# ORIGIN OF HYDROCARBON ACCUMULATIONS IN PRECAMBRIAN OF EASTERN SIBERIA

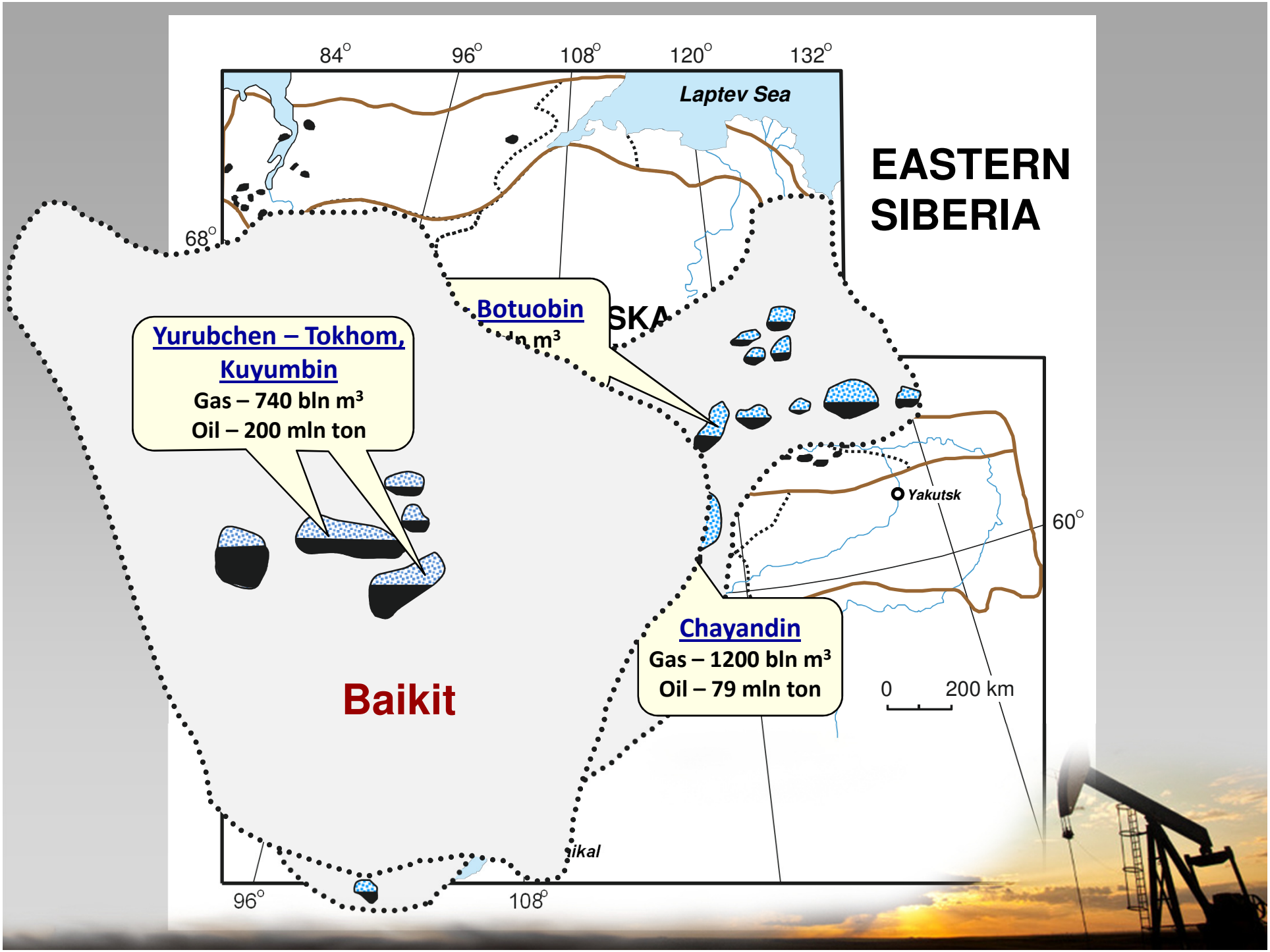
E.M.Galimov



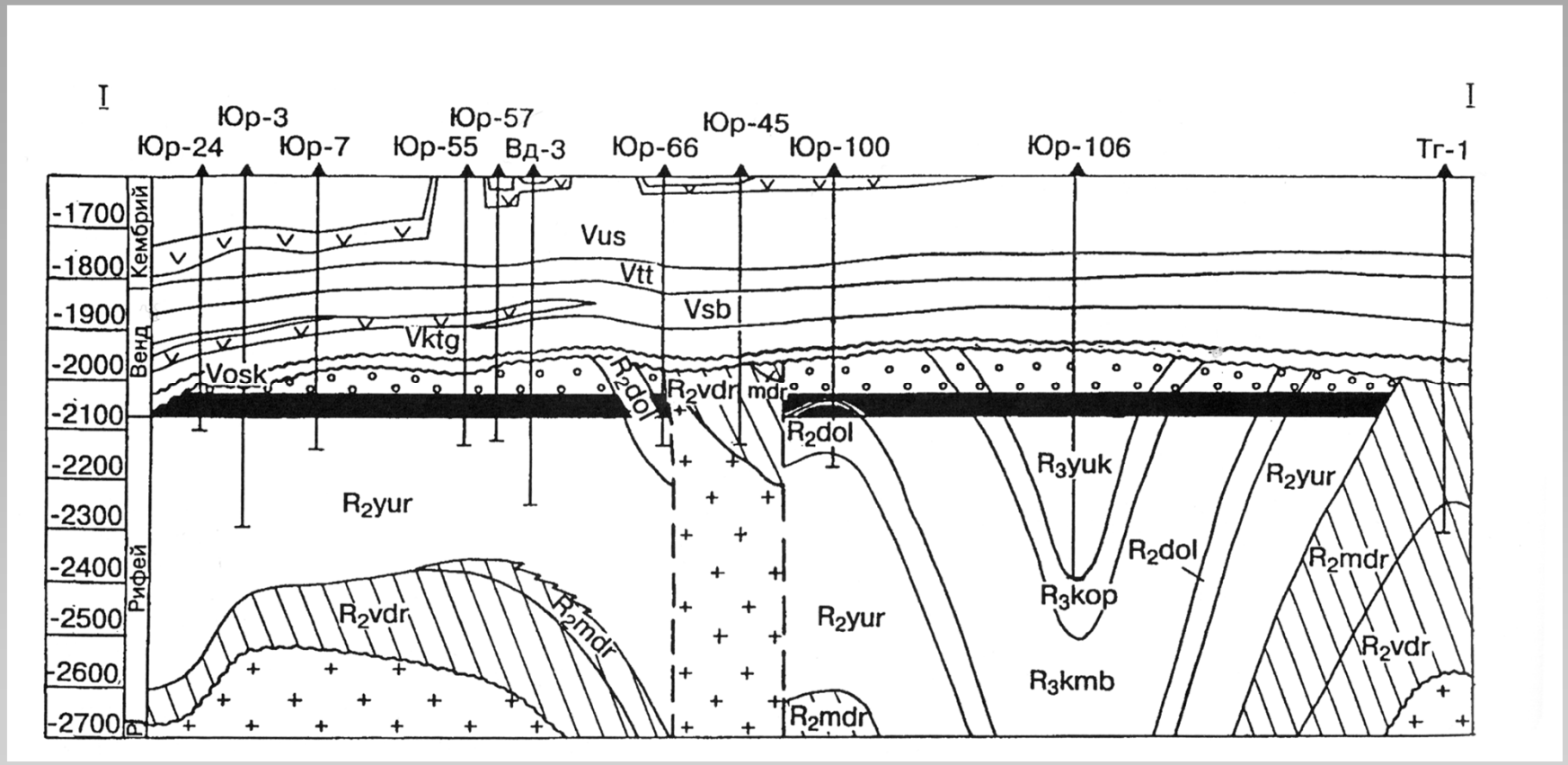
# Precambrian Petroleum Basins in the World



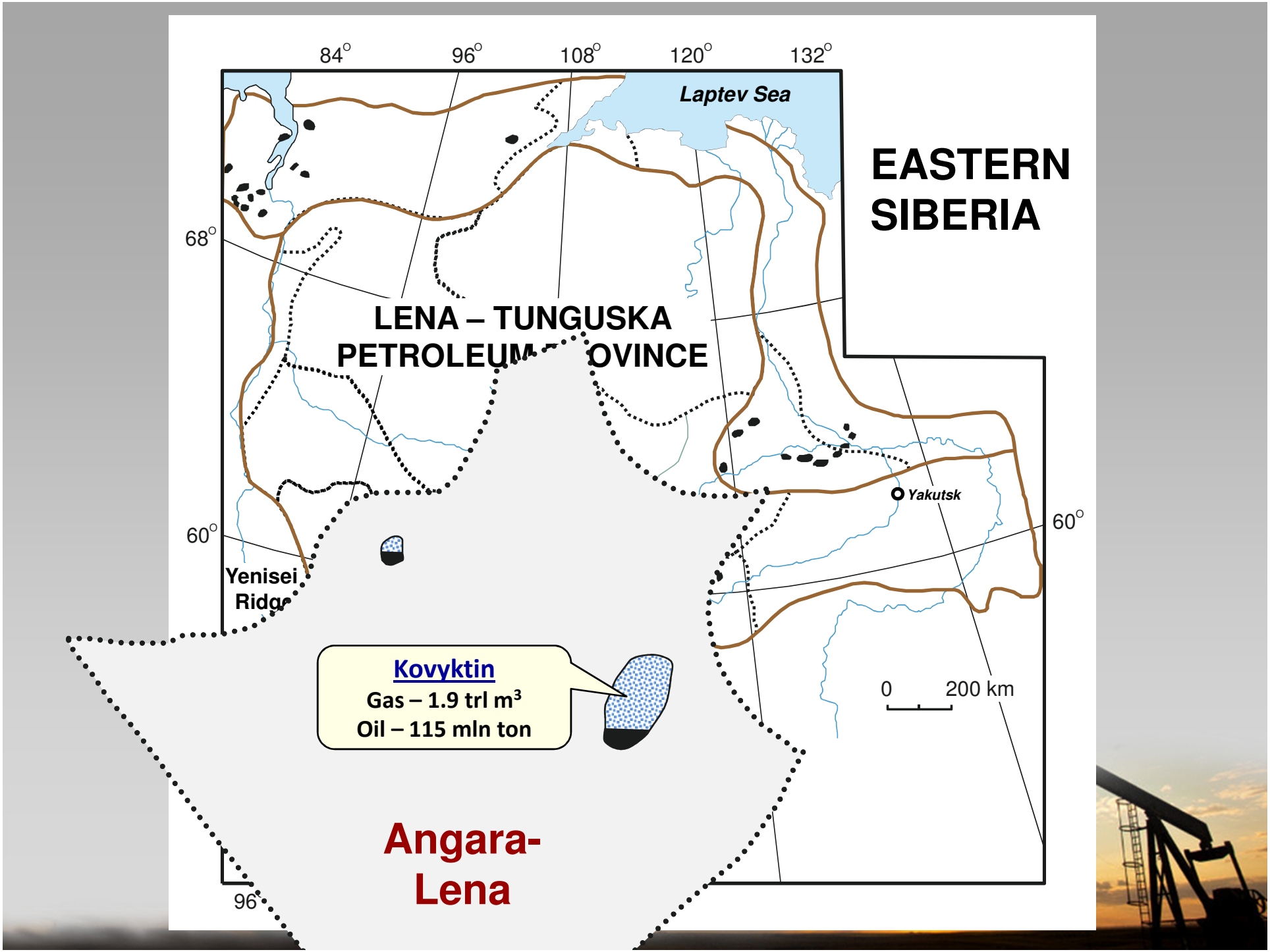

LENA – TUNGUSKA
PETROLEUM
PROVINCE
Yakutsk
Katanga
Nepa-
Botuobin
Baikit
Baikal - Patom upland
Angara-
Lena
Krasnoyarsk
L.Baikal
Irkutsk
RUSSIA
KAZAKHSTAN
MONGOLIA
CHINA


EASTERN SIBERIA
84°
96°
108°
120°
132°
68°
60°
Laptev Sea
Botuobin
Yurubchen – Tokhom, Kuyumbin
Gas – 740 bln m³
Oil – 200 mln ton
Chayandin
Gas – 1200 bln m³
Oil – 79 mln ton
Yakutsk
Baikit
0
200 km

