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Organic Petrology: An Overview

Suárez-Ruiz Isabel

*Instituto Nacional del Carbón (INCAR-CSIC) Oviedo
Spain*

1. Introduction

Organic Petrology is a branch of the Earth Science that studies fossil organic matter in sedimentary sequences including coal and the finely dispersed organic matter in rocks (DOM). It was developed from coal petrology that dates back to the end of the 19th century. The organic petrology is usually expressed by two fundamental parameters: the nature and proportions of the organic constituents, and by the rank or maturity of these organic components. In the case of coals the amount and composition of its mineral matter (grade of a coal) is another parameter to be taken into account. The work carried out by the International Committee for Coal and Organic Petrology (ICCP) related to the development of the maceral nomenclature, classification, standardization and the use of petrographic methods has been reported in various editions of the “ International Handbook of Coal Petrology” (ICCP, 1963, 1971, 1975, 1993) and other publications such as ICCP (1998, 2001) and Sýkorová et al. (2005). There are also several monographs focused on organic petrology such as those by Stach et al., (1982) and Taylor et al., (1998). Recently Suárez-Ruiz and Crelling (2008) edited a book on coal petrology and coal utilization. Other references in which organic petrology and/or coal petrology are discussed at some length include Ward (1984); Bustin et al. (1985); Falcon and Snyman (1986); Diessel (1992) and Teichmüller (1989). This chapter is an overview focused on organic petrology (including coal petrology), its fundamental concepts, the analytical techniques and the main current applications.

2. Fundamentals and general considerations

The particulate organic matter in sedimentary sequences ranges from disseminated occurrences of organic particles to concentrated organic matter in coals. The classification of the organic matter based on H/C and O/C atomic ratios (van Krevelen, 1993) distinguishes three main types of kerogens (Type I, Type II and Type III) that initially were associated to specific geological settings (Tissot and Welte, 1984). Vandenbroucke and Largeau (2007) revised this classification indicating that Type I kerogen may derive from various highly specific precursors characterized by a common high aliphaticity in different sedimentary environments, Type II kerogen can be associated with planktonic organic matter in open marine and fresh water lacustrine environments, and that Type III kerogen from higher plants can be associated with terrestrial inputs into lacustrine or marine settings. The kerogen classification (Fig. 1) is important because kerogen types (organic matter types) are directly related to total hydrocarbon potential, oil chemistry, and hydrocarbon generation kinetics. Coal, usually described as Type III kerogen, is a combustible sedimentary rock

composed of lithified plant debris. This plant debris was originally deposited in a swampy depositional environment. The prolonged burial of the peat at depths of up to several kilometers, compaction, pressure and the influence of elevated temperatures for long periods of time (million years) are known as the coalification process that change peat into coal. Coal did not appear until the Devonian period due to the lack of terrestrial plants, although some organic matter derived from marine algae occurs in Precambrian sedimentary rocks.

Fig. 1. Scheme of kerogen (organic matter) evolution on the van Krevelen's diagram. (Source: Petroleum Formation and Occurrence. 1984. By B.P. Tissot and D.H., Welte. 2nd ed., Springer-Verlag, 699 pp. This figure is from Chapter 7, Fig. II.7.2 in p. 216 (modified after Tissot, 1973). Copyright 1984, with kind permission from Springer Science and Business Media).

2.1 Origin, type and properties of organic components

Macerals are the microscopic organic components typically identified in coals. They derive from terrestrial, lacustrine and marine plant remains, and their appearance is a function of the parent material, of initial decomposition before and during the peat stages and also of the degree of evolution undergone. Macerals are distinguished from one to another on the basis of their physico-optical properties and universal acceptance is given to the ICCP classification of macerals (ICCP, 1963, 1971, 1975, 1998, 2001; Sýkorová et al., 2005) in three groups: liptinite, inertinite and huminite/vitrinite. These groups are subdivided into a variety of maceral sub-groups, macerals, and maceral varieties (Table 1).

The liptinite maceral group (Fig. 2) includes the optically distinct parts of plants such as spores, cuticles, suberine, etc., some degradation products, and those generated during the coalification/maturation process. Liptinite macerals show the highest content in hydrogen, contain compounds of mainly an aliphatic nature, and by thermal evolution they produce hydrocarbons (Tissot and Welte, 1984; Taylor et al., 1998; Wilkins and George, 2002). The inertinite maceral group derives from plant material that was strongly altered and degraded

before deposition, or at the peat stage (Taylor et al., 1998; ICCP, 2001). Inertinite macerals (Fig. 2) exhibit a high degree of aromatization and condensation. The huminite/vitrinite maceral groups (Fig. 2) originate mainly from lignin and cellulose, partly also from tannins of the woody tissues of plants, and from colloidal humic gels (ICCP, 1971, 1998; Sýkorová et al., 2005). The formation of huminite /vitrinite macerals requires a set of successive processes such as humification, and biochemical and geochemical gelification. Huminite is only identified in low rank coals and is the precursor of the vitrinite macerals in medium and high rank coals. The chemical structure of the huminite/vitrinite is represented by aromatic and hydroaromatics compounds in low-rank coals, but with increasing coal rank the aromaticity, condensation and order of the polyaromatic units notably increase. Different maceral groups have different chemical and physical properties (Stach et al., 1982; van Krevelen, 1993; ICCP, 1998, 2001; Taylor et al., 1998; Sýkorová et al., 2005, and Suárez-Ruiz and Crelling, 2008).

Liptinite Group	Inertinite Group	Huminite Group		Vitrinite Group	
Sporinite	Fusinite	Telohuminite	Textinite	Telovitrinite	Telinite
Cutinite	Semifusinite		Ulminite		Collotelinite
Resinite	Funginite	Detrohuminite	Attrinite	Detrovitrinite	Vitrodetrinite
Alginite	Secretinite		Densinite		Collodetrinite
Suberinite	Macrinite	Gelohuminite	Corpohuminite	Gelovitrinite	Corpogelinite
Chlorophyllinite	Micrinite		Gelinite		Gelinite
Fluorinite	Inertoditrinite				
Bituminite					
Exudatinite					
Liptodetrinite					

Table 1. Main components of maceral groups. (Compiled from ICCP, 1971, 1975, 1998, 2001 and Sýkorová et al., 2005).

