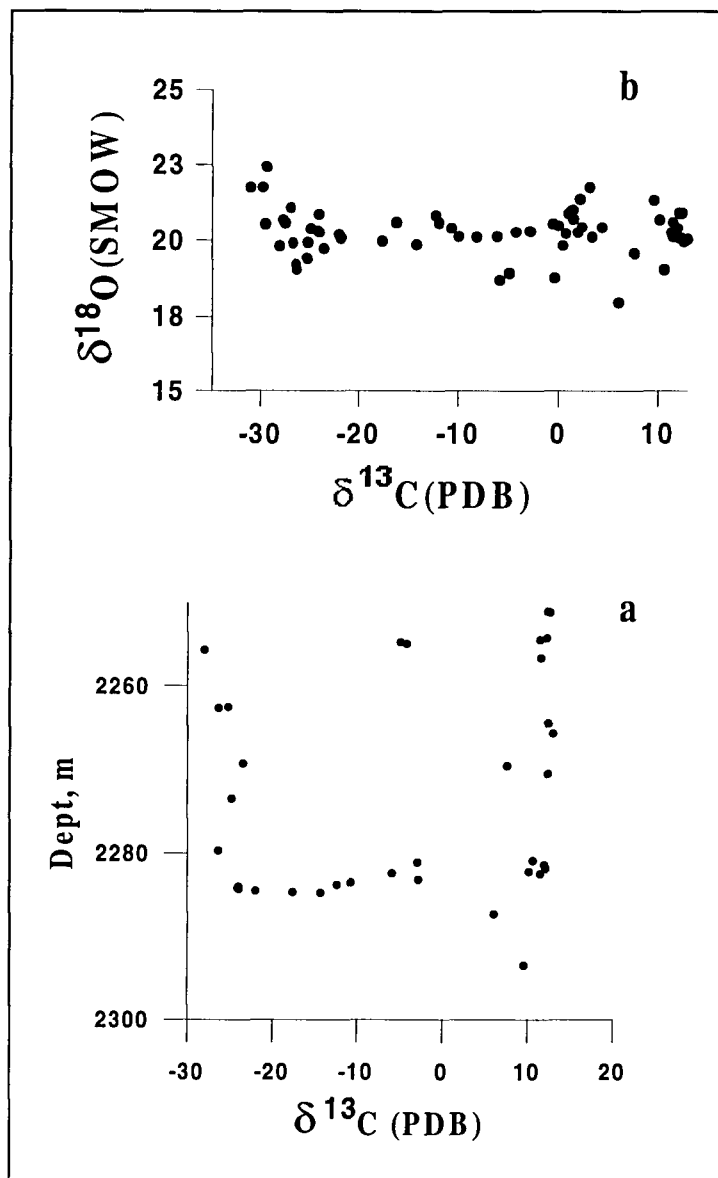


Fig. 12. $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ cross-plot (a) and $\delta^{13}\text{C}$ vs. depth (b) for Forth carbonates - North Sea (data are from Watson et al. 1995).

of carbon isotopes in deposited aragonite, from -7.7 to +3.5‰, coupled with extremely heavy oxygen, 32.4-38.1‰ (Fig. 13). The latter is higher by 3‰ in average than $\delta^{18}\text{O}$ of the Dead Sea which was dictated by a higher rate of evaporation (Katz et al. 1977).

Another example of rocks originating in highly evaporative environments are the calcium and magnesium carbonate sediments formed in coastal sabkhas of Abu Dhabi, the Arabian side of the Persian Gulf (McKenzie 1981). The carbon isotopes of the Abu Dhabi carbonates is fairly constant. The average $\delta^{13}\text{C}$ value for the calcium-carbonate components is $+3.2\pm 0.6\text{‰}$ and that for diagenetic dolomite is $+2.8\pm 0.6\text{‰}$ which coincide with isotopically heavy oxygen values ranging between +30.4 and +34.5‰ (Fig. 13).

From the data reviewed above it can be inferred that evaporation does not always lead to marked ^{13}C enrichment. Even in the highly evaporated system of Lake Lisian the $\delta^{13}\text{C}$ values that are generally negative and the highest $\delta^{13}\text{C}$ value is below +3.5‰ (Fig. 13). The $\delta^{13}\text{C}$ values of known evaporitic carbonates do not exceed +5‰. This feature has also been discussed by Magaritz et al. (1983) who emphasised that evaporitic environments in the Baja California (Pierre 1982) and the Afar Depression (Bonatti et al. 1971) have carbonates with negative to slightly positive $\delta^{13}\text{C}$.

Furthermore, a few additional arguments conflict with an evaporitic origin of the Tulomozerskaya carbonate rocks. Firstly, it would appear that most evaporitic carbonates are not marked by substantial enrichment in ^{13}C but have highly elevated $\delta^{18}\text{O}$ averaging around 32-37‰. The high $\delta^{18}\text{O}$ are very characteristic features of evaporitic carbonates that definitively distinguish them from those of the Tulomozerskaya Formation which are marked by an 'average Precambrian' figure of 22.3‰ (Fig. 13). Secondly, the members B, C, D and E of the Tulomozerskaya Formation, in which evaporites and sedimentological evidence of evaporitic conditions are recorded, are not characterised by the maximum of enrichment in ^{13}C . The carbonates most enriched in ^{13}C are located in less evaporitic Member A. The Member H carbonates formed in marine environments are as rich in ^{13}C as carbonates from evaporitic Members C, D and E. Thirdly, the Tulomozerskaya carbonates were formed in a very sustainable system which was able to maintain $\delta^{13}\text{C}$ between +6 and +16‰. This is not the case

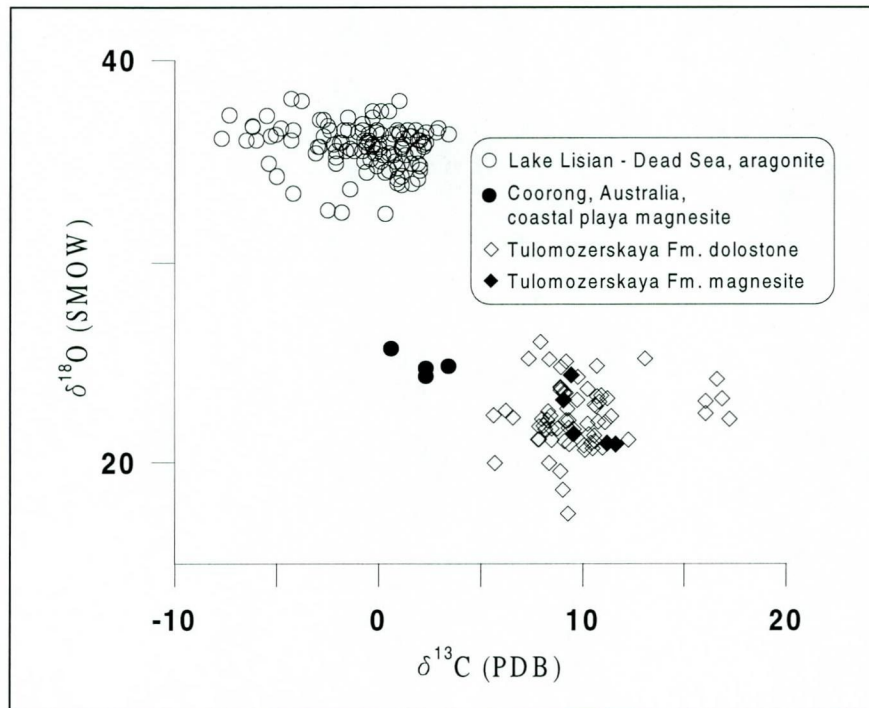


Fig. 13. $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot for Ca- and Mg-carbonates of some typical recent evaporitic environments, and the Tulomozerskaya Formation. Data are from: Lake Lisian-Dead Sea, Israel - Katz et al. 1977; Coorong Lagoon, South Austria - Zachmann 1989.

for any known recent evaporitic basins, even for the highly evaporative Lake Lisian - Dead Sea environments.

Therefore we conclude that an evaporitic origin of ^{13}C enrichment of Tulomozerskaya carbonates can be rejected on the grounds that it is not supported by the available data. The fractionation capability of the natural evaporitic systems is too low, and the average figure of +9.9‰ is too high to have been produced by evaporation. However an evaporitic model may be verified by investigation and comparison of distal carbonates studied here with those deposited in proximal parts of the Onega palaeobasin, and hence in more evaporitic conditions.

7.3 *Model of restricted basin with high bioproduction*

Primary shift in the isotopic composition of sedimentary carbon can also be caused by enhanced rates of burial of organic material leading to the enrichment of deposited carbonates in ^{13}C (e.g. Scholle & Arthur 1980). The scale of this effect can be global or basinal and assessment of these alternatives is crucial for the interpretation of the carbon excursion.

The discrimination between open and restricted lacustrine environments may be achieved by a combination of sedimentological and isotopic data. Sokolov (1987), Akhmedov et al. (1993) and many others have assembled sedimentological evidence to indicate that part of the succession of the Onega palaeobasin (Member A, E, partly B) must have accumulated in a closed lacustrine environments. Carbonates of Member B, C, D, E are associated with accumulation of evaporates which also indicates some periods of negative water balance, and is highly suggestive of closed-basin conditions.

