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World-wide 2 billion-year-old isotopically heavy carbonate carbon: the evolutionary significance and driving forces (final report).

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REPORT

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World-wide 2 billion-year-old isotopically heavy carbonate carbon: the evolutionary significance and driving forces (final report).

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Summary:

This report shows the activities carried out and the results obtained within the project. The results shown in this report have been obtained within period of time from 30.11.96 to 15.09.99. The main objectives were to reach an understanding of the Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$, its significance in the Earth evolution and driving forces using stable and radiogenic isotope systematics of 2.3-1.9 Ga-old sedimentary formations. Evolutionary significance of the isotope excursion has been exemplified by its inter-link with dramatic climatic changes, a world-wide continental rift expansion, extensive development of shallow-water carbonate platphorms and world-wide' red beds', widespread dolostones and evaporites, along with anprecedented in Earth history lateral expansion of cyanobacterial ecosystems, free oxygen increase, the earliest appearances of phosphorites, formation of Fe, Mn, P and $CaCO_3$ concretions. The excursion is a unique event both in terms of long duration (>300 Ma) and an extreme ^{13}C enrichment (up to +18‰), though superficially resembles the Precambrian/Cambrian transition events. Several 2.40-2.06 Ma Palaeoproterozoic positive excursions of $\delta^{13}C_{carb}$ have been suggested by new data. Three positive shifts of $\delta^{13}C_{carb}$ separated by returns to 0‰ have been recognised. Differentiation between global and local factors suggests that the isotopic excursion with global $\delta^{13}C_{carb}$ value of +5‰ might have been driven by accelerated accumulation of organic material combined with onset of intensive methane cycling resulting in Δ_c change. Palaeoproterozoic shallow water environments and bordering oceans were apparently decoupled, shallow water carbonates with extreme enrichment in ^{13}C (up to +18‰) from restricted environments should not be applied for reconstruction of secular $\delta^{13}C$ variations. Current problems are related to the fact that the isotope anomaly cannot be balanced by only C_{org} burial (f_{org}). A significant change in δ_{in} seems implausible. $^{87}Sr/^{86}Sr$ ratios do not support enhanced erosional rate and concomitant enhanced accumulation of C_{org}. The isotope excursion was apparently driven by a different mechanism involved in the primary production of C_{org} , i.e. change in Δ_c.

Keywords: Palaeoproterozoic,	Isotopes	Evaporites
Carbon	Stromatolites	Shallow-water environments
Strontium	Red beds	Final report

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INTRODUCTION

1. TITLE, REFERENCE NUMBER

World-wide 2 billion-year-old isotopically heavy carbonate carbon: the evolutionary significance and driving forces;

INTAS-RFBR 95-928;
Victor A. Melezhik;

Total period of time: 30th of November 1996 - 15th of September 1999;

Period of time since the last report: 30th of November 1996 - 15th of September 1999.

2. RESEARCH

2.1. Scientific Objectives

The main objectives were to reach an understanding of the Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$, its significance in the evolution of the biosphere and driving forces using: (*I*) stable and radiogenic isotope systematics of 2.3-1.9 Ga-old sedimentary formations, (*II*) modelling of anomalous heavy carbonate carbon formation, which occurred at around 2.3-2.06 Ga ago: global phenomenon versus local development.

The project is devoted to a study of one of the most remarkable and enigmatic Palaeoproterozoic phenomena: wide-spread unusually heavy carbonate carbon (Schidlowski 1975; Baker & Fallick 1989a, 1989b; Yudovich et al. 1991; Karhu, 1993; Melezhik & Fallick 1996; Buick et el. 1998). The Early Proterozoic $\delta^{13}C_{carb}$ excursion together with a series of major global palaeoenviromental changes resembles, but is more intense than, the Precambrian/Cambrian transition events (Melezhik and Fallick 1994). This phenomenon is

related to a fundamental problem of the global carbon cycle, biological evolution and oxygenation of hydrosphere-atmosphere system in the Precambrian.

Previously it has been suggested that the isotopically positive carbon anomaly might be attributed to: (*I*) an increase of the 'Ronov ratio' or 'Broecker ratio' (reduced carbon/oxidised carbon ratio), (*II*) generally different carbon pathways within the global ecosystem, possibly associated with the minimal oxygenation of the environment; or (*III*) enzymological and/or physiological differences in primary products, (*IV*) as well as other various possible models still under discussion. The possibility of diachronism in deposition of high $\delta^{13}C_{carb}$ carbonates has also been considered.

The main area of study is indicated on Fig. 1.

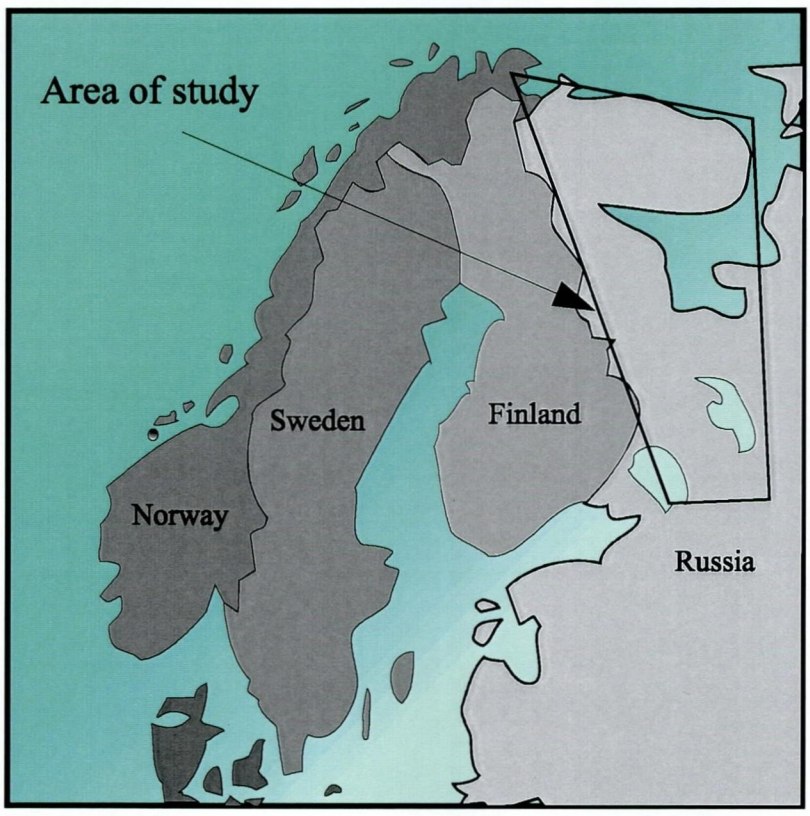

Figure 1. ***Geographic positions of the study areas.***

2.2. Research Activities

Five institutions were involved in the research: the Geological Survey of Norway (participant 1), the Scottish Universities Research and Reactor Centre (participant 2), the Institute of Precambrian Geology and Geochronology, St. Petersburg (participant 3), the Geological Institute, Moscow (participant 4), the Institute of Geology, Petrozavodsk (participant 5).

