Organic Facies: Palynofacies and Organic Geochemistry Approaches

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1. Introduction

The concept of organic facies, as well as the definitions and means of the different facies became a very important tool to palaeoenvironmental characterization, basin analysis and fossil fuel exploration. The application of this concept is the best way to integrate microscopy and geochemical techniques to study kerogen contained in sedimentary rocks. Thus, palynofacies analysis and bulk geochemical methods (organic facies) are used to characterize the sedimentary organic matter (kerogen and bitumen). Palynofacies analysis involves the integrated study of all aspects of the kerogen assemblage: identification of the individual particulate components, assessment of their absolute and relative proportions and preservation states. The correlation between palynofacies and geochemical data provides the organic facies models that point out the depositional environmental conditions and hydrocarbon source rock potential.

2. Organic matter: Concepts and definitions

2.1 Origin and characterization of the sedimentary organic matter

Organic matter present in sedimentary rocks usually represents the lowest proportion of the sedimentary fraction. It is constituted by organic molecules (under the form of monomers and polymers) deriving directly or indirectly from the organic part of the organisms (composed by the elements C – carbon, H – hydrogen, O – oxygen, N – nitrogen, and S – sulfur). Skeletal parts, shells, bones, spines, and teeth are not included (Tissot & Welte, 1984; Tyson, 1995).

According to Tyson (1995), the study of the organic matter in sediments and sedimentary rocks focuses on the interaction between the biosphere and geosphere. A proper appreciation of the subject requires an understanding of the environmental controls which govern the production of organic matter in the biosphere, the ecological and sedimentological processes which control its deposition and distribution, the biogeochemical, and geomicrobiological factors which influence its preservation and

geochemical and physical processes which determine its modification during its incorporation in the geosphere. The characterization of the organic matter contained in sediments and sedimentary rocks is an important issue for many different types of biological, geological, and environmental scientists. The method used depend largely upon the age of the organic matter (or of the host sediment), the background of the investigators and the objectives of any given study. The integrated use of microscopy and geochemical techniques is particularly under-utilized.

2.2 Organic matter and biosphere evolution

From the Precambrian till the Devonian, the main producers of organic carbon were blue-green algae and photosynthetic bacteria. Since the Devonian an increasing amount of primary production has been contributed by higher terrestrial plants (Tissot & Welte, 1984). Throughout the Early Paleozoic (Cambrian, Ordovician, and Silurian), a variety of marine phytoplanktonic organisms, bacteria, and blue-green algae (Cyanophyta) were the dominant sources of organic carbon until land plants appeared on the continents and spread sufficiently by the Middle Devonian (Zimmermann, 1959). Vallentyne (1965) estimated that even today the marine phytoplankton and bacteria are responsible for 50 to 60% of the world organic carbon production.

The fossil records are inadequate to quantify the productivity of bacteria throughout the geological time. Because of microscopic size, and the lack of hard parts, the bacteria are rarely fossilized (Tissot & Welte, 1984). According to Moore (1967), fossilized bacteria are often associated with organic matter such as plant tissues, and animal and insect remains. Bacteria may be heterotrophic, autotrophic (photosynthesis without production of oxygen), or both.

Following phytoplankton and bacteria, higher plants are the third important contributor to organic matter in sediments. Quantitatively, the four most important contributors to organic matter in sediments are phytoplankton, zooplankton, higher plants and bacteria. Higher organized animals (e.g. fishes) contribute on the average so little to organic matter in sediments that they can practically be neglected (Tissot & Welte, 1984).

2.3 Biomass: Chemical composition

The sedimentary organic matter is derived from live organic matter and its metabolic products. The type of organic matter deposited and incorporated in sediments depends on biological productivity. The chemical composition of the biomass in a given area, and at a given time, is mainly dependent on the physical and chemical environment of the biological habitat and the evolutionary level of the organisms. Determining environmental factors include light, temperature, nutrients, and conditions of water (e.g. currents, temperature, etc.), besides the presence of groups of organisms (Tissot & Welte, 1984).

According Tissot & Welte (1984), basically all organisms are composed of the same chemical constituents e.g. proteins, carbohydrates, lipids, and lignins-tannins. However, differences exist between the chemical composition of marine planktonic algae and terrestrial higher plants. The organic matter of marine plankton is mainly composed of proteins (up to 50% and more), a variable amount of lipids (5 to 25%), and generally not more than 40% carbohydrates. Higher terrestrial plants are largely composed of cellulose (30 to 50%) and lignin (15 to 25%).

2.4 Organic matter accumulation

The accumulation of organic matter in sediments is controlled by a limited number of geological conditions (Tissot & Welte, 1984). The main factors that control the accumulation of organic matter include the production of the biomass and the degradation processes and transport of the organic matter. The quantity and quality of the organic matter accumulated in sediment are basically the result of the combined influence of the biomass productivity, biochemical degradation and of the organic matter depositional processes. The accumulation is practically restricted to sediment deposited in aquatic environments, which must receive a certain minimum amount of organic matter. In subaerial sediments, organic matter is easily destroyed by chemical or microbial oxidation. It is necessary balanced conditions between the energy level in a body of water and rate sedimentation to preserve and concentrate organic matter in sediments. This organic matter can be supplied on the form of particulate organic matter (in particles) or as dissolved organic matter (dissolved organic components).

2.5 Organic matter transformation

Among the liberation of biological products in the adjacent environment and its incorporation to the sediments, occurs the intervention of a number of physicochemical and biological factors, which will influence its chemical structure and will determine its space distribution in the deposits. Organic matter consists of a diverse variety of compounds, each differing in its inherent biochemical characteristics and susceptibility to microbial attack (Tyson, 1995).

Living tissues are composed of a biomolecules assembly which is thermodynamically unstable. When such molecules are secreted or excreted by the organisms, or even after the death of the organism, they tend to lose its integrity and they can be transformed in simple stable components such as CO_2, CH_4, NH_3, H_2S, H_2O, etc. This process of degradation can be accomplished by the physicochemical processes (oxidation, photolysis, thermolysis, etc). Biological Molecules suffer modifications, of which the resulting products could be presented on the form of several components. The proportions and reactivity of these individual constituents determine the overall pattern of degradation, the most metabolizable compounds disappearing first and at faster rates (Tyson, 1995).

3. Thermal maturity

The physiochemical transformation of organic matter during the geological history of sedimentary basins cannot be considered as an isolated process. Such transformation is controlled by the same factors that also determine the variations of composition of the mineral fraction (solid inorganic phase) and of the interstitial water of the sediments: biological activity in an early stage, then temperature and pressure (Tissot & Welte, 1984). The chemistry of organic matter contained within a sedimentary rock changes over time, reflecting its temperature and burial history. This change or thermal maturity is measured and can be combined with quality of organic matter. The maturity level is the product of a number of variables, such as tectonic setting, burial history, and thermal history.

From the start of buried, organic matter in sedimentary rocks suffers numerous compositional changes, which are caused initially by the biological activity (microbial)

following for the action of the temperature and pressure. This continuous series of processes is denominated of thermal maturation and it is divided in consecutive stages of evolution: diagenesis, catagenesis, metagenesis and metamorphism. These consecutive stages of evolution act on the carbon cycle and cause, of irreversible way, progressive changes in the composition of sedimentary organic matter. Each stage is characterized by different types of chemical processes (Tissot & Welte, 1984). There is a correlation of various maturation indicators for organic matter in coal and kerogen and their relation to the organic maturation stages and the hydrocarbons generated based on Staplin, 1969, Teichmüller, 1974, Hunt, 1979, 1985, Mukhopadhyay, 1994, Pearson, 1990, Peters & Moldawan, 1993, etc.

3.1 Diagenesis

The physical, chemical, and microbiological changes, which occur during the deposition in the order of a few hundred meters of overburden, are called diagenesis. Diagenesis is a process through which the system tends to approach equilibrium under conditions of shallow burial, low temperature and pressure, and through which the sediment normally becomes consolidated. In the diagenetic interval, the increase of temperature and pressure is small, and transformations occur under mild conditions. During early diagenesis, one of the main agents of transformation is microbial activity, and a whole series of low-temperature reactions occur; such as decarboxylation, deamination, polymeralization, and reduction. These contribute the kerogen of ancient rocks (Hunt, 1995). Within the sediment, organic material proceeds also towards equilibrium, previous biogenic polymers or "biopolymers" (proteins, carbohydrates) are destroyed by microbial activity during sedimentation and early diagenesis. Then their constituents become progressively engaged in new polycondensed structures ("geopolymers") precursing kerogen (Tissot & Welte, 1984).

3.2 Catagenesis

Catagenesis results from an increase in temperature during burial in sedimentary basins. Organic matter is subjected to increasingly higher temperatures with greater depth of burial. Consecutive deposition of sediments results in burial of previous beds to a depth that reaching several kilometers of overburden in subsiding basins. This means a considerable increase in temperature and pressure. Over time, these higher temperatures cause the thermal degradation of kerogen to yield petroleum-range hydrocarbons under reducing conditions (Hunt, 1995). Tectonics may also contribute to this increase. The temperature may range from about 50 to the 150°C and geostatic pressure due to overburden may vary from 300 to 1500 bars. Such increase again places the system out of equilibrium and results in new changes (Tissot & Welte, 1984). During the catagenesis organic matter experiences major changes and thermal degradation of kerogen is responsible for the generation of most hydrocarbons. Progressive evolution of the kerogen produces first liquid petroleum; then in a later stage "wet gas" and condensate; both liquid oil and condensate are accompanied by significant amounts of methane. This stage corresponds to the main stage of formation of oil and also wet gas.

3.3 Metagenesis

The final stage, after catagenesis and before metamorphism, is the metagenesis. Matagenesis is reached only at great depth and represents the last stage in the significant thermal

alteration of organic matter (Hunt, 1995). This stage of evolution of organic matter begins earlier than metamorphism of the mineral phase. At this stage the organic matter is composed only of methane and a carbon residue, where some crystalline ordering begins to develop. Methane generation diminishes and graphitic structures begin to form. Metagenesis is only concerned with the stage precursing metamorphism, which has been variously characterized and designated as early metamorphism, epimetamorphism, anchimetamorphism, etc. (Tissot & Welte, 1984).

3.4 Metamorphism

Metamorphism is the last stage of the evolution of sediments, where temperature and pressure reach high values in deep zones. In addition, rocks are exposed to the influence of magma and hydrothermal effects. True conditions of metamorphism result in greenchist, and amphibolites facies development. Constituents of the residual kerogen are converted to graphitic carbon (Tissot & Welte, 1984).