Concerning the isotopic data, the most comprehensive study on this subject has been made by Talbot (1990) and Talbot & Kelts (1990). They have reported that isotopic covariance is most typical of carbonates from lakes that are hydrologically closed. Two examples shown in Fig. 14, namely carbonates from Lake Turkana, Kenya (Halfman et al. 1989) and Great Salt Lake, Utah, USA (McKenzie 1985), are characterised by the high correlation coefficient ($r=0.86$ and 0.87 respectively, Talbot 1990) for covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. All sorts of isotopic

fractionation during carbonate precipitation are of secondary importance and generally masked

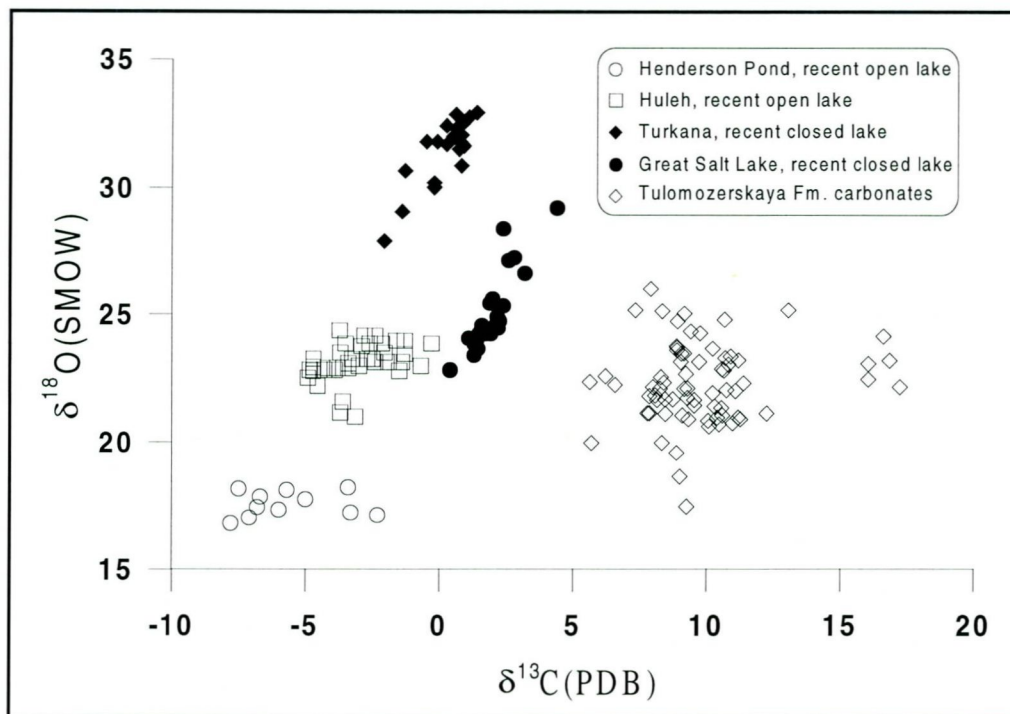


Fig. 14. $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ cross-plot for carbonates of some typical 'open' and 'closed' recent lakes, and for the Tulomozerskaya Formation. Data are from: Henderson Pond, USA - Stuiever 1970; Huleh, Israel - Stiller and Hutchinson 1980; Turkana, Kenya - Halfman et al. 1989; Great Salt Lake, Utah, USA - McKenzie 1985.

by evaporative- and residence-related effects (Talbot 1990 and references therein). For comparison, Fig. 14 shows also data for carbonates from two hydrologically open lakes, Henderson Pond, USA (Stuiver 1970) and Haleh, Israel (Stiller and Hutchinson 1980). These contain carbonates which exhibit no covariation between oxygen and carbon isotopes, although there are relatively large changes in $\delta^{13}\text{C}$ and only small variations in $\delta^{18}\text{O}$. Relatively invariant carbonate oxygen isotopic values suggest relatively fixed lake water composition and short residence time (Talbot 1990).

Based on the data discussed above one may conclude that C-O isotopic patterns of the Tulomozerskaya carbonate display almost no covariation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ($r=0.12$) and therefore on the isotopic grounds no similarity can be seen to carbonates of the typical hydrologically closed basins (Fig. 14). Furthermore, closed system lacustrine carbonates never have $\delta^{13}\text{C}$ values exceeding $+5\text{‰}$. More resemblance in terms of O-C covariance may be observed between carbonates of hydrologically open lakes and those of the Tulomozerskaya Formation carbonates, both of which are characterised by little covariance between $\delta^{13}\text{C}$ - and $\delta^{18}\text{O}$ -values (Fig. 14). However the Tulomozerskaya Formation exhibits a wider range in $\delta^{13}\text{C}$ and highly anomalous $\delta^{13}\text{C}$ values such as $+10$ to $+17\text{‰}$. Such values have never been observed in the open lake system unless they were subjected either to a global or local change in the carbon cycle.

Nevertheless, in a small restricted basin biological fixation and removal of reduced carbon may lead to isotopic disequilibrium between the basin and the open atmosphere-hydrosphere system. This will cause enrichment of ^{13}C in precipitated carbonates. Isotopically heavy carbonates ($\delta^{13}\text{C}$ up to 13.6‰) are forming today by this mechanism in the Lake Kivu, the great western rift zone of East Africa (Botz et al. 1988). Those carbonates which were precipitated in isotopic equilibrium with the lake water bicarbonate have $\delta^{13}\text{C}$ values around 5‰ (Fig. 15a). The most ^{13}C -rich carbonates were formed during times of low water-level stands in those parts of the lake which were isolated from the main lake and their waters were 'chemically' stratified. In all cases ^{13}C -rich sediments contain 2-19% of C_{org} (Botz et al. 1988). At depths of 1.2 m to 4.2 m the first carbonates have been detected with negative $\delta^{13}\text{C}$ of -1.2 to -2.3‰ (Fig. 15b) reflecting the contribution of CO_2 derived from oxidation of organic matter (Botz et al. 1988).

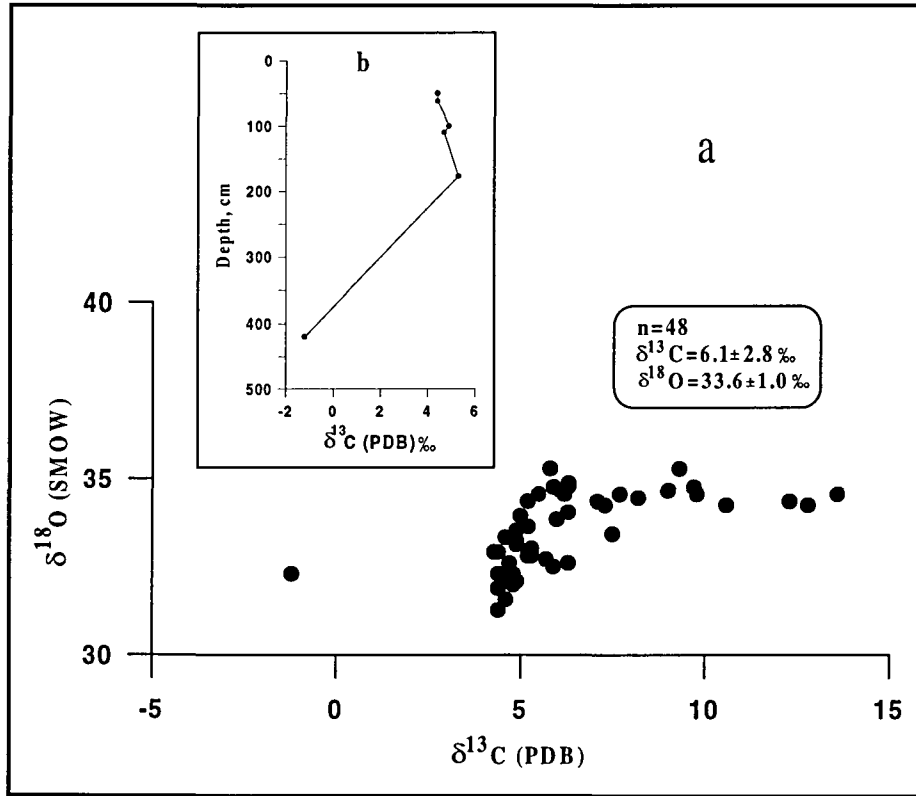


Fig. 15. $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ cross-plot (a) and $\delta^{13}\text{C}$ vs. depth (b) for the Lake Kivu carbonates (analytical data are from Botz et al. 1988).

The data which have been obtained from the Tulomozerskaya Formation carbonates militate with the geochemical features of carbonates reported for the Lake Kivu environments. Firstly, no negative values of carbon isotopes have been measured in the Tulomozerskaya carbonates. Secondly, C_{org} content in carbonate rocks is less than 0.05% (Karhu 1992). Thirdly, no other rocks containing detectable amount of C_{org} have been found to be deposited prior to or simultaneously with ^{13}C -rich carbonates in the Onega palaeobasin (Golubev et al. 1984). On the contrary, all rocks are highly oxidised 'red beds'. Considering that all initial C_{org} mass buried in a closed lake system was eventually oxidised in the course of the post-depositional alteration, then the three crucial questions can hardly be answered: when, why and how it happened without isotopically depleting previously deposited and/or without forming a new generation of carbonates depleted in ^{13}C ?

Thus the model of restricted basin with high bioproduction has to be rejected as not supported by the available data.

7.4 Tectonic model (*Des Marais' model*)

The operation of the carbon cycle can be monitored through an isotopic mass balance (Broecker 1970; Schidlowski et al. 1983; Summons & Hayes 1992)

$$\delta_{in} = f_{carb} \delta_{carb} + f_{org} \delta_{org} \quad (1)$$

where δ_{in} represents the isotopic composition of carbon entering the global surface environment, δ_{carb} and δ_{org} represents the weighted-average isotopic composition of two carbon forms buried in sediments, f_{carb} and f_{org} the fractions of carbon buried in inorganic and organic forms ($f_{carb} = 1 - f_{org}$). Carbon enters the surface environment over time scales longer than 100 Myr, $\delta_{in} = -5\text{‰}$, the average value for crustal carbon (Holser et al. 1988).

It has been established (eg. Schidlowski & Aharon 1992) that δ_{carb} values have been varying around 0‰ throughout geological history within a long-mid-term time scale (10^9 - 10^6 a). A mean δ_{carb} value is considered to be around -25‰. As follows from the relationship given in Eq.(1), a rise in δ_{carb} from -5‰ (δ_{in}) to 0‰ would imply that 20% of total carbon ($C_{org}/C_{carb} = 0.2$, 'Ronov ratio') entering surface environments has to be transformed to C_{org} .

Des Marais et al. (1992b) recently published the result of a total organic carbon isotope study for the Precambrian, based on 731 analyses. In this work δ_{Org} was corrected for the post-depositional thermal degradation of the kerogen. When the reconstructed initial δ_{Org} was used to calculate values of f_{carb} , results indicate a considerable episodic increase between 2.1 and 1.8 Ga ago. The f_{carb} value changed from 0.1 at 2.5 Ga to c. 0.2 at 2.0 Ga and then dropped again to 0.11 after 1.8 Ga ago. Des Marais et al. (1992b) and Des Marais (1994) have linked inferred episodic growth in the reservoir of sedimentary organic carbon and concomitant availability of 'oxidising power' to major changes in tectonism (especially times of global rifting and orogeny).