The three maceral groups are found in highest concentrations in sediments of terrestrial origin such as coals and carbonaceous shales, but they are nearly absent in most of carbonate rocks. In sedimentary rocks with DOM in addition to the described maceral groups, and secondary products, faunal relics and microfossils of various composition such as zooclasts, dinoflagellates and acritarchs can be found. Moreover, the non-structured organic matter or amorphous organic matter (Bertrand et al., 1993), intimately associated with the fine grain-minerals such as clays is also present in rocks with DOM. Another component of the DOM is the solid bitumen which appear in the macropores of the rocks, and as vein fillings. They are secondary products of the coalification/maturation processes and derive from the cracking of the macromolecular structure of organic matter into liquid hydrocarbons (of which they are the solid residue).

Fig. 2. Photomicrographs: 1,2,3,5: reflected white light; 4,6: fluorescence.

1,2) Bituminous coal with vitrinite, inertinite and liptinite. Carboniferous age, North Spain.

3,4) Telohuminite and resinite (liptinite) in a carbonaceous shale. Cretaceous, North Spain.

5,6) Oil shale (Tasmanite algae, Liptinite, right image). Jurassic, North Spain.

2.2 Mineral matter and microlithotypes in coals

Macerals in coals are accompanied by inorganic components that may appear as fine disseminations and as discrete partings. The inorganic fraction of coals should be taken into account due to its influence in coal utilization. Conventionally the mineral matter in coals has been differentiated on the basis of its origin into two major categories (ICCP, 1963; Stach et al., 1982; Bustin et al., 1985; Falcon and Snyman, 1986): i) the intrinsic inorganic matter which was present in the original plant tissues, and ii) the extrinsic or introduced forms of mineral matter that can be primary or secondary. The major groups of minerals in coals include clays, carbonates, iron sulphides and silicas. Other groups occur more rarely. Trace elements are also present in coals (Swaine, 1990; Finkelman, 1993).

The natural associations of macerals in coals are called microlithotypes. They are identified by optical microscopy and by definition (ICCP, 1963, 1971; Stach et al. 1982; Taylor et al., 1998) microlithotypes should form bands greater than 50 microns in width and should contain at least 5% of a maceral group. Microlithotypes are classified into three groups: mono-, bi-, and trimaceralic (or trimacerites) depending on whether their composition is made up of elements from one, two or three maceral groups. Macerals and microlithotypes that appear associated with minerals are named carbominerites.

2.3 Types of coal and lithotypes

The macroscopic composition of coals and their homogeneous / heterogeneous appearance is related to their composition. Macroscopically, all coals are classified in two categories or coal types: humic and sapropelic coals. Humic coals or banded coals are the most common in nature. Sapropelic coals are scarce and homogeneous in appearance. Lithotypes are the macroscopically recognizable bands in humic coals (ICCP, 1963) and four different lithotypes (vitrain, clarain, durain and fusain) have been described. Stach et al. (1982) extended the definition of lithotypes to include two varieties for sapropelic coals: cannel and boghead coals.

2.4 Evolution of the organic matter

Coalification / maturation is a process that affects the organic matter after its deposition. This process is the result of the organic matter burial, and the corresponding increase in temperature and the time of this temperature influence. Pressure also at some stages of the coalification has some influence. Through the coalification process the original peat swamp is transformed, and passes through the progressive stages of evolution known as lignite, sub-bituminous, bituminous, anthracite and meta-anthracite (Fig. 3). With continued burial coalification may be followed by the graphitization process. The level of evolution reached by a coal through the coalification process is termed rank. The term coalification (Taylor et al., 1998) applies to coal evolution while the term maturation has been long used to describe the diagenetic evolution of the dispersed organic matter in sedimentary rocks leading to the formation of oil and gas (Tissot and Welte, 1984; Taylor et al., 1998; Vandenbroucke and Largeau, 2007).

As for the evolution (maturation) of dispersed organic matter in sedimentary rocks, the process is parallel to the coalification of coals although the nomenclature of the various stages of maturity is different. Thus with increasing maturity of DOM in sedimentary rocks the following main stages were initially described (Tissot and Welte, 1984) and reviewed by Vandenbroucke and Largeau (2007): i) early diagenesis with a major loss of N and a potential incorporation of inorganic S and O into the organic matter, ii) diagenesis "sensu stricto" with a significant loss of O mainly as CO₂ and H₂O and it develops until the equivalent boundary in coals of sub-bituminous/bituminous rank stage; iii) catagenesis with a loss of H and C because the generation of oil and wet gas by thermal degradation of the organic matter due to the increase in temperature with burial in sedimentary basins. This stage follows the diagenesis and develops until the equivalent boundary in coals of bituminous/anthracite rank stage; and iv) metagenesis in which a reorganization of the aromatic network of the residual organic matter occurs increasing its aromaticity with production of CH₄ and non-hydrocarbon gases (CO₂, H₂S and N₂). It is the last stage of organic matter maturation and it is reached at great depths. With the increase of the organic evolution (diagenesis, catagenesis and metagenesis phases) the organic matter is progressively described as immature, mature and overmature.

This information in combination with the amount and type of kerogen (organic matter) is of capital importance for oil and gas exploration (Fig. 3).

Fig. 3. Rank stages determined from microscopic rank/maturity parameters in relation to oil and gas production. (Source: Organic Petrology. 1998. By G.H. Taylor, M. Teichmüller, A. Davis, C.F.K. Diessel, R. Littke, P. Robert. Gebrüder Borntraeger. Berlin. 704 pp. This figure is from Chapter 3, Fig. 3.40 in p.135 (from Teichmüller 1987, after Dow 1977). Copyright 1998, with kind permission from Gebrüder Borntraeger. www.borntraeger-cramer.de).

