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Basics and Application of Rock-Eval/TOC Pyrolysis: an example from the uppermost Paleocene/lowermost Eocene In The Basque Basin, Western Pyrenees

Fundamentos y Aplicación de la Pirólisis Rock-Eval/TOC: un ejemplo del Paleoceno final/Eoceno basal de la Cuenca Vasca, Pirineos Occidentales

PALABRAS CLAVE: Materia orgánica sedimentaria, Pirólisis Rock-Eval/TOC, Paleoceno final/Eoceno basal, Cuenca Vasca.

GAKO-HITZAK: Materia organiko sedimentarioa, Rock-Eval/TOC Pirólisis, Paleozeno goien/Eozeno behearena, Euskal Arroa.

KEY WORDS: Organic sedimentary matter, Rock-Eval/TOC Pyrolysis, uppermost Paleocene/lowermost Eocene, Basque Basin.

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RESUMEN:

Se han recogido un total de 18 muestras para la realización de pirólisis Rock-Eval/TOC en cuatro secciones representativas del final del Paleoceno y el comienzo del Eoceno en la Cuenca Vasca (secciones de Ermua, Aixola, Alto de Trabakua y Zumaia). El análisis de estas muestras se ha realizado con el fin de definir la cantidad y tipo de materia orgánica a lo largo de la sucesión estratigráfica que incluye el límite Paleoceno/Eoceno.

De las cuatro secciones, se ha escogido la de Ermua para el análisis de pirólisis detallado (10 muestras), habiéndose establecido previamente su datación y caracterización en base a palinomorfos. Todas estas muestras han presentado unos valores bajos en el contenido Total de Carbono Orgánico (TOC), Índice de Hidrocarburos Generados (S2), Índice de Producción (PI) e Índice de Hidrógeno (HI). De las 8 muestras restantes correspondientes a las otras tres secciones, se han obtenido valores similares en todas menos en una de la sección de Aixola. Esta muestra presenta un valor de TOC de 2.5% en peso y un temperatura máxima (Tmax) alrededor de 450° C, conteniendo por lo tanto materia orgánica madura.

A pesar de que todas las muestras recogidas corresponden a facies marinas profundas, el análisis de pirólisis ha revelado un origen continental para la materia orgánica que contienen. El medio ambiente en que se depositaron estas rocas estaba bien oxigenado y la productividad orgánica era baja. Atendiendo a los datos obtenidos de la maduración, y al contenido y tipo de materia orgánica, solo pequeñas cantidades de gas se podrían haber generado a partir de estos materiales.

ABSTRACT:

Eighteen samples from four uppermost Paleocene-lowermost Eocene outcrop sections (Ermua, Aixola, Trabakua Pass, and Zumaia) were collected in the Basque Basin for Rock-Eval/TOC pyrolysis. The analysis of these samples intends to define the organic matter amount and type across the Paleocene/Eocene boundary contained in rocks of this stratigraphic position.

The Ermua section was selected for detailed pyrolysis analysis after micropaleontological characterisation and datation. Ten mudstone samples from the Ermua section were analysed. All these samples showed very low Total Organic Carbon (TOC), S1, S2, and Hydrogen Index (HI) values. Eight mudstone samples were analysed from the other three sections and yielded pyrolysis values very similar to most of those from the Ermua section. These samples showed low TOC, S1, S2, and HI values. However, one sample from the Aixola section contains about 2.5 wt. % of TOC and shows a Tmax value around 450° C and, thus, this sample contains mature organic matter.

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Despite the deep-marine origin of all the samples of this study their organic matter has a marked terrestrial character as reflected by the pyrolysis data. These data indicate that the environment was well oxygenated and there was no major organic production. Owing to the maturation level, organic content, and type, only small amounts of gas could be generated.

LABURPENA

Euskal Arroko Paleozeno goien/Eozeno behereneko lau mendi-sekzioetan (hain zuzen, Ermua, Aixola, Trabakuako Gaina. eta Zumaian) 18 lagin bildu ziren Rock-Eval/TOC pirolisi azterketa burutzeko. Paleozeno/Eozeno mugaren ondoko harri sedimentarioen materia organikoaren kantitate eta moeta finkatzeko bete zen ikerlan hau.

Karakterizazio eta datazio palinologikoaren ondorioz Ermua sekzioa aukeratu zen pirolisi azterketa zehatz batetarako. Sekzio honetako harbeletako hamar lagin aztertu ziren. Lagin guzti hauek Karbono Organiko Totala (TOC) zein Sortutako Hidrokarburo (S₂), Produkzio-Indize (PI) eta Hidrogeno-Indize (HI) txikiak eman zituzten. Bestalde, beste hiru sekzioetako harbeletako zortzi lagin aztertu baziren ere lagin gehienetan Ermuko laginen pareko emaitzak lortu ziren. Zortzi lagin hauetako zazpiren TOC, S₂ eta PI baloreak oso txikiak izan ziren. Aldiz, Aixola sekzioko lagin batetan TOC balorea pisuaren 2.5% zen eta Tmax temperatura-balorea 450° C inguru agertu zen. Beraz, azken lagin honek arroko materia organikoa heldua dela azaltzen digu.

Ikerketa honetako lagin guztiak itsasokoak badira ere, bertan daukaten materia organiko, gehiena lehorrekoa dela adierazten du azterketa pirolitikoak. Halaber, ingurunea ongi oxigenaturik zegoela eta materia organiko gutxi sortzen zela ere erakusten du laginen pirolisiak. Bestalde, heldutasun organikoaren maila, edukin organikoa eta materia-moeta kontutan harturik gasa besterik ez da sortu harri hauetatik, eta gainera kantitate txikian.

INTRODUCTION

This study reviews the basics of accumulation and preservation of organic matter in sedimentary rocks, the generation of hydrocarbons, and the application of the Rock-Eval/TOC pyrolysis technique to the characterisation of sedimentary organic matter. Also an example of the use of the pyrolysis technique is presented herein through the study of the organic matter content of the uppermost Paleocene/lowermost Eocene in the Basque Basin.

The latest Cretaceous-early Eocene Basque Basin constituted an interplate deep-water trough surrounded by shallow carbonate shelf areas (North Iberian Platform and Aquitaine Platform) except on its western opening towards the present day Bay of Biscay (PLAZIAT, 1981). The general and detailed stratigraphy, paleogeography, and biostratigraphy of the Paleogene for this basin have been previously described (PUJALTE et al., 1989, 1993a, and 1993b; ORUE-ETXEBARRIA, 1983; BACETA et al., 1991a and 1991b; ROBADOR et al., 1991) and they will not be discussed further in this paper.

The four sections (Ermua, Aixola, Trabakua Pass, and Zumaia) covered in this study (Fig. 1) represent Paleocene/Eocene basal deposits. The former two sections correspond to a carbonate solpe apron on the base-of-slope of the North Iberian Platform and the latter two represent the basin-floor environment. All four sections largely consist of hemipelagic limestones, marlstones and claystones. However, some calcareous and siliciclastic turbidites interbeds occur in the Ermua and Aixola sections (Fig. 2).

The objective of this study was to obtain basic information about the type and amount of organic matter contained in rocks of the uppermost Paleocene/lowermost Eocene interval of the Basque basin (Fig. 1) to study any possible changes across the Paleocene/Eocene boundary that could be reflected by the organic matter type and composition. The four sections (Ermua, Aixola, Trabakua Pass, and Zumaia) were sampled for Rock-Eval Pyrolysis

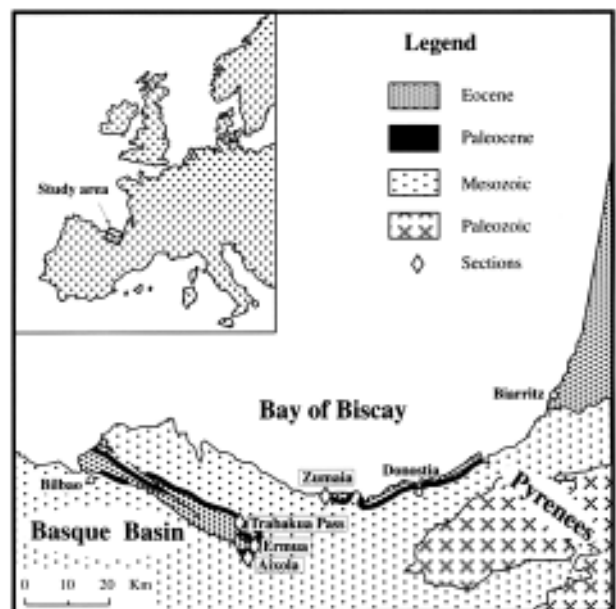


Fig. 1. Location map of study area (Northern Iberian Peninsula). The sections analysed in this study are: Ermua, Aixola, Trabakua Pass, and Zumaia. Only major stratigraphic units are presented on the geological map. Major cities (Bilbo, Donostia, and Biarritz) presented for geographical reference only.

analyses. The information obtained from these analyses will reinforce ongoing previous micropaleontological studies based on micro and macroforaminifera, calcareous nannoplankton, and palynology.

