### **D.P. Dimitrov**

Institute of Oceanology - BAS, Varna, Bulgaria

### RADIOCARBON DATING (14C) OF THE SHELF AND DEEP SEE SEDIMENTS OF THE BLACK SEA

Numerous radiocarbon ( $^{14}$ C) dating organic material of mollusk and bottom sediments were made. Objective of the research was absolute age determinination for geocatastrofic occurense and the beginning of sapropele formation. It took place in geochronological interval — 8—9 thousand years. Holocene and LatePleistocene strata is stratified.

**Key words:** Radiocarbon dating  $(^{14}C)$ , shelf sediments, deep see sediments, diatoms analyses, mollusk fauna, palynological analyses.

Many drills of the shelf and its periphery in the bar zone, where the most complete cross-section of the Upper Pleistocene sediments was established, underwent radiocarbon datings to determine the age of sediments (table 1).

The published results from the estimates of the absolute age of sediments on the coast and in the northwestern part of the shelf (Semenenko, Koyumdzhieva, Kovalyuh, 1976; Shterbakov et al., 1978) as well as in the deep valley of the Black Sea were also taken into account (Degens, Ross, 1972, Shimkus et al., 1976; Ross, Neprochnov, 1978; Dimitrov, 1978, 1982). Special attention was paid to the age segmenation of the Neoeuxinian littoral and clayey sediments, reaching highest thickness of 330 cm on the periphery of the shelf in drill 2345 (fig. 1), (Filipova, 2003). The estimation of the absolute age of the sediments was performed at the laboratory of physical and geological properties of the Institute of Oceanology «P.P. Shirshov» in Russia under the supervision of Professor A. P. Lisitsin using the scintillation version of the radiocarbon dating technique and in the Woods Hole Geological Laboratory (USA). The results of the 14C absolute datings using were published later (Dimitrov, 1982).

The radiocarbon datings of sediments containing Chaudian fauna show that the age of mollusc shells exceeds 50 thousand years and thus the determination of their age goes beyond the capabilities of the method.

The estimation of the absolute age of the Karangatian sediments, found by drills along the coast of Varna Lake (Semenenko, Koyumdzhieva, Kovalyuh, 1976) indicate that their age is  $30200 \pm 950 - 39100 \pm 900$  years.

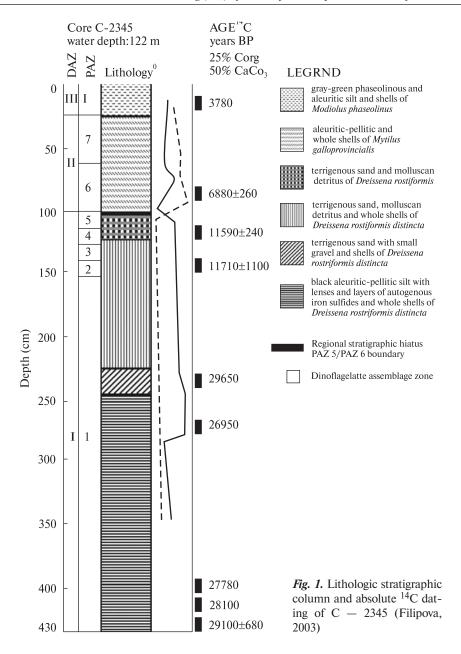
Table 1. Summarized geochronological (stratigraphic) scale of sediments in the Black Sea (Nevesskiy, 1967; Fedorov, 1978)