# Yurubcheno – Tokhom field




*From A.E.Kontorovich et al., 1996*

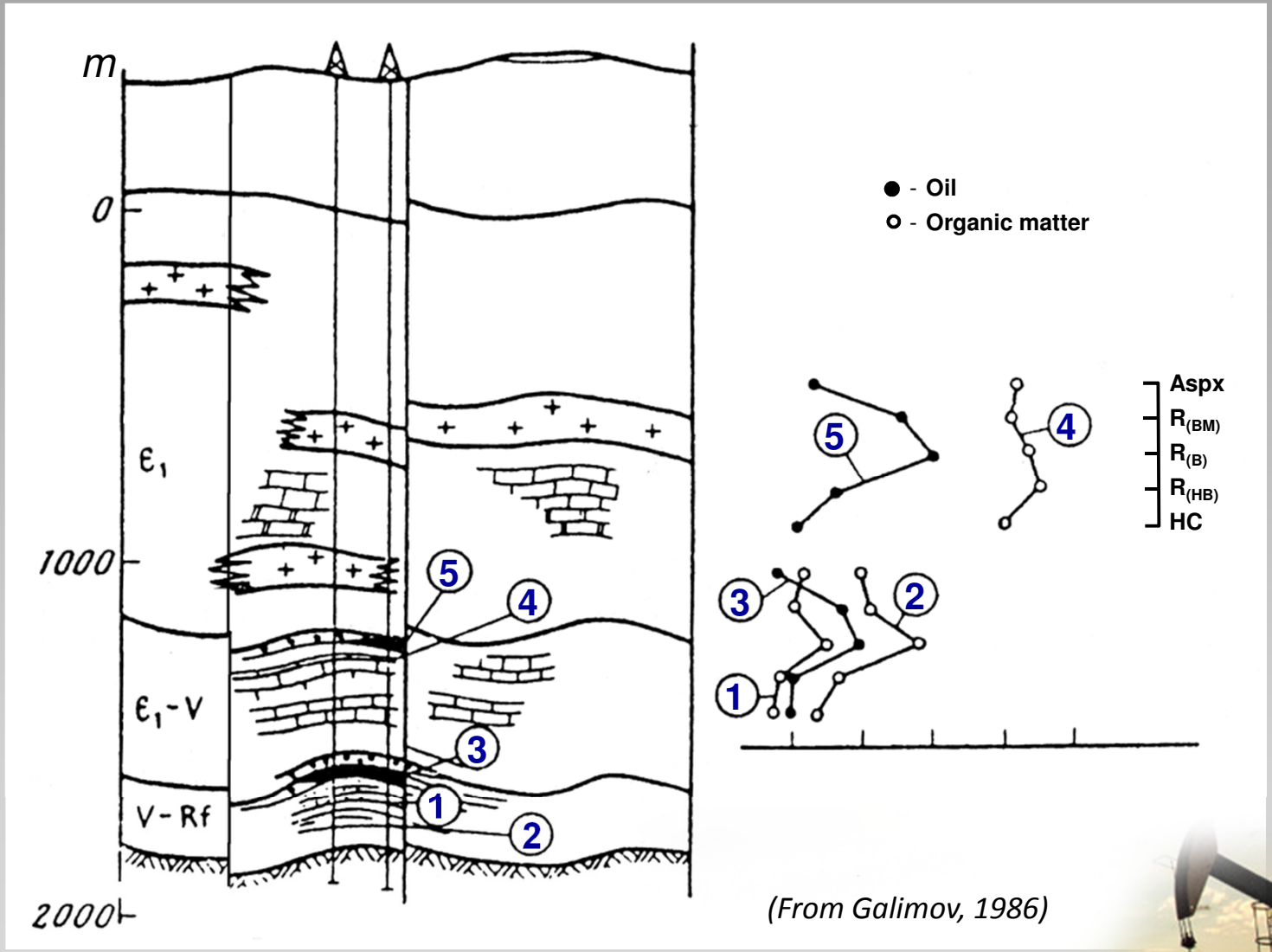

84°
96°
108°
120°
132°
Laptev Sea
EASTERN SIBERIA
68°
LENA – TUNGUSKA PETROLEUM PROVINCE
Yakutsk
60°
60°
Yenisei Ridge
Kovyktin
Gas – 1.9 trl m³
Oil – 115 mln ton
0
200 km
Angara-Lena
96°

# Reserves of the largest oil-gas fields in Eastern Siberia

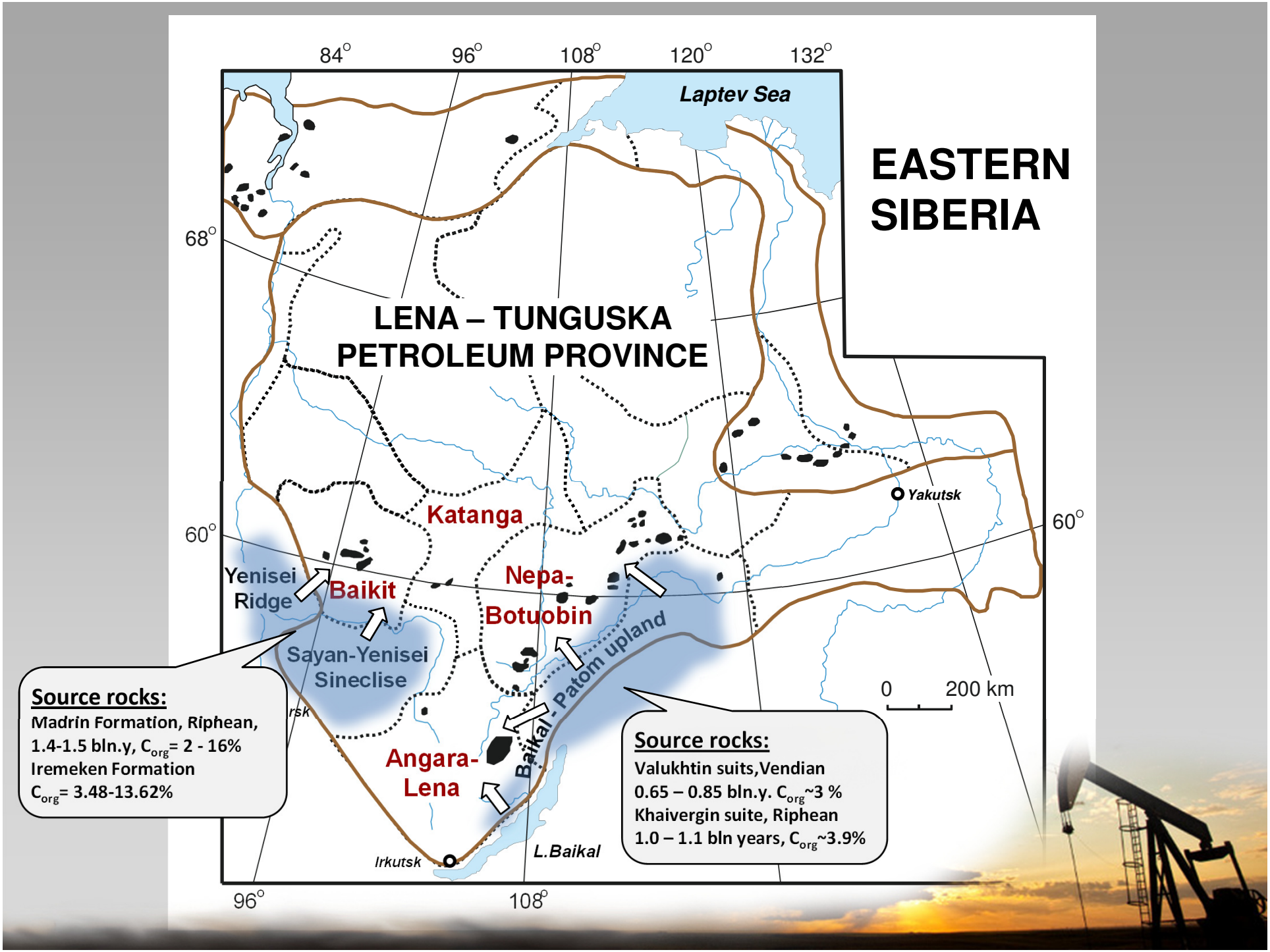
| Region, field | | Gas Bln $m^3$ | Oil Mln ton |
|---|---|---|---|
| **Nepa-Botuobin** | | | |
| | ***Chayandin*** | **1240** | **50** |
| | ***Verkhnechon/Talakon*** | **760** | **370** |
| **Baikit** | | | |
| | ***Yurubchen/Tokhom/Kuyumbin*** | **740** | **200** |
| **Angara-Lena** | | | |
| | ***Kovyktin*** | **1900** | **115** |
| **Explored reserves** | | **6 -7 trl** | **1 bln** |
| **Estimated total potential** | | **> 20 trl** | **>5 bln** |

*(From different sources)*

# Sredne – Botuobin oil-gas field



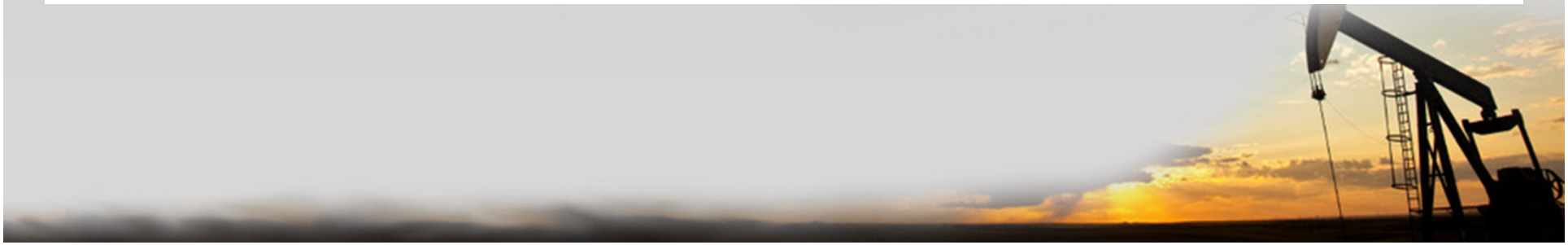

*(From Galimov, 1986)*


EASTERN SIBERIA
LENA – TUNGUSKA PETROLEUM PROVINCE
84°
96°
108°
120°
132°
68°
60°
Laptev Sea
Yakutsk
Katanga
Nepa-Botuobin
Yenisei Ridge
Baikit
Sayan-Yenisei Sineclise
Baikal - Patom upland
Angara-Lena
Irkutsk
L.Baikal
0
200 km
Source rocks:
Madrin Formation, Riphean,
1.4-1.5 bln.y, Corg= 2 - 16%
Iremeken Formation
Corg= 3.48-13.62%
Source rocks:
Valukhtin suits,Vendian
0.65 – 0.85 bln.y. Corg~3 %
Khaivergin suite, Riphean
1.0 – 1.1 bln years, Corg~3.9%

# Precambrian oil-source rocks in Eastern Siberia

| Geological structure | Oil source | $\delta^{13}C$, ‰ |
|---|---|---|
| Patom Upland<br>Nepa-Botuobin<br>anticlise | Zherbin suite (Vendian shale), $C_{org}$ = 2.4% [2] | **-36** |
| | Jemikukan and Valukhtin suits (Baykal horizon, 0.65 – 0.85 bln.y.), $C_{org}$ up to 3 % [2] | |
| | Bugarikhtin suite (Lakhandin horizon, 0.85 – 1.0 bln.y) $C_{org}$ up to 12.9% | |
| | Khaivergin suite (Kerpul horizon, 1.0-1.1bln.y.), black shale, $C_{org}$ – 1,7% | |
| Yenisey Ridge<br>Sayan-Yenisei syneclise<br>Baikit anticlise | Lakhandin horizon (0.82 – 1.1 bln.y) black shale, $C_{org}$ up to 15% | **-31** |
| | Madrin Formation (1.4-1.5 bln.y) $C_{org}$= 0.73 up to 2.1% [1] | **-34.4 ÷ - 27.1** |
| | Iremeken Formation $C_{org}$= 3.48-13.62% [3] | |

*1 – Kontorovich et.al., 1999; 2 – Timoshina, 2004; 3 – Philiptsov et.al., 1999.*



# Carbon isotope composition of oil and gas in the fields of Lena-Tunguska Province.

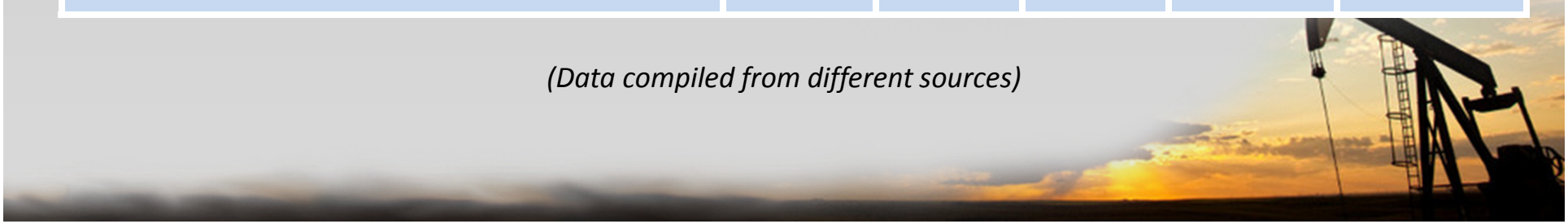
| Region, field | | $\delta^{13}C$, ‰ | | Age of reservoir |
|---|---|---|---|---|
| | | Oil | Gas | |
| **Nepa-Botuobin** | | | | |
| | ***average of 12 fields*** | **-36.0…-32.9<br>-34.5** | **-42.6…-30.1** | **V -∈** |
| **Baikit** | | | | |
| | ***Yurobchen<br>Kuymbin*** | **-33.5** | **-42.5…-38.5** | **R** |
| **Katanga** | | | | |
| | ***Sobin*** | **-34.1** | **-41.1…-37.5** | **V** |
| **Angara-Lena** | | | | |
| | ***Kovyktin*** | **-35.5** | **-38.4…-28.4** | **V -∈** |

*Data compiled from: Zor'kin et al., 1984; Starobinets et al., 1980; Galyshev, 2010; Dakhnova et al., 2011.*

# Chemical composition of gases from the fields of Lena-Tunguska Province

| Region, field | | $CH_4$ % | $C_2H_6$ % | $C_{3+}$ % | Incombustible | |
|---|---|---|---|---|---|---|
| | | | | | $N_2$, % | He, % |
| **Nepa-Botuobin** | | | | | | |
| | ***Chayandin*** | **85.48** | **4.57** | **2.58** | **6.44** | **0.58** |
| | ***Srednei - Botuobian*** | **88.61** | **4.95** | **3.12** | **2.93** | **0.45** |
| **Baikit** | | | | | | |
| | ***Yurobchin - Takhom*** | **81.10** | **7.31** | **5.06** | **6.32** | **0.18** |
| **Katanga** | | | | | | |
| | ***Sobin - Paygin*** | **67.73** | **3.43** | **1.55** | **26.29** | **0.58** |
| **Angara-Lena** | | | | | | |
| | ***Kovyktin*** | **91.39** | **4.91** | **1.78** | **1.52** | **0.28** |