4. Kerogen: Composition and classification

The organic matter is composed by two fractions: kerogen (fraction of the organic matter insoluble in organic solvents), and bitumen (fraction of the organic matter soluble in organic solvents). The most common term used to describe the fossil organic matter in sedimentary rocks is kerogen. In the absence of migrant hydrocarbons, kerogen is usually 95% or more of total organic matter in sedimentary rocks (Tyson, 1995). Kerogen was originally named in 1912, but one of the first definitions was presented by Forsman and Hunt (1958) defining kerogen as the dispersed OM of ancient sediments insoluble in the usual organic solvents, in contrast to extractable OM (bitumen). Other definitions as those introduced by Durand (1980), Tissot & Welte (1984) and Vandenbroucke and Largeau (2007) or even those of the Organic Petrologists and Palynologists point out to the same concepts: insoluble fraction of the organic matter or residue isolated from a sedimentary rock after complete dissolution of the rock matrix by HCl and HF acids. The researchers that participants of Open Workshop on Organic Matter Classification (University of Amsterdam, June of 1991) decided to use the term *palynological organic matter* to describe the *kerogen* has been observed under transmitted white light.

Using a more simple and practical definition, kerogen is composed by particulate organic matter (organic constituent of the sedimentary rocks) and bitumen is composed by molecular organic matter (molecular organic compounds: saturated; aromatic and polar compounds - resins and asphaltenes). Owing to the characteristics of each fraction from the organic matter, they are studied using different techniques. For study of bitumen are used organic geochemical techniques; such as solvent extraction; liquid chromatography (LC); gas chromatography (GC); gas chromatography coupled to mass spectrometry (GC-MS), etc. Now, for the kerogen studies are used an association of microscopic and geochemical techniques. Techniques of microscopic examination (transmitted white light, reflected white light and fluorescence mode) can be applied to both kerogen-containing rock and previously isolated kerogen. There are many others techniques that can be used in the characterization of the kerogen, the appropriate technique will depend on the objective of the study.

About the kerogen composition and classification, different physical and chemical techniques of analysis are able to give valuable information on the structure and

composition of kerogen; such as: Elemental Analysis (C, H and O); Infra-Red Spectroscopy; Microscopic Examination; Degradative Oxidation; Various Experiments of Pyrolysis (Rock-Eval, Hydrous-pyrolysis, Laser Micro-pyrolysis, etc.).

Through the elementary ratios it is possible to define the 3 types of kerogen using the global atomic composition of 3 major elements (C, H and O). This plot was first used by van Krevelen (1961) to characterize coals and their coalification path. Tissot & Welte (1984) proposed to call this diagram as "van Krevelen diagram" that can be represented the 3 principal types and evolution paths of kerogen using *Hydrogen Index* (*HI*) and *Oxygen Index* (*OI*) from Rock-Eval pyrolysis analysis.

Kerogen Type I (Plate 1) presents a high initial H/C atomic ratio and low initial O/C ratio; it comprises much lipidic material, particularly aliphatic chains; the content of polyaromatic nuclei and heteroatomic bonds is low; this type of kerogen is either mainly derived from algal lipids (fresh water algae) or from organic matter enriched in lipids by microbial activity (AOM); it presents a high potential to hydrocarbon generation;

Kerogen Type II (Plate 2) is particularly frequent in many petroleum source rocks with relatively high H/C and low O/C ratios; aliphatic chains of moderate length and naphthenic rings; the content of polyaromatic nuclei and heteroatomic ketone and carboxylic acid groups are more important than those are in type I, but less than in type III; it comprises pollen grains, spores, cuticles and marine organic matter deposited in a reducing environment, with medium to high Sulphur content; it presents a high potential to hydrocarbon generation;

Kerogen Type III (Plate 3) presents low H/C ratio, O/C ratio is comparatively higher than is the other 2 types of kerogen; it contains mostly condensed polyaromatic and oxygenated functional groups, with aliphatic chains; the organic matter is mostly derived from terrestrial higher plants; oil potential is moderate, although this kerogen may still generate abundant gas at greater depths;

Kerogens of intermediate composition can also occur, besides one type of Kerogen (type IV), which is a secondary type of kerogen.

| Plate 1 | Plate 2 | Plate 3 | Plate 4 |
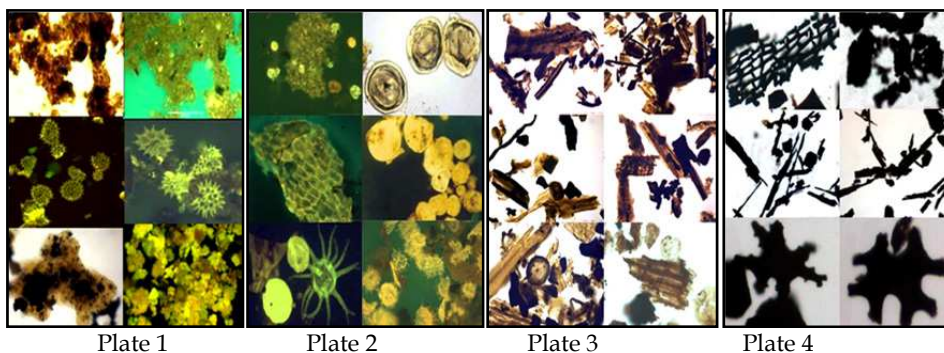
Plate 1: Organic matter (AOM, *Pediastrum* and *Botryococcus* Algae) related to the Kerogen Type I
Plate 2: Organic matter (AOM, Pollen Grain, Cuticle, Prasinophyte Algae, Acritarchae and Dinocysts) related to the Kerogen Type II
Plate 3: Organic matter (wood tissues: non-opaque phytoclasts) related to the Kerogen Type III
Plate 4: Organic matter (carbonized wood tissues: opaque phytoclasts) related to the Kerogen Type IV

Kerogen Type IV (Plate 4) is a secondary type of kerogen; it contains practically only aromatic components; the organic matter is carbonized through the combustion/natural pyrolysis and /or oxidation (pre-depositional); it present no potential to hydrocarbon source rock.

4.1 Techniques used in the kerogen study

Techniques of microscopic examination (natural light reflectance and transmittance, or UV fluorescence) can be applied to both kerogen-containing rock and previously isolated kerogen. The evaluation of the kerogen in ancient sediments uses microscopy techniques that allow the analysis so much in samples that organic matter was isolated from the rock matrix.

4.2 Microscopy

Techniques of microscopic examination (natural light reflectance and transmittance, or UV fluorescence) can be applied to both kerogen-containing rock and previously isolated kerogen (Tissot & Welte, 1984). The evaluation of the kerogen in ancient sediments uses microscopy techniques that allow the analysis so much in samples that organic matter was isolated from the rock matrix, Palynofacies Analysis (e.g. Tyson, 1984, 1987; Oboh, 1992; Batten, 1996; Follows and Tyson, 1998; Mendonça Filho, 1999; Oliveira, 2003; Menezes & Mendonça Filho, 2004; Meyer *et al.*, 2005; Carvalho *et al.*, 2006; Mendonça Filho *et al.* 2010a) as in whole rock samples through the Organic Petrology (Chow *et al.*, 1995; Stasiuk, 1996, 1999; Stasiuk & Fowler, 2004).

According to Tyson (1995), the main advantages of the microscopy analysis of kerogen are: provides information on the relative abundance, as well as characteristics, of the different components of the organic matter assemblage; optical data is better correlated with the bulk geochemical composition than *vice versa*; solid insoluble organic matter represents 95% or more of the total organic matter in most sediment; the origin, preservation state, and degree of thermal alteration of the organic matter can often be determined by direct visual observation; the industry standard procedures for determining the level of organic maturation are optical (vitrinite reflectance and palynomorph color); microscopy can provide valuable information even when the techniques used are relatively "low tech" and inexpensive; and it can be done with only a few grams of sample.

The characterization of the origin of the organic matter (botanical precursors) and the all aspects of the palynological organic matter assemblage are achieved using a combination of the morphology and optical properties (reflectance, fluorescence, and translucency). Examination of kerogen concentrates isolated from the minerals shows that, except in certain types of sediments formed by massive accumulation of a single type of organism, heterogeneity of kerogen is common in sedimentary rocks; the size, shape, color and structure of the organic remnants vary (Tissot & Welte, 1984).

4.2.1 Transmitted light microscopy

For isolated kerogen examination (palynological organic matter assemblage), based on palynological type preparation, the microscopy analyses are performed on strewn slides of kerogen concentrate sample using transmitted white light and fluorescence mode.

According Combaz (1964), the study of kerogen using transmitted light is derived from palynological examinations.

The type of organic matter is identified, using the translucency and shape of particles, and in some cases their fluorescence. The results of transmitted light studies mainly give information on the type of organic particles present and their thermal maturity. The characterization of the origin of the organic matter (botanical precursors) and the all aspects of the palynological organic matter assemblage, in transmitted white light microscopy and fluorescence mode, are achieved using a combination of the morphology and optical properties (qualitative fluorescence and translucency).

4.2.2 Fluorescence mode

Fluorescence microscopy is an important tool in the evaluation of thermal maturation and hydrocarbon generation potential of dispersed organic matter in sedimentary rocks. This is because organic components in coals and dispersed organic matter display fluorescence when illuminated with ultraviolet and/or blue light. This property is variable in intensity and color, and it depends on the composition and maturity level of the organic matter (see a summary in Taylor *et al.*, 1998).

The intensity of the fluorescence is influenced by the surrounding medium; less "quenching" occurs in oil-prone matrices. The most intense autofluorescence occurs in liptinitic oil-prone kerogen; vitrinite can also fluoresce, but much more weakly, such that it normally appears non-fluorescent to the eye (except in recent to sub-recent sediments) (Tyson, 1995).

The combination of transmittance and fluorescence microscopy makes possible the distinction the different individual organic constituents from the kerogen assemblage. According to Tyson (1995), autofluorescence always reflects a combination of three factors: biological origin, preservation state, and level of maturation and is also good for a 3D morphology observation, recognition of palynomorphs masked by amorphous organic matter (AOM) matrix, and helping to distinguish sporomorphs (spores and pollen grains) and plankton. In this case, when immature, organic-walled microplankton often shows more intense and more greenish fluorescence color than sporomorphs and sporomorphs show more variable fluorescence colors. The fluorescent intensity of palynomorphs is usually greater than that of AOM, except in oil shale with very high hydrogen indices.

Fluorescence can be used in the study of organic matter for diagnosis of hydrogen-rich organic particles, mainly to identify AOM, particles of algal or bacterial origin. Fluorescence is also an important method in determining the level of maturity of kerogen by estimating the intensity and color of fluorescence (qualitative) or by quantitative measurement of the fluorescence spectrum (photometric microscope). Qualitative fluorescence is intense in immature samples and decreases during diagenesis and most of catagenesis, disappearing completely at the end of catagenesis. However the color of spectrum (quantitative fluorescence) is progressively changed, the wavelength range of the fluorescence light moves towards the red with increasing catagenesis.

5. Organic composition: Palynofacies analysis

Combaz (1964) introduced the term *palynofacies* in an important period for creation of Organic Petrology, because at beginning was Palynology and Coal Petrology. Following the

work of Combaz at *Compagnie française des pétroles*, the palynofacies means the total assemblage of microscopic organic constituents presents in a rock that remain after maceration in hydrochloric acid (HCl) for carbonates and by hydrofluoric acid - (HF) for silicates, concentration and mounting using normal palynological preparation procedures. This author used the microscope technique to observe, in organic debris isolated from sedimentary rocks after the destruction of their minerals regularities in proportions of the different components: spores, pollens, wood fragments, plant cells, amorphous organic matter. Combaz called palynofacies the diagram of the proportions of the different components (Durand, 2003).

