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An Organic Geochemical Study of Austrian Bituminous Rocks

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With 7 Text-Figures and 3 Tables

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Tirol
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Bituminöse Gesteine
Ölschiefer
Faziesanalyse
Bächental Schichten
Seefelder Schichten
Häringer Schichten
Kainacher Gosau
Lagerstättengenese
Erdölmuttergesteine

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Zusammenfassung

Im Rahmen des Projektes ÜLG 19 „Aufsuchung von Alginit in Österreich" wurden zahlreiche Vorkommen bituminöser Gesteine unterschiedlicher stratigraphischer Stellung geologsich und in Richtung potentieller agrargeologischer Nutzung untersucht und zum Teil auch einer organisch-geochemischen Analyse unterzogen. Dieser Bericht vermittelt in aller Kürze erste orientierende Untersuchungsergebnisse hinsichtlich Bitumengehalt und in HCl-unlöslichem Rückstand aus Probenmaterial der Seefelder Schichten, des Häringer Bitumenmergels, des Lias-„Ölschiefers" des Grünbachgrabens am Untersberg, Salzburg sowie von bituminösen Kalken aus der Kainacher Gosau, die allesamt hinsichtlich ihrer hohen Bitumenausbringung mit guten Erdölmuttergesteinen verglichen werden können.

Über den einzigen zur Zeit in Österreich im Betrieb befindlichen „Ölschiefer"-Abbau (sieht man von der Mitgewinnung bituminöser Mergel bzw. Mergelkalke als Zementrohstoff in Bad Häring ab) in Bächental im Karwendelgebirge werden detaillierte Ergebnisse organisch-geochemischer Untersuchungen mitgeteilt und – ergänzt durch mikrofazielle Untersuchungen im Dünnschliff und Raster-Elektronen-Mikroskop – hinsichtlich ihrer faziellen Aussagekraft diskutiert. Neue Ammonitenfunde lassen ein Einsetzen des anoxischen Events bereits im Pliensbachien – Hauptphase wohl im Toarcien – als möglich erscheinen. Lithofaziell zeigen die im 2–3 dm-Bereich gebankten, dunkel-schokoladebraunen, biomikritischen Bitumenmergel von Bächental meist ein gut ausgeprägtes sedimentäres Parallelgefüge; nicht selten ist auch Druckflaserung zu beobachten. Der HCl-unlösliche Rückstand schwankt von 38–71 Gew.-%. Montmorillonit und Illit dominieren den Schichtsilikatanteil; auffallend ist der hohe Pyritgehalt. Die biofazielle Analyse zeigt auffallende Benthos-Armut bei Dominanz von Radiolarien, Schwammnadeln und gelegentlich Echinodermen-Detritus. Untergeordnet finden sich noch Ammoniten, kleine Bivalven, Ostrakoden, Foraminiferen, Filamente, Calcisphären sowie Schalendetritus indet. Nannofossilien (*Striatomarginis speciosus*) konnten ebenso nur sehr selten beobachtet werden.

Die organisch-geochemische Analyse der Bächentaler Bitumenmergel zeigt stark schwankende Bitumenausbringung von 1700–13300 ppm. Die Kohlenstoffisotopen-Untersuchung weist alle Fraktionen organischer Substanz – Bitumen und Kerogen – als an leichten Kohlenstoff-Isotopen ($\delta^{13}C$) angereichert aus, was für Herkunft der organischen Substanz von Lipiden einzelligen Phytoplanktons (Grün- oder Blaugrünalgen) spricht. Auch die Bitumen-Fraktionen sind einander in der Kohlenstoffisotopen-Zusammensetzung ähnlich, wobei diese Konfiguration charakteristisch für organische Substanzen ist, die unter O_2-verarmten Ablagerungsbedingungen bei hohen Konzentrationen von Phytoplankton-Resten im Sediment entstehen. Die Molekularstruktur der organischen Substanz wur-

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de mit Hilfe spektroskopischer Methoden untersucht. Gesättigte Kohlenwasserstoffe sind in der Hexan-löslichen Fraktion weit verbreitet. Von besonderem Interesse ist auch der Nachweis von Metallporphyrinen, wobei Vanadyl-Porphyrine dominieren. Weiters kann geschlossen werden, daß gemeinsam mit Etioporphyrinen auch DPEP-Porphyrine vorhanden sind, in deren Molekülen jener isozyklische Ring nachweisbar ist, der von einem Chlorophyll-Molekül herleitbar ist. Die Anreicherung von organischen Substanzen in den Porphyrinen gemeinsam mit hohem Schwefelgehalt kann als Hinweis auf anoxische Verhältnisse und reduzierende Diagenesebedingungen im Sediment angesehen werden. Die Anwesenheit von Perylen spricht jedoch dafür, daß keine stagnierenden Sedimentationsbedingungen herrschten. Das Nichtvorhandensein von Kupfer-Porphyrinen im Bitumen wird als Hinweis gewertet, daß kein terrigener Einfluß im Sediment nachweisbar ist.

Zusammenfassend kann festgehalten werden, daß die organisch-geochemische Analyse in Verbindung mit litho- und biofaziellen Daten die Aussage zuläßt, daß die Bitumenmergel von Bächental ihren Bitumenanteil hohen Konzentrationen von einzelligem Phytoplankton verdanken. Es herrschten sapropelitische Ablagerungsbedingungen. Ein niedrig-energetischer Ablagerungsbereich mit geringen O_2-Gehalten im Bodenwasser, jedoch nicht stagnierenden Sedimentationsbedingungen und gleichzeitiger hoher Biomasse-Produktion erscheint ebenso erforderlich gewesen zu sein. Die biofazielle Analyse deutet auf einen Ablagerungsraum im äußeren Neritikum bzw. Pelagikum.

Hohe Bitumengehalte, die extrem hohe Konzentrationen geochemisch reifer Petroporphyrine (Ni- und VO-Komplexe) zeigen, werden als Zeugen hohen Sedimentreifegrads angesehen.

Abstract

The main goal of this study is a detailed organo-geochemical investigation of the classical locality of the organic-rich Upper Liassic sediments – the socalled Bächental Schichten in Tyrol. In addition also data on HCl-insoluble residues and bitumen yield from various Alpine formations are provided, namely of the Upper Triassic (Norian) Seefelder Schichten, the Upper Liassic of Grünbachgraben in Salzburg, the Upper Cretaceous bituminous limestones of Kainacher Gosau, Styria, and the coal-bearing bituminous Häringer Schichten of Oligocene age. In respect to bitumen content all these organic-rich sediments are comparable with good oil source rocks.

The anoxic "event" of the Bächental Schichten seems to start in the Upper Pliensbachian, as indicated by recent findings of *Arieticeras* sp. and (?)*Leptaleoceras* sp. The main stratigraphic interval of organic-rich sedimentation, however, most probably was in the Lower Toarcian stage. The dark chocolate-brown Bächental Schichten consist of well bedded (2-dm range) bituminous marls or marly limestones and very often show well expressed lamination. Radiolarians and sponge spicules are the dominant biota. The biofacies indicates outer neritic/pelagic depositional environment.