This episode of enhanced organic sedimentation between 2.1 and 1.8 Ga ago, described by Des Marais et al. (1992b), is roughly coupled with the Tulomozerskaya ^{13}C -rich carbonates deposited prior to 2.0 Ga. It also coincides with the major phase of rifting recorded on the Fennoscandian Shield (e.g. Melezhik & Sturt 1994). Such an episode of enhanced organic sedimentation at around Jatulian time might be represented by ^{13}C -rich carbonates of the Tulomozerskay Formations as well as other ^{13}C -rich carbonates of approximately that age reported from Simbabwe (Schidlowski et al. 1976), Norway (Baker & Fallick 1989b), Karelia (Yudovich et al. 1991), Scotland (Baker & Fallick 1989a), Finland (Karhu 1993), Kola (Karhu & Melezhik 1992; Pokrovsky & Melezhik 1995; Melezhik & Fallick 1996) and Canada (Melezhik et al. a, submitted). However, the estimated buried C_{Org} mass in the Precambrian on the Fennoscandian Shield from Melezhik et al. (1988) shows an increase in organic carbon accumulation does not coincide with the Jatulian 'heavy' carbon excursion. Instead the positive $\delta^{13}\text{C}_{\text{carb}}$ anomalies correspond with a minimum of buried C_{Org} mass. The extensive world review by Salop (1982) showed that the required c. 2.2 ± 0.2 Ga C_{Org} -rich sediments are also unreported elsewhere in the world. Therefore Des Marais' model, being an attractive approach for the explanation of isotopically heavy carbonates occurring at around 2.2 ± 0.2 Ga, suffers from the problem as delineated above which really comes into focus unless 2.2 ± 0.2 Gyr-old C_{Org} -rich rocks would be found somewhere on the globe.

7.5 *Model of oceanic anoxic event*

An oceanic anoxic event normally should result in a stratified ocean with high preservation of organic material. According to Keith (1982) changes from a well-mixed aerated ocean to a

stratified ocean provide a counterbalance between deep reduction and shallow oxidation as well as conditions that favour maximal formation of deep-water C_{org}-rich black sulphidic shales and protopetroleum coupled with shallow-water barite, iron ores, cherty iron formations and 'red beds'. Keith (1982), based on the Permo-Triassic and Late Cretaceous-Early Tertiary stagnant episodes, showed that a stratified oceanic environments were indicated by mesopelagic limestones notably depleted in ¹³C (opposite to prior conclusions, e.g. Tappan 1968; Scholle & Arthur 1980; Jenkyns 1980; Schidlowski & Junge 1981) and ¹³C-rich atmospheric CO₂. If Keith's model is correct then ¹³C-rich CO₂ of the atmosphere must have a tremendous reverberation on isotopic composition of shallow water carbonates. One may expect that some shallow water non-oceanic carbonates and particularly all carbonates deposited in closed lake environment have to be enriched in ¹³C. The lacustrine carbonates, as deduced from Keith's model, are also associated with highly oxidised evaporitic deposits and 'red beds'.

One component of Keith's model is definitely present in the Onega palaeobasin, where widespread lacustrine 'red beds' with evaporitic affinities are associated with extensively developed ¹³C-rich dolostones. However the lack of any kind of evidence of the second component, namely a ca. 2.3-2.1 billion year-old stratified oceanic environment resulting in deep-water C_{org}-rich black sulphidic shales and oceanic limestones depleted in ¹³C, has puzzled scientists since ¹³C-rich carbonates were discovered on the Fennoscandian Shield (e.g. Yudovich et al. 1991; Karhu 1993, Melezhik & Fallick 1996). Therefore the applicability of an oceanic anoxic event as the mechanism leading to development of ¹³C-rich carbonates in Jatulian time remains an open question until synchronously formed C_{org}-rich sediments are found on the Fennoscandian Shield or elsewhere.

7.6 *Model of stromatolite basin (Shark Bay model)*

Primary shift in the isotopic composition of sedimentary carbon can also be due to preferential biological fixation of ¹²C into organic material (e.g. Hayes, 1983; Broecker, 1970). On a basinal scale enrichment of heavy isotopes may be caused by widespread stromatolite-forming bacteria in shallow-water environments. Fig. 16 shows isotopic data on Late Pleistocene and early Holocene stromatolites from the Natron-Magadi (Kenya-Tanzania) basin (Hillaire-Marcel & Casanova 1987; data cited in Talbot 1990). These stromatolites have the similar

isotopic signature to some non-stromatolitic carbonates from evaporitic environments, e.g. Abu Dhali coastal sabkha carbonates which have been discussed earlier (Fig. 13). There is very little

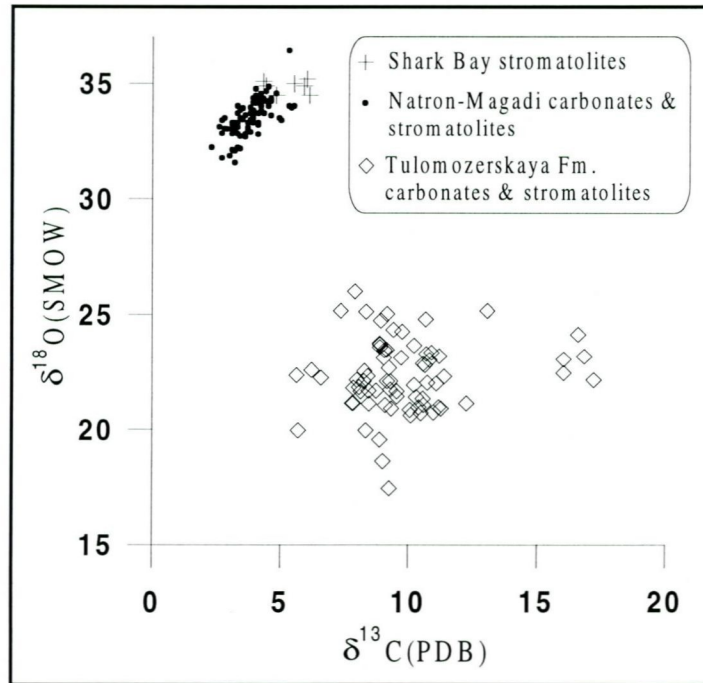


Fig. 16. $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ cross-plot for carbonates of some typical recent and ancient stromatolites, and for carbonates of the Tulomozerskaya Formation. Data are from: Shark Bay, Western Australia - Des Marais et al. 1992; Pokrovsky and Krylov, (unpublished data); Natron (Kenya)-Magadi (Tanzania) - Hillaire-Marcel and Casanova 1987.

a:str-is.grf

control as to whether enrichment in ^{13}C was mediated by evaporative processes or if it could have been assigned to the activity of stromatolite-forming bacteria. The high $\delta^{18}\text{O}$ values support an evaporitic rather than biological impact. However, isotopically heavy carbonates ($\delta^{13}\text{C}$ from 3.0 to +5.6‰) are forming today by this mechanism in Shark Bay, Western Australia (J. Ferguson, L.A. Plumb and M.R. Walter, unpublished data cited in Knoll et al. 1986). Des Marais et al. (1992a) have reported that both $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ of recent stromatolitic mats, including those of Shark Bay, are rather enriched in ^{13}C , from -19.1 to 3‰, and from +2.5 to +6.6‰ (Fig. 17) respectively. Krylov & Pokrovsky's unpublished data (Fig. 18) demonstrates that not only are stromatolitic carbonates of Shark Bay are enriched in ^{13}C but carbonates of living shales are also isotopically heavy, from +4.3 to 4.8‰. Des Marais et al. (1992a) have reported that net dissolved carbon fluxes in a Guerrero stromatolitic pond include day (water to mat) input of HCO_3^- and night (mat to water, in an amount of 80% from the initial HCO_3^- day flux) outflow of carbon component with $\delta^{13}\text{C}$ of -6‰ and +1‰ respectively. From here one may conclude that biologically induced enrichment in ^{13}C may take place in aerobic environments. However, the future, diagenetic, fate of Shark Bay isotopically heavy stromatolitic and shale carbonates as well as accumulated organic matter have not been yet studied. Therefore it is unclear how ^{13}C -rich carbonates and organic matter will cooperate in the course of middle to deep burial and what kind of $\delta^{13}\text{C}$ diagenetic distribution pattern will be seen then in rock record.

Nevertheless, despite of all these questions the Shark Bay stromatolitic basin provides evidence of both direct precipitation of ^{13}C -rich stromatolitic carbonates (up to 6.0‰) and a ^{13}C -enriched carbon component escaping into the water column, which apparently causes the ^{13}C -rich shale carbonates. Theoretically this ^{13}C -rich water environment can be maintained during long periods of time, as long as a stromatolitic community functions, and therefore the system seems to be capable of producing a large amount of ^{13}C -rich carbonates.

The Onega palaeobasin possesses all indispensable components of the Shark Bay environment, namely that the Tulomozerskaya Formation carbonates are essentially stromatolitic rocks formed in shallow-water conditions. Although the studied carbonate formations are approximately three times richer in ^{13}C than the stromatolitic carbonates of

Shark Bay, there is apparently no restriction for employing the Shark Bay model as a principle mechanism leading

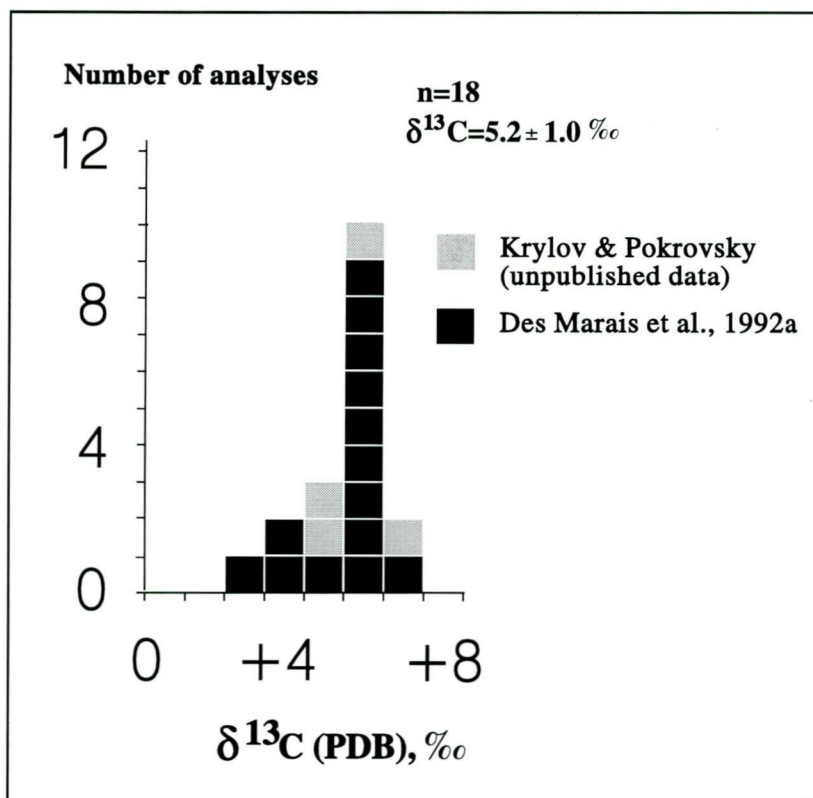


Fig. 17. Histogram of $\delta^{13}\text{C}$ values of carbonates from stromatolites of Shark Bay.