The following work has been carried out by the participants:

Participant 1: Co-ordinating the work on the project; sedimentological research, major and trace element analyses, sulphide separation, cathode-luminescent microscope study, electron microprobe study.

Participant 2: Conventional isotope analyses of carbonate and organic carbon, and sulphur; laser isotope analysis of carbonate carbon.

Participant 3: Pb-Pb age determination of carbonate rocks; Rb and Sr contents in carbonate phases, strontium isotope analysis of carbonates.

Participant 4: Wet chemical analysis of carbonates including AAS determination of Mn and Fe contents; taxonomic treatment, palaeoenvironmental interpretation, and dynamics of taxanomic diversity of Palaeoproterozoic stromatolites.

Participant 5: Field work, taxonomic treatment of Palaeoproterozoic stromatolites, sedimentological and geochemical studies.

The major components of the programme for the years 1996-1999 are indicated in Table 1. Almost all the activities of the programme have been accomplished apart from laser isotope analyses. These were not carried out due to the lack of suitable material to be analysed.

Table 1. 24month programme for the years 1996-1999 starting 30/11/96*.

Period	Activity	Participants	Remark
	Co-ordinating work		
1	Co-ordinating meeting of all participants in St. Petersburg	All	Accomplished
	Compilation work		
1	Compiling available data on $\delta^{13}C_{carb}$ for the Fennoscandian Shield	1 & 5	«
	Experimental work, Onega area, Karelian carbonate platform		
1	Field work	5	«
1	Sample preparation for main and trace element analyses	1 & 5	«
1	Main and trace element analyses	1 & 4	«
2	Conventional isotope analysis of carbonate carbon	2	«
2	Rb-Sr systematics and strontium isotope analysis	3	«
2	Sample preparation for Pb-Pb age determinartion	1, 3 & 5	«
2	U-Pb systematics and Pb-Pb age determination	3	«
3	Cathode-luminescent study	1	«

* There were no activity on the project from August 1998 till April 1999 due to the economic crisis in Russia and the temporal termination in funding of the project.

Table 1. (continued).

Period	Activity	Participants	Remark
3	Sample selection for sulphur isotope analyses of sulphides and sulphates	1 & 5	«
3	Sulphide extraction	1	«
3	Sulphur isotope analyses of sulphides and sulphates	2	«
3	U-Pb systematics and Pb-Pb age determination	3	«
3	Rb-Sr systematics and strontium isotopes analyses	3	«
3	Conventional isotope analyses of carbonate carbon	2	«
	Compilation work		
2	Compiling data on Fennoscandian Palaeoproterozoic stromatolites	4, 1 & 5	Accomplished
2	Compiling data on depositional environments of Fennoscandian Palaeoproterozoic carbonate formations	1, 4 & 5	«
	Co-ordinating work		
4	Co-ordinating meeting in St. Petersburg (all participants)	All	«
	Reporting		
4	Annual report on activity	1 & 3	«

Table 1. (continued).

Period	Activity	Participants	Remark
	Experimental work, the Pechenga Belt		
5	Field work	5	«
5	Major and trace element analyses	1, 4	«
5	Conventional isotope analyses of carbonate carbon	2	«
5	Rb-Sr systematics and strontium isotope analyses	3	«
5	U-Pb systematics and Pb-Pb age determination	3	«
6	Cathode-luminescent study	1	«
6	Sample preparation for laser isotope analyses	1	Do not accomplished
6	Laser isotope analysis	2	«
6	U-Pb systematics and Pb-Pb age determination	3	Accomplished
6	Rb-Sr systematics and strontium isotope analyses	3	«
6	Sample selection for sulphur isotope analysis	1	«
6	Sulphur isotope analysis	2	«
7	U-Pb systematics and Pb-Pb age determination	3	«
7	Rb-Sr systematics and strontium isotope analyses	3	«

2.3. Scientific Results

2.3.1. Main results

A series of scientific results have been achieved with the summary provided below.

A global character of the 2.4-2.06 Ga positive excursion of $\delta^{13}C_{carb}$.

New, well-studied occurrences of ^{13}C-rich carbonates from the area of investigation have been added to those previously reported. Together these cover nearly the whole globe (Fig. 2), confirming the earlier conclusions by Baker & Fallick (1989) that the Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$ is global in nature.

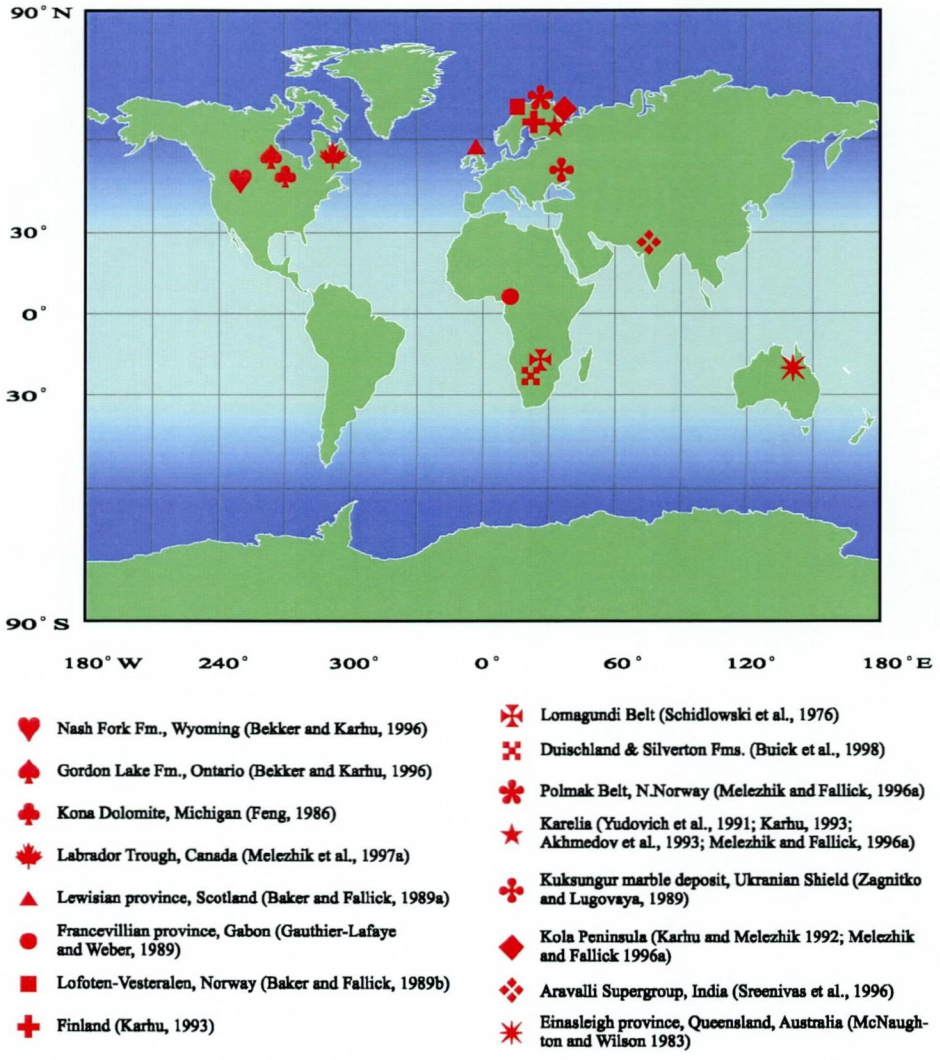

Figure 2. ***World-wide distribution of the Palaeoproterozoic (2.40-2.06 Ga) ^{13}C-rich carbonate rocks (modified from Melezhik et al. 1997).***

Differentiation between global and local factors involved in the formation of ^{13}C-rich carbonates.