Palynological analyses only permitted the establishment of the age of the Ermua section which includes the Paleocene/Eocene boundary as defined in other European localities. This palynological datation is based on comparison with palynomorph ranges and zonation schemes from other European sections (CARO, 1973; CAVALIER and POMEROL, 1983; COSTA and DOWNIE, 1976 and 1979; POWELL, 1992). However, the palynological recovery was poor for the Aixola, Trabakua, and Zumaia sections and no detailed datation was possible.

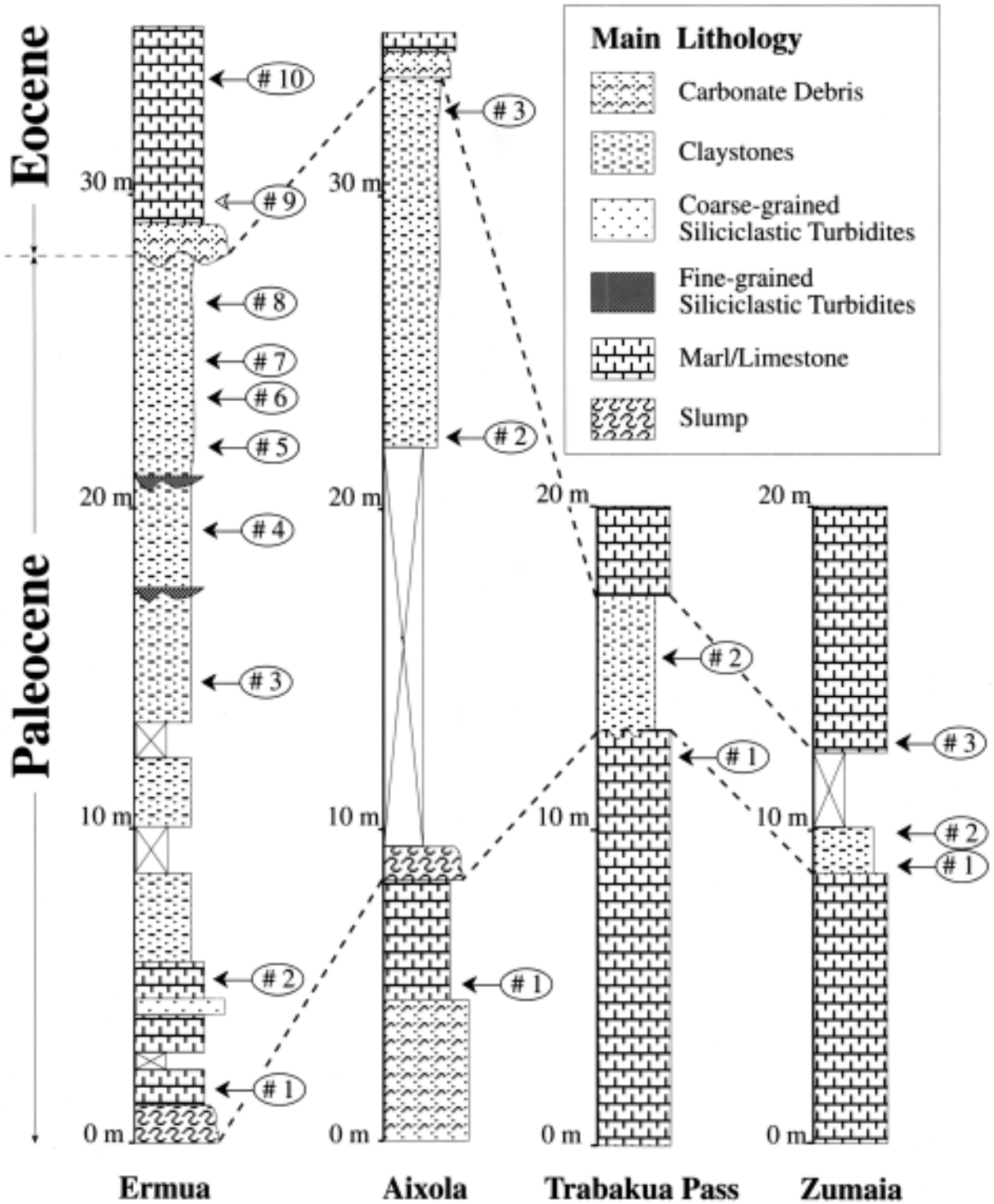


Fig. 2. Simplified lithological representation of the four uppermost Paleocene/lowest Eocene sections covered in this study. Crossed blank areas represent covered intervals; encircled numbers correspond to pyrolysis samples. The entire Aixola, Trabakua Pass, and Zumaia sections can be roughly correlated to the uppermost Paleocene as defined for the Ermua section.

ORGANIC MATTER CONTENT: BASIC INTERPRETATIONS

Basically all sedimentary rocks contain organic matter and although a few unusual occurrences of hydrocarbons may have an inorganic origin, practically all economic petroleum accumulations originated from organic matter deposited with sedimentary rocks. The occurrences of hydrocarbon accumulations in igneous and metamorphic rocks are linked to sedimentary source beds and posterior migration and accumulation in crystalline rocks. Any organic matter will generate gas if buried deeply enough but at intermediate depths the type of organic matter exercises primary control over the nature of the petroleum products.

To know if a sedimentary rock may have any petroleum potential laboratory analyses of the organic compounds contained in the rock are necessary. A problem with evaluating natural samples is that some of the products generated are lost during the thermal maturation process that occurs in the subsurface, and only the remaining organic matter is available for analysis in the laboratory (HARWOOD, 1982). In the subsurface, hydrocarbons are produced by thermal alteration of the organic matter at temperatures between 50° and 175° C through a long period of time. The substitution of the natural conditions by unnaturally high temperatures in the laboratory is necessary so that hydrocarbons can be produced over practical periods of time. Despite these deviations from natural conditions, the laboratory results appear to be generally comparable to those resulting from natural catagenesis and therefore are useful in interpreting natural data (HARWOOD, 1982). However, if the entire organic matter contained in a sedimentary rock has already been spent for the formation of hydrocarbons and if this sedimentary rock has already undergone high temperatures only carbon-rich compounds such as heavy condensed residues and graphite will remain in the rock, and no further hydrocarbons will be obtained in the laboratory (TISSOT et al., 1971).

The Rock-Eval Pyrolysis method is the most basic organic geochemical analysis of sedimentary organic matter. Laboratory pyrolysis of the organic matter in sedimentary rocks aims to parallel the changes in the subsurface (BAJOR et al., 1969) and provides a useful technique for characterising organic matter. In this study this method is intended as a primary laboratory analysis of the organic matter of the stratigraphic units across the Paleocene/Eocene boundary. This provides a base for further geochemical analyses. More complete information on the hydrocarbon potential of the units included in this study would be obtained by combining the pyrolysis data with kerogen elemental composition analysis, vitrinite reflectance, and gas chromatography.

The pyrolysis method is based on a steady heating of rock samples so that the total evolved hydrocarbons can be monitored as a function of temperature. In fact, pyrolysis is the thermally induced break-up of large molecules to give lower molecular weight products (BARKER, 1979). The hydrocarbons naturally produced and already stored in the rock, are released at temperatures lower than the ones needed to break down the kerogen to produce more hydrocarbon. Thus, laboratory monitoring of the hydrocarbons released by steadily increasing temperature provides a way of obtaining the amount of generated hydrocarbons relative to the total potential to generate.

The natural petroleum generation process can be simulated in the laboratory by heating rock samples in the absence of oxygen, but then it is necessary to use experimental temperatures considerably higher than those normally found in the subsurface so that appreciable reaction can occur in a reasonably short time. This is the basis for the various pyrolysis techniques used to characterise the organic matter in sedimentary rocks (BARKER, 1974). Usually the process of generation of hydrocarbons is incomplete at depths of interest to the petroleum industry so that when shale samples are heated in the laboratory, they still release hydrocarbons. This release includes the most volatile elements, namely the hydrocarbons which already have been generated in the subsurface and that are stored in the pores of the rock, as well as newly produced hydrocarbons caused by the thermal breakdown of kerogen. The hydrocarbons already present are represented as S1 in pyrolysis and the hydrocarbons produced during pyrolysis are known as S2. These processes can be monitored by heating the samples in a stream of helium which sweeps the evolved hydrocarbons into a flame-ionisation detector. The hydrocarbon release curve, thus, show two peaks, the first one for the hydrocarbons S1 already present in the rock and the second one for those hydrocarbons S2 thermally induced by the pyrolysis process. The relative amounts of S1 and S2 will depend on the type of organic matter and on the thermal energy (time and temperature) the rock has already gone through in the subsurface. The temperature reached in the subsurface is in turn controlled by depth and heat flow. The temperature needed to produce hydrocarbons in the subsurface is much lower than that used in the pyrolysis process. Yet, the temperature corresponding to the maximum production of hydrocarbons during pyrolysis of the kerogen gives an indication of maturity of the studied organic matter.

The origin of petroleum can be ascribed generally by four successive stages: (1) formation of organic-rich, fine-grained sediments through photosynthesis, deposi-

tion, and preservation of abundant organic matter; (2) thermal degradation of that organic matter during burial to increasing temperatures, with formation of petroleum molecules; (3) expulsion of oil and gas from the fine-grained source rock, and migration through and entrapment in porous permeable reservoir rock; and (4) physical, thermal, and/or biological alteration of petroleum in reservoir rock (HOOD et al., 1975). Therefore, the oil source capacity of a possible source rock depends of four factors: quantity, quality, and thermal maturity of kerogen, and expulsion efficiency of the source sequence (WAPLES, 1979).