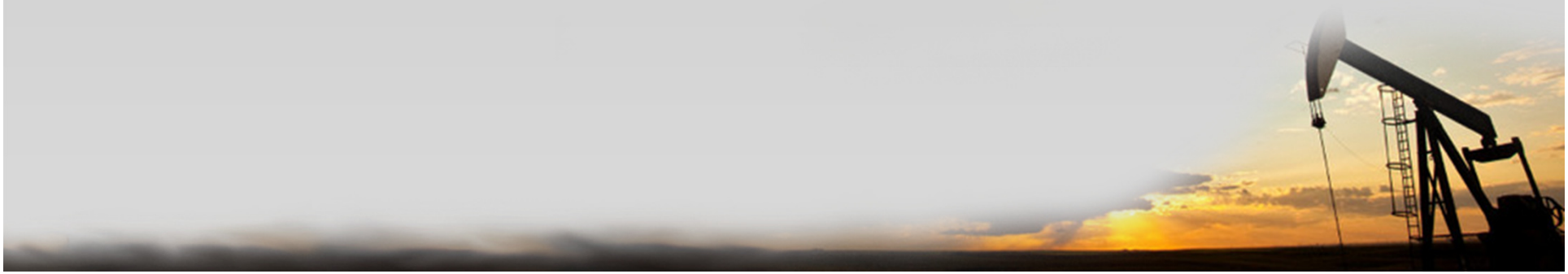
*(Data compiled from different sources)*



# Some characteristics of gas from Baikit region

| $\delta^{13}C‰$ | $\delta$ D ‰ | He% | $\frac{^3He}{^4He}$ |
|---|---|---|---|
| -37.16<br>-40.65…-32.9 | -140<br>-157…-132 | up to 0.22 | $10^{-8}$ |

The upper figure stands for average, the lower ones show the range of variation.
(*Lukin and Dontsov, 2009).*



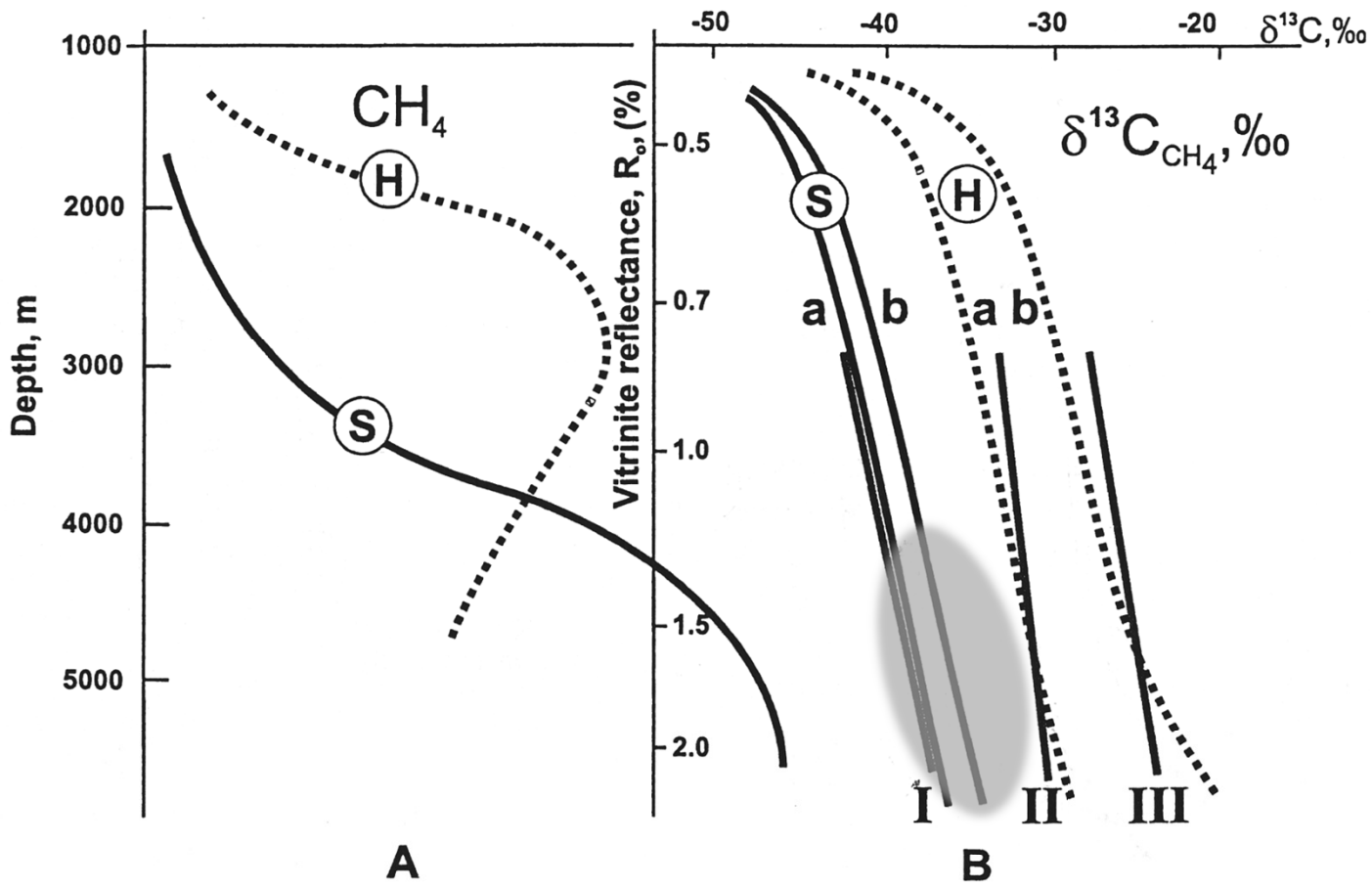
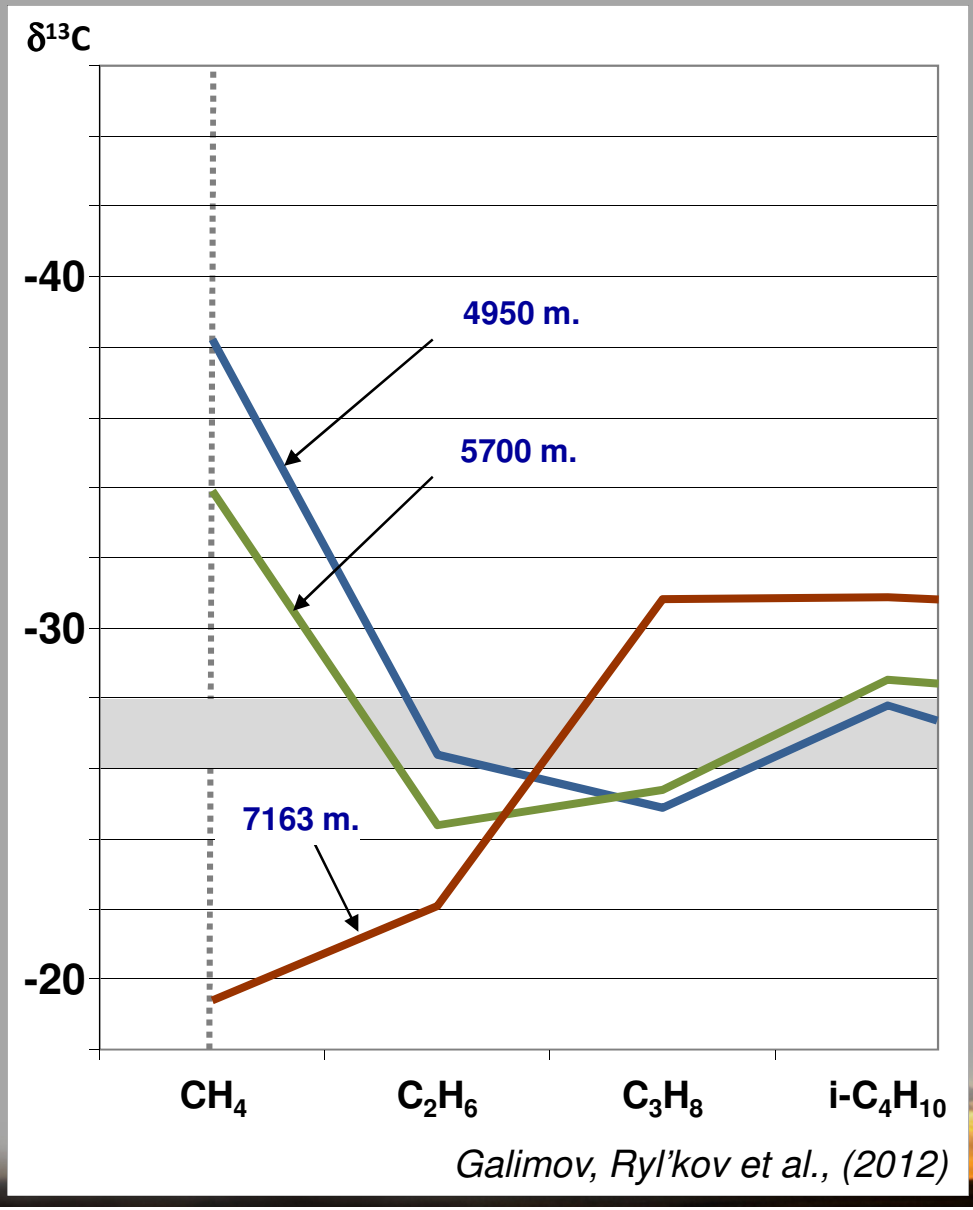



Fig. 37. Methane evolution (A) and carbon isotope composition (B) trends resulting from the model implying different distributions of activation energies for sapropelic (S) and humic (H) organic matter: $a$ = "cumulative" curve, $b$ = "instantaneous" curve (Galimov et al., 1988). Isotopic composition of the initial organic carbon: $\delta^{13}C_0 = -25‰$; the kinetic isotope effect of methane formation is $-30‰$.

*Modified from E.M. Galimov (Organic Geochemistry, 2006)*

# Change of carbon isotope composition of hydrocarbon gases with depth (СГ-7 superdeep hole, West Siberia)




*Galimov, Ryl'kov et al., (2012)*

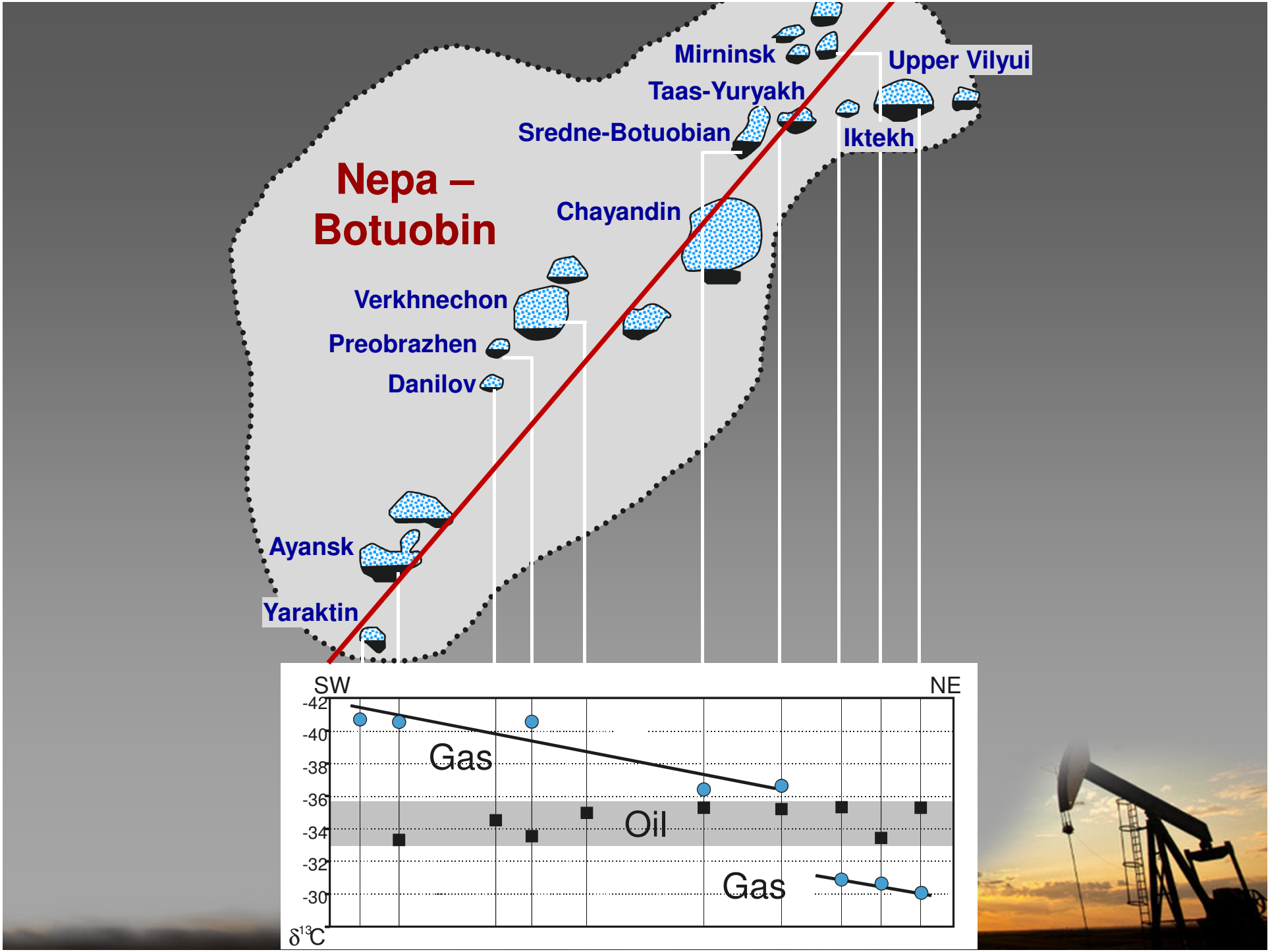

Nepa –
Botuobin
Mirninsk
Upper Vilyui
Taas-Yuryakh
Sredne-Botuobian
Iktekh
Chayandin
Verkhnechon
Preobrazhen
Danilov
Ayansk
Yaraktin
SW
NE
-42
-40
-38
-36
-34
-32
-30
Gas
Oil
Gas
δ13C