Era Eratema	Period System	Epoch Series	Subepoch Subseries	Age stage	Sub-age Sub-stage		Index	Chron. Scale, million years
	Quaternary	Holocene		Chernomorian	Newcher nomorian Oldchern omorian Orian	Djemetinian Kalamitian Vityazevian Bugazian	Q <sub>iv kl</sub> Q <sub>iv vt</sub> (Hl <sub>2</sub> ) Q <sub>iv</sub>	0.003 0,007 0.01
Neozoic		Pleistocene	Upper	Neoeuxine Karangatian	Upper Lower Upper Middle Lower		bg(Hl <sub>1</sub> ) Q <sub>III nev</sub> Q <sub>III krg</sub>	0,03
			Middle	Uzunlar Ancient Euxine			Q <sub>II uz</sub> Q <sub>II dev</sub>	0,20 0,35
			Lower	Chaudian	Upper Lower		Q <sub>I tsch</sub>	0,73
	Neogene	eoPleistocene Pliocene Miocene	Upper Lower Middle Upper	Gurian Kujalnik Kimerian Pont 2,3 Pont 1			$\begin{array}{c} {\rm Q_g} \\ {\rm N_{2\;ku}} \\ {\rm N_{2\;k}} \\ {\rm N_{2p}} \\ {\rm N_{1p}} \end{array}$	1,81 3,40 5,30 6,50 7,50
		Paleogene	Lower Middle Oligocene Eocene Paleocene	Meotian Sarmatian Maykop			$N_{1m}$ $N_{1s}$ $Pg_3 + N_1$ $Pg_2$ $Pg_1$	11,2 16,3 35,4 54,8 65,0
Mesozoic	Cretaceous						K	

The age of the muds containing *Dreissena rostriformis distincta* found in the lower part of drill 2362 in the periphery of the shelf turned out to be nearly 30 thousand years. Probably they are lie over muds with Mediterranean fauna.

On the basis of shells of *Dreissena polymorha* was estimated an age of 17 thousand years on the periphery of the shelf, at a depth of 102 m, in the layer of Neoeuxinian shelly detritus, under the base of Bugazian layers; that age probably reflects the period of the Post-Karangatian regression (fig. 1).

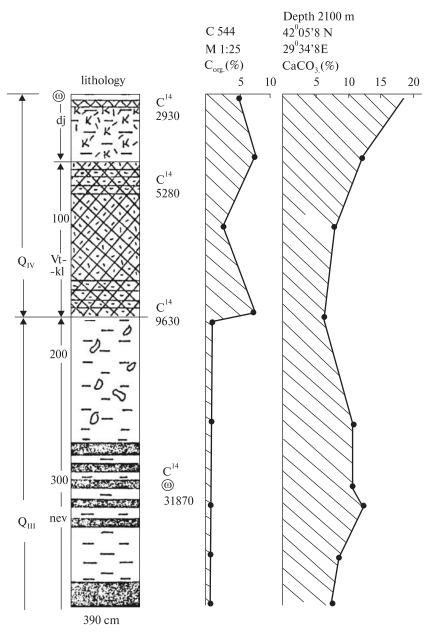
The age of fine aleurite silt with detritus and Vityazevian fauna found within the interval of 80-90 cm in drill 2345 was estimated at  $6880\pm260$  years. At the same time, sediments from the base of Bugazian layers are aged at 7000 years on the basis of *Monodacna* and >11000 years on the basis of *Dreissena*). Thus the so called Bugazian (transitional) layer is characterized on the basis of mixed fauna as a result of the catastrophic events and its existence as an independent layer is not proven. The age of the lower boundary of the Djemetinian layers in different sections of the shelf is about 3000 years (fig. 2). Analogical data of the age of Upper Pleistocene sediments using the radiocarbon method were produced regarding the deep water sediments of the Black Sea



(Ross, Degens, 1974; Shimkus et al., 1976; Ryan, Pitman 1998; Cagatay et al., 2000; Dimitrov, Dimitrov, 2003; Atanasova, 2005; Dimitrov, 2010).

Further estimations of the absolute age using the radiocarbon method were made in drill 544 (Dimitrov, 1990) situated at a depth of 2100 m (fig. 2). The samples were taken from Neoeuxinian silt interbeds alternating with autogenous ferrous sulfides in the interval 300—305 cm, the lower part (165—170 cm) and the upper part (65—70 cm) of the sapropelic horizon and the lower part of the Djemetinian layers (fig. 2).

The age of the Neoeuxinian sediments with interbeds of autogenous ferrous sulfides is estimated at 31,870. The lower part of the sapropelic horizon, lying over an eroded



*Fig. 2.* Lithologic stratigraphic column and distribution of Corg. and carbonates in C—544 (Dimitrov, 1990)

surface of Neoeuxinian ooze of the seekreide type is approximately 9,600 years old, while is upper part is 5280 years old. Probably the age of the quoted horizons in C-544 is quite exaggerated due to the so called reservoir effect (Slavova, 2002). Appendix 1 to this paper lists by calendar years the  $^{14}C$  datings published so far.