The organic content of such sediments, which eventually become source beds of petroleum generally ranges between 0.5 and 5.0 %, with a mean around 1.5 %. The largest quantity of petroleum hydrocarbons is formed from organic matter heated for a period of time in the earth to temperatures between about 60° and 150° C.

ACCUMULATION AND DEGRADATION OF ORGANIC MATTER

When organisms die, their organic matter undergoes degradation through a variety of mechanisms. Some of these mechanisms are microbial such as the formation of methane by anaerobes, and some are purely physical or chemical, such as dehydration and oxidation. In high-energy oxygenated environments, most organic matter is consumed by benthic filter feeders and by burrowing organisms in near-surface sediments. The more resistant organic matter, including humic material, resins, waxes, and lipids are preferentially preserved. Environments that preserve unusually large amounts of organic matter are large, stagnant water areas and silled basins, where the bottom waters, owing to anoxia, are strongly reducing, for example the Black Sea. In such areas, the organic content of the sediment frequently exceeds 15.0 wt. %. At the other extreme are the red clays of the oceanic abyssal plains, where slow rates of deposition, aerobic waters, and little contribution of organic matter results in sedimentary organic content of less than 0.1 wt. % (HUNT, 1979).

Heterotrophic microorganisms, mainly bacteria, play a critical role in decomposing organic matter in the water column, in the interstitial water of sediments, and in the digestive tracts of animal scavengers. In marine basins bacterial biomass approaches that of the phytoplankton (BORDOVSKY, 1965). Bacterial degradation proceeds quickly and efficiently in aerobic water. When the oxygen supply becomes exhausted, oxidation of organic matter by anaerobic bacteria uses nitrates, then sulphates, and finally fermentation that is the least efficient mechanism of oxidation of organic matter.

Anaerobic degradation results in a more lipid-rich and more reduced (hydrogen-rich) organic residue than does aerobic degradation (FOREE and McCARTY, 1970; PELET and DEBYSER, 1977). Moreover, under such conditions, a significant fraction of the preserved organic matter consists of remains of the bacterial biomass itself (LIJMBACH, 1975).

Bacterial activity is also influenced by granulometry. Fine-grained sediments, where diffusibility of oxidising agents is restrained have lower levels of bacterial activity than coarse-grained sediments (BORDOVSKY, 1965). Therefore anoxic environments in which very fine-grained sediments are deposited have the best potential for preservation of organic matter.

ANOXIC ENVIRONMENTS AND ORGANIC MATTER ACCUMULATION

The organic content of Recent sediments can be attributed to three factors: (1) rate of organic deposition versus mineral deposition, (2) availability of oxygen, and (3) level of biological activity. The critical factor related to preservation of organic matter in the subaquatic sediments is the development of anoxicity (DEMAISON and MOORE, 1980).

The anoxic aquatic environment is a mass of water so depleted in oxygen that virtually all aerobic biologic activity has ceased. Anoxic conditions occur where the demand for oxygen in the water column exceeds the supply. Oxygen demand relates to surface biologic productivity, whereas oxygen supply largely depends on water circulation, which is governed by global climatic patterns and the Coriolis force (DEMAISON and MOORE, 1980).

Organic matter in sediments below anoxic water is commonly more abundant and more lipid-rich than under oxygenated water mainly because of the absence of benthonic scavenging. The specific cause for preferential lipid enrichment probably relates to the biochemistry of anaerobic bacterial activity. Geochemical-sedimentological evidence suggests that potential oil source beds are presently and have been deposited in the geologic past in four main anoxic settings as follows:

1. Large anoxic lakes: permanent stratification promotes development of anoxic bottom water. This anoxic environment occurs nowadays in Lake Tanganyika (DEGENS et al., 1971).

2. Anoxic silled basins: only those landlocked silled basins with positive water balance tend to become anoxic. Typical examples are the Baltic Sea (GRASSHOFF, 1975), Black Sea (DEGENS and ROSS, 1974), and Saanich Inlet of British Columbia (NISSENBAUM et al., 1972). Anoxic conditions in silled basins on oceanic shelves al-

so depend upon overall climatic and water-circulation patterns. Silled basins should be prone to oil source bed deposition at times of worldwide transgression, both at high and low paleolatitudes.

3. Anoxic layers caused for upwelling. These develop only when the oxygen supply in deep water cannot match demand owing to high surface biologic productivity. Oil source beds and phosphorites resulting from upwelling are present preferentially at low paleolatitudes and at times of worldwide transgression.

4. Open-ocean anoxic layers. These are present in the oxygen-minimum layers of the north-eastern Pacific and northern Indian oceans, far from deep, oxygenated polar water sources. They are analogous, on a reduced scale, to "worldwide anoxic events" which occurred at global climatic warm-ups and major transgression. Known marine oil source bed systems are not randomly distributed in time but tend to coincide with periods of worldwide transgression and oceanic anoxia. Evidence of worldwide oceanic anoxic events in the generally warm Mesozoic Era is indicated by remarkably widespread organic-rich black shales like those from the Late Jurassic and middle Cretaceous (SCHLANGER and JENKYN, 1976). Identical worldwide oceanic anoxic events are inferred to have prevailed intermittently in Paleozoic time because the widespread Lower Ordovician, Silurian, and Lower Carboniferous organic-rich marine black shales coincide with times of widespread marine transgression and ice cap melting (BERRY and WILDE, 1978).

Basins with a positive water balance have strong salinity contrast between fresher outflowing surface water and deeper ingoing more saline and nutrient-rich oceanic water (DEMAISON and MOORE, 1980). The development of permanent or intermittent anoxic condition is a general feature of those semi-enclosed seas which have a positive water balance. Basins with a positive water balance also act as nutrient traps, thus enhancing both productivity and preservation of organic matter. The Black and Baltic Seas would be modern examples of this type of basin.

In basins with a negative water balance, resulting from a hot, arid climate, there is a constant inflow of shallow oceanic water to compensate for high levels of evaporation. As shallow oceanic water enters, it replaces the hypersaline water which sinks and flows out as a density undercurrent into the ocean. Therefore, the basin bottom is both oxygenated and nutrient depleted. The Red and Mediterranean Seas, and the Persian Gulf constitute modern examples of this type of basins.

Bioturbation is ubiquitous under oxic water where it has been observed at all water depths, including the de-

ep-sea sediments of the abyssal realm. Under an anoxic water column, however, oxygen depletion depresses and eliminates benthonic life, and thus, there is no bioturbation of bottom sediments. Lack of bioturbation under anoxic water results in laminated and organic-rich sediments.

Silled depressions also occur in oxic open oceans. Many anoxic silled basins are suspected in the geologic record like the Lower Jurassic of Yorkshire (England). Based on the sedimentological features the apparently monotonous, 60 m thick shale sequence was subdivided into three facies: normal, restricted, and bituminous (MORRIS, 1979). These three facies occur in cycles and are indicative of variations in the position of the oxic-anoxic boundary within the water column. The section was also analysed for pyrolysis data and found that the degree of maturation of these three facies is late immature to early mature (DEMAISON and MOORE, 1980).

The normal shale facies is a homogeneous, bioturbated sediment with abundant benthic body-fossils and common sideritic nodules. This facies is indicative of well-oxygenated bottom waters. This shale contains only "gas-prone" type III kerogen (TOC: 0.66-3.40 wt. %, and HI 83-134 mg HC/g Corg).

The restricted shale facies consists of poorly laminated sediments with scattered calcareous concretions, sparse benthic fauna, and thin discrete pyritic burrows. This facies was deposited under oxygen-depleted waters. This facies contains type II and type III "mixed" kerogen (TOC: 2.59-6.75 %, HI: 135-216 mg HC/g Corg).

The bituminous shale facies is a finely laminated sediment with pyritic concretions, little or no bioturbation and a benthic fauna which is sparse and does not include burrowing organisms. This facies reflects anoxic conditions in the water column. This shale contains highly "oil-prone" type II kerogen (TOC: 5.61-11.42 %, HI: 253-584 mg HC/g Corg).

Anoxic, bituminous shales of very widespread aerial extent were also deposited during the Late Jurassic in parts of the North Sea and in the Western Siberian Basin, and during the latest Albian in the Mowry Sea of North America. These bituminous shales are linked to many important hydrocarbon source beds around the world.

SEDIMENTARY ORGANIC MATTER

The organic matter contained in sedimentary rocks may have two different provenances, continental and marine. The majority of organic matter preserved in the rocks is of vegetal origin in a broad sense, and since marine and terrestrial vegetal organisms have different

structure and elemental composition their residues are also very characteristic and can be easily identified. Continental organic matter (which gives products rich in aromatics) and marine organic matter (which produced more paraffinic hydrocarbons) can be differentiated by low temperature pyrolysis (BORDENAVE et al., 1970).

Practically all sedimentary organic matter may be classified into two major types, sapropelic and humic. The term sapropelic refers to decomposition and polymerisation products of fatty lipid organic materials such as sporomorphs, amorphous organic matter, planktonic algae, and herbal components deposited in subaquatic muds (marine or lacustrine), usually under oxygen-restricted conditions. The term humic refers to products of peat formation, mainly land plant material deposited in swamps in the presence of oxygen.

