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ISOTOPIC APPROACH TO IDENTIFICATION OF OIL
SOURCE ROCKS AS APPLIED IN SEVERAL OIL-BEARING
BASINS OF THE USSR

by

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Isotopic approach to identification of oil source rocks as applied in several oil-bearing basins of the USSR

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Identification of oil source rocks is of crucial importance for petroleum exploration.

The geological and geochemical analysis necessary for the prognosis of petroleum generating potential of sediments is to a great extent based on modern organic geochemical data. The type of kerogene, its maturation degree petroleum generating potential are estimated by means of a number of well developed techniques^{see} (for examples Tissot and Welte, 1982; Tissot, 1984).

The most difficult and at the same time a decisive link in the oil source rock identification procedure is recognition of direct genetic relationships between crude oils and the specific oil source beds in a given section, called "crude oil - source rock correlation". If such a relationship is recognized, a number of problems can be solved: from general questions of petroleum origin, through the analysis of conditions and facies favourable for petroleum generation, to practical tasks of the estimation of reserves and effective prospecting and exploration.

Two approaches to solving this problem exist at present. The first one consists in comparative analysis of some characteristic compounds (and their ratios) present in crude oils and

sedimentary organic matter. These usually are normal alkanes, isoprenoids, tetrapyrrol compounds (those of sterane and triterpane series), several groups of aromatic hydrocarbons. The second approach is based on the study of the isotopic composition of the matter, and first of all-carbon isotope composition. The isotopic approach has the advantage of characterizing the chemical element accounting to the bulk of matter contrary to investigation of individual compounds and structures which may be unrepresentative for the organic matter studied. Moreover, isotopic ratio are less subjected to changes caused by secondary processes.

In earlier studies we mainly considered the isotopic composition of oil on the whole, and these data served basis for conclusions about the presence of different genetic types of crude oils in a given section and their relation to specific oil source beds (Kvenvolden, Squires, 1967; Galimov et al., 1972; Williams, 1974). Carbon isotopic composition of crude oils seemed to be useful for identification the type of the source matter. Carbon of marine organisms (in the first place plankton) is known to have $\delta^{13}\text{C}$ values predominantly in the range from -19 to -22‰ , while carbon of land plants has $\delta^{13}\text{C}$ values mainly by from -24 to -28‰ . Since the appearance of the work by Silverman and Epstein (Silverman, Epstein, 1958), this difference has served basis for differentiating between crude oils of marine and continental facies. However, this criterion has appeared to be ambiguous. Several scientists in the Soviet Union who studied crude oils of West Siberia expressed contradicting opinions. Some of them believed that crude oils of continental origin were enriched in lighter isotopes compared

with those of the marine origin (Trofimuk, Vyshemirsky, 1975), while others (A.E.Kontorovich and coworkers, e.g. see Bogorodskaja et al., 1980), on the contrary, considered the enrichment in lighter isotopes to be characteristic of namely marine oils. In fact, both groups of researchers were but partly right. We shall dwell on this point a little later here.

The study of carbon isotope composition of petroleum hydrocarbons having different chemical composition and structure, as well as non-hydrocarbon compounds (resins, asphaltenes) present in oils has revealed a characteristic differences between these components (Galimov, 1973). On the basis of our data, a West German scientist, W. Stahl, proposed a practical method for petroleum source rock identification, more exactly, for recognizing the isotopic composition of the original organic matter (Stahl, 1977, 1978). He proceeded from an empirical rule according to which the ^{12}C content decreases from methane and naphthene hydrocarbons through aromatics resins and asphaltenes. Extrapolation of this relationship in the direction of the continuing increase in polarity allows, according to this scientist, to identify the isotopic composition of petroleum source rock kerogen. Such direct relationship between the above mentioned fractions of crude oil, however, exists in only some cases, as we shall see below.

Explanations for the ambiguity of isotopic data in several cases or their contradictory interpretation eventually lie in the complexity of the processes accounting for the isotope composition of organic matter and crude oil. In order to make an adequate estimation of possibilities and limitations of this method, it is necessary to understand the essential aspects of

the processes of isotope fractionation leading to the observed isotope distribution in naturally occurring organic compounds. This has been the purpose of our investigations for some time. The results of these studies have been summarized in a number of works (Galimov, 1980; Galimov, 1981; Galimov and Kodina, 1982).

It is advisable now to dwell on some regularities in the processes forming isotope composition of fossil organic matter. These regularities are considered as being important, and they lie in the basis of our method for identification of oil and gas source rocks.

Principal regularity of biological fractionation of isotopes

It has long been found, that different biochemical components have different isotopic compositions. Lipids, for example, are most enriched in the light isotope. Carbohydrates and proteins are enriched in much less extent.

We have shown that this is only a particular manifestation of the dependence of carbon isotope composition of biomolecules upon the value of the thermodynamic isotopic factor (reduced partition function ratio). For the latter we use a designation β with a symbol of the isotope under consideration (in case of carbon - $\beta^{13}\text{C}$). This value estimates the affinity of a compound to the heavier isotope in isotope exchange reactions. It depends on what type of chemical bonds the carbon atoms in a given molecule form. The $\delta^{13}\text{C}$ value is lower if carbon is predominantly bound to hydrogen, as is the case in low polar lipids. It increases in the case of carbon-carbon bonds or carbon-oxygen and carbon-nitrogen bonds predominating in proteins

and carbohydrates as well as in polar lipids. The β -factor values are calculated by solving of spectrum problem for various isotopic forms of molecules (Urey, 1947). β -Factor may be calculated by the additive method (Galimov, 1982) that provides satisfactory accuracy in many cases.

Correlation between isotopic composition and the β -factor value has been demonstrated for many biological objects (Galimov, 1981). It has been found both on the intermolecular and intramolecular level. Fig. 1 illustrates the intramolecular correlation between $\beta^{13}\text{C}$ and $\delta^{13}\text{C}$.

Existence of such correlations is a highly untrivial fact. In common case the correspondence between isotope distribution and values of β -factors takes place in equilibrium systems. It was, therefore, unexpected to find this phenomenon in biological systems which are considered as essentially non-equilibrium ones. We attribute this phenomenon to special properties of enzymatic reaction (Galimov, 1981; Galimov, 1982).

Possibility to distinguish biogenous and abiogenous substances

The above regularity is a characteristic feature of biological systems. Comparison of biogenous compounds with their synthesized counterparts shows that carbon isotope characteristics of various structural groups in biogenous compounds correlate with their β -factors, whereas in the synthesized molecules those are random (Fig. 2).

Therefore, a pattern of intramolecular isotope distribution may be used for differentiation of biogenous and abiogenous substances.

It is natural to apply this criterion to petroleum which organic or inorganic origin is still a matter of discussion (Kropotkin, Valyaev, 1984; Gold, 1984). For this purpose we have selected a number of petroleum samples from several oil fields of the USSR. It is seen Fig. 3, (left) that carbon isotope composition of the fractions studied reveals the dependence on the $\beta^{13}\text{C}$ value that is typical of biogenous systems. Fig. 3 (right) shows also the data for various fractions of synthesized hydrocarbon mixture generated by thermocatalysis at 200°C . The single source of all hydrocarbons present in this mixture was oleic acid. The $\beta^{13}\text{C} - \delta^{13}\text{C}$ correlation is absent in this case.

It is important to note in this connection that crude oils contain compounds having undoubtedly biological origin. These include porphyrins, isoprenoids and other chemical fossils. The advocates of inorganic origin of petroleum recognize this fact. However, they suggest that such compounds are washed out from rocks by hydrocarbon flows ascending from greater depth, i.e. that biological substances are foreign to the bulk of crude oil. This is how an American scientist, T. Gold who made his report supporting the hypothesis of inorganic origin of petroleum at the 27th Session of the International Geological Congress (Gold, 1984, p.185) explained the presence of evidently biological compounds in petroleum. However, it can be seen from Fig. 3 that the data points of the isotopic composition of porphyrins and isoprenoids from each of the crude oils studied plot on the correlation line for a given oil. This proves a genetic relationship between biological compounds, such as porphyrins and isoprenoids, and hydrocarbons making up the bulk of petroleum.

Changes in isotopic composition of organic matter during diagenesis: Effects of the type of organic matter and diagenetic conditions

From the point of view of the problem discussed in this work, an important consequence from the principal regularity of isotope fractionation in biological systems is that the ^{13}C content in biogenous substances increases with increasing polarity.

Indeed, the study of organic matter from oceanic sediments that we carried out on the DSDP core samples taken by "Glomar Challenger" has shown a regular isotope distribution in isolated fractions with increase in their polarity (Galimov, 1980; Galimov and Kodina, 1982). The analytical procedure we use includes extraction of the bitumen from rock samples with alcohol-benzene, mixture (1:1). The extract was treated with pentane to separate the most polar fraction, asphaltenes (A), which remained in residue. Then, the deasphaltized bitumen was inserted into a silica gel column and its fractions were successively eluted from the column with solvents of increasing polarity: hydrocarbons (HC) were eluted with hexane and fractions of resins - with a mixture of hexane and benzene (HB resins), with benzene (B resins) and benzene-methanol (BM resins). Fig. 4 presents several examples of the relationship between the isotopic composition and the degree of polarity of fractions isolated from oceanic sediments. One can see that isotope distribution corresponds to biological trend. However, a linear, inherited from biological precursors, trend of isotope distribution in fossil organic matter is not always observed. Processes of diagenesis may considerably change the pattern of isotope

distribution in some cases.

Several types of organic matter are recognized in sedimentary rocks. They differ in chemical composition, petrographic characteristic, geological conditions and nature of their biological precursors. These characteristics are interrelated. Thus, organic matter derived from marine plankton has most frequently a colloform structure and contains predominantly aliphatic and alicyclic components. In stagnant conditions developing in a basin of sedimentation, organic matter is reworked by anaerobic microorganisms. It receives substantial contribution of their biomass and accumulates as organic rich interlayers.

This substantially polymerlipid matter is attributed to sapropelic type.

Marine organic matter derived from plankton can give other fossil forms if during deposition in sediments it is highly diluted by mineral phase, in particular impregnated in shells of skeletal planktonic organisms (diatoms, radiolarian, coccolithophorids etc.). In this case it is less subjected to attack of anaerobic microorganisms. The protein-carbohydrate fraction is transformed by the melanoidin reaction mechanism (Nissenbaum, Kaplan, 1972). The resulting disseminated organic matter of sediments has heteropolycyclic structure similar to that of humic matter. We call it here aquahumic.

Humic matter proper is a product of transformation of the remains of higher plants. It is derived from cellulose and lignin components and receives a polyaromatic structure during humification.

Naturally occurring organic matter represents a mixture of various types of material. A considerable admixture of land derived humic organic matter is found even in sediments of typical oceanic basins. Marine organic matter proper contains various proportions of sapropelic and aquahumic material. Specific sources of organic matter, such as spores, pollen, cuticles, resinous components, are sometimes a predominant component of organic material and produce a matter of exinite, or liptinite, type. Nevertheless, in spite of intricate paths of transformation and a diversity of organic matter sources, three main types of organic matter can be recognized: sapropelic, aquahumic and terrestrial humic matter. They correspond to three types of elemental composition evolution on the well-known Van Krevelen diagram.

Our studies have revealed different patterns of carbon isotope fractionation for these three types of organic matter.

Coalified remains of plant tissues essentially inherit the isotopic composition of the original carbon during fossilization of terrestrial organic matter (Fig. 5). The $\delta^{13}\text{C}$ values of lignin are in the range from -25 to -27‰ . Disseminated humic matter has lower $\delta^{13}\text{C}$ values, if it is enriched in remains of spores, pollen and cuticle, since these components represent that part of plants, which is enriched in the light isotope: the $\delta^{13}\text{C}$ value ranges from -26 to -30‰ (Generalova et al., 1974).

In marine environments the main bioproduction is provided by lower organisms. They do not contain lignin, but are enriched in lipids. The isotopic composition values of the marine plankton lipids are approximately -24 to -28‰ . Proteins and carbo-

hydrates are depleted in the light isotope ($\delta^{13}\text{C}$ range from -16 to -21‰). When organisms die, their complex biopolymers break into simpler fragments and monomers. Part of them undergoes repolymerization producing geopolymers, stable under geological conditions. With regard to the isotopic composition of sedimentary organic matter, the fate of the most isotopically heavy protein-carbohydrate fraction appears to be very important. These components are readily degraded by microorganisms. However in skeleton bearing organisms the protein-carbohydrate material being impregnated into mineral matrix can, as has been noted earlier in this paper, survive a severe microbial attack at the early stage of sedimentation and eventually give a stable geopolymer due to melanoidin formation reaction.