Hughes & Moody-Stuart (1967) proposed the term palynological facies in the same general sense as "palynofacies" of Combaz (1964) to include all organic elements. These authors and Batten (1973) also applied the term in the concept of Combaz to refer to the general aspect of kerogen preparation. Quadros (1975) took the words *Organopalynology* and *Organopalynofacies* for the investigation of organic matter in sedimentary rocks using techniques of microscopy towards Organic Geochemistry in Petrobras Company. Batten (1982a, 1982b) applied this concept not only for palaeoenvironmental and biostratigraphic studies, as well as, for thermal maturity determination and source potential studies. Leopold *et al.* (1982) showed that a palynofacies does not necessarily reflect the biologic environment of the area near the basin of deposition but instead can be produced by a variety of geological and geochemical taphonomic processes associated with sedimentation. This sort of palynofacies is a product of the total sedimentary environment and is unlikely to be a *palynobiofacies*. Powell *et al.* (1990) defined palynofacies as a "distinctive assemblage of HCl- and HF-insoluble particulate organic matter (*palynoclasts*) whose composition reflects a particular sedimentary environment". Traverse (1988) defined a palynofacies as "the assemblage of palynomorphs *taxa* in a portion of a sediment, representing local environmental conditions and not typical of the regional palynoflora". Tyson in 1993 published a pioneering contribution in the area of palynofacies analysis. Traverse (1994) reported that since 1960 used the term palynofacies to refer to a more or less local concentration of particular palynomorphs, indicating a sort of *biofacies*. The author believes that the application of the word since then has been geologically oriented, and palynofacies is used primarily to indicate information about the enclosing *rock*, especially its environment of deposition should be called *palynolithofacies*. Beside this, the several papers edited by Alfred Traverse in 1994 (*Sedimentation of Organic Particles*) ranging from general overviews to detailed sequence-stratigraphic studies.

The book published by Tyson (1995) contains summation of the geochemical aspects of organic facies analysis. This work integrates the geological and biological aspects of palynofacies research. The modern palynofacies concept was introduced by Tyson (1995) and his definition of palynofacies is: "a body of sediment containing a distinctive assemblage of palynological organic matter thought to reflect a specific set of environmental conditions or to be associated with a characteristic range of hydrocarbon-generating potential" and the definition of palynofacies analysis is: "the palynological study of depositional environments and hydrocarbon source rock potential based upon the total assemblage of particulate organic matter". Furthermore, the third volume of Jansonius and McGregor's (1996) compendium of palynology include two chapters (Batten, 1996a, 1996b) with succinct and profusely illustrated summaries and exposition of the subject, including its application to petroleum exploration.

According Mendonça Filho (1999) the palynofacies term refers to the study of the particulate organic matter presents in sediments and sedimentary rocks using the organic matter isolation methods for sample preparation (kerogen concentration) and applying microscopy techniques as principal tool for acquiring data and statistical methods for its interpretation.

According to Batten and Stead (2005), palynofacies are "associations of palynological matter (PM) in sediments, considered primarily in terms of the reasons for the association, which is usually geological, but may be connected to the biological origin of the particles".

Palynofacies is a powerful analytical tool when used in conjunction with geological and geophysical information. It can be applied in the determination of kerogen types and their abundance, providing clues concerning depositional environment and hydrocarbon-generating potential. Palynofacies analysis involves the integrated study of all aspects of the palynological organic matter assemblage, which include the identification of the individual particulate components, assessment of their absolute and relative proportions, particle sizes, and their preservation states. It can be used in diverse studies, such as: geology (stratigraphy, sedimentology and palaeoenvironmental studies), paleontology (biostratigraphic studies), petroleum exploration, environmental studies, etc. (Tyson, 1995). According to Fleisher & Lane (1999), palynofacies data can be still combined with ancillary biostratigraphic information in a sequence-stratigraphic framework to help recognize reservoir–source rock geometry.

5.1 Kerogen groups

The classification of organic particles has always been rather subjective. Classifications often have a particular objective. Particles have been divided by their modification and thermal alteration, their depositional environments, botanical classification, degree of terrigenous supply and thereby distance from land, degree of degradation, and allochthonous and autochthonous fractions. It is essentially a morphological classification but it also incorporates the broad areas of provenance of particles (Tyson, 1993, 1995).

The classification of kerogen constituents is based primarily on their appearance and preservation state, using transmitted white light with ancillary observation employing fluorescence methods (UV mode). Many classification strategies have been proposed (Staplin, 1969; Correia, 1971; Burgess, 1974; Hart, 1979; Combaz, 1980; Masran & Pocock, 1981; Batten, 1981, 1982a; Batten & Morrison, 1983; Whitaker, 1984; Tyson, 1984; Boulter & Riddick, 1986; Hart, 1986; Traverse, 1988; Tyson, 1993; 1995, Mendonça Filho 1999, Mendonça Filho et al., 2010b; 2011a) based on degradational state and biological derivation (i.e., plants debris, phytoplankton, etc.). However, the classification systems are still not standardized between studies.

There are many published kerogen classifications. According to Tyson (1993), a generally acceptable terminology for transmitted light work has proved elusive and they differ by the degree of emphasis placed on different aspects of kerogen assemblage providing more detailed subdivisions of the palynomorph, phytoclast and amorphous organic matter components by greater attention to botanical source, morphology, and/or preservation states. The much more standardized and systematic maceral terminology used by organic petrologists (in reflected light studies) should never be used in transmitted light work. Macerals can only be properly defined on reflected light characteristics; any other usage can

produce pseudo-accuracy, unnecessary confusion and futile controversy. However, regarding the kerogen groups and subgroups it is important to use a classification system which gives the maximum information about the variables involved. This means the classification system shall also emphasize the most relevant factors having in mind the objectives of the study. In that case, a rigorous subdivision of the categories should be present to identify any quantitative variation related to the main controls on the distribution of the organic matter and thus use those factors in the determination of the palaeoenvironmental meaning. According to Tyson (1995), in the case of palynofacies the main objectives of microscopy are to determine: the origin of the organic matter (in terms of its botanical precursors); the relative percentages of the different constituents; the preservation state of the different constituents; the hydrocarbon generating potential of the organic matter; the degree of thermal alteration (maturity) of the organic matter; the nature of the deposition palaeoenvironment (terrestrial inputs); the redox conditions (reducing versus oxidizing); and the palaeosalinity (to differentiate fresh water, brackish or marine environments).

In transmitted white light microscopy, the three main groups of morphologic constituents recognized within kerogen assemblage are: palynomorphs (organic walled constituents that remain after maceration using HCl and HF acids), phytoclasts (fragments of tissues derived from higher plants or fungi), and amorphous organic matter - AOM (structureless material derived from non-fossilizing algae, or advanced tissue biodegradation, phytoplankton or bacterially derived AOM, higher plants resins and amorphous products of the diagenesis of macrophyte tissues).

Tables 1, 2, and 3 show the detailed classification system of the individual palynological components based on Tyson (1995), Vincent (1995), Mendonça Filho (1999), and Mendonça Filho *et al.* (2002, 2010b), indicating the appropriate use of the nomenclature for the observation of kerogen under transmitted white light.

5.1.1 Phytoclast group

The phytoclast term was introduced by Bostick (1971) to describe all particles with size clay or fine-sand derived from higher plants or fungi. They are fragments of tissues derived from higher plants or fungi and its autofluorescence depends on derived tissue. Phytoclasts can be translucent (non-opaque) or opaque (black) and non-biostructured, biostructured, structured or "pseudoamorphous". Most are derived from the highly lignified mechanical support tissue of higher plants, i.e. wood (xylem), once lignin is highly resistant to decay and tends to become selectively preserved and therefore concentrated during decay. According to Tyson (1993, 1995), the original lignin content is 25-35% in softwood and 18-25% in hardwood, but up to 70% or more in subfossil (archaeological) wood. Lignin decay is mainly through "mouldering" by "white rot" fungi; this process requires oxygen. Wherever oxygen is in short supply, e.g. in water (26 times less 02 than air), especially disoxic-anoxic water, lignin/wood preservation is enhanced. This is why coals are formed in wet swampy environments. Because it is mainly only the lignin-rich secondary cell walls that survives, even anaerobic degradation of wood produces a major weight loss (70-80%), due to degradation of the cellulosic tissues. Except in coals, it is mainly dispersed tracheid and other woody tissues which form the bulk of the phytoclast population. Other tissues may also be present, e.g. the thinner-walled material derived from "ray" tissues, but these

are produced in lower amounts, and are less well preserved (due to their lower lignin content). Gymnosperm (softwood/conifer) xylem is composed largely of tracheids-elongate cylindrical cells. These often show characteristic "bordered pits", pores in the cell wall by which adjacent cells communicate. Their pores have membranes, but these rarely survive, leaving only holes. Now, angiosperm (flowering plant) wood contains less tracheid, but has similar but larger structures called "vessels". Overall it has less lignin and is thus often less well preserved compared to gymnosperm wood.

GROUP		SUBGROUPS		DESCRIPTION
P H Y T O C L A S T	Opaque	**Equidimensional (Equant)** length: width ratio < 2		Black or opaque in colour even at grain boundary. Sharp outline; mostly no internal structure.
		Lath length: width ratio > 2		Black or opaque in colour even at grain boundary. Sharp outline; it may show pits.
		Corroded		Black in colour. More diffuse outline; irregular.
	Non-Opaque (Translucent) [Fragments of Tissues Derived from Higher Plants or Fungi]		**Fungal Hyphae**	Fragments of hyphae. Brown in colour. Individual filaments of the mycelium of the vegetative phase of eumycote (higher) fungi.
		Undegraded Sharp outline (may be slightly irregular). May be splintered. or *Degraded* Irregular and diffuse outline or *Pseudoamorphous/ "Amorphous"* Diffuse outline, it may be light brown, brown to dark brown in colour. Starting to show some features of AOM, but homogenous in apperance (*flat fluorescence*), not pyrite specked, no inclusions. It may exhibit fluorescence. or *In decomposition "Highly preserved"* Irregular outline in transmitted white light, it exhibits coloration of fluorescence. The characteristics indicate a highly degree of chemistry preservation due to specific conditions.	**Non-biostructured**	No botanical structure. Translucent, generally brown in colour. Lath or equant in shape.
			Cuticle	Epidermal tissue of higher plants. Pale yellow-green, yellow, reddish-yellow in colour. Regular cell outlines; occur as sheet-like, in some cases with visible stomata. It may occur as thick translucent phytoclasts that present a yellow fluorescing cuticle coating. This particular feature (cuticular layer fragments associated with innermost part of epiderms) could be indicating that the land plant fragments derived from leaves.
			Membrane	Pale yellow in colour; thin; sheet-like; irregular. Often fluorescent; highly translucent. Lack of diagnostic internal structure.
			Biostructured	Generally brown in colour; lath to equant in shape; clearly visible internal structure. *Striate:* thin (regular fibrous lineation). *Striped:* Irregular or unequal stripes (may be thickenings). *Banded:* Regular and equal parallel sided thickenings. *Pitted:* Bordered or scalariform pits.
	Sclereids	Generally opaque, but may be translucent (dark brown). Sclerenchymatic tissue cells, with thickened secondary wall and impregnated with lignin. Found in different parts of the plant (root, stem and leaf) with the sustentation function and mechanical resistance.		