3. Procedures in organic petrology

3.1 Sampling and preparation of samples for microscopic analysis

For petrographic studies of organic material, samples can be taken from the outcrops and open pit mines (surface samples) or from the underground mines, boreholes and exploration wells (subsurface samples). In some cases washed well cuttings may be used although special care is needed because cuttings can be contaminated by caved materials or drilling mud additives. In surface samples the main problem are weathering and oxidation processes that can lead to an extensive physical deterioration of the coals, particularly in case of low-rank coals. Adequate and precise guidelines for sampling procedures are given by international standards (ISO or ASTM norms).

The most widespread method of petrographic examination of coal and DOM in sedimentary rocks is the use of reflected white light microscopy on polished surfaces of high quality, under oil immersion to enhance component or maceral reflectance differences. The polished surfaces can be obtained from polished epoxy-mounted samples which are prepared from

whole rock, crushed material (coals or sedimentary rocks) or from concentrates of organic matter. The procedures of sample preparation for this type of analysis are standardized in ISO and ASTM norms.

3.2 Petrographic methods: Identification of organic matter

Petrographic analysis in incident light microscopy involves the identification of organic components, its quantification and rank/maturity determinations.

The identification of the organic matter types and the observation of all their physico-optical characteristics provides information about its source. Among these characteristics it should be mentioned (*e.g.*) the organic and mineral matter associations; the shape and morphology of the organic components, intergrowths, organic distribution, porosity, internal reflections, texture and structures, fluorescence properties, optical isotropy/anisotropy, oxidation traces, etc. The optical texture (isotropic/anisotropic character) of the organic matter is a property to be considered in the case of organic components in rocks or in coals of high rank. This is especially significant in the case of anthracitic coals, bitumens in paragenesis with ore minerals, etc. With the coalification, the organic matter (initially isotropic and structurally disordered) becomes more ordered and tends to develop optical anisotropy.

3.3 Maceral and microlithotype analysis in coals

In geological research on coal basins, in the evaluation of coal seam quality or for coal utilization it is always necessary to know the quantitative composition of a coal in terms of macerals (and minerals in some cases) or maceral groups. This is because differences in maceral composition indicate differences in chemical composition and therefore in the technological properties of the coal. The maceral analysis in coals is performed using optical microscopy with a point-counter coupled to the microscope stage. The microscope stage is moved through the point-counter in a series of fixed intervals according to the total points to be recorded on the whole sample, and the identity of the maceral falling beneath the cross-hairs or micrometer after each advance is recorded. For that the microscope should be equipped with incident white light, oil immersion objectives (25x-50x magnification) and 8x to 10x oculars, one of which must contain an adjustable eyepiece with a micrometer or cross-hair. The analytical procedure for maceral analysis is standardized by the ISO and ASTM normative protocols. Automated methods using computerized image analysis were also developed in the last decades for maceral analysis although the manual point-counting method is the most extensively used. Although maceral analysis is carried out in white light, supplementary observations in fluorescence mode are recommended. Results of maceral analysis are reported on a volume percent basis.

Microlithotypes, and coal-mineral associations, carbominerites, can be also quantified via microlithotype analysis. The analytical procedures are standardized in the ISO norm. Microlithotype analysis is carried out in a similar way as maceral analysis. However, a suitable 20 points reticule (ICCP 1963; Stach et al. 1982) must be placed in one of the oculars in substitution of the micrometer or cross-hairs. In microlithotype analysis it is necessary to consider two conventions: i)- the minimum band width of the association to be measured must be 50 microns, and ii)- the 5% rule, which indicates that macerals present in the association in amounts smaller than 5% should be disregarded. Each observation on a 20-intersection or reticule is regarded as a point in the analysis. Under these circumstances each

intersection of the reticule represents 5% of the total number of intersections (20) according to the 5% rule. For each set of readings at least ten reticule intersections must cover the coal particles. Microlithotype analysis may also include coal-mineral associations. Results from microlithotype analysis are also expressed as volume percent.

3.4 Quantification of organic component in organic-rich rocks other than coals

Quantification of organic components present in non-coal rock samples in reflected light microscopy and on particulate pellets can be also performed following the method of maceral analysis. However, taking into account that the organic matter in non-coal samples is disperse, and that many components are only visible in fluorescence mode results will not be as accurate and some components will be under- or over-estimated. To improve this type of analysis Boucsein and Stein (2009) used the point-counting method but only counting organic components versus minerals obtaining good results in their study of a black shale formation.

3.5 Optical methods to evaluate the coal rank and thermal maturity of DOM

The determination of thermal maturation of organic matter in coals and organic-rich rocks is essential to the geothermal studies in basin analysis, in the evaluation of natural fossil fuel resources, etc.,.

3.5.1 Vitrinite reflectance measurements

The degree of evolution of the organic matter is commonly expressed in terms of vitrinite reflectance. Vitrinite reflectance is measured in incident white light microscopy and therefore, is an optical parameter that serves to describe the degree of coalification reached by a coal, the class of coals (ISO 11760, 2005), and the level of maturity of sedimentary rocks with DOM (ICCP, 1971; Stach et al., 1982; Taylor et al., 1998). The reflectance is a property related to the aromaticity of the organic components and it increases for all macerals as the level of coalification/maturation increases and the atomic O/C and H/C ratios decrease. However, reflectance usually is measured on vitrinite in coals and in rocks younger than Upper Silurian which marks the first appearance of vascular plants and so the precursor material of huminite and vitrinite. The procedure used for vitrinite reflectance measurements is standardized in ISO and ASTM norms for coals. Measurements of reflectance are carried out by comparing the amount of light reflected from a maceral (vitrinite) with the amount of light reflected by a standard and these measurements must be achieved in monochromatic green light (546 nm), in oil immersion and objectives with magnifications between 25x and 50 x. Two types of reflectance measurements can be made to quantify the reflectance of a vitrinite: i) the random reflectance (R_o , %), and ii) the maximum reflectance ($R_{v_{max}}$, %). Random reflectance is the reflectance of a particle in the orientation in which it is encountered (polarizer is removed from the microscope). For measurements of maximum reflectance the polarizer should be placed in the 45° position into the incident light beam. When the microscope stage is rotated through 360° the maximum reflectance can be taken (twice).