The resulting marine kerogen will be relatively depleted in the light isotope. The melanoidin formation is accompanied by isotopic effects. Isotopic effects of polymerization have been studied in our laboratory in sufficient details (Galimov, 1980). They sometimes lead to an enrichment of the resulting polymer by $3\text{--}8\text{‰}$ relative to the starting monomer. During a simulated melanoidin formation successive enrichment of carbon in the light isotope takes place from fulvic acids through humic acids to insoluble melanoidin (counterpart of kerogen); so as it occurs in the corresponding natural process (Nissenbaum, 1974). The resulting kerogen is slightly enriched in the light isotope relative to carbon of the original planktonic biomass. This enrichment is not high. The shift in isotopic composition is from -20‰ (the average value for marine plankton) to about -24‰ . The marine kerogene is in this case isotopically heavier than terrestrial organic matter, which is characterized

by $\delta^{13}\text{C}$ values from -25 to -27‰. Lipidic components in complex with humins make part of the forming geopolymer. Its bitumen fraction derived mainly from lipids is markedly enriched in the light isotope relative to the kerogen. The isotopic composition of bitumen fractions shows a linear dependence on the degree of polarity, which is normal for biological systems. Examples of this have been presented above (Fig. 4). Fig. 6 presents the data on the isotopic composition of organic matter in the Angola Basin sediments (the Atlantic Ocean, site 530 DSDP). The core samples had been presented by the Advisory Panel on Organic Geochemistry (JOIDES), and the studies carried out in our laboratory were a part of the International Deep Sea Drilling Program. Sediments in the upper part of the section are represented by diatomaceous ooze. The pattern of curves is the same as that for diatomaceous sediments from the Gulf of California. The isotopic composition of the bitumen appreciably differ from that of the kerogen. The range of the $\delta^{13}\text{C}$ values for the fractions of different polarity is narrower (the curves are steeper) for samples from the lower part of the section including layers of black shales. This is due to the presence of land derived humic material in the black shales. Smoothing of the isotopic composition of the bitumen fractions having different polarity is partly a consequence of the increasing level of catagenesis as well (Galimov, Kodina, 1983).

Isotope fractionation accompanying the formation of sapropelic organic matter proceeds differently. The protein-carbohydrate fraction is almost completely eliminated. This alone leads to a noticeable shift in carbon isotope composition of sapropelic matter to lower $\delta^{13}\text{C}$ values. An additional enrichment

in the light isotope results from polymerization of lipids by microorganisms. Therefore, kerogen of sapropelic type, in spite of the fact that it has derived from marine organisms, can be substantially enriched in the light isotope: from -28 to -33‰ and lower. It becomes isotopically lighter than carbon of continental origin.

Thus, the above mentioned problem, whether marine organic matter is lighter or heavier than continental one, may be solved by stating that marine kerogen can be both lighter and heavier relative to continental one depending on the type of biological precursors and diagenetic evolution of organic matter.

Polar components of sapropelic organic matter are mainly produced by microbial oxidation of the initially isotopically light compounds of aliphatic structure (e.g. fatty acids). Therefore, both the whole kerogen and asphaltenes of bitumen may be enriched in the light isotope to the same extent as hydrocarbons. This leads to a specific unlinear isotope distribution in fractions of increasing polarity.

The isotope distribution in bitumen fractions of the sapropelic oil shales corresponds to this model (Fig. 7).

Another characteristic feature of sapropelic organic matter is essential identity of isotopic compositions of bitumen and kerogen.

It is interesting that the finding that different types of organic diagenesis are responsible for different isotope distributions allowed to explain an earlier found, but not completely understood regularity in the change of organic matter and bitumen with the geologic time. In Fig. 8 the data on carbon isotopic composition of kerogen and bitumen from sediments of different

geological age within the Russian platform are reproduced. In the Carboniferous and the younger sediments the $\delta^{13}\text{C}$ values for kerogen and bitumen are appreciably different while in more ancient rocks they are practically coincide. It is clear now that this is due to the predominance of environments favourable for accumulation of sapropelic matter in Precarboniferous time whereas the younger sediments contain humic matter including aquahumic one. It should be noted, that attempt to interpret the revealed regularity only as a consequence of the change in the level of organic matter catagenesis with depth of burial (Arnett, 1984) cannot be accepted, as it leaves the facial differences without consideration.

Oil-source rock correlation

Fractions of different polarity can be isolated from crude oil, and the corresponding fractions can be isolated from bitumen of sedimentary organic matter using the same solvents. Comparison of the isotope distributions among the corresponding fractions of crude oil and organic matter provides a basis for conclusion whether the oil and organic matter are genetically related.

We carried out such investigations for a number of oil fields in various oil and gas regions of the USSR.

Volga-Urals. The Perm Kama oil fields.

This region includes the eastern margin of the Russian platform with the Permian and Bashkirian domes and the Preurals trough. The age of sediments is Paleozoic. Seven producing horizons have been identified. More than half of the reserves are within the Yasnopolanan beds of Lower Carboniferous age

(Abrikosov, 1966). Carbonate reservoirs of the Middle Carboniferous, Tournaisian and terrigenous Devonian (Kynov-Pashian beds) also contain petroleum.

Several sequences of this section are rich in organic matter, and they could have been the source of petroleum. Two sequences have the highest organic content. These are the Frasnian beds of the Upper Devonian, including domanikoid beds, and the terrigenous Visean, including the Tulian and Bobrikovian units of the Yasnopolianian superhorizon and the Malinovian beds. These two sequences have a high organic content throughout the most of the Russian platform. According to E.S. Larskaya (1983), the Upper Devonian sediments contain $700 \cdot 10^{16}$ g of organic matter and the terrigenous Visean contain $344 \cdot 10^{16}$ g of organic matter, which constitutes correspondingly almost a half and a quarter of all organic matter present in sediments of the Russian platform.

The investigation has shown that carbon isotope distribution for the organic matter fractions from the Malinovian and Yasnopolianian beds has a pattern corresponding to that of humic organic matter (Fig. 9). Crude oils from the Yasnopolianian producing horizon are clearly different in the isotopic distribution from the organic matter of Yasnopolianian age. No do they show a similarity to the Tournaisian organic matter. Only organic matter from the Upper Devonian sediments is isotopically similar to the cruds in the Yasnopolianian.

The pattern of isotopic curves of crude oils studied is characteristic of the sapropelic type of the initial organic matter. This agrees to the facial characteristic of the Upper Devonian domanicoid sediments, which many workers have already considered as petroleum source rocks in Volga-Urals.

Attention should be drawn to one advantage of the approach applied. Methods based on the material analysis when applied to the characterization of a bed require a great number of measurements, since the composition of samples may vary from place to place. The pattern of the isotope distribution curve is dependent, as has been noted earlier in this paper, on the type of the original organic matter and its diagenetic history, i.e. those factors, that are characteristic to the whole basin. Therefore, it may be expected, that the pattern of the curve based even on a few sample data would be representative for the corresponding sediments. Indeed, it is visible in Fig. 9, that all the curves corresponding to organic matter from the Yasnopolan horizon are similar although samples for analyses were taken from fields scattered over a large territory.

Sakhalin. Okruzhnoe field.

The Okruzhnoe field is situated at the eastern coast of the Sakhalin Island. Main production is from the Miocene Pilen-gian Formation consisting of argillaceous siliceous rocks with tuff and siltstone interlayers. The oil contained deposits are overlain by shales of the Borian Formation. The trap is 600 m high.

Siliceous rocks result from lithification of sediments containing biogenic silica. predominantly from diatom oozes. This sediments are widespread in sedimentary basins of the northern Pacific mobil belt and are, evidently, associated with upwelling zones. A well-known counterpart of these beds is the Monterey Formation in California also of Miocene age.

This object was interesting in two respects. Firstly, our intention was to test our theoretical model predicting a linear

isotope distribution among fractions of the bitumen and the crudes for this type of sediments. Secondly, most workers believe that the source of the Pilengian oil are the siliceous rocks of the Pilengian sequence itself (Bazhenova et al., 1976). It was advisable to apply our isotopic method to demonstrate this genetic correlation. A sample of organic matter was taken in fact outside the Okruzhnoe field within the Khuzcnian area. A sample of crude oil originates from a producing horizon of the Pilengian formation. Fig. 10 demonstrates a clear similarity in isotope distribution among fractions of the oil and organic matter. The distribution has a linear pattern, and the oil and organic matter are relatively depleted in the light isotope. In other words, the carbon isotope distribution is in accordance with the above model as well as it confirms that the siliceous rocks of the Pilengian Formation were the source of the oil.

West Siberia. The Paleozoic oil problem.

At the Corelaya area near Khanty-Mansiysk city oil blow from Paleozoic sediments have occurred. An adequate estimation of the Paleozoic prospects is essential for further development of petroleum prospecting in the northern West Siberian Basin.

Our purpose was to find out whether the crude oil discovered in the Paleozoic sediments had been generated in the Paleozoic rock itself or it migrated by anyway from the Jurassic.

The analysis has shown that oil from the Paleozoic sediments (sample I, Fig. 11) by its isotopic characteristic is similar to organic matter from the lower part of the overlying Tyumenian formation of the Lower-Middle Jurassic age (Sample 4). Comparison of oil from the Paleozoic sediments with an undoubtedly Jurassic oil (sample 2, the Sherkalinian horizon of the Talin-

skoe field) shows that the carbon isotope distribution among the fractions studied is essentially identical. Therefore, it has been concluded that a probable source for the oil discovered in the Paleozoic of the Gorelaja area is in the overlying Lower-Middle Jurassic sequence.

West. Siberia. The Middle Obian area.

The Salyk field contains an oil accumulation in the Bazhenovian formation. This sequence is rich in organic matter of sapropelic type and is considered by many workers as possible source of oil.

Our analysis showed that carbon isotope distributions among fractions of oil from this accumulation and those of the bitumen isolated from the Bazhenovian rocks of the Salyk field are completely identical (Fig. 12). The pattern of the isotopic curve is characteristic of oil derived from organic matter of sapropelic type. It is interesting to note that average carbon isotope values for this oil and bitumen markedly differ, which additionally emphasizes a relatively low efficiency of the approach based on study of only total oil and bitumen.

Oils from producing horizons of a number of other Middle Obian fields have been studied. These include the East-Surgut field (horizon BC-10) and Samotlor (horizon B-8). The isotopic curves 3 and 4 have a pattern similar to that of organic matter of the Bazhenovian formation. Therefore, it may not be excluded, that it was the Bazhenovian formation that generated oil of the accumulations studied.

East Siberia. The Middlebotuobinian field.

East Siberia, as a new promising petroleum region of the USSR has some interesting features one of which is that oil is present in ancient sediments: Cambrian and Proterozoic.

The Middlebotuobian field is situated in the north-Eastern part of the Nep-Botuobinian anteklise. Two producing horizons: Osinian (Lower Cambrian) and Botuobian (Upper Proterozoic), have been recognized in the field. Oils from these horizons and organic matter from the immediately underlying sediments have been studied (Fig. 13).

The results of the studies indicated that the Upper Proterozoic oil (the Botuobian horizon) was generated in the Upper Proterozoic argillites.

Oils of the Osinian and Botuobian horizons seem to be genetically related. The isotopic characteristic of the Osinian oil is similar to that of the Botuobian oil, but is different from the isotopic characteristic of organic matter within the dolomite sequence underlying the Osinian producing horizon.

The isotopic curve pattern points to a sapropelic type for the original organic matter. Since the Precambrian source for this oil has been proved, the earlier opinion (Kropotkin, Valiyev, 1984) that the ancient oils of the Nep-Botuobian anticlise have a deep-seated inorganic source has no scientific basis.

Effects of biodegradation and thermal metamorphism
on the isotope distribution among bitumen and oil
fractions

Application of the discussed isotope method for crude oil-source rock correlation has its limitations. The latter are

primarily due to those hypergene and catagenen transformations of crude oil and organic matter that take place after oil migration from source rocks. Such oils may be recognized by their characteristic features, and possible secondary alteration of the isotopic composition may be taken into account during interpretation of isotopic data.

Biodegradation is known to lead to the loss of normal alkanes. The remaining n-alkane fraction is depleted in the ^{12}C isotope resulting from the predominant rupture of ^{12}C - ^{12}C bonds. Microbial activity results in the enrichment of oil in polar components (Bayley et al., 1973). This is accompanied by a shift in isotopic composition of the oil toward higher ^{12}C content and an increase in optical activity of the oil (Winters, Williams, 1969), since high-molecular-weight compounds are usually most capable of rotating the polarization plane of light. Thus, the change in isotope distribution among fractions due to biodegradation consists in the depletion of saturated hydrocarbons in the light isotope and enrichment of polar components in this isotope, while aromatics remain essentially unchanged (Fuex, 1977; Stahl, 1980).