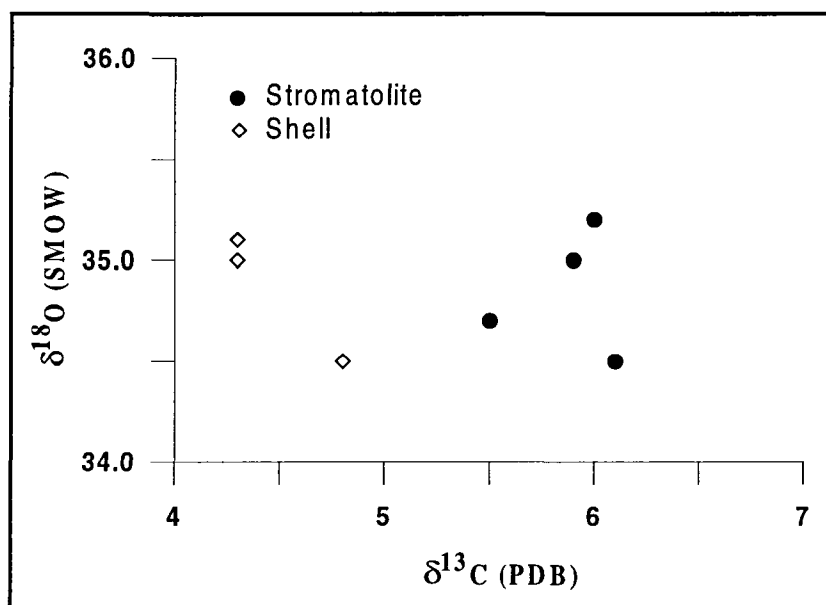


Fig. 18. $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ cross-plot for stromatolitic and shell carbonates of Shark Bay. Unpublished data are from Pokrovsky and Krylov.

to the formation of isotopically heavy carbonates in the Onega palaeobasin on the local scale. However it is unlikely that this mechanism can have influenced the isotopic signature of carbonates deposited on the global scale, as synchronously accumulated isotopically light organic carbon has to be returned to the global carbon cycle in the long run and maintain $\delta^{13}\text{C}$ of the oceanic bicarbonate at around 0‰. On the other hand, Melezhik et al. (a, submitted) have documented that a maximum in diversity and abundance of stromatolite between 2.33-2.06 Ga ago (Jatulian biomass fertility) is synchronised with the positive $\delta^{13}\text{C}_{\text{carb}}$ shift of Jatulian age carbonates, including those of the Tulomozerskaya Formation. It has been also noted that the time interval 2.33 to 2.06 Ga is marked on the Fennoscandian Shield by high diversity and abundance of stromatolites and by both isotopically heavy carbonates and unusually high $\delta^{13}\text{C}$ values of organic matter (up to -4.6‰, Melezhik et al., b, submitted). This indicates an even greater similarity between the Fennoscandian and Shark Bay environments, although the Fennoscandian stromatolitic basins were developed on an area of 850,000 km² and can be extended further NW via Scotland (Baker & Fallick 1989a) to the Labrador Trough (Melezhik et al. a, submitted), which manifests quite a global scale.

8 ORIGIN OF Mg-RICH CARBONATES

Five layers of magnesite or magnesite-bearing dolostones, all less than 2 m in thickness, were detected. Four layers were documented in the drillhole 5177 within the Members D and B at the depth of 553.5, 568.5, 598.7, and 799.0 m (Fig. 5). In drillhole 4699 magnesite-bearing dolostone was observed in Member B at the depth of 537.5 m (Fig. 6). In all cases Mg-rich rocks are white to yellow, medium-grained carbonates which are not distinguished in the drill-core from hosting dolostones. Coarse-grained magnesite observed in natural exposures typically displays replacement relations towards the country rocks, namely dolostones with smaller grain-size. The magnesites and dolostones are similar in major and trace elements as well as in oxygen and carbon isotopes. The only difference between these two carbonate species is the essentially lower Na₂O and F contents of the magnesites; both components are below the detection limit of 0.01% (Appendix 1 and 2). Magnesites are also depleted in Sr (Fig. 8).

As evidenced by sedimentological data the depositional environment of the Tulomozerskaya Formation magnesite (Member B and D) resembles that of a sabkha to playa situations. Consequently diagenesis had to result in a hypersaline environment. It has been documented that magnesite in the Tulomozerskaya Formation replaced dolomite. The latter, as we discussed above, was either chemically precipitated or formed in the course of early diagenesis. Thus magnesite being a secondary phase should have formed during either diagenesis or metamorphism. Oxygen and carbon isotopic results (Fig. 13) suggest that basically one and the same fluids contributed to the precipitation of both dolomite and magnesite. The slightly increased $\delta^{18}\text{O}$ values of the samples with the highest MgO/CaO ratio (23.1 and 24.3‰ compare to 22.3‰ of an average dolomite) may indicate an increased salinity control. Therefore the precipitation of magnesite in the Tulomozerskaya Formation is considered to have been an early diagenetic phenomenon, caused by pore waters isotopically comparable to that of water from which dolomite was formed. Depletion in the Na and F as compare with dolomite apparently indicates deficiency in these components in magnesite forming solutions.

Known and studied magnesite deposits and occurrences appear in a wide variety of geological environments, although the typical sedimentary developments are confined to ancient marine platform carbonates (Veitsh type, Pohl 1989), lacustrine sediments nearby or overlying ultramafites (Belaya Stena type), marine evaporates (e.g. Sebkh el Melah, east coast of Tunisia, Perthuisot 1980), recent coastal salt flats in arid regions (e.g. sabkhas of Abu Dhabi, Bush 1973) and to continental and coastal lakes (e.g. playas in Coorong Lagoon area, South Australia, Schroll 1989). Most magnesite is formed during diagenesis in a hypersaline environment. Magnesite may also be formed in freshwater lakes although this type of mineralization is of recent to Tertiary age and is strictly confined to areas with an extensive development of ultramafic complexes (Zachmann 1989). Only Veitsh and Belaya Stena types are of economic importance (Pohl 1989).

The origin of Mg-bearing solutions is not yet well understood, although it has been stated that magnesite formation as a primary precipitate at low temperature seems to be impossible (e.g. Möller 1989). The formation of magnesite depends first of all on the predominance of Mg in relation to Ca in the solution (Müller et al. 1972; Möller 1989). It is well known that Mg^{2+} is

enriched in seawater in the course of carbonate sedimentation. This process enhances dolomitisation of carbonate muds (Carpenter 1980) and may proceed towards magnesitisation. The influence of algae in producing high pH-values in the water may be an important factor for magnesite formation; major fossil magnesite deposits are intimately associated with biohermal algae dolomite (Greensmith 1979). Salinity of the diagenetic pore solutions is very important, as rising salinity increases the Mg/Ca-ratio and enlarges the stability field of magnesite as compared to that of dolomite. Although the salinity may be either positively correlated with Mg-carbonate formation, for instance in sabkhas of Abu Dhabi, Persian Gulf, or not correlated, as is the case in coastal salt lakes (playas) in the Coorong district, South Australia (Pohl 1989). The Mg/Ca-ratio is raised even more if sulphates crystallised (Bathurst, 1975) leading to the development of dense, Mg-enriched residual brines.

A consideration of the sedimentological data shows that the Tulomozerskaya Formation magnesite mineralisation was formed in sabkha to playa environments. Therefore, on palaeobasinal grounds it may be comparable to that of either sabkhas of Abu Dhabi, or playas in the Coorong Lagoon area, South Australia. Data on C- and O-isotopes of magnesites from the Coorong playas, shown in Fig. 13, display that the O-isotope values of Coorong magnesite are similar to those of the Tulomozerskaya Formation. However $\delta^{13}\text{C}$ differs, as the studied magnesites are richer in ^{13}C as has been discussed above in the connection with a general problem of carbon anomalous values for the whole set of carbonate rocks of the Tulomozerskaya Formation. If the mechanism for magnesite precipitation in the Tulomozerskaya Formation is interpreted as similar to the South Australian Coorong Lake (Schroll 1989), then the Tulomozerskaya type of magnesite mineralisation is of non- or subeconomic quality and quantity.

9 CONCLUSIONS

The Palaeoproterozoic Tulomozerskaya Formation studied herein represents a 800 m-thick terrigenous-carbonate succession formed in lacustrine evaporitic settings that has prograded into sabkha, and then into marine environments. All carbonate rocks, which lithologically are predominantly dolostones and to a lesser extent magnesites, despite their depositional settings,

exhibit only isotopically positive, highly anomalous $\delta^{13}\text{C}$ values. The carbon isotope data mostly fall within the +8 and +10‰ range, with large stratigraphic oscillations only at the base (between 12 and +17.2‰) and in the uppermost part of the sequence (between +5.6 and +9‰). These are coupled with $\delta^{18}\text{O}$ ranging between 17.5 and 26.0‰ with 22.3‰ as a mean, which is a normal Palaeoproterozoic value. Dolostones were precipitated either from the basinal waters or from the diagenetic pore-water which was apparently isotopically similar to the basinal water. Magnesite occurs in a number of 1 to 2 m-thick layers. It was apparently formed as a secondary phase during early diagenesis. Magnesitisation was accomplished under evaporitic conditions similar to those in modern sabkha and playa lakes. The magnesite mineralisation is considered to be similar to the Coorong type and evaluated as sub-economic.

None of the recent environments developed under normal conditions can provide a model which may result in the formation of large amount of carbonates with $\delta^{13}\text{C}$ falling between +5 and +17‰ such as is the case for the Tulomozerskaya dolostones. Among the various theoretical possibilities from global- to basinal-scale models, we definitely exclude diagenetic and evaporative origins as well as a model of restricted basin with high bioproduction, as they are in conflict with the existing data.

The rise of $\delta^{13}\text{C}$ in the Onega palaeobasin must have generated in a global or semi-global scale as indicated by its continuity across the Fennoscandian Shield through Scotland and Canada. The excess of C_{org} deposition which must have caused the $\delta^{13}\text{C}$ anomaly and took place in an area external to the Onega Palaeobasin as shown by a lack of C_{org} within the Tulomozerskaya sequence. The tectonic model by Des Marais (Des Marais et al. 1992b; Des Marais 1994) might be considered as a possible mechanism leading to enhanced rate of organic carbon buried and resulting in a disbalance of the global carbon reservoir. The stratified ocean as proposed by Keith (1992), is also a favourable global model which may provide a counterbalance between deep-water reduction with deposition of ^{13}C -depleted limestones and shallowwater oxidation with deposition of ^{13}C -rich dolostones. However, these two models discussed are theoretical considerations rather than the real solutions to the problem: a lack of C_{org} -rich sediments (for the tectonic model), and lack of isotopically light limestones coupled with C_{org} -rich oceanic sediments (for the stratified oceanic model) of that age on the Fennoscandian Shield or elsewhere on the globe.