Measurements of vitrinite reflectance in sedimentary rocks with DOM follows a similar procedure as in coals. Vitrinite reflectance directly correlates with the other physico-chemical rank/maturity parameters and has been extensively and worldwide used to assess rock strata across a broad range of thermal maturity stages, ranging from early diagenesis through catagenesis to low grades of metamorphism in coals, oil shales, source rocks, etc.,

Anisotropy. Vitrinite in high rank coals and in rocks with overmature organic matter shows an anisotropic behavior and exhibits bi-reflectance. This is because with the increase in rank or maturity the structure of the carbonaceous material is reorganized and consequently almost all of its physical properties vary according to the considered section of the particle. With data of the true maximum and minimum reflectances, the anisotropy can be calculated as the difference: $R_{\max} - R_{\min}$. The anisotropy is linked to the overlying pressure of the strata and tectonic stress.

3.5.2 Reflectance measurements on zooclasts and solid bitumens

In absence of vitrinite in pre-Devonian rocks or when the sedimentary sequence is vitrinite-poor, the reflectance of zooclasts such as graptolites, chitinozoans, and scolecodonts have been used as rank/maturity parameter. Zooclast reflectance has been found to increase with the depth of burial and the increase in temperature. Graptolites possess weak to strong anisotropic character (Goodarzi and Norford, 1985) and its maximum reflectance also correlates with the Conodont Alteration Index (CAI) and optical properties of co-occurring coal macerals and solid bitumen. Other microfossils that have been used as maturation indicators are the chitinozoans and scolecodonts (Goodarzi and Higgins, 1987; Bertrand, 1990; Tricker et al., 1992). The reflectance of these microfossils increases at different rates depending on zooclast type.

Thermal evolution causes regular changes in the chemical composition of solid bitumens as well as an increase in its aromaticity and therefore, in the reflectance values. Several correlations have been developed between the reflectances of solid bitumen and vitrinite (Jacob, 1989, 1993; Bertrand, 1993; Landis and Castaño, 1995). However, the use of solid bitumen reflectance as a maturity parameter has been also a subject of some debate. For example, different relationships found between solid bitumen and vitrinite reflectances are thought to be due to the existence of various genetic types of solid bitumens with different optical properties. Despite of this, there are many studies that have used the reflectance properties of solid bitumens in conjunction with other thermal maturity parameters.

3.5.3 Fluorescence properties of organic constituents

Fluorescence microscopy is employed in coal petrology and in organic matter studies for characterization of liptinite macerals, organic matter composition, rank/maturation studies (as an essential criterion for oil and gas formation), hydrocarbon detection, and for correlation of technological properties of coals (thermoplastic, coking and oxidation features) to vitrinite fluorescence characteristics. Fluorescence analyses should be carried out using a reflected light microscope coupled to a photomultiplier (ICCP, 1975, 1993) or camera detector. The microscope must be equipped with a high pressure mercury or xenon lamp for illumination with the corresponding excitation filters to select the UV or blue light, barrier filters and also a variable interference filter covering the range of 400 to 700 nm. The fluorescence properties are primarily estimated on a qualitative basis (organic component diagnosis) using blue light excitation. Because the fluorescence of organic components is variable in intensity and color depending on the type and maturity level of the organic matter, these characteristics can be measured by monochromatic fluorescence microscopy and spectral fluorescence. The former includes quantitative measurements of fluorescence intensity at a specific wavelength (546 nm) recorded in relation to a standard (Jacob, 1980). Spectral fluorescence measurements determine changes in fluorescence color by recording

the emission of the spectrum (Ottenjann, et al., 1975) between 400 - 700 nm. They also measure the spectral alteration or changes in fluorescence properties after 30 minutes of irradiation of organic substances (Teichmüller and Ottenjann, 1977). The classical reported parameters (Teichmüller, 1987) of fluorescence emission are: I = Fluorescence intensity at 546 nm; Lambda max = Spectral maximum; Q = Spectral quotient (red/green ratio); AI = Alteration of fluorescence intensity at 546 nm, and AS = Spectral alteration, in each case for a period of 30 minutes irradiation. Other spectral parameters are described by Teichmüller and Durand (1983) and Bertrand et al. (1993).

3.6 Other analysis in organic-rich rocks and coals

In transmitted light microscopy the organic matter is characterized by means of palynofacies analysis (Combaz, 1980; Tyson, 1993, 1995). The main populations identified in palynological residues were initially classified (Combaz, 1980) as: terrestrial organic fragments, pelagic and benthic microfossils and the so-called amorphous organic matter or amorphous fraction, and later reorganized as phytoclasts, palynomorphs and amorphous organic matter by Tyson (1993, 1995). The palynofacies analysis combined with studies of organic petrography, geochemical investigations, stratigraphy and paleontology, is a tool in the interdisciplinary analysis of organic matter providing accurate information in the investigation of organic facies and depositional paleoenvironments, paleoclimate reconstructions, origin and transfer studies of fossil organic matter in recent environments, hydrocarbon source rock potential and petroleum exploration.

In organic geochemistry one of the most commonly techniques to investigate DOM in rocks is the Rock-Eval pyrolysis (Espitalié and Bordenave, 1993 and references therein). Biomarkers obtained from gas chromatography and gas chromatography/mass spectrometry techniques have been found to be a powerful tool for source rocks to oil correlation (e.g., Philp, 1985a,b; Bordenave, 1993). The pyrolysis gas chromatography/mass spectrometry is another method to analyze the organic-rich rocks that provides more detailed information about the chemical composition of the organic components (e.g., Iglesias et al., 2002; Peters et al., 2005). Other bulk geochemical analyses used to characterize dispersed organic matter include total organic carbon determinations (TOC), elemental analysis (C, H, O, N, S), infrared spectroscopic analysis, nuclear magnetic resonance for characterizing the chemical structures and functional groups (e.g., Iglesias et al., 2006; Kelemen et al., 2007), electron paramagnetic resonance, and isotopic analyses (e.g., Galimov, 2006). Thermogravimetric analysis have been also used for characterization of organic matter in sedimentary rocks.