However, it should be born in mind, that the enrichment of asphaltenes in the light isotope does not prove that an oil was biodegraded, as is sometimes argued (Stahl, 1980). In common case this is an indication of the sapropelic type of the initial organic matter.

Enrichment of asphaltenes in the light isotope is asquired at an early stage of the formation of sapropelic organic matter. As can be seen in Fig. 14, hydrocarbons of bitumen isolated from a limnic sapropelic mud (Bitjukov, Galimov, 1982)

are depleted in ^{12}C . The asphaltenes are enriched in this isotope. And the resins of the low polarity (HB), including also aromatic hydrocarbons, remain unchanged relative to the normal biological trend. Hydrocarbons generated at more advanced stages of diagenesis and catagenesis, after the extinction of ^{the} microbial activity in sediments, preserve their isotopic composition, and isotope distribution among bitumen fractions takes the pattern typical of sapropelic organic matter and crude oils derived from it.

A number of investigators discussed effects of catagenesis and thermal metamorphism on isotopic composition of crude oil and its fractions (Lewan, 1983; Chang et al., 1981; Orr, 1974). Thermal transformation of oil results in the loss of isotopically light low molecular weight fragments eliminated as a gas phase. Liquid petroleum hydrocarbons, in particular the low-boiling hydrocarbons of the gasoline fraction, are consequently depleted in the light isotope. It is especially pronounced in the highly altered condensate oils (Galimov, 1973).

Fig. 15 shows some curves of isotope distribution among fractions of bitumen isolated from the sediments of the Gulf of California. Samples used for our study were taken during the 64th Leg of "Glomar Challenger" (Galimov, Kodina, 1983). Organic matter of these sediments show different degree of thermal transformation depending on a local magnitude of heat flow and the proximity to magmatic intrusions. Fig. 15 shows samples from 478-6(1) to 477-16(5) arranged according to increase in the degree of their thermal alteration. It can be seen that hydrocarbon fraction of the samples is being pro-

gressively depleted in the light isotope in this direction. However, the whole pattern of the isotope distribution between fractions is preserved up to sample 477-16(5). The latter represents a rock that has undergone a strong hydrothermal alteration. Its organic matter has to a considerable extent burnt out. The content of the isoprenoids has sharply decreased. The Porphyrins are absent. As thermodestruction involves a disproportionation process, the low molecular fragments enriched in ^{12}C not only escape into the gas phase, but also ^{joint} the high molecular weight fraction, promoting polymerization processes (Galimov, 1973). Therefore ^{the} asphaltenes are being enriched in the light isotope.

The pattern of isotope redistribution among fractions of thermally altered organic matter is similar to that of biodegraded matter. However, thermally altered oils in contrast to biodegraded ones have a lower optical activity and an increased alkane content. There is also a number of hydrocarbon characteristics (n-alkane/isoprenoid ratio, relative content of porphyrins and other biomarkers) that make it possible to distinguish biodegraded and thermally altered oils. It should be noted that some differences in oils attributed to their thermal alteration (Koons et al., 1974; Chang et al., 1981; Arnett, Matzgate, 1984) may in fact reflect different nature of the initial organic matter.

Thus, the isotopic method based on the discovered regularities of isotope fractionation in biological systems and during organic matter fossilization may be successfully used for the identification of oil source beds. It makes possible not only crude oil-source rock correlation but provides

information on the facial type of organic matter and oil.

In combination with other geochemical data this method provides an adequate interpretation even ⁱⁿ the cases when isotope distribution is affected by secondary processes.

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Captions

Fig. 1. Intramolecular correlation of $\delta^{13}\text{C}$ and $\beta^{13}\text{C}$ -values for biomolecules: (a) - chlorophyll fragments (Bogacheva and Galimov, 1979); (b) - carbon in various structural positions within acetoin molecule (experimental data of Rinaldi et al., 1974); (c) - carbon in various structural positions within the malic acid, isolated from apples (left curve) and sorghum (after Meinschein et al., 1984).

Fig. 2. $\delta^{13}\text{C}$ and $\beta^{13}\text{C}$ -values for synthesized preparations (structural groups studied are connected with dashed lines) and their biological counterparts (the corresponding groups are connected with continuous line):
★ - acetic acid, ● - vanillin, ◻ - anethole,
▨ - amino acids synthesized in electric discharge.
The shaded area is that of biogenic compounds.

Fig. 3. $\beta^{13}\text{C}$ - $\delta^{13}\text{C}$ correlation for natural oil (left) and synthesized hydrocarbon mixture by thermocatalysis of oleic acid (200°C, 50 h, $\delta^{13}\text{C}$ of oleic acid -25,1‰). The oil samples have been taken from the North Ostrovnoye (1), East-Surgut (2) and Kokuy (3) fields. The synthesized hydrocarbon mixture has been distilled into fractions boiling in the range: 210-330°C (▽), 330-355°C (⊗). 355-435°C (△). The hydrocarbons separated are: polyaromatics (Ar III), diaromatics (Ar II), bicyclic naphthenes (Na II), monoaromatics (Ar I), monocyclic naphthenes (Na I), n-alkanes (n-Alk).

Fig. 4. Carbon isotope distribution among the fractions of the bitumens isolated from diatom oozes of the Gulf of California (Leg 64, DSDP). Diatom ooze, Site 477, depth 300 m - (1); slightly consolidated clayey-diatomaceous sediment, Site 474a, depth 350 m - (2); slightly consolidated diatomaceous sediment, Site 481a, depth 330 m - (3); consolidated diatomites, Site 478, depth 305 m - (4). The complete geochemical characterization of these samples is presented in an earlier work by Galimov et al., (1981).

Fig. 5. A model of the processes responsible for carbon isotope composition of the various types of organic matter.

Fig. 6. Carbon isotope composition of the bitumen fractions (○), the whole bitumen (▨) and kerogen (□) from sediments of the Angola Basin (the Atlantic ocean) Site 530, Leg 75 of DSDP (Galimov et al., 1984).

Fig. 7. Carbon isotope composition of the bitumen fractions (○) the whole bitumen - (▨) and kerogen - (□) from sapropelic organic matter of different geological age and setting (Galimov et al., 1984).

Fig. 8. Change in the isotope composition of kerogen (□) and bitumen (▨) with depth of burial in sediments of the Russian platform (Galimov et al., 1975).

Fig. 9. Comparison of isotope distribution among bitumen fractions of sedimentary organic matter (light symbols) and fractions of crude oil (dark symbols) in sedimentary succession of the Perm Kama district (Volga-Ural Region). Relative petroleum resources

(in %) in reservoir rocks are shown (after Abrikosov, 1966).

The fields studied: Kustovskoye - 1, Savinskoye - 2, Khatymskoye - 3, Rodnikovskoye - 4, Kalmiyarskoye - 5, Sokolovskoye - 6.

Fig.10. Comparison of isotope distribution among the fractions of crude oil (1) and bitumen from the sedimentary rocks (2) of the Pilengian formation (the Okruzhnoye field, Sakhalin island.).

Fig.11. Comparison of isotope distribution among fractions of crude oils from the Paleozoic sediments of the Goreloe area (1), Lower-Middle Jurassic sediments of the Talinskoe area (2) and organic matter from sediments of Early-Middle Jurassic (3) and Paleozoic (4) age.

Fig. 12. Comparison of isotope distribution among fractions of crude oil from the accumulation in the Bazhenovian formation of the Salym field (2), the accumulation in the Vartovian formation of the E-Surgut field (4), the accumulation in the Megionian formation of the Samotlor field (3) and bitumen from sedimentary rocks of the Bazhenovian formation (1).

Fig.13. Comparison of the isotope distribution among the fractions of crude oil from the Botuobian (3) and Osinian horizons (5) and bitumen from rocks of Precambrian (Vend-Riphean) (1) and (2) and Early Cambrian (4) age (the Srednebotuobinskoye field, East Siberia).

Fig.14. Isotope distribution among the fractions of bitumen from a Recent saprophelic mud (the Lakhapere Lake, Estonia).

Fig.15. Comparison of isotopic characteristics of bitumens from sediments that experienced different thermal alteration (the Gulf of California, Leg 64, DSDP). The degree of transformation increases in the following order: 478-6(1), 479-43(2), 474-40(3), 477-7(4), 477-16(5). The first three samples contain immature organic matter. Sample (4) exposed to moderate heating contains mature organic matter corresponding to peak oil generation. Sample (5) contains "overcooked" organic matter (no pigments, the phytan/n-C₁₈ ratio is low). A detailed description of these samples is given elsewhere (Galimov, Kodina, 1982).

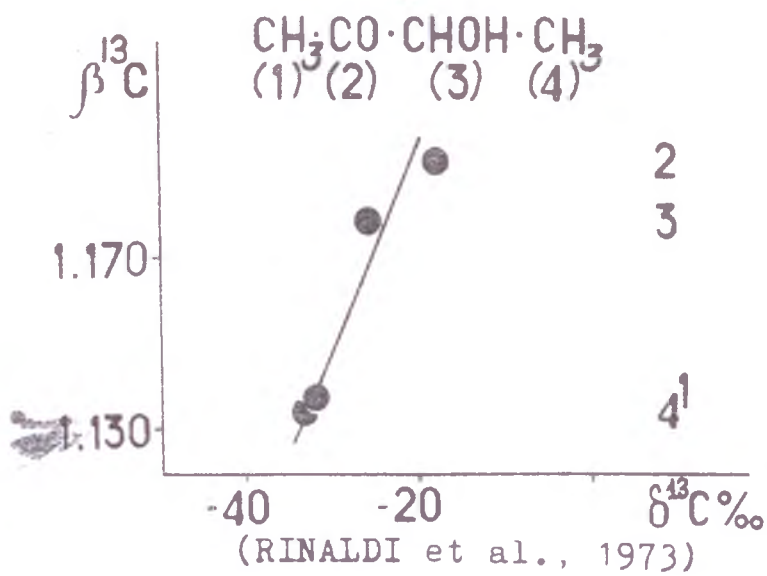
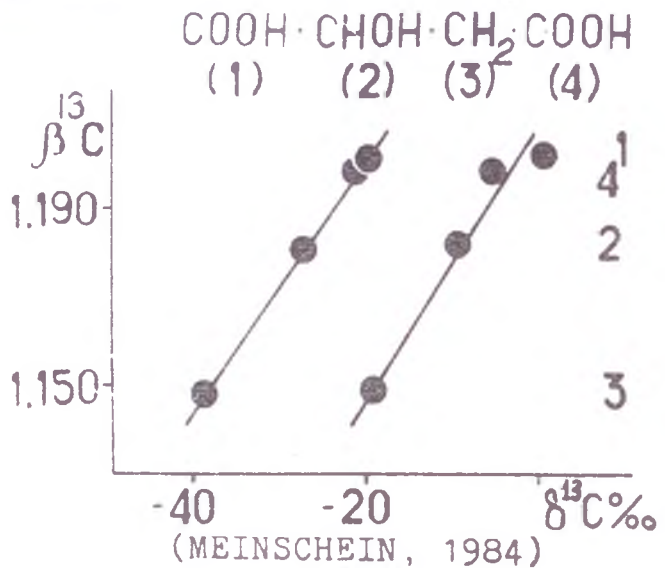
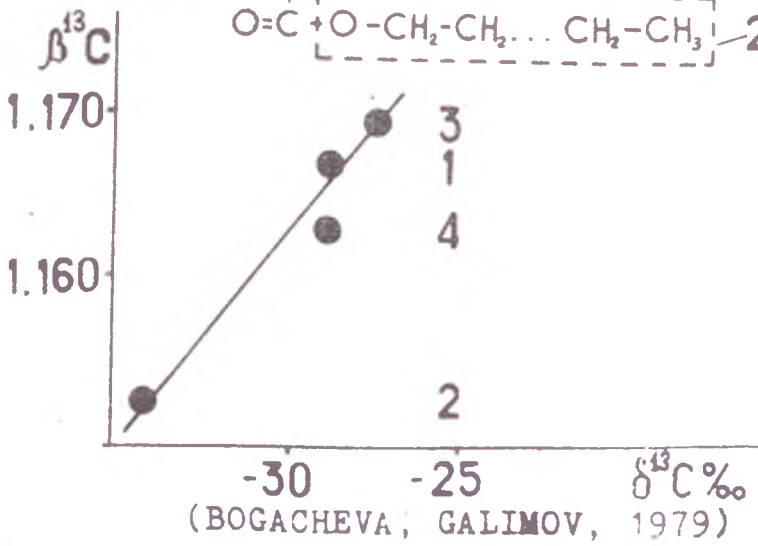
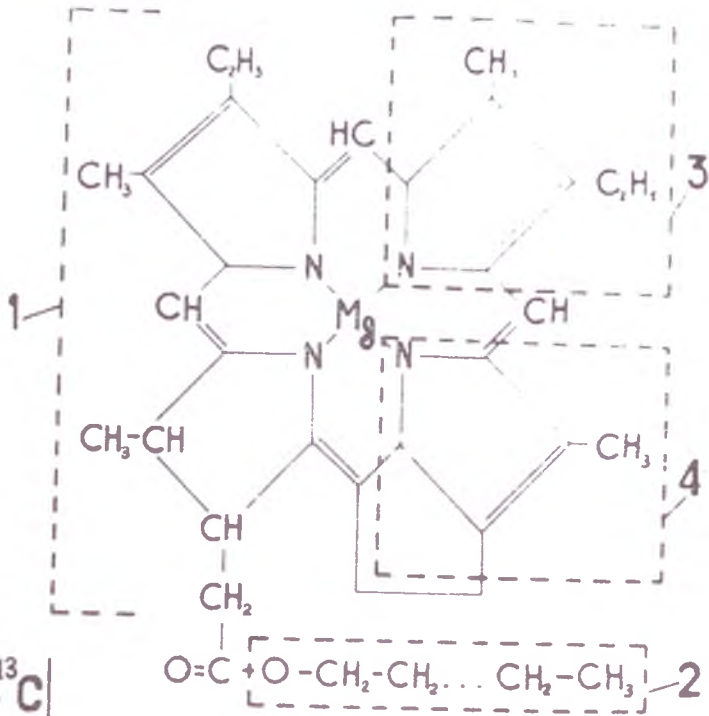
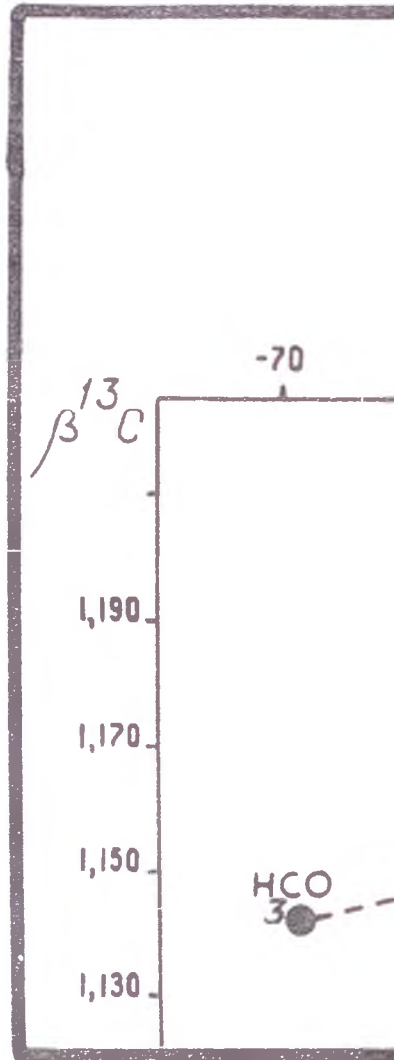