The carbon isotope composition of the organic matter of Bächental Schichten is enriched in the light carbon isotope up to a $\delta^{13}C$-value of –32.2 ‰, the carbonates up to –2.75 ‰. All the fractions of organic-rich matter – bitumen and kerogen – are enriched in the light carbon isotope. This feature is typical for organic matter of sapropelic type, originating from lipids of plankton biomasse residues. The principal source of organic matter are unicellular, organic-walled green- and bluegreen algae. The established distribution of carbon isotopes in the bitumen fractions is charateristic for sapropelic organic matter deposited under O_2-depletetd conditions in low-energy environments.

The molecular structure analysis of Bächental organic matter shows abundant saturated hydrocarbons. An aliphatic nature of organic matter is manifested in all rest bitumen fractions. A further peculiarity in the molecular composition is a high content of metalporphyrins, especially of vanadyl porphyrins. Also etioporphyrins are present together with DPEP-porphyrins, the latter confirm the inheritage from a bioprecursor chlorophyll molecule. Enrichment of porpyhrins in organic matter together with high sulfur content is considered as proof for anoxic conditions and reductive diagenesis in the sediment. However, the presence of perylene points to a non-existence of stagnant sedimentation. The absence of copper porphyrins in the bitumen can be considered as indication for the absence or terrigeneous input to the sediment. High yield of bitumen which is extremely rich in geochemically mature petroporphyrins – Ni- and VO-complexes – gives evidence of the high maturation stage of Bächental Schichten.

1. Introduction

The modern level in organic geochemistry allows one to investigate organic matter of sedimentary rocks at molecular and isotopic levels. The data obtained bear information on bioprecursors of the matter, the depositional environment and some features of diagenesis and geochemical history of rocks. Therefore organic geochemistry penetrates thoroughly into sedimentary geological sciences. Its data are used now to resolve different problems in stratigraphy, sedimentology, ore formation as well as oil and gas geochemistry, including geochemical correlation and identification of oil-source rocks.

Isotopy gives a wider chance for research in the geochemistry of organic matter in which the parent biomolecules are practically entirely destroyed and disappeared (GALIMOV, 1980). The theory and experimental approaches of molecular-isotopic geochemistry allows one to get information on the source of fossil organic matter and its geochemical transformation on the basis of organic carbon isotope composition and carbon isotope distribution between the fractions of organic matter (KODINA & GALIMOV, 1985; GALIMOV, 1980, 1984, 1986). Inasmuch as any transformation of biomaterial to fossil organic matter is accompanied by isotopic effects, an investigation of preserved individual molecules and some structural groups is considered to be essential for reliable interpretation of isotopic data. In this investigation the chromatographic and spectroscopic methods are used.

In the frame of the present study organic matter of bituminous carbonate rocks from several localities in Tyrol, Styria, Salzburg and Carinthia was selected for research. The samples were collected in quarries, roadcuts and field exposures. Because about 40 % of the world oil resources are connected with carbonate rocks – including the giant oil-fields in the Jurassic and Tertiary of the Near East (CHILINGAR et al., 1967) – the study of organic matter of Austrian organic-rich rock samples seems to be of sufficient interest not only from a regional viewpoint.

2. Bituminous Rocks of Austria – A Short Review

Only very scarce data relate to organic rich carbonates in Paleozoic sequences of the Carnic Alps. However, bituminous rocks occur in various stratigraphic levels of Mesozoic and Cenozoic sedimentary sequences of the Austrian Alps and their foredeeps. The most complete review was given by BITTERLI (1962) and a short but informative summary has been compiled by HEINRICH (1980). Only very little and scattered informa-

Table 1.
Synopsis of HCl-insoluble residue and bitumen content of selected representative Austrian Mesozoic and Cenozoic organic-rich sediments.

Formation and Locality	Stratigraphic Age	Lithology	HCl-insoluble residue [weight-%]	Yield of bitumen [ppm]
Seefelder Schichten next to Nördlinger Hütte, Tyrol	Upper Triassic (Norian Stage)	Organic-rich dark grey intercalations in Hauptdolomite, ±sandy-silty shales, often calcareous and/or dolomitic; basin-edge facies	2–67	1.500–18.800
"Bächental Schichten" of classical locality, Tyrol	Upper Liassic (?Upper Pliensbachian) – Lower Toarcian	Chocolate-brown marls, marly shales and marly limestones, micritic with deeper water fauna (ammonites, radiolarians, sponge spicules); outer neritic/pelagic environment	38–71	1.700–13.300
"Bächental Schichten", Grünbachgraben, Salzburg	See above	See above	69	10.600
Häringer Schichten, Perlmooser Cement Plant Quarry, Bad Häring, Tyrol	Tertiary (Oligocene)	Partly coal-bearing bituminous marls and marly limestones of brackish to fully marine environment	8–18	630– 4.500
Gosau Limestone, Geistthal, Kainacher Gosau, Styria	Upper Cretaceous (probably Santonian/ Campanian)	Black organic-rich micritic limestone without ecologically characteristic biota; most probably fully marine environment	32	3.900

tion exists also on their organic geochemistry (BITTERLI, 1962; GRÄF, 1975 [data provided by ÖMV-AG], KRATOCHVIL & LADWEIN, 1984). In Austria the most conspicuous stratigraphic level of bituminous rocks are the Seefelder Schichten, an organic-rich member of the Tethyan Norian Hauptdolomite Formation (e. g. BITTERLI, 1962; BRANDNER & POLESCHINSKI, 1986; CZURDA, 1972; DALLATORRE, 1926; FISCHER, 1957; FRUTH & SCHERREIKS, 1984; HRADIL, 1929, 1949, HRADIL & FALSER, 1930; ISSER, 1888; KLEBELSBERG, 1935; KRATOCHVIL & LADWEIN, 1984; KURRE, 1935; SANDER, 1921, 1922; TOLLMANN, 1976). The second important organic-rich sediment type are the Upper Liassic bituminous marls of Tyrol and Salzburg. Both the Norian Seefelder Schichten and the (Upper Pliensbachian?)–Toarcian Bächental Schichten achieved local importance for their usage in the cosmetic and pharmaceutical field. The Liassic oil-bearing marls of Bächental-type have been treated by ALBRECHT, 1984; BITTERLI, 1962; GÜNTHER & TICHY, 1979; HRADIL & FALSER, 1930; KLEBELSBERG, 1935; PLÖCHINGER & OBERHAUSER, 1956; SANDER, 1921, 1922 and TOLLMANN, 1976. Quarrying of the Seefelder Schichten has been terminated as a consequence of uneconomic thicknesses of highly bituminous layers. The Liassic Bächental Schichten, however, are still mined.

Uneconomic layers of high grade bituminous rocks are also known from different stratigraphic levels of the Upper Cretaceous Gosau formation (e. g. BITTERLI, 1962; GRÄF, 1975 – with data on organic geochemistry! HEINRICH, 1975; see also Table 1). Oligocene bituminous marls and marly limestones are mined as cement raw material in Bad Häring/Tyrol (SANDER, 1922; SCHNABEL & DRAXLER, 1976; see also Table 1). Bituminous "fishshales" of Upper Egerian ("Aquitanian") age are known in the Molasse Zone and have been encountered extensively in hydrocarbon exploration drillholes.

