

Palaeozoic and Mesozoic Carbon-Isotopic Macrorhythms and Macrocycles of Solar Activity

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It has been realized that the high $\delta^{13}\text{C}$ values in organogenic carbonates from selected Upper Palaeozoic and Mesozoic horizons are the testimony of an abundance of organic carbon in ocean of appropriate time and that the sharp drop of the $\delta^{13}\text{C}$ values at Permian-Triassic and Cretaceous-Tertiary boundary transitions coincides with reduction of organic carbon accumulation (Magaritz et al., 1981, 1983, 1986, 1988, 1991; Magaritz & Turner, 1982; Anderson & Arthur, 1983; Holser, 1984; Holser & Magaritz, 1985; Holser et al., 1986, 1991; Zachos & Arthur, 1986; Baud et al., 1989, 1995; Zachos et al., 1989; Magaritz & Holser, 1991; Alcalá-Herrera et al., 1992; Yang, 1992; Anderson et al., 1994; Jenkyns et al., 1994; Naidin & Kiyashko, 1994; Hirano & Takagi, 1995; Jenkyns et al., 1995; Hirano & Fukuju, 1997; Foster et al., 1998; Atudorei, 1999; Baud et al., 1999; Jenkins, 2000; Ando et al., 2000; Zakharov et al., 2000a; Zakharov et al., 2001a, in press among others). According to the opinions by previous authors, the degree of enrichment by a heavy isotope ^{13}C appears to reflect intensity of exception of a light isotope ^{12}C during photosynthesis, i.e. intensity of organic production.

As suggested by Alcalá-Herrera et al. (1992), some variations in $^{13}\text{C}/^{12}\text{C}$ ratios recorded in deep-water marine organogenic carbonates might be controlled by such environmental factors as the carbon budget, upwelling and primary productivity. It is difficult to separate the effect of each of these factors in deep-water conditions; but when worldwide carbon isotope shifts are observed in shallow-water carbonates, they are generally attributed to changes in primary biological productivity, first of all in phytoplankton one. Therefore, $\delta^{13}\text{C}$ value can

be used for a measure of biological productivity of ancient shallow seas. Agreeing with such rough, approximate estimation of the data on $\delta^{13}\text{C}$, Weimarn et al. (1998), however, scored that not any weighting of carbonate carbon can be treated so, as the carbon-isotopic anomalies in number of cases grow out of composite effect of many factors.

The peculiarities in distribution of some producers (phytoplankton), one of main utilizators of a solar energy on the surface of the present day ocean, are now well investigated (Bogorov, 1974). Their main biomass is contained in an upper 100-meter water mass that is connected with a feature of photosynthesis, but their location in it depends first of all on a degree of hydrological intermixing of waters under influence of considerable thermal gradients and winds and their distribution. The phytoplankton productivity is great in areas characterized by an intensive vertical circulation (boreal realms and the zone of equatorial uprising of waters between 10-12° of Northern latitudes and 7-8° of Southern latitudes). The uprising of deep waters reduces enrichment of surface layer by nutritious substances that promotes increase of phytoplankton production and intensity of its photosynthesis. The small amount of plankton in Recent Arctic and Antarctic seems to be originated in the short vegetal period of a phytoplankton of high latitudes.

In time of absence of polar ice on the Earth (it is expected at least for the significant part of Late Palaeozoic and Mesozoic) hydrological conditions, probably, considerably differed from Recent ones first of all in an "unusual" poleward transport of large equatorial warm water masses and weaker vertical circulation of waters in some climatic zones. During that time, another sort of regularities in distribution of phytoplankton in the surface layer of the ocean, apparently, took place, therefore the actual method for isotopic investigation of Phanerozoic organogenic carbonates can be applied only with considerable stipulation.

