

Review article

Review and update of the applications of organic petrology: Part 2, geological and multidisciplinary applications

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ABSTRACT

The present paper is focused on organic petrology applied to unconventional and multidisciplinary investigations and is the second part of a two part review that describes the geological applications and uses of this branch of earth sciences. Therefore, this paper reviews the use of organic petrology in investigations of: (i) ore genesis when organic matter occurs associated with mineralization; (ii) the behavior of organic matter in coal fires (self-heating and self-combustion); (iii) environmental and anthropogenic impacts associated with the management and industrial utilization of coal; (iv) archeology and the nature and geographical provenance of objects of organic nature such as jet, amber, other artifacts and coal from archeological sites; and (v) forensic science connected with criminal behavior or disasters. This second part of the review outlines the most recent research and applications of organic petrology in those fields.

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1. Introduction

In a previous paper (Suárez-Ruiz et al., 2012) focused on geological applications of organic petrology two of the main fields of application were described: depositional paleoenvironments (including organic facies and geothermal history of basins), and fossil fuel exploration (source and reservoir rocks). These are the traditional fields in which organic petrology has been applied and developed. The present paper is a continuation of the previous, but in this case the discussion is focused on application of organic petrology to less well-known disciplines. The first section of this manuscript is dedicated to applications of organic petrology to ore genetical investigation examining cases when organic matter is associated with ore deposits. The second section gathers applications of organic petrology to multidisciplinary fields unrelated to geology but of increasing societal interest such as the coal fires (self-heating and self-combustion), environmental science, archeology, and forensics (including forensic geology). These later disciplines can be described as unconventional applications of organic petrology. The range of unconventional applications and the amount of published contributions have been growing in the last 15 years.

As indicated in the previous paper (part 1, Suárez-Ruiz et al., 2012), in this review (part 2), the application of organic petrology to coal utilization is not considered given that a monograph focused on this subject was recently published (Suárez-Ruiz and Crelling, 2008).

When organic petrology is applied to investigations of ore genesis and other unconventional fields the technique and optical microscopy approach is the same as that conventionally applied to the study of the coal or dispersed organic matter as was described in part 1. This approach includes: i) observations in incident light to determine the type, source, and physico-optical properties of organic matter; ii) analysis of the optical textures (isotropy/anisotropy) in order to establish mineral and organic matter paragenesis in ore deposits, or to establish an anthropogenic source of organic material; iii) analysis of the fluorescence properties of organic matter, and iv) quantitative petrographic determinations such as reflectance measurements which are an organic indicator of thermal evolution and can be used to establish paragenetic sequences in the case of ore deposits.

Observations in transmitted light (thin sections) are infrequently used in the study of organic matter in ore deposits. However, such observations may provide additional information regarding thermal maturity because the color of some organic components irreversibly changes from light yellow to black with increasing maturity. For example, Gize (1993) reported the potential for simple coloration studies to outline thermal anomalies associated with hydrothermal mineralization although such studies require detailed investigation and must be interpreted with caution. On the other hand, analysis of organic matter in transmitted light is a classic tool in forensic investigations, particularly in the use of palynological studies to diagnose organic components. In all ore-related and unconventional applications, organic microscopy studies normally are used in combination with geochemical analysis.

2. Applications of organic petrology

2.1. Ore genesis and organic matter

2.1.1. Introduction

The formation of an ore deposit necessarily requires that the concentration of metallic elements is above average crustal levels (Meyers et al., 1992). It is well-known that some ore deposits occur associated with organic matter and that some of these deposits are of economic interest. Therefore in the 1980s, Dean (1986) edited a book examining organic matter associated with ore deposits including study of processes

involved in concentration and accumulation of metals by organisms, methods used in the study of organic matter, and focused case studies. Some associations are well-documented, for example the Kupferschiefer in Central Europe (e.g., Heppenheim et al., 1995; Sawlowicz et al., 2000) which hosts the Cu–Pb–Zn–S mineralization with noble metals (e.g., Kucha, 1993), the organic matter (kerogen and bitumen) occurring with gold and uraninite in the Witwatersrand ore deposits in South Africa (Eakin and Gize, 1992; Mossman et al., 2008; Parnell, 2001; Spangenberg and Frimmel, 2001, among others), hydrocarbons associated with Carlin-Type disseminated gold deposits (mentioned in Gize, 1993), and bitumens associated with various Cu deposits in Chile (Cisternas and Hermosilla, 2006; Wilson, 2000; Wilson and Zentilli, 2006).

Nature of the involvement of organic matter in some aspects of 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 organic matter unrelated to the ore forming process. According to Mossman (1999) mechanisms by which the organic matter may concentrate metals include metal accumulation in living organisms (biomineralization processes, not discussed herein), metal absorption, and organic matter facilitation of reduction reactions through electron donation. Organic matter interacts with metals due to their inherent reducing, acidic and chelating properties. Redox reactions are important mechanism in diagenetic and epigenetic ore-forming environments wherein organic matter acts as a reducing agent for example for soluble metal sulfates in the generation of metal-sulfide deposits and/or the reduction of soluble metal cations to the insoluble native element. In all cases organic matter becomes oxidized. Leventhal (1986) described the physico-chemical processes (mobilization, transportation, concentration, reduction and preservation) and the role of organic matter in ore deposits (Table 1). Disnar and Sureau (1990) reviewed relationships between organic matter and uranium, gold, zinc, lead and copper in large ore deposits with special reference to the Witwatersrand (South Africa), Blind River–Elliot Lake (Ontario, Canada), Pine Point (Northwestern Territories, Canada, see also Macqueen, 1986), Jumbo Mine (Kansas, USA), Mississippi Valley-type ore deposits, and the Kupferschiefer deposit. They discussed the occurrence and role of the organic matter in metallic ore concentration, concluding that the key to understanding processes of ore genesis was the identification of specific alteration traits of the organic materials and criteria of the redox processes participating in metal concentration.