In Austria up to present only uneconomic indications of "alginite" sensu SOLTI (1985) have been traced in the Neogene (Badenian [?]) of Weingraben/Burgenland and in the Pannonian at Fehring (Mataschen clay-pit) in Styria (SOLTI, LOBITZER et al., 1987). In Hungary "alginite" is used successfully for soil melioration in agriculture (SOLTI, 1985).

The term "oil-shale" in Austria is often used incorrectly synonymous to bituminous rocks. However, only very few of the rocks in question in fact are really true shales. Many of them are bituminous marls, marly limestones and/or dolomites. The yield of HCl-insoluble residue is representative for the proportion of clay- and carbonate matter in a rock sample. In Table 1 the corresponding data of some characteristic bituminous rock formations of the Austrian Alps are presented together with the data on bitumen content.

As it follows from the table, all rock samples investigated have high bitumen contents. The organic-rich marl samples are comparable with good oil source rocks in respect to bitumen yield. In some cases, as for example, in at least part of the Seefeld rock samples, the high bitumen yield is due to surface bitumen appearances. Samples from other localities of bituminous smelling Triassic rocks investigated are much poorer in C_{org}-content and predominantly carbonatic with only small contents of clay material (Seefelder Schichten intercalations in the Hauptdolomite of Windische Höhe and of Bleiberg-Erlachgraben; Carnian bituminous dolomite of Rubland section, Carinthia).

3. The Liassic Bituminous Marls of Bächental ("Bächental-Schichten")

The (?Upper Pliensbachian)–Toarcian bituminous marls and marly Limestones of Bächental in the marvellous Karwendel Mountains/Tyrol, are mined in small scale by Gebrüder Albrecht Ltd. (ALBRECHT, 1984) mainly for the production of cosmetic and pharmaceutic products. The "Bächental Schichten" are understood as a member of the Allgäuschichten-Formation. They constitute a mappable unit and seem to differ considerably enough from the thin-bedded age-equivalent and also often highly bituminous Sachranger Schiefer (TOLLMANN, 1976) of the Bavarian Limestone Alps. The Bächental Schichten can be considered as Alpine equivalent of the various ±epicontinental Toarcian "oilshales" of Europe as e. g. of the

Posidonienschichten in Germany (HALLAM, 1987; JENKYNS, 1985, a. o.).

3.1. Lithology and Stratigraphy

Lithologically the organic-rich Bächental Schichten are well bedded in the two-decimeter-range comprising bituminous marls and marly limestones of dark chocolate-brown colour. The weathered surfaces mostly show light blueish appearance. The microfabric very often demonstrates a pronounced parallel texture which predominantly is of sedimentary origin and much less frequent flasered due to pressure solution. According to the oilshale-classification of HUTTON (1987) the Bächental Schichten belong to the group of marinites. As demonstrated in Text-Fig. 1 the carbonate matrix is truely micritic.

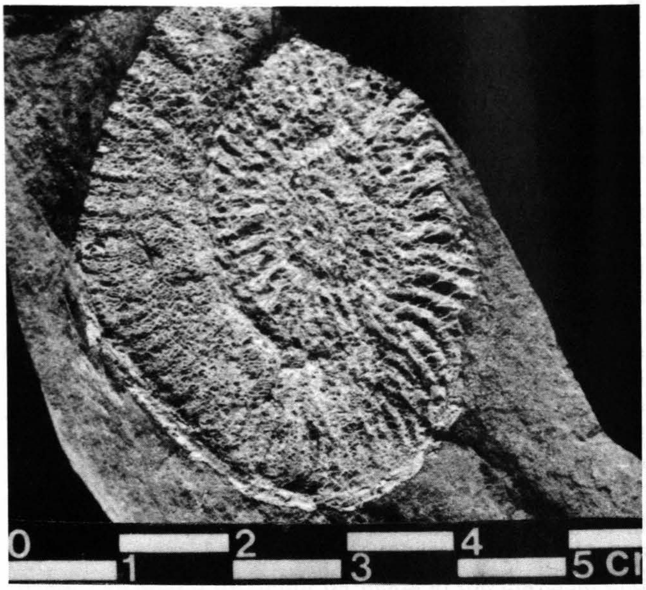
Text-Fig. 1.
SEM-photomicrograph of sample Bächental AL16 showing the nannofossil *Striatomarginis speciosus* PRINZ 1969 (det. H. STRADNER) in micritic carbonate matrix and flakes of phyllosilicates.
Scale bar = 4 micron.
Photomicrograph: R. SURENIAN.

In addition to the mineralogical analysis of sample Bächental AL 16, which is documented in chapter 3.2., two samples collected also in the Bächental mine are demonstrated in Table 2 (XRD-analyses courtesy of Prof. B. SCHWAIGHOFER, University of Agriculture, Vienna).

In addition to the mineral phases detected by XRD-analysis, also some glauconite grains have been observed in thin sections.

In contrast to the bituminous Bächental Schichten, in the Norian Seefelder Schichten of Nördlinger Hütte profile carbonates predominate. The phyllosilicates (15 % respectively 25 % in the samples analysed) consist about 100 % of illite which shows random widening of the crystals. Mixed layer clay minerals are present only in trace amounts (XRD-data courtesy of Prof. B. SCHWAIGHOFER).

The fauna of the Bächental Schichten is extremely poor in benthic organisms. The macrofauna consists in scarce findings of ammonites. KLEBELSBERG (1935) reports *Harpoceras* which proves Toarcian age for at least part of the Bächental Schichten. New findings by the present authors have been determined by Dr. M. RAKUS (GUDS Bratislava) as *Arieticeras* sp. and *Arieticeras* sp. or *Leptaleoceras* sp. (Text-Fig. 2). The recent findings point to Upper Pliensbachian (Middle to Upper Domerian) age for part of the Bächental Schichten. Also small and uncharacteristic pelecypods have been collected. The microfauna is dominated by radiolarians and sponge spicules. Echinoderm-debris, foraminifera, ostracods, calcispheres, filaments and shell debris indet. are present only in subordinate quantities. The same ist true for nannofossils. Prof. H. STRADNER could only identify one taxon, namely *Striatomarginis speciosus* PRINZ 1969 which indicates Middle-Upper Liassic age.



Text-Fig. 2.
Arieticeras sp. or *Leptaleoceras* sp. (det. M. RAKUS, GUDS Bratislava) from sample Bächental No. 5.
This taxon confirms Middle to Upper Domerian Age.

Table 2.
Lithology of two samples of Bächental Schichten.

Sample No.	Lithology	Bulk-Mineralogy		Clay mineral distribution <2 micron	
Bächental 2	Laminated bituminous marl without macrofauna. In thin sections abundant radiolarians, scarce echinoderm debris.	Phyllosilicates	35 %	Illite	48 %
		Quartz	11 %	Montmorillonite	52 %
		Calcite	49 %	Mixed Layer	Traces
		Pyrite	5 %		
Bächental 5	Thin-bedded (cm-range) laminated bituminous marly shale with ammonites (Text-Fig. 2). Radiolarians in thin sections prevailing sponge spicules.	Phyllosilicates	40 %	Illite	51 %
		Quartz	15 %	Montmorillonite	40 %
		Calcite	35 %	Kaolinite	9 %
		Pyrite	10 %	Mixed Layer	Traces

According to the present state of knowledge it seems, that the anoxic event represented by the Bächental Schichten started in the Upper Pliensbachian and persisted through the Lower Toarcian stage. The fauna points to an outer neritic/pelagic environment of deposition.