Recently, Pokrovsky, Letnikov and Samylin (1999) proposed a model which is compatible with observations on the Recent ocean and with the data on Quaternary glacial period: the high $\delta^{13}\text{C}$ values in carbonates of the Lower Proterozoic, Upper Rhyphen, Vendian and Permian seem to be connected with conditions of largest glacial epochs. We must briefly remark that their reference to Bauds et al. (1989) who examined the isotopic compositions of Upper Permian carbonates is not appropriate, but there is another publication (Rao, 1988) showing that Lower Permian Berriedale Limestone of Tasmania, formed, as they believed, during Main Gondwanian glacial epoch, is also char-

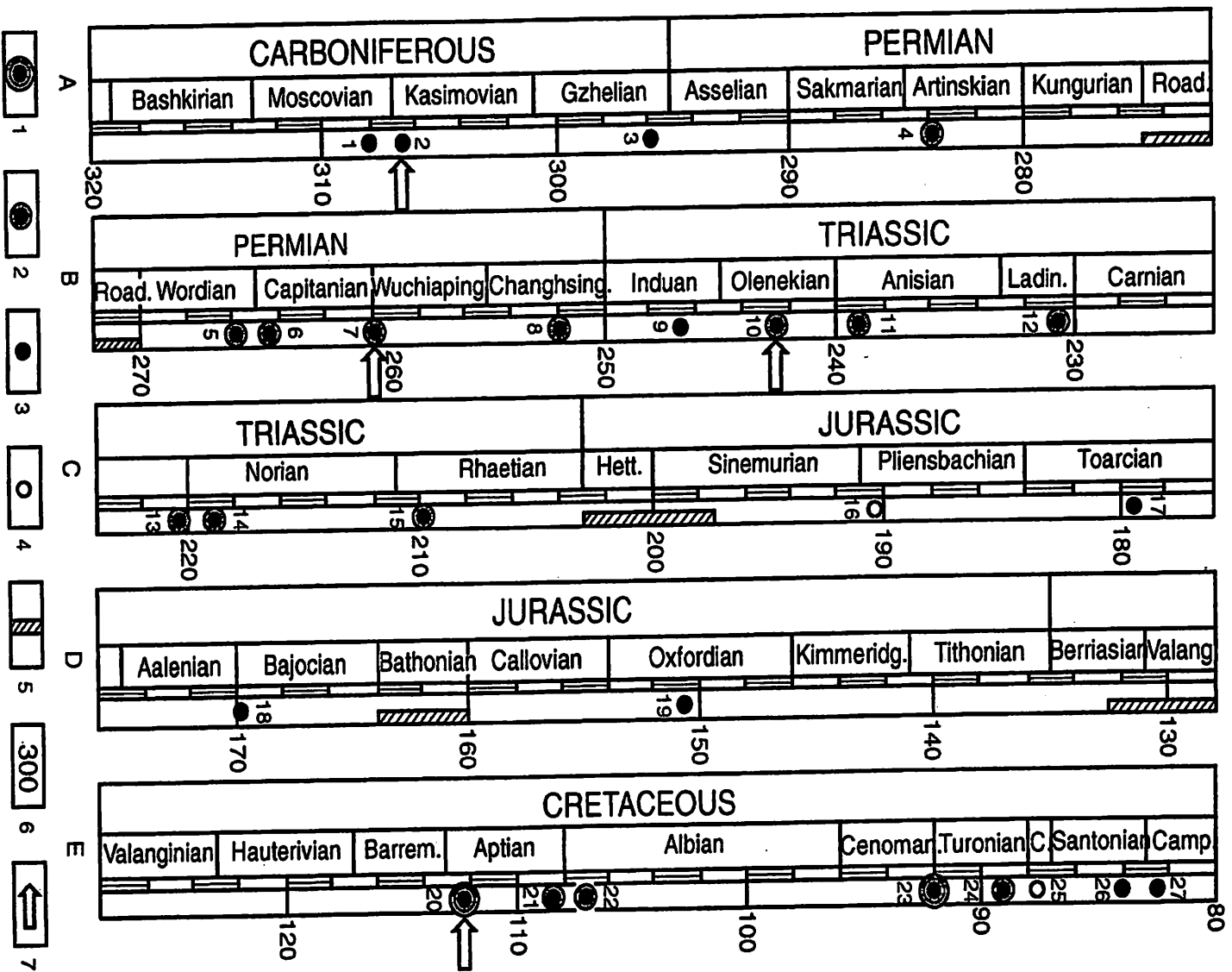


Figure 1: Late Palaeozoic and Mesozoic $\delta^{13}C$ anomalies. 1 - anomalies discovered in many localities and their number, 2 - anomalies discovered in some (2-7) localities and their number, 3 - anomaly discovered in a single locality and its number, 4 - anomaly in question and its number, 5 - brightest Phanerozoic event ($\delta^{13}C$ more than 6‰, 6 - uninspected interval, 7 - age in Ma. Road - Roadian, Wuchiaping - Wuchiapingian, Valang. - Changhsing - Changhsingian, Ladin - Ladinian, Hett. - Hettangian, Kimmeridg. - Kimmeridgian, Valang. - Valanginian, Barrem. - Barremian, Cenoman. - Cenomanian, C. - Coniacian, Camp. - Campanian. Information on 1-27 see in the text.

acterized by anomalously high $\delta^{13}C$ values (up to +5.4‰).

However, the present study, based on data from selected horizons of post-Sakmarian carbonates,

characterized by high $\delta^{13}C$ values suggests that they were formed in more or less warm climate during eustatic transgressions. This interpretation is supported by following facts: (1) the primary concentration of a heavy oxygen-isotope in them is low, being

No	Type	Duration MA
1	Microcycle of solar activity (levels 1-3)	11 ⁶ -1 ³
2	Macrocycle of solar activity	1.5-12.0, less often up to 15-18
3	Megacycle of solar activity	About 300