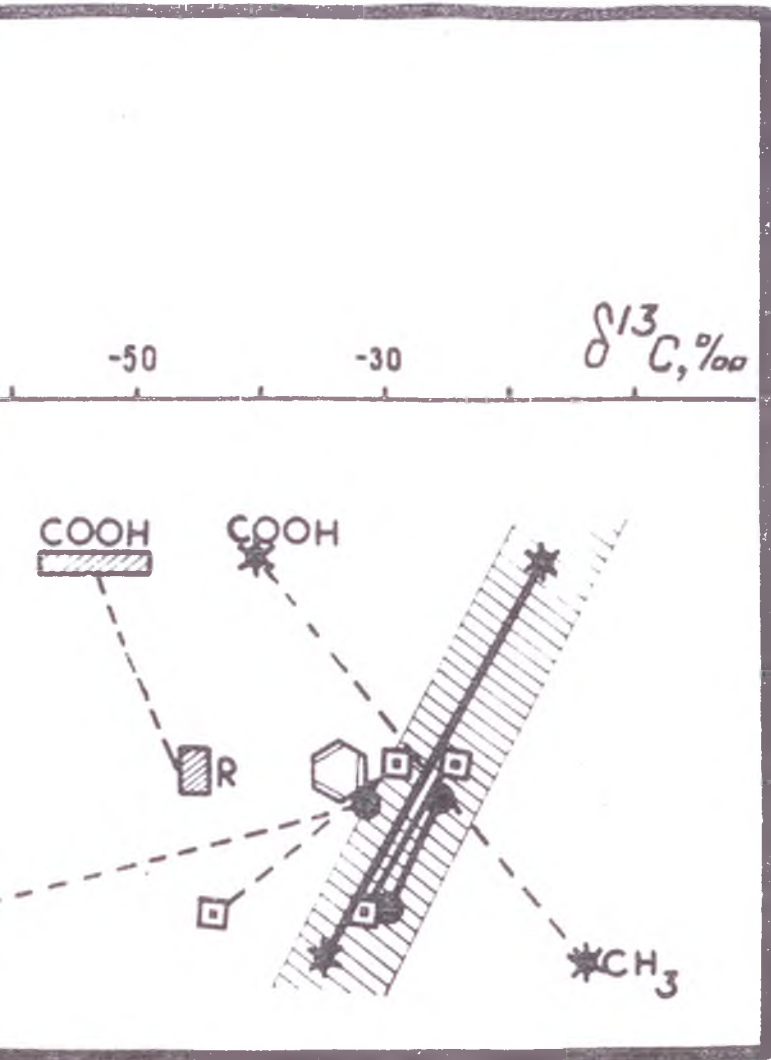
Fig.