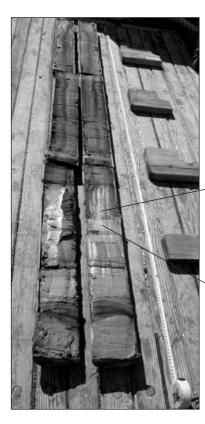
Considerable contribution to the <sup>14</sup>C dating of the Black Sea sediments is attributed to Ryan, Pitman (1998) thanks to the marine Accelerator Mass Spectrometry (AMS) developed by Glen Jones (Jones et al., 1994) on the basis of cryogenic vacuum technologies. AMS measures the ratio between the stable <sup>12</sup>C and the unstable <sup>14</sup>C contained in

the samples. It produces highly accurate measurements and is capable of analyzing minimum sample amounts for minimum time periods (less than 5 min). This state-of-theart technology allowed Ryan, Pitman (1998) to obtain a series of radiocarbon datings using the mussel Mytilus galloprovincialis from the Kim shelf. At depths from 123 m to 68 m they performed 5 datings and established the following calendar ages respectively 7500, 7580, 7510, 7510 and 5470 years. These data confirm the catastrophic course of the event according to the obtain <sup>14</sup>C datings from the Bulgarian shelf.

The complex approach to the stratigraphic segmenation of cross-sections allowed for the achievement of a high degree of reliability in the determination of the separate stratigraphic boundaries. The analysis of mollusc fauna remains as the main technique especially for the shelf where the other methods complement and clarify some aspects of the paleooceanological conditions. When describing the classical approach to the segmentation of the sediment complex we should also mention the litho-stratigrpahic technique (Khristchev, Shopov, 1978) that makes use of informal litho-stratigrpahic units without defining their rank. While developing the approach of Arhangelskiy and Strakhov (1938), Degens and Ross, (1972), Khrischev et al., (1988) separate the following three stratigrpahic units that reflect the vertical variations in the studied stratigraphic range: Ia (UNIT 1) — present-day layers, Ib (UNIT 2) — Oldchernomorian layers and Ic (UNIT 3) — Neoeuxinian layers. Without going into any discussions we should note that the litho-stratigrpahic technique is more suitable for the deep waters where the variation of the area is insignificant.

The comparison of the different stratigraphic methods shows that the reference stratigraphic boundaries (e.g. the Holocene-Pleistocene boundary) are confidently correlated.

For example, the Vityazevian and the Kalamitian layers on the shelf are characterized by similar mollusc complexes and their segregation will require quantitative evaluations. It is difficult to separate these layers also in the deep areas on the basis of diatom analyses because of the uniform complexes. The situation with the separation of the Bugazian layers from the ian layers on the basis of foraminiferous benthic fauna is the same. On the shelf, where the littoral sediments are developed and the spore-pollen grains are eroded, it is preferable to perform segmentation of the cross-section on the basis of mollusc fauna. For deep water sediments without presence of mollusc fauna the analyses of the nanoplankton are believed to be reliable. The studies of coccolithophorids performed by M. Ushakova (Geology and hydrology ... 1979) indicate existence of 2 zones — 1. Emiliania huxleyi acme (0-0,07 million years) and 2. Emiliania huxleyi (0,07-0,27 million years). The lowest part of the cross-section disclosed Braurudosphaera bigelowi, which is a typical reference layer for the Black Sea. It is known that the so called stratigraphic hiatuses affecting mainly the transgression complexes may be found anywhere on the shelf and especially in its peripheral zone. The shelf zone has suffered the influence of subaerial processes many times during regressions as well as the destructive influence of sea waves along the shore. As a result of that the sediments deposited earlier are eroded and some of them can be found as fragments or as relic sediments. Such is the case with the absence of Karangatian and, in some cases, of Ancient Euxinian sediments in the stratigraphic range between the Chaudian and the Neoeuxinian layers on the shelf. Usually the age on the Holocene-Pleistocene boundary, the lower part of Bugazian layers, is 7,5 thousand years, while the upper part of the underlying Neoeuxinian layers is aged 10—11 thousand years. The stratification of the sediments in the deep areas of the basin, below the 200-meter isobath, (fig. 3.) that have not suffered any subaerial influences except the erosion boundary