Table 1. Detailed classification system of the individual palynological components from Phytoclast Group based on Tyson (1995), Vincent (1995), Mendonça Filho (1999), and Mendonça Filho *et al.* (2002, 2010b, 2011a).

5.1.2 Palynomorph group

Palynomorphs are organic-walled microfossils present in a rock that remain after maceration using HCl acid for carbonates and HF acid for silicates**.** Organic-walled

microfossils are composed of entirely unmineralized proteinaceous material, such as: chitinozoans, spores and pollen, prasinophytes, acritarchs, and dinoflagellates. The term of palynomorph was introduced by Tchudy (1961) to refer to all discrete HCl and HF-resistant, organic-walled (unicellular, multicellular, or colonial) microfossil that may be present in palynological preparations. They are discrete, coherent, individual or colonial entities and it can be subdivided into: terrestrial (sporomorphs) and aquatic (marine and fresh water) subgroups (Tyson, 1995).

Sporomorph Subgroup (terrestrial palynomorphs)

The term sporomorphs was originally defined as a useful collective term for all terrestrial spores and pollen grains. In this case, it would be all palynomorphs produced by land plants (although some would exclude fungal spores). This subgroup is composed by two components: spores and pollen grains (spores and pollen grains are not the same thing, they have a different position in the life cycle, but both are a means of indirect or direct dispersal of gametes), with variable fluorescence properties (Tyson, 1995).

Spores and pollen grains are parts of the reproductive cycle of plants and range in age from Late Ordovician and Carboniferous, respectively, to Holocene. Although land derived, the grains can be carried by wind and water currents into marine and nonmarine environments. The type and relative abundance of spores and pollen grains provide useful paleoenvironmental and paleoclimatic information, and they are widely used for basinal and regional stratigraphic correlation.

Spores are produced by Bryophyte, Pteridophyte (fern type) plants and their primitive ancestors. They first appear in the late Ordovician and continue to the present day. They are formed in tetrads. About the shape, spores are mostly triangular or circular; the most common type is the trilete spore, which has a Y-shaped mark. Monolete spores (oval and have an "I"-shaped mark) are less common. Different forms, sizes and ornamentation can occur and they may have a wide diversity of ornament on their outer ("distal") surface (spines, ridges, etc.).

Pollen Grain are produced by the seed-producing plants, such as Gymnosperms (e.g. Conifers), Carboniferous-Present; Angiosperms (flowering plants), Early Cretaceous-Present (dominate global flora from Late Cretaceous onwards). They are produced in dyad, tetrads and polyads, but only very rarely is a trilete mark visible. They are produced by the seed-producing plants. The presence of dyad, tetrads and polyads (pollen grain agglomerates) are an indication of proximity of a source area. Most pollen is circular or oval in outline.

Fungal Spore

According to Tyson (1995), the presence of fungal spores can indicate a close proximity to, or redeposition from, active fluvio-deltaic source areas (especially deltaic, estuarine, or lagoonal oxic facies). When these organic particles are associated with high numbers of dinocysts and foraminiferal linings, they can indicate upwelling areas.

Freshwater (Organic-Walled) Microplankton

Other subgroup from the palynomorph group is the fresh water microplankton. They belong to the aquatic constituents from this group. The main components from this group belong to the Chlorococcale Algae. There are 2 common forms, both colonial and exclusively freshwater: *Botryococcus* and *Pediastrum*.

Botryococcus **(Carboniferous to Recent)**

Algae from *Botryococcus* genus are irregular globular colonies of variable size (30-2,000µm). The colonies often have several lobes (like miniature cauliflower heads) and they may show a vaguely radial texture. More structure, including circular pits on the surface (cell cups), may be visible under fluorescence. Usually a yellow glossy appearance in immature sediments and they can be orange-brown, presenting a typically strong fluorescence. The stratigraphic record of the colonial freshwater alga *Botryococcus* spans the Carboniferous to the present (about 360 Ma) and they occur widely in lagoonal and lacustrine facies (they occur in marine sediments only by redeposition or transportation, e.g. prodeltaic facies). They can tolerate elevated salinities, but only in lakes. Large modern blooms occur in temporary lakes in the Australian Coorong Region; drying out of the lakes deposits the buoyant algae, sometimes forming a rubbery mat-like deposit known as Coorongite. No equivalent ancient sediments are known. *Botryococcus*-rich oil shale is referred to as Torbanite (first described from carboniferous of the Edinburgh region); however, most of their kerogen is usually "AOM". Torbanites have type I kerogen (organic facies A or AB) and are excellent source rocks in some rift basins (Tyson, 1995). *Botryococcus* algae are very rich in lipids (hydrogen) and they can liberate hydrocarbons (oil) in life (Canter-Lund & Lund, 1998).

Pediastrum **(Early Cretaceous-Recent)**

The other most common genus of fossilizing Chlorococcale algae is *Pediastrum*. Flat "cog-wheel"-shaped colonies (coenobia). According to Evitt (1963), the geological record of this genus extends back to the Early Cretaceous, and at least as early as the Late Barremian. The colonies of *Pediastrum* form characteristic non-mucilaginous, flat, discoidal units, which are one cell layer thick and have a "cog wheel shaped" outline. The flat "cog- wheel"-shaped colonies are called coenobia. The polygonal cells have a concentric arrangement and the outer cells have one or two triangular points each (giving the teeth of the "cogs"). Mostly 30-200µm in diameter and they are common in lacustrine facies, although rarely in the same samples as abundant *Botryococcus*, because they compete to the same environment. Most species prefer higher nutrient concentrations and reflect higher productivity settings. Nevertheless, they cannot tolerate elevated salinities, and thus tend to occur in lakes of wetter climates and can be redeposited into marine sediments. *Pediastrum*-rich sediments often have a type I or type II composition. They can represent important source rocks in Cretaceous and Cenozoic rift basins (e.g. W. Africa, China, Indonesia and Brazil). *Pediastrum*-rich oil shales do not have a specific name (Tyson, 1995).

Zygnemataceae Family (Carboniferous-Recent)

The Zygnemataceae are an extant Family of hydro-terrestrial, filamentous green algae which produce acid-resistant spores. Palynomorphs of probable zygnematacean affinity often referred to as "acritarchs", occur frequently in sediments of Late Palaeozoic to Holocene age. Only the filamentous algae spores are preserved. In Recent zygnematacean algae the form, size and markings of the spore wall are very important for species identification. The majority of species have spores of constant form, only a very few are polymorphic. The forms are of four primary types (globose, obovoid, ellipsoid and quadrangular) of which a number of variation are known (Grenfell, 1995). The filamentous Zygnemataceae algae inhabit a great variety of freshwater habitats including cold, swift flowing streams; warm,

stagnant pools and moist soils and peats. Most species prefer stagnant pools, ponds and ditches (Hoshaw and MacCourt, 1988).

Most Recent species of the Zygnemataceae form zygospores in clean, oxygen rich, stagnant and shallow freshwater. In the fossil record, the presence of a non-marine depositional environment may be inferred when the following are fairly abundant. Such non-marine environment would include fluvial and lacustrine facies where swamps, marsh and shallow, stagnant yet oxygenated water bodies persisted. Studies of extant Zygnemataceae indicate that they inhabit a wide range of hydro-terrestrial habitats but most species prefer fluvial and lacustrine facies. The presence and abundance of fossil zygnematacean spores are potential indicators of palaeoenvironment (Grenfell, 1995).

Marine (Organic-Walled) Microplankton

Other subgroup from the Palynomorph Group is the marine organic-walled microplankton. They belong to the aquatic constituents from this group as well as freshwater organic-walled microplankton (*Botryococcus* and *Pediastrum*).

The fossil record of the organic-walled microplankton (OWM) is very incomplete. Only a fraction of the original plankton biomass and taxa are preserved, generally only those parts of the life cycle that produce resistant "cysts" or similar structures, probably made of Algaenan- type substances (Tyson, 1995). Marine Microplankton includes dinocysts, acritarchs and prasinophytes. They exhibit variable fluorescence properties and some taxa may tolerate brackish conditions. Late Precambrian and Palaeozoic OWM are dominated by the Acritarchs and Prasinophytes. The period of low global sea levels in the carboniferous to E. Triassic resulted in elimination of most Acritarchs, and sediments of this age contain very little OWM. In the Mid-Late Triassic, as sea-level raised again, the cyst-forming dinoflagellate cysts (dinocysts) "evolved", becoming common and diverse by the end of the M. Jurassic, dominating over the Acritarchs except in marginal marine environments. Dinocyst diversity is correlated with the global sea level and was highest during the Mid Late Cretaceous; they continue to the present day. Prasinophyte algae range in age from Precambrian to the present (Tyson, 1995; Mendonça Filho *et al.*, 2011a).

Prasinophyte algae

Prasinophyte algae are present an Age range from Precambrian to Recent. Fossilizing structures produced by small quadriflagellate phytoplankton which do not themselves fossilize. Modern flagellates occur in fresh to hypersaline waters, but fossil forms are exclusively marines. The fossilizing structures are referred to as phycomata (singular: phycoma) to distinguish them from cysts; this is because they are not dormant, but the cell contents are actively dividing and growing during life. The phycomata are buoyant (due to internal lipid globule), float and thus have a pelagic distribution, occurring widely in shallow or deep waters. They are only sedimented when ingested or the living content has emerged. As the whole life cycle occurs in the surface water, it is described as "holoplanktic". The mero/holo plankton (i.e. Dinocyst or Acritarch to Prasinophyte) ratio decreases offshore. Although occur a wide distribution, seldom these algae are common except in marine organic rich black shales (AOM-rich), where they may be the dominant OWM. Phycomata have a very oil prone composition; this may result in a rich organic facies (Tyson, 1995).

Acritarchs

Evitt (1963) introduced the name Acritarchs to describe a variety of diverse OWM which do not have characteristic dinocyst features (i.e. no paratabulation). They are marine microplankton of unknown biological affinity. Acritarchs are a polyphyletic group of palynomorphs whose name means "of uncertain origin" (*incertae sedis*) and may include cysts, egg cases, etc. They range from Precambrian to Holocene in age (Tyson, 1995).

They are excellent biostratigraphic indices for Proterozoic through Devonian strata but are less important in the Mesozoic and Cenozoic. They are most diverse during the Ordovician-Silurian. Distribution pattern indicates they were mostly marine phytoplankton. As they have no formal taxonomic status, and the organisms which produced these palynomorphs are either extinct or unknown, the acritarchs have been classified entirely on the basis of morphological characteristics. Post-Palaeozoic Acritarchs are less diverse, mostly simple, small (10-20μm), spiny forms with a central spherical body. Acritarchs occur abundantly in fine-grained rocks and are geographically widespread (Tyson, 1995).