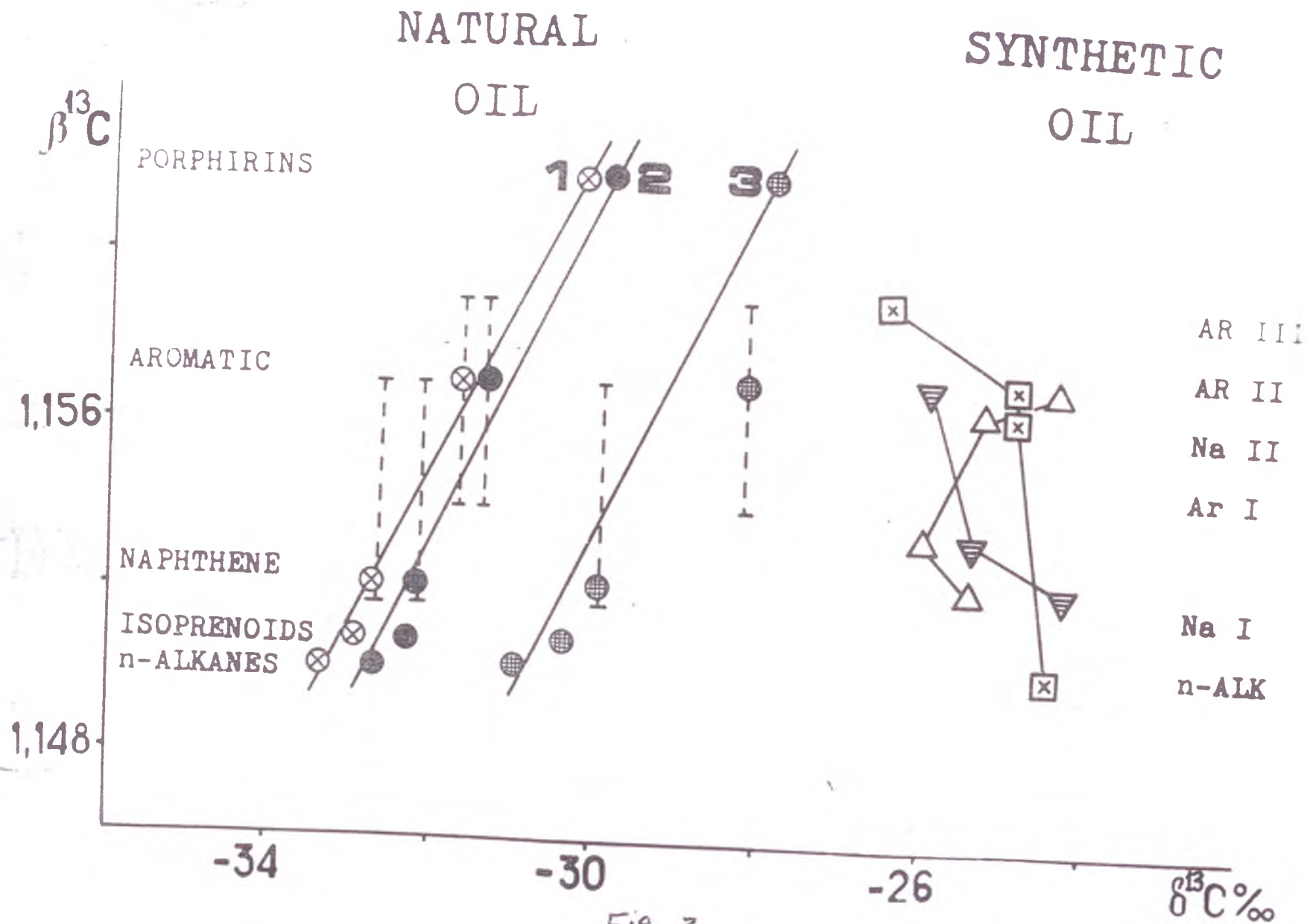
● - VANILLIN

□ - ANETOL



- ★ - ACETIC ACID
- ▨ - AMINO ACIDS

Fig 2



Asph

R_{BM}

R_B

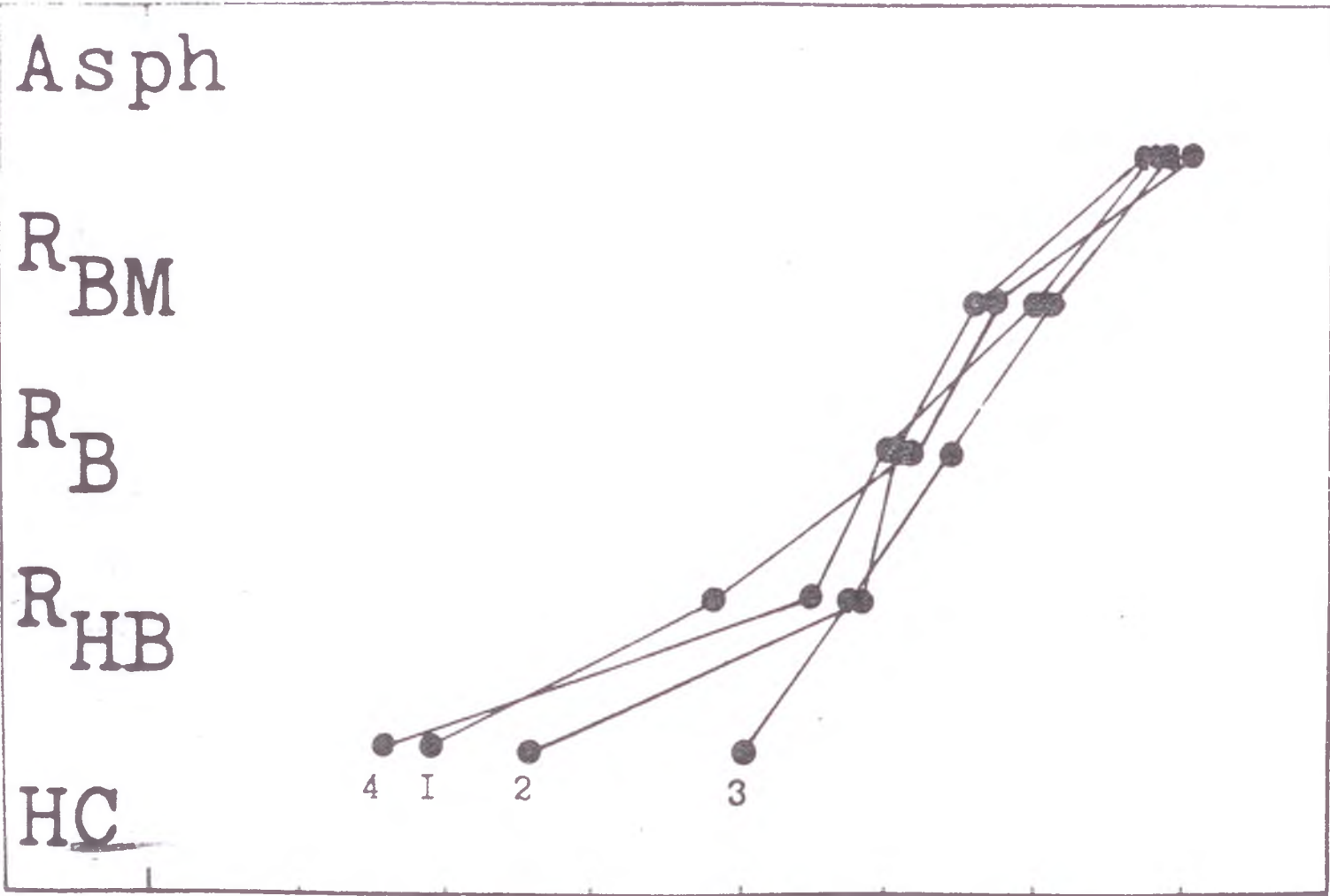
R_{HB}

HC

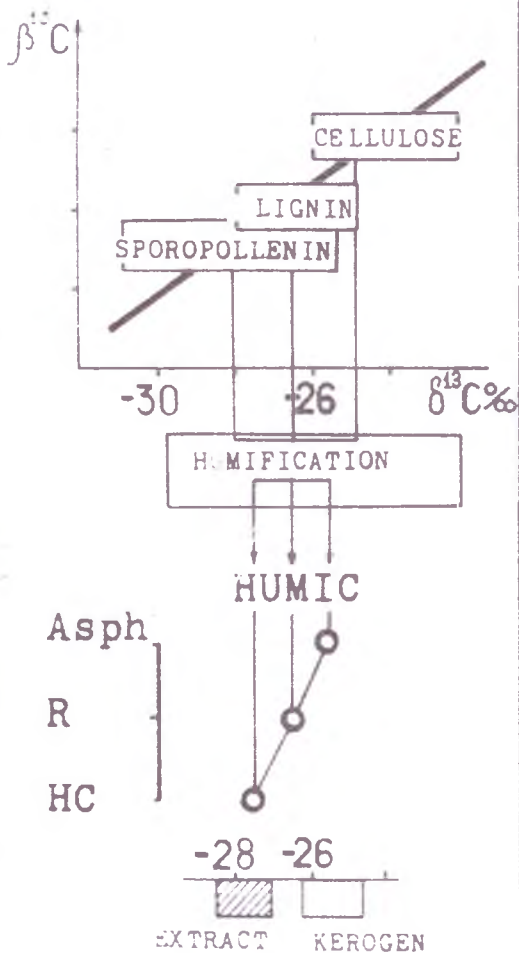
4 I 2 3

-30 -28 -26 -24 $\delta^{13}\text{C}, \text{‰}$

Fig. 4



LAND PLANTS



MARINE PLANKTON

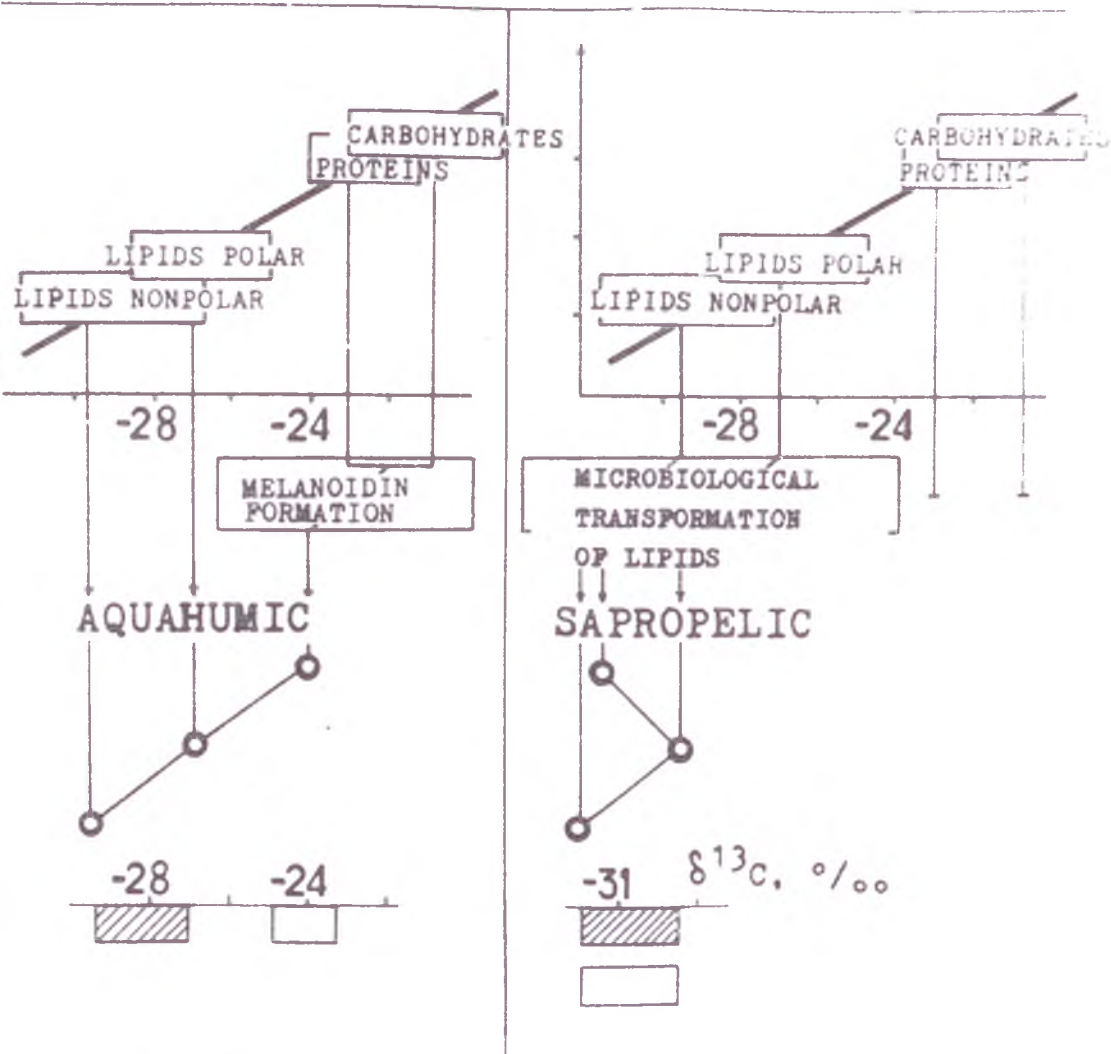