01.09.2006
Station 2
Core — 04 — with nylon
= 42°24,00 N
= 29°33,90 E
dept — 2096 m
lost first 100 cm — Unit I
Unit II — 0 — 83 cm — sapropel,
alternate with mud layers and cocolitic
83—163 cm turbidite layers from mud volcances,
gray—black resedimentation layers
163—180 cm — turbidites,
transition layer between Unit II and Unit III
Unit III seekreide —180—230 cm Neoeuxine gray density mud,

Fig. 3. Lithologo-stratigraphic borderline between units. Ib (Unit II) and Ic (Unit III), (Dimitrov, 2010)

between units Ib and Ic, is intact. The possible erosion boundaries may be due to underwater erosion processes or landslides and material supplied by mud volcanoes.

with black turbidite layers

Let's go back to the already discussed Chaudian layers. Since the radiocarbon dating method turned out to be inapplicable, the age segmenation is made on the basis of mollusc fauna, spore-pollen and diatom analysis (C-194). The determination of the Chaudian mollusc fauna was performed consecutively by E. Koyumdzhieva, L. Govberg, V. Kaneva-Abadzhieva and Vl. Shopov in consultation with P. V. Fedorov and L. A. Nevesskaya. The initial comparisons with the fauna from the terrace complexes of Cape Chauda and the Caucasian shores turned out to be wrong as this concerns a new regional type in the development of the basin. Most researchers of the Chaudian cross-section of Cape Chauda yield data of Lower Chaudian age of the sediments, formed under warm climatic conditions (Fedorov, 1978) at a stage of trasgression. According to the paleomagnetic data Zubakov and Kochegura (1973) also relate them to the Lower Chaudian. Besides that the spore-pollen analyses of the late Chaudian sediments indicate dominance of cold climatic conditions (Filipova, Bozilova, Dimitrov, 1979). The spectra of Chaudian sediments obtained from the deep water depression and described by Koreneva, Kartachova (1978), are analogical.

The diatom analysis of samples from the Chaudian layers (Filipova, Bozilova, Dimitrov, 1979) shows presence of three species: *Stephanodiscus astraea, Stephanodiscus hantzschii* and *Cyclotella corona*, characterizing a temperate and cold climate and conditions close to freshwater conditions. The same species are typical of the Chaudian sediments in C-380A (Jouse, Mukhina, 1978). In this way the stratigraphic schema and the diagram of the geohistorical development undergo an essential correction. A new

regional stage in the development of the basin (Chaudian) is introduced: it occurred during a period of glaciation (Mindelian) and regression of the basin and pervaded completely the depths within the range of 80-100 m. The palynological analysis of the native oozes on the continental slope in the southwestern part of the Black Sea allowed Komarov (1978) to relate the obtained spectra to the end of the Lower and the onset of the Middle Pleistocene. He isolated four horizons - Mindelian (M I-II-III), Mindel-Riss (M-R) Rissian and Riss-W?rmian (R-W). The spore-pollen spectra of these horizons are well correlated with the Chaudian, the Ancient Euxinian and the Karangatian spore-pollen zones on the western Black Sea shelf.

The Ancient Euxinian layers, isolated in C-8 (Khrischev, Shopov, 1978) are characterized by Caspian and Mediterranean elements gradually replaced by stenohaline Karangatian species up along the cross-section. This is a typical stratotype support cross-section of the Middle and Upper Pleistocene formed during the gradual change of environmental factors. Unfortunately Khrischev, Shopov (1979) do not provide any other biostratigraphic techniques that would characterize more fully the conditions that led to the formation of the sediments.

In terms of time the Neoeuxinian sediments correspond to the powerful Neoeuxinian regression that occurred during the Würmian glaciation and caused a drop of sea level down to -90...-120 m. The boundaries of the Neoeuxinian basin were established on the basis of the complex biostratigraphic analysis and the absolute <sup>14</sup>C datings (Dimitrov, Govberg, 1979; Khrischev, Shopov, 1979). The shoreside boundary of the Neoeuxinian basin is traced to a depth of 25 m while the seaside boundary reaches modern depths of 90—120 m. The boundaries of the late Chaudian basin reached depths of 20—30 m off the modern shore, and on the outer (sea) side the boundary reached depths of 80—100 m. Everything points to the fact that the maximums of the regressive cycle of the Neoeuxinian and the Chaudian basins had similar range.