Dinoflagellate Cysts (Dinocysts)

Dinoflagellates are the resting cysts of marine, unicellular red algae. Dinoflagellates present a cellulosic composition and do not fossilize; only the resistant resting cyst produced during the sexual part of the life cycle survives. The life cycle alternates between active asexual planktic flagellate cells which live in the surface waters (using their flagellae to swim), and the dormant benthic resting cysts (zygotes) produced during the sexual phase of the life cycle. This part planktic and part benthic life cycle is described as "meroplanktic" (spending part of their life as a motile flagellate phase, and part as a benthic resting cyst). The fossil record of dinoflagellates is almost entirely confined to forms that have a meroplanktonic life; cysts are produced abundantly only by these forms. They occur abundantly in Upper Triassic to Holocene sediments and are excellent biostratigraphic indices because of their rapid evolution and widespread geographic distribution. Dinoflagellate cysts occur predominantly in marine rocks but also are present in Cretaceous and Cenozoic lacustrine facies. Cysts are produced abundantly only by those meroplanktic. Even those dinoflagellates that produce cysts do not do so to the same extent; in some species 50-85% of the motile individuals may produce cysts (e.g. *Operculodinium*), whereas in others (e.g. *Spiniferites*) the corresponding value may be only 0,2-3,0% (Dodge & Harland, 1991). Dinoflagellates live in unstable shallow shelf waters. Organic walled cysts are not produced in permanently stratified waters like the modern (oxic) ocean, nor apparently in some ancient deep shelf basins. Most dinocysts in ocean sediments have been redeposited from the shelf. The morphology and diversity of dinoflagellate assemblages can be used to differentiate marine environments (Tyson, 1995; Vincent, 1995).

Zoomorph Subgroup

Zoomorph subgroup is composed by animal-derived palynomorphs (discrete unitary animal-derived particles, whether whole or damaged, are classified as zoomorph palynomorphs) including foraminiferal linings, chitinozoa and scolecodonts (Müller, 1959; Tschudy, 1969. It is identifiable as fragment zoomorph palynomorphs (Tyson, 1989, 1995).

Zooclast Group

Zooclast Group is a different group from the organic matter comprising animal-derived organic particles (e.g. graptolites, crustacean eggs, tintinnids, insect cuticle fragments, and

other arthropod cuticle fragments). They are material of definite animal origin (has specific morphological characteristics). Zooclasts are unknown organic particle, structured, fragmentary particle (clast), angular broken outline, obviously not a whole discrete entity (spines, slits, hairs, joints, etc.) and those particles identifiable as fragmented zoomorph palynomorphs are not classified as zooclasts. The most common varieties of zooclasts include arthropod exoskeletal debris, organic linings from some bivalve shells and ostracod carapaces and graptolite fragments (Tyson, 1989, 1995).

GROUP	SUBGROUPS		DESCRIPTION
P A L Y N O M O R P H / Sporomorph	**Spores**	Terrestrial Palynomorph produced by Pteridophyte, Briophyte and Fungi.	Triangular or circular form palynomorph, trilete mark ("Y") or monolete (scar). They can occur as massulae of the freshwater fern (Azolla), agglomerates and tetrad. "First spores" (Cambrian): Cryptospores (spore-like bodies) and Embryophyte Spores: Upper Ordovician-Recent.
	Pollen Grain	Terrestrial Palynomorph produced by Gymnosperms and Angiosperms	Palynomorph with varied ornamentation, most with circular or oval outline; could present opening or not. They can occur as agglomerates or tetrads. Devonian-Recent.
Freshwater Microplanckon	*Botryococcus*	Chlorococcales Algae	Irregular globular colonies; size 30 to 2000 μm, sometimes with several lobes (like miniature cauliflower); Ordovician-Recent.
	Pediastrum		Colonial green algae (coenobia). Rounded colonies with 30-200 μm diameter. In polygonal form the cells have a concentric arrangement; cells present two horns in the side external. Jurassic (?) - Recent.
Marine Microplankton	**Dinoflagellate Cysts**	Cell produced during the sexual phase of the dinoflagellate life cycle	The fossil record of dinocysts is almost entirely confined to forms that have a meroplanktonic life cycle. Major dinogellate cyst morphotypes: Proximate, Cavate and Chorate. Triassic-Recent.
	Prasinophyte	Fossilized structure produced by small quadri-flagellate motile phase.	Majority, like *Tasmanites*, are spherical; diameter 50 to 2000 μm. Modern species include freshwater. Precambrian-Recent.
	Acritarchs	Unicellular fossilized cysts with organic cell walls. They have no formal taxonomic status.	The acritarchs are a polyphyletic group of palynomorphs whose name means "of uncertain origin". Acritarcha (*akritos* = uncertain, mixed and *arche* = origin). Small dimension organism (5 a 150 μm). Simmetrically shaped with varied ornamentation. They first appeared in the late Precambrian, attained their acme during the Ordovician-Devonian.
Zoomorph	**Foraminiferal Test-Linings**	Chitinous organic linings to calcareous shells of foraminifera.	The linings are typically dark brown colour, although their outer chambers are often more thin-walled and translucent. Good indicator of marine conditions.
	Scolecodonts	Elements of the jaw of benthic polychaete annelid worms.	They are the part-calcified and scleroprotenaceous ("chitinous") mouth parts ("pharyngeal jaws") of benthic polychaete annelid worms. Ordovician - Recent.
	Chitinozoa	Vesicles in format of flasks or small hollow bottles (30 to 2000 μm). Uncertain affinity.	They constitute an extinct group of organic-walled microfossils found in Palaeozoic marine sediments. Early Ordovician - Late Devonian.
Others	**Zooclasts (Graptolite, Crustacean eggs); *Spongiophyton*.**		

Table 2. Detailed classification system of the individual palynological components from Palynomorph Group based on Tyson (1995), Vincent (1995), Mendonça Filho (1999) and Mendonça Filho *et al.* (2002, 2010a, 2011a).

5.1.3 Amorphous Group (Amorphous Organic Matter)

The Amorphous Group consists of all particulate organic components that appear structureless at the scale of light microscopy; including phytoplankton derived amorphous organic matter (traditionally referred to as "AOM"), bacterially derived amorphous organic matter (also traditionally referred to as "AOM"), higher plant resins, and amorphous products of the diagenesis of macrophyte tissues (Tyson, 1995).

Typical AOM (Amorphous Organic Matter) is directly or indirectly derived from phytoplankton (taxa or parts which do not fossilize as recognizable structures, i.e. not as palynomorphs) or bacteria (autotrophic or heterotrophic bacteria). They may be yellow, orange, brown or grey in color; irregular particles; rounded to angular; gradational margins; homogeneous or heterogeneous; varied common micro-inclusions; often strongly fluorescent, but can be variable. The amorphous material (especially "AOM") commonly acts as a matrix for a diversity of structured. AOM is the single most important source of hydrocarbons, and the main type of kerogen in source rocks. The main sources of AOM are the degradation of phytoplankton or bacteria; reworking of organic matter (phytoplankton) by heterotrophic bacteria and bacteria activity products (Tyson, 1995; Mendonça Filho *et al.*, 2010b).

GROUP	SUBGROUP		DESCRIPTION
AMORPHOUS ORGANIC MATTER	**"AOM"** Phytoplankton or bacterially derived amorphous organic matter - derived from reworked microbiological matter.		Structureless material with no morphology or form; color: yellow-orange-red; orange-brown, ash; often has palynomorphs and pyrite inclusions, may sometimes exhibit fluorescence.
	Resin Mostly produced by terrestrial higher plants in tropical climates.		Structureless particle (glassy shards), hyaline, usually round, homogeneous, strongly fluorescent.
	Amorphous Products	Products of macrophyte tissues (*Pseudoamorphous/ "Amorphous"*)	Diffuse outline, light brown, brown and dark brown in colour. Starting to show some features of AOM, but homogenous in apperance (*flat fluorescence*), not pyrite specked, no inclusions. It may exhibit fluorescence.
		Microbial mats	They consist predominantly of the maceral lamalginite when examined in reflected white light. They form rather uniformly and strongly fluorescent cohesive particles which show relatively sharp and distinct (sometimes quite angular) outlines after maceration.
		Products from bacteria *Bacterial Extracellular Polymeric Substance (EPS)*	Mucilagenous sheet. Diffuse outline, thin, pale yellow, yellow, orange, ash in colour. Not pyrite specked, no inclusions. Exhibits intense fluorescence.

Table 3. Detailed classification system of the individual palynological components from AOM Group based on Tyson (1995), Vincent (1995), Mendonça Filho (1999), and Mendonça Filho *et al.* (2002, 2010b, 2011a).

The other component is amorphous organic matter terrestrially derived, which has been reworked to different extent exhibiting high content of carbohydrates. This AOM undergoes a microbiologic reworked in reducing conditions (plant material reworked by heterotrophic

bacteria colony), where various amorphization stages can be distinguished ranging from subangular particles with neat boundaries to particles with diffuse limits and is associated predominantly to shales. In this case the derived amorphous organic matter is generally associated with the highest TOC content (Mendonça Filho *et al*., 2010a, 2010b).

AOM can be derived by bacterial activity (autotrophic-photosynthetic bacteria) producing a bacterial mucilage and is associated with predominantly carbonate sediments. The mucilage, Extracellular Polymeric Substance (EPS), is rich in lipids and proteins and extremely resistant (higher preservation potential). Cyanobacterias (blue-green algae) and thiobacterias (sulphur bacteria) are the main responsible for the production of the EPS (Mendonça Filho *et al*., 2010a). These organisms do not normally fossilize as recognizable entities, but the dominant forms have a filamentous growth habit (each filament consisting of a trichome – a chain of cells) surrounded by a mucilagenous sheath (cover), and under certain conditions, their constituent cyanobacteria and thiobacteria may be important sources of oil-prone amorphous organic matter and the microbial mats are among the most productive ecosystems in the world (Tyson, 1995). This type of material can appear in a pelicular AOM (*sensu* Combaz, 1980); imprinting the organic matter with a crater aspect, due to impression of the carbonate minerals following dissolution with HCl. The pelicular AOM is generally associated with low organic content (Mendonça Filho *et al*., 2010a). The mucilaginous material also can suffer a microbiological reworking in reduction conditions (heterotrophic bacteria colonies reworking the EPS produced by the autotrophic bacteria) and appear as a dense, highly-fluorescent aspect, in a plate form, at times, with angular outlines. In this case the derived amorphous organic matter is usually associated with the highest organic content (Mendonça Filho *et al*., 2010a).

Resin and Amber

Resins are natural products of higher plants which occur either as internal cell- or void-filling secretions, or as extracellular exudations on the plant (stem or leaf) surface and they are classified within the Amorphous Group because they are inherently structureless. They should not be referred to by the abbreviation "AOM", which is traditionally reserved solely for material of a phytoplankton or bacterial origin. Higher plant resins (microscopic amber) can be intracellular or extracellular; resistant if not exposed to air; glassy (hyaline) shards easily rounded to beads; mostly produced by Angiosperm trees in tropical climates and very oil-prone, but usually minor component (Tyson, 1995).