Fig. 5

SOUTH ATLANTIC, ANGOLA BASIN
 LEG 75, DSDP. SITE 530

AQUAHUMIC OM

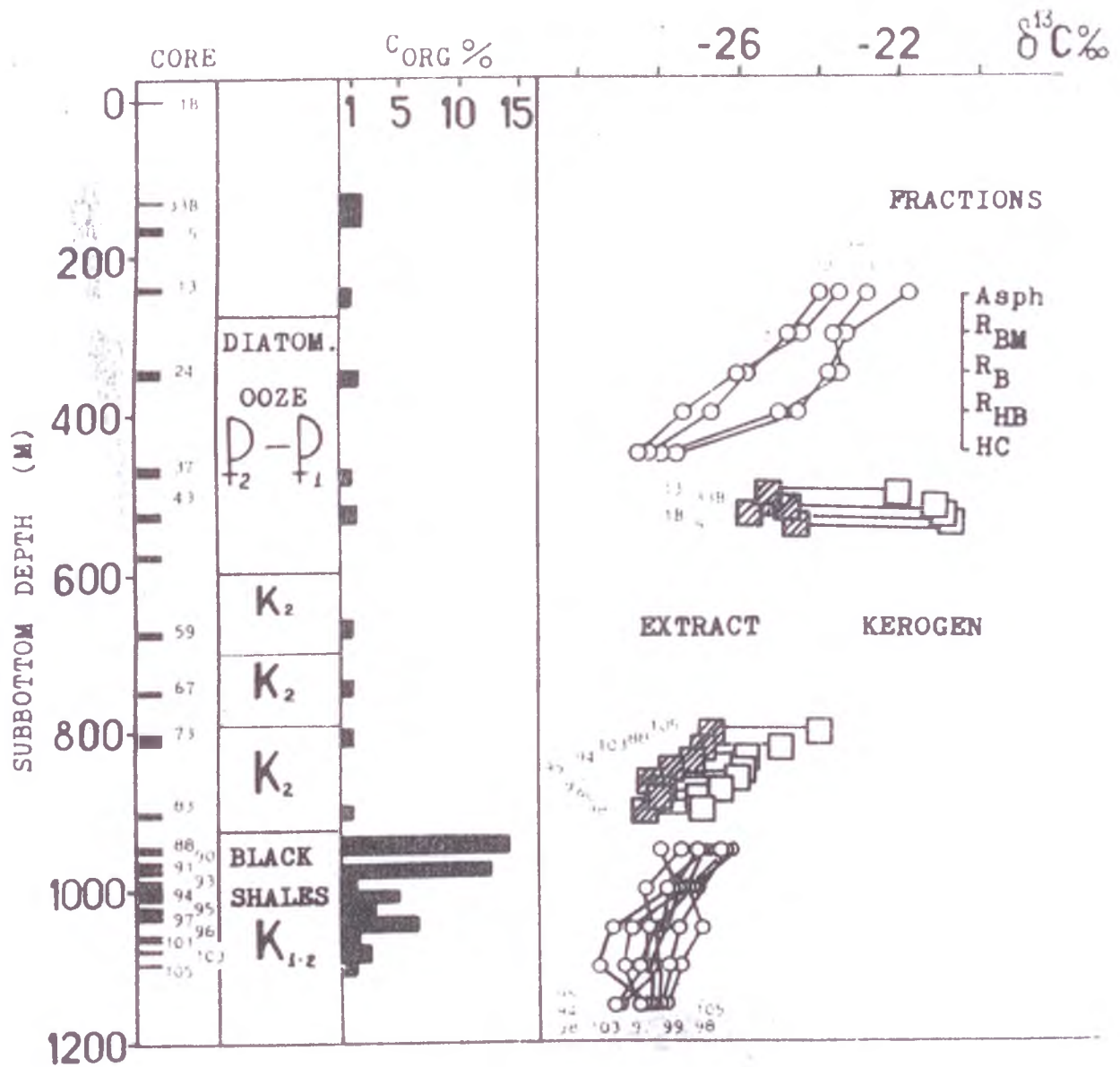


Fig. 6

SAPROPELIC ORG. MATTER

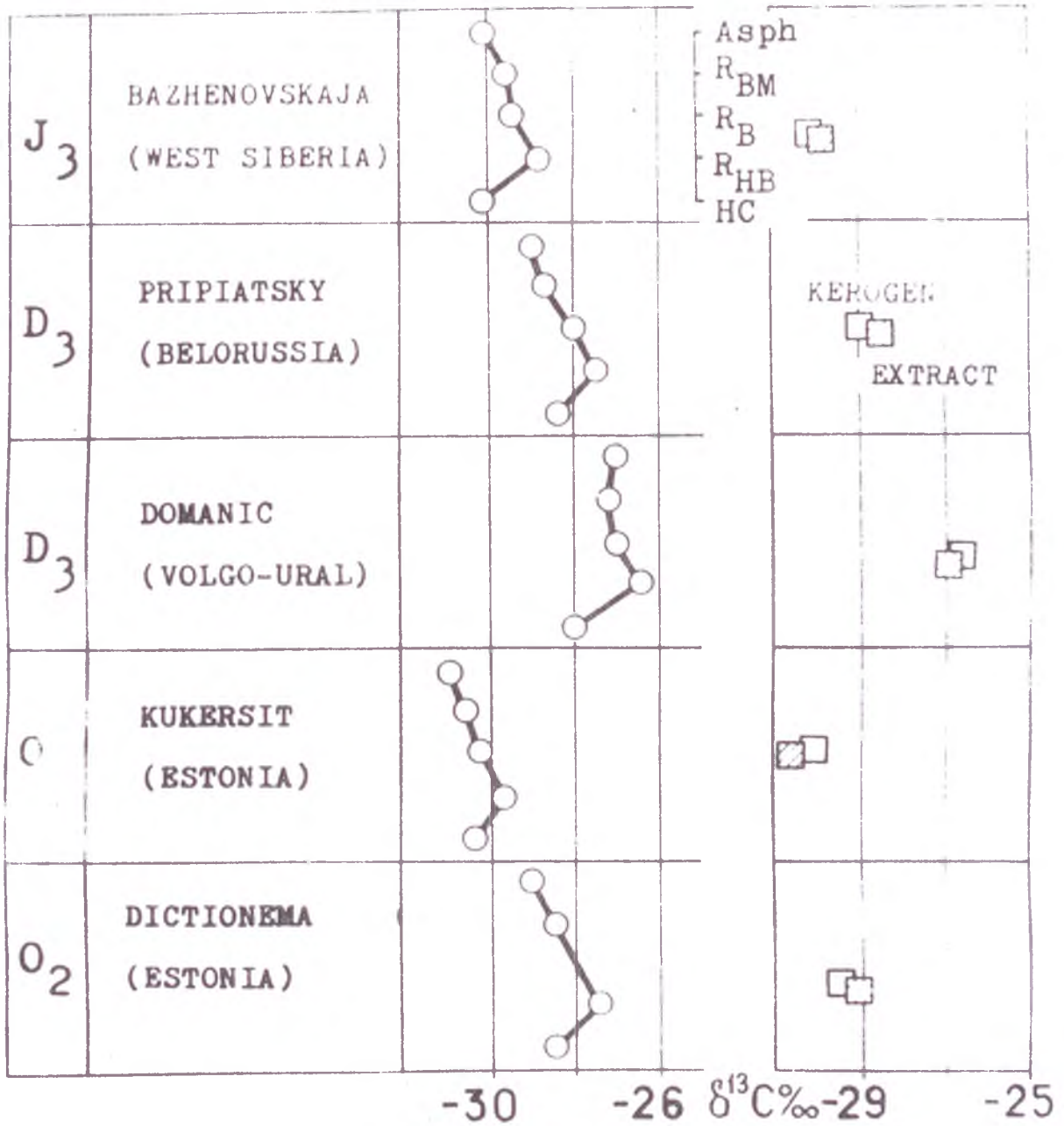


Fig. 7

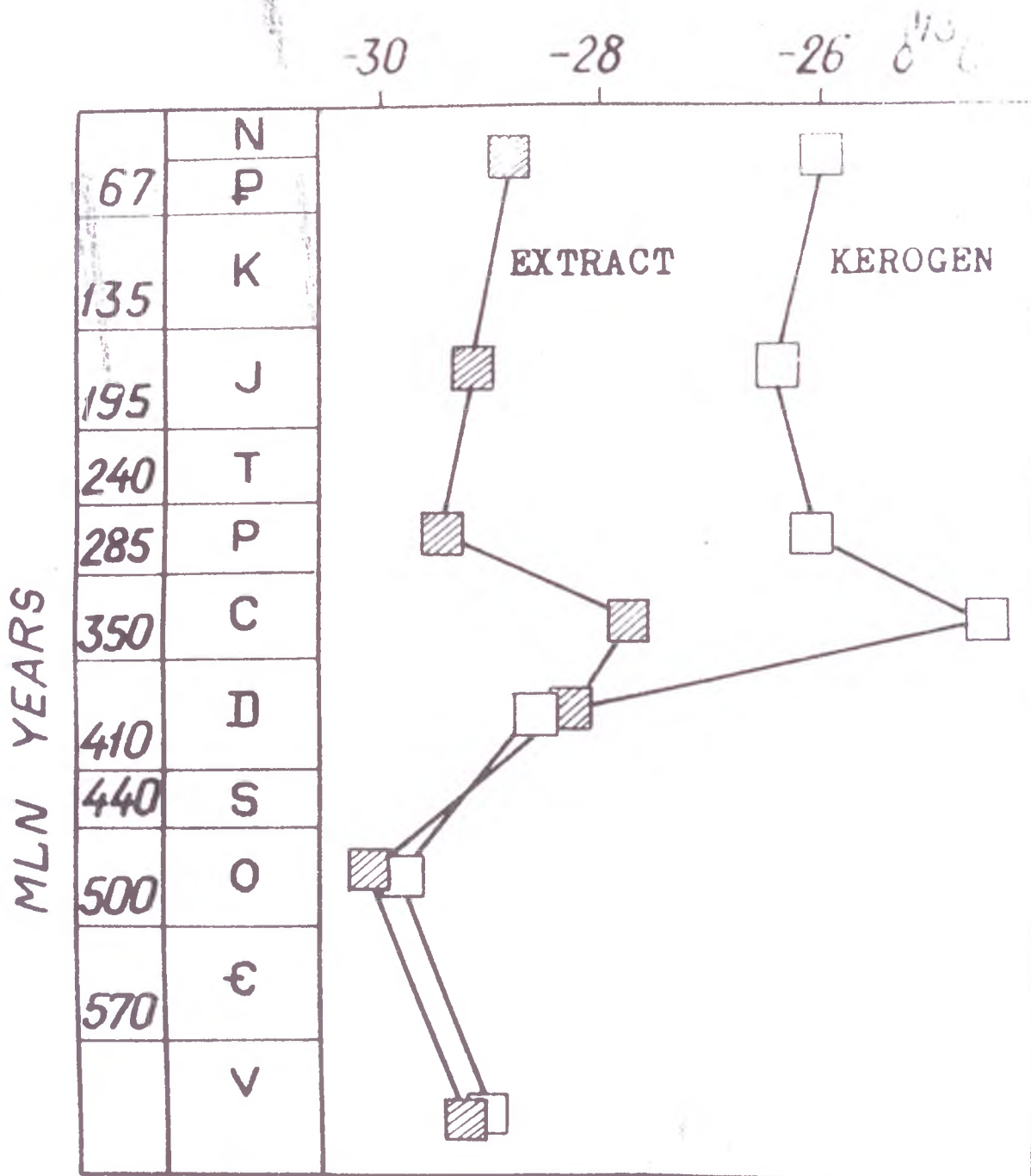


Fig. 8

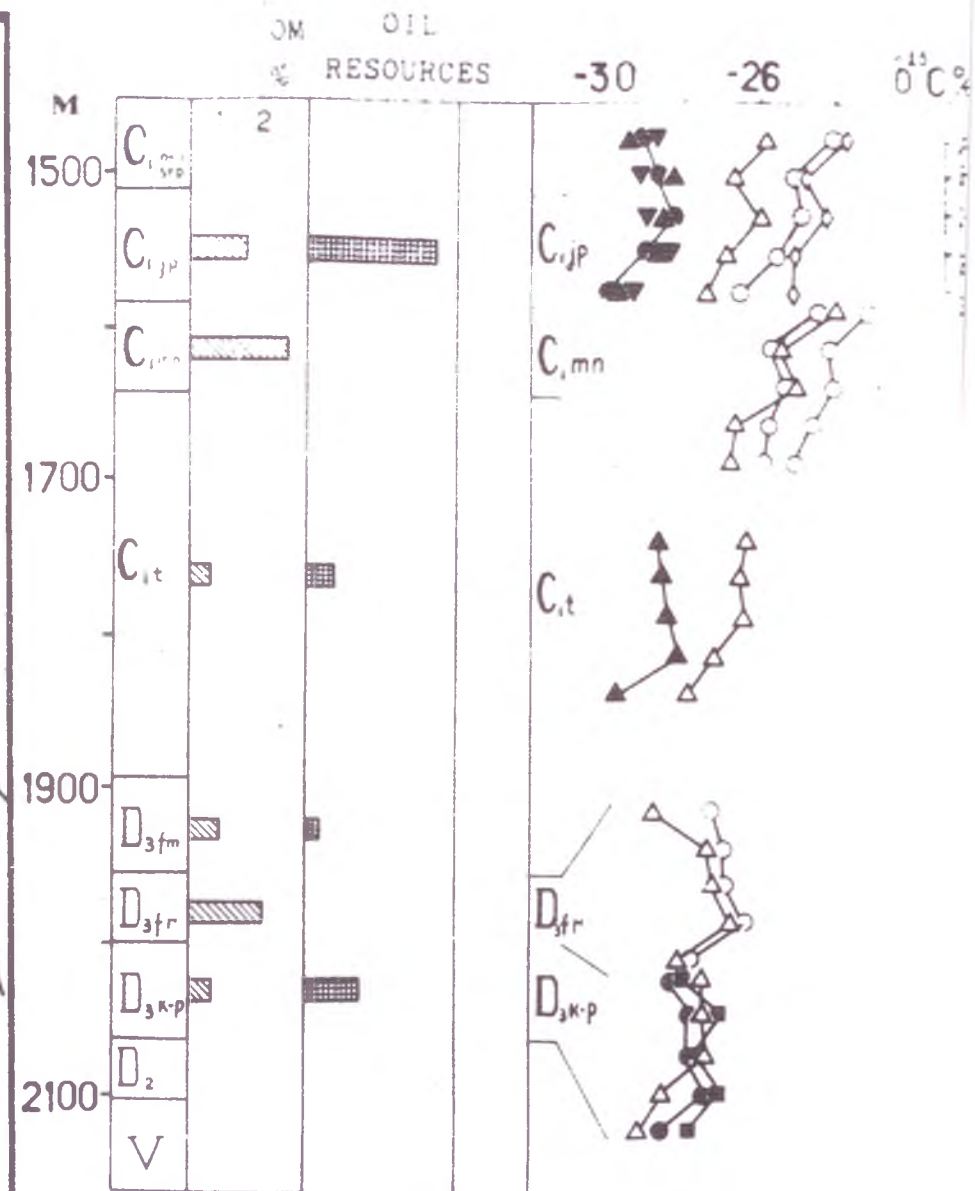
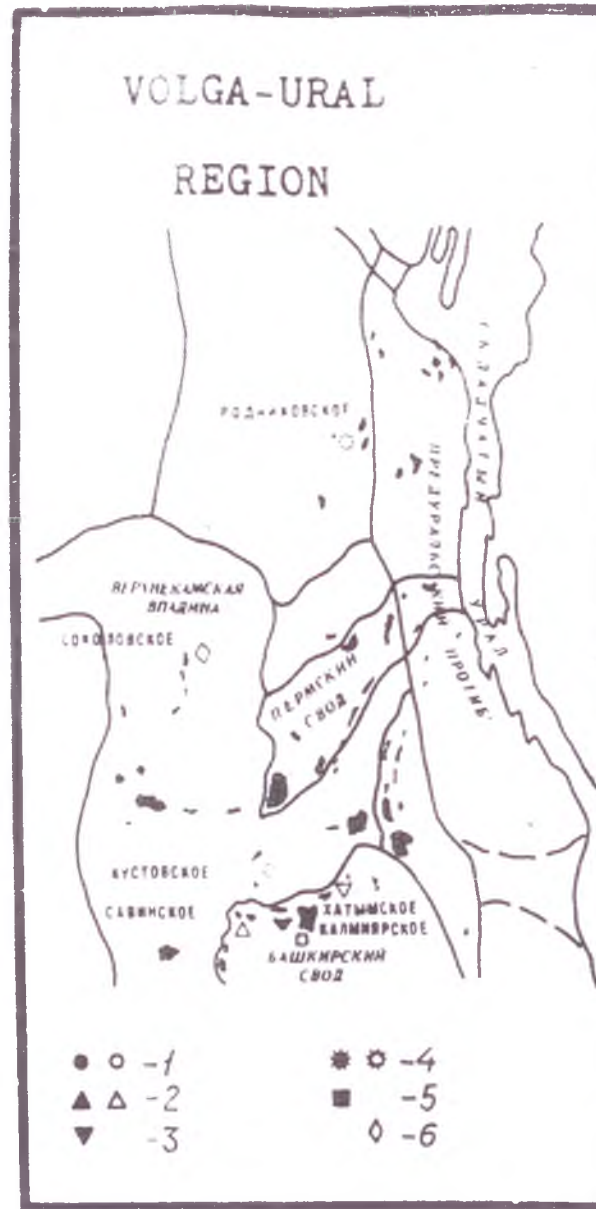