In the last 30 years many researchers have tried to determine relationships between organic matter and ore deposits mainly using organic geochemistry techniques (TOC and CHNOS determinations, Rock-Eval Pyrolysis, GC–MS analysis, stable isotopes such as C, O, among others) including e.g., Ben Hassen et al. (2009), Bostick and Clayton (1986), Brocks et al. (2003), Giordano (1985, 2000), Hatch et al. (1986), Ho et al. (1990), Ho and Mauk (1996), Kríbek (1989), Kettler et al. (1990), Kremenetsky and Maksimuk (2006), Landais et al. (1990), Macqueen and Powell (1983), Gize (1986a), Spangenberg and Frimmel (2001), and Strmic Palinkas et al. (2009), among others. Others have recognized the potential of organic petrology applications in studies of metal concentration and have incorporated additional microscopy techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in combination with organic geochemical analysis to investigate the role of organic matter. Examples include the investigations of Aizawa (2000), Bechtel et al. (1998), Cortial et al. (1990), Cunningham et al. (2004), Eakin and Gize (1992), Forbes et al. (1988), Glikson et al. (2000a, b), Glikson and Taylor (2000), Golding et al. (2000), Hausen and Park (1986), Heppenheim et al. (1995), Héroux et al. (2000), Hu et al. (1998), Jochum (2000), Mauk and Hieshima (1992), Meunier et al. (1990), Monson and Parnell (1992), Mossman et al. (1993a,b), Mossman et al. (2008), Parnell (1992, 1999, 2001), Parnell and McCready (2000), Pasava et

Table 1

Roles of organic matter in ore deposits compared to roles of inorganic substances (from Leventhal, 1986, Table 2, page 11).

Source: Roles of organic matter in ore deposits, by J.S. Leventhal, in: Organics and ore deposits, W.E., Dean (Ed.), Proceedings of the Denver Region Exploration Geologists Society Symposium, 7–20, copyright 1986, reprinted with kind permission of Denver Region Exploration Geologists Society.

Process	Roles of organic matter	Roles of inorganic matter
Mobilization	Decomposition of organic material raises CO ₂ partial pressure in ground water and soil and adds organic CO ₂ and organic acids, which leach and mobilize uranium and other metals from source rocks.	Atmospheric CO ₂ (in meteoric water) and hydrothermal fluids may leach metals.
Transportation	Metal cations held by ion exchange to fulvic or humic acids can be transported with organic matter. Uranium is transported as dicarbonate anion or as soluble organic complex in ground water and surface water.	Cold or hot water may transport metals in inorganic complexes (e.g., with Cl [−] , or PO ₄ ^{3−}).
Concentration	Where pH is suitable, organic materials with functional groups (such as humic acids) may bind Uranium and other metals by ion exchange or by chelation. These types of organic compounds can precipitate at the interface of recharge aquifer waters, where pH becomes more acid, where dissolved solids increases (through evaporation or influx of other water), or on clay surfaces.	Clays, iron oxides, and manganese oxides are effective concentrators of some metals by adsorption.
Reduction	Organic matter may reduce metals directly or through the reduction (biogenic or chemical) of sulfate to sulfide, which in turns reduces the metals.	Allogenic hydrogen sulfide (from hydrothermal fluids or petroleum reservoirs) may serve as a reductant.
Preservation	Reduced metal sulfides or uranium intimately mixed with organic matter are protected from oxidation or remobilization by oxygenated ground water, particularly if the organic matter becomes refractory through burial or aging.	Carbonate cements and clays can decrease porosity and impede water flow.

al. (2003, 2008), Piqué et al. (2009), Sawlowicz et al. (2000), Sherlock (2000), Smieja-Król et al. (2009), Wilson (2000), and Wilson and Zentilli (1999, 2006), among others. However, studies of ore genesis and organic matter using optical microscopy are more scarce, although some authors have demonstrated the usefulness of this approach in the last fifteen years.

2.1.2. Organic petrography in the study of ore deposits

Macqueen (1984) stated that a detailed characterization of the organic matter present in ore deposits would help in evaluation of the time–temperature burial history of ores and would elucidate the active or passive role of organic matter in ore deposition, thereby helping to determine the source of metals, transportation and precipitation mechanisms, and indications of the thermal history of the host rocks. In this type of characterization, organic petrography is revealed as a powerful tool as demonstrated in the papers cited herein.

2.1.2.1. Parameters determined from study of the organic matter associated with ore deposits. There are two key parameters analyzed in the organic matter present in an ore deposit: i) the source and type of organic matter, and ii) its degree of thermal evolution.

i) The source and type of organic matter found in association with ore deposits. The identification of organic matter in incident light is straightforward due to its low reflectance and its polishing softness compared to associated metallic ore minerals (Fig. 1). Following contextual identification, the type of organic matter (e.g., kerogen, oil, bitumen) associated with the ore mineralization and its source are determined (e.g., organoclasts such as graptolites and chitinozoans with high reflectance were described by Bierlein and Cartwright, 2001 in gold mineralizations of the Western Lachlan Orogen in Australia; alginite and its residue after oil generation, and solid bitumens/pyrobitumens remaining from oil migration and cracking were described by Glikson et al., 2000a,b also from Australian ore deposits).