Table 1. Typification of cycles of solar activity, established in the present paper.

comparable to temperatures of 19.6-27.9°C; which came from calcite of well-preserved brachiopod shells from the Capitanian-Wuchiapingian transition beds in Transcaucasia (Zakharov et al., 1997), upper Lower Changhsingian of Transcaucasia (Zakharov et al., 1997) and North Caucasus (Zakharov et al., 2000a), and aragonitic portion of Inoceramus shells from the upper Santonian of Hokkaido (Zakharov et al., 1999), (2) calcitic material from the positive $\delta^{13}\text{C}$ anomalies is mostly characterized by high content of magnesium (Zakharov et al., 1997, 2000a); (3) sediment rocks showing positive anomalies record tracks of particular biological events, being represented by high taxonomic diversity of their fossils, which is common for assemblages of tropical and subtropical facies (Zakharov et al., 2001a, in press).

The stably warm climatic conditions at the time of eustatic transgressions promoted a high bioproductivity of the seas, and intensive photosynthesis, repeatedly arose during Phanerozoic. As was shown by Gao (1993), the Lower Devonian limestone of Central Oklahoma with approximately +2.6‰ $\delta^{13}\text{C}$ values was formed at temperature of about 25°C. The analysis of many positive carbon isotopic anomalies made it possible to assume that during Late Palaeozoic and Mesozoic there were at least about 27 events, fixed by them, most part of which proved to be global.

(1) Moscovian. The anomaly (5.6‰) was discovered in Spain (Scotese et al., 1979) (Fig.1).

(2) Kasimovian. The anomaly (6.2‰) locates in Spain (Scotese et al., 1979). There are some problems in correlating the anomaly with the anomaly (5.6‰) known in the Winchell Formation (Missourian) in Texas (Grossman et al., 1991).

(3) Gzhelian (middle-late Virgilian) anomaly is known from the Colony Creek shale (5.6‰), shales of the Finis (4.3‰), Necessity (4.5‰) and Wayland (5.5‰) members of the Graham Formation (Virgilian) of Texas (Grossman et al., 1991).