Fig. 9

SAKHALIN ILD. OKRUZHNOE

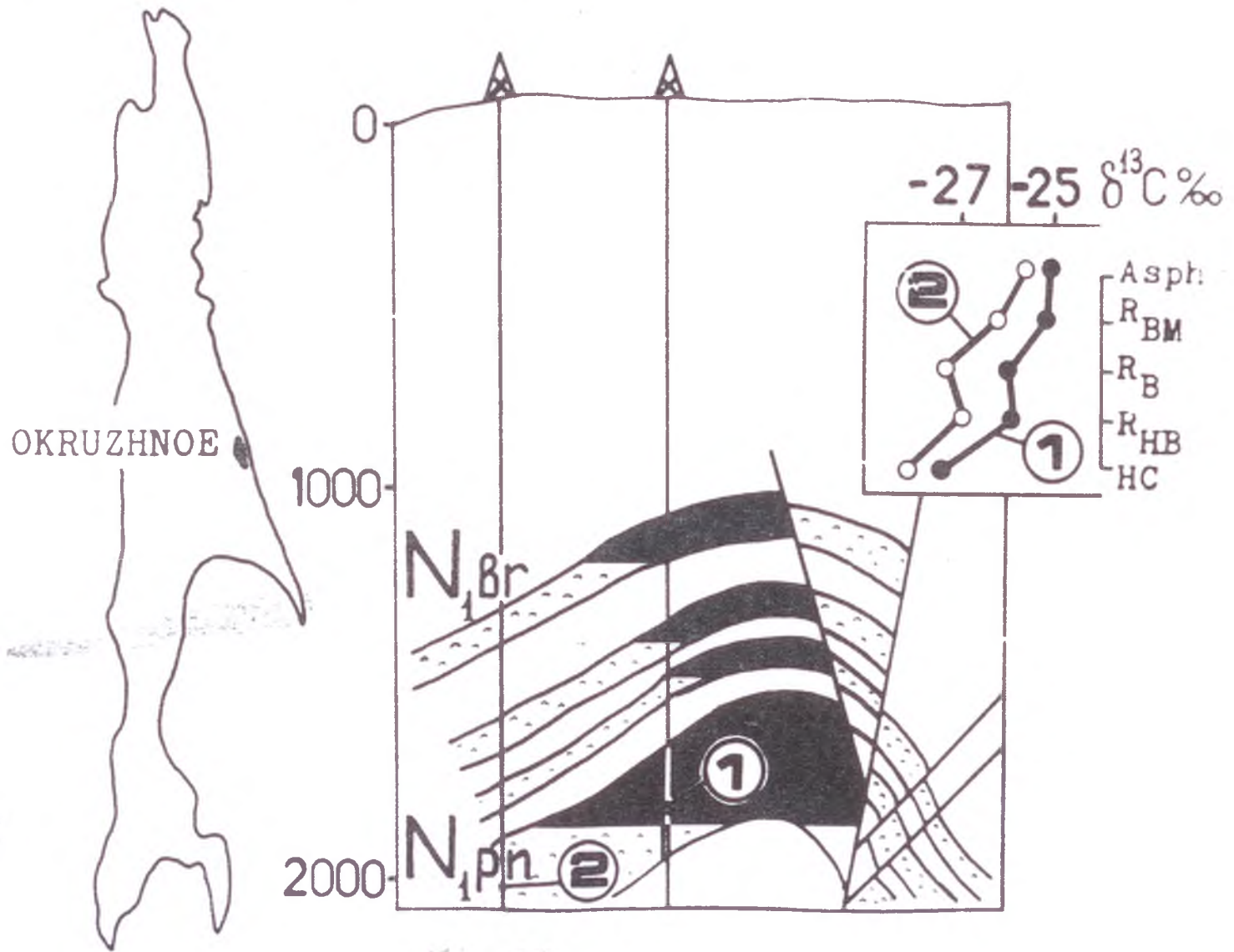


Fig. 10

WEST SIBERIA

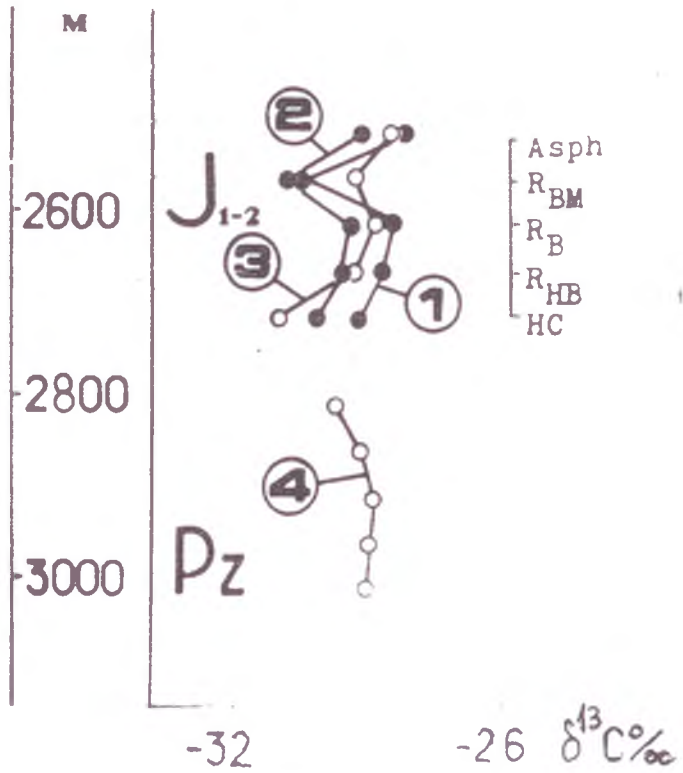
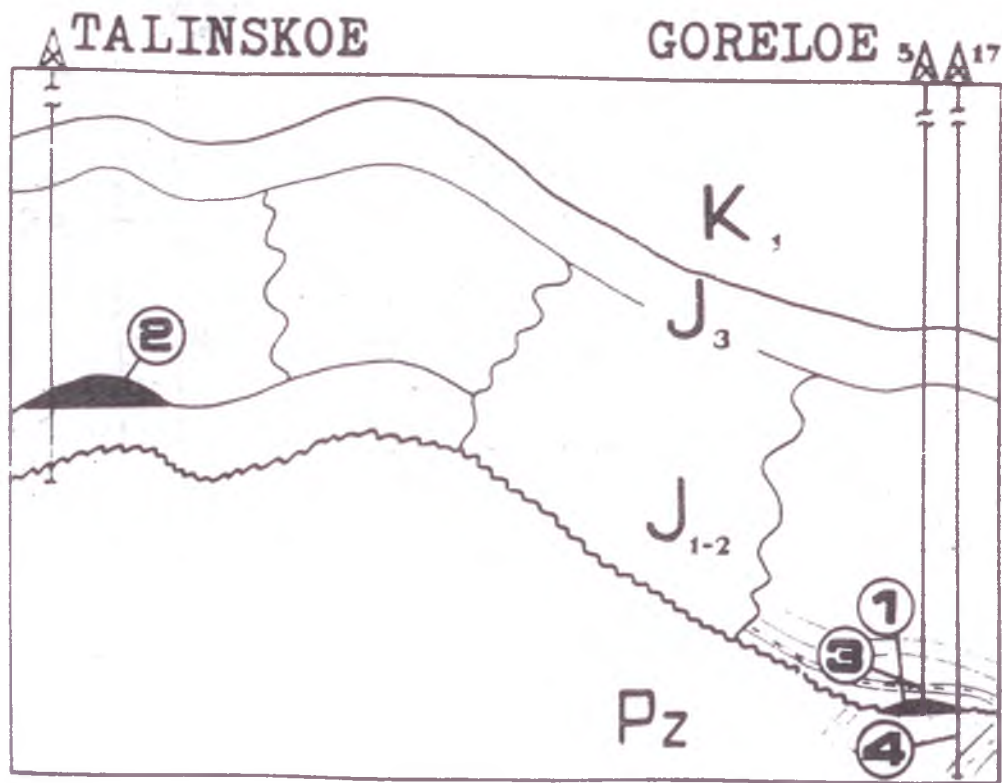


Fig. 11

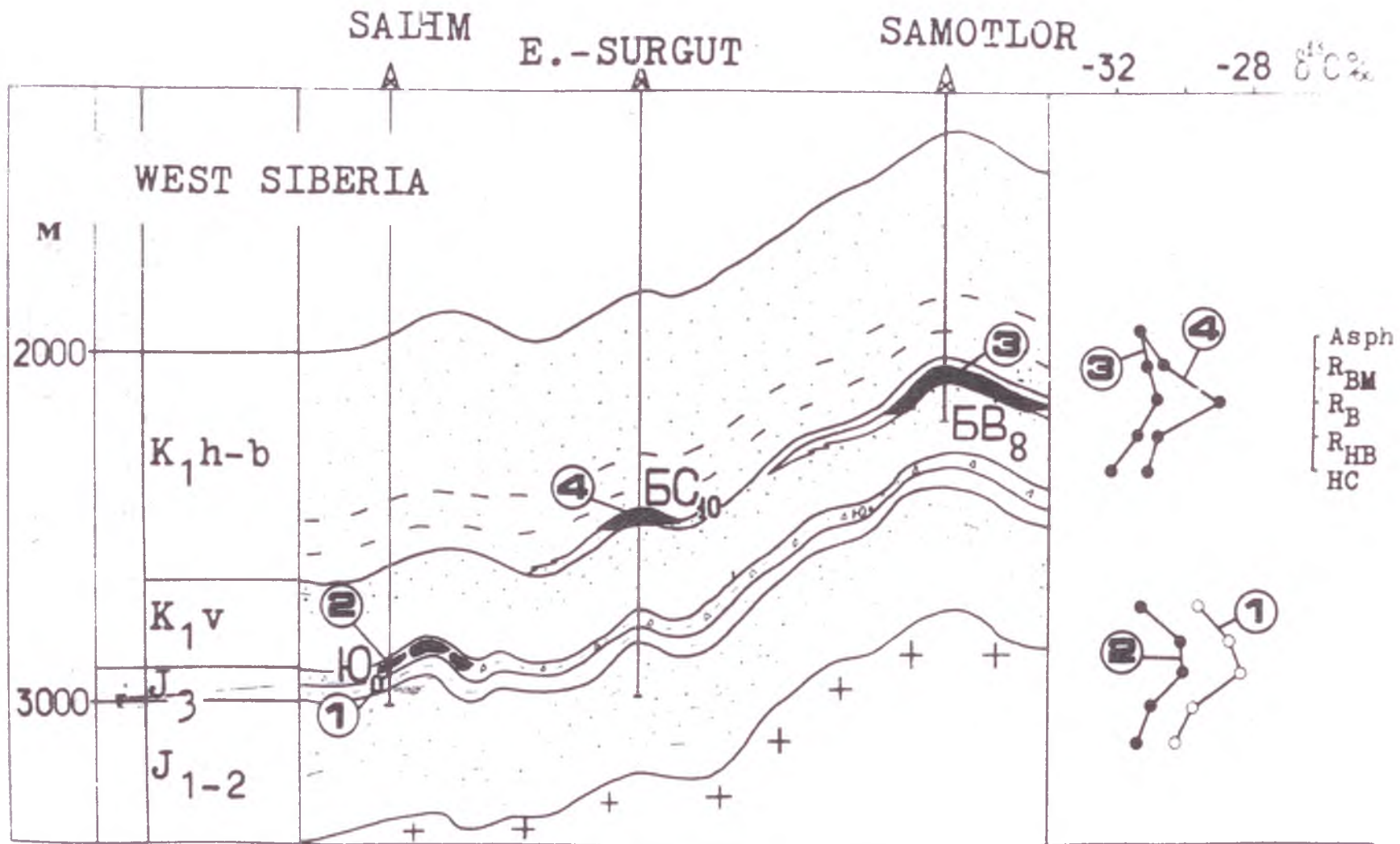
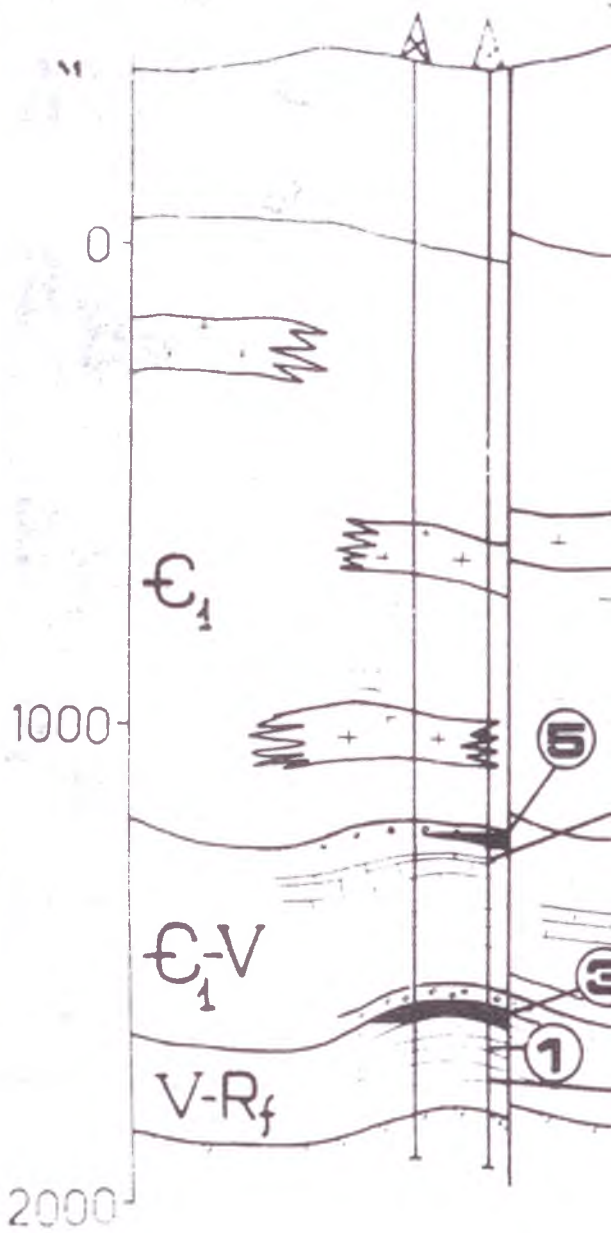