Globally, organic matter occurring in association with ore deposits varies from living plants and animals (not discussed herein) to fossil organic matter of various sources. The fossil organic matter in ore deposits can be indigenous (syngenetic) as in the cases of the Akouta uranium deposit (Niger) with Type-III (land-derived) organic matter (Forbes et al., 1988); coals and coal-bearing strata with the polymetallic deposit (Nb(Ta)–Zr(Hf)–REE–Ga) occurring in the late Permian of southwestern China (Dai et al., 2010); the organic matter in black shales as in the stratiform Cu–Ag deposits described by Püttmann and GoBel (1990), and the tin-polymetallic sulfide deposits in Devonian black shales of the

Dachang area in South China described by Pasava et al. (2003). More frequently the organic matter associated with ore deposits corresponds to secondary organic products such as oils/hydrocarbons, bitumens, and pyrobitumens (Figs. 1 and 2a–c). This is the case with copper mineralization at White Pine (Michigan, USA) described by Mauk and Hieshima (1992); the El Soldado–Cu deposit (Wilson, 2000; Wilson and Zentilli, 1999) and the strata-bound copper deposits (Copiapo area) (Cisternas and Hermosilla, 2006) both in Chile; the uranium ore deposits in the Oklo area of Gabon (Mossman et al., 1993b); the Mount Isa ore deposits in Australia described by Glikson et al. (2000a); the Athabasca uranium deposits in Canada described by Wilson et al. (2007); and the Itxaspe Zn–(Pb) MVT occurrence in North Spain described by Piqué et al. (2009). Occurrences of graphite and graphitic carbon associated with ore minerals were reported by Bierlein and Cartwright (2001) and Wilson and Zentilli (1999), among others.

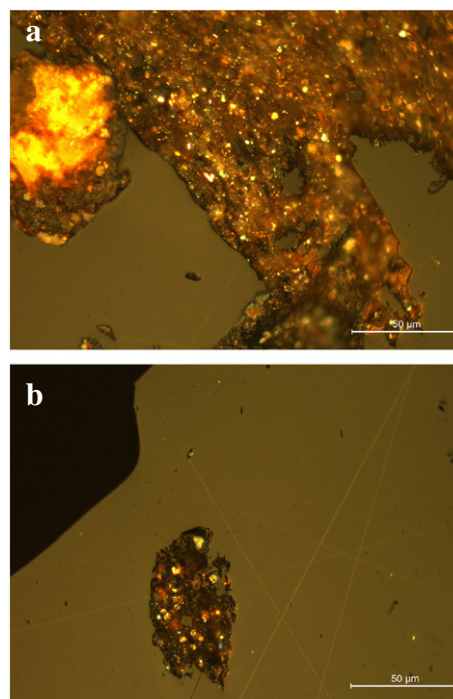


Fig. 1. Optical microscopy. Photomicrographs (a–b) taken in reflected white light. Example of an intergrowth of bitumen and inorganics containing iron. Bitumen is albertite with a measured random reflectance (in oil) of 0.36%. Sample from Albert Mines in the Mississippian Frederick Brook Member, Albert Formation, near Moncton, New Brunswick, Canada.

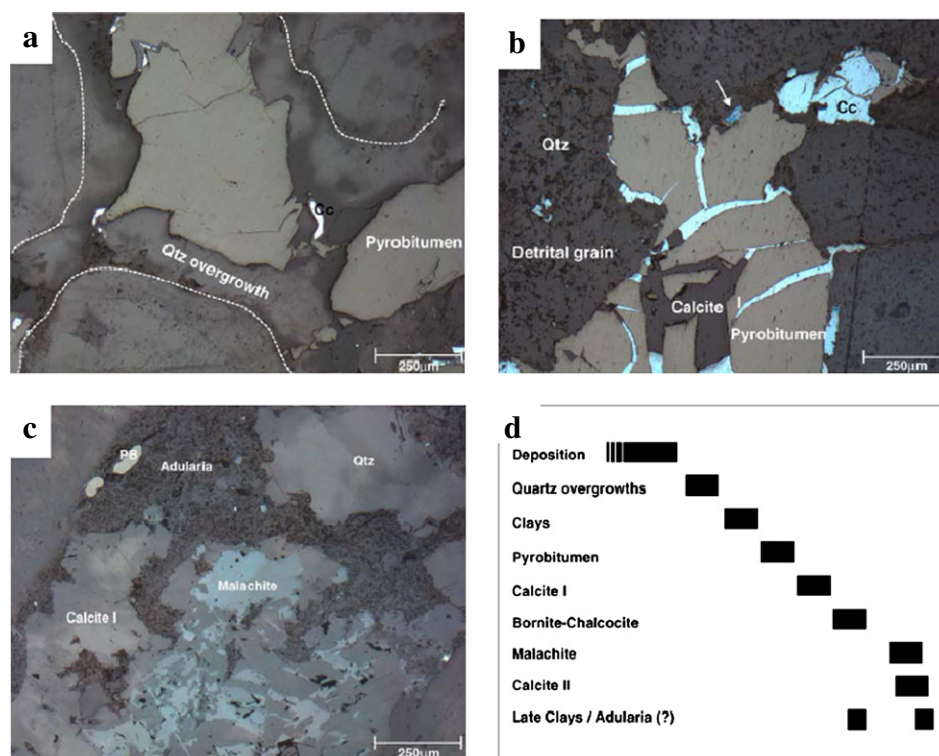


Fig. 2. Example of an association of pyrobitumen with copper mineralization in central Chile developed by Wilson and Zentilli (2006) in which optical microscopy contributed to establishment of the paragenetic sequence. Optical microscopy. Photomicrographs in reflected white light. a): early quartz (qtz) overgrowing detrital grains with porosity filled by pyrobitumen and minor chalcocite (Cc); b): pyrobitumen filling the pore space crosscut by chalcocite (minor digenite; arrow); c): clay (adularia) crosscutting calcite and including pyrobitumen (PB), and d): paragenetic sequence.

From Wilson and Zentilli, (2006, Fig. 4, page 163). Source: Association of pyrobitumen with copper mineralization from the Uchumi and Talcuna districts, central Chile, by N.S.F. Wilson and M., Zentilli. International Journal of Coal Geology 65, 158–169, copyright 2006, with kind permission from Elsevier, www.elsevier.com.