Marine organic matter is rich in amorphous material and include hydrogen-rich organic carbon. Terrestrial organic matter is rich in woody material and waxes. These elements are absent from aquatic organic matter. Wood is made up of cellulose and lignine, and smaller amounts of lipids. Cellulose can be biodegraded but the lignine is much more resistant and survives deep into the subsurface where rising temperature breaks it down into methane and ethane, and coal. Much of the gas of the southern North Sea and Holland was formed by this mechanism (LUTZ et al., 1975). On the other side, plant waxes give very long chain n-paraffins after thermal degradation and, therefore, crude oils containing high percentages of long chain paraffins have high pour points, and are generally associated with near-shore sedimentation especially in deltaic settings (HEDBERG, 1968). Kerogen of phytoplanktonic and algal origin generates the range of normal crude oils.

In the Miocene Cruse Formation of the proto-Orinoco delta all the gas fields are nearer to the shoreline than the oil fields which are located farther away from the paleoshoreline (MICHELSON, 1976). Other examples are provided by the Eocene deltaic Latrobe Formation of the Australian Gippsland Basin (HEDBERG, 1968) and the Mahakan delta (MAGNIER et al., 1975). With time deltas prograde seawards and terrestrial organic material is deposited over the previously deposited aquatic material producing a trend from oil generating to gas generating with decreasing depth.

In the aquatic environments organic matter occurs as three different forms: (1) in true solution as dissolved matter; (2) as particulate material; and (3) as colloidal material. The first one is the most abundant type. Dissolved organic matter is adsorbed by clay particles as these particles settle down. Most organic matter is incorporated directly into the sediments through this

mechanism. The colloidal organic matter first flocculates and then settles, and the particulate organic matter settles directly to the bottom. However, all organic matter types are vulnerable to organisms that feed on them, so that only relatively resistant organic matter is preserved in the sediments. Thus, the amount and type of organic matter preserved in the sediments is controlled in part by the depositional environment but also by the productivity of the waters, the sediment grain size, the physical conditions in the area of deposition, and the mineralogy of the sediments (BARKER, 1979).

Most of the organic matter in the sediments comes from the autochthonous organisms so that much organic matter is available in areas of high productivity. The principal source of aquatic organic matter is phytoplankton (BORDOVSKY, 1965) composed largely of single-cell algae residing in the uppermost layers of water illuminated by sunlight, the euphotic zone. The main limiting factor to planktonic productivity, in addition to light is the availability of mineral nutrients, particularly nitrates and phosphates, which are in short supply in the euphotic zone. Phytoplankton are intensively grazed by zooplankton. Both phytoplankton and zooplankton are then consumed by large invertebrates and fish.

The other source of organic matter in the aquatic environment is transported terrestrial organic matter from streams and rivers. Land-plant productivity is largely dependent on the amount of rainfall on supporting landmasses. Because terrestrial organic matter has undergone considerable degradation in subaerial soils prior to and during its transport, it is usually hydrogen depleted and refractory in nature.

Shallow inland seas, narrow seaways between continents, and restricted areas of quiet deposition are the typical environment for source beds of petroleum. The low-energy coastal areas and inland sedimentary basins where fine-grained clay and carbonate muds are deposited generally contain 0.5 to 5.0 wt. % organic matter and, thus, in the range of most oil-forming sediments.

TYPES OF ORGANIC MATTER

The quantity of organic matter as measured by the Total Organic Content (TOC) is the basic quantitative parameter that must be used when determining the petroleum generation potential of a stratigraphic unit. However, although organic matter content in sediments is usually estimated by a determination of organic carbon, the limiting element in the petroleum forming reaction is not carbon but hydrogen. The reason for analysing carbon, however, is that only the hydrogen bonded in organic molecules is active in the petroleum forming processes. The hydrogen content in comparison to the

carbon content is measured as the Hydrogen/Carbon (H/C) ratio. Hydrogen which is present in water or mineral phases is not active at temperatures normally associated with oil generation (below 175° C) and, therefore, does not contribute to the H/C ratio. The amount of organic hydrogen is essentially controlled by the nature of the organic matter present in the sediment, and thus, the kerogen has been broadly classified in four types (I, II, III, and IV) depending on the relative content of organic hydrogen. These four kerogen types correspond to distinct biological source materials.

Type I kerogen is derived from algal debris (Tasmanites in marine waters and Botryococcus in fresh water). The Triassic mudstones and siltstones of the Schei Point Formation of southern Ellesmere Island contain this type of kerogen (BROOKS et al., 1992). The H/C ratio of the type I kerogen is the highest for all types of kerogens and, thus, this kerogen has the highest petroleum generation potential, even though higher levels of thermal maturation are needed for the formation of hydrocarbons from type I kerogen than from the other three types of kerogen.

Type II kerogen corresponds to common marine organic matter and is derived mainly from phytoplanktonic organisms. This type of kerogen is far more common than type I and, is considered as the typical "oil" source kerogen.

Type III kerogen corresponds to "common" terrestrial organic matter and is derived from higher land plants. This type of organic matter is rich in lignin and cellulose and, unless the plant remains are enriched in cuticles, sporomorphs, or resinite, this type of kerogen only yields gas. However, if this type of kerogen is enriched with waxy materials (i.e., plant cuticles) from higher plants waxy oil can be produced from terrestrial organic matter. Despite its terrestrial origin the type III may happen to be the dominant kerogen type in a marine shale (BARKER, 1974).

The fourth type (type IV) of organic matter contains the lowest H/C level and has been defined after Pennsylvanian coal. Type IV kerogen consists mainly of black, opaque debris of angular shape which are derived from lignified precursors, such as altered woody material, highly altered mainly by oxidation and/or high levels of alteration (COPE, 1981). This type of kerogen corresponds mainly to inertinite and is often called "dead-carbon". It has no effective potential for oil and very little, if any, for gas (BROOKS et al., 1987).

MATURATION OF ORGANIC MATTER

Not only the amount and type of organic matter are important for the generation of hydrocarbons but also

the level of thermal maturation. Only dry gas and possibly heavy oil will be found in the immature facies; oil and wet gas in the mature facies; and only dry gas in the metamorphosed facies. These definitions refer only to source rock characteristics and do not take into account vertical migration of oil or gas.

The evolution of the organic matter in the rock involves a process of continuous, irreversible change, usually called "maturation" (BARKER, 1979). Temperatures and duration of exposure to various heat intensities are the most important factors controlling thermal maturation of organic matter (PHILIPPI, 1965; LOUIS and TISSOT, 1967; VASSOYEVICH et al., 1970; BOSTIC, 1973, 1974; CASTAÑO and SPARKS, 1974; CONNAN, 1974; WAPLES and CONNAN, 1976; DEROO et al., 1977, WAPLES, 1980; HÉROUX et al., 1982). The generation of petroleum hydrocarbons from thermally reactive organic matter (mainly kerogen) during burial is a part of the overall process of thermal metamorphism of organic matter and is often referred to as "organic metamorphism" (HOOD et al., 1975). This process has also been called "transformation" (DOBRYANSKY, 1963), "eometamorphism" (LANDES, 1966, 1967), "thermal alteration" (HENDERSON et al., 1968; STAPLIN, 1969), "incipient metamorphism" (BAKER and CLAYPOOL, 1970), "katagenesis" (VASSOYEVICH et al., 1970), and frequently just "maturation". There are many scales such as those based on coal rank (SUGGATE, 1959), spore and pollen carbonisation (GUTJAHN, 1966; STAPLIN, 1969), elemental composition and colour of kerogen (TISSOT et al., 1974; PETERS et al., 1982), vitrinite reflectance (MCCARTNEY and TEICHMÜLLER, 1972; SHIBAOKA et al., 1973), electron spin resonance (PUSEY, 1973a, 1973b), and chemical maturity indicators (TISSOT et al., 1974) which reflect irreversible effects of organic metamorphism. When spores are subjected to increasing temperatures and pressures in the laboratory, they undergo the colour changes observed in nature, along with size reduction, shape deformation and ultimate amalgamation and crystallisation (SENGUPTA, 1975). The reduction of spore sizes appears to occur about the same time as the blackening of spores and loss of gaseous decomposition products. Obviously as maturation is a breakdown process the lower the temperature reached in the subsurface the less mature is the organic matter contained in the rock since thermal alteration is a continuous process.

Crude oils are not equilibrium mixtures and as temperature increases they readjust towards equilibrium at an increasing rate by redistributing hydrogen. They ultimately give methane and a solid carbon-rich residue that eventually becomes graphite. Therefore, a consequence of the maturation process is that oil is only produced over a limited temperature range below which

there is no generation of oil, and above which there is only gas. This temperature range is called the "oil window" (PUSEY, 1973b). But temperature is not the only constrain of the "oil window"; time (age), and pressure (depth) constitute the other two parameters to reconstruct the oil generation range.

Also the level of thermal maturation of the organic matter contained in a rock may give important information about the features of the basin where the hydrocarbons have been formed. Therefore, one important application of studies of organic metamorphism of potential petroleum source rocks is the determination of subsurface depths and the temperatures at which oil and gas are generated from the kerogens of those rocks.