It is also worth mentioning, that all occurrences of Upper Liassic bituminous rocks in the Northern Limestone Alps show close spatial relationship with manganese shales (socalled Strubbergschichten [cf. BITTERLI, 1962; GÜNTHER & TICHY, 1979; HRADIL & FALSER, 1930; KLEBELSBERG, 1935, PLÖCHINGER & OBERHAUSER, 1956; TOLLMANN, 1976]). The manganese shales were also mined in small scale, however, they prove to be uneconomic in the present.

In the context of stratigraphy of Austrian bituminous rocks a paper by GÜNTHER & TICHY (1979) has to be mentioned. Strange enough, these authors attribute the Bächental Schichten of the classical locality to the Triassic Hauptdolomite. The bituminous marls of Grünbachgraben (Table 1) are considered by them as of Lower Cretaceous age. Because they do not offer any new paleontological data to prove this opinion, we still have to consider both localities as typical representatives of the (Upper Pliensbachian?)–Lower Toarcian anoxic event.

3.2. Organic Geochemistry

In the following paragraphs the detailed results of organo-geochemical investigations of marl sample Bächental No. AL 16 are presented. Organic-rich rocks of Upper Liassic (especially Toarcian) age are known to be widely distributed in Europe (JENKYNS, 1985; JENKYNS & CLAYTON, 1986; HALLAM, 1987). In Paris Basin, for example, they are excellent oil source rocks (TISSOT & WELTE, 1978).

In the sample Bächental AL 16 $C_{org.}$-content is 13 per cent by weight, bitumen yield 13300 ppm, HCl-insoluble residue 50 per cent of the rock. The mineralogical composition of the sample (per cent): montmorillonite: 16, illite-montmorillonite: 3, illite: 4, kaolinite: 1, quartz: 34, plagioclase: 4, calcite: 24, pyrite: 6, amorphous: 8 (XRD-data courtesy of Dr. G. SOLTI, Budapest; cf. SOLTI, LOBITZER et al., 1987).

Some inorganic elements were determined (%): Mg: 0.76, Ti: 0.22, P: 0.18, Mn: 0.32, S: 3.07, Cr: 0.003, Ni: 0.0064, V: 0.0165, Cu: 0.007, Zn: 0.0068.

An increased content of some elements, in comparison with other sedimentary rocks, was determined in the samples from Seefeld too, with the highest enrichment in V (0.1), Ni (0.01), Cr (0.01), Mo and Ti (0.1) in the shales with the highest $C_{org.}$-content.

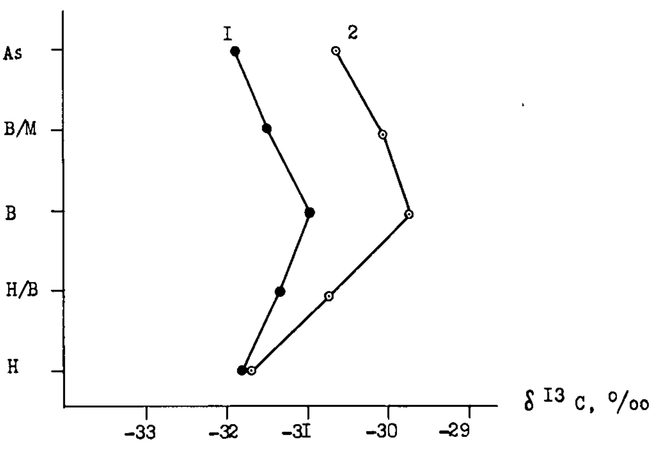
Determination of the element content in bitumen of sample Bächental AL 16 showed that about 100 % of Cr and Ni of the rock, 13 % of V, 3 % of Fe and Mn are concentrated in the bitumen. It is known that the rocks enriched in the sapropelic-type organic matter often have enhanced content of some elements (P, S, Mo, V, Cu, Ni, Cr, Co, U etc.) as compared with other types of sedimentary rocks (BRUMSACK, 1980; NERUTCHEV, 1982).

3.2.1. Carbon Isotope Composition

Organic matter of sample Bächental AL 16 was investigated by UV-, visible-, IR- and ESR-spectroscopy and gas-liquid chromatography. Carbon isotope composition of organic matter in total, bitumen and bitumen fractions were determined. Bitumen was Soxlet extracted with 9 : 1 benzene-methanol mixture from crushed rock samples, asphaltenes were precipitated with pentane and the pentane-soluble fraction was divided into four fractions by silica column absorption chromatography using solvents of increasing polarity as eluents.

The organic matter of the Bächental's sample is enriched in the light carbon isotope up to the $\delta\,^{13}C$-value of −32.2 per mille, carbonates up to −2.75 per mille. For the Seefeld samples the $\delta\,^{13}C_{org.}$-values range from −27.9 to −30.5 ‰. All the fractions of organic matter are enriched in the light carbon isotope. The bitumen and kerogen are really indistinguishable in this respect. This feature is common to organic matter of sapropelic type, originating from lipids of plankton biomasse residues (KODINA & GALIMOV, 1985). The bitumen fractions are isotopically similar to each other too (Table 3).

The benzene-soluble fraction which is intermediate in its polarity is the most depleted in the light carbon isotope. A similar picture is observed in many oil shales and oil-source rocks which contain isotopically light planktonogenic organic matter (GALIMOV, 1986). This is examplified by the core samples of oil-source



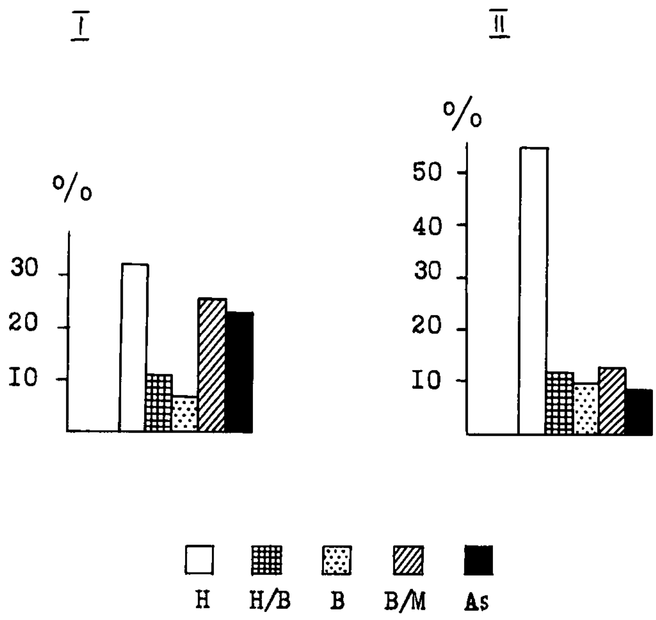
Text-Fig. 3.
Carbon isotope distribution of bitumen fractions from the bituminous marl sample Bächental AL16 (1) and oil-source rock sample from Salym oil deposit, West Siberia, J_{3v} (2).
Explanation of the fractions: As = asphaltenes; B/M = benzene-methanol soluble resins; B = benzene soluble fraction; H/B = hexane-benzene soluble fraction; H = hexane soluble fraction.