Amorphous Terrestrial Humic Materials

The biodegradation of land plants (phytoclast degradation products, see pseudo-amorphous and amorphous phytoclasts) often results in the production of primary intra and extracellular amorphous material. They are rare even in coals, except when intracellular; they tend to be more homogeneous than "AOM" and present no organic inclusions (Tyson, 1995).

6. Organic composition: Geochemical analyses

6.1 Total Organic Carbon (TOC)

The abundance of organic matter in sediments is usually expressed as the relative percentage of organic carbon on a dry weight basis. The TOC is a measure of total organic

carbon in a sample (Jarvie, 1991; Bordenave *et al.*, 1993). The Total Organic Carbon (TOC) is determined on a device through the combustion of the organic carbon to CO_2 in an oxygen atmosphere using the decarbonated residue of powdered sample (after carbonate carbon has been removed by HCl acid treatment). The organic carbon analyses are performed on finely ground rock samples in a combustion apparatus utilizing an induction furnace and a thermal conductivity cell to measure the evolved CO_2. However, this procedure really determines only organic carbon content, and not the total organic matter or kerogen. In some cases, extractable organic matter (bitumen) is removed prior to determination of organic carbon. The percentage of organic carbon corresponding to bitumen is usually not more than 0.1% or 0.2% of the total (Tissot & Welte, 1984). Only part of the organic matter is carbon (the rest, in order of importance, is mostly O, H, N, and S). Even if there is 100% OM, there will not be 100% TOC. The carbon content of OM varies from 60-80% for kerogens and 30-75% for modern OM. It is high in both type I and type IV ancient kerogens (Tyson, 1989, 1995). The elemental composition of kerogen depends on type and level of evolution (thermal maturation). Thus, to compensate for other elements present in kerogen, the value found for organic carbon should be multiplied by a conversion factor (Tissot & Welte, 1984). The conversion factors can range from 1.07 (metamorphosed rocks) up to 1.40 for non-metamorphosed organic matter rich in oxygen (Forsman and Hunt, 1958).

The TOC determination technique provides a simple measure of organic matter content of sediments, however there are some problems with the interpretation of TOC data. According to Tyson (1995), the main problem is that of dilution; because TOC is expressed as a relative percentage, it depends not only on the supply and preservation of organic matter but also on the supply and preservation of siliciclastic and biogenic material. It is a purely relative concentration parameter, affected by the relative absolute accumulation of both organic matter and sediment. TOC is always controlled by a set of three master variables: the input of OM, the preservation of the supplied OM, and the dilution of this OM by mineral matter (Tyson, 1989, 1995). Besides, geochemically significant changes in the organic matter may not be represented by a change in the TOC. Despite these problems TOC% is widely used to express the quantity of organic matter and its analysis gives an excellent base for further other organic geochemical methods. The TOC analysis must be used in conjunction with other methods, e.g. Rock-Eval Pyrolysis or data from optical studies, in order to evaluate the nature of the organic matter present (Bustin, 1988; Tyson, 1989, 1995; Bordenave *et al.*, 1993), and TOC% can also provide an extra element of quantification to palynofacies studies when combined with percentage abundance data of the organic matter constituents.

6.2 Rock-eval pyrolysis and hidrouspyrolysis

Pyrolysis is defined as the thermal decomposition of organic matter through the application of heat in the absence of oxygen. This technique does allow the simulation of natural processes in laboratory under controlled experimental conditions; time, temperature, pressure and reaction system (Tissot & Welte, 1985).

In petroleum exploration, pyrolysis is a useful tool to study and understand petroleum system processes such as: hydrocarbon generation; cracking of oil to gas in reservoirs and

generation of carbon dioxide and organic acids. Experimental data can be used for basin modeling purposes, like kinetic of hydrocarbon generation or oil to gas cracking; vitrinite reflectance evolution or prediction of porosity and permeability.

Open-system and closed-system pyrolysis are the main pyrolysis methods which lend itself well to tasks in petroleum geochemistry. The open-system pyrolysis is an analytical technique which is conducted at high temperatures and over short heating times in a flowing stream of inert gas, is used to break down kerogen into volatile products. An example of analytical pyrolysis is the Rock-Eval Pyrolysis equipment. The closed-system or pyrolysis of simulation, differently of the open-system, is conducted at low temperatures and over longer heating times in a closed system. These conditions are used to gradually break down kerogen into volatile products. This process is considered to mimic natural petroleum formation. There are numerous closed-systems pyrolysis such as: hydrous pyrolysis confined (gold tube) pyrolysis and Micro Scale Sealed Vessel (MSSV).

Rock-Eval Pyrolysis

Espitalié *et al.* (1977) published the first paper on the development and application of the Rock-Eval Pyrolysis. This technique is considered a more cost-effective means of geochemical kerogen typing than elemental analysis because prior kerogen separation is not required. Rock-Eval pyrolysis is the one of the standard petroleum industry organic geochemical screening methods; when combined with TOC data it allows the identification of potential source rocks and gives an idea of their quality. The products from pyrolysis resulting in 3 different peaks: P_1, P_2, and P_3 and their correspondent areas S_1, S_2, and S_3, respectively and thus their mass (mg) can be determined:

Peak P1 (S1) represents any free hydrocarbons in the rock that either was present at time of deposition or was generated from the kerogen since deposition (S1 is the amount of free hydrocarbons originally present in the rock - mg HC/g of rock).

Peak P2 (S2) represents the amount of milligrams of hydrocarbons per gram of rock that can be generated by pyrolytic degradation of the kerogen normalised to the weight of the samples; providing a reasonable evaluation of source rock potential.

Peak P3 (S3) represents the CO_2 yielded through the break of carboxyl groups from the kerogen the amount of CO_2 released from resistant components of the kerogen (mg CO_2/g of rock).

Normalization of the Rock-Eval Pyrolysis yields to the sample TOC permits the calculation of several parameters. According Espitalié *et al.* (1977), the ratio of mg HC in S2/g TOC is called *Hydrogen Index* (*HI*). The ratio of mg CO_2 in S3/g TOC is called *Oxygen Index* (*OI*).

Production index (*PI*) is defined as the ratio S1/(S1+S2). This ratio is used as a maturity parameter when migration process did not occur.

The temperature corresponding to the maximum of hydrocarbon generation during the pyrolysis (maximum amount of hydrocarbons is generated – S2) is considered a parameter for evaluation of the maturation stage. This parameter is called maximum temperature of pyrolysis (*T_{max}*).

T_{max} is the common parameter used to estimate the thermal evolution of the organic matter. Values increase with maturity. T_{max} values < 435^0C represents immature organic matter; values between 435^0C-470^0C represents the oil window (mature organic matter) and T_{max}>470^0C represents the overmature zone. However, T_{max} is partially dependent on other factors, such as type of organic matter (Tissot & Welte, 1984) and concentration of S2 peak (<0.2 mg HC/g rock, Peters, 1986).

Hydrous pyrolysis

Simulation pyrolysis is conducted at low temperatures and over longer heating times in a closed system to gradually break down kerogen into volatile products. This simulation can be performed in the presence (hydrous pyrolysis) or absence (anhydrous pyrolysis) of water. Hydrous pyrolysis experiments are conducted in autoclaves using water excess. The pressure of the system is equal of the water pressure. In a different way, anhydrous pyrolysis is performed in sealed gold tubes load in autoclaves without water (confined pyrolysis). In these experiments the pressure of the system is controlled and several samples can be heated at the same time. In this section only the hydrous pyrolysis technique will be discussed.

Hydrous pyrolysis technique can be defined as a hydrothermal experiment which allows the pyrolysis of potential petroleum-source rocks in the presence of water. Specific conditions of weight of sample and water, reactor volume and reaction temperature are necessary to ensure the liquid phase of water during heating (Lewan, 1993). The equipment is a simple system which basically consists in autoclaves with variable volumes and wall composition, an oven, manometer and a temperature controller.

For these experiments are necessary an immature sample with higher values of TOC and potential generation. This type of pyrolysis is normally undertaken over a period of 72 hours at one specific temperature.

A series of temperatures can be used to increase the thermal evolution of the organic matter in a source rock at different maturity levels. The amount and type of hydrocarbons produced can be measured and analyzed. Most immature source rocks will produce measurable amounts of oil and gas in such experiments. This analysis is probably the most useful for a complete evaluation of the amount and type of hydrocarbons that a source rock will produce at various maturity levels. Bitumens and expelled oils generated during hydrous pyrolysis experiments show the chemical composition trend similar to observed in natural samples. Bitumens are enriched in high-molecular-weight hydrocarbons and heteroatom compounds (resins and asphaltenes) while expelled oils are enriched in saturated hydrocarbons.

Hydrous pyrolysis products allow a better understanding of the petroleum systems. Comparative studies between the generated bitumen and its correspondent expelled oil are possible without interferences attributable to organic facies variations in the source rock or secondary process, such as biodegradation, water washing, migration or additional maturation, mixing with other oils or bitumens (Peters *et al.*, 1990).

Lewan (1993) determined through the monitoring of the hydrous pyrolysis products (expelled oil, heated sample or kerogen and retained bitumen) that petroleum generation involves two mainly reactions:

Kerogen → Thermal decomposition → **Bitumen** → Thermal decomposition → **Oil**

These reactions are also suggested in natural systems (Tissot & Welte, 1984). According to Lewan (1993) four stages can be described for petroleum formation:

1. Pre-oil generation: in this stage the organic matter occurs as an immature solid kerogen;
2. Incipient-oil generation: represents the beginning of thermal decomposition of the kerogen into a bitumen;
3. Primary-oil generation: this stage represents the thermal decomposition of bitumen into oil. During this decomposition the kerogen concentration remains constant;
4. Post-oil generation: in this stage bitumen and expelled oil are thermally decomposed into gas and pyrobitumen.

The role of the water during simulation of oil generation and expulsion was observed in the experiments reported by Comet *et al.* (1986), Tannenbaum *et al.* (1986), Lewan (1993) and Lewan & Roy (2011). These authors observed that the yields of products obtained by hydrous pyrolysis were higher than those obtained with the anhydrous pyrolysis. The presence of pyrobitumen was obtained when experiments were performed in the absence of water (anhydrous pyrolysis) and, no expelled oil was observed in these conditions. According to Lewan (1997), the presence of a pyrobitumen in anhydrous and an expelled oil in hydrous conditions suggests that two reactions pathways may occur during the experiments: cross-linking reactions (covalent bonds are made between carbon atoms intra- or inter-adjacent), and cracking reactions (bonds between carbon atoms are broken). These reactions are responsible for the products obtained in experiments under hydrous or anhydrous conditions. Cross-linking reactions promote the formation of insoluble products of high molecular weight (pyrobitumen or char) while cracking reactions promote the formation of soluble products with low molecular weight. Both reactions compete in conditions of heat stress and occur by free radical mechanisms (Lewan, 1997).