During the analysis of the type and source of organic matter in ore deposits all optical characteristics usually are taken into account. This includes the relationships between organic matter and metals in the host rock as reported by e.g., Eakin and Gize (1992), Wilson (2000), and Wilson and Zentilli (1999, 2006), shape and morphology of the organic matter (e.g., Bierlein and Cartwright, 2001; Hansley and Spirakis, 1992); the intergrowth, distribution, porosity types (pores, cracks and shape of cracks), degassing vesicles (Cisternas and Hermosilla, 2006; Wilson, 2000; Wilson and Zentilli, 1999, 2006), and internal reflections, flow textures, fluorescence color and optical isotropy/anisotropy. Such characteristics are used to establish the mineral and organic matter paragenesis in ore deposits (Figs. 2 and 3). Some examples where incident light observations were employed include Jakobsen and Ohmoto (1993), Liu et al. (1993), Mancuso et al. (1993), Parnell (1993, 2001), Parnell and McCready (2000), and Percy and Burruss (1993) for organic matter in ore deposits; and Spirakis and Heyl (1993) in studies of paragenetic sequences to determine mineralization temperatures and stages.

Petrographical and geochemical analyses of organic matter associated with the Upper Silesian Zn–Pb sulfide deposits (northwest of Krakow) which are hosted in dolomitized Middle Triassic limestones were carried out by Kwiecinska et al. (1997), and Sass-Gustkiewicz and Kwiecinska (1994). The organic matter is of humic and allochthonous nature and experienced migration under oxidizing conditions. It was identified as eugelinite, with a reflectance lower than 0.3%, of the variety dopplerite (calcium humate), which precipitated from humic acids migrating downwards in aqueous solution and loaded with Ca cations released from surrounding carbonates by ascending hydrothermal solutions. The organic matter and sulfide ores were both deposited within karst collapse structures contemporaneously and are genetically related. The authors concluded

that organic matter and humic acids play a critical role in precipitation of sulfide ore minerals as reductants of partly oxidized, sulfur- and metal-bearing, ascending hydrothermal solutions.

Solid bitumens may capture metals in ore deposits. Therefore, elucidation of the character of mineral matter and bitumen intergrowths, development of porosity features including linear and irregular

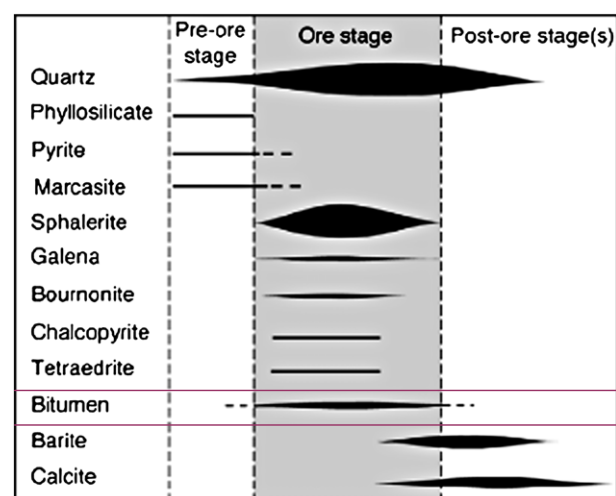


Fig. 3. Paragenetic sequence of the Itxaspe Zn–(Pb) mineralization in the MVT occurrence, Basque–Cantabrian Basin, Northern Spain.

From Piqué et al. (2009; Fig. 4, page 437). Source: In situ thermochemical sulfate reduction during ore formation at the Itxaspe Zn–(Pb) MVT occurrence (Basque–Cantabrian basin, Northern Spain) by A. Piqué, A. Canals, J.R. Disnar, and F. Grandia, in *Geologica Acta* 7/4, 431–449, copyright 2009, with kind permission from *Geologica Acta*, www.geologica-acta.com.

voids, internal reflections, optical isotropy/anisotropy, and flow textures may aid in the study of paragenetic ore and organic matter sequences. Jacob (1989, 1993) reported a genetic classification of solid bitumens [ozocerite, asphalt, asphaltites (gilsonite, glance pitch, and grahamite), wurtzilite, albertite, and impsenites (epi-, meso- and cata-impsonite)] that is useful when they are found in paragenesis with metals. He also described the corresponding source and optical properties of solid bitumens including reflectance, fluorescence intensity, microsolubility in immersion oil and micro-flowpoint. Some of these properties are shown in Table 2. Ozocerite is rare in paragenesis with minerals while asphalt usually is described in intergrowths with ore and gangue minerals. Gilsonite and glance pitch have the same genesis but the latter is a more mature solid bitumen than gilsonite; both usually occur in intergrowths with ore and other minerals. Grahamite is best known from Paleozoic rocks and its occurrence in rocks of Mesozoic and Cenozoic age is rare. Wurtzilite and albertite (see albertite in Fig. 1) typically occur in intergrowths with low temperature ore minerals. The impsenites are metamorphic bitumens that require progressively higher temperatures in their formation. Epi-impsonite is the first stage of the metamorphic solid bitumens followed by meso-impsonite and cata-impsonite. The impsenites are porous due to degassing processes, they show higher reflectance, and their fluorescence is completely lost. The impsenites also appear as intergrowths with ore minerals and other minerals. The most mature bitumen, cata-impsonite, occurs as intergrowths with ore minerals of hydrothermal to pneumatolytic-pegmatitic origin. Weathering of bitumens changes their properties e.g., lowering or increasing the reflectance, and their assignment to a specific genetic class of bitumen becomes more difficult.