A model of stromatolitic basin (Shark Bay model) is regarded as another possibility. Stromatolites may provide the accumulation of ^{13}C -rich carbonates and continuous outflow of carbon component enriched in ^{13}C . We assume that an intensive preferential biological removal of ^{12}C into living biomass of stromatolites must have caused ^{13}C enrichment of water on the local scale. In this respect the Tulomozerskaya carbonates together with others on the Fennoscandian Shield and elsewhere, represent a phenomenon caused by local, although widespread, factors.

REFERENCES

Akhmedov, A.M., Krupenik, V.A., Makarikhin, V.V. & Medvedev, P.V. 1993: Carbon isotope composition of carbonates in the early Proterozoic sedimentary basins. Printed report, Institute of Geology of the Karelian Scientific Centre, Petrozavodsk, 58 p. (in Russian).

Aksenov E.M., Ignat'ev, S.V., Negruzta, V.Z. & Solonzov, L.F. 1975: On magnesite in Jatulian carbonate formations in South Karelia. *Transactions of the USSR Academy of Sciences, Earth Sciences Section*, 227 (3), 672-675.

Baker, A. J. & Fallick, A. E. 1989a: Evidence from Lewisian limestone for isotopically heavy carbon in two-thousand-million-year-old sea water. *Nature*, 337, 352-354.

Baker, A. J. & Fallick, A. E. 1989b: Heavy carbon in two-billion-year-old marbles from Lofoten-Vesterålen, Norway: Implications for the Precambrian carbon cycle. *Geochim. Cosmochim. Acta.*, 53, 1111-1115.

Bathurst, R.G.C. 1975: *Carbonate sediments and their diagenesis*. 2nd ed. Dev. Sedimentol., 12, Elsevier, Amsterdam, 658 pp.

Botz, R., Stoffers, P., Faber, E. & Tietze, K. 1988: Isotope geochemistry of carbonate sediments from lake Kivu (East-Central Africa). *Chemical Geol.*, 69, 299-308.

Brand, U and Veizer, J. 1980: Chemical diagenesis of multicomponent carbonate system - 1. Trace elements. *Journal of Sedimentary Petrology*, 50, 1219-1250.

Bonatti, C., Emiliani, C., Ostlund, G. & Rydel, H. 1971: Final dessication of the Afar Rift, Ethiopia, *Science*, 1972, 468-469

Broecker, W.S. 1970: A boundary condition on the evolution of atmospheric oxygen. *Journal of Geophysical Research*, 75(18), 3553-3557.

Bush, P., 1973: Some aspects of the diagenetic history of the Sabkha in Abu Dhabi, Persian Gulf. In: Pursur, B.H.. (ed.), *The Persian Gulf*, Springer-Verlag, New York, pp. 395-407.

Carpenter, A.B. 1980: The chemistry of dolomite formation I: The stability of dolomite. *SEPM Spec. Publ*, 28, 111-121.

Des Marais D.J. 1994: Tectonic control of the crustal organic carbon reservoir during the Precambrian. *Chem. Geol.*, 114, 303-314.

Des Marais, D.J., Bauld, J, Palmisano, A.C., Summons, R.E. & Ward, D.M. 1992a: The biochemistry of carbon in modern microbial mats. In: Schopf, J.W. & Klein, C.(eds.), *The Proterozoic Biosphere*, Cambridge University Press, 287-293.

Des Marais, D. J., Strauss, H, Summons, R. E. & Hayes, J. M. 1992b: Carbon isotope evidence for the stepwise oxidation of the Proterozoic environment. *Nature (London)*, 359, 605-609.

Eskola, P. 1919: Hufvuddragen av Onega Karelians geologi. *Teknikern*, 29.

Friedman, I. 1970: Some investigations of deposition of travertine from hot springs - I: The isotopic chemistry of a travertine-depositing spring. *Geochim. Cosmochim. Acta.*, 34, 1303-1315.

Golubev, A.I., Akhmedov. A.M. & Galdobina, L.P. 1984: *Geochemistry of the early Proterozoic 'black shale' complexes of the Karelo-Kola Region*. Leningrad: Nauka, 193 pp (in Russian).

Greensmith, J.T. 1979: Petrology of the sedimentary rocks. In: *Textbook of Petrology, Vol. 2, 6th ed.*, G.Allen & Uniwin Ltd. London, 241 pp.

Halfman, J.D., Johnsos, T.C., Showers, W.J. & Lister, G.S. 1989: Authigenic low-Mg calcite in Lake Turkana, Kenya. *J.Afr. Earth Sci.*

Hillaire-Marcel, C. & Casanova, J. 1987: Isotopic hydrology and paleohydrology of the Magadi (Kenya)-Natron (tanzania) basin during the Late Quaternary. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 58, 155-181.

Hayes, J.M. 1983: Geochemical evidence bearing on the origin of aerobiosis, a speculative hypothesis. In: Schopf, J.W. (ed), *Earth's Earliest Biosphere: Its Origin and Evolution* Princeton University Press, NJ, 291-301.

Holser, W.T., Schidlowski, M., Mackenzie, F.T. & Maynard, J.B. 1988: Geochemical cycles of carbon and sulphur. In: Gregor, C.B., Garrels, R.M., Mackenzie, F.T. & Maynard J.B. (eds.) *Chemical Cycles in the Evolution of the Earth*, Wiley NY, 106-173.

Hudson, J.D. 1977: Stable isotopes and limestone lithification. *Journal of Geological Society, London*, 133, 637-660.

Irwin, H., Curtis, C. & Coleman, M. 1977: Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature*, 260, 209-213.

ISSC (International Subcommision on Stratigraphic Classification of IUGS Commission on Stratigraphy), 1976: *International Stratigraphic Guide: A Guide to Stratigraphic Classification, Terminology and Procedure* (ed. Hedberg, H.D.), John Willey & Sons. New York, 200 pp.

Jenkyns, H.C. 1980: Cretaceous anoxic events from continents to oceans. *J. Geol. Soc. London*, 137, 171-188.

Karhu, J.A. 1989: Extensive early Proterozoic carbon isotope anomaly recorded in sedimentary carbonates and kerogens from the Fennoscandian Shield. *Epstein 70th Birthday Symposium, Abstracts with Program*. Pasadena: California Institute of Technology, 80-82.

Karhu, J.A. 1993: Palaeoproterozoic evolution of the carbon isotope ratios of sedimentary carbonates in the Fennoscandian Shield. *Geol. Surv. Finland, Bull.*, 371, 1-87.

Karhu, J.A. & Melezhik, V.A. 1992: Carbon isotope systematics of early Proterozoic sedimentary carbonates in the Kola Peninsula, Russia: Correlations with Jatulian formations in Karelia. In: Balagansky, V.V. & Mitrofanov F.P. (eds.), *Correlations of Precambrian formations of the Kola-Karelia region and Finland*, Apatity: Kola Scientific Centre of the Russian Academy of Sciences, 48-53.

Katz, A., Kolodny, Y. & Nissenbaum, A. 1977: The geochemical evolution of the Pleistocene Lake Lisan - Dead Sea system. *Geochimica and Cosmochimica Acta*, 41, 1609-1626.

Kratz, K.O. 1963: Geology of the Karelian Karelides. *Transactions of the Laboratory of Precambrian Geology of the USSR Academy of Sciences*, 16, 205 pp. (in Russian).

Keith, M.L. 1982: Violent volcanism, stagnant oceans and some inferences regarding petroleum, strata-bound ores and mass extinctions. *Geochim. Cosmochim. Acta*, 46, 2621-2637.

Knoll, A.H., Hayes, J.M., Kaufman, A.J., Swett, K. & Lambert, I.B. 1986: Secular variation in carbon isotope ratios from Upper Proterozoic successions of Svalbard and East Greenland. *Nature (London)*, 321, 832-838.

Laajoki, K. 1986: The Precambrian supracrustal rocks of Finland and their tectono-exogenic evolution. *Precambrian Res.*, 33, 67-85.

Magaritz, M., Anderson, R.Y., Holser, W.T., Saltzman E.S. & Garber, J. 1983: Isotope shift in the Late Permian of the Delaware Basin, Texas, precisely timed by varved sediments. *Earth and Planetary Science Letters*, 66, 111-124.

Makarikhin, V. V. & Kononova, G. M. 1983: *Early Proterozoic Phytolithes of Karelia*. Leningrad, 'Nauka', 180 pp. (in Russian).

Makarikhin, V. V., Medvedev, P.V., Lavrov, B.S. & Satzuk, Yu.I. 1994: Palaeontological characteristic of the Tulomozero Formations of the Onega Zone as based on drillcore material. In: Rybakov, S.I., (ed.), *Problems of the Precambrian Geology, Magmatism and Metamorphism, Karelia*. Institute of Geology, Petrozavodsk, pp. 9-14 (in Russian).

McKenzie, J.A. 1981: Holocene dolomitisation of calcium carbonate sediments from coastal sabkhas of Abu Dhabi, U.A.E. - a stable isotope study. *J. Geol.*, 89, 185-198.

McKenzie, J.A. 1985: Carbon isotopes and productivity in the lacustrine and marine environment. In: Stumm, W. (ed.), *Chemical Processes in Lakes*. Wiley, New York, N.Y., 99-118.

Melezhik, V.A., 1993: Magnesite potential in the Jatulian carbonate formations of the Fennoscandian Shield. Geological Survey of Norway, *Unpublished report 93.151*, 66 pp.

Melezhik, V.A. & Fallick, A.E., 1996. A widespread positive $\delta^{13}\text{C}_{\text{carb}}$ anomaly at around 2.33-2.06 Ga on the Fennoscandian Shield: a paradox? *Terra Nova*, 8, in press.

Melezhik, V.A. & Sturt, B.A. 1994: General geology and evolutionary history of the Early Proterozoic Polmak-Pasvik-Pechenga-Imandra/Varzuga-Ust'Ponoy Greenstone Belt in the north-eastern Baltic Shield. *Earth Science Reviews*, 36, 205-241.