The conventional method to quantify the mineral matter in coals is the low temperature ashing that removes the organic matter by exposing the coal sample to a reactive oxygen plasma. The residue remaining (LTA) is evaluated by X-ray diffraction techniques (Renton, 1986). Mineral particles in coal can be also analyzed by scanning electron microscopy and similar techniques (e.g., Ward et al., 1996) such computer-controlled scanning electron microscopy (CCSEM) techniques (Gupta et al., 1999) and the advanced QEM*SEM and QEM Scan systems (Creelman and Ward, 1996) that allow the integration of SEM data with image analysis methods. The composition of specific minerals may be obtained from electron microprobe analysis using methods outlined by Reed (1996). Mössbauer spectroscopy, thermal analysis, Fourier-transform infra-red spectrometry, proton microprobe using proton-induced X-ray emission, the ion microprobe mass

analyzer, the laser microprobe mass analyzer, laser ablation microprobe-inductively coupled plasma- mass spectrometry, the high-resolution ion microprobe, and X-ray absorption fine structure spectroscopy have also been used to identify the minerals, inorganic elements and trace elements in coals. To determine the concentration of individual inorganic elements in coal and in coals-ash (HTA, high temperature ashes) at major and trace levels (Huggins, 2002) several techniques are in use such as: X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, optical emission spectrometry and inductively coupled plasma vaporization combined with atomic emission spectrometry or mass spectrometry.

3.7 Technological assays in coal utilization

The characterization of coals for industrial utilization requires specific analysis and tests (see Ward, 1984; Suárez-Ruiz and Crelling, 2008). Chemical analysis such as proximate analysis (moisture, ash, volatile matter, and fixed carbon contents), ultimate analysis (C, H, N, S, and O contents), and Calorific value (heating value) are conventional and routine determinations that are carried out in coal characterization. These analysis are normalized by the ISO and ASTM standards. Other coal quality parameters are obtained from specific assays such as: the Hardgrove grindability index (HGI) which indicates the ease by which the coal can be ground to fine powder; the ash fusion temperatures (AFT) that indicate the behavior of the ash residues from the coal at high temperatures; the free swelling index (FSI) or crucible swelling number (CSN) which measures the increase in volume of the coal when it is heated in a small crucible in the absence of air; the Roga index that provides information on the caking properties of the coal; the Gray-King and Fischer assays which determine the proportions of coke or char (solids), tar (organic liquids), liquor (ammonia-rich solutions) and gas produced when the coal is carbonized in the absence of air; and the Gieseler plastometer and Audibert-Arnu dilatometer tests that inform how the coal behaves in specific conditions. The Gieseler plastometer measures the coal's fluidity whereas the Audibert-Arnu dilatometer measures the contraction and coal's expansion.

4. Applications of organic petrology

The organic petrology studies throughout the identification and characterization of organic components, quantification, and assessment of rank/maturation stage of organic matter are mainly applied to geosciences investigations (*e.g.*, basin analysis), fossil fuel resources exploration and coal utilization. In the last years organic petrology has been also used in other fields such as environmental pollution and anthropogenic impacts, coal fires, archaeologic aspects and forensics.

4.1 Basin analysis

In the reconstruction of the palaeoenvironment of coal bearing sequences, in addition to the sedimentology and stratigraphy, the intrinsic characteristics of coals which are linked with the original vegetation and accumulation conditions should be considered. Petrographic composition of coal (macerals and microlithotypes) contributes to the definition of facies peat-forming for the palaeoenvironmental interpretation. On the basis of maceral composition of coals Diessel (1986); Mukhopadhyay (1986); Calder et al. (1991); Kalkreuth et al. (1991); Hacquebard (1993), and Jasper et al. (2010) have proposed a series of petrographic

indices. By correlation of these indices the authors have defined facies and palaeoenvironmental diagrams that permit the assessment of the depositional environment and paleoconditions at the time of peat formation such as the vegetation type, preservation, the relative water level (relative dryness or wetness), the rates of peat accumulation and the basin subsidence. Many authors have used those petrographic indices in studies of coal-bearing sequences such as (*e.g.*) Diessel (1992); Jiménez et al. (1999); Piedad-Sánchez et al. (2004); Kalaitzidis et al. (2010). In the definition of coal facies and for palaeoenvironmental interpretations other authors have used the microlithotypes associations and lithotypes (*e.g.*, Hacquebard and Donaldson, 1969; Marchioni and Kalkreuth, 1991).

Taking into account the relationship between the degree of coalification/maturation and the rock temperature to which the organic matter has been heated during its geological history, many attempts have been carried out to reconstruct paleogeothermicity using vitrinite reflectance as the rank/maturity parameter. Sweeney and Burnham (1990) early indicated the need of using kinetic calculations for the evolution of vitrinite reflectance rather than simple vitrinite reflectance gradients in order to obtain reliable geothermal data because the measures of rank/maturity cannot be directly converted into paleotemperatures values. These authors proposed the kinetic EASY%R algorithm that permits the comparison of measured and calculated vitrinite reflectance values and thus the effective calibration of the thermal and burial histories. This model has been used (*e.g.*) by Hertle and Littke (2000); Petersen et al. (2009). Carr (2003) noticed that in overpressure systems a pressure-dependent kinetic model should be used for modeling. Models based on heat flow but also including data on compaction, pressure, temperature, maturation of organic matter, petroleum generation, migration and accumulation through time have been used to simulate the burial history of sediments by Tissot and Welte (1984); Baur et al. (2010), among others. However, in tectonically active basins, the resulting maturation patterns are the sum of a wide set of processes that should be taken into account in basin modeling.