6.3 Organic matter extraction (bitumen)

Analysis of bitumen (e.g. sedimentary biomarkers) involves extracting the sediment with a suitable combination of organic solvents, usually followed by some separation procedure in order to aid component identification by proving less complex mixtures. Organic matter is extracted from rocks using Soxhlet apparatus and dichloromethane as solvent. Numerous solvent mixtures have been used by organic geochemists to extract bitumen from environmental and geological samples (e.g., benzene/MeOH, toluene/MeOH, chloroform/MeOH, dichloromethane and DCM/MeOH).

A crushed and dried rock sample is extracted by Soxhlet apparatus with an organic solvent such as dichloromethane. The sample is transferred to a cellulose extraction thimble, and covered with glass wool. The thimble is placed in the extraction tube, which itself sits on a flask containing an organic solvent (like dichloromethane). The solvent is boiled, and its

vapour travels upward through the extraction tube into the condenser tube. The cool water flowing around the outside of the condenser tube condenses the vapor, which then drips into the thimble, containing the sample. These samples are run in a Soxhlet extractor for 8 hours; reflux events occurred every 10-15 minutes. Removal of free sulphur is performed by simultaneous treatment with active copper filings. The Extractable Organic Matter (EOM) is weighed after removal of the solvent by evaporation. Although some light compounds are lost during evaporation step, steranes and triterpanes are unaffected by evaporative loss.

6.4 Liquid Chromatography (LC)

Biomarkers are commonly trace components in oils and bitumens and normally must be concentrated prior to analysis (Peters *et al.*, 2005; Bastow *et al.*, 2007). These types of separations are also useful when characterizing samples with large unresolved complex mixtures (UCMs) that are typical of biodegraded petroleum and can be difficult to characterize using a gas chromatograph-flame ionizing detector (GC-FID) or gas chromatograph–mass spectrometer (GC–MS) alone (Bastow *et al.*, 2007).

Some laboratories routinely use open-column chromatography with activated silica gel to separate saturated, aromatic and NSO compounds (**N**itrogen, **S**ulphur and **O**xygen containing non-hydrocarbons) from crude oils and rock extracts. The saturate fraction represents the non-aromatic compounds including normal, branched and cycloalkanes. The aromatic fraction contains organic compounds with one or more unsaturated rings such as monoaromatics and polycyclic aromatic hydrocarbons. In column chromatography, the bitumen sample is poured on to silica gel adsorbent in a glass column, and fractions are collected by successive elution of solvents with increasing polarity. Therefore, molecular separation in silica gel chromatography is based upon the polarity of a particular molecule.

In the procedure a 25 mm i.d. column is packed with pre-activated silica gel (28–200 mesh). Organic solvents such as *n*-Hexane, *n*-hexane / dichloromethame (8:2,v/v) and dichloromethane / methanol (1:1, v/v) are used to elute saturated, aromatic hydrocarbons and polar NSO fractions, respectively.

6.5 Gas Chromatography (GC)

Gas chromatography (GC) is the principal method of analysis for thermally stable volatile organic compounds present in mixtures that can span a wide range of complexity (Poole *et al.*, 1992).

The saturated fraction to be analyzed is injected into the gas chromatograph. Each injected sample is vaporized and mixed with an inert carrier gas (helium) and then moves through a capillary column. It is inside the column where the separation of the individual chemical components takes place.

The different compounds are separated during the movement down the column as they are repeatedly retained by stationary phase and release into the mobile phase depending on their volatility and affinity for each phase. Therefore, the separation of the hydrocarbons is

achieved primarily according to molecular weight and volatility. The separated compounds leave the gas chromatograph and achieve a flame ionization detector (FID) that responds any compound with C-H bond.

The whole extract analysis by GC is particularly useful for identifying the presence of polar contaminants which are removed by liquid chromatographic separation prior to saturate GC-MS analysis. This technique provides a fingerprint of all compounds which are solvent extractable from rocks.

6.6 Gas Chromatography coupled to Mass Spectrometry (GC-MS)

The separated compounds leave the gas chromatograph in sequence and enter the mass spectrometer's ion chamber, where they are analyzed in the same sequence. Each compound entering the mass spectrometer is bombarded with a high-energy electron beam that ionizes the molecules by knocking off one electron. The molecular ions formed in this manner are unstable, however; most break apart to give a variety of smaller fragment ions. The molecule and fragment ions produced in this manner differ in mass, but most bear a +1 charge. Because of the differences in their mass/charge caused by differences in mass, they can be separated by a magnetic field or quadrupole mass filters. The separated ions move sequentially to the detector where the relative abundances of each mass are recorded (Waples & Machihara, 1991).

The various classes of biomarkers fragment in characteristic ways in the mass spectrometer, depending upon their molecular structures (e.g. m/z 85, 191, 217 e 218 to n-alkanes, terpanes and steranes, respectively). The determination of biomarkers is generally accomplished using gas chromatography-mass spectrometry and techniques such as multiple-ion detection (selected-ion monitoring). High resolution mass spectrometry (HRMS) is often used to analyze biomarkers in petroleum, due to its ability to provide quantitative data for compounds present in complex mixtures. However, HRMS requires a significant financial investment as well as highly trained operators to assure valid results (Philp *et al.*, 1990).

6.7 Biomarkers

Biomarkers (chemical fossils) are sedimentary organic compounds whose basic skeletons suggest an unambiguous link with known contemporary natural products, and were synthesized by biota present at the time of the deposition of the sediment (Kohnen *et al.*, 1991). Lipids derived from organisms contributing organic matter to depositional environments can be preserve in the sedimentary record where they can act as biological markers (biomarkers) for both the organisms and the environmental conditions prevailing at the time of deposition (Farrimond *et al.*, 2003). As a result organic matter deposited in different environments is characterized by different molecular signals, depending upon both the assemblage of organisms contributing organic material to the sediment and the environmental conditions.

Therefore, organic geochemical study of organic matter preserved in sediments can provide valuable information which includes the biological source organisms that generated the organic matter, the environmental conditions that prevailed in the water column and

sediment at the time, the thermal history of both the rock and the oil, and the degree of microbial biodegradation.

Since biomarkers provide unique clues to the identity of source rocks from which petroleum samples are derived the fingerprints from migrated oil and source-rock extracts can be compared to infer genetic relationships, which represent an important tool in the search for petroleum, especially in areas with complex depositional and structural histories. In addition, when samples of proposed source rocks are unavailable, biomarkers in oils can still be used to constrain the identity of the source (Picha & Peters, 1998).

For these studies some biomarker parameters are arranged by groups of related compounds in order to identify characteristics of the source rocks (e.g. lithology, geologic age, type of organic matter, redox conditions). However these parameters are used in conjunction with other geochemical parameters to help solve oil exploration, development, and production problems (Peters *et al.*, 1986).

In studies of the effects of the diagenesis on biomarker composition initial variations due to depositional conditions have to be taken into account (Moldowan *et al.*, 1986). These studies have typically focused on transformations between individual precursors and products in the solvent-soluble organic matter (bitumen) of sediments and sedimentary rocks (Philp *et al.*, 1988).

During diagenesis biomarkers undergo the same main types of reactions as other biogenic organic compounds: defunctionalization, aromatization and isomerization. Oxygen-containing functional groups predominate among lipid components at the start of diagenesis and their loss involves reactions such as dehydration and decarboxylation. At the end of diagenesis, these defunctionalization process lead to the formation of hydrocarbons, either saturated or aromatic. However the reducing and oxidizing conditions, i.e. Eh and pH in the sediment, exert an influence on several biomarker precursor-product pathways.

6.8 Biogeochemistry

Bacteria are the oldest life form on the planet. They appeared 3.8 Gy, when the atmosphere of Earth was being reduced and gases like carbon dioxide, methane, nitrogen and ammonia were abundant (Crapez, 2009). Thanks to their activity throughout the course of evolution and geological time, microorganisms have been interacting with and modifying the physical environment ever since (Dilek *et al.*, 2008).

These organisms are considered geological agents and function as concentrators, dispersers and fractionators of mineral and organic matter. As *concentrating agents*, their activity results in a localized accumulation of mineral matter. As *dispersing agents*, they promote the dissolution of insoluble mineral matter. Finally, as fractionizing agents, they operate on several inorganic compounds promoting selective chemical changes involving one or more minerals (Ehrlich, 1996).

These matter-microbial life interactions are studied within the context of Geomicrobiology, defined as a scientific field concerned with the participation of microorganisms, both in the past and currently, in a wide variety of geological processes (Ehrlich, 1996). The main goals of studies in this new area of the Earth Sciences are identifying the role of microorganisms in

mineral formation and dissolution; in weathering and rock alteration; in the generation of sulfide minerals; in the fractioning of stable isotopes that facilitates mineral and rock diagenesis; the generation of porosity in deep sedimentary packages; in the formation of the aerobic biosphere; in the generation of fossils that record the evolution of microorganisms; in bioremediation process; in the cycling of biogeochemical elements; in the degradation of hydrocarbons and in the transformation of sedimentary organic carbon for the formation of fossil fuels (Dilek *et al.* 2008).

6.9 Bacterial activity in the degradation and cycling of organic carbon

Microorganisms are the main agents in the diagenesis of organic matter in soils, sediments (including the deepest layers of these), oceans and freshwater bodies. They take part in the recycling of inorganic elements that have limited availability in the environment, are nutritionally important and essential for life, like C, N, P and S (Ehrlich, 1996).

The composition of organic matter (OM) in sediments can be classified, regarding its solubility in organic solvents, in soluble (labile and refractory) and insoluble (labile and refractory) components, whose relative concentrations change according to origin, degradation, use, transformation, accumulation and exportation. It is comprised of an autotrophic fraction (primary organic matter), derived from photosynthesis, and a heterotrophic fraction (secondary organic matter) (Killops & Killops, 1993, Danovaro, 2000, Mendonça Filho *et al.*, 2010a, 2010b).

The labile fraction of the OM is organic carbon fraction most rapidly available to the organisms and is comprised of biopolymer molecules (lipids, proteins and carbohydrates (Dell'Anno, 2002). These three biochemical classes together make up the biopolymeric carbon (BPC) and respond for 10%-70% of all the organic carbon in the marine sediments (Danovaro, 2000). These fractions are more abundant in superficial sediments and in the early phases of diagenesis. Their concentration decreases as the burial and diagenesis processes advance (Tyson, 1995).

The remaining labile material, for geological and geochemical studies in older sediments, has been preserved due to special circumstances, such as dysoxic-anoxic sedimentary facies, and its quality and preservation has no direct bearing on its metabolization potential. This fraction of the metabolizable material can be adsorbed, chemically bonded or physically captured in protokerogen, kerogen or mineral constituents that restrain the action of microorganisms, protecting it from degradation and making it recalcitrant (Tyson, 1995; Danovaro *et al.*, 2001).

Biochemical analyses to verify the quality of the organic matter, i.e., the three main classes of biomolecules (lipids, proteins and carbohydrates), and enzymatic analyses to assess the acquisition and transformation of this energy are the procedures most widely employed (Tyson, 1995; Danovaro *et al.*, 2001).