Melezhik, V.A., Basalae, A.A., Predovsky, A.A., Balabonin, N.L., Bolotov, V.I., Pavlova, M.A., Gavrilenko, B.V. & Abzalov, M.Z. 1988: *Carbonaceous Deposits of Early Stages of the Earth's Evolution (Geochemistry and Conditions of Accumulation on the Baltic Shield)*. Leningrad, 'Nauka', 200 pp. (in Russian).

Melezhik, V.A., Fallick, A.E. & Clark, T. A new province shows 2 billion-year-old isotopically heavy carbon: evidence from the Labrador Trough, Canada. *Canadian Journal of the Earth Sciences*, (a, submitted).

- Melezhik, V.A., Fallick, A.E., Makarikhin, V.V. & Lubtsov, V.V. Links between palaeoproterozoic palaeogeography and rise and decline of stromatolites: Fennoscandian Shield. *Precambrian Research*, (b, submitted).
- Möller, P. 1989: Nucleation process of magnesite. *Monograph Series on Mineral Deposits*, 28, 287-292.
- Müller, G., Irion, G. and Förstner, U. 1972: Formation and diagenesis of inorganic Ca-Mg-carbonates in lacustrine environment. *Naturwiss.*, 59, 158-164.
- Negrutza, V. Z. 1984: *Early Proterozoic Development of the Eastern Part of the Baltic Shield*. Leningrad, Nedra, 270 pp. (in Russian).
- Peirre, C. 1982: Teneurs en isotopes stables (^{18}O , ^2H , ^{13}C , ^{34}S) et conditions de génèse des évaporites marines: application à quelques milieux actuels et au Messinien de la Méditerranée, *D.S.N. Thesis*, Université de Paris-Sud, Orsay, 226 pp.
- Perthuisot, J.P. 1980: Sebkh el Melah near Zaris, a recent paralic salt basin (Tunisia). In: *Editions Technip, Evaporite Deposits*, Paris, pp. 11-17.
- Pohl, W. 1989: Comparative geology of magnesite deposits and occurrences. *Monograph Series on Mineral Deposits*, 28, 1-13.
- Pokrovsky, B.G. & Melezhik, V.A., 1995 Variations of oxygen and carbon isotopes in Palaeoproterozoic carbonate rocks of the Kola Peninsula. *Stratigraphy and Geological Correlation*, 3(5); 42-53.
- Pukhtel', I.S., Zhuravlev, D.Z., Ashikhmina, N.A., Kulikov, V.S. & Kulikova V.V. 1992: Sm-Nd age of the Suisarskay suite on the Baltic Shield. *Transections of the Russian Academy of Sciences*, 326, 706-711

- Reitsema, R.H. 1980: Dolomite and nahcolite formation in organic rich sediments: isotopically heavy carbonates. *Geochim. Cosmochim. Acta*, 44, 2045-2049.
- Salop, L. I. 1982: *Geological Development of the Earth in Precambrian*, Leningrad, Nedra, 343 pp. (in Russian).
- Satzuk, Yu. I., Makarikhin, V.V. & Medvedev, P.V. 1988: *Geology of the Jatuli (Onego-Segozero watershed)*. Leningrad, Nauka, 96 pp. (in Russian).
- Schidlowski, M. & Aharon, P. 1992: Carbon cycle and carbon isotope record: geochemical impact of life over 3.8 Ga of Earth history. In: Schidlowski, M., Golubich, S., Kimberley, M.M. & Trudinger, P.A (eds.), *Early Organic Evolution: Implications for Mineral and Energy Resources* Berlin Heidelberg: Springer-Verlag, 145-175.
- Schidlowski, M., Eichmann, R. & Junge, C.E. 1975: Precambrian sedimentary carbonates: Carbon and oxygen isotope geochemistry and implications for the terrestrial oxygen budget. *Precambrian Res.*, 2, 1-69.
- Schidlowski, M., Eichmann, R. & Junge, C.E. 1976: Carbon isotope geochemistry of the Precambrian Lomagundi carbonate province, Rhodesia. *Geochim. Cosmochim. Acta.*, 40, 449-455.
- Schidlowski, M & Junge, C.E. 1981: Coupling among the terrestrial sulphur, carbon and oxygen cycles: numerical modeling based on revised carbon isotope record. *Geochim. Cosmochim. Acta*, 45: 589-594.
- Schidlowski, M., Hayes, J.M. and Kaplan, I.R. 1983: Isotopic inference of ancient biochemistries: carbon, sulphur, hydrogen and nitrogen. In: Schopf, J. W. (ed.), *Earth's earliest biosphere: its origin and evolution* University Press, Princeton, NJ, pp.149-186.

Scholle, P.A. & Arthur, M.A. 1980: Carbon isotope fluctuations in Cretaceous pelagic limestones: potential stratigraphic and petroleum exploration tool. *Bull. Am. Assoc. Pet. Geol. Bull.*, 64(1), 64-78.

Schroll, E. 1989: Recent formation of magnesite in evaporitic environment. The example of the the Coorong Lagoon (South Australia). *Monograph Series on Mineral Deposits*, 28, 29-34.

Sederholm, J.J. 1899: Über eine archaische Sediment Formation in sudwestlichen Finland and ihre Bedeutung fur die Erklärung der Entstehungsweise des Grundgebirges. *Bull. Comm. Géol. Finlande*, 6, 254 S.

Sokolov, V.A. 1970: Jatuli of Karelia and vicinities. *D. Sc. Thesis*, Geological Institute of the USSR Academy of Sciences, Moscow, 52 pp. (in Russian).

Sokolov, V.A. 1980: Jatulian formations of the Karelian ASSR. In: Silvennoinen, A. (ed.), *Jatulian Geology in the Eastern Part of the Baltic Shield*, Proceedings of a Finnish-Soviet Symposium held in Finland, 21th-26th August, 1979. Rovaniemi: The Committee for Scientific and Technical Cooperation between Finland and Soviet Union, 163-220.

Sokolov, V.A. 1987: The Jatulian Superhorizon. In: Sokolov, V.A., (ed.). *The Geology of Karelia*. Leningrad, Nauka, pp. 51-59. (in Russian).

Stiller, M. & Hutchinson, G.E., 1980: The waters of Merom: a study of Lake Huleh, 1. Stable isotopic composition of carbonates of a 54 m core: Paleoclimatic and paleotrophic implications. *Arch. Hydrobiol.*, 89, 257-302.

Stiller, M., Rounick, J.S. & Shasha, S. 1985: Extreme carbon-isotope enrichments in evaporitic brines. *Nature (London)*, 316, 434-435.

Stuiver, M. 1970: Oxygen and carbon isotope ratios of fresh-water carbonates as climatic indicators. *Journal of Geophys. Res.*, 75, 5247-5257.

Summons, R.E. & Hayes, J.M. 1992: Principles of molecular and isotopic biogeochemistry. In: *The Proterozoic Biosphere* (ed. by Schopf, J.W. & Klein, C.). Cambridge University Press, 155-153.

Talbot, M.R. 1990: A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Isotope Geoscience*, 80, 261-279.

Talbot, M.R. & Kelts, K. 1990: Palaeolimnological signatures from carbon and oxygen isotopic ratios in carbonates from organic carbon-rich lacustrine sediments. In: Katz, B.J (ed.), *Lacustrine Basin Exploration: Case Studies and Modern Analogues*. Tulsa, AAPG Memoir, 50: 99-112.

Tappan, H. 1968: Primary production, isotopes, extinctions and the atmosphere. *Paleogeogr., Paleoclimatol., Paleoecol.*, 4, 187-210.

Tikhomirova, M. & Makarikhin, V.V. 1993: Possible reasons for the $\delta^{13}\text{C}$ anomaly of lower Proterozoic sedimentary carbonates. *Terra Nova*, 5, 244-248.

Veizer, J. 1978: Strontium: Abundance in common sediments and sedimentary rock types. In Wedepohl, K.H. (ed.), *Handbook of Geochemistry III/5 Section 38 L*. Springer Verlag.

Veizer, J., Clayton, R.N. & Hinton, R.W. 1992b: Geochemistry of Precambrian carbonates: IV. Early Paleoproterozoic (2.25±0.25 Ga) seawater. *Geochemica and Cosmochimica Acta*, 56, 875-885.

Veizer, J. & Hoefs, J. 1976: The nature of $\text{O}^{16}/\text{O}^{18}$ and $\text{C}^{13}/\text{C}^{12}$ secular trends in sedimentary carbonate rocks. *Geochemica and Cosmochimica Acta*, 40, 1387-1395.

Veizer, J., Lemieux J., Jones, B., Gibling, R.M. & Savelle J. 1978: Palaeosalinity and dolomitisation of a Lower Paleozoic carbonate sequence, Somerest and Prince of Wales Islands, Arctic Canada. *Canadian Journal of Earth Sciences*, 15, 1448-1461.

Veizer, J., Clayton, R.N. and Hinton, R.W., Von Brunn, V., Mason, T.R., Buck, S.G. & Hoefs, J. 1990: Geochemistry of Precambrian carbonates: III. Shelf seas and non-marine environments of the Archean. *Geochemica and Cosmochimica Acta*, 54, 2717-2729.

Veizer, J., Plumb, K.A., Clayton, R.N., Hinton, R.W. & Grotzinger, J.P. 1992b: Geochemistry of Precambrian carbonates: V. Late Paleoproterozoic seawater. *Geochemica and Cosmochimica Acta*, 56, 2487-2501.

Väyrynen, H. 1933: Über die Stratigraphie der Karelischen Formationen. *Bull. Comm. Géol. Finlande*, 101, 54-78.

Watson, R.S., Trewin, N.H & Fallick, A.E. 1995: The formation of carbonate cement in the Forth and Balmoral Fields, northern North Sea: a case for biodegradation, carbonate cementation and oil leakage during early burial. In: Harley, A.J. and Prosser, D.J. (eds), *Characterization of Deep Marine Clastic Systems, Geological Society Special Publication*, 94, 177-200.

Yudovich, Ya.E., Makarikhin, V.V., Medvedev, P.V. & Sukhanov, N.V. 1991: Carbon isotope anomalies in carbonates of the Karelian Complex. *Geoch. Intl.*, 28(2), 56-62.

Zachmann, D.W. 1989: Mg-carbonate deposit in freshwater environment. *Monograph Series on Mineral Deposits*, 28, 61-94

Appendix 1. Chemical composition of carbonate rocks, drill holes 5177 from Onega area, Karelia
(continued).