(4) Early Permian (Artinskian?). An anomaly was found in Kabayama Limestone of the Sakamotozawa Formation in Kitakami, Japan (4.7‰; Zakharov et al., 2000c). Anomaly (up to 5.4‰) discovered in Lower Permian Berriedale Limestone of Tasmania (Rao, 1988) seems to be

the same age.

(5) Wordian. Anomalies of the Wordian level were observed on the basis of limestones of the two sections in Oman: in the Member A of the Maquam Formation (5.4‰) in the Wadi Maquam section and in the Unit 2 of the Wordian in the Wadi Wasit section (5.1‰) (Atudorei, 1999). It seems to be present also in the same level (Unit 2 of the Wargal Formation) of Salt Range (4.8‰) (Atudorei, 1999).

(6) Early Capitanian. Abnormally high $\delta^{13}\text{C}$ values were recognized in limestones of the Kattisawa member of the Kanokura Formation (4.5‰) (Zakharov et al., 2000c) and member 4a of the Wargal Formation in Salt Range (5.3‰) (Baud et al., 1995; Atudorei, 1999).

(7) Latest Capitanian - Earliest Wuchiapingian. Anomalies of the Capitanian-Wuchiapingian boundary transition were found in organogenic carbonates of many localities: Bell Canyon (upper part) (more than 3‰) and Castile (lower part) (6.5‰) Formations in Texas (Magaritz et al., 1983), Iwaizaki member of the Kanokura Formation in Kitakami (4.1‰) (Zakharov et al., 2000c), upper Chandalez Formation (3.8‰) and Nakhodka reef limestone (4.1‰) in South Primorye (Zakharov et al., 1996), upper Khachik Formation in Transcaucasia (4.0‰) (Zakharov et al., 1997), lower unit of the Bellerophon Formation in the Alps (3.5‰) (Holser & Magaritz, 1985), Zechstein Formation of western Europe (Magaritz & Turner, 1982) and, apparently, the upper part of the Wargal Formation in Salt Range (5.4‰) (Baud et al., 1995; Atudorei, 1999) and the middle part of the Kapp Starostin Formation in West Spitsbergen (7.3‰) (Gruszczynski et al. 1983; Wignall et al., 1998).

(8) Early Late Changhsingian. Anomalies of the Upper Changhsingian level were discovered from organogenic carbonates of the three localities: Nikitin Limestone of North Caucasus (4.7‰) (Zakharov et al., 2000a), upper Akhura Formation in Transcaucasia (2.8‰) and lower Upper Changhsingian in South China (5.1‰) (Chen et al., 1984).

(9) Middle Induan - ?Early Olenekian. The 3.2-4.0‰ shifts of approximately Middle Induan-Lower Olenekian level were recorded in limestone exotics of Oman (Atudorei, 1999).