Fig 12



EAST SIBERIA

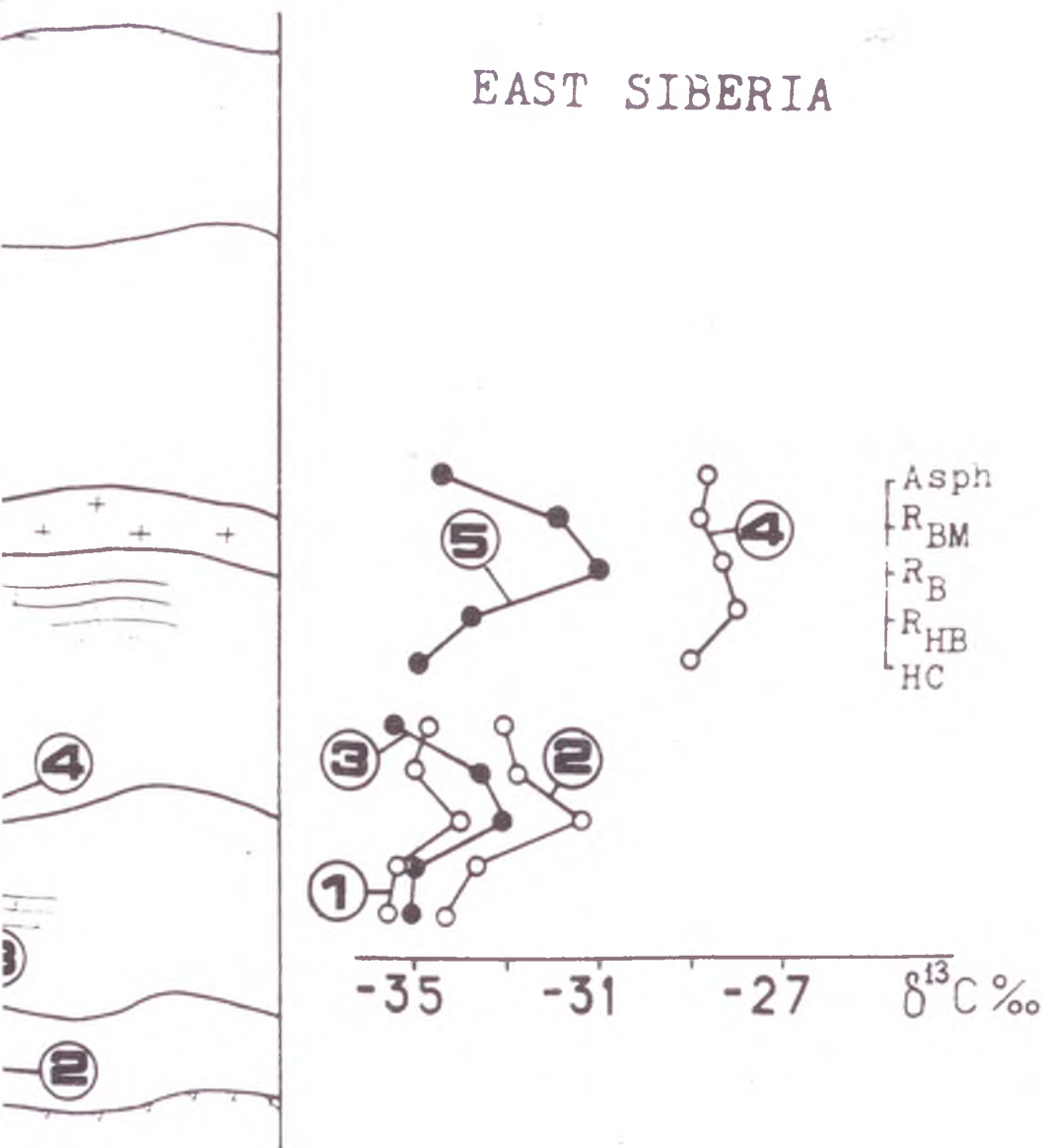


Fig 13

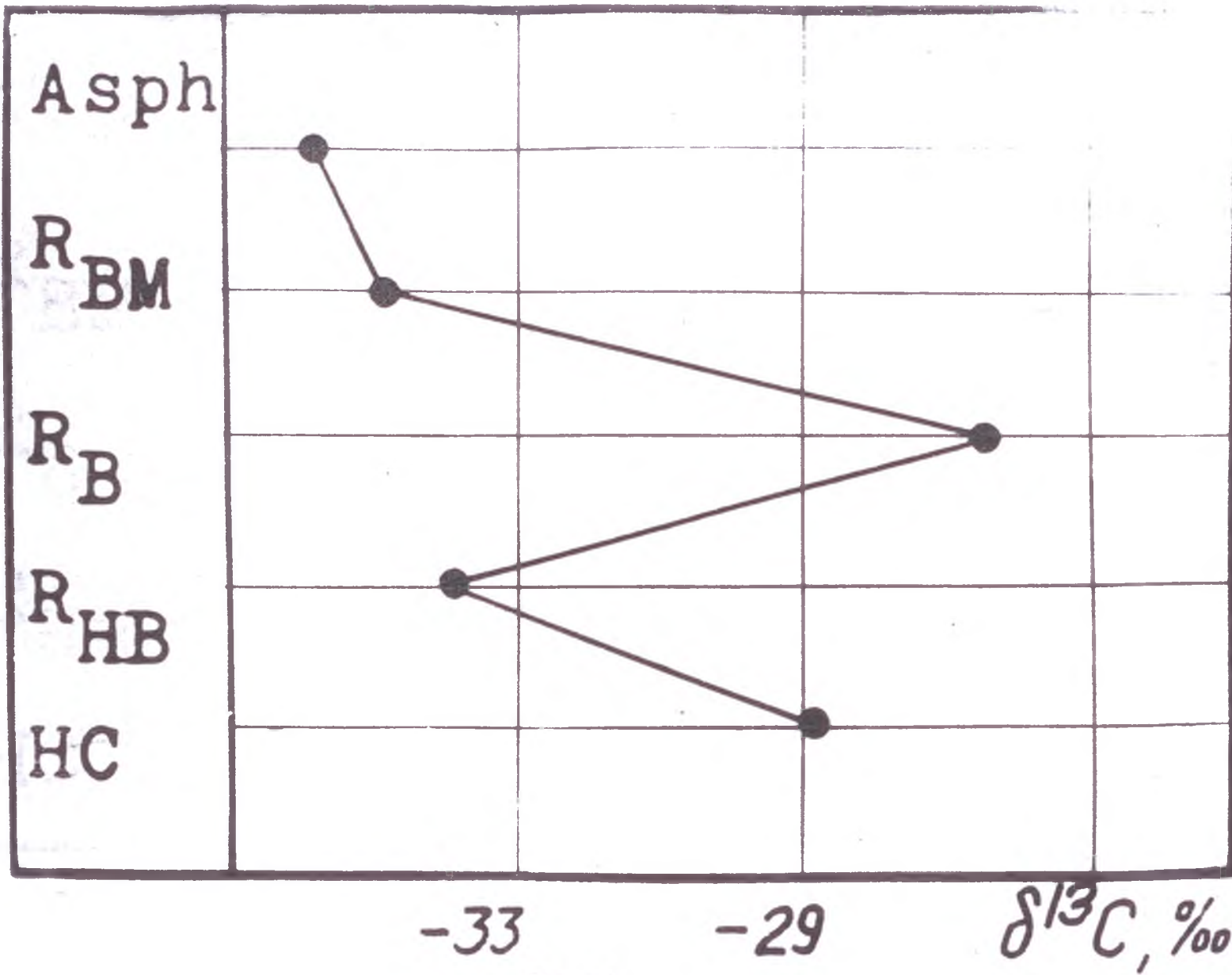


Fig 14

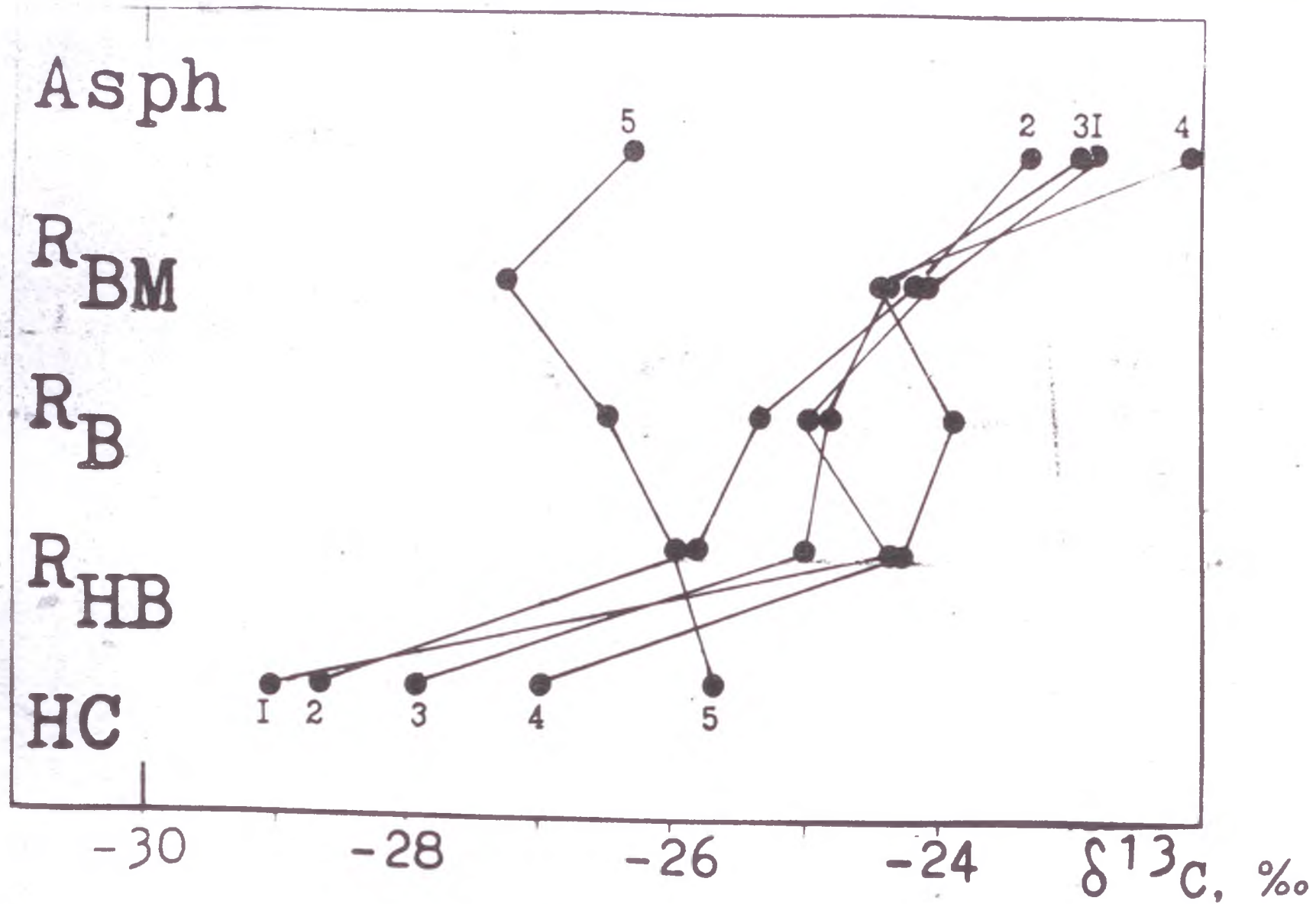


Fig 15