Depth, m	K ₂ O	MnO	P ₂ O ₅	Total	δ ¹³ C, ‰	δ ¹⁸ O, ‰	Mo	Nb
335	n.d.	n.d.	n.d.	n.d.	8.34	19.97	n.d.	n.d.
337.5	n.d.	n.d.	n.d.	n.d.	9.17	25.03	n.d.	n.d.
344	0.16	0.01	0.09	58.81	9.1	21.05	<0.0005	<0.0005
344.6	0.05	0.02	0.09	56.24	5.68	19.97	<0.0005	<0.0005
347	0.05	0.01	0.1	56.67	8.47	21.11	<0.0005	<0.0005
349.5	0.02	0.03	0.09	55.16	6.21	22.57	<0.0005	<0.0005
351.2	0.05	0.02	0.07	69.39	6.57	22.24	<0.0005	<0.0005
351.7	0.02	0.03	0.11	55.47	5.62	22.35	<0.0005	<0.0005
356	0.01	0.02	0.1	56.06	8.9	23.69	<0.0005	<0.0005
359.6	0.01	0.01	0.09	55.51	8.93	24.74	<0.0005	<0.0005
360	n.d.	n.d.	n.d.	n.d.	9.16	23.46	n.d.	n.d.
366	<0.01	0.04	0.1	55.64	9.17	22.09	<0.0005	<0.0005
380.4	0.01	0.03	0.1	55.18	8.89	23.75	<0.0005	<0.0005
391.5	0.01	0.04	0.09	55.23	8.35	25.13	<0.0005	<0.0005
392	0.02	0.02	0.07	56.56	7.92	26.01	<0.0005	<0.0005
392.7	0.02	0.03	0.08	56.36	7.34	25.17	<0.0005	<0.0005
395.2	0.02	0.04	0.08	56.38	8.46	21.68	<0.0005	<0.0005
360	<0.01	0.04	0.15	56.1	n.d.	n.d.	<0.0005	<0.0005
403.2	0.07	0.37	0.1	56.46	9.24	22.67	<0.0005	<0.0005
448	0.03	0.15	0.08	56.07	8.41	22.32	<0.0005	<0.0005
449.8	0.05	0.17	0.08	55.44	8.75	21.68	<0.0005	<0.0005
520	0.21	0.02	0.15	57.88	10.06	20.85	<0.0005	<0.0005
542	0.04	0.25	0.09	55.47	9.01	18.65	<0.0005	<0.0005
542.5	0.03	0.17	0.1	55.48	8.89	19.57	<0.0005	<0.0005
553.5	0.01	0.17	0.01	40.86	9.05	23.12	<0.0005	<0.0005
554.5	0.03	0.08	0.1	55.27	7.86	21.8	<0.0005	<0.0005
555.5	0.04	0.07	0.08	55.65	8.08	21.83	<0.0005	<0.0005
556	0.04	0.07	0.09	55.06	8	22.15	<0.0005	<0.0005
560.5	0.06	0.07	0.18	55.49	9.29	21.72	<0.0005	<0.0005
563	0.06	0.01	0.08	56.27	9.26	17.47	<0.0005	<0.0005
568.5	0.04	0.19	0.04	33.82	9.42	24.34	<0.0005	<0.0005
569.5	0.07	0.06	0.14	55.38	n.d.	n.d.	<0.0005	<0.0005
584.5	0.14	0.09	0.13	69.62	7.86	21.14	<0.0005	<0.0005
593	0.06	0.05	0.1	55.78	8.15	21.65	<0.0005	<0.0005
598.7	1.06	0.05	0.08	47.31	9.55	21.44	<0.0005	<0.0005
599	0.3	0.06	0.09	56.64	8.3	22.54	<0.0005	<0.0005
654	0.06	0.03	0.11	68.4	7.8	21.14	<0.0005	<0.0005
678.5	0.32	0.02	0.07	69.98	8.26	22.09	<0.0005	<0.0005
718	1.74	0.07	0.22	61.25	9.07	23.45	<0.0005	<0.0005
720	0.96	0.09	0.18	59.45	8.9	23.59	<0.0005	<0.0005
724.5	0.92	0.09	0.13	58.95	10.68	24.8	<0.0005	<0.0005
727	3.63	0.09	0.32	84.26	9.29	22.1	<0.0005	<0.0005
729	1.49	0.08	0.11	62.58	9.72	23.12	<0.0005	<0.0005
732.5	0.28	0.1	0.09	57.07	9.76	24.26	<0.0005	<0.0005
757	0.26	0.02	0.11	70.53	10.48	20.71	<0.0005	<0.0005
760	0.01	0.02	0.05	70.9	16.04	23.05	<0.0005	<0.0005
764.5	0.22	<0.01	0.31	56.19	10.7	23.28	<0.0005	<0.0005
766.5	0.21	<0.01	0.17	56.33	10.58	22.85	<0.0005	<0.0005
767.5	0.2	<0.01	0.24	56.17	10.23	23.65	<0.0005	<0.0005
796.5	n.d.	n.d.	n.d.	n.d.	10.65	22.8	n.d.	n.d.
799	n.d.	n.d.	n.d.	n.d.	10.74	22.03	n.d.	n.d.

Appendix 1. Chemical composition of carbonate rocks, drill holes 5177 from Onega area, Karelia
(continued)

Depth, m	Zr	Y	Sr	Rb	U	Th	Pb	Cr
335	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
337.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
344	<0.0005	<0.0005	0.0101	<0.0005	0.0037	0.002	<0.0010	<0.0005
344.6	<0.0005	0.0007	0.0115	<0.0005	0.0028	<0.0010	<0.0010	<0.0005
347	<0.0005	<0.0005	0.0134	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005
349.5	<0.0005	<0.0005	0.0047	<0.0005	0.0041	<0.0010	0.0022	<0.0005
351.2	<0.0005	<0.0005	0.0024	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005
351.7	<0.0005	0.0006	0.0039	<0.0005	0.0039	<0.0010	<0.0010	<0.0005
356	<0.0005	<0.0005	0.007	<0.0005	0.0017	0.001	<0.0010	<0.0005
359.6	<0.0005	0.0006	0.0051	<0.0005	0.0036	0.0011	<0.0010	<0.0005
360	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
366	<0.0005	<0.0005	0.0077	<0.0005	0.0051	0.0015	<0.0010	<0.0005
380.4	<0.0005	<0.0005	0.0044	<0.0005	<0.0010	0.0014	<0.0010	<0.0005
391.5	<0.0005	<0.0005	0.0049	<0.0005	0.0022	0.0019	<0.0010	<0.0005
392	<0.0005	<0.0005	0.002	<0.0005	0.0025	<0.0010	<0.0010	<0.0005
392.7	<0.0005	<0.0005	0.0024	<0.0005	0.0016	0.0011	<0.0010	<0.0005
395.2	<0.0005	0.0008	0.0015	<0.0005	0.004	<0.0010	<0.0010	<0.0005
360	<0.0005	<0.0005	0.0029	<0.0005	0.0034	<0.0010	<0.0010	<0.0005
403.2	<0.0005	0.0009	0.0021	<0.0005	0.0024	<0.0010	<0.0010	<0.0005
448	<0.0005	<0.0005	0.0087	<0.0005	0.0016	<0.0010	<0.0010	<0.0005
449.8	<0.0005	<0.0005	0.0203	<0.0005	0.0024	<0.0010	<0.0010	<0.0005
520	<0.0005	0.0006	0.0097	0.0007	0.0035	0.0012	<0.0010	0.0007
542	<0.0005	<0.0005	0.0219	<0.0005	0.004	<0.0010	0.0014	<0.0005
542.5	<0.0005	<0.0005	0.0185	<0.0005	0.0049	<0.0010	0.0013	<0.0005
553.5	<0.0005	<0.0005	<0.0005	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005
554.5	<0.0005	<0.0005	0.0169	<0.0005	0.0047	<0.0010	0.002	<0.0005
555.5	<0.0005	<0.0005	0.0158	<0.0005	0.0026	<0.0010	0.0033	<0.0005
556	<0.0005	0.0009	0.0166	<0.0005	<0.0010	<0.0010	0.0038	<0.0005
560.5	<0.0005	<0.0005	0.0118	<0.0005	0.0019	<0.0010	0.0023	<0.0005
563	<0.0005	<0.0005	0.0083	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005
568.5	<0.0005	<0.0005	0.0011	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005
569.5	<0.0005	<0.0005	0.0193	<0.0005	0.0041	<0.0010	0.0019	<0.0005
584.5	<0.0005	<0.0005	0.0082	<0.0005	0.001	<0.0010	<0.0010	<0.0005
593	<0.0005	<0.0005	0.0181	<0.0005	<0.0010	<0.0010	0.0022	<0.0005
598.7	<0.0005	<0.0005	0.0062	0.0028	<0.0010	<0.0010	<0.0010	<0.0005
599	<0.0005	<0.0005	0.0193	0.0007	0.0017	<0.0010	<0.0010	<0.0005
654	<0.0005	<0.0005	0.0073	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005
678.5	<0.0005	<0.0005	0.0081	0.0015	0.0016	0.001	<0.0010	0.0023
718	0.0018	0.0013	0.0087	0.0038	0.0037	0.0011	<0.0010	0.0023
720	<0.0005	0.0009	0.0083	0.0019	0.0013	0.0012	<0.0010	0.0011
724.5	0.0011	0.0011	0.008	0.0019	0.0021	0.0012	<0.0010	0.0014
727	0.0064	0.0017	0.005	0.0088	<0.0010	<0.0010	<0.0010	0.0091
729	0.0019	0.0014	0.0082	0.0029	<0.0010	<0.0010	<0.0010	0.0026
732.5	<0.0005	0.0008	0.0107	<0.0005	0.0025	<0.0010	<0.0010	<0.0005
757	<0.0005	<0.0005	0.0144	0.0011	0.0025	0.0012	0.0012	<0.0005
760	<0.0005	0.0008	0.0112	<0.0005	0.0013	<0.0010	<0.0010	<0.0005
764.5	<0.0005	<0.0005	0.0065	0.0008	<0.0010	<0.0010	<0.0010	<0.0005
766.5	<0.0005	<0.0005	0.0069	0.0007	0.0037	0.0013	<0.0010	<0.0005
767.5	<0.0005	<0.0005	0.0066	0.0008	0.0037	<0.0010	<0.0010	<0.0005
788	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
796.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Appendix 1. Chemical composition of carbonate rocks, drill holes 5177 from Onega area, Karelia.