Under crossed polars, organic matter may appear either isotropic or anisotropic depending on its internal structure and the ordering of its basic structural units (BSUs). With thermal and burial evolution, the organic matter becomes increasingly ordered and develops optical anisotropy. The final product of maturation of organic matter may be graphite, which is chemically homogeneous, structurally ordered, and optically anisotropic. Analysis of the optical texture (isotropy/anisotropy) is especially significant in the case of solid bitumens in paragenesis with ore minerals. In ore deposits in which the temperature has been low or moderate (approximately 200 °C or less) solid bitumens tend to be optically isotropic reflecting structural heterogeneity at the molecular level (Gize, 1993). Solid bitumens associated with higher temperature ore deposits may show the transition from isotropic to anisotropic and to graphite. Some examples were reported by Wilson (2000) for solid bitumens in the El Soldado Cu deposits and by Cisternas and Hermosilla (2006) for isotropic and anisotropic bitumens related to hydrothermal events in stratabound copper deposits at the

Copiapó area (northern Chile). Other examples of solid bitumens with anisotropic optical texture and development of thermal mesophase in high temperature ore deposits were described by Gize (1986b). Solid anisotropic bitumens with fine mosaic character also were reported by Bierlein and Cartwright (2001) in a study focused on the genesis of gold mineralizations in Victoria (Australia). Other cases of anisotropic bitumens in ore deposits were described by Cortial et al. (1990), Kríbek et al. (1993), and Smieja-Król et al. (2009).

- ii) Maturation of the organic matter. The maturation of organic matter present in ore deposits is the second parameter usually considered after source and type. The advantage of maturation studies in ore deposits is that if the thermal history is known (e.g., from fluid inclusions) the timing of occurrence and paragenesis chronology can be evaluated (e.g., Cisternas and Hermosilla, 2006; Wilson, 2000; Wilson and Zentilli, 1999, 2006). In the case of a hydrothermal event the duration also may be approximated. Maturation studies permitted determination of the phases of bitumen generation and their influence on metal concentrations as reported by Hansley and Spirakis (1992) in a study of the organic diagenesis and its role in uranium concentration.

Studies of organic maturity using reflectance measurements include e.g., Yang and Liu (1993) in which reflectance and organic matter type provided valuable information related to the formation of some strata bound ore deposits in China. Reflectance of the organic matter increases with thermal maturity through the effect of temperature (burial, hydrothermal activity, dykes and sill intrusions), in addition to radiolysis events (as in the case of uraniferous bitumens, e.g., Eakin and Gize, 1992; Landais, 1993). Reflectance may also increase or decrease due to the oxidation and weathering processes (e.g., Cortial et al., 1990; Wilson and Zentilli, 1999). Reflectance values also are very important in assessment of spatial variations in organic maturity and detection of thermal anomalies in ore deposits or describing thermal evolution of bitumens that actively participated in mineralization (Gize, 1993). Some examples of studies are presented in Table 3.

The organic matter in ore deposits may also fluoresce and measurement of fluorescence color and intensity may help to determine source and thermal maturity. In a study of metallogenesis and hydrocarbon generation in Mount Isa Basin (Australia) Glikson et al. (2000a) used fluorescence to identify and describe autochthonous immature alginite in a regional context in which the predominant organic matter was an overmature solid bitumen. Fluorescence microscopy is applied not only in the differentiation of co-existing types of the organic matter (e.g., kerogen and bitumens, immature and mature organic matter) but also in the detection of hydrocarbon present in fluid inclusions (Sousa et al., 2007) and oil staining in minerals. In addition to organic

Table 2

Main physico-chemical characteristics of bitumens ("migrabitumens"). Data from Jacob (1989), Table 2, page 69.

Source: Classification, structure, genesis and practical importance of natural solid oil bitumen, "migrabitumen", by H. Jacob, International Journal of Coal Geology 11, 65–79, copyright 1989, reprinted with kind permission from Elsevier, www.elsevier.com.

	Rr % (oil)	Fluorescence ^a intensity	Microsolubility ^b	Density (g/cm ³)	Vol. mat. (% daf)	C (% daf)	H (% daf)
Ozocerite	<0.01–ca. 0.02	ca. 9.0–>50	Soluble	~0.8–0.9	>99	84–89	11–17
Wurtzilite	<0.01–ca. 0.10	ca. 0.1–>2.0	Insoluble	~1.0–1.1	95–75	72–84	8–13
Albertite	ca. 0.1–ca. 0.7	≤0.1	Insoluble	~1.1–1.2	75–45	83–92	6–13
Asphalt	ca. 0.02–ca. 0.07	ca. 0.4–>4.0	Soluble	~1.0–1.1	>90	75–86	11–13
Gilsonite	ca. 0.07–ca. 0.11	ca. 0.05–ca. 0.4	Soluble	~1.0–1.1	90–80	85–86	9–11
Glance pitch	ca. 0.11–ca. 0.3	ca. 0.05–ca. 0.2	Soluble	~1.1–1.15	80–65	80–85	7–11
Grahamite	ca. 0.3–ca. 0.7	≤0.05	Slightly soluble or insoluble	~1.15–1.25	65–45	83–90	6–9
Epi-impsonite	ca. 0.7–2.0	≤0.02	Insoluble	~1.2–1.7	45–19	88–93	2–6
Meso-impsonite	2.0–3.5	<0.01	Insoluble	~1.2–1.7	19–8	88–93	2–6
Cata-impsonite	3.5–ca. 10	<0.01	Insoluble	~1.2–1.7	<8	88–93	2–6

Rr: random reflectance. Vol. Mat.: volatile matter.

^a Special masked uranyl glass standard = 1%.

^b In immersion oil and petroleum ether.

Table 3

Some examples of the application of organic maturity to understanding the formation of ore deposits.