Sedimentological and isotopic evidence obtained suggests an apparent geochemical decoupling between Palaeoproterozoic shallow water environments and bordering oceans; shallow water red beds, evaporites and stromatolite-rich carbonates from restricted environments should not be applied for reconstruction of secular $\delta^{13}C$ curves. The extreme enrichment in ^{13}C (up to +18‰) has been caused by local factors such as an intensive development of cyanobacteria, coupled with evaporation in restricted basins which were apparently not in full equilibrium with atmospheric CO_2 (Fig. 3)

Evolutionary significance the Palaeoproterozoic positive excursion of $\delta^{13}C_{car}$.

Fig. 4 lists some of the major Palaeoproterozoic events which are interlinked to the Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$, and clearly demonstrates the evolutionary significance of the excursion. A world-wide continental rift expansion, development of large shallow-water intercontinental seas and the Huronian glaciation preceded the Palaeoproterozoic isotope excursion (Fig. 3).

Onset of the isotope excursion coincides with the development of shallow-water carbonate platforms, widespread deposition of dolostones and evaporites, world-wide development of 'red beds', and anprecedented in Earth history lateral expansion of cyanobacterial ecosystems reflected in stromatolite record. Contrary to the latest Mesoproterozoic-Neoproterozoic positive shifts in $\delta^{13}C_{carb}$ values (up to 10-12‰), the 2.4-2.06 Ga positive excursions do not seem to have been related to obvious evolutionary events in the biota.

The level of oxygen in the atmosphere rose between 2.2 and 2.0 Ga by factor of 15 (Holland 1994). This coincides with the onset of diagenetic alterations rather similar to present diagenetic processes, in that they are manifested by formation of abundant concretions with highly oxidised iron and manganese, phosphate concretions and carbonate concretions, as a result of organic carbon recycling during diagenesis under oxic conditions.

One of the earliest (2.1 Ga) appearances of organelle-bearing eukaryotic cells corresponding to the formation of sedimentary and diagenetic phosphorites are assigned to the second half of the isotope excursion.

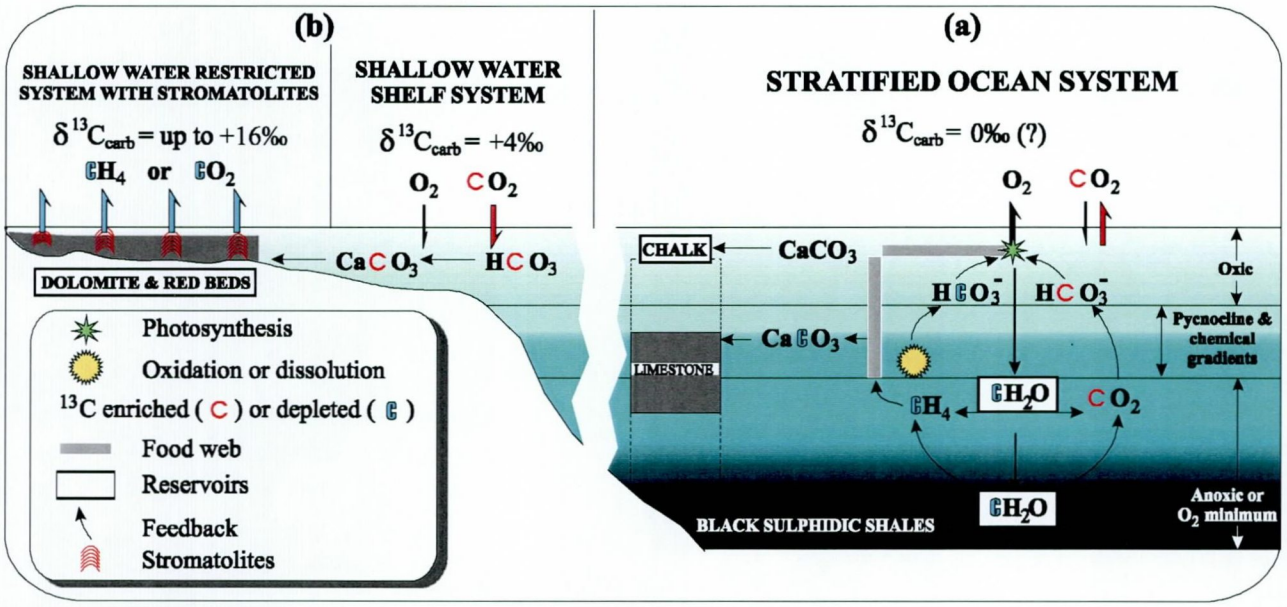

Figure 3. ***Simplified model illustrating enrichment of Palaeoproterozoic carbonates in ^{13}C as compared to inferred global background value of +5‰ (modified from Melezhik & Fallick 1997). Diagram also shows carbon transfers and reservoirs in (a) a stagnant ocean and (b) in developing marginal seas. A horizontal food-web pattern represents dominant phytoplankton components, and a vertical pattern dominant bacterial components. Carbon isotope fractionation is shown schematically by contour-face and bold-face carbon symbols.***

Termination of the Palaeoproterozoic isotopic shift at 2.06 Ga (Karhu 1993) is concurrent with decline of banded iron formation and detrital uraninite and pyrite.

A sharp increase in dispersal of $\delta^{34}S$ clearly coincides with the first appearance of isotopically heavy carbonates suggesting that (*i*) sulphate was widely available in seawater and (*ii*) sulphides abundantly formed via bacterial sulphate reduction in restricted environments with a limited SO_4^{2-} supply.

The Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$ is a unique event.