7. Organic facies

The concept of "Organic Facies" was introduced during the increase of the integration between microscopy and organic geochemistry methods. The primary objective of organic

facies studies is the prediction of the likely occurrence (and lateral variability) of hydrocarbon source potential as a function of depositional environment (Tyson, 1995).

Depending on the objectives of the study and the parameters used for its definition, geoscientists observe the lateral variations of a certain organic facies both at the "basin scale" and at "slide scale". Based on a paleoecological and paleoclimatic vision, an organic facies can identify both small and large cycles related to transgressive-regressive events. However, its characterization is also related with the depositional paleoenvironments and with the deposition of the stratigraphic units responsible for the generation of oil. In this manner, the application of this concept is wide and several authors consider the introduction of this term in the literature considering it is an indispensable exploration tool (Tyson, 1995).

According Peters & Cassa (1994), many authors use the term *organic facies* as a synonym of *kerogen facies*, based on chemical data, or *palynofacies* or *facies of the maceral association*, based on petrographic data.

The term organic facies was first used by Rogers (1980). Organic facies were defined by "the organic matter content (primarily type, less frequently amount), its source and depositional environment". Cornford (1979) used the organic facies term, without questioning the concept, just for comparison the methods of studying organic matter and inter-related the interpretations. Cornford *et al.* (1980) summarized the group of organic parameters (organic petrography and geochemistry parameters) that characterize an association of sediments as "Organofacies".

According to Peters *et al.* (1981), a sedimentary organic facies is determined in the type of the precursor organism, in the depositional paleoenvironments, and in the initial conditions of diagenesis of the organic matter.

Habib (1982) considered organic facies a particular aspect of the organic faciology (which can be determined by the palynological study of organic matter), and it can be considered as "palynologically defined organic facies".

A formal definition was proposed by Jones & Damaison (1982), where an "organic facies is a detectable subdivision of a certain stratigraphic unit which can be discriminated by the characteristics of the organic constituents without considering the aspects of the inorganic fraction of the sediments".

Powell (1987) presents the same concepts in his definition of organic facies, considering the effect of the depositional control on the composition of organic matter of potentially hydrocarbon source rocks. This effect regards to the nature of the primary biomass (algal, bacterial, or from land plants/higher plants), to the extent of bacterial degradation (reworking) during deposition and to the lithology of the source rock, and to the chemical composition of the waters present in the depositional palaeoenvironment (salinity, pH, alkalinity and oxygenation).

Tuweni & Tyson (1994) consider that TOC and pyrolysis data combined with palynofacies analysis provides an excellent means of characterizing organic facies.

According to Tyson (1995), the concept of organic facies can be defined as a "group of sediments having a distinctive set of organic constituents that can be recognized by microscopy or be associated to a characteristic organogeochemical composition".

7.1 Organic facies *sensu* Jones (1987)

Jones (1987) in a study developed the organic facies concept and defined seven organic facies using geochemical, and to a lesser extent optical data (microscopy). These organic facies have been assigned to either individual samples, groups of samples or whole stratigraphic units and the parameters used correspond to sedimentary intervals with low thermal maturity. This organic facies approach is probably more realistic than kerogen type in attempting to classify different kerogen assemblages as it takes into account the fact that the assemblages are controlled by preservational factors as well as their source, and that changes between assemblages are often gradational (Tyson, 1995).

According to Pasley (1991), the definition of organic facies presented by Jones is more appropriate due to the similarities of the organic facies with the detectable stratigraphic units discriminated by the composition of its organic matter. This author integrates the organic petrography and organic geochemistry data in the concept of sequence stratigraphy, not only to improve the better understanding of the occurrence of oil source rocks, but also to use as a prediction tool (Tyson, 1995).

The seven organic facies defined by Jones (1987) are: A, AB, B, BC, C, CD and D. According to Tyson (1995), the three main divisions are into anoxic-dysoxic (A, AB, B, BC), proximal fluvio-deltaic to prodeltaic-oxic shelf (C, CD), and distal deposited, oxic facies (D).

According to Tyson (1995) the major palaeoenvironmental controls on organic facies are:

1. Palaeoxygenation and redox conditions in the basin;
2. Relative proximity of the depositional site to active siliciclastic sediment (and terrestrial OM) sources;
3. Climatic controls on the production, preservation and export of terrestrial organic matter;

The main characteristics of each facies from Jones (1987) were discussed by Jacobson (1991) and Tyson (1995, 1996) and are presented below:

Organic Facies A: this organic facies presents H/C ≥ 1.45 and HI ≥ 850. The rocks are usually laminated and organic rich and are found in alkaline lakes and marine palaeoenvironment with persistent bottom water anoxia. The organic matter, often brightly fluorescent, is derived primarily from a single type of algae or bacteria. Organic facies A commonly occurs in carbonate settings. It is found in condensed sections of lakes and marine margins that are protected from oxygenated waters.

Organic Facies AB: this organic facies presents H/C ~ 1.45-1.35 and HI ~ 850-650. Rocks forming this facies are often laminated and organic rich. The organic matter is similar to that in organic facies A, except that it is diluted either with organic input of lesser quality or by partial degradation. It is volumetrically more important than Organic Facies A because its slightly lower H/C ratio can be tolerate a small amount of terrestrial input and/or oxidization of the OM. Organic facies AB is found in both carbonates and shales deposited under a well-developed and persistent anoxic water column.

Organic Facies B: this organic facies presents H/C ~ 1.35-1.15 and HI ~ 650-400. This facies is the source of petroleum for the majority of the world's oil fields, although organic facies AB may have contributed more of the world's oil (Jones, 1987). It is often laminated

and may contain some terrestrial organic matter. It can be interbedded with less oil-prone facies, reflecting either fluctuations in bottom water anoxia or introduction of sediments with associated oxygen or poorer quality organic matter. Organic facies B and its systematic neighboring facies AB and BC can be mixtures representing biological source variation, some transported organic matter, or variations in preservation. Organic facies B encompasses most of the earth's best petroleum source rocks and is predominantly found in marine rocks, especially in deep water palaeoenvironment associated with upwelling.

Organic Facies BC: this organic facies presents H/C ~ 1.15-0.95 and HI ~ 400-250. This facies is found in both marine and lacustrine palaeoenvironment. It is often deposited in fine-grained siliciclastics where rapid deposition captures small oxygen volumes in the sediments. This "sedimentary oxygen" encourages biological activity in the sediments. Terrestrial organic matter can be a significant contributor, but bioturbation of bottom sediments may be sufficient to degrade marine organic matter to this quality.

Organic Facies C: this organic facies presents H/C ~ 0.95-0.75 and HI ~ 250-125. This facies is predominantly gas prone. The organic matter is primarily woody and terrestrial and makes up most coals. Organic facies C is found in marine environments on Tertiary and Mesozoic shelf margins where it includes mixtures of hydrogen-rich and hydrogen-poor macerals or degraded hydrogen rich macerals. Organic facies C and neighboring facies BC and CD are found in coal-forming swamp deposits, deltaic deposits, and bioturbated marine mudstones. The types of environments in which this facies occurs often correspond to the transgressive and early highstand systems tracts where some oxidation occurs and where different kerogen components can be deposited together.

Organic Facies CD: this organic facies presents H/C ~ 0.75-0.60 and HI ~ 125-50. It is heavily oxidized and frequently represents terrestrial organic matter that has been transported through oxidizing environments. This facies may represent recycled organic matter that has been eroded one or more times from sediments.

Organic Facies D: this organic facies presents H/C ≤ 0.60 and HI ≤ 50. This facies contains highly oxidized organic matter, which may represent burnt wood (charcoal), recycled terrestrial material, and thermally postmature constituents. It may include fragments of larger woody components recycled from porous sandy units where oxidation prevailed. This facies is usually encountered in small concentrations and has no hydrocarbon generative capacity. It occurs in prograding sediments associated with sea level highstands and redeposited sediments of lowstands. Organic facies D is the regionally distributed type IV kerogen. It is frequently found in fluvial palaeoenvironment, on offshore toes of deltas, and where organic carbon has been recycled. Sediments containing this kerogen can be found in all systems tracts, including the fine-grained parts of turbidites in lowstand systems tracts and the silts and muds of highstand prograding sediments. The oxidization can occur in innumerable depositional environments ranging from the deep ocean to terrestrial.

According to Jacobson (1991), organic facies are mappable units and their distribution reflects varying influences of biological productivity, preservation, and geological processes. Hydrogen-rich organic facies reflect hydrocarbon generative potential that helps exploration geologists map the distributions of possible petroleum source rock candidates. Petroleum

source rocks form where appropriate conditions for organic productivity and preservation of organic matter occur.

Tyson (1995) showed the relationship between some selected palynofacies kerogen parameters and organic facies *sensu* Jones (1987) in idealized marine siliciclastic facies. This relationship is represented in Table 4.

ORGANIC FACIES	A	AB	B	BC	C	CD	D
Palynofacies characteristics							
% 'AOM' of kerogen	dominant			mod	usually low/absent		
'AOM' matrix fluorescence	highest		mod-weak		weak	usually absent	
% prasinophytes of plankton	highest	mod	rare	usually very rare			
% phytoclasts of kerogen	low (dilution)			mod	usually dominant		
opaque:translucent phytoclasts	often high			usually low		increases	
Geochemical characteristics (for immature sediments)							
Hydrogen index	≥ 850	≥ 650	≥ 400	≥250	≥125	50-125	≤ 50
Kerogen type	I	I/II	II	II/III	III	III/IV	IV
TOC%	5-20+	3-10+		3-3+	≤ 3	< 0.5	
Environmental factors							
Proximal-distal trend	Distal			Proximal		Distal	
Oxygen regime	Anoxic	Anoxic-dysoxic		Oxic			V. Oxic
Sediment accumulation rate	Low	Varies		High		Mod	Low
ORGANIC FACIES	A	AB	B	BC	C	CD	D

Table 4. Relationship between some selected palynofacies kerogen parameters and organic facies sensu Jones (1987) in idealized marine siliciclastic facies (generalized relative trends only) (Tyson, 1995; 1996).

8. Summary and conclusions

Organic facies is a discipline of Geosciences that has been   increasingly applied in studies devoted to the fossil fuels exploration and basin analysis. The present paper has intended to provide a general view of organic facies in relation to the techniques used for its applications in the field of geosciences, emphasizing its contribution to both fundamental and applied scientific knowledge. The scope of organic facies is broad, however encompasses some fundamental concepts, such as the organic content characterization, in terms of type and quality. Organic facies investigation uses techniques from microscopy (Palynofacies analysis) and organic geochemistry (TOC, Biomarkers, Biogeochemistry, etc.) and the application of these techniques mainly in the palaeoenvironmental characterization, basin analysis and fossil fuel exploration.

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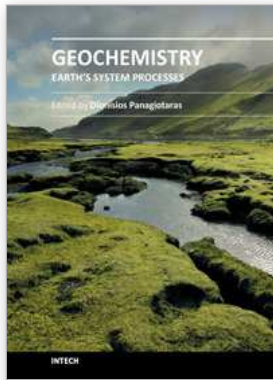
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