GENERATION OF PETROLEUM IN NATURE

The origin of petroleum hydrocarbons with increasing depth and temperature has been documented in many sedimentary basins. Methane is formed biogenically at the surface and accumulates in sediments along with hydrocarbons derived from the living organisms and a complex mixture of nitrogen, sulphur, and oxygen compounds which represent microbiologically degraded organic matter. Some generation of hydrocarbons occurs in the first hundred metres of burial from reactions requiring very low activation energies. The quantities are small, and it is not until the burial temperature rises to the threshold of intense generation that large quantities of hydrocarbon are formed. This threshold varies somewhat in different sedimentary basins, depending on the rate of sedimentation. In a typical basin intense oil generation might start around 50° C, peak at about 90° C, and terminate at about 175° C (BARKER, 1979).

In all sedimentary rocks, about 3 % of the organic matter is converted to hydrocarbons with an equal amount converted to nitrogen, sulphur, and oxygen compounds. The generation of hydrocarbons is more efficient in carbonates because their organic matter is almost entirely amorphous material derived from plankton. Shales have large amounts of woody and coaly material which forms fewer hydrocarbons. However, carbonates contain less organic matter than shales. Shale source rocks typically contain 0.5 to 5.0 wt. % organic carbon whereas carbonate source rocks may have as little as 0.3 wt. %. Since most rocks contain much recycled organic carbon which is carbonized and cannot produce petroleum. Some geochemists have contended that the minimum organic carbon content of source rocks should be in the 1.0-1.5 wt. % range.

About 90 % of the organic matter preserved in sediments is a high molecular weight, insoluble, polymeric material called kerogen (Fig. 3), and the rest is solvent

soluble and is called bitumen (BARKER, 1979). Bitumens are native substances of variable colour, hardness, and volatility, composed principally of the elements carbon and hydrogen and sometimes associated with mineral matter. The bitumens are also called "lipids" or simply "extractables" and are soluble in organic solvents such as benzene, methanol, and carbon disulphide. Bitumens include compounds such as the n-paraffins derived from fatty acids, waxes, hydrocarbons (saturated, unsaturated, cyclic, or aromatic), and also fats, alcohols, and pigments.

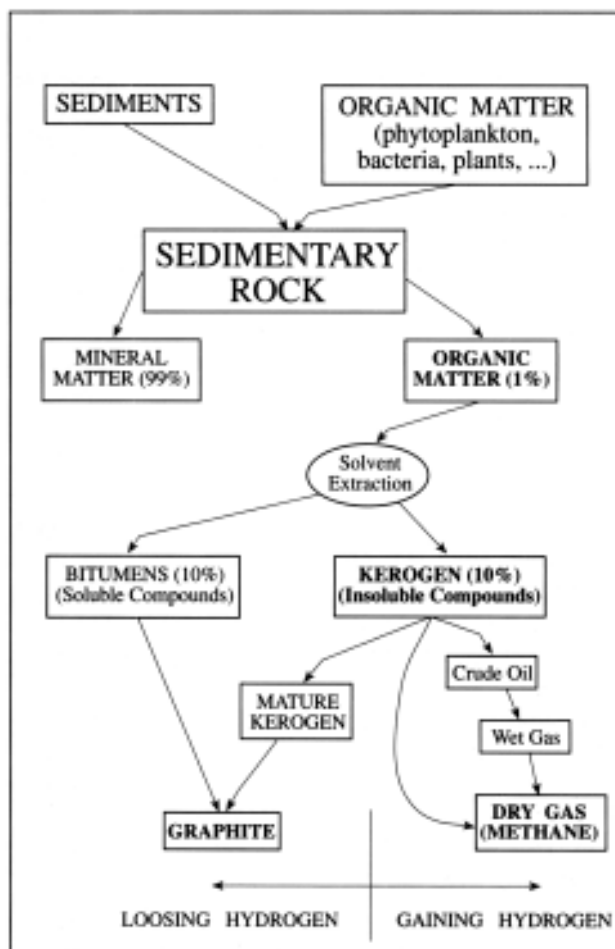


Fig. 3. Basic scheme of organic maturation process and formation of petroleum hydrocarbons in nature. This diagram has been modified after BARKER (1979) and BROOKS et al. (1987).

As temperature increases with increasing depth the kerogen gets progressively richer in carbon by becoming more condensed and developing more aromatic structures whereas the bitumen gets richer in hydrogen. The transfer of hydrogen from kerogen to bitumen, and consequently the increase in the amount of bitumens is the base of the process of petroleum generation.

Kerogens that were derived from lower plants and animals with high lipid and high hydrogen contents generate much bitumen and appear to be oil sources. In contrast, kerogens derived from remains of higher vascular plants have low lipid and low hydrogen contents, and apparently are gas sources with little capability for generation of liquid hydrocarbons.

DEFINITION OF SOURCE ROCKS

The colour of a rock is a rough, but not always reliable, indicator of its organic content. For many years the oil industry's rule of thumb has been that "black shales" are source rocks but there are many source rocks which are not black and some black shales which contain little organic matter (TRASK and PATNODE, 1942). Black colours may be caused by a high manganese oxide content or abundant micropyrite content (de GRACIANSKY et al., 1987).

Rocks that generate petroleum are "potential source rocks" and only can be classed as "source rocks" after commercial quantities of petroleum have migrated out of them. A more detailed definition of "potential source rock" was given by Dow (1977): "A unit of rock that has the capacity to generate oil or gas in sufficient quantities to form commercial accumulations but has not yet done so because of insufficient thermal alteration". Thus, "source rocks" would be those that have already generated and expelled hydrocarbons in commercial quantities. A source bed that is still in the process of generating hydrocarbons would be called "active" but if the process of hydrocarbon generation is already completed it would be called "spent source rock". The source rock may be also a "limited source rock" because it meets all the prerequisites to be a source bed except volume or an "inactive source rock" if the process of generation of hydrocarbons has stopped prior to becoming spent. A hydrocarbon-bearing rock may become a source rock based on market interests more than on the geological features of the rock because the rock has to be able to produce hydrocarbons in commercial quantities and this varies based on oil and gas prices, advances in technology, commercial and political interests, etc.

The relationship between high organic matter in the rocks and occurrence of reservoir petroleum is well documented and although some source rocks have carbon contents as high as 10 % most are between 0.8 and 2.0 %, and it seems to require a minimum of about 0.4% organic carbon to form a source rock. Potential oil source beds are organic-rich sediments containing a kerogen type that is sufficiently hydrogen-rich (type I or type II; TISSOT et al., 1974) to convert mainly to oil during thermal maturation. Kerogen type and thus oil source character in ancient sediments is identified through ele-

mental analysis of kerogen and whole-rock pyrolysis with additional support from microscopic organic analysis (TISSOT and WELTE, 1978; HUNT, 1979). Documented oil source beds and oil shales around the world always contain hydrogen-rich kerogen and fall into a range of organic carbon content between about 1wt. % and over 20% by weight (DEMAISON and MOORE, 1980).

The measurement of organic carbon in sediments alone is insufficient to identify potential oil source beds. Transported terrestrial organic matter, oxidised aquatic organic matter, and reworked organic matter from a previous sedimentary cycle can create levels of organic carbon in marine sediments up to about 4%. Yet this organic matter is hydrogen-poor, gas-prone, and without significant oil generating potential (TISSOT et al., 1974; DEMAISON and SHIBAOKA, 1975; DOW, 1977). This is essentially the organic facies that has been described in middle Cretaceous marine black shales encountered by several Deep Sea Drilling Project holes in the north-western Atlantic Basin. An identical situation is present today on the Arctic Shelf of the USSR where high organic carbon concentrations in marine sediments result from the influx of large fluvial discharge. In summary, a high TOC content in sediment is not necessarily an indication of oil source rock precursor character.

WHOLE SAMPLE ROCK-EVAL PYROLYSIS TECHNIQUE

The rock-eval pyrolysis technique followed in this study is based on the methodology described by ESPITALIÉ et al. (1977, 1985), ESPITALIÉ (1986), PETERS (1986), and RIEDEGER (1991). This technique provides data on the quantity, type, and thermal maturity of the associated organic matter. This is a simple and quick technique that can be carried out in the laboratory and in the well site since it does not require especially expensive or highly sophisticated equipment. Furthermore, the pyrolysis analyser uses whole rock samples that do not need any previous treatment.

Following this technique each sample was pulverised and 100.0 mg (+/-0.1 mg) were weighed into stainless steel crucibles. These crucibles have a fritted or screened top and bottom which allow the passage of helium carrier gas and air for oxidation through the sample. A group of 22 samples, their duplicates and intercalated standards are placed in the programmed Delsil pyrolysis unit which automatically runs them. These 48 samples are, one at a time, placed in an oven, and the generated data is sent to a connected computer set. After a sample is automatically placed in the oven, this is closed and the air purged with a flow of helium. Analysis of each sample requires about 20 min.