Table 3.
Carbon isotope composition of the organic matter fractions from bituminous marl sample Bächental AL16.

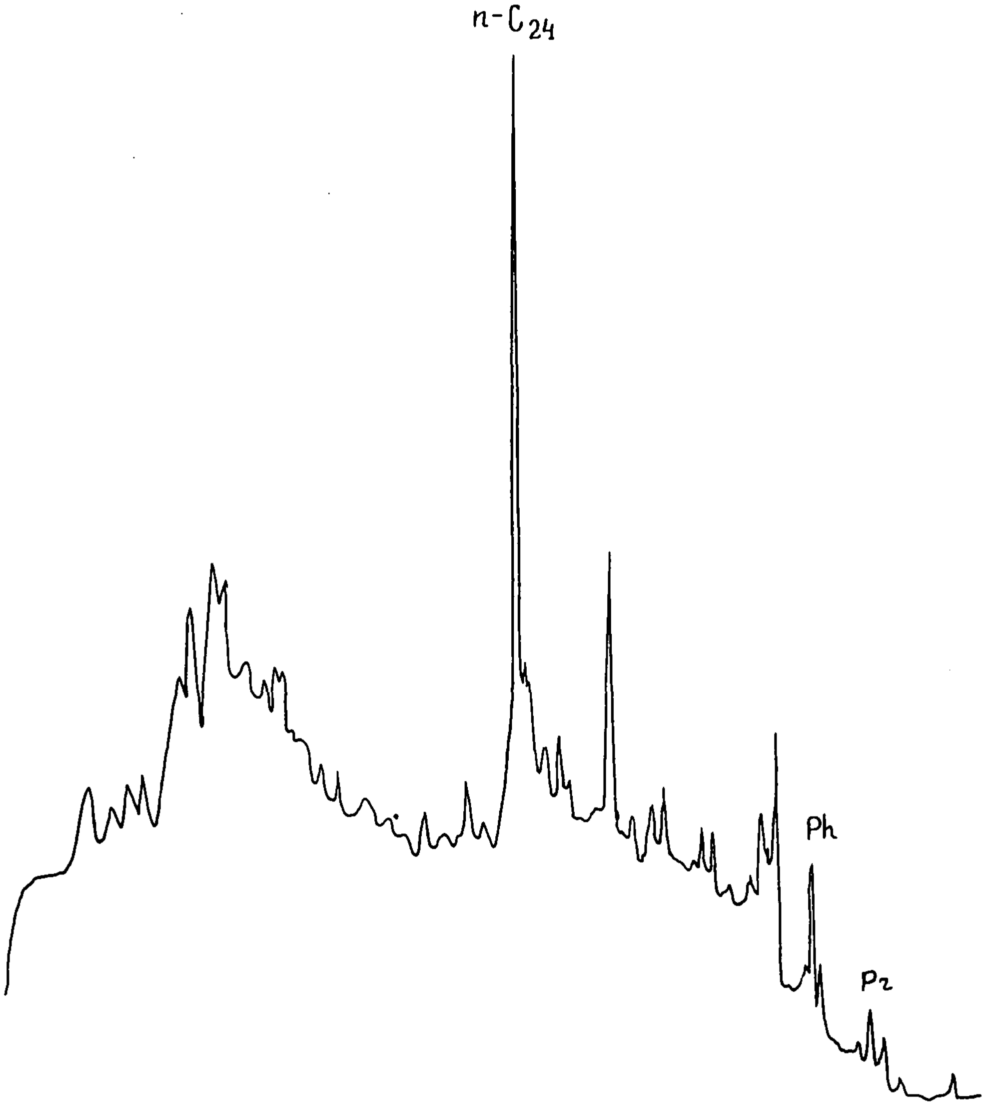
Fraction	Kerogen	Bitumen (total)	Bitumen fractions				
			Asphaltenes	Benzene-methanole-soluble	Benzene-soluble	Hexane-benzene-soluble	Hexane-soluble
$\delta^{13}C$, per mille	−32.2	−31.7	−31.8	−31.4	−30.8	−31.2	−31.7

rock from Bazchenovskaja suit (Volgian stage of the Upper Jurassic) in Salym oil-field, West Siberia. In Text-Fig. 3 two curves are presented, which show the carbon isotope distribution between the bitumen fractions of the bituminous rock under study and oil-source rock mentioned above. The established distribution of carbon isotopes in the bitumen fractions is peculiar to the sapropelic-type organic matter which is deposited under O_2-depleted conditions with abundant incorporation of phytoplankton biomasse residues in sediments. The principal source of organic matter are unicellular, organic-walled green or blue-green algae, deprived of protective mineralized cell walls. As a consequence the most susceptible substances such as proteins and carbonhydrates, which are mostly enriched in the heavy carbon isotope fraction are mostly microbially destructed, and lipids are accumulated in sediments, oxidatively polymerized with formation of the isotopically light, lipid-rich kerogen corresponding to I- or II-types of kerogens, according to TISSOT's classification (KODINA & GALIMOV, 1985; GALIMOV, 1986).

Comparing the two curves (Text-Fig. 3) we can see their similarity. It is indicative of the common facial-genetic type of organic matter in the two cases. However, the distinction between the two curves is quite obvious. The distinction consists in the following: The hexane bitumen fraction of sample AL 16 is isotopically



Text-Fig. 4.
Percentage of the bitumen fractions in the bituminous marl sample Bächental AL16 (1) and oil-source rock sample from West Siberia (2).
Explanation of the fractions as in Text-Fig. 3.



Text-Fig. 5.
Chromatogram of the hexane soluble fraction from sample Bächental AL16, with n-C_{24} added as an internal standard.

heavier than asphaltenes, whereas in an oil-source rock bitumen the hexane fraction is sufficiently more enriched in the light isotope, than asphaltenes are. There is a difference in the fractional composition of both bitumens too. As follows from Text-Fig. 4, the percentage of hexane fraction in the bituminous marl is sufficiently lower, but of the asphaltenes and benzene-methanol resin fraction it is correspondingly higher than in an oil-source rock. The differences stated above may result from one of two following phenomena:

1) Migration of the more labile and less polar part of bitumen enriched in the light carbon isotope
   or
2) biodegradation and other hypergenic activities.