**Таблица 1.** Средние значения и разброс геохимических показателей семейств протерозойских нефтей Лено-Тунгусской провинции

| Семейство | Число | 20 | | | (Pr+Ph)/(*n*-$C_{17}$+ | | |
|---|---|---|---|---|---|---|---|
| I | | | | | | | |
| II | | | | | | | |
| Семейство | | | | | | | |
| I | | | | | | | |
| II | | | | | | | |

Примечан
углерода
нормальн
шение сум
сумме гоп
$\Sigma St_{27-29}/\Sigma$
ме гопано
21β); $St_{29}$

ДОКЛАДЫ АКАДЕМИИ НАУК том 370 № 1 2000

# East – Siberian Proterozoic Oils

| Lena-Tunguska petroleum province | $\delta^{13}C$, ‰ | 12-13 mma, % | $St_{29}/St_{27}$ |
|---|---|---|---|
| **Baikit anticlise** | **-33,3** | **6,8** | **4,2** |
| **Nepa-Botuobin anticlise** | **-34,6** | **12,3** | **5,4** |

## In Fanerozoic

| | | |
|---|---|---|
| **-29 ÷ - 26** | **no** | **< 1** |

# Geochemistry of oil from Precambrian deposits of different fields in the world.

| Geological setting | | Geochemistry of oil | $\delta^{13}C$, % |
|---|---|---|---|
| **Eastern Siberia**<br>***Nepa-Botuobin anticlise*** | Vendian-Riphean | ρ = 0.82 S = 0.25%<br>Rr/Rh = 0.93<br>$St_{29}/St_{-27}$ = 4.2<br>$C_{12}$-$C_{13}$-mma = 6.8% | **-33.3** [1] |
| **Eastern Siberia**<br>***Baikit anticlise*** | Vendian-Riphean | ρ= 0.84 S = 0.65%, Rr/Ph =0.89<br>$St_{29}/St_{27}$ = 5.4<br>$C_{12}$-$C_{13}$- mma= 12.3% | **-34.6** [1] |
| **India**<br>***Bikaner-Nagaur Baghevala-1*** | Vendian sandstone (infracambrian)<br>Jodhpur suite | S = 1.21% Pr/Ph = 0.9<br>Steranes: $C_{27}(20):C_{28}(21):C_{29}(59)$ | **-32.4** [2] |
| **Pakistan**<br>***Punjab Basin, Karampur-1*** | Infracambrian<br>Salt Range Series | Heavy oil (tar), S = 5.1%<br>Steranes: $C_{27}(14):C_{28}(14):C_{29}(72)$<br>Pr/Ph = 0.4 | **-37.0** [2] |
| **Oman** | Huqt Group Pre-Cambrian shallow marine clastics and carbonates | S = 1.3 to 6.2% Pr/Ph = 0.8<br>Steranes: $C_{27}(20):C_{28}(20):C_{29}(60)$ | **-33.7 ÷ -37.2** [3] |
| **Northern America**<br>***Grand Canyon*** | Chuar Group<br>1.3-1.4 bln.y | Steranes: $Ct_{27}$ predominates<br>Presence of gammacerane | **-25,5 ÷ -28,0** [4] |
| **Northern America**<br>***White Pine Mine*** | Nonesuch Formation (1.1 bln.y)<br>Lacnstrine deposits, sandstone | Bitumen, seep of oil | **-30.8 ÷ -34.1** [5] |
| **Australia**<br>***McArtur Basin*** | McArtur Group<br>(1.4-1.8 bln. y.) | Pr/Ph < 1,<br>12-13 – monomethylalkanes<br>St29 predominates | **-32 ÷ -34** [6] |
| **China**<br>***Jibei, Huabei Basin, Yangtze Platform, Sichuan Basin*** | Xiamolin, Teiling<br>Umishan formations,<br>Late Sinian dolomites<br>Weiyan Gas Field | $St_{29}$ predominates | **-33.3** [7] |
| **Volga-Ural**<br>***Sivinskaya Shirkan*** | Vendian,<br>Riphean | ρ=0.96 Res.+Asph=30.84%<br>High viscous oil | **-30.5 ÷ -32.2** [8] |

1 – Kontorovich et.al., 2000; 2 – Peters et.al., 1995; 3 – Grantham et al., 1987; 4 – Summons and Capon, 1988;
5 – Imbus et.al., 1987; 6 – Jackson et.al., 1986; 7 – Korsch, 1991; 8 - Galimov, 1973.

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# The Causes of the Global Variations of Carbon Isotopic Composition in the Biosphere

E. M. Galimov

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Received December 19, 1998

**Abstract**—Global trends in the carbon isotopic composition of carbonate and organic materials are considered. The unusual causes of opposite directions of $\delta^{13}C$ trends for carbonate and organic carbons are of particular interest. We have examined in detail two observations: (1) the anomalous enrichment of Precambrian carbonates in $^{13}C$ with the simultaneous enrichment of organic carbon in $^{12}C$ and (2) the depletion of Late Cenozoic organic carbon in $^{12}C$ with the simultaneous depletion of carbonates in $^{13}C$. The proposed model accounts for these phenomena by a combination of changes in the isotope fractionation in the biosphere with changes in the proportions of carbonate and organic carbons. We also considered specific geochemical processes that could cause the observed relationships. The anomalous enrichment of the Precambrian carbonates in $^{13}C$ corresponds to the epochs of active volcanism. The volcanism was accompanied by a vast inflow of nutrients, increase of bioprpductivity, and accumulation of organic carbon on the seafloor. Under the conditions of limited oxygen

THE CAUSES OF THE GLOBAL VARIATIONS

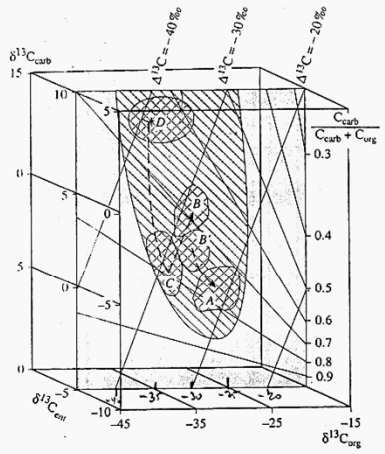



Fig. 1. The dependence of the isotopic compositions of carbonate ($\delta^{13}C_{carb}$) and organic ($\delta^{13}C_{org}$) carbons on the mass ratio of carbonate and organic carbons $C_{carb}/(C_{carb} + C_{org})$ and the value of isotope fractionation $\Delta^{13}C$ between organic and inorganic materials in the exosphere at the constant composition of bulk carbon, –5‰. See text for explanation.

blage have an average $\delta^{13}C = -4.5‰$ [30]. The isotopic composition of diamonds of the ultrabasic paragenesis, from different parts of the world varies within a very narrow interval. Apparently, the isotopic compositions of both mantle-derived carbon and sedimentary carbon remobilized due to metamorphism, which have been added to the exosphere during geologic history, were close to $\delta^{13}C = -5‰$.

If the isotopic composition of entering carbon ($\delta^{13}C_{ent}$) is taken to be constant, we obtain the following equations, which are used as the basis for the diagram of Fig. 1:

$$\delta^{13}C_{org} = \delta^{13}C_{ent} + \frac{C_{carb}}{C_{carb} + C_{org}}\Delta^{13}C,$$

$$\delta^{13}C_{carb} = \delta^{13}C_{ent} - \frac{C_{org}}{C_{carb} + C_{org}}\Delta^{13}C,$$

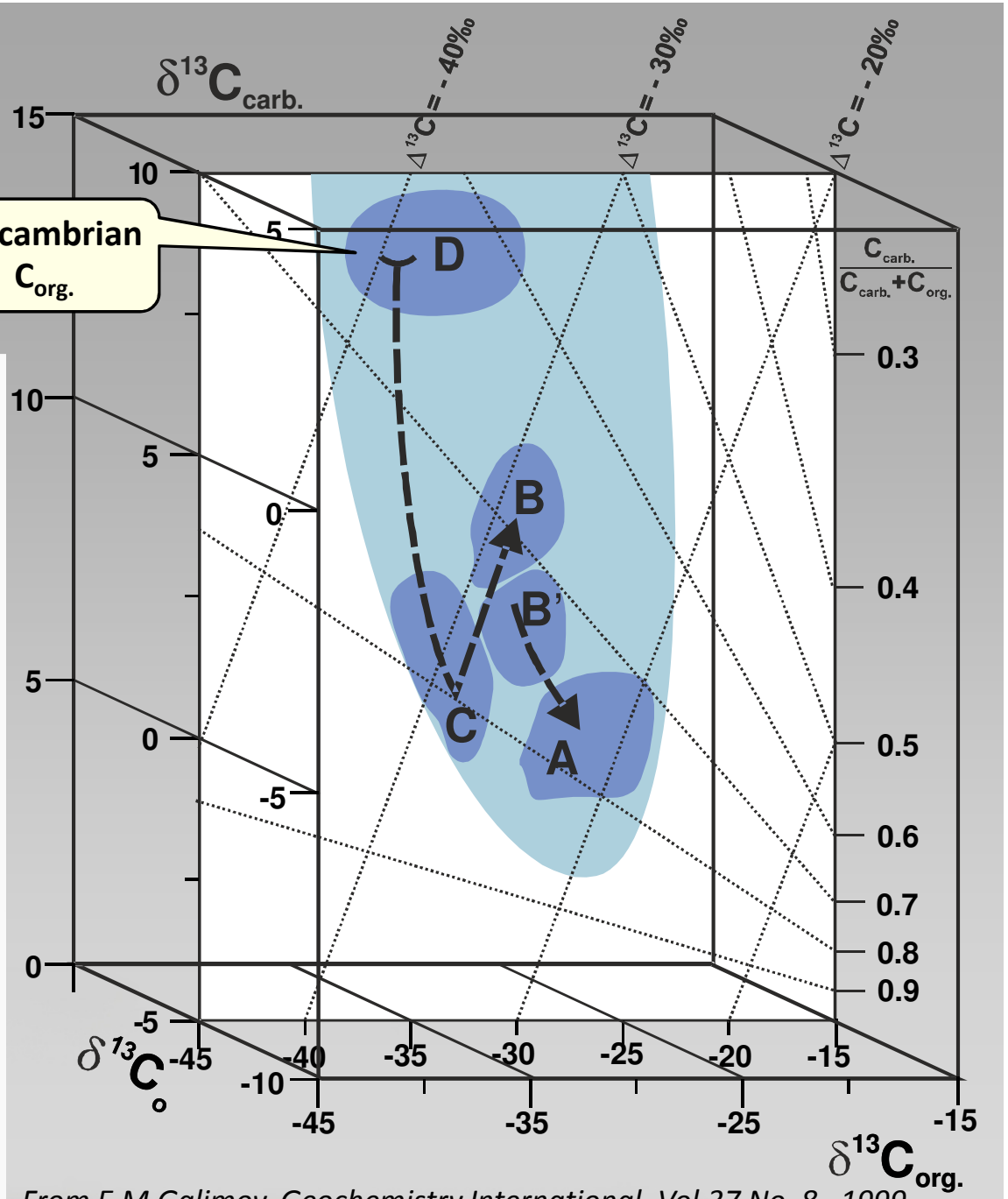
where $\Delta^{13}C = \Delta^{13}C_{org} - \Delta^{13}C_{carb}$ and, in turn, $\Delta^{13}C_{org} = \delta^{13}C_{org} - \delta^{13}C_{exosphere}$ and $\Delta^{13}C_{carb} = \delta^{13}C_{carb} - \delta^{13}C_{exosphere}$ characterize isotope fractionation in the processes of the transition of organic and carbonate carbons from the exosphere to the sedimentary shell. Formally, $\Delta^{13}C = \delta^{13}C_{org} - \delta^{13}C_{carb}$. The main diagram is drawn for the most probable value of $\delta^{13}C_{ent} = -5‰$.

If $\delta^{13}C_{ent}$ is not equal to –5‰, the $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ axes shift correspondingly, while the structure of the net formed by $\Delta^{13}C$ and $C_{carb}/(C_{carb} + C_{org})$ isolines remains invariable. In other words, $\delta^{13}C_{ent}$ forms the third axis.

The hatched area shows the most typical ranges of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ during geologic history. The diagram shows that variations in the proportions of organic and carbonate carbons [i.e., $C_{carb}/(C_{carb} + C_{org})$ value], which are usually considered as a possible cause for global changes in carbon isotope composition with the geologic time, cannot alone produce the whole range of $\delta^{13}C$ of carbonate and organic carbons observed in nature. This field requires variations in the extent of isotope fractionation in the biosphere and, in some cases, of $\delta^{13}C_{ent}$ values.