The Palaeoproterozoic $\delta^{13}C_{carb}$ excursions together with a series of major global palaeoenvironmental changes superficially resemble the Precambrian/Cambrian transition events (Melezhik & Fallick 1996; Buick et al. 1998). However, the Palaeoproterozoic

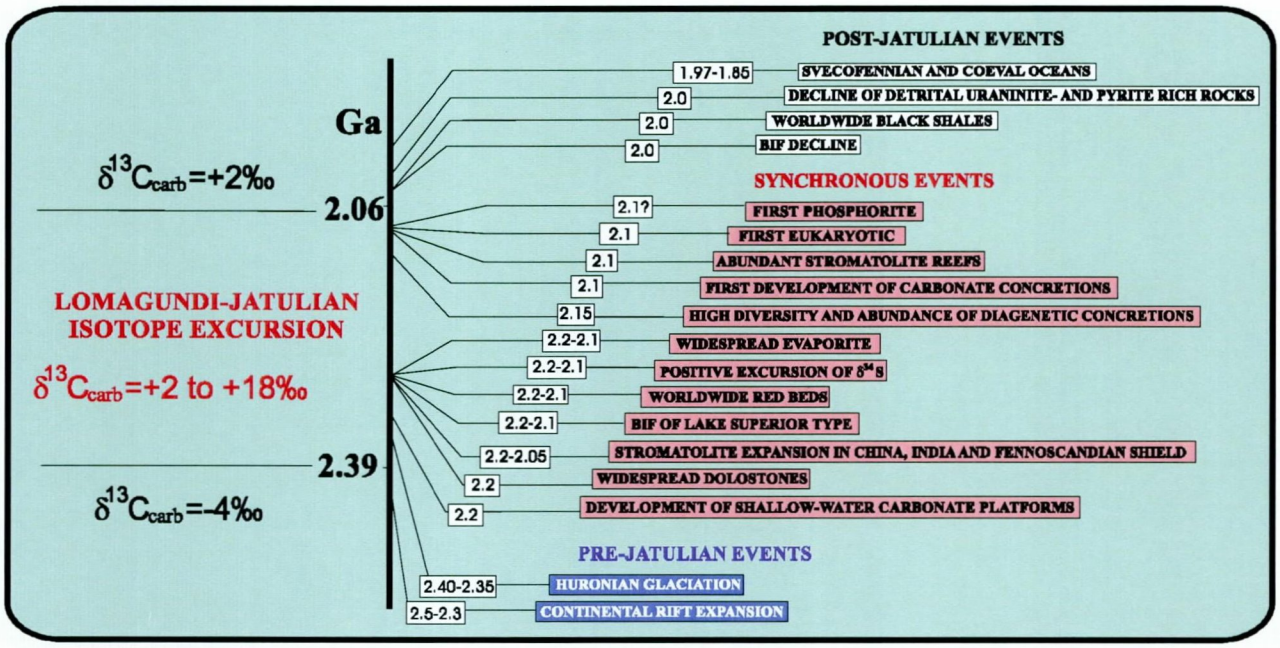

Figure 4. ***Major phenomena interrelated to the Palaeoproterozoic (Lomagundi-Jatulian) isotopic event (modified from Melezhik et al. 1997).***

isotopic event is unique in terms of both duration (>300 Ma) and ^{13}C enrichment (up to +18‰) (Fig. 5).

Several Palaeoproterozoic positive excursions of $\delta^{13}C_{carb}$.

New data obtained within the projects (Melezhik et al., 1999) and by Buick et al. (1998) suggest that the single Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$ is now considered as three positive shifts of $\delta^{13}C_{carb}$ separated by returns to 0‰, which all occurred between 2.40 and 2.06 Ma (Fig. 6).

2.3.2. Current problems

The mechanism responsible for one of the most significant carbon isotopic shifts in Earth history remains highly debatable. The isotope anomaly cannot be balanced by organic carbon burial (f_{org} in equation) as there is no geological evidence for an enhanced C_{org} accumulation prior to or synchronous with the excursion:

$$\delta_{carb} = \delta_{in} + f_{org}\Delta_c,$$

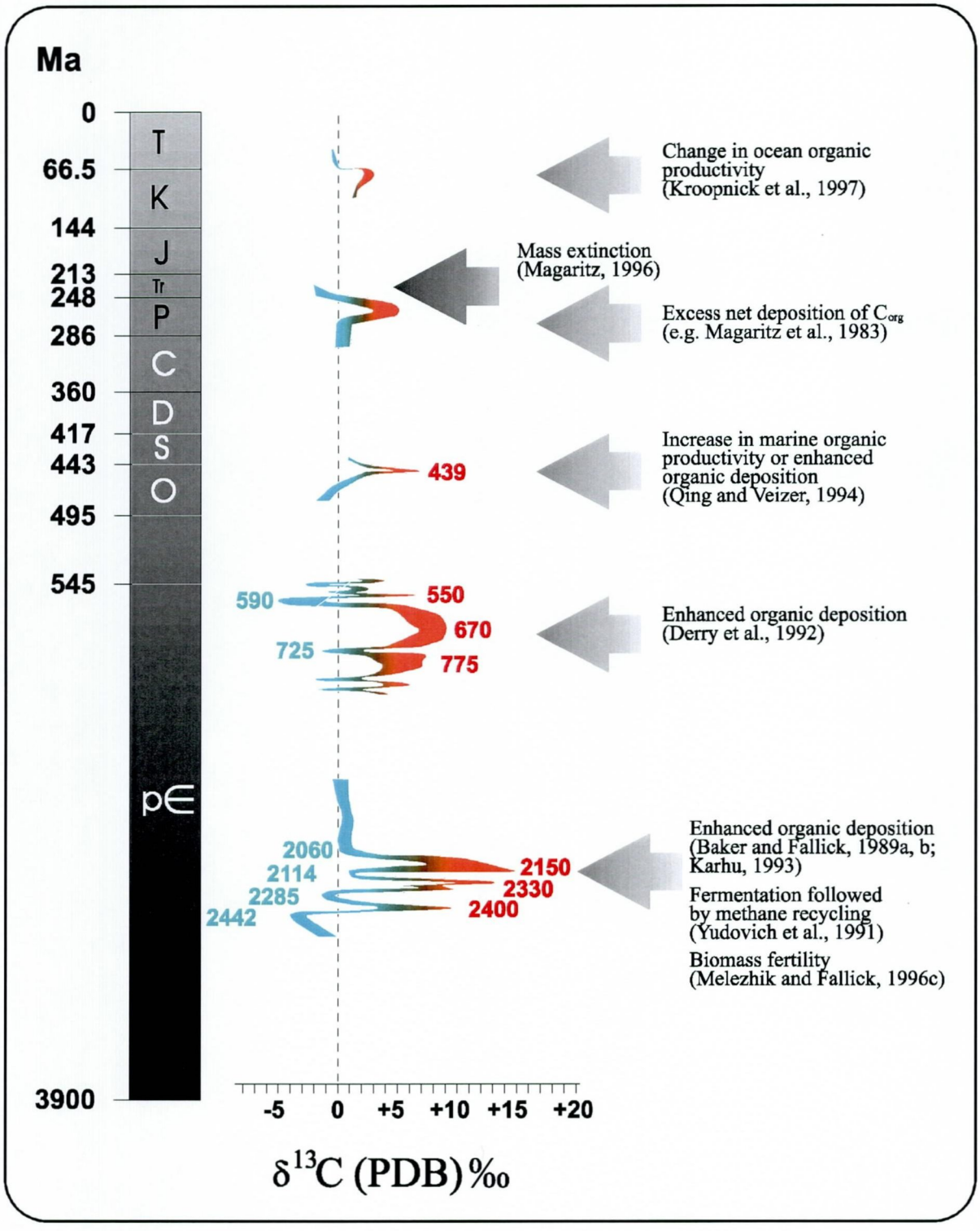

Figure 5. *Major $\delta^{13}C_{carb}$ anomalies in Earth history based on published material (after Melezhik et al. 1999).*