Authors	Material/parameter used/event detected	Ore deposit
Spirakis (1986)	Occurrence and processes involving organic carbon in paragenesis of Mississippi Valley deposits	Mississippi Valley-type sulfide deposits in US and Canada districts
Ilchick et al. (1986)	Late hydrothermal event	Alligator Ridge Carlin-type disseminated gold deposit
Gize (1986b)	Development of thermal mesophase in bitumens	High temperature ore deposits from various places
Cortial et al. (1990), Glikson et al. (2000a,b), Kribek et al. (1993)	Maturity or thermal evolution of bitumens	Different type of ore deposits
Liu et al. (1993), Yang and Liu (1993)	Maturity of kerogens and bitumens	Chinese mineral deposits
Glikson and Taylor (2000)	Reflectance data from the kerogen	North Pole chert-barite deposit (Western Australia)
Sawlowicz et al. (2000)	Reflectance data from the kerogen	Copper deposits in the Kupferschiefer of Central Europe
Mastalerz et al. (2000)	Maturity of organic matter	Hydrothermal systems
Héroux et al. (2000)	Thermal anomalies	Sulfide Polaris deposit in the Canadian Arctic
Cunningham et al. (2004)	Thermal anomalies	Disseminated gold deposits associated with a porphyry Cu–Au–Mo system in Utah
Glikson and Golding (2006)	Reflectance as an indicator of the maximum temperature and mode of heating and heating rate	Ore deposits in the Isa Superbasin of Australia
Wilson et al. (2007)	Maturity of bitumens	Uranium deposits in the Athabasca Basin (Canada)

fluorescence some ore and gangue minerals may fluoresce (e.g., sphalerite and carbonates), enhancing description of color banding and growth features. The observation of fluorescence properties in combination with reflectance measurements (e.g., Jacob, 1993) has also served to differentiate various generations of bitumens. Gize (1993) described bitumen inclusions in sphalerite which displayed different reflectances between an outer zone (1.3%) and an inner core (0.3%), interpreted as a consequence of two generations of petroleum. This interpretation was confirmed and expanded in fluorescence observations because the thermally mature outer zone did not show any fluorescence but the inner immature core contained two zones emitting at different wavelengths and representing two distinct solid bitumens with compositional differences. Another example of the utilization of fluorescence properties of the organic matter were provided by Percy and Burruss (1993) in a study of relationships between hydrocarbons and bitumens occurring in California gold deposits. Rasmussen et al. (1993) used fluorescence of solid bitumen to determine the degree of polymerization of oil by radioactive minerals in three cases from Western Australia. Heppenheimer et al. (1995) analyzed fluorescence characteristics of organic matter extracts in a study of the influence of organic matter on metal accumulation processes in two areas (Poland and Germany) of the Kupferschiefer ore deposit to show the influence of fluids. Wilson et al. (2007) used fluorescence microscopy to identify petroleum inclusions trapped in fractures, intergrowths and within cements associated with kerogen in the Proterozoic Douglas Formation in the Athabasca Basin (Canada). The results helped in the estimation of formation temperatures and helped to establish the paragenetic sequence and chronological relationships between the occurrence of graphite, petroleum generation, pyrobitumen formation and the uranium mineralization.

Uranium, vanadium and organic matter in copper deposits are associated with thucholite and coffinite (Banas et al., 2005; Hansley and Spirakis, 1992). The organic matter (reflectance values between 3.6 and 3.8%) occurs in anisotropic shapeless accumulations metasomatically replacing quartz grains and is characterized by a high degree of structural ordering (Banas et al., 2005).

2.1.2.2. Relevant cases of the organic petrology used in the study of organic matter contained in ore deposits. In addition to the research already cited herein there are two comprehensive volumes edited by Parnell et al. (1993) and Glikson and Mastalerz (2000) that provided examples of the applications of the petrographic methods to investigation of the role of organic matter in concentration of metals from different ore deposits around the world. In the present review,

some examples in which organic petrographic techniques were used in metalliferous deposits are discussed below.

The degree of involvement (nature, source, and time of emplacement) of various types of organic matter in ore deposits determined using the petrographic methods alone or in combination with other geochemical techniques is well documented in investigations by Wilson and Zentilli (1999) and Wilson (2000). These authors investigated the solid bitumens (Fig. 2) associated with the strata-bound Cu deposits hosted in rhyolites and andesites of the Lower Cretaceous Lo Prado Formation in El Soldado (central Chile). Two main stages of evolution were identified: i) Stage I occurred at low temperatures (<100 °C) during burial of the basin in which petroleum was generated from basal marine organic-rich shales and migrated into the primary rock porosity, accompanied by development of framboidal pyrite through biodegradation of the petroleum. The processes of Stage I occurred at low temperatures before Cu mineralization and so, within the oil window. ii) Stage II occurred due to regional low-grade metamorphism (~300 °C) which introduced Cu into the system through fluid influx, crosscutting and thermally altering the bitumen, notably increasing its reflectance as a function of the magnitude of hydrothermal circulation and Cu mineralization. As a result, bitumens developed anisotropy with textures related to the amount of Cu concentration, incorporated other metal components from the mineralizing fluids, and experienced local graphitization. Throughout Stage II bitumen was oxidized while reducing the mineralizing fluids. Wilson and Zentilli (2006) developed a similar petrographic study on association of bitumen with copper mineralizations in other Chilean districts (Uchumi and Tulcuma) concluding that degraded petroleum reservoirs are important controls for metallic mineralizations derived from hydrothermal solutions of different sources particularly if the biodegradation process generated pyrite.

Organic matter associated with some Au deposits has also been documented but its participation in the genesis of gold mineralizations is still under discussion. Percy and Burruss (1993) used fluorescence microscopy and observations in incident white light in a study on the hydrocarbons occurring in gold deposits of California (USA) to establish the time of hydrocarbon trapping relative to mineralogical paragenesis. They concluded that the timing of gold mineralization does not correlate well with hydrocarbon genesis in the paragenetic sequence despite that high gold concentrations occurred in the associated bitumen. Bierlein and Cartwright (2001) investigated the role of the various types of organic matter (bitumens, graptolites and chitinozoans, and graphite) with different thermal maturities as indicated by their reflectance values in the mesothermal gold deposits of central Victoria (Southeastern Australia). They found that the highest gold grades were not coincident with the presence of the organic matter and, in the cases where gold mineralization was associated with the high