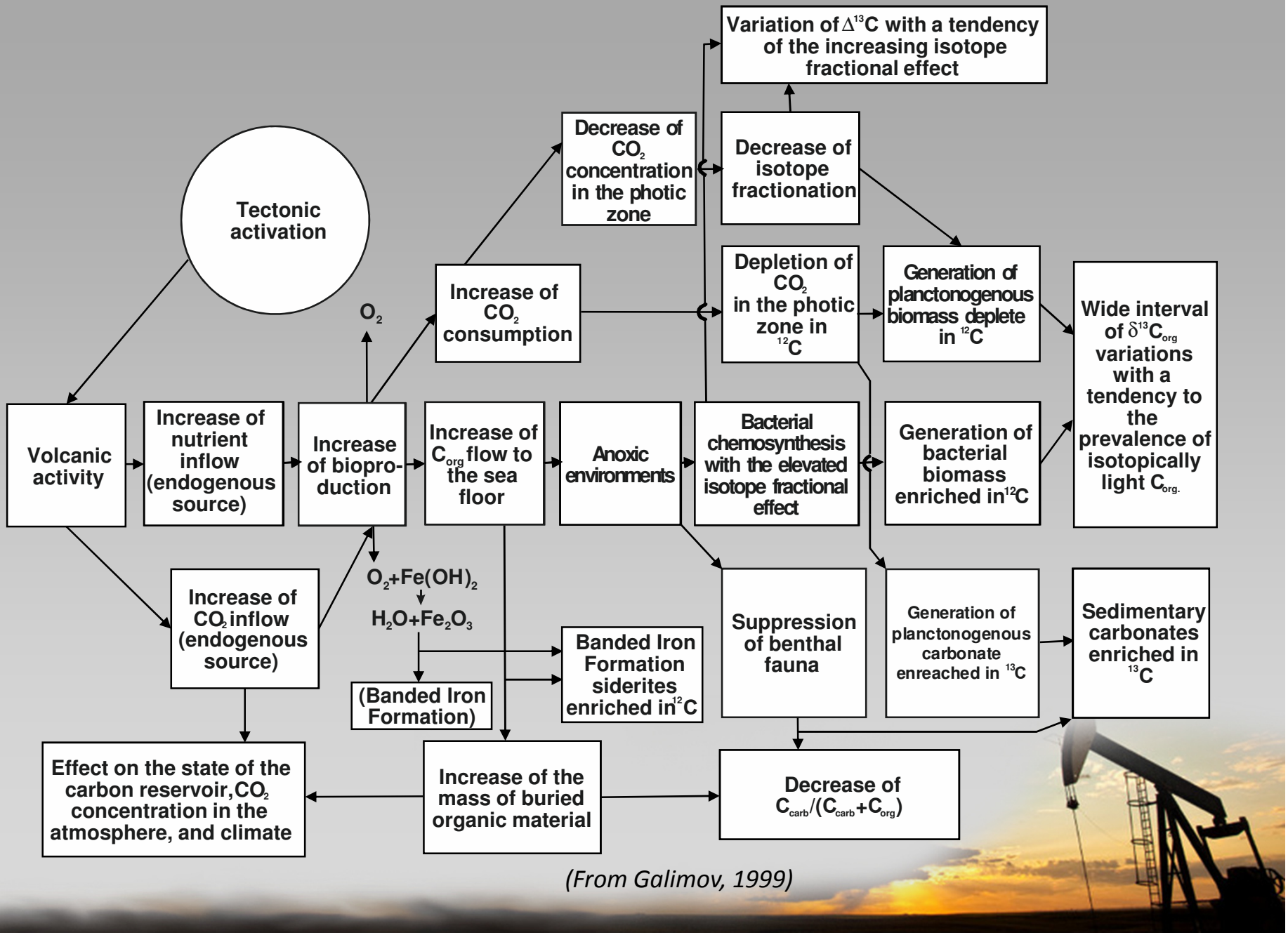
On the diagram for $\delta^{13}C_{ent} = -5‰$, data points for the present-day biosphere plot within field A with the center at $\delta^{13}C_{carb} = 0‰$ and $\delta^{13}C_{org} = -22‰$. Thus, the present-day ratio of carbonate to organic carbons is



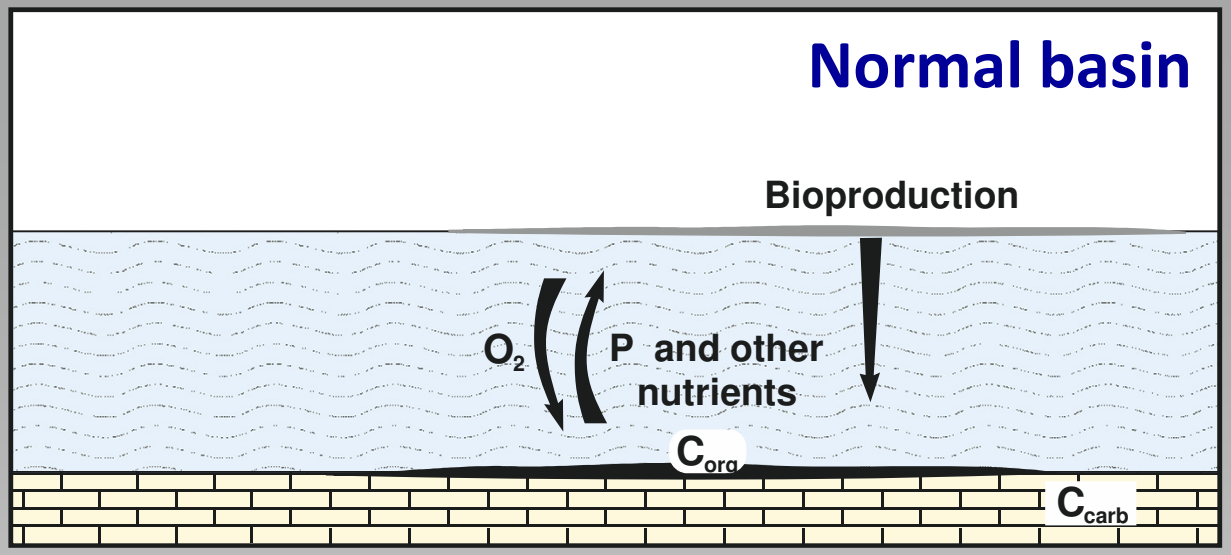


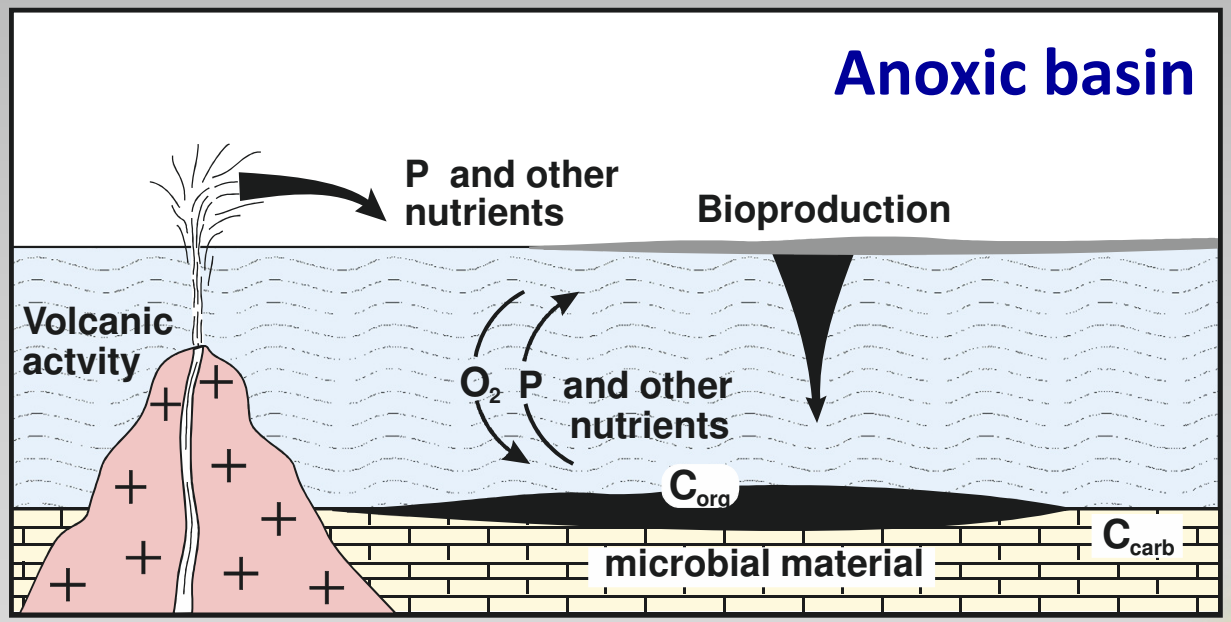

*From E.M.Galimov, Geochemistry International. Vol.37 No. 8 , 1999*

# Sequence of events leading to enlarged isotope fractionation

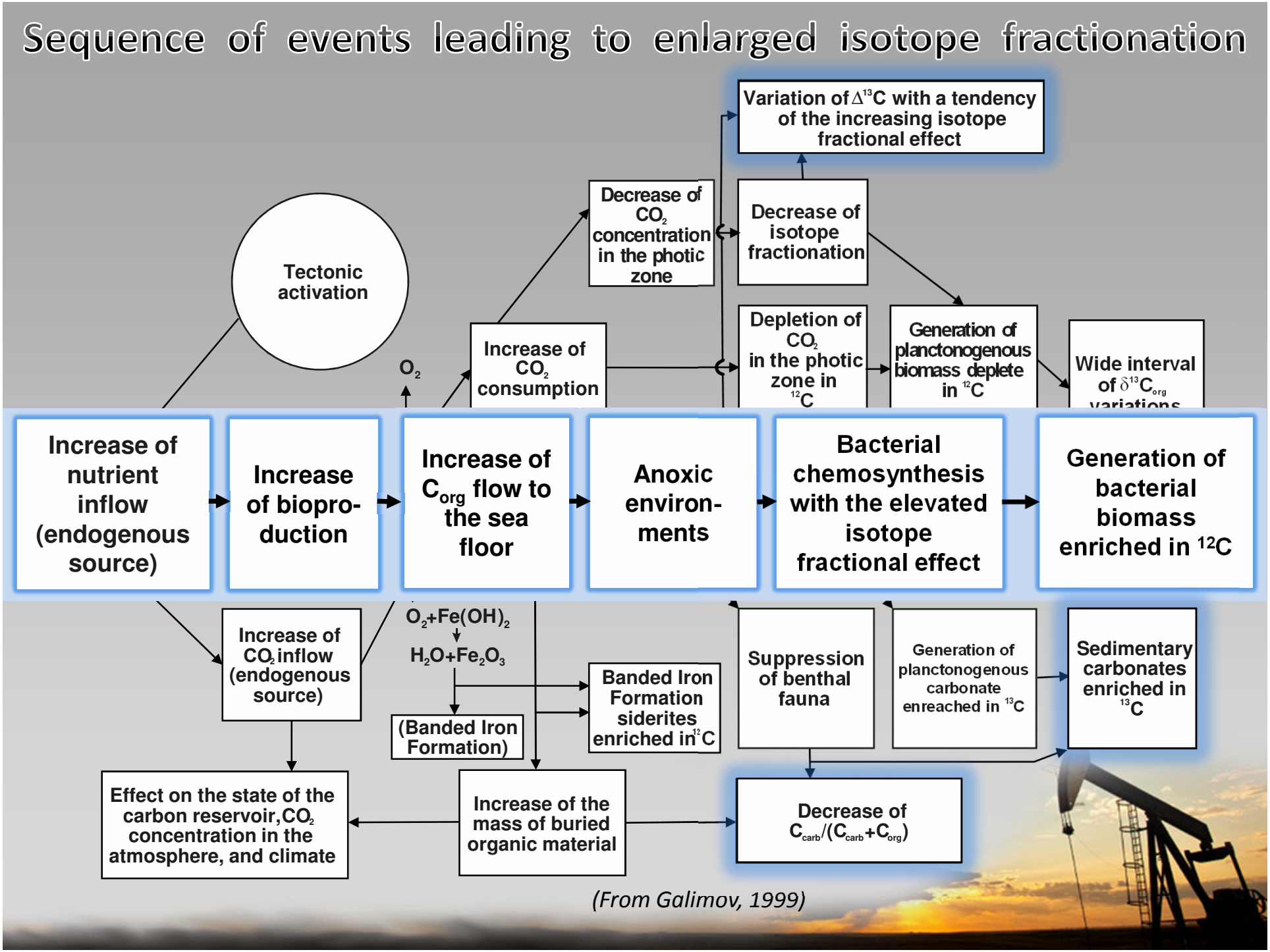



*(From Galimov, 1999)*


Normal basin
Bioproduction
O2
P and other nutrients
Corg
Ccarb


Anoxic basin
P and other nutrients
Bioproduction
Volcanic actvity
O2
P and other nutrients
Corg
Ccarb
microbial material

# Sequence of events leading to enlarged isotope fractionation




*(From Galimov, 1999)*

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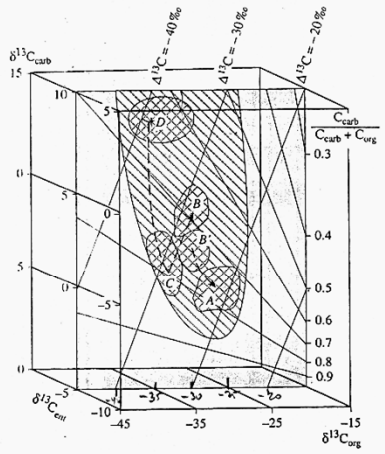



Fig. 1. The dependence of the isotopic compositions of carbonate ($\delta^{13}C_{carb}$) and organic ($\delta^{13}C_{org}$) carbons on the mass ratio of carbonate and organic carbons $C_{carb}/(C_{carb} + C_{org})$ and the value of isotope fractionation $\Delta^{13}C$ between organic and inorganic materials in the exosphere at the constant composition of bulk carbon, –5‰. See text for explanation.

blage have an average $\delta^{13}C = -4.5‰$ [30]. The isotopic composition of diamonds of the ultrabasic paragenesis, from different parts of the world varies within a very narrow interval. Apparently, the isotopic compositions of both mantle-derived carbon and sedimentary carbon remobilized due to metamorphism, which have been added to the exosphere during geologic history, were close to $\delta^{13}C = -5‰$.