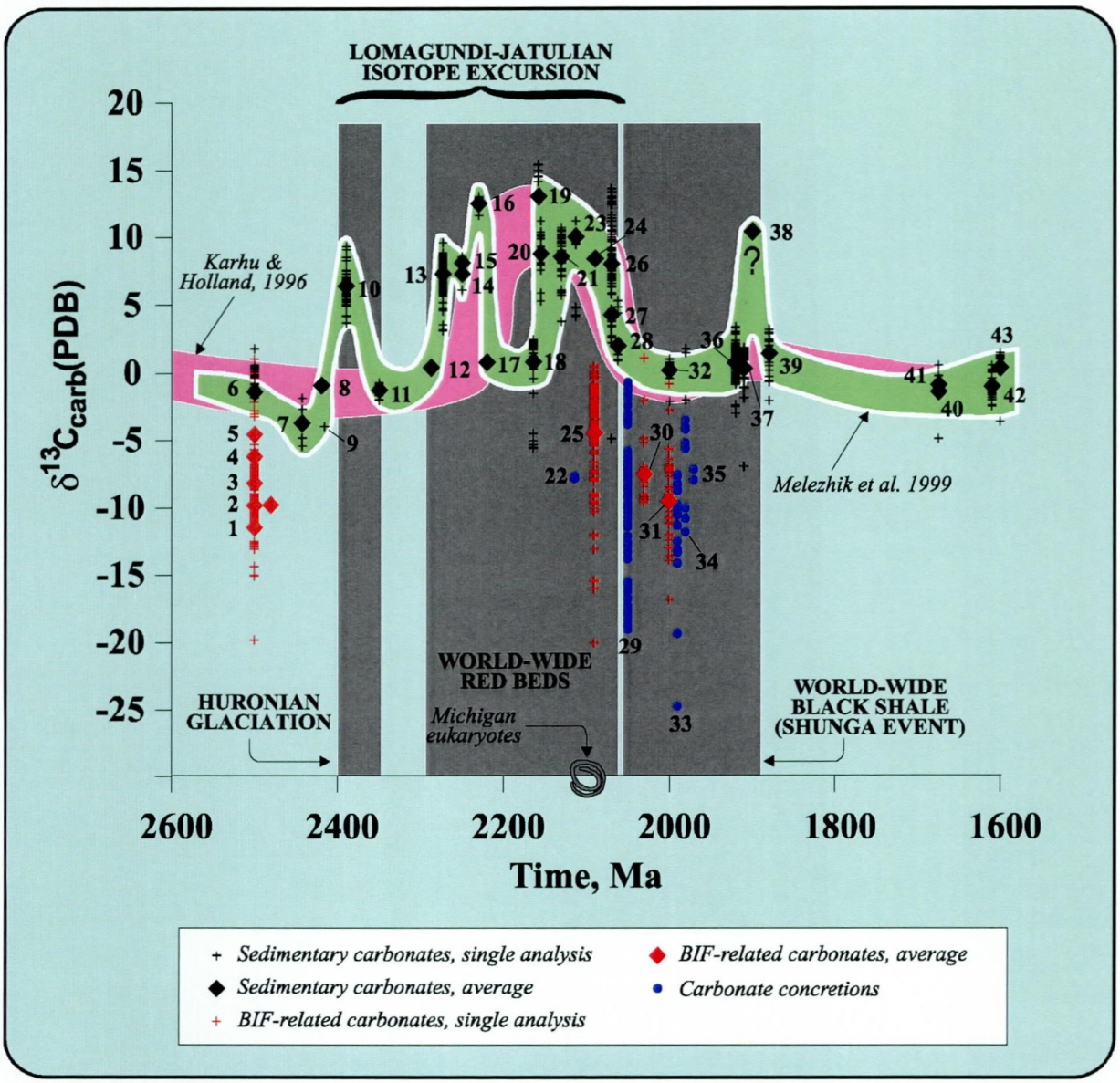

Figure 6. ***$\delta^{13}C$ variation of sedimentary and diagenetic carbonates through the Palaeoproterozoic, and some interrelated phenomena.***

where δ_{in} is the isotopic composition of C entering the global surface environment, δ_{carb} represent the isotopic composition of C_{carb}, f_{org} is the fraction of C buried in C_{org} form, and Δ_c is the isotopic difference between C_{carb} and C_{org}.

Strontium isotope ratios obtained from ^{13}C-rich carbonates are too low (Gorokhov et al. 1998) to be consistent with enhanced erosional rate and concomitant enhanced accumulation of C_{org} as suggested by Des Marais (1992).

None of the three positive excursions of $\delta^{13}C_{carb}$ is followed by a negative isotopic shift significantly below 0‰ (Fig. 6), as has usually been observed in younger isotopic events (Fig. 5) reflecting an overturn of a major marine carbon reservoirs.

2.3.3. Possible solution and direction for future work

A significant change in δ_{in} seems implausible. It has been suggested that the traditional approach via f_{org} change is also not applicable to 2.40-2.06 Ga. Instead, the Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$ could have been driven by a radical change in the mechanism involved in the primary production of organic carbon. Onset of intensive methane cycling (e.g., Hayes 1993) resulting in Δ_c change is another possibility.

2.3.4. Scientific significance of the results

1. The single long-lasting 2.40-2.06 Ma Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$ has been demonstrated to consist of three positive shifts of $\delta^{13}C_{carb}$ separated by returns to 0‰.

2. The three Palaeoproterozoic isotopic excursions are inter-linked to a series of first-order palaeoenvironmental changes which all together are categorised as one of the major isotopic-environmental events in Earth history.

3. Strontium isotope data suggest that the formation of the Palaeoproterozoic ^{13}C-rich carbonates was not associated with enhanced erosional rate.

4. The isotopic excursions might have been driven by onset of intensive methane cycling resulting in Δ_c change combined with accelerated accumulation of organic material. The change in Δ_c has been suggested as a new possibility to explain the Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$.

5. The global $\delta^{13}C_{carb}$ value (background value) of 2.2-2.1 Ga carbonates has been estimated at around +5‰.

6. Palaeoproterozoic shallow water environments and bordering oceans were decoupled; shallow water red beds, evaporites and stromatolite-rich carbonates from restricted environments should not be applied for reconstruction of secular $\delta^{13}C$ curves.