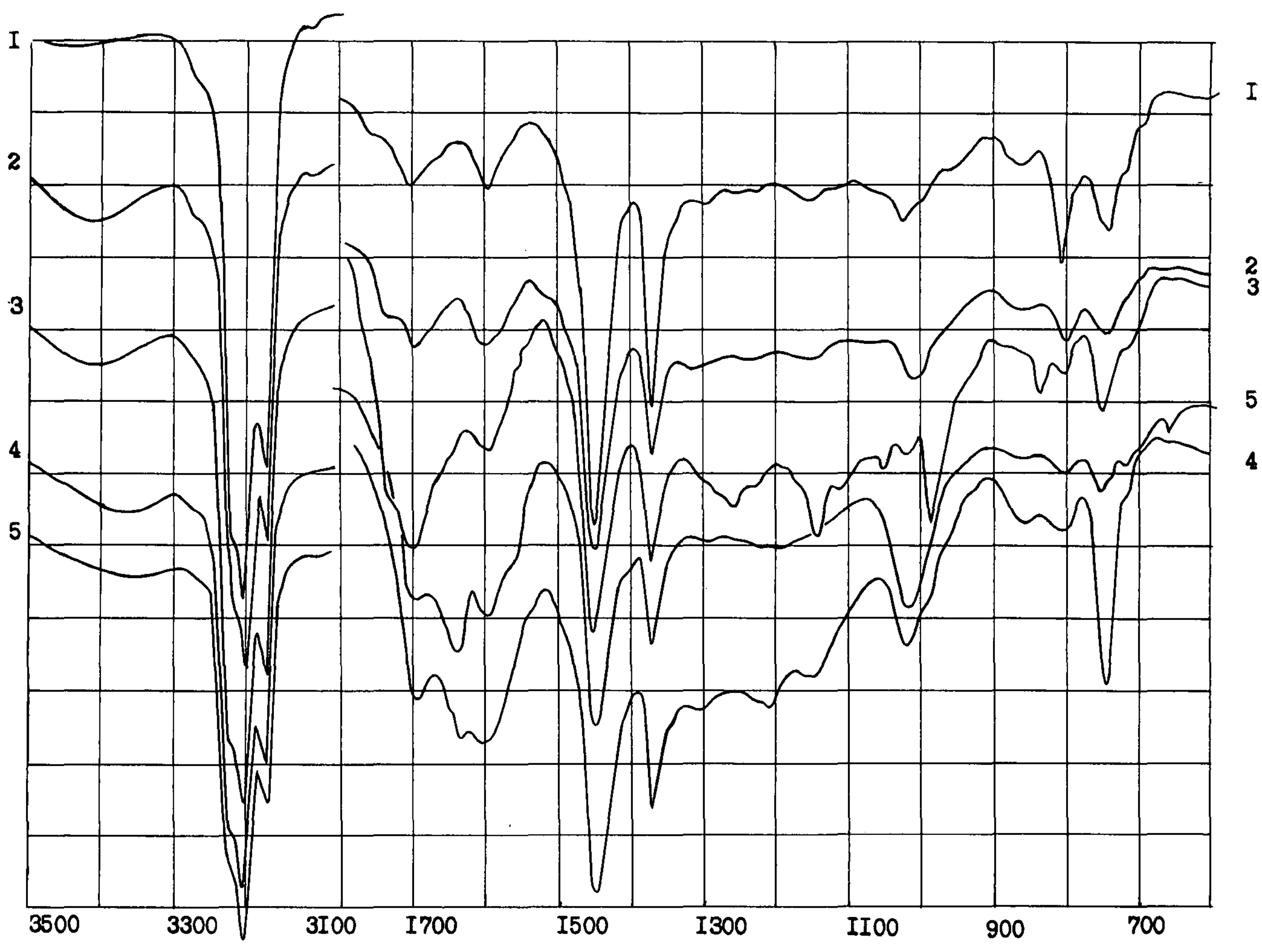
It is known that the most isotopically light oil compounds, the n-alkanes, are mostly susceptible to microbial attack. In microbially altered oils n-alkanes disappear in the first place. The chromatographic investigation of the hexane fraction of the Bächental bituminous marl shows a picture which is very similar to biodegraded oil (Text-Fig. 5). n-Alkanes are almost entirely absent, iso-alkanes are only partly preserved. A large two-peaked unresolved hump on the chromatogram gives evidence of a high proportion of branch-chain cyclic and aromatic molecules in the fraction. The same is evident from IR-data.

3.2.2. Molecular Structure of Organic Matter

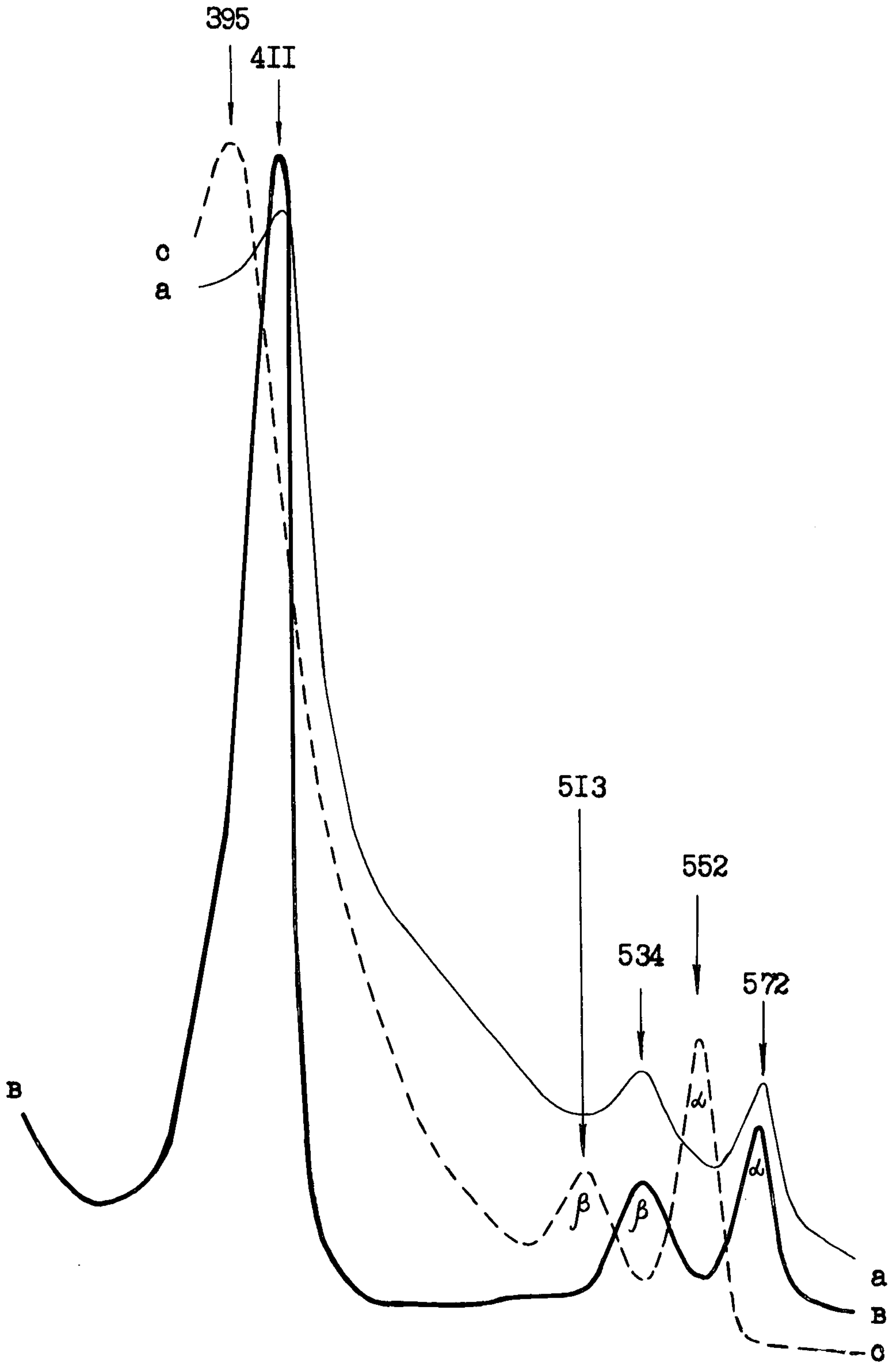
Infra-red spectroscopy is one of the several important techniques for the elucidation of molecular structure of organic matter. As can be seen in Text-Fig. 6, saturated hydrocarbons are abundant in the hexane-soluble fraction. The presence of methyl and methylene groups (CH_3 and CH_2) gives strong absorption bands in the regions 2960–2860, 1460 and 1370 cm^{-1}. However, long-chain paraffinic molecules (n-alkanes) are in subordinate position: the deformation vibration band of CH_2-groups in compounds containing the methylene chain – $(CH_2)_n$ – where $n \geq 4$, is strongly reduced.