If the isotopic composition of entering carbon ($\delta^{13}C_{ent}$) is taken to be constant, we obtain the following equations, which are used as the basis for the diagram of Fig. 1:

$$\delta^{13}C_{org} = \delta^{13}C_{ent} + \frac{C_{carb}}{C_{carb} + C_{org}}\Delta^{13}C,$$

$$\delta^{13}C_{carb} = \delta^{13}C_{ent} - \frac{C_{org}}{C_{carb} + C_{org}}\Delta^{13}C,$$

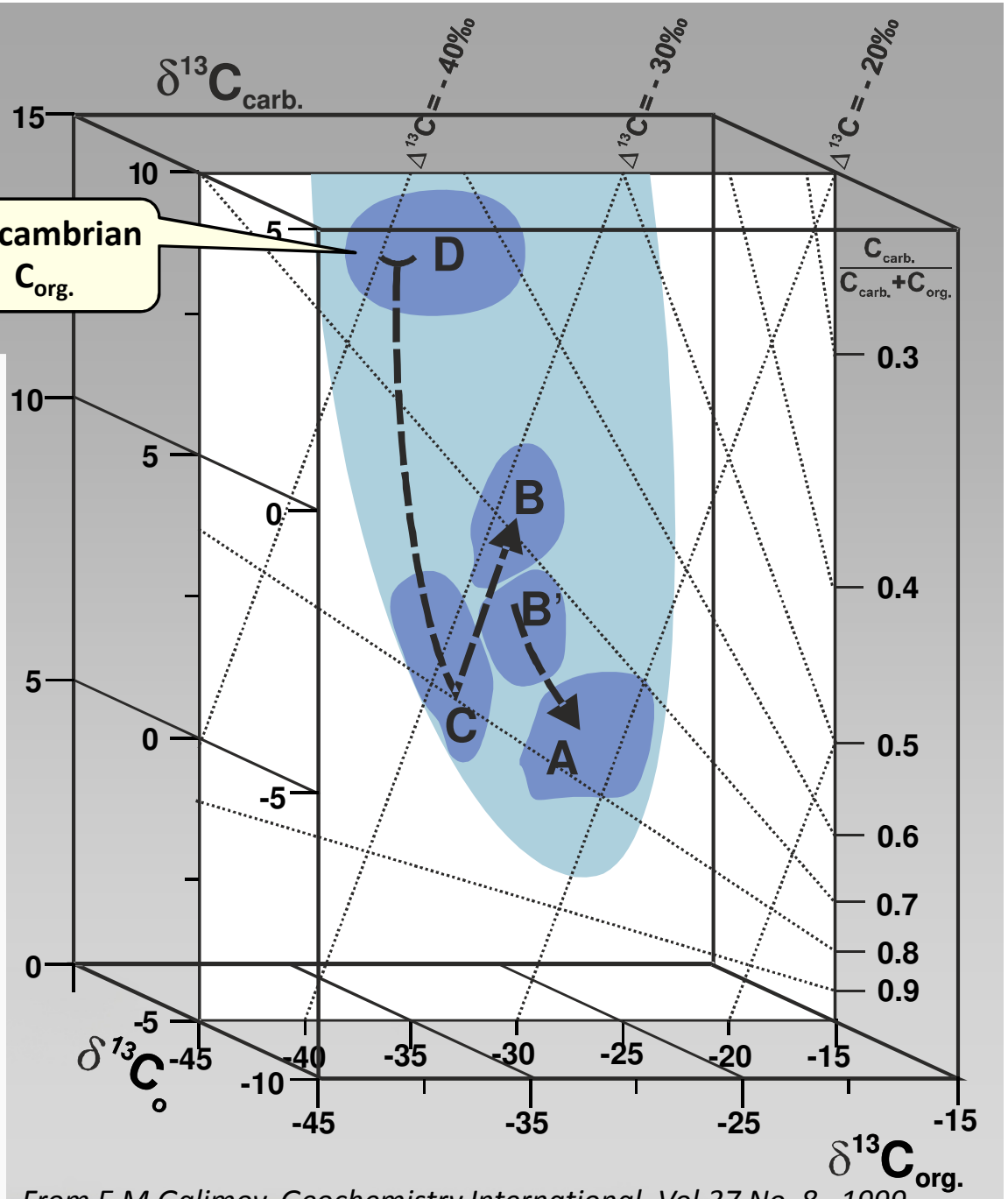
where $\Delta^{13}C = \Delta^{13}C_{org} - \Delta^{13}C_{carb}$ and, in turn, $\Delta^{13}C_{org} = \delta^{13}C_{org} - \delta^{13}C_{exosphere}$ and $\Delta^{13}C_{carb} = \delta^{13}C_{carb} - \delta^{13}C_{exosphere}$ characterize isotope fractionation in the processes of the transition of organic and carbonate carbons from the exosphere to the sedimentary shell. Formally, $\Delta^{13}C = \delta^{13}C_{org} - \delta^{13}C_{carb}$. The main diagram is drawn for the most probable value of $\delta^{13}C_{ent} = -5‰$.

If $\delta^{13}C_{ent}$ is not equal to –5‰, the $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ axes shift correspondingly, while the structure of the net formed by $\Delta^{13}C$ and $C_{carb}/(C_{carb} + C_{org})$ isolines remains invariable. In other words, $\delta^{13}C_{ent}$ forms the third axis.

The hatched area shows the most typical ranges of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ during geologic history. The diagram shows that variations in the proportions of organic and carbonate carbons [i.e., $C_{carb}/(C_{carb} + C_{org})$ value], which are usually considered as a possible cause for global changes in carbon isotope composition with the geologic time, cannot alone produce the whole range of $\delta^{13}C$ of carbonate and organic carbons observed in nature. This field requires variations in the extent of isotope fractionation in the biosphere and, in some cases, of $\delta^{13}C_{ent}$ values.

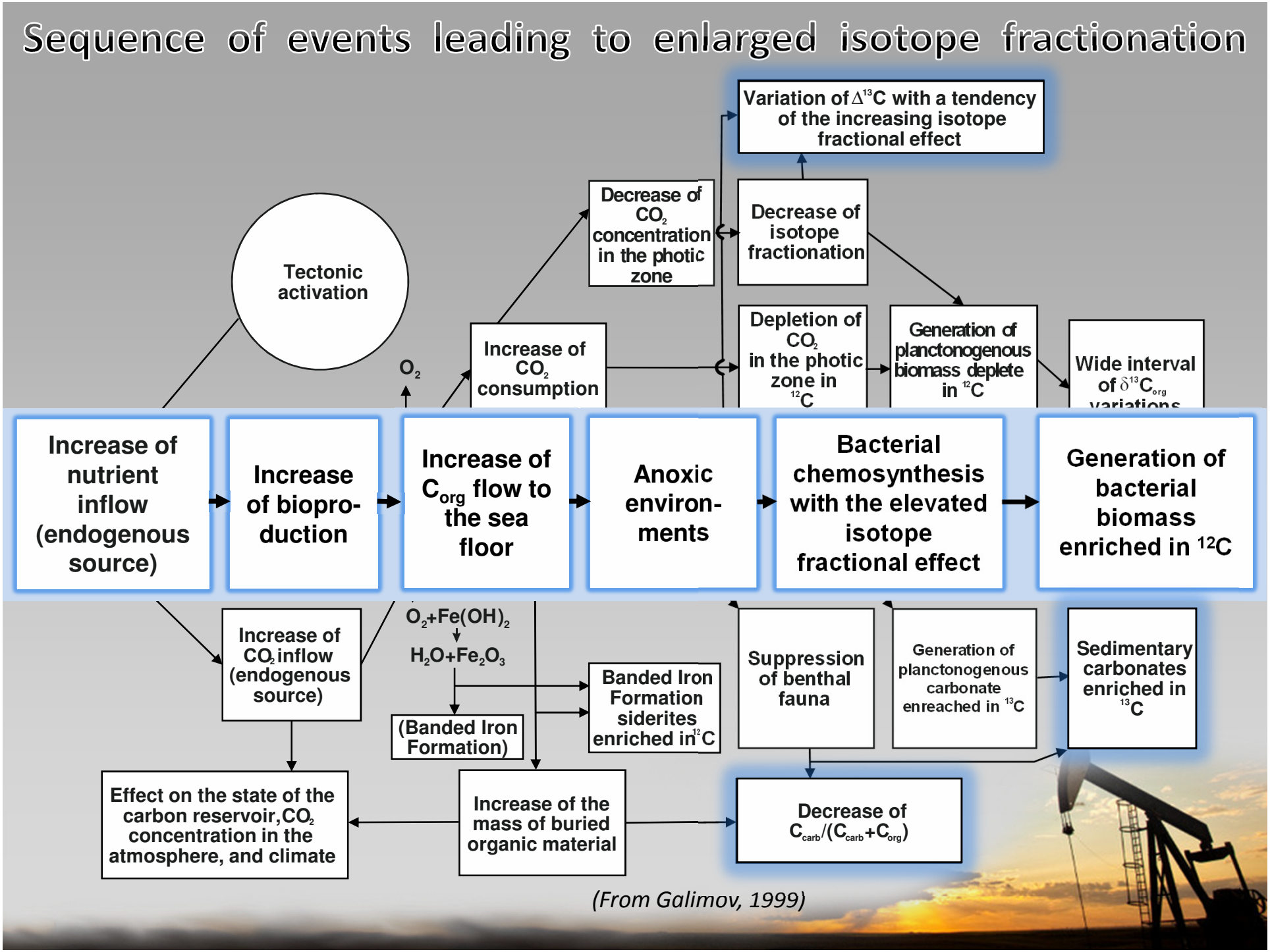
On the diagram for $\delta^{13}C_{ent} = -5‰$, data points for the present-day biosphere plot within field A with the center at $\delta^{13}C_{carb} = 0‰$ and $\delta^{13}C_{org} = -22‰$. Thus, the present-day ratio of carbonate to organic carbons is






*From E.M.Galimov, Geochemistry International. Vol.37 No. 8 , 1999*

# Sequence of events leading to enlarged isotope fractionation




*(From Galimov, 1999)*

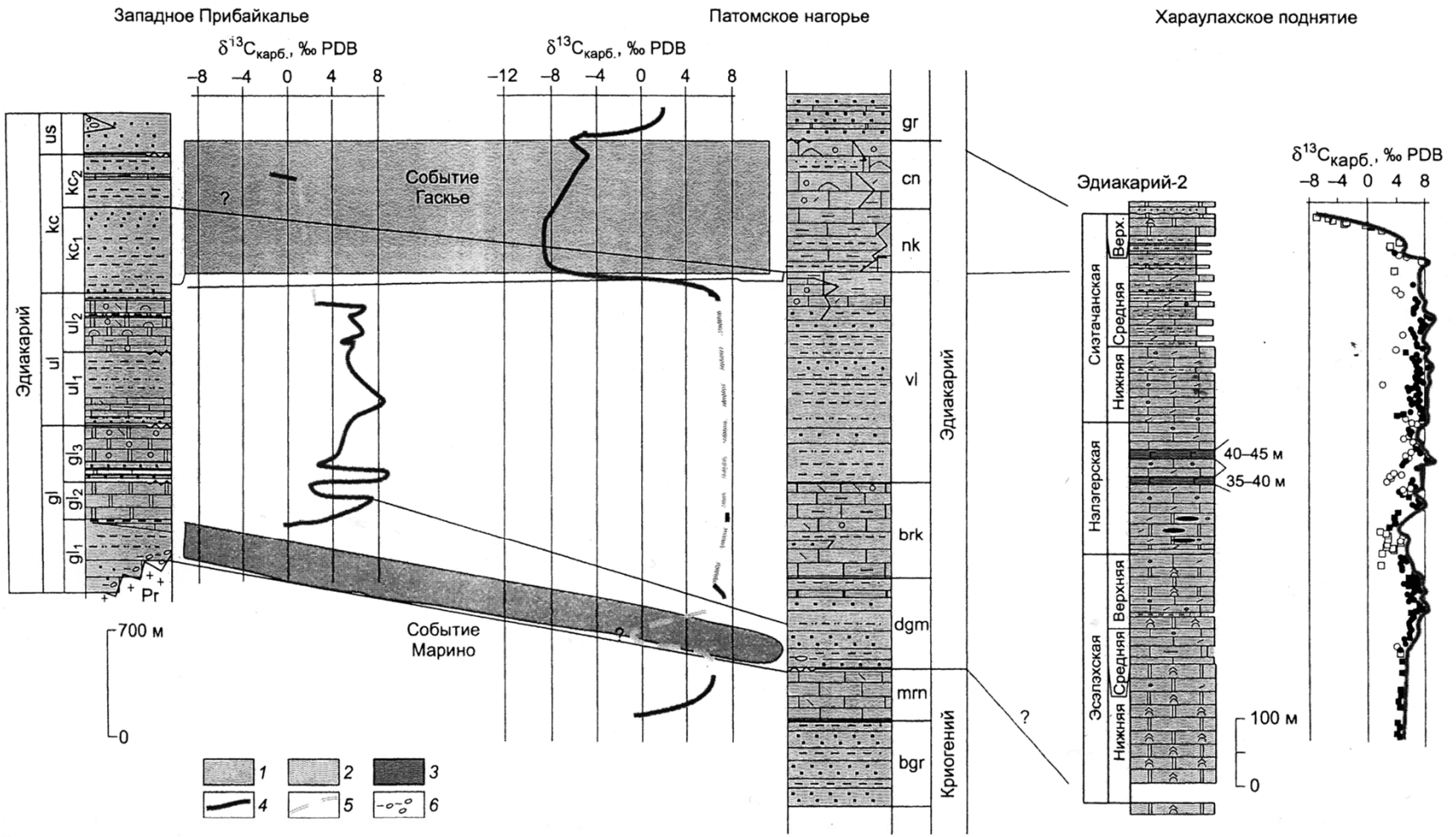
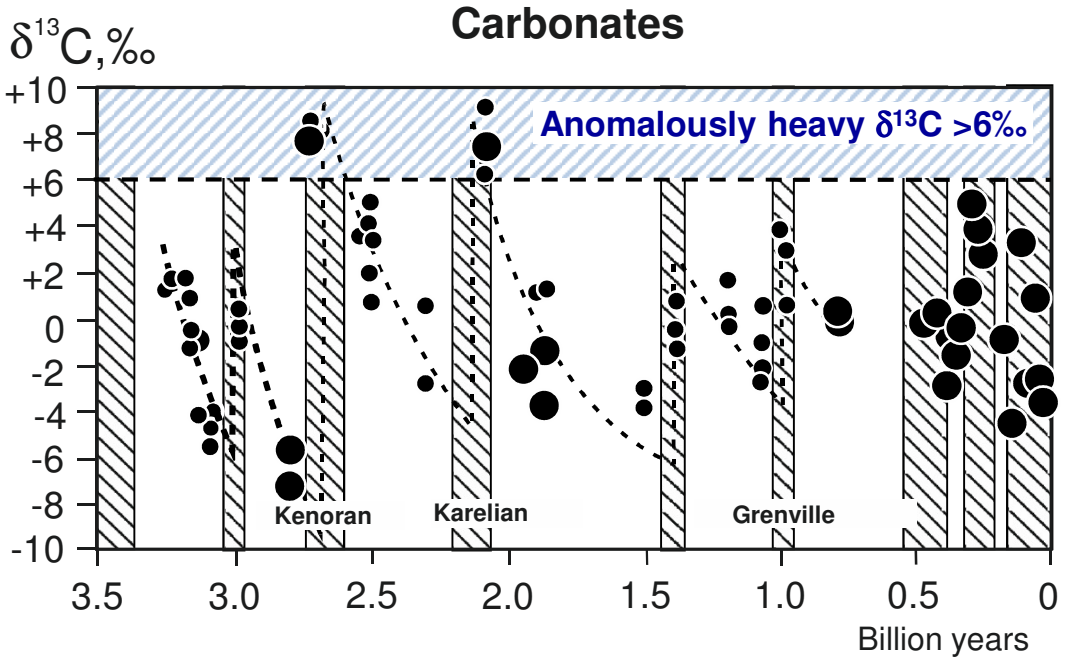