7. The extreme enrichment in ^{13}C (up to +18‰) was caused by local factors such as an intensive development of cyanobacteria, coupled with evaporation in restricted basins which were apparently not in full equilibrium with atmospheric CO_2.

2.3.5. Publications of results

The following scientific papers and presentations resulted directly from this project are listed below:

Articles in international journals.

Published

1. Melezhik, V.A., Fallick, A.E., Filippov, M.M., & O. Larsen, O., 1999. Karelian shungite–an indication of 2000 Ma-year-old metamorphosed oil-shale and generation of petroleum: geology, lithology and geochemistry. *Earth Sci. Reviews*, 47, 1-40.

In press

1. Melezhik, V.A., Fallick, A.E., Medvedev, P.V & Makarikhin, V.V., 1999. Extreme $^{13}C_{carb}$ enrichment in ca. 2.0 Ga magnesite-stromatolite-dolomite-'red beds' association in a global context: a case for the world-wide signal enhanced by a local environment. *Earth Sci. Reviews.*

Submitted

1. Melezhik, V.A., Fallick, A.E., Medvedev, P.V. & Makarikhin, V.V., 1999. Palaeoproterozoic magnesite: lithological and isotopic evidence for playa/sabkha environments. *Sedimentology.*
2. Melezhik, V.A. & Fallick, A.E., 1999. Palaeoproterozoic ^{13}C-rich travertines from a rift lake environment. *Chemical Geology.*

In preparation

1. Kuznetsov A.B., Gorokhov I.M., Melezhik V.A., Konstantinova G.V., Melnikov N.N., Kislova I.V. Chemical and Sr isotope evidence for depositional environments of Palaeoproterozoic ^{13}C-rich carbonates from theTulomozerskaya Formation, Russian Karelia. *Precambrian Research.*
2. Melezhik, V.A., Fallick, A.E., Heiskanen, K.I., Rychanchik, D. & Makarikhin, V.V. 2.0 billion year old isotopically heavy carbonate carbon: comparison of distal and proximal carbonate sequences from the Onega palaeobasin, Karelia, Russia. *Chemical Geology.*
3. Melezhik, V.A. and Fallick, A.E. Sulphur isotope composition of clastic pyrite from 2.4 Ga fluviatile sequence: Pechenga, north-west Russia. *Chemical Geology.*
4. Ovchinnikova G.V., Melezhik V.A., Gorokhov I.M., Kuznetsov A.B., Vasilyeva I.M. & Gorokhovsky B.M. Uranium and lead geochemistry and Pb-Pb dating of Palaeoproterozoic ^{13}C-rich carbonate rocks from the Tulomozerskaya Formation, Russian Karelia. *Chemical Geology.*

Articles in Russian journals

Published

1. Gorokhov, I.M., Kuznetsov, A.B., Melezhik, V.A., Konstantinova, G.V. & Melnikov, N.N., 1998. Sr isotopic composition in the Upper Jatulian (Early Paleoproterozoic) dolomites of the Tulomozero Formation, southeastern Karelia. *Transactions (Doklady) of the Russian Academy of Sciences, Earth Science Sections, 360 (4)*, 609-612. (in English and Russian).
2. Semikhatov, M.A., Raaben, M.E., Sergeev, V.N., Veis, A.F. & Artemova O.V., 1999. Biotic events and $\delta^{13}C_{carb}$ positive anomaly 2.3-2.05 Ga ago. *Stratigraphy and Geological Correlation, 7(5),* 3-24. (in English and Russian).

In press

1. Heiskanen, K.I. & Rychanchik, D.V., 1999. Jatulian (Early Proterozoic), isotopicaly heavy carbonates of the Baltic Shield: stratigraphic position and geographic distribution. *Stratigraphy & Geological Correlation.*

Submitted

1. Semikhatov, M.A., Raaben, M.E., Sergeev, V.N. & Veis, A.F., 1999. Riphean and Vendian paleontological and $\delta^{13}C_{carb}$ record: A comparison. *Stratigraphy and Geological correlation.*

In preparation

1. Ovchinnikova G.V., Melezhik V.A., Gorokhov I.M., Kuznetsov A.B., Vasilyeva I.M. & Gorokhovsky B.M. U-Pb systematics of Palaeoproterozoic ^{13}C-rich carbonate rocks from the Kuetsjarvi Formation Kola Peninsula. *Lithology and Mineral Deposits.*

Articles in national Norwegian/Nordic journals

Published

1. Melezhik V.A., Fallick A.E. & Semikhatov M.A. 1997. Could stromatolite-forming cyanobacteria have influenced the global carbon cycle at 2300-2060 Ma? (extended abstract), *Norges geologiske undersøkelse Bull. 433,* 30-31.

Submitted

1. Melezhik, V.A., Fallick, A.E., Medvedev, P.V. & Makarikhin, V.V., 1999. Palaeoproterozoic magnesite-stromatolite-dolomite-'red beds' association, Russian Karelia: palaeoenvironmental constraints on the 2.0 Ga positive carbon isotope shift. *Norsk Geologisk Tidsskrift.*

Oral presentations and abstracts in proceedings of international conferences

1. Gorokhov, I.M., Melezhik, V.A., Kuznetsov, A.B., Konstantinova, G.V. & Melnikov, N.N., 1998. $^{87}Sr/^{86}Sr$ ratio in early Palaeoproterozoic seawater: implications for the $\delta^{13}C_{carb}$ positive anomaly. *Abstracts of the Ninth International Conference on Geochronology, Cosmochronology and Isotope Geology, 20-26 August, 1998, Beijing, China. Chinese Science Bulletin, 43, Supplement,* p. 47.
2. Heiskanen, K.I., 1998. Paleogeography of Early Proterozoic carbonaceous sedimentation in the Baltic Shield. *Abstracts Volume, International Symposium on Carbonaceous Formations in Geological History, June 2-7,1998, Petrozavodsk, Russia*, p. 11-12.
3. Heiskanen, K.I. & Rychanchik, D.V., 1998. Geological restrictions to the hypotheses of the shungite origin. *Abstracts Volume, International Symposium on Carbonaceous Formations in Geological History, June 2-7,1998, Petrozavodsk, Russia*, p.61-62.
4. Kuznetsov, A.B., Gorokhov, I.M., Melezhik, V.A., Ovchinnikova, G.V., Melnikov, N.N. & Kislova, I.V., 1999. Evolution of the Palaeoproterozoic Tulomozero palaeobasin, south-eastern Karelia, Russia: chemical and isotopic evidence. *EUG-10, European Union of Geosciences, March 28 - April 1, 1999, Strasbourg, France. Journal of Conference Abstracts, 4*, p. 810.
5. Makarikhin, V.V., 1998. Type localities of stromatolites in Europe. *Abstracts Volume, PROGEO'98, Sofia, Bulgaria*, p. 33-34.
6. Makarikhin, V.V., 1999. Elements of the Mopanyu stromatolite assemblage in the Baltic Shield. *Abstracts Volume, 7th International Symposium on Fossil Algae, October 13-17, 1999, Nanjing, China*, submitted.
7. Makarikhin, V.V. & Medvedev, P.V., 1998. Stiriolites in Early Precambrian sequences. *Abstracts Volume, 23rd Nordic Geological Meeting, January 13-16, 1998, Arhus, Denmark*, p.192.
8. Makarikhin, V.V. & Medvedev, P.V., 1999. System of stromatolites. *Abstracts Volume, 7th International Symposium on Fossil Algae, October 13-17, 1999, Nanjing, China*, submitted.
9. Makarikhin, V.V. & Medvedev, P.V., 1998. Litophytes as environmental indicators. *Abstracts Volume, International Symposium on Paleoclimates and the Evolution of Paleogeographic Environments in the Earth's Geological History, August 27-31, 1998, Petrozavodsk, Russia*, p. 57.
10. Medvedev, P.V. & Makarikhin, V.V., 1998. Signs of life in Early Proterozoic carbon-bearing sequences. *Abstracts Volume, International Symposium on Carbonaceous Formations in Geological History, June 2-7,1998, Petrozavodsk, Russia*, p.27.