Organic facies, palaeoenvironment interpretations and rank/maturation data are necessary for the reconstruction of geological history of sedimentary basins. Rank profiles and rank maps illustrating the regional rank variations (*e.g.*, Suárez-Ruiz and Prado, 1995; Colmenero et al., 2008; Ruppert et al., 2010) provide important information in basin studies and modeling. Detailed research focused on the palaeogeography and/or the palaeothermal conditions during the geological evolution of basins all over the world have been reported (*e.g.*) by Büker et al. (1996); Baur et al. (2010).

4.2 Fossil fuel resources

For fossil fuel resources exploration the knowledge of all the characteristics of the sedimentary basins is a pre-requisite. These natural resources are related with coal, source rocks, petroleum (oil and gas), reservoir rocks including coal as reservoir, oil shales, shale gas, black shales, carbonaceous shales, and coal bed methane. The quantification of their reserves is approached through exploration activities which include the creation of geological maps of the areas containing the natural resource (geological settings), the organic facies and sedimentary paleoenvironment investigations, geophysical surveys, and finally the exploration drilling. The last step is the construction of a geological model of the basin which provides with an accurate report of the area to be developed and reduce the exploratory risks.

4.2.1 Source rocks

The source rocks are organic-rich sediments that can be originated in various sedimentary environments such as deep marine, lacustrine and deltaic paleoenvironments. According to Law (1999) source rocks can be divided into four major categories: i) potential source rocks, that include rocks containing organic matter in sufficient quantity to generate and expel hydrocarbons if subjected to an increase in thermal maturation, ii) effective rocks with organic matter that are generating and/or expelling hydrocarbons forming commercial accumulations, iii) relic effective rocks, which describes an effective source rock that ceased the generation and expulsion of hydrocarbons because a thermal cooling event such as uplift or erosion before exhausting its organic matter, and iv) spent rock which describes an exhausted source rock due to the lack of sufficient organic matter or because the rock is in an overmature state. The main information to be obtained in the characterization of potential source rocks is: i) amount of organic matter in the rock, ii) quality and type of organic matter capable of yielding hydrocarbons (different types of organic matter have different hydrocarbon potentials), and iii) maturity of organic matter. Examples can be found in (*e.g.*,) Tissot and Welte (1984); Bordenave (1993); Suárez-Ruiz and Prado (1995); Hakimi et al. (2010).

Tissot and Welte (1984) described oil shales as any immature rock that yields oil in commercial amounts upon pyrolysis. Oil shales are generated in a wide range of sedimentary environments, from terrestrial swamps and pools, transitional zones between land and sea and to deep marine basins. The organic matter is frequently marine or freshwater algae, but other planktonic organisms and also bacterial biomass may contribute significantly. Oil shales are widely distributed around the world and hundreds of deposits are known (*e.g.*, Kruge and Suárez-Ruiz, 1991; Fu et al., 2009).

Black shale is a dark-colored mudrock containing more or less transformed organic matter and silt- and clay-size mineral grains that accumulated together. The content of organic matter rarely exceeds a few percentages. If the content in organic matter is higher, the rock may yield petroleum by pyrolysis and then it is described as oil shale. In these shales the organic matter is made up of structureless and carbonized organic components, in which terrestrially-derived fragments may be present together with microplankton. Black shales can be originated in different depositional paleoenvironments. However, the most appropriate conditions include anoxic bottom waters with low energy, in which the sulphate-reducing bacteria generate hydrogen sulphide after oxygen has been used up, and the benthic life is inhibited (Hallam, 1980). Black shales are in some cases source rocks of metals but its major interest is that they may be important source for petroleum (*e.g.*, Kolonic et al., 2002). If they have generated liquid and/or gaseous hydrocarbons these products can be found in reservoir rocks. Recently the potential of black shale itself as a reservoir for gas hydrocarbons has been recognized.

Carbonaceous shales are a transition from humic coals into coaly shale. Taylor et al. (1998) published a detailed microscopic classification of organic matter-rich sediments designating the organic matter-rich rocks as carbonaceous when they contained terrigenous organic matter. There is an economic importance attached to these carbonaceous rocks, because they may be an important source of natural gas or methane (*e.g.*, Lee et al., 2010).

4.2.2 Reservoir rocks

Reservoir rocks are one of the elements of the petroleum system. Any permeable and porous rock may act as a reservoir for hydrocarbon and may be detrital or clastic rocks or

precipitated rocks such as carbonates. Occasionally shale, volcanic rocks, and fractured basement can act as reservoir rocks. The characterization of a reservoir rock is fundamental for all kind of studies related to hydrocarbon field exploration. The two most essential elements of a reservoir rock are porosity and permeability. The majority of petroleum accumulations are found in clastic reservoir rocks being sandstones the most common. However, more than 40% of the so-called giant oil and gas fields are found in carbonates (Tissot and Welte, 1984). The study of reservoir rocks includes the analyses of secondary organic matter products (solid bitumens), and gaseous hydrocarbons which in the case of coals are called coalbed methane (Ayers, 2002). Coal is classified as a continuous-type, unconventional natural gas reservoir, with complex reservoir properties in which coalbed methane is stored dominantly in an adsorbed state rather than a free state. In coal reservoir studies diverse geologic factors influence storage capacity, hydrocarbon content, and production performance. The variability of those geologic factors is conditioning the specific strategies for both coalbed methane development and carbon sequestration in each basin. Coalbed methane (CBM) has diverse origins, namely thermogenic and biogenic and isotopic analysis helps in its differentiation (Whiticar, 1996). On CBM there is a large amount of papers (*e.g.*, Gentzis et al., 2006; Alsaab et al., 2008)

Shale gas is an unconventional natural-gas reservoir, and refers to in situ hydrocarbon gas present in fine grained and organic rich sedimentary rocks. Gas produced from organic-rich shales is of both biogenic and thermogenic origin and is stored in situ, in shales as both adsorbed gas (on organic matter) and free gas (in fractures or pores). The issues to be taken into account when characterizing shale gas are: the organic richness, its type or quality, and the thermal maturity which may be approached via organic petrology. Organic geochemistry and isotopic composition of gas are also a need for determining the hydrocarbon type and composition. Finally, generation and retention of hydrocarbons in the system are assessed via hydrocarbon modeling.