- (10) Middle Olenekian. Anomalies of the *Tirolites* beds were discovered in limestones of the four Russian localities: Schmidt Formation of Primorye region (4.9‰) (Zakharov et al., 2000b), Yatyrgvart Formation of Belaya River (3.6‰), Sakhray River (4.2‰), and Malaya Laba River (6.9‰) basins in North Caucasus (Zakharov et al., 2000a). According to N.-V. Atudorei's (1999) data, the two additional positive excursions apparently of the same level in the Himalaya occur: in limestones of the middle part of the Mianwali Formation in Salt Range (4.7‰) and the middle part of the Tamba Kurkur Formation in Spiti (2.6‰).
- (11) Early Anisian. Lower Anisian anomalies were discovered from limestones of the four localities: lower Malotkhachskaya Formation of Kapustin Ravine in North Caucasus (3.5‰) (Zakharov et al., 2000a), base of Nity Limestone of the Kurkur Formation in Kashmir (2.6‰) (Atudorei, 1999), member A2 of Mottled Limestone in North Dobrogea (more than 4‰) (Atudorei, 1999) and lower part of the Aegean of Albania (4.3‰) (Atudorei, 1999).
- (12) Latest Ladinian – Lowermost Carnian. Anomalies of this level were discovered in Coryphyllia moiseevi beds of a large olistolite in the Lower Cretaceous olistostrome of Sikhote-Alin (2.6‰) (Zakharov et al., 2000b) and lower part of Enisala Limestone of North Dobrogea (3.2‰) (Atudorei, 1999).
- (13) Late Carnian. Upper Carnian anomalies have been discovered in limestones at the two localities: Opponiz Formation in the Alps (3.5‰) (Zakharov et al., 2000b) and Congaz Formation in Dobrogea (3.9‰) (Atudorei, 1999).
- (14) Early Norian. Lower Norian anomalies are known only in Russian territory: in *Margarosmia melnikovae* beds of a large olistolith in the Lower Cretaceous olistostrome of Sikhote-Alin (3.1‰) (Zakharov et al., 2000b) and limestones of the Shapkinskaya Formation of the Kuna River in North Caucasus (2.6‰).
- (15) Early Rhaetian. Abnormally high $\delta^{13}\text{C}$ values of the Norian-Rhaetian transition beds of the Shapkinskaya Formation in North Caucasus were discovered in limestones at the three localities: Bzhebs (2.8‰) and Sakhray (2.5‰) Rivers, and Tkhach-Bakh River watershed (2.5‰) (Zakharov et al., 2000a). The high $\delta^{13}\text{C}$ value (2.79‰) was identified also in the carbonates of the lower unit of the Koessen Formation in the Alps (Morante & Hallam, 1996).
- (16) Early Pliensbachian. High $\delta^{13}\text{C}$ values (up to 2.6‰) were discovered recently at the Sinemurian-Pliensbachian boundary horizon (Redcar Mudstone Formation, bed 73) (Hesselbo et al., 2000).
- (17) Toarcian. High positive $\delta^{13}\text{C}$ values (up to 4.4‰) occur in the Toarcian limestones of Siberia (Ignatiev et al., 1982).
- (18) Aalenian-Bajocian. Abnormally high $\delta^{13}\text{C}$ values (about 4.0‰) were discovered in belemnite rostra from Passet member of KongsØya Formation of Kong Karls Land, Svalbard (Ditchfield, 1997).
- (19) Oxfordian. The shift of $\delta^{13}\text{C}$ (3.0‰) was recognized in Oxfordian carbonates of England (Anderson et al., 1994).
- (20) Early Aptian. Lower Aptian anomalies were discovered in organogenic carbonates from various regions of the world, including the Alps (4.5‰) (Erbacher, 1994) and the Koryak Upland (6.8‰) (Zakharov et al., 2001b, in press).
- (21) Late Aptian, Upper Aptian anomalies were also distinguished in carbonates of western Europe (4.0‰) (Erbacher, 1994).
- (22) Early Albian. Lower Albian anomaly (3.0‰) is known from carbonates of western Europe (Erbacher, 1994). Within large interval, from upper Albian to upper Cenomanian no $\delta^{13}\text{C}$ anomalies have been discovered (Price et al., 1998).
- (23) Cenomanian-Turonian. Abnormally high $\delta^{13}\text{C}$ values (up to 4.7‰) were discovered from the Cenomanian-Turonian transition beds in carbonates of many regions of the world, including the Alps, South England and Tibet (Boersma & Schackleton, 1981; Douglas & Savin, 1973, 1975; Zachos & Arthur, 1986; Erbacher, 1994; Naidin & Kiyashko, 1994; Weimarn et al., 1998; Wan & Wang, 2000).
- (24) Late Turonian. Upper Turonian $\delta^{13}\text{C}$ anomalies were discovered in the upper Penzhinskaya Formation of the Mamet River, Koryak Upland (up to 3.9‰) (Zakharov et al., 2001b, in press); Lewes Marl (3.46‰), Southstreet Marl (5.51‰), Zoophycus bed (3.61‰) and Snowdrop Flint 1 (3.15‰) of Navigation Pit, England; Bridgewick Marl 3 (3.64‰), Lewes Marl (4.18‰) and Navigation Marl 1 (3.34‰) of Shoreham, England; Bridgewick 2 (3.72‰) of Dover, England; Bridgewick 2 (3.04‰) of St. Margaret's Bay, England; Hitchwood Hardground ((3.29‰) of Kensworth, England; Glynde Marl 4 (3.08‰) of New Pit, England (Voigt, 2000); Micraster Marl (3.82‰) of Soehlide quarry, Germany; and upper Turonian (3.77‰) of Salzgitter-Salder quarry, Germany (Voigt, 2000).
- (25) Coniacian. Abnormally high $\delta^{13}\text{C}$ value (up to 5.0‰) was recently discovered by us only in aragonite of the single Coniacian inoceramid shell from the lower Haborogawa Formation, Inoceramus uwajimensis Zone in the Yutakazawa River, Hokkaido and therefore the existence of the Coniacian anomaly needs in verification (Zakharov