11. Medvedev, P.V. & Makarikhin, V.V., 1999. Stromatolites in terrigeneous-carbonate sediments of the Early Precambrian (Baltic Shield). *Abstracts Volume, 19th Regional European Meeting on Sedimentology, August 24-26, 1999, Copenhagen, Denmark.*

12. Melezhik, V.A. & Fallick, A.E., 1999. The Palaeoproterozoic positive isotopic excursion of carbonate $^{13}C/^{12}C$: three positive excursions instead of one, though still a paradox. *Abstract Volume, 3rd International Symposium on Applied Isotope Geochemistry. September 21-25, 1999, Orleans, France, p. 125-126.*

13. Melezhik, V.A. & Fallick, A.E., 1999. Three Palaeoproterozoic positive isotopic excursions of carbonate $^{13}C/^{12}C$: still a paradox. *Abstract Volume, Ninth Annual V.M. Goldschmidt Conference, August 22-27, 1999, Cambridge, Massachusetts.*

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Guide books

1. Heiskanen, K.I., Demidov, I.N., Makarikhin, V.V., Medvedev, P.V. & Bondar, L.F., 1998. *Field Trip Guide-Book.* International Symposium on Paleoclimates and the Evolution of Paleogeographic Environments in the Earth's Geological History, August 27-31, 1998, Petrozavodsk, Russia, 22 pp.
2. Rychanchik D.V., Philippov, M.M. & Heiskanen, K.I., 1998. *Field Trip Guide-Book.* International Symposium on Carbonaceous Formations in Geological History, June 2-7, 1998, Petrozavodsk, Russia.

Public Lecture

1. Semikhatov, M.A. Appearance and disappearance of the largest $\delta^{13}C_{carb}$ positive anomaly 2,3-2,05 Ga ago versus biotic and biologically-induced events. Annual meeting of the Russian Government Scientific Programe Global Environmental and Climatic Changes. Moscow, 8-11 February, 1999.

Table 2. Summary of the scientific output.

Scientific Output	published	in press/accepted	submitted	in preparation
Paper in an International Journal	1	1	2	4
Paper in National Russian Journals (in Russian)	2	1	1	1
Paper in National Norwegian/Nordic Journals (in English)	1		1	
Abstract in proceedings of a conference	27			
Guide Book	2			
Internal Report	2			
Thesis (MSc, PhD, etc.)				
Patent				
Oral Presentation, Public Lecture	26			

2.4. Practical applications.

The global distribution of 2.4-2.06 Ga ^{13}C-rich carbonates developed on different continents provide a possibility to use such carbonates for intercontinental correlation of those carbonate sequences which cannot be dated.

The recorded impact of a lateral expansion of ancient cyanobacterial ecosystems on the global biogeochemical carbon cycle has to be taken into account in modeling of the evolution of the CO_2 regime in the atmosphere in the Recent and past.

3. MANAGEMENT

3.1. Meetings and visits

The first co-ordinating meeting took place in St. Petersburg (01/12/96-04/12/96). One participant from each organisation involved in the project participated in the meeting. The second co-ordinating meeting took place in St. Petersburg (16/10/97-22/10/97) with the participation of all members of the project.

P. Medvedev studied geological material from the project at the University of Vienna (8 months in 1998-1999) and the Geological Survey of Finland (4 months in 1998).

Table 3. Summary of the meetings and visits.

Visits	Number of scientists	Number of person days
West ==> East	2	386
East ==> West	3	24
West ==> West	5	37
East ==> East	7	21

Major fieldwork took place in the Karelia and Kola regions with the summary given in Table 4.

Table 4. Summary of fieldwork.

Area	Duration	Persons
Karelia: Panajarvy, Likhta, Onega Lake area	10 July-15 August, 1997	Heiskanen, Makarikhin, Medvedev, Rychanchik
Karelia: drill core logging , Onega Lake area	5-8 August, 1998	Heiskanen, Melezhik, Rychanchik
Karelia: Segozero, Kukasozero, Panajarvi	7-18 September, 1998	Heiskanen, Kolesov, Makarikhin, Medvedev, Rychanchik
Karelia: drill core logging , Onega Lake area	26 June-30 July, 1999	Heiskanen, Makarikhin, Medvedev, Rychanchik
Karelia: drill core logging , Onega Lake area	16 August-14 September, 1999	Heiskanen, Makarikhin, Medvedev, Rychanchik
Karelia: Kizhi Island, Velikaya Guba	22 August-27 August, 1999	Rychanchik
Kola Peninsula: Pechenga	7-11 September, 1998	Melezhik
Kola Peninsula: Pechenga, Imandra/Varzuga	31 Agust-7 September, 1999	Melezhik

3.2. Collaboration

Table 5. Intensity of the collaboration among the different Participants

Intensity of Collaboration	high	rather high	rather low	low
West <=> East		x		
West <=> West	x			
East <=> East		x		

The project participants cooperated to a major extent with additional Russian organisations which were not mentioned in the Co-operation Agreement. These are the Scientific Industrial Centre 'Kola Superdeep', Zapolyarny, Russia; the University of Vienna; and the Geological Survey of Finland.

3.3. Time Schedule

The overall time planning has been in accordance with the Work Programme. Some deviation and delay has been caused by the economic crisis in Russia, in August 1998. This

resulted in substantial obstacles in funding transfer and caused 9 months delay in the time planning.

3.4. Problems encountered

I did not encounter any major problems with regard to quality and quantity of the scientific contributions of the different Participants, telecommunication, the transfer of funds and goods, taxation, customs and withholding of overheads. The only problem, which seriously affected the work process and caused nine months delay, was an economic crisis in Russia in August 1998. Additionally, in 1999 RFBR paid to the project in roubles with very low exchange rate: 9Rbls for 1ECU whereas the actual exchange rate was 27 Rbls for 1ECU.