4.3 Coal utilization

Coal is another fossil fuel resource. Their physico-chemical properties are related to three independent parameters: rank, type and grade (Ward, 1984; Taylor et al., 1998). Coal quality is a function of these factors. The role of coal petrology in coal utilization has been recently compiled by Suárez-Ruiz and Crelling (2008).

4.3.1 Coal Mining and coal preparation

Coal composition and rank influence its behavior during mining and beneficiation. During mining coal is liberated from the host clastic rock and through beneficiation process a higher grade coal is obtained. The coal quality can be assessed by understanding the distribution of coal lithotypes relative to the thickness and splitting characteristics of a coal seam which is related to the original depositional controls. Microscopically, changes in maceral composition can also help in predicting splitting in advance of mining (Esterle and Ferm, 1986). Abrupt changes in coal rank or trace element content may indicate intrusive bodies and dykes and in some cases faults by a change in vitrinite reflectance. Development of anisotropy may also record changes in palaeo stress.

The analysis of the distribution of coal lithotypes, coal rank and grade may serve to predict the behavior of a coal seam at all stages of the mining and beneficiation chain. A significant hazard during mining, transport and storage of coal is the self-heating of coal that led to

spontaneous combustion. Lower rank coals are generally more prone to self-heating than higher rank coals, but this is not a linear relationship and coal type, coal particle size and climate are important factors that influence this process. Coals with high contents in reactive macerals, (liptinites and vitrinites) are more prone to self-heating than inertinite- rich macerals. Beamish and Arisoy (2007) also demonstrated the importance of mineral type and content for self-heating.

4.3.2 Coal combustion

In coal combustion, coal rank is fundamental because it influences the heating value of a coal, and the combustion characteristics. The maceral composition is also fundamental to the combustion properties, as different maceral groups combust at different temperatures and rates. The inorganic composition is also basic to the heating rate of the coal. Mineral matter type and contents influence the ash yield, as well as the emission of gaseous oxides and trace elements in the combustion process. Neavel (1981) described a series of coal properties that are important in combustion such as: calorific value, grindability, combustibility (combustion properties of macerals), and ash properties. An important issue in coal combustion is the production of fly ash (Fig. 4). The characteristics of these fly ash will depend on the type and grade of combusted coals and the combustion conditions. Fly ash can be re-used and methods used in organic petrology serves to control the composition and properties of fly ash (Suárez-Ruiz-and Crelling, 2008).

Fig. 4. Images in optical microscopy. Polarized light and retarder plate of 1λ . 1,2) Fly ash from pulverized coal combustion of bituminous coals; left: unburned carbon, right: inorganic particles. 3) Metallurgical coke. 4) Gasification residue of a subbituminous coal.

4.3.3 Coal carbonization

Coal carbonization is the process for producing metallurgical coke (Fig. 4) for use in iron-making blast furnaces and other metal smelting processes. Coal carbonization is developed when coal is heated to temperatures as high as 1100°C in the absence of oxygen. In addition to coke, the by-products obtained in this process are tars, light oils, coke oven gas along with ammonia, water, and sulfur compounds that are also thermally removed from the coal. Coal petrology has been applied to general aspects of carbonization such as to evaluate the suitability of a given coal for coking, in the prediction of the strength of cokes made from both single coals and coal blends, the peak coking pressures, and the coke reactivity. Coke shows distinct optical textures and structures and these features can be investigated by petrographic analysis to understand the behavior of coke. There are classification systems of the coke structures published in the literature. Coal petrology has been also incorporated into models for prediction of coke strength of single coals and coal blends. In coke making the peak coking pressure is a factor to be considered, and Benedict and Thompson (1976) developed petrographic methods to predict peak coking pressure.

4.3.4 Coal gasification

Gasification is a conversion process that is described as the reaction of solid fuels with air, oxygen, steam, carbon dioxide, or a mixture of these gases at temperatures exceeding 800°C in a reducing environment where the air/oxygen ratio is controlled. The obtained gaseous products are further processed for use as an energy source or as a raw material. The chemical composition of the gas produced depends on coal composition and rank, coal preparation; gasification agents, gasification conditions, and plant configuration. The performance of the gasification process is also dependent on the type of the coal and the gasifier configuration. Elemental composition (organic and inorganic) is one of the relevant coal properties together with surface characteristics and porosity, and intrinsic reactivity (van Heek and Muhlen, 1986). Coal rank affects hydrogen and oxygen ratios, gasifier performance and the char morphology (Harris et al., 2006). Char morphology can be predicted from the initial maceral and microlithotype composition because they behave in specific ways when exposed to increasing temperatures and oxygen-rich or oxygen-depleted environments. The analysis of the type and amount of mineral matter in coals permits the prediction of the ash or slag properties, the conversion rate, the size of the ash bed in the reactor, and ash / slag handling facilities following conversion.

4.3.5 Direct coal liquefaction

Coal liquefaction can be carried out by different processes (directly by hydrogenation, indirectly by the Fischer-Tropsch synthesis, and removing some carbon from coal by pyrolysis) which differ in their requirements, technology, yield of fuel and final products. The objective of direct coal liquefaction (conversion of coal to liquids by hydrogenation) is to add hydrogen to the organic structure of the coal, breaking it down to produce distillable liquids to be used as transportation fuels or chemicals. A series of coal characteristics should be controlled such as coal rank and composition which are primary factors that influence the liquefaction behavior (*e.g.*, Cudmore 1984). The maceral composition of the coals has also a strong influence on the composition of the resulting products (liquid yield), and the mineral matter content of the coal influence the

liquefaction behavior. The coal liquefaction process also produces solid residues and their study provide information on the physical and chemical transformation of coal macerals and minerals in the process. Moreover the study of solid residues by petrography also informs about the efficiency of the conversion process. In 1993 the ICCP published a Classification of Hydrogenation Residues in order to standardize the terminology and organize the residue components by their degree of reaction or mode of formation.