The sample is first heated under an inert atmosphere of helium at 300° C for 3-4 min and then pyrolysed at 25° C/minute to 600° C, followed by posterior cooling down for the next sample to be run. The heating of organic matter in the absence of oxygen yields organic compounds. In the first stage of pyrolysis when the sample is maintained at 300° C the free organic compounds (bitumen) already present in the rock are distilled. In the second stage of increase heating to 600° C the insoluble organic matter (kerogen) is cracked down into pyrolytic products. Flame ionisation and thermal conductivity detectors sense any organic compounds and CO₂ generated during the two stages. In the first stage the helium gas flow sweeps the volatile products out of the oven to a splitter. The first half of the split effluent is sent to water scrubber and then to a CO₂ trap. The second half is directed into a hydrogen flame ionisation detector where hydrocarbons volatile at 300° C are detected and quantitatively measured. After 2 minutes the oven increases its temperature at a rate of 25° C/minute up to 600° C. Once this temperature has been reached the CO₂ trap is dumped onto a thermal conductivity detector and the amount of thermally evolved organic CO₂ is measured.

The pyrolysis values collected on the computer are presented in a table that includes values such as Tmax, S1, S2, S3, PI, S2/S3, PC, TOC, HI, and OI. All these values are indicative of the level of maturity of the organic matter, the type or types of organic matter, and the amount of hydrocarbons already produced or that can be produced from a studied rock sample.

The first value, Tmax, represents the temperature at which the maximum amount of hydrocarbons degraded from kerogen are generated (Fig. 4). Tmax does not represent the actual burial temperature of the rock but rather a relative value of the level of thermal maturity. If the rock has not been subject of oil generation then the organic matter has been little altered and, therefore, if heated during pyrolysis it will produce hydrocarbons. In turn, if the organic matter is more mature it will take more temperature to make it produce hydrocarbons since it has already been impoverished.

The second value is S1 and represents milligrams of hydrocarbons that are thermally distilled from one gram of rock. The S1 peak is measured during the first stage of pyrolysis at the fixed temperature of 300° C. As rocks are buried they are subjected to increasing temperatures and hydrocarbons start to be generated. These hydrocarbons are the ones that form the S1 peak.

The third value is S2 and indicates the milligrams of hydrocarbons generated from degrading the kerogen in one gram of rock during the second stage of pyrolysis. Tmax is the temperature at the maximum of the S2 pe-

ak. The larger the S1 peak the deeper (up to a point) and more mature the organic matter is. This increase occurs at the expense of the S2 peak which not only decreases in size but also moves to higher temperatures as the less thermally stable material has already broken down during natural maturation leaving a thermally more stable kerogen residue in the rock. If there is very little organic matter in the rock (below 0.3 wt. %) a very limited amount of hydrocarbons can be produced and thus, the S1 and S2 peaks will be very low and form a wide gentle hump. The pyrolysis analyser, then, will have difficulties to pick the highest point of the hump and will present unreliable, scattered data. Both the ratio S1/S2 and Tmax indicate the level of maturity of the organic matter.

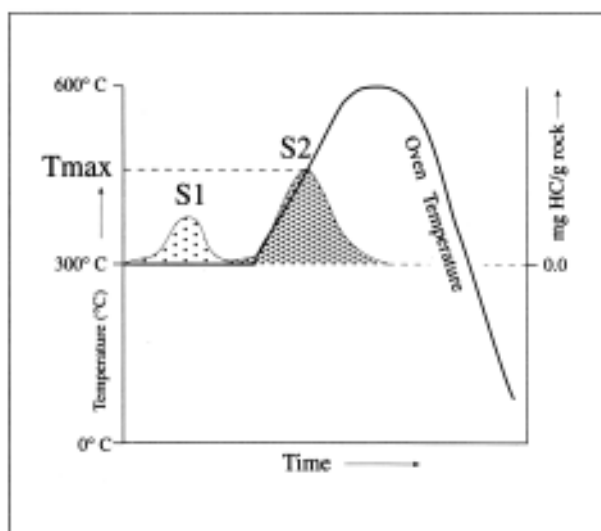


Fig. 4. Response of organic matter to controlled heating during pyrolysis. S1 corresponds to hydrocarbons formed in the subsurface and already present in the rock, whereas S2 represents hydrocarbons generated during the pyrolysis process. Tmax corresponds to the maximum generation of hydrocarbons during pyrolysis and is much higher than the temperatures governing the formation of hydrocarbons in nature (Modified after BARKER, 1974).

The fourth value is called S3 and expresses the milligrams of carbon dioxide generated from a gram of rock during temperature programming up to 390° C. Next comes the production index (PI) which is defined as the ratio S1/(S1+S2). PI is an indication of the amount of hydrocarbon which has been produced geologically relative to the total amount of hydrocarbon which the sample can produce.

The S2/S3 ratio is the sixth value and represents a measure of the amount of hydrocarbons which can be generated from a rock relative to the amount of organic CO₂ released during temperature programming up to 390° C. S2/S3 ratios are considerably lower for Type III kerogen than for Type II and Type I because terrestrially

derived organic matter contains substantially more oxygen than the other types of organic matter. The Pyrolysed Carbon (PC) is defined as the ratio $(S1 + S2)/10$ and is another organic type indicator. Type I kerogen yields PC values of about 80 %, Type II of about 50 %, and Type III between 10-30 %.

After pyrolysis is complete the sample is transferred to an oxidation oven where is heated to 600° C in the presence of air. There the residual organic matter generates CO₂ which is quantitatively measured by passing the effluent over a series of traps and catalysts. The amount of this carbon is added to S1 and S2 to obtain the Total Organic Carbon (TOC) content that is given in weight percentages. Two other obtained values are the Hydrocarbon Index (HI) and Oxygen Index (OI). HI is defined as the ratio $S2/TOC$, and represents the quantity of pyrolysable organic compounds from S2 relative to TOC in the sample. OI is defined as $S3/TOC$ and corresponds to the quantity of carbon dioxide from S3 relative to TOC.

INTERPRETATION OF ROCK-EVAL PYROLYSIS DATA

Petroleum generation results from the transformation of sedimentary organic matter in the subsurface under the influence of both temperature and geologic time. This transformation can be ascribed to the thermal cracking of the kerogen which releases micropetroleum into the pore system of the source rock (TISSOT and WELTE, 1984; HUC, 1990).

Rock-*eval* pyrolysis permits rapid evaluation of the organic matter type, quantity and maturity and, thus, yields information on the petroleum-generative potential. However, a minimum amount of organic matter is needed to obtain reliable results. This technique is based on the production of hydrocarbons from a rock sample by steadily heating it. However, if the amount of organic matter present in the rock is very small or is completely burned little information can be obtained. If high thermal maturation values (expressed as high, R₀, vitrinite reflectance values) are suspected other techniques should be more appropriate to the study of the organic matter.

Oil shales and most organic-rich sedimentary rocks can be studied by the Rock-Eval pyrolysis technique. In the context of hydrocarbon studies the most important data are concerned with the amount, type, and thermal maturation level of organic matter. Information on amount and type of kerogen is readily given on the computer by collecting the data provided by the pyrolysis unit.

The amount of organic matter is expressed by the TOC values which represent the total amount of organic

carbon present in the rock. For shales, usually a TOC of 2.0 % is considered to be good, and a TOC value higher than 4 % is considered as very good. For limestones even lower values are good.

The T_{max} value represents the temperature at which the largest amount of hydrocarbons is produced in the laboratory when a whole rock sample undergoes a pyrolysis treatment. The production of these hydrocarbon by pyrolysis is linked to the amount of hydrogen the rock still contains and, therefore, to its level of maturation since the more mature the rock is the lower amount of hydrogen it contains and the highest amount of energy it needs to liberate hydrocarbons. The thermal maturation level is deduced from the T_{max} values. In general, T_{max} values lower than 435° C indicate immature organic matter (organic matter). T_{max} values between 435° C and 455° C indicate "oil window" conditions (mature organic matter). Values between 455 and 470° are considered transitional. A T_{max} higher than 470° C represents the wet-gas zone and overmature organic matter (PETERS, 1986). The thermal maturation level for oil-prone type I kerogens is often higher than for the other types of kerogen (TISSOT et al., 1978).

T_{max} data for samples with S₂ peaks less than 0.2 mg HC/g rock may be inaccurate because the S₂ peak becomes so broad and low that there is no sharp top and, thus, the analyser takes any point as the top of the peak. For this reason if there is very little organic matter in the rock, the S₂ peak is very low and broad, and T_{max} values are scattered and unreliable. T_{max} values may also be depressed by the presence of resinite from fossil tree resin or they may be increased by the presence of other organic compounds such as gilsonite. For the same maturation level, carbonate-rich rocks usually yield lower T_{max} values than clay-rich samples.

At present two types of diagrams are widely used to interpret the type of organic matter. Of these two diagrams one is the Hydrogen Index (HI) versus T_{max} diagram, and the other is the Hydrogen Index (HI) versus Oxygen Index (OI) diagram. Both diagrams offer information on the dominant type of kerogen, although the first one also gives an approximate idea of the maturation level. For samples containing less than 0.5 wt. % TOC the Oxygen Index values may be anomalous because of adsorption of carbon dioxide or oxygen. Drawing of both types of diagrams provides a reliable comparison of results that helps detecting anomalies.