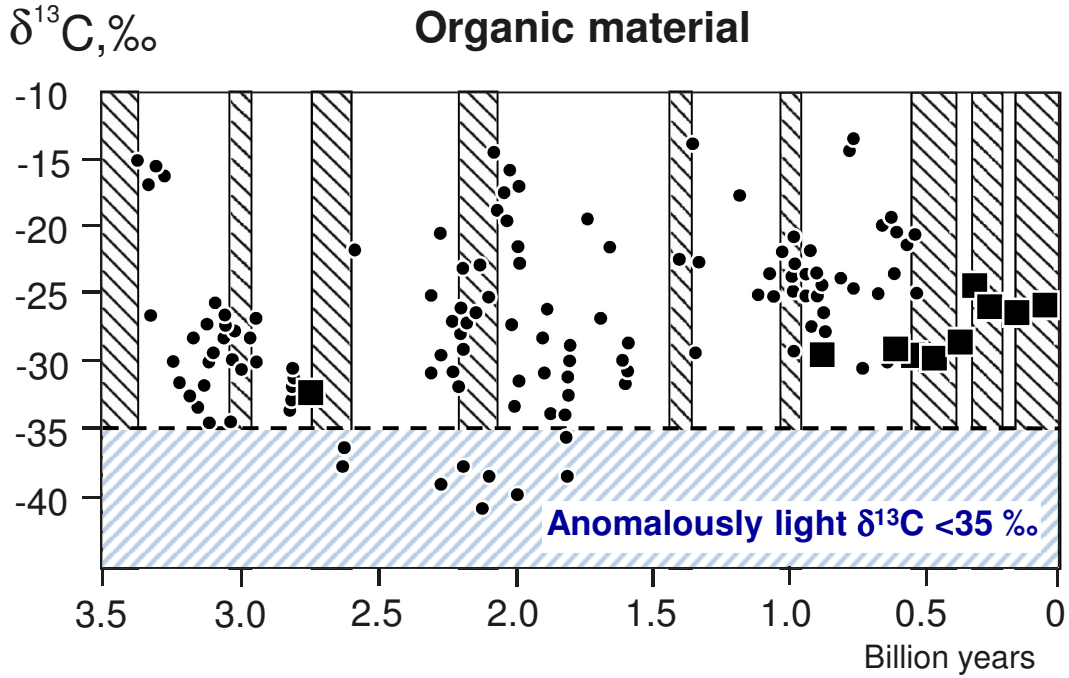

**Рис. 8. Вероятная корреляция разрезов верхнего докембрия Хараулахского поднятия, Патомского нагорья и Западного Прибайкалья по $\delta^{13}C_{карб.}$**

*1* — силикокластические породы; *2* — карбонатные породы; *3* — долериты; *4*, *5* — кривые $\delta^{13}C$: *4* — установленные, *5* — предполагаемые; *6* — грубообломочные породы с песчано-глинистым матриксом. Остальные усл. обозн. см. на рис. 2, 6.

Свиты: gl — голоустенская, ul — улунтуйская, kc — качергатская, us — ушаковская, bgr — бугариктинская, mrn — мариинская, dgm — джемкуканская, brk — баракунская, vl — валюхтинская, nk — никольская, cn — ченчинская, gr — жербинская.

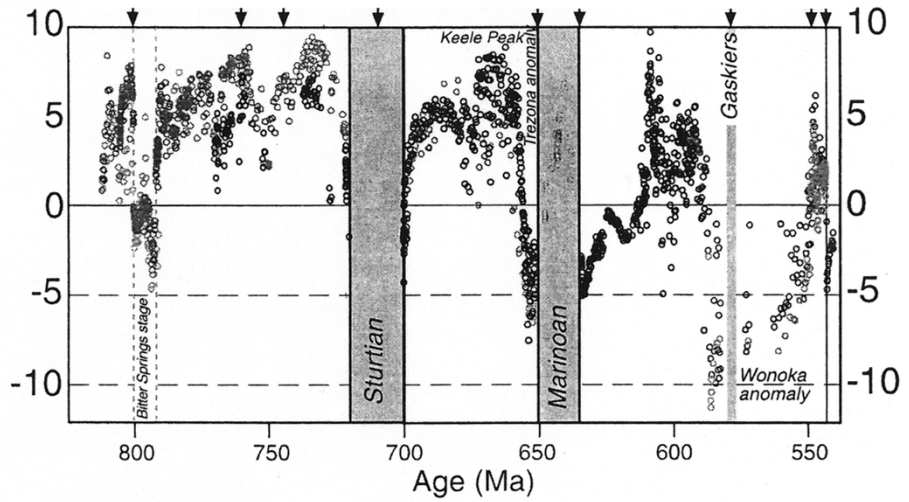
*(From Khabarov and Izokh, 2014)*



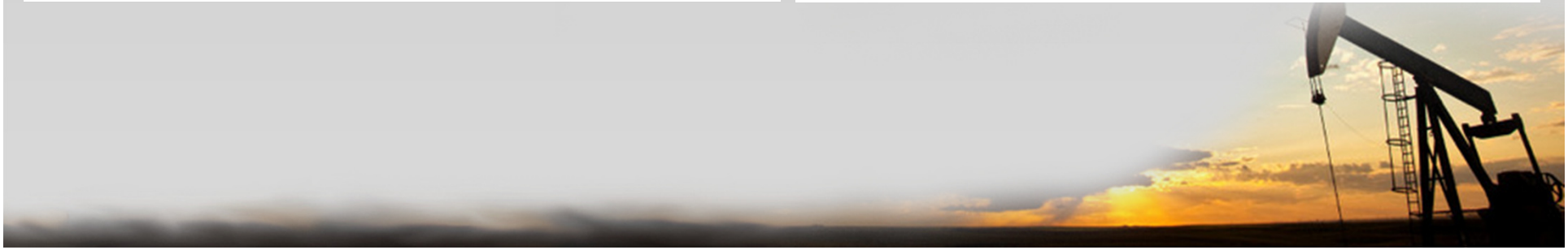

*(From Galimov, Ronov, Migdisov (1973)*

## Carbonates




*(From Halverson et al., 2005)*

| Glaciations | | | | Mln. y |
|---|---|---|---|---|
| Neoproterozoic | Ediacaran | Vendian | Gaskiers | 580 |
| | Cryogenian | Riphean-3 | Marinoan | 635 |
| Mezoproterozoic | Stenian | Riphean-2 | Sturtian | 730 |



## ИЗОТОПНЫЙ СОСТАВ C, O, Sr И S В ПОЗДНЕДОКЕМБРИЙСКИХ ОТЛОЖЕНИЯХ

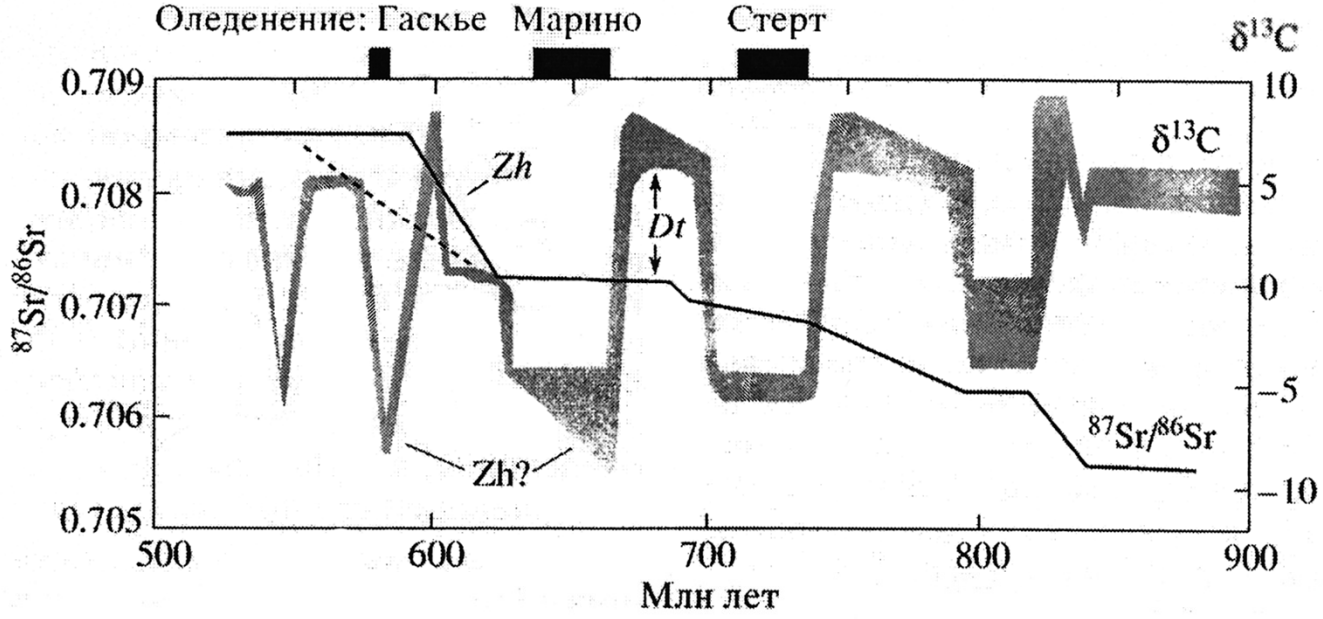



**Рис. 9.** Эволюционные кривые $^{87}Sr/^{86}Sr$ и $\delta^{13}C$, пересмотренные с учетом новых изотопных данных и последних U-Pb определений возраста неопротерозойских оледенений по цирконам [Halverson et al., 2005, 2006].

Dt – дальнетайгинская серия; Zh – жуинская серия. Пунктирной линией показана вероятная эволюция изотопного состава стронция в неопротерозойском океане, в том случае, если жуинская серия по возрасту близка к формации Вонока в Австралии (~580 млн. лет).