Aromatic compounds do not give strong absorption pattern in the regions 750-870, 1600 and 3050 cm^{-1}. Oxygen-containing groups are not representative of this nonpolar fraction (weak absorption in the regions 3100–3500, 1700, 1000–1200 cm^{-1}). An aliphatic nature of the matter is manifested in the spectra of all the rest bitumen fractions. But by the transition from the nonpolar hexane fraction to the most polar benzene-methanol resins appears an enhancement of the O-, N-, S- containing groups as it is seen from strong complex absorption in the region 1500–1800 cm^{-1} being especially strong for the benzene-methanol fraction.

A further peculiarity in molecular composition of organic matter of bituminous shales is revealed by visible



Text-Fig. 6.
IR-spectra of the bitumen fractions, sample Bächental AL16.
1 = hexane soluble fraction; 2 = hexane-benzene soluble fraction; 3 = benzene soluble fraction; 4 = benzene-methanol soluble fraction; 5 = asphaltenes.



Text-Fig. 7.
Visible absorption spectra of the bitumen in total sample Bächental AL16 (a), benzene soluble fraction of the bitumen (vanadyl porphyrins) (b), and hexane-benzene soluble fraction of the bitumen (Ni-porphyrins) (c) in chloroform solution.

spectroscopy. It is a high content of metalporphyrins, which give rise to the bright orange-red colour of the bitumen in solution. In Text-Fig. 7a the absorption (electronic) spectrum of the bitumen in total is given. The absorption bands in the regions 410, 530 and 570 nm are characteristic of vanadyl prophyrins which are dominating in the sample. Vanadyl prophyrins are concentrated in the benzene-soluble fraction (Text-Fig. 7b) by the column chromatographic fractionation of the bitumen, whereas less polar nickel porphyrins appear in the hexane-benzene soluble fraction (Text-Fig. 7c). The spectrum has maxima in the shorter-wave regions (395, 513, 552 nm). From the ratio of the band α and β-intensities it is possible to conclude that along with the etio-porphyrins also DPEP-porphyrins are present in the specimen. In the molecule of the latter the isocyclic ring is present which is inherited from the bioprecursor chlorophyll molecule. Enrichment of organic matter in porphyrins along with high sulfur content is considered to be an evidence of anoxic condition and reductive diagenesis in sediment (DEMAISON & MOORE, 1980). It is necessary to note, however, that it doesn't include stagnation during sedimentation, which is proved by the presence of perylene, which was detected by the visible-spectroscopy in the hexane fraction (absorption maxima 408, 428, 435 nm). The absence of copper porphyrins (ESR data) in the bitumen is considered to be an indication of the absence of noticeable terrigeneous input in the sediment (BAKER & LOUDA, 1984). Large predominance of vanadyl porphyrins over nickel complexes, the presence of trace of the freebase porphyrins are indicative of the soft thermal regime during all the period of sedimentation and geological history of the sediment.

3.3. Conclusions

The data presented above describe the organic matter of one of the main types of Austrian bituminous rocks, namely of the bituminous Bächental marls. There is, however, not enough material so far for general conclusions on organic geochemistry of bituminous rocks of Austria. It will be a matter of future concern.

Nevertheless, the data show an experimental approach and information character of the molecular-isotopic method in organic geochemistry, which is being developed in the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the U. S. S. R. The data reveal some specific features of the definite facial-genetic type of organic matter on one hand and its geochemical transformation of the organic-rich sediments of ancient Tethys during the stage of hypergenesis on the other.

The organic matter of Bächental bituminous marls is a representative of sapropelic-type matter, which is composed of aliphatic structures. Geochemically mature aliphatic kerogen produces a lot of bitumen enriched in aliphatic compounds, too. The sapropelic nature of the organic matter of the Bächental bituminous marl is manifested in the enrichment of $C_{org.}$ in the light carbon isotope fraction and pattern of carbon isotopes distribution between the bitumen fractions and confirmed by IR-spectra and specific composition of macro- and microelements. High yield of bitumen that is extremely rich in geochemically mature petroporphyrins – Ni and VO-complexes – is considered to be a geochemical sign of the high maturation degree of sediment.

Sediments which contain high concentration of planktonogenic sapropelic organic matter are formed in marine or epicontinental basins in low-energy environments, with a low O_2-content in subbottom water and high surface productivity. In accordance with the litho- and biofacies data for the Bächental Schichten an outer neritic/pelagic depositional environment can be postulated.

Favourable conditions for organic matter preservation and accumulation arose in the ancient Tethys repeatedly and were rather prolonged as indicated by numerous occurrences of high-bituminous beds in the Austrian Alps.

Other special features of the bitumen are some peculiarities in its composition related to influence of the factors of hypergenesis and biodegradation in the first place. The peculiarities are evident in enrichment of the hydrocarbon fraction by the heavy carbon isotope at the expense of elimination of n-alkanes resulting in the specific deformation of the isotopic-fractional curve.

n-Alkanes are the most isotopically light bitumen compounds and at the same time they are the most microbially susceptible fraction. Relatively high contents of the polar, oxygen-bearing compounds in bitumen, as can be seen from IR-spectra, are considered to be a consequence of oxidative processes in the zone of hypergenesis.

Extensive migration of fluid bitumen is peculiar to carbonate rocks. Numerous fissures and voids in carbonate matrix are usual migration ways. Sometimes they are filled up with fluids. In some cases an outstanding high bitumen concentration is observed. Examples are numerous in the Seefeld samples. The bitumen migration through micro- and macrofissures is not accompanied by chemical and isotopic fractionation as it is often observed in clays during specific capillar diffusion. The data presented above show, that the most organic-rich carbonate rocks are mostly enriched in clay minerals.

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References

ALBRECHT, Gebr.: 80 Jahre Tiroler Steinölwerke. Die Steinölbrenner vom Bächental in Pertisau am Achensee. – 28 p., Pertisau 1984.

BAKER, E. W. & LOUDA, J. W.: Highly alkylated copper and nickel etioporphyrins in marine sediments. – Organic Geochem., **6**, 183–193, 1984.

BITTERLI, P.: Studien an bituminösen Gesteinen aus Österreich und benachbarten Gebieten. – Erdöl-Z., **78**, 405–416, Wien 1962.