The Hydrogen Index (HI) versus T_{max} diagram (GORIN and FEIST-BUKHARDT, 1990) is based on the amount of hydrogen that the kerogen contains and the amount of energy necessary to produce hydrocarbons from that type of kerogen in the laboratory over a short period of time. ESPITALIÉ et al. (1977) defined the

Hydrogen Index (HI) versus Oxygen Index (OI) pyrogram where HI and OI are $(S_2/TOC) \times 100$ and $(S_3/TOC) \times 100$ respectively. This diagram provides rough information on the type of organic matter which represents the proportion of hydrogen bound in the organic structure. The HI represents the hydrogen richness and the OI depicts the organic oxygen content of the sample, both relative to the total organic carbon content (SNOWDON, 1989).

The type of organic hydrogen is controlled by the nature of the organic matter. Aquatic organic matter has a high hydrogen content whereas terrestrially derived organic matter has a low hydrogen content and a variable high oxygen content.

The type I kerogen has a monospecific algal origin and presents the highest hydrogen content. Thus, this type of kerogen usually gives the highest HI values. In the HI versus Tmax diagram this type occurs in the upper part. Based on its maturation level the sample will plot to the right (more mature) or to the left (less mature). In the HI versus OI pyrogram of PETERS (1986) this type of kerogen occurs in the upper left owing to its high hydrogen and low oxygen contents.

Type II of kerogen is originated mainly from phytoplanktonic organisms and has a relatively high hydrogen content but not as high as type I. Therefore, HI values for this type of kerogen are intermediate and occupy the central part of the both pyrograms. This is usually the oil forming kerogen. The HI versus Tmax diagram also will provide information about the maturation level, and, thus, the oil generation expectancies.

Type III of kerogen corresponds to terrestrially produced organic matter, especially material from higher plants. The majority of the terrestrial plant material has less hydrogen than the aquatic plant material. In addition, the terrestrial plant organic matter is transported (usually by fluvial systems) for relatively long distances before it is deposited in subaquatic basins. During transport the terrestrial organic matter is partly degraded and impoverished in hydrogen. Due to its nature and the degradation suffered during transport, terrestrial organic matter and, therefore, its sedimentary counterpart, the type III kerogen, present low HI values. Type III kerogen commonly plots on the lower part of both pyrograms. This type of kerogen usually is a source of gas rather than oil. The maturation level will offer information on the gas forming capability of the studied sample.

Type IV of kerogen represents an extreme of type III and contains very little hydrogen. If plotted on the pyrograms it occurs on the bottom of the diagrams. The only difference with type III is that type IV organic matter usually has high Tmax values or lacks the S₂ peak. Type IV kerogen behaves as oxidised, highly mature kerogen.

The Production Index (PI) is also in part indicative of the degree of thermal maturity (Peters, 1986). In general, PI values below 0.4 indicate immature organic matter; PI values between 0.4 and 1.0 indicate mature organic matter; and PI values above 1.0 are indicative of overmature organic matter. Outcrop samples commonly show depletion in S₁ and S₂ and high S₃ values due to weathering. PI is defined as the ratio $S_1/(S_1+S_2)$, and, hence, depletion of S₁ and S₂ may induce changes on actual PI values. Immature sediments commonly yield poorly separated S₁ and S₂ peaks which can lead to anomalous results. Oxidation is the most common form of degradation of organic matter. Oxidation removes hydrogen and adds oxygen to the kerogen, and, therefore, HI values are usually lower and OI values higher for outcrop samples than for fresh-core samples.

Most coals correspond to type III organic matter but do not generally react during pyrolysis as dispersed Type III organic matter does. Often coals give misleading results and plot as mixtures of type II and type III organic matter

LIMITATIONS OF THE ROCK-EVAL/TOC PYROLYSIS TECHNIQUE

The origin of the dominant type of organic matter found in a sample may be defined based on pyrolysis data. In many studies (e.g., TISSOT et al., 1980) values such as Hydrogen Index (HI) have been used to assess the organic matter type. High HI are generally interpreted as representative of lipid-rich marine organic matter whereas low HI values are commonly interpreted as indicative of terrestrial organic matter. Therefore, variations in HI may often be indicative of fluctuations on distance to continental areas and shifting of environments of deposition. Decreasing HI is commonly interpreted as increasing proximity to paleo-shoreline, and conversely, HI increases with deepening of sedimentation setting (MILLER, 1990). The shoreward fall in HI is probably due as much to poorer preservation in shallower water as to increased terrigenous input. Turbidity influxes of terrestrial organic matter with simultaneous replenishment of the pore-water surface may induce anomalously low HI values.

However, there is a risk of oversimplification in the interpretation of pyrolysis data which should be supported by other data such as sedimentology and paleontology. For instance type II marine organic matter may chemically degrade to a mixture of types II and III. In fact, variations in the mineral matrix and organic enrichment affect both the absolute and relative hydrocarbon, and CO₂ yields and, therefore, also affect the HI and OI indices (KATZ, 1983). For instance, the presence of some elements such as elemental sulfur produce a subs-

tantial decrease in HI values and an increase in OI values, so that type I kerogen gives a response typical of type III kerogen. Pyrolysis indicators of thermal maturation level such as Tmax and PI are also affected by the presence of elemental sulfur in the matrix of the studied rock sample. High levels of elemental sulfur induce decreased values of Tmax and increased values of PI (SASSEN and CHINN, 1989).

ROCK-EVAL PYROLYSIS OF THE UPPERMOST PALEOCENE/ LOWERMOST EOCENE: METHODOLOGY AND RESULTS

This pyrolysis analysis intended to obtain information on the amount and type of organic matter contained in the stratigraphic interval covered in this study. A total of 18 mudstone samples (Fig. 2) were collected from well exposed outcrops trying to avoid weathered zones to obtain "fresh rock". Sample collection included ten samples from Ermua and eight from the Aixola, Trabakua Pass, and Zumaia sections. The Ermua section was sampled in more detail than the other three sections because it contains a rich-palynomorph assemblage that allowed precise datation of the section. The palynological content of the other three sections is poor. The Ermua section includes more dark mudstone rocks than the other three sections what was preliminarily interpreted as more organic-rich. All samples are stored at the Department of Geology and Geophysics, The University of Calgary, Alberta, Canada.

All whole rock samples were pulverised and analysed on a Delsi II Rock-Eval/TOC pyrolysis unit equipped with a Total Organic Carbon (TOC) analysis module at the Institute of Sedimentary and Petroleum Geology (Geological Survey of Canada) in Calgary (Alberta, Canada). All samples were run in duplicate (Table 1) to ensure that data were constant. However, Tmax values for all samples but one were very erratic owing to the low TOC values. All data from the four sections are plotted on HI versus Tmax and HI versus OI pyrograms respectively (Fig. 5) to establish the type of organic matter contained in these rocks.

One in-house standard (# 9107) was run to ensure that the analytical conditions remained constant (Table 1). The standard was run at the beginning, in the middle, and at the end of the analysis.

All samples of this study but one are very similar in organic matter content and type. These samples show very erratic Tmax and PI values, and low pyrolysis values such as S1 about 0.02 mg HC/g rock, S2 about 0.08 mg HC/g rock, S3 about 0.5 mg HC/g rock, TOC about 0.15 wt. %, HI about 25 mg HC/g rock, and highly variable OI.

Only one sample from the Aixola section is relatively organic-rich and allows the establishment of the level of thermal maturation for this interval. For this sample Tmax values are about 455° C, TOC is about 2.55 wt. %, S1 is about 0.25, S2 about 0.29, S3 about 0.87, PI about 0.48, HI about 11, and OI about 34.

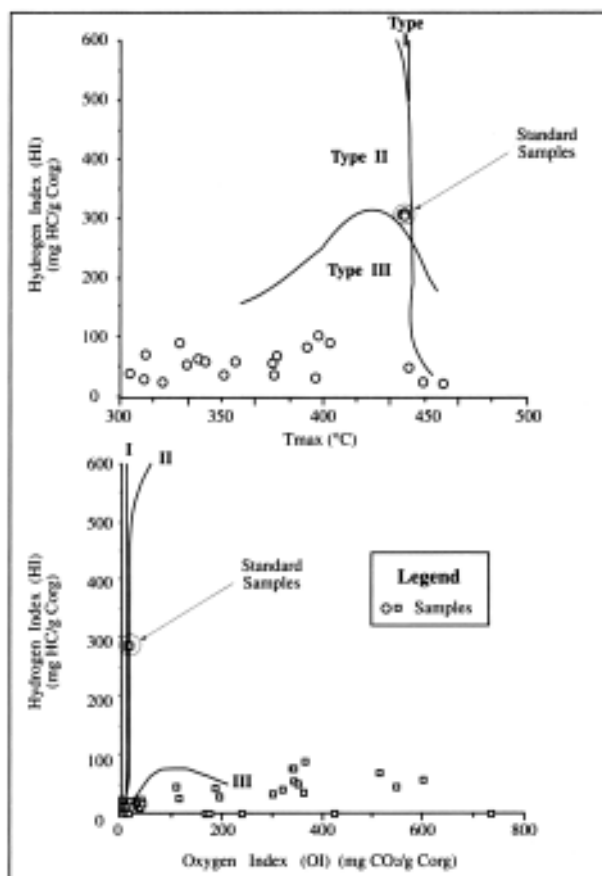


Fig. 5. Diagrams for Hydrogen Index (HI) versus Tmax and Hydrogen Index (HI) versus Oxygen Index (OI) for the uppermost Paleocene/lowermost Eocene of the Basque Basin. Organic Matter Type curve for HI/Tmax from GORIN and FEIST-BURKHARDT (1990), and for HI/OI from PETERS (1986).