*(From Pokrovski et al., 2014)*

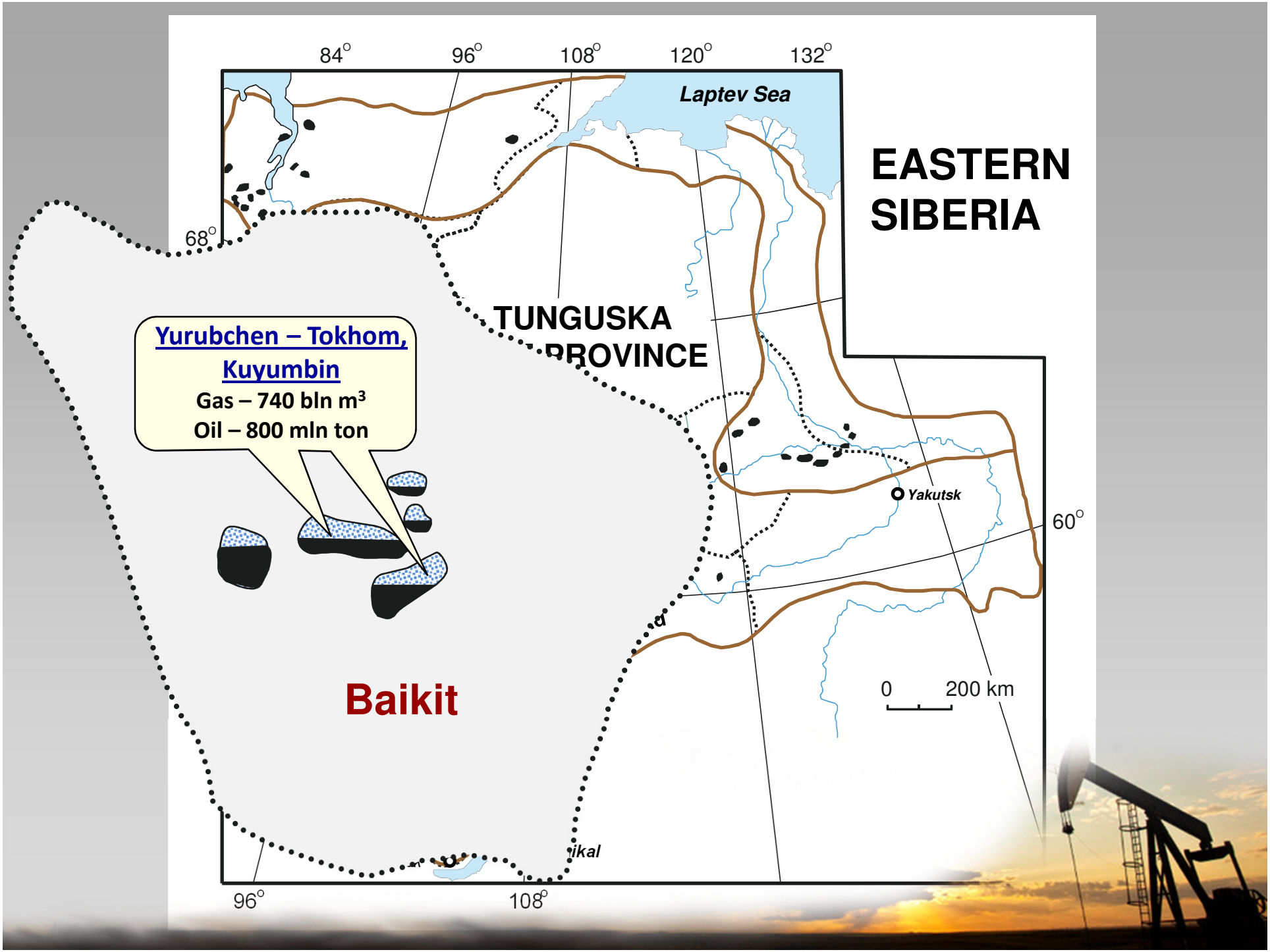
# Conclusion

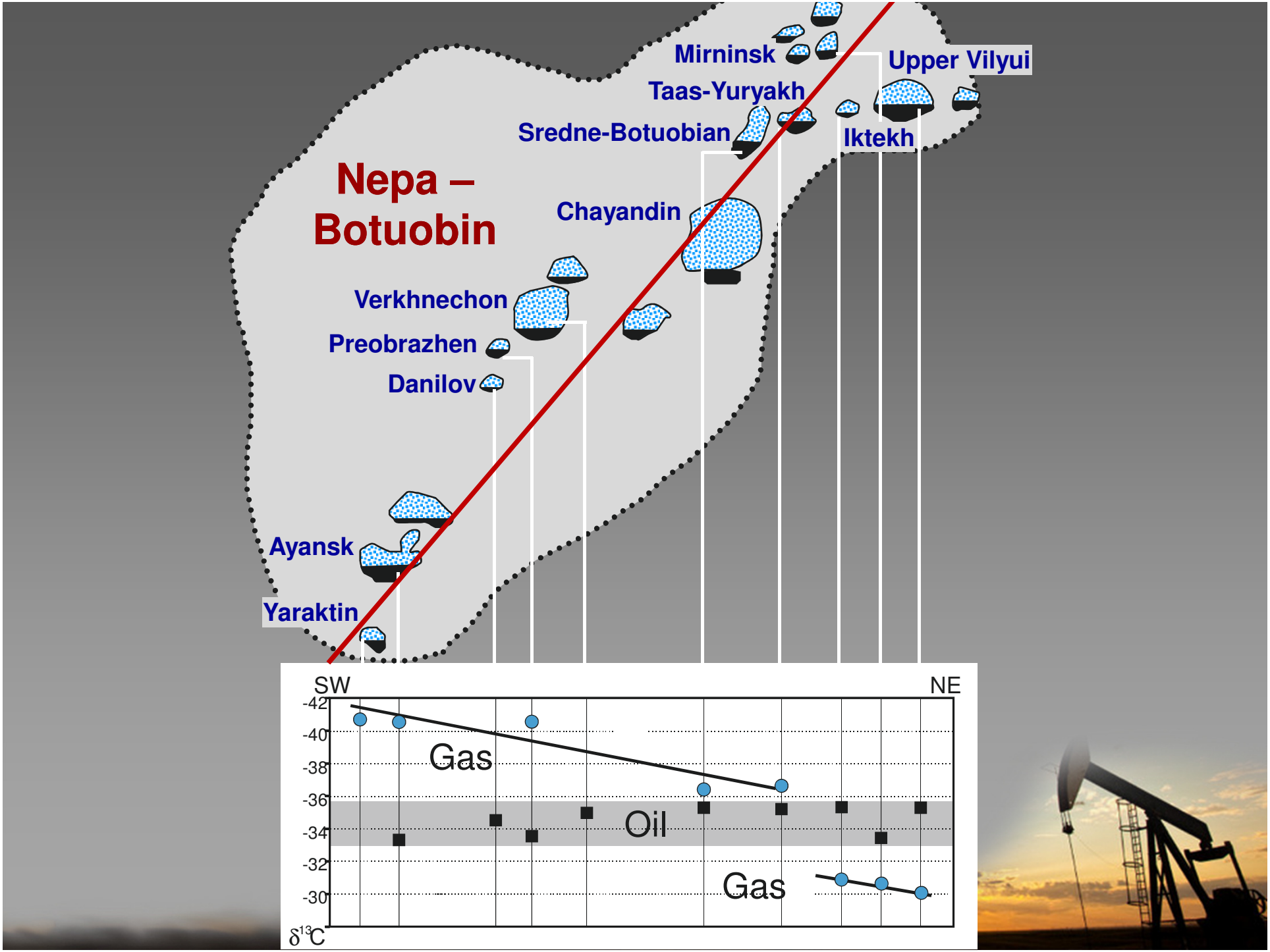
Hydrocarbons in the Precambrian rocks of Eastern Siberia originated from bacterial type of organic matter deposited in anoxic basins in periods of the volcanic activity.

Initial oils are subjected to partial destruction that led to formation of the present gas-condensate accumulations.

I believe that many Precambrian oil-gas fields in the world could have the similar geological history.




84°
96°
108°
120°
132°
68°
Laptev Sea
EASTERN SIBERIA
TUNGUSKA PROVINCE
Yurubchen – Tokhom, Kuyumbin
Gas – 740 bln m³
Oil – 800 mln ton
Yakutsk
60°
Baikit
0
200 km
96°
108°


Nepa –
Botuobin
Mirninsk
Upper Vilyui
Taas-Yuryakh
Sredne-Botuobian
Iktekh
Chayandin
Verkhnechon
Preobrazhen
Danilov
Ayansk
Yaraktin
SW
NE
-42
-40
-38
-36
-34
-32
-30
Gas
Oil
Gas
δ13C

Geochemistry International, Vol. 37, No. 8, 1999, pp. 699–713. Translated from Geokhimiya, No. 8, 1999, pp. 787–803.
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# The Causes of the Global Variations of Carbon Isotopic Composition in the Biosphere

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Received December 19, 1998

**Abstract**—Global trends in the carbon isotopic composition of carbonate and organic materials are considered. The unusual causes of opposite directions of $\delta^{13}C$ trends for carbonate and organic carbons are of particular interest. We have examined in detail two observations: (1) the anomalous enrichment of Precambrian carbonates in $^{13}C$ with the simultaneous enrichment of organic carbon in $^{12}C$ and (2) the depletion of Late Cenozoic organic carbon in $^{12}C$ with the simultaneous depletion of carbonates in $^{13}C$. The proposed model accounts for these phenomena by a combination of changes in the isotope fractionation in the biosphere with changes in the proportions of carbonate and organic carbons. We also considered specific geochemical processes that could cause the observed relationships. The anomalous enrichment of the Precambrian carbonates in $^{13}C$ corresponds to the epochs of active volcanism. The volcanism was accompanied by a vast inflow of nutrients, increase of bioprpductivity, and accumulation of organic carbon on the seafloor. Under the conditions of limited oxygen



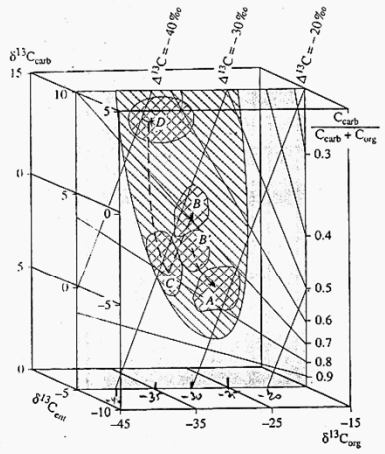



Fig. 1. The dependence of the isotopic compositions of carbonate ($\delta^{13}C_{carb}$) and organic ($\delta^{13}C_{org}$) carbons on the mass ratio of carbonate and organic carbons $C_{carb}/(C_{carb} + C_{org})$ and the value of isotope fractionation $\Delta^{13}C$ between organic and inorganic materials in the exosphere at the constant composition of bulk carbon, –5‰. See text for explanation.

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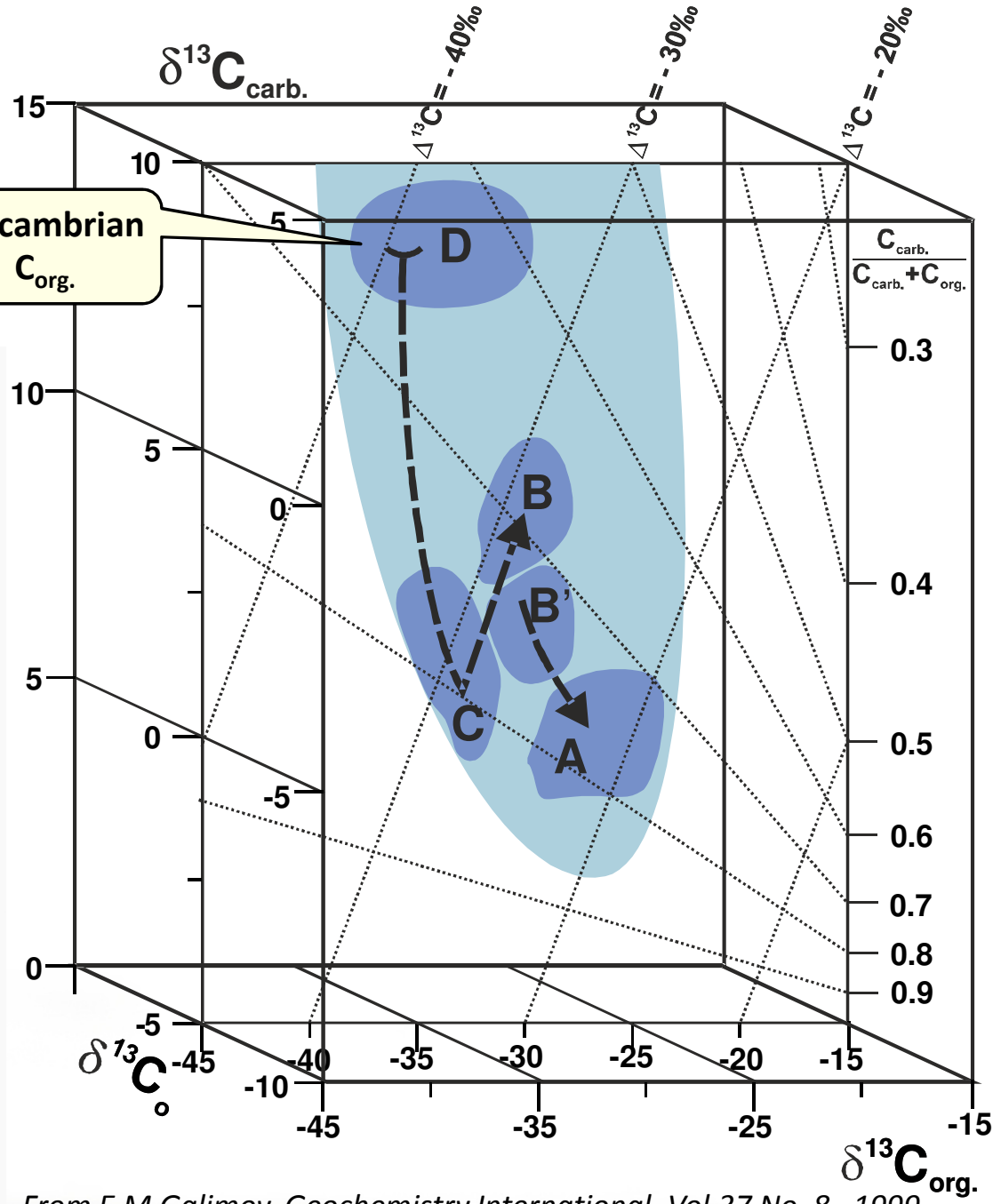
where $\Delta^{13}C = \Delta^{13}C_{org} - \Delta^{13}C_{carb}$ and, in turn, $\Delta^{13}C_{org} = \delta^{13}C_{org} - \delta^{13}C_{exosphere}$ and $\Delta^{13}C_{carb} = \delta^{13}C_{carb} - \delta^{13}C_{exosphere}$ characterize isotope fractionation in the processes of the transition of organic and carbonate carbons from the exosphere to the sedimentary shell. Formally, $\Delta^{13}C = \delta^{13}C_{org} - \delta^{13}C_{carb}$. The main diagram is drawn for the most probable value of $\delta^{13}C_{ent} = -5‰$.

If $\delta^{13}C_{ent}$ is not equal to –5‰, the $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ axes shift correspondingly, while the structure of the net formed by $\Delta^{13}C$ and $C_{carb}/(C_{carb} + C_{org})$ isolines remains invariable. In other words, $\delta^{13}C_{ent}$ forms the third axis.

The hatched area shows the most typical ranges of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ during geologic history. The diagram shows that variations in the proportions of organic and carbonate carbons [i.e., $C_{carb}/(C_{carb} + C_{org})$ value], which are usually considered as a possible cause for global changes in carbon isotope composition with the geologic time, cannot alone produce the whole range of $\delta^{13}C$ of carbonate and organic carbons observed in nature. This field requires variations in the extent of isotope fractionation in the biosphere and, in some cases, of $\delta^{13}C_{ent}$ values.

On the diagram for $\delta^{13}C_{ent} = -5‰$, data points for the present-day biosphere plot within field A with the center at $\delta^{13}C_{carb} = 0‰$ and $\delta^{13}C_{org} = -22‰$. Thus, the present-day ratio of carbonate to organic carbons is






*From E.M.Galimov, Geochemistry International. Vol.37 No. 8 , 1999*