et al., in prep.).

(26) Late Santonian. Comparatively high $\delta^{13}\text{C}$ values (up 2.5‰) were recognized in some ammonoid shells from the middle Upper Yezo Group of Hokkaido (Zakharov et al., 1999).

(27) Early Campanian. Abnormally high $\delta^{13}\text{C}$ values (3.0-3.7‰) were obtained from lower Campanian planktonic foraminifers of Falkland Plateau, South Atlantic (Huber et al., 1995).

We can consider the four brightest Phanerozoic events, which were probably reflected by the greatest phytoplankton heyday and, accordingly, by an intensive photosynthesis: Kasimovian ($\delta^{13}\text{C} = 6.2\text{‰}$) (Scotese et al., 1979), Capitanian-Wuchiapingian (6.5-7.3‰) (Gruszczynski et al., 1983; Magaritz et al., 1983), middle Olenekian (6.9‰) (Zakharov et al., 2000a) and Early Aptian (6.8‰) (Zakharov et al., 2001b, in press).

Thus, the data on isotopic composition of organogenic carbonates testify that the carbon-isotopic anomalies in many periods of the Phanerozoic appreciably are reflection of climatic fluctuation. Their positive maxima during the end of Paleozoic and Mesozoic fell, probably, on warm epochs caused by several factors, main of which seem to be: (1) rise of solar activity (Shcherbinovskij, 1964; Chistyakov, 1997), (2) macropulsations of an energy core of the sun (Chistyakov, 1997) and (3) number of astronomical variations (Milankovich, 1939; Lengershausen, 1964; Naidin, 1989; Bolshakov & Bolshakov, 1999).

About eight solar cycles (Chistyakov, 1997, 1999) distinguishing on their duration are known now.

All eleven-year, secular and thousand-year cycles, confirmed by data on oxygen-isotopic rhythms of Quaternary carbonates (Naidin, 1989), sediment recurrence of evaporites of the Permian Zechstein Formation (Richter-Bernburg, 1968), and tape-clay and some other sediments of the Upper Cenozoic (Lengershausen, 1964; Zubakov, 1984; Chistyakov, 1997), we offer to name as solar microcycles of the different levels.

300 Ma-year cycles (Chistyakov, 1997), based on periodicity of largest glacial epochs, can be called, in our opinion, as solar megacycles (Table 1).

Carbon-isotopic macrorhythms of Late Palaeozoic and Mesozoic demonstrated here (Fig. 1) may testify to the existence of also cycles of solar activity of an intermediate type (solar macrocycles) by duration from 1.5 up to 12 Ma, less often up to 15-18 Ma.

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