Ermua Section											
Sample	Qty.	Tmax	S1	S2	S3	PI	S2/S3	PC	TOC	HI	OI
1	100.0	397	0.01	0.03	0.05	0.25	0.60	0.00	0.15	20	33
1	100.0	***	0.00	0.00	0.02	***	0.00	0.00	0.15	0	13
2	100.0	***	0.02	0.04	0.03	0.33	1.33	0.00	0.18	22	16
2	100.1	***	0.00	0.00	0.00	***	***	0.00	0.17	0	0
3	100.0	306	0.01	0.05	0.22	0.17	0.22	0.00	0.19	26	115
3	100.0	343	0.02	0.10	0.23	0.17	0.43	0.01	0.21	47	109
4	100.0	352	0.01	0.07	0.09	0.12	0.77	0.00	0.29	24	31
4	100.0	322	0.00	0.03	0.09	0.00	0.33	0.00	0.27	11	33
5	100.0	404	0.02	0.26	1.12	0.07	0.23	0.02	0.33	78	339
5	100.1	398	0.01	0.28	1.13	0.04	0.24	0.02	0.31	90	364
6	100.0	340	0.00	0.04	0.28	0.00	0.14	0.00	0.08	50	350
6	100.0	331	0.01	0.07	0.31	0.12	0.22	0.00	0.09	77	344
7	100.0	***	0.00	0.00	0.00	***	***	0.00	0.04	0	0
7	100.0	***	0.01	0.01	0.00	0.50	***	0.00	0.04	25	0
8	100.0	***	0.00	0.00	0.17	***	0.00	0.00	0.04	0	425
8	100.0	***	0.00	0.00	0.07	***	0.00	0.00	0.04	0	175
9	100.1	***	0.00	0.00	0.12	***	0.00	0.00	0.05	0	240
9	100.0	***	0.00	0.02	0.18	0.00	0.11	0.00	0.06	33	300
10	100.1	313	0.00	0.06	0.14	0.00	0.42	0.00	0.32	18	43
10	100.0	377	0.01	0.08	0.12	0.12	0.66	0.00	0.31	25	38
Aixola Section											
11	100.1	449	0.26	0.32	0.85	0.45	0.37	0.04	2.58	12	32
11	100.1	459	0.24	0.25	0.88	0.50	0.28	0.04	2.47	10	35
12	100.1	378	0.01	0.05	0.31	0.17	0.16	0.00	0.09	55	344
12	100.0	334	0.01	0.04	0.32	0.25	0.12	0.00	0.10	40	320
13	100.1	***	0.00	0.00	0.00	***	***	0.00	0.26	0	0
13	100.0	***	0.01	0.03	0.00	0.25	***	0.00	0.24	12	0
Trabakua Pass Section											
14	100.1	***	0.00	0.00	0.02	***	0.00	0.00	0.17	0	11
14	100.1	***	0.00	0.02	0.02	0.00	1.00	0.00	0.18	11	11
15	100.0	442	0.00	0.03	0.29	0.00	0.10	0.00	0.08	37	362
15	100.0	376	0.00	0.04	0.17	0.00	0.23	0.00	0.09	44	188
Zumaia Section											
16	100.0	***	0.01	0.05	0.33	0.17	0.15	0.00	0.17	29	194
16	100.1	***	0.00	0.00	0.30	***	0.00	0.00	0.18	0	166
17	100.0	393	0.01	0.10	0.72	0.10	0.13	0.00	0.14	71	514
17	100.0	358	0.00	0.06	0.71	0.00	0.08	0.00	0.13	46	546
18	100.0	***	0.00	0.00	0.44	***	0.00	0.00	0.06	0	733
18	100.0	314	0.02	0.04	0.42	0.33	0.09	0.00	0.07	57	600
Standard Samples											
9107	100.0	439	1.18	12.79	0.74	0.08	17.28	1.16	4.40	290	16
9107	100.0	440	1.23	12.98	0.51	0.09	25.45	1.18	4.50	288	11
9107	100.0	440	1.27	13.32	0.49	0.09	27.18	1.21	4.54	293	10

Table 1. Rock-Eval Pyrolysis data for Ermua, Aixola, Trabakua, and Zumaia sections of the uppermost Paleocene/lowermost Eocene of the Basque Basin.

DISCUSSION

The study of sedimentary organic matter is based on comparison with the mechanisms of production, accumulation and preservation of organic matter in the different environments of modern basins. These studies are aimed at the characterisation of organic matter to establish the environmental features of past geological basins, and the petroleum generation potential of sedimentary rocks. The Rock-Eval Pyrolysis technique is the most basic method to characterise sedimentary organic matter and yields preliminary information that can later be completed by other organic geochemistry techniques.

Despite the great applications of the Rock-Eval Pyrolysis technique there are also some limitations owing to technical specifications of the pyrolysis units. The most important limitations are due to low organic contents. The quantity of organic matter as measured by the Total Organic Content (TOC) is the basic quantitative parameter that must be used when determining the petroleum generation potential of a stratigraphic unit. If there is very little organic matter in the rock (below 0.3 %) a very limited amount of hydrocarbons can be produced and thus, the S1 and S2 peaks will be very low and form a wide gentle hump. Tmax data for samples with S2 peaks less than 0.2 mg HC/g rock may be inaccurate because the S2 peak becomes so broad and low that there is no sharp top and, thus, the analyser takes any point as the top of the peak. This explains the erratic Tmax values obtained in this study. However, one sample from the Aixola section contains about 2.5 wt. % and shows consistent Tmax values around 455° C. This is likely indicative of the thermal maturation level of the studied samples. Also, for samples containing less than 0.5 % TOC the Oxygen Index values may be anomalous because of adsorption of carbon dioxide or oxygen, and therefore the OI values of all samples but one may not be precise.

The pyrolysis data can also be interpreted to obtain information about the environment of deposition. The critical factor related to preservation of organic matter in the subaquatic sediments is the development of anoxicity (DEMAISON and MOORE, 1980). Anoxicity is linked to several parameters such as basin geometry, high organic productivity rates, and climatic conditions. In fact, the latest Paleocene to earliest Eocene interval records the warmest surface temperatures of the Cenozoic in an ice-free greenhouse world (MILLER et al., 1987). This produced major modifications in ocean circulation (BENJAMINI, 1992). The distinct warming and the change in ocean circulation coincide with a major extinction event in benthic foraminifera (NOMURA, 1991) and may be explained by a decrease of surface ocean producti-

ivity, a cessation of the deep-water flow, and a concomitant inflow of warm, saline water from low latitudes (MILLER et al., 1987; THOMAS, 1989).

The latest Cretaceous-Early Eocene Basque Basin constituted an interplate deep-water trough surrounded by shallow carbonate shelf areas except on its western opening towards the present day Bay of Biscay (PLAZIAT, 1981; PUJALTE et al., 1993a and 1993b). The pyrolysis data collected in this study may well reflect the climatic conditions of the semi-enclosed Basque Sea. These climatic conditions would be similar to those already postulated for other oceanic basins of that age. The pyrolysis data may be interpreted as indicative of a probable negative water balance in the Basque Basin. This negative balance was due to high evaporation levels and induced a circulation pattern with a relative constant influx of oceanic water into the basin to compensate for evaporation levels as nowadays occurs in the Mediterranean Sea. This constant renovation of the water mass in the Basque Basin and the lack of any sills in its western opening prevented the formation of anoxic conditions.

The palynological analyses yielded a rich palynomorph assemblage that comprised 77,80 % marine specimens and the rest terrestrial. However, this may be misleading. In fact, the pyrolysis data indicate that continentally derived matter is the main organic matter contained in these rocks. The different results are due to the techniques used to process organic matter for palynology that try to oxidise all amorphous organic matter and concentrate only palynomorphs. Yet, the dominance of terrestrially originated organic matter (Type III) indicates low marine productivity in the Basque Sea. Since there were relatively good oxygenation levels and low organic productivity in the Basque Basin little amounts of organic matter were preserved in the sedimentary rocks of the uppermost Paleocene/ lowermost Eocene.

CONCLUSIONS

This paper presents basic information on sedimentary organic matter and its characterisation through Rock-Eval Pyrolysis. This laboratory technique has been applied to the uppermost Paleocene/lowermost Eocene of the Basque Basin to study the nature of the organic matter across this stratigraphic boundary.

This first analysis of the uppermost Paleocene/lowermost Eocene of the Basque Basin from the deep-water Ermua, Aixola, Trabakua Pass, and Zumaia sections indicates that the organic matter contained in these rocks is mature and of type III. All samples but one are organic-poor and, therefore, do not constitute a "potential sour-

ce rock". Only small amounts of gas may have been originated from these rocks.

In contrast with palynological data mainly terrestrially derived organic matter accumulated in the Basque Sea. During the latest Paleocene/Earliest Eocene the climate was warm and the Basque Sea was well oxygenated with low levels of productivity.

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