The Bugazian or the lower part of the Oldchernomorian layers are not found everywhere in the cross-section. They are best represented in the interior of the shelf where shelly terrigenous aleurite oozes were found. The Bugazian layers in the central part of the shelf, under the 10-12 m of Holocene sediments, are represented symbolically (20-30 cm), while on the periphery of the shelf and the continental slope they are eroded. The Holocene-Upper Pleistocene boundary is usually eroded. For that reason the Holocene — Pleistocene boundary is marked along the boundary of contrasting lithological varieties and mollusc communities aged approximately 7.5-8 thousand years.

In some case the Vityazevian layers (according to the mollusc fauna) are united with the Kalamitian, while in other cases — according to the benthic foraminifera — with the Bugazian. The age of the upper part of the Vityazevian layers according to <sup>14</sup>C dating is 5 thousand years (fig. 2).

There is a lithofacial transition in the periphery of the shelf and the upper part of the continental slope from Kalamitian-Vityazevian shelf sediments with vegetation detritus and *Mutilus* shells to deep water sapropelic oozes whose stratigraphic position is determined on the basis of nanoplankton studies. The Djemetinian or Newchernomorian (New Black Sea) layers are spread everywhere in the water area (fig. 3.). In most cases they reflect modern climatic and oceanographic factors in the water area.

In the central part of the shelf their thickness exceeds 20 m however on the periphery of the shelf they are thin or completely absent, and on the continental slope, in the axes of underwater valleys they slide due to the gravitational processes. Their absolute age is deter-

mined by the presence of the stenohaline species of *Modiolus phaseolunus* and is about 3 thousand years or near the age of the coccolith oozes and the appearance of *Emiliania huxleyi*. According to Ryan, Pitman (1998) the intrusion of the *Emiliania huxleyi* species in the Black Sea is due to the bilge water discharged from Ancient Greek ships.

The water area of the western part of the Black Sea disclosed a full specter of sediments where the separate stratigraphic boundaries are well correlated by the applied stratigraphic methods. A summarized stratigraphic scale of the Black Sea sediments (table. 1) was elaborated on this basis reflecting the current views based on the interpretation of the acquired results.

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Received 01.04.2015

#### Димитр Петков Димитров

# РАДИОУГЛЕРОДНОЕ ( $^{14}$ С) ДАТИРОВАНИЕ ШЕЛЬФОВЫХ И ГЛУБОКОВОДНЫХ ОСАДКОВ ЧЕРНОГО МОРЯ

Выполнены многочисленные определения абсолютного возраста радиоуглеродным (<sup>14</sup>C) методом органичиского вещества моллюсков и донных осадков. Радиоуглеродными анализами определены возраст геокатастрофических событий и начала образования сапропелевых илов — 8—9 тыс. лет тому назад. Стратифицирована вся толща голоцена и верхнего плейстоцена.

**Ключевые слова:** радиоуглеродный (<sup>14</sup>C) анализ, шельфовые осадки, глубоководные осадки, диатомовый анализ, моллюски, полинологический анализ.

#### Дімітр Пєтков Дімітров

# РАДІОВУГЛЕЦЕВЕ (<sup>14</sup>C) ДАТУВАННЯ ШЕЛЬФОВИХ ТА ГЛИБОКОВОДНИХ ОСАДІВ ЧОРНОГО МОРЯ

Виконано численні визначення радіовуглецевим ( $^{14}$ С) методом абсолютного віку органічної речовини молюсків і донних осадів. Радіовуглецевим аналізом встановлено вік геокатастрофічних подій та початку утворення сапропелевих мулів — 8—9 тис. років тому. Стратифіковано всю товщу голоцену та верхнього плейстоцену.

**Ключові слова:** радіовуглецевий ( $^{14}$ C) аналіз, шельфові осади, глибоководні осади, діатомовий аналіз, молюски, палінологічний аналіз.