carbon accumulations the cause was epigenetic remobilization during hydrothermal alteration and ore genesis. In the case of the Early Proterozoic gold and uranium deposits of Witwatersrand (South Africa), the presence of organic matter and its role in mineralization have been a subject of debate for many years. Petrographic studies by Parnell (1999, 2001) showed that the gold mineralization was late in the paragenetic sequence and post-dated the emplacement of uraninite and the organic matter. Mossman et al. (2008) included petrographic observations and reflectance measurements in their effort to distinguish the kerogen from bitumen in Witwatersrand ore deposits and concluded that the carbon (organic matter) associated with these deposits was an indigenous biogenic marker that grew contemporaneously with the placer development. Lastly Smieja-Król et al. (2009) developed a work focused on the texture, microtexture and structure of organic matter from the Witwatersrand gold and uranium deposits and included reflectance and anisotropy analysis in addition to TEM and X-ray diffraction (XRD) determinations. The authors indicated that the advanced rearrangement of the polyaromatic units of the organic matter (already in a solid state), occurred under stress in high pressure, low temperature conditions and in the presence of ionizing radiation.

The involvement of the organic matter in uranium mineralization has also been a well-researched subject for many years. Eakin and Gize (1992) used the incident light microscopy to study uraniferous bitumens from Great Britain, Scandinavia and also the Witwatersrand (South Africa) deposits. They observed a relationship between the petrographic textures in the uraniferous bitumens and their genesis and alteration, in particular noting an increase in reflectance values induced by the radiolytic effect of the uraniferous minerals. Mossman et al. (1993b) focused their study on the relationship between organic matter (solid bitumen) and the natural fission reactors at Oklo (Gabon) using incident light microscopy to determine that the bitumen came from the transformation of liquid petroleum which, in its turn, was generated from a kerogen (and protokerogen) derived from abundant cyanobacteria in tidal and deltaic sediments in the Francevillian Formation. The solid bitumens played a role in the genesis of the uranium deposit and also constrained the loss of fissile and fissionogenic isotopes from the organic-rich natural reactors. Another example of the importance of differentiation of organic matter types was reported by Mossman et al. (1993a) in their multidisciplinary study of the organic matter in the uranium ores from the Elliot Lake (Canada). They used organic petrography (texture analysis and reflectance) to differentiate two forms of kerogen derived from Precambrian cyanobacterial mats plus solid bitumen. They demonstrated a positive relationship between higher reflectance and degree of kerogen anisotropy developed as a result of the ionizing radiation from U-bearing minerals. However, the solid bitumens were not affected by radiation because they did not contain radioactive elements or minerals.

Heppenheimer et al. (1995) used reflectance measurements of organic matter and spectral fluorescence microscopy to study the Kupferschiefer in the Hessian depression (Germany) and in the North Sudetic Syncline (Poland) and showed that the dominant processes for metal enrichment in both areas were the same (thermochemical sulfate reduction). They determined that the maturation of the organic matter in both areas was not related to the degree of metal enrichment. Vitrinite reflectance indicated that the temperature in the Hessian depression was slightly higher than in the North Sudetic Syncline. Strong fluorescence in samples from the Kupferschiefer of the North Sudetic Syncline was interpreted as a consequence of the introduction of strongly fluorescent hydrocarbons present in the mineralizing solutions. Cunningham et al. (2004) investigated relationships between metals and the organic matter in disseminated gold deposits associated with a porphyry Cu–Au–Mo system. They documented the presence of solid bitumens in an area of Utah (USA) that was not regionally heated beyond the “oil window” (temperatures lower than 150 °C) as indicated by a combination of maturity parameters

including conodont color alteration indices and mean random reflectance of solid bitumen.

An understanding of the relationships between the organic matter and metals is critical in the exploration for ore deposits. As has been shown in the examples included herein, organic petrographic techniques are a powerful tool that when used in combination with geochemical analysis may contribute to answering two key questions: the source and type of organic matter, and the active or passive role that it has in the concentration of metals in a specific ore deposit.

2.2. Multidisciplinary investigations

2.2.1. Introduction

There are other applications of organic petrology not strictly related to the geology that are less known but of increasing interest. Because organic petrography is a versatile tool, in the last 15 years it has become a useful technique which can be complementary (e.g., to palynological, and geochemical studies) when applied to investigations in fields only partially related with geology or totally unrelated. This section of the review is focused on these unconventional applications and therefore, will describe the ways in which organic petrology contributes to a range of issues so diverse as coal fires and self-heating, environmental pollution, archeology, and forensics.

2.2.2. Coal fires and self-heating

Coal fires in un-mined outcrops, abandoned mines and coal waste piles constitute a serious safety and environmental hazard (Fig. 4). Coal fires have been a problem for hundreds of years and in addition to the loss of energy resources they cause other problems such as: ground subsidence, the emission of greenhouse gases (CO, CO₂, H₂S, SO_x, CH₄, VOCs, PAHs, phenols and dust); the genesis of sublimates (deposits from coal fire gases) (Fig. 5); and also source of particulate matter into the atmosphere (dust) constituting hazard issues with consequences for both human health (e.g. Finkelman, 2004; Mysz-Kennan and Fabianska, 2011; Pone et al., 2007) and environment and ecosystems preservation (e.g. Bell et al., 2001; Pone et al., 2007). Table 4 shows the volatile organic compound (VOC) composition in vents close to burning zones in the Lomba and San Pedro da Cova coal waste piles in Portugal.