4.3.6 Coal-derived carbon materials

Coal and its by-products may also be employed as a source of organic chemicals and carbon based-materials (Schobert and Song, 2002) such as carbon fibers and carbon-carbon composites, graphites, activated carbons, and carbon foams among others. Carbon materials are composed of a high percentage of carbon and taking into account that coals by definition are carbon-rich solids a wide range of solid carbon materials can be obtained from coal and its by-products. Depending on the rank and composition, coals may be used directly as precursors to obtain solid carbon materials. Solid residues with a high carbon content from coal utilization are also investigated as precursors of carbon materials. In the case of coal by-products, coal-tar is produced during coal conversion to obtain metallurgical coke. Pitches obtained from coal-tar are in turn used as precursors for chemicals and carbon materials. In addition, mesophase pitches (the anisotropic fraction of pitches) obtained from coal-tar pitches, are also used as precursors of carbon materials. In the study of the physico-optical properties of solid carbon materials and their precursors, the procedures used in organic petrography play a major role. This is because the relevant parameters obtained from microscopic analysis of a material or precursor can be correlated with other analytical information assisting in the interpretation of the properties and behaviour of a particular carbon material. The most relevant characteristics analysed by the microscopic examination of carbon materials and their precursors are reported in Suárez-Ruiz and Crelling (2008).

4.4 Ore deposits

It is known that some ore deposits occur associated to the organic matter in variable amounts and that some of them are of economic interest. The involvement of the organic matter in some aspects of the ore formation (*e.g.*, Meyers et al., 1992; Mossman, 1999) varies from active participation in the emplacement of ore deposits to post-depositional alteration of the organic matter that may be related or unrelated with the ore forming process. The incorporation of organic petrology methods in studies of metal concentration may assist in the evaluation of the time-temperature burial history of ores and may elucidate the active or passive role of the organic matter in ore deposition, thereby helping to determine the source of metals, transportation and precipitation mechanisms, and provides indications of the thermal history of the host rocks. The microscopic approach is the same as that conventionally applied to coal/ coke and for the dispersed organic matter in sedimentary rocks. Some examples of this type of studies include (*e.g.*) Parnell et al. (1993); Parnell (2001) and Glikson and Mastalerz (2000).

4.5 Other fields of organic petrology application

In the last years organic petrology studies also complements investigations developed in other different fields not strictly related to those previously described such as coal fires, environmental impacts, archaeology and provenance of organic artifacts, and forensics.

Coal fires in un-mined outcrops, abandoned mines and coal waste piles constitute a serious safety and environmental hazard. There is an increasing interest in the self-heating processes (*e.g.*), Stracher and Taylor (2004). Critical coal properties requisite for spontaneous combustion are summarized in Suárez-Ruiz and Crelling (2008) and include: high moisture and volatile matter contents; particle size and available surface area which permits the permeation of air and water; mineral matter type; petrographic composition (presence of reactive macerals), and coal rank.

Organic petrology has been also used in combination with other analytical techniques in investigations of environmental pollution due to anthropogenic activities. Some examples include those by Cohen et al. (1999a,b) and Carrie et al. (2009). The identification of organic particulates derived from industrial activities such as coal mining, preparation, transport, blending, storage and utilization, coke, coal-tar, pitches, etc., is important due to the existing relationships between such organic particulates, their sorption properties, and the presence of PCBs, PAHs, and PCDD/Fs organic pollutants (*e.g.*, Yang et al., 2008). Taking into account this Crelling et al. (2006) published an atlas focused on organic particles from anthropogenic activities that can be identified by using petrographic methods.

The possibilities of the organic petrology to investigate the archaeological objects of organic nature such as jet have been revised by Teichmüller (1992) and recently by Suárez-Ruiz and Crelling (2008). Most of the scientific research into the occurrences of jet from different countries, its nature, origin, properties and quality has been carried out in the last three decades (*e.g.*, Petrova et al., 1985; Suárez-Ruiz et al., 1994 among others). The organic petrography in combination with organic geochemistry has demonstrated that jet is a perhydrous coal with suppressed reflectance, high H/C atomic ratio and high oil yields. Because the scarcity of this material, jet ornaments are very appreciated and organic petrology helps to differentiate jet from other apparently similar materials.

Petrologic methods have been also used to investigate the provenance of organic objects and artifacts from archeological and similar sites (*e.g.*, Smith, 2005). Moreover, the organic petrography also helped in the assessment of trading patterns of coals during the past two centuries in relation to (*e.g.*) the shipwrecks (Erskine et al., 2008).

Forensic geology is mainly concerned with studies of rocks, sediments, minerals, soils and dusts and it can be defined as the discipline that uses geological methods and materials in the analysis of samples and places that maybe connected with criminal behavior or disasters (Murray, 2004; Ruffell, 2010). Therefore forensic geology includes geological methods of analysis such as geophysics, petrography, geochemistry, microscopy and micropaleontology (Ruffell, 2010).

5. Summary

This paper provides a general picture of organic petrology and the significant role it plays in contributing to scientific knowledge. Organic petrology is a subject of broad scope that started out as coal petrology for coal research (coal exploration and utilization). This discipline dates back to the end of the 19th century. The two basic concepts of the organic petrology, composition and rank/maturation of organic matter and the undeniable economic interest shown in fossil fuels have extended its application to the field of hydrocarbon resources. In the last few decades, due to its high versatility, the organic

petrology has been increasingly branching out into other fields of studies such as coal fires, environmental impacts, archaeology and provenance of organic artifacts, and forensics. Consequently a great deal of research has been carried out in both, fundamental and applied organic petrology as it is reflected in hundreds of published papers, and monographs.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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