Depth, m	V	As	Sc	S	Cl	F
335	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
337.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
344	0.0012	<0.0010	0.0013	<0.10	<0.10	0.54
344.6	0.0015	<0.0010	0.0011	<0.10	<0.10	0.48
347	0.0013	<0.0010	<0.0010	<0.10	<0.10	0.51
349.5	0.0015	<0.0010	0.001	<0.10	<0.10	0.46
351.2	0.0007	<0.0010	<0.0010	<0.10	<0.10	0.27
351.7	0.0021	<0.0010	0.001	<0.10	<0.10	0.47
356	0.0005	<0.0010	0.0011	<0.10	<0.10	0.46
359.6	0.0011	<0.0010	0.0012	<0.10	<0.10	0.4
360	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
366	0.0008	<0.0010	<0.0010	<0.10	<0.10	0.48
380.4	0.0009	<0.0010	<0.0010	<0.10	<0.10	0.43
391.5	0.0007	<0.0010	<0.0010	<0.10	<0.10	0.44
392	<0.0005	<0.0010	0.0012	<0.10	<0.10	0.33
392.7	0.0007	<0.0010	0.0013	<0.10	<0.10	0.34
395.2	0.0006	<0.0010	0.0012	<0.10	<0.10	0.35
360	0.0009	<0.0010	0.001	<0.10	<0.10	0.37
403.2	0.0008	<0.0010	0.0013	<0.10	<0.10	0.35
448	0.0008	<0.0010	0.001	<0.10	<0.10	0.34
449.8	0.0009	<0.0010	<0.0010	<0.10	<0.10	0.45
520	0.0012	<0.0010	0.0011	<0.10	<0.10	0.38
542	<0.0005	<0.0010	<0.0010	<0.10	<0.10	0.43
542.5	0.0009	<0.0010	0.001	<0.10	<0.10	0.41
553.5	0.0005	<0.0010	<0.0010	<0.10	<0.10	<0.10
554.5	0.0007	<0.0010	<0.0010	<0.10	<0.10	0.44
555.5	0.001	<0.0010	0.001	<0.10	<0.10	0.45
556	0.0009	<0.0010	<0.0010	<0.10	<0.10	0.46
560.5	0.001	<0.0010	0.0011	<0.10	<0.10	0.4
563	0.0009	<0.0010	0.0011	<0.10	<0.10	0.34
568.5	0.0005	<0.0010	<0.0010	<0.10	<0.10	<0.10
569.5	0.0011	<0.0010	<0.0010	<0.10	<0.10	0.46
584.5	0.0009	<0.0010	0.0012	<0.10	<0.10	0.25
593	0.001	<0.0010	0.0012	<0.10	<0.10	0.38
598.7	0.0013	<0.0010	0.0011	<0.10	<0.10	<0.10
599	0.0014	<0.0010	0.0011	<0.10	<0.10	0.43
654	0.0008	<0.0010	0.001	<0.10	<0.10	0.2
678.5	0.0011	<0.0010	0.0012	<0.10	<0.10	0.27
718	0.0017	<0.0010	0.0013	<0.10	<0.10	0.43
720	0.0013	<0.0010	0.0013	<0.10	<0.10	0.42
724.5	0.0016	<0.0010	0.0012	<0.10	<0.10	0.42
727	0.0052	<0.0010	0.0012	<0.10	<0.10	0.5
729	0.0019	<0.0010	0.0014	<0.10	<0.10	0.4
732.5	0.0009	<0.0010	<0.0010	<0.10	<0.10	0.43
757	0.0006	<0.0010	0.0013	<0.10	<0.10	0.33
760	0.0007	<0.0010	0.0011	<0.10	<0.10	<0.10
764.5	0.0012	<0.0010	0.0011	<0.10	<0.10	0.55
766.5	0.0012	<0.0010	0.001	<0.10	<0.10	0.52
767.5	0.0011	<0.0010	0.001	<0.10	<0.10	0.53
788	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
796.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
799	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Appendix 2. Chemical composition of carbonate rocks, drill hole 4699 from Onega area, Karelia
(continued).

Depth, m	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	CaO	MgO/CaO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	Total	δ ¹³ C, ‰	δ ¹⁸ O, ‰
493.5	34.12	0.88	0.32	0.04	16.3	19.19	0.85	0.2	0.26	0.03	0.1	71.44	10.3	21.4
497.5	39.83	0.28	0.15	0.02	12.11	16.38	0.74	<0.10	0.25	0.02	0.08	69.22	10.1	20.62
506	13.35	<0.01	0.05	<0.01	17.69	25.39	0.70	0.13	0.11	0.03	0.15	56.89	10.4	20.97
512	0.22	<0.01	0.04	<0.01	22.56	32.08	0.70	0.14	0.09	0.02	0.16	55.27	10.23	21.92
514	18.46	0.31	0.14	0.02	15.66	22.52	0.70	0.13	0.17	0.01	0.09	57.51	10.59	21.05
516.5	37.27	0.15	0.08	<0.01	12.54	18.26	0.69	0.11	0.09	<0.01	0.08	68.6	10.56	21.34
522.5	15.3	0.1	0.08	0.01	17.05	24.75	0.69	0.14	0.05	0.04	0.23	57.76	9.55	21.65
524.1	7.79	<0.01	0.02	<0.01	19.41	28.32	0.69	0.15	0.05	0.06	0.16	55.89	9.33	20.91
527.5	4.51	<0.01	0.06	0.01	21.43	29.65	0.72	0.13	0.14	0.04	0.15	56.12	10.82	23.02
530	1.47	<0.01	0.04	<0.01	21.99	31.36	0.70	0.13	0.09	0.04	0.12	55.2	10.9	23.34
535.5	14.7	<0.01	0.02	<0.01	17.47	24.56	0.71	0.12	0.03	0.04	0.07	56.89	11.09	22.00
537.5	1.5	<0.01	0.02	<0.01	32.8	10.58	3.10	<0.10	0.05	0.05	0.08	45.02	11.18	20.96
560	37.51	<0.01	0.03	<0.01	12.2	18.45	0.66	0.11	0.07	0.03	0.18	68.54	10.97	20.74
566.5	36.15	0.83	0.16	0.02	18.58	15.92	1.17	<0.10	0.61	0.03	0.06	72.44	13.07	25.17
589	8.31	0.04	0.08	0.01	19.85	27.76	0.72	0.14	0.08	0.12	0.13	56.53	11.2	23.19
595.5	45.92	2.39	0.28	0.08	8.94	12.95	0.69	0.14	1.73	0.05	0.08	72.56	11.39	22.3
660	1.38	0.48	0.26	0.04	22.78	31.2	0.73	0.13	0.3	0.18	0.23	56.98	12.25	21.13
732	2.25	0.03	0.02	0.01	22.04	30.89	0.71	0.15	0.03	0.05	0.11	55.6	16.6	24.14
750	15.13	5.47	1.5	0.21	17.79	21.17	0.84	0.13	3.49	0.07	0.15	65.11	16.84	23.17
756	16.55	1.46	0.43	0.06	17.45	22.86	0.76	0.12	0.7	0.04	0.08	59.75	n.d.	n.d.
758	6.7	0.6	0.13	0.02	26.09	19.75	1.32	0.12	0.24	0.04	0.17	53.86	17.21	22.15
761.5	16.2	<0.01	0.01	<0.01	16.61	23.76	0.70	0.16	0.03	0.05	0.08	56.87	16.04	22.45

Appendix 2. Chemical composition of carbonate rocks, drill hole 4699 from Onega area, Russian Karelia

Depth, m	Zr	Y	Sr	Rb	U	Th	Pb	Cr	V	Sc	F
493.5	<0.0005	<0.0005	0.0097	0.001	<0.0010	0.0011	<0.0010	<0.0005	0.0013	<0.0010	0.35
497.5	<0.0005	<0.0005	0.0071	0.0012	0.0018	0.0012	<0.0010	<0.0005	0.0011	<0.0010	0.27
506	<0.0005	<0.0005	0.0109	<0.0005	0.0036	<0.0010	0.0012	<0.0005	0.001	0.001	0.41
512	<0.0005	<0.0005	0.013	<0.0005	0.0036	<0.0010	<0.0010	<0.0005	0.0011	<0.0010	0.52
514	<0.0005	<0.0005	0.0092	0.0006	0.0029	<0.0010	<0.0010	<0.0005	0.0011	0.0012	0.3
516.5	<0.0005	0.0005	0.0067	<0.0005	0.0015	<0.0010	<0.0010	<0.0005	0.0008	0.0014	0.22
522.5	<0.0005	<0.0005	0.0055	<0.0005	0.0023	<0.0010	<0.0010	<0.0005	0.0007	0.0012	0.32
524.1	<0.0005	<0.0005	0.0075	<0.0005	0.0023	0.0017	<0.0010	<0.0005	0.0009	0.0012	0.43
527.5	<0.0005	0.0009	0.0491	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005	0.0011	0.0011	0.55
530	<0.0005	0.0006	0.0449	<0.0005	0.0019	<0.0010	<0.0010	<0.0005	0.0013	<0.0010	0.53
535.5	<0.0005	0.0005	0.0396	<0.0005	0.0026	<0.0010	<0.0010	<0.0005	0.0008	0.0011	0.34
537.5	<0.0005	<0.0005	0.0151	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005	<0.0005	<0.0010	<0.10
560	<0.0005	0.0007	0.007	<0.0005	0.0026	0.0011	0.0011	<0.0005	0.0007	0.0012	0.24
566.5	<0.0005	0.0005	0.012	0.003	<0.0010	0.0011	<0.0010	0.0008	0.0012	0.0013	0.43
589	<0.0005	0.0007	0.0173	<0.0005	0.0039	<0.0010	0.0016	<0.0005	0.0009	0.0013	0.41
595.5	0.0043	0.0007	0.0189	0.0027	<0.0010	0.0011	<0.0010	<0.0005	0.0009	<0.0010	0.11
660	<0.0005	0.0007	0.0033	0.0013	0.0037	0.0016	<0.0010	0.0007	0.001	<0.0010	0.54
732	<0.0005	0.0011	0.0406	<0.0005	0.0024	0.001	<0.0010	<0.0005	0.0009	<0.0010	0.43
750	0.0046	0.0016	0.0381	0.0056	0.0039	0.0017	<0.0010	0.0026	0.0027	0.0013	0.35
756	0.0005	0.0012	0.0097	0.0011	0.0012	<0.0010	<0.0010	<0.0005	0.0007	0.0013	0.33
758	<0.0005	0.0024	0.0308	<0.0005	<0.0010	<0.0010	<0.0010	<0.0005	0.0005	0.0012	0.26
761.5	<0.0005	0.0011	0.0215	<0.0005	0.0039	<0.0010	<0.0010	<0.0005	0.0009	0.0011	0.29

S, Cl, As, Mo, Nb are below detection limit, <0.10, <0.10, <0.0010, <0.0005, <0.0005 respectively