Table 6. Summary of my experiences

Problems encountered	major	minor	none	not applicable
Co-operation of team members			x	
Transfer of funds		x		
Telecommunication			x	
Transfer of goods			x	

3.5. Actions required

No suggestions.

3.6. Manpower invested

Participant 1: 1.0 person-year, none - due to the funding received from this grant.
Participant 2: 0.5 person-year, none - due to the funding received from this grant.
Participant 3: 7.8 person-year, 7.8 - due to the funding received from this grant.
Participant 4: 0.54 person/years, 0.54 – due to the funding received from this grant.
Participant 5: 5 person-year, 1.63 - due to the funding received from this grant.

4. FINANCES (in ECU)

4.1 This grant

Participant		Cost Category						TOTAL (ECU)
# *)	Name of Participant *)	Individ. Grants Labour Costs	Overheads	Travel and Subsistence	Equipment	Consumables	Other Costs	
1	Participant 1	0	688	*4 039*	**)	0	0	*4 727*
2	Participant 2	0	1 300	2 668	**)	2 000	0	5 968
3	Participant 3	*8 752*	156	2 028	1 861	6 440	2	*19 239*
4	Participant 4	*5 143*	103		4 143	884	0	*10 273*
5	Participant 5	*4 427*	496	2 538	1 461	242		*9 164*
TOTAL (ECU)		***18 322***	**2 743**	***11 273***	**7 465**	**9 566**	**2**	***49 371***

Remarks: Figures shown in italics include the final 10% not yet received.

The difference between the received and spent sums is largely due to variations in EURO, USD and roubles rates.

All Participants except Participant 4 have the spending in accordance with the one foreseen in the Work Programme. Participants 4 spent all the money which were allocated for travel, on equipment for the following reason. The main goal of Participant 4 was to set up an extensive data base on global time-and-space distribution of Archaean and Proterozoic microfossils and stromatolite-bearing formations. When the work has already been in progress Participant 4 realised the need for two powerful PC. However, the travel costs (e.g. participations in two co-ordinating meetings) were covered by M.A. Semikhatov's RFBR grant.

4.2 Other funding

Additional, though essential, financial support was given by the Geological Survey of Norway (ca. 60000 ECU, for fieldwork, sample preparation, XRF major and trace elements, electron microscopy, microprobe analyses) and by the Scottish Universities Research & Reactor Centre (ca. 40000 ECU, for isotope analyses). Participant 4 and 5 received 6000 ECU additionally through the RFBR system.

5. SUMMARY OF RESULTS AND KEY REFERENCES

World-wide 2 billion-year-old isotopically heavy carbonate carbon: the evolutionary significance and driving forces; INTAS-RFBR 95-928; 30/11/96-15/09/99; Prof. Victor A. Melezhik, Geological Survey of Norway, Leiv Erikssons vei 39, N-7491 Trondheim, Norway; tel.: +47-73 91 40 11; fax: +47-73 92 16 20; e-mail: victor.melezhik@ngu.no

A global character of the 2.4-2.06 Ga positive excursion of $\delta^{13}C_{carb}$, earlier suggested by Baker and Fallick (1989), has been confirmed by new, well-studied, occurrences of ^{13}C-rich carbonates from the area of investigation.

The evolutionary significance of the isotope excursion is exemplified by its inter-link with dramatic climatic changes, a world-wide continental rift expansion, extensive development of shallow-water carbonate platforms and world-wide 'red beds', widespread dolostones and evaporites, along with anprecedented in Earth history lateral expansion of cyanobacterial ecosystems, free oxygen increase, the earliest appearances of phosphorites, formation of Fe, Mn, P and $CaCO_3$ concretions.

The excursion is a unique event in terms of both long duration (>300 Ma) and an extreme ^{13}C enrichment (up to +18‰), though it superficially resembles the Precambrian/Cambrian transition events.

Several 2.40-2.06 Ma Palaeoproterozoic positive excursions of $\delta^{13}C_{carb}$ ***have*** been suggested by the new data. Three positive shifts of $\delta^{13}C_{carb}$ separated by returns to 0‰ have been recognised.

Differentiation between global and local factors suggests that the isotopic excursion with global $\delta^{13}C_{carb}$ value of +5‰ might have been driven by accelerated accumulation of organic material combined with onset of intensive methane cycling resulting in Δ_c change. Palaeoproterozoic shallow water environments and bordering oceans were apparently decoupled, and shallow water carbonates with extreme enrichment in ^{13}C (up to +18‰) from restricted environments should not be applied for reconstructions of secular $\delta^{13}C$ variations and chemostratigraphic purposes.

Current problems are related to the fact that the isotope anomaly cannot be balanced by only C_{org} burial (f_{org}). A significant change in δ_{in} seems implausible. $^{87}Sr/^{86}Sr$ ratios do not support enhanced erosional rate and concomitant enhanced accumulation of C_{org} at around 2.1 Ga.

Future work is suggested to investigate whether the isotope excursion was driven by a different mechanism involved in the primary production of C_{org}, i.e. change in Δ_c.

Key words: Palaeoproterozoic, carbon, strontium, isotopes, stromatolites, evaporites.

6. ROLE AND IMPACT OF INTAS

Table 7. **Importance of <u>this</u> grant for starting and carrying out the project.**

Role of INTAS	definitely yes	rather yes	rather not	definitely not
Would the project have been started without funding by INTAS?				x
Would the project have been carried out without funding from INTAS?				x

Table 8. **The most important achievements of the project.**

Main achievement of the project	very important	quite important	less important	not important
exciting science	x			
new international contacts		x		
additional prestige for my lab		x		
additional funds for my lab			x	
helping scientists in NIS	x			

One of the results, namely, that the Palaeoproterozoic positive excursion of $\delta^{13}C_{carb}$ was apparently driven by a radical change in the mechanism involved in the production of organic carbon has resulted in the application of a new INTAS project proposal. In this sense, the research started in this project will be continued if the new application is accepted and financed.

The co-operation among the project participants will definitely continue in the future.

7. RECOMMENDATIONS TO INTAS

The financial management was good and should not be changed.

The financial co-operation with the Russian Foundation for Basic Research was not particularly good, and this organisation is not considered as a reliable partner.

8. ANNEXES

The following articles are included:

5. Sr isotope composition in the upper Jatulian (Early Proterozoic) dolomites of the Trulomozero Formation, south-eastern Karelia.
6. Could stromatolite-forming cyanobacteria have influenced the global carbon cycle at 2300-2060 Ma?
7. Karelian shungite–an indication of 2.0-Ca-old metamorphosed oil-shale and generation of petroleum: geology, lithology and geochemistry.
8. Extreme $^{13}C_{carb}$ enrichment in ca. 2.0 Ga magnesite-stromatolite-dolomite-'red beds' association in a global context: a case for the world-wide signal enhanced by a local environment.