BRANDNER, R. & POLESCHINSKI, W.: Stratigraphie und Tektonik am Kalkalpensüdrand zwischen Zirl und Seefeld in Tirol (Exkursion D am 3. April 1986). – Jber. Mitt. oberrhein. geol. Ver., N. F., **68**, 67–92, 12 figs., Stuttgart 1986.

BRUMSACK, H.J.: Geochemistry of Cretaceous black shales from the Altantic Ocean (DSDP Legs 11, 14, 36 and 41). – Chem. Geol., **31**, 1–25, 1980.

CHILINGAR, V., BISSEL, H. J. & FAIRBRIDGE, R. W. (eds.): Carbonate Rocks – Physical and Chemical Aspects. – Vol. **2**, Amsterdam – London – New York (Elsevier) 1967.

CZURDA, K.: Parameter und Prozesse der Bildung bituminöser Karbonate (Bituminöser Hauptdolomit). – Mitt. Ges. Geol. Bergbaustud., **21**, 235–250, Innsbruck 1972.

DALLATORRE, K. W. von: Zur Geschichte der Ichthyolgewinnung in Seefeld (Tirol). – Tiroler Heimatblätter, **4**, 162–165, Innsbruck 1926.

DEMAISON, G. J. & MOORE, G. T.: Anoxic environments and oil source bed genesis. – Amer. Ass. Petrol. Geol. Bull, **64**, 1179–1209, Tulsa 1980.

DOLPHIN, D. (ed.): The Porphyrins. – Vol. 1, New York (Academic Press) 1978.

FISCHER, G.: Über die Bitumenmergel von Seefeld in Tirol. – Geol. Jb., **74**, 63–74, Hannover 1957.

FRUTH, J. & SCHERREIKS, R.: Hauptdolomit – sedimentary and paleogeographic models (Norian, Northern Calcareous Alps). – Geol. Rdsch., **73**, 305–318, 14 figs., Stuttgart 1984.

GALIMOV, E. M.: $^{13}C/^{12}C$ in Kerogen. – In: DURAND, B. (Ed.): Kerogen, 271–299, Paris (Editions Technip) 1980.

GALIMOV, E. M.: Biological Fractionation of Isotopes. – New York (Academic Press) 1984.

GALIMOV, E. M.: Isotopic method of oil source rocks identification examplified by some oil fields in the U. S. S. R. – Izvestija Akademii Nauk U. S. S. R., Ser. Geol., No. **4**, 3–22, Moscow 1986 (in Russian).

GRÄF, W.: Ablagerungen der Gosau von Kainach. – In: FLÜGEL, H. W. (ed.): Erläuterungen zur Geologischen Wanderkarte des Grazer Berglandes 1 : 100.000. – 83–102, Wien – Graz 1975.

GÜNTHER, W. & TICHY, G.: Die Ölschieferschurfbaue im Bundesland Salzburg. – Mitt. Ges. Salzburger Landeskunde, **119**, 375–381, Salzburg 1979.

HALLAM, A.: Mesozoic marine organic-rich shales. – In: BROOKS, J. & FLEET, A. J. (eds.): Marine Petroleum Source Rocks. – Geol. Soc. Spec. Publ., **26**, 251–261, London 1987.

HEINRICH, M.: Ölschiefer. – In: OBERHAUSER, R. (ed.): Der Geologische Aufbau Österreichs, 547–548, Wien – New York (Springer) 1980.

HRADIL, G.: Über "Dirschenit" und die Verbreitung des Bitumengehaltes im Ölschiefer von Seefeld in Tirol. – Petroleum, 25. Jg., Nr. 14, 431–436, Berlin 1929.

HRADIL, G.: Die Ölschiefer Tirols. – Veröff. Mus. Ferd., **26**, 25–32, Innsbruck 1949.

HRADIL, G. & FALSER, H. v.: Die Ölschiefer Tirols. – VIII+121 p., Leipzig 1930.

HUTTON, A. C.: Petrographic Classification of Oil Shales. – Internat. J. Coal Geology, **8**, 203–231, Amsterdam 1987.

ISSER, M. von: Die Bitumenschätze von Seefeld. – Berg- und Hüttenmänn. Jb., **36**, 1–31, Wien 1888.

JENKYNS, H. C.: The Early Toarcian and Cenomanian–Turonian anoxic events in Europe: comparisons and contrasts. – Geol. Rdsch., **74**, 505–518, Stuttgart 1985.

JENKYNS, H. C. & CLAYTON, Ch. J.: Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic. – Sedimentology, **33**, 87–106, 14 figs., Oxford etc. 1986.

KLEBELSBERG, R. v.: Geologie von Tirol. – XII+872 p., Berlin (Gebr. Borntraeger) 1935.

KODINA, L. A. & GALIMOV, E. M.: Origin of carbon isotope composition in organic matter of humic and sapropelic types in marine sediments. – Internat. Geochem., **2**, 87–100, Moscow 1985.

KRATOCHVIL, H. & LADWEIN, H. W.: The Vienna Basin hydrocarbon source rocks and their importance for future exploration. – Erdoel-Erdgas, **100**, 107–115, 18 figs., Hamburg 1984.

KURRE, B.: Ölschiefergewinnung in den Alpen. – Petroleum, **31**, No. 7, 4–6, Berlin 1935.

NERUTCHEV, S. G.: Uranium and Life in the Earth History. – Leningrad (Nedra) 1982 (in Russian).

PLÖCHINGER, B. & OBERHAUSER, R.: Ein bemerkenswertes Profil mit rhätisch-liassischen Mergeln am Untersberg-Ostfuß (Salzburg). – Verh. Geol. B.-A., 275–283, Wien 1956.

SANDER, B.: Über bituminöse Mergel. – Jb. Geol. Staatsanst., **71**, 135–148, Wien 1921.

SANDER, B.: Bemerkungen zur Petrographie der Häringer Bitumenmergel. – Jb. Geol. B.-A., **72**, 147–150, Wien 1922.

SANDER, B.: Über bituminöse und kohlige Gesteine. – Mitt. Geol. Ges. Wien, **15**, 1–50, Wien 1922.

SCHNABEL, W. & DRAXLER, I.: Sedimentologische, palynologische und Nannofossil-Untersuchungen in der Inneralpinen Molasse des Unterinntales unter besonderer Berücksichtigung von Umlagerungsfaktoren. – N. Jb. Geol. Paläont. Abh., **151**, 325–357, Stuttgart 1976.

SOLTI, G.: Prospection and utilization of alginite and oil shale in Hungary. – In: Neogene Mineral Resources in the Carpathian Basin, VIIIth RCMNS Congress, 503–517, Budapest 1985.

SOLTI, G., LOBITZER, H. et al.: Aufsuchung von Alginit in Österreich. Bericht 1986 über die österreichisch-ungarische Zusammenarbeit in der Ölschiefer/Alginit-Forschung. – VIII+176 p., (unpublished report) Budapest – Wien 1987.

TISSOT, B. P. & WELTE, D. H.: Petroleum Formation and Occurrence. A New Approach to Oil and Gas Exploration. – XVIII+538 p., Berlin – Heidelberg – New York (Springer Verlag) 1978.

TOLLMANN, A.: Analyse des klassischen nordalpinen Mesozoikums. Stratigraphie, Fauna and Fazies der Nördlichen Kalkalpen. – XV+580 p., Wien (Deuticke) 1976.

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