There is an increasing interest in the self-heating processes of coals and coal wastes and a great body of work has been generated on the different aspects and consequences of spontaneous combustion (e.g., Chandra and Prasad, 1990; Gentzis and Goodarzi, 1989; Hanak and Nowak, 2008; Kus, 2008; Mysz-Kennan and Fabianska, 2010, 2011; Mysz et al., 2007; Misra and Singh, 1994; O’Keefe et al., 2010; Pone et al., 2007; Querol et al., 2008, 2011; Ribeiro et al., 2010a,b; Silva et al., 2011; Skret et al., 2010; Stracher and Taylor, 2004, among others). In 2004, a special issue of the International Journal of Coal Geology (Stracher, 2004) addressed this topic and later Stracher (2007) documented several case studies from around the world. The first volume of a planned four volume book set dedicated to this global problem entitled “Coal and Peat Fire: a Global Perspective” was recently published by Stracher et al. (2011). And finally, the Second International Conference on Coal Fire Research – ICCFR 2, was held in 2010 (Berlin, Germany) to gather the international community engaged in coal fire research. Mysz-Kennan (2010) and Mysz-Kennan and Fabianska (2010) described in detail the thermal alteration of organic matter in coal wastes from Upper Silesia (Poland) subjected to self-combustion, and Mysz-Kennan and Fabianska (2011) recently presented a very complete review focused on application of organic petrology and geochemistry to the study of coal wastes. These authors describe and illustrate with great detail the transformations of various components of the organic matter during self-heating. Some examples are shown in Fig. 6.

Intrinsic and/or external factors both can cause ignition of organic matter. The weathering/oxidation of coal is the most common intrinsic factor contributing to the ignition of the coals seams and coal

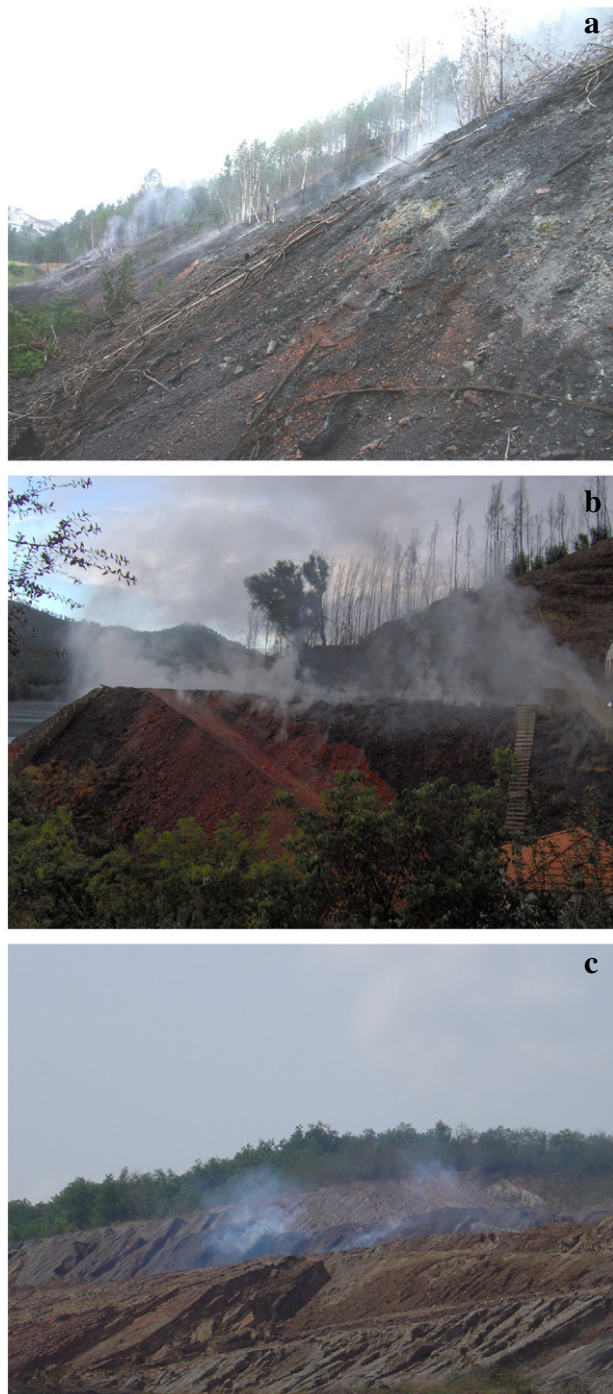


Fig. 4. Self-combustion of: a) San Pedro da Cova, and b) Lomba coal waste piles as consequence of fires occurred in 2005 in Portugal. Note the red colored material, destroyed vegetation and gas exhalations, and c) coal in an Indonesian coal mine. For panels a and b, photo credits: Joana Ribeiro.

waste piles. As this process is exothermic, heat generated during weathering and oxidation raises the temperature and self-heating may start. During this complex and uncontrolled process both the organic and mineral matter experiences a range of alteration which is dependent on petrographic composition and the heating rate, temperature, and duration of exposure.

Critical coal properties requisite for spontaneous combustion were summarized in Beamish and Arisoy (2007), Mastalerz et al. (2011), Misz-Kennan and Fabianska (2011), Suárez-Ruiz and Crelling (2008) and references therein, 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 (mainly pyrite because its oxidation accelerates self-heating); petrographic composition (presence of reactive macerals such as liptinite and vitrinite); and coal rank. High moisture and volatile matter content as well as the presence of reactive macerals (mainly liptinite) are common characteristics of low-rank coals including lignite and subbituminous coals. Thus, it has been widely recognized that lower rank coals have the highest susceptibility to spontaneous combustion. However, extrinsic factors associated to the mining practice (Suárez-Ruiz and Crelling, 2008) and forest fires and lightning strikes (Gentzis and Goodarzi, 1989; Stracher, 2007) also are responsible for the ignition of many coal seams and coal waste piles, even of high rank coals such as meta-anthracites (Ribeiro et al., 2010a).

In study of coal fires, organic petrology contributes to the evaluation of factors responsible for spontaneous combustion and also can be used to assess the changes that are taking place in coal and coal waste material as a result of coal fires. Therefore, Commission III of the International Committee for Coal and Organic Petrology (ICCP), in its ICCP-TSOP Joint Meeting held in Oviedo (2008), decided to create a Working Group on Self-heating of Coal and Coal Wastes (Misz-Kennan et al., 2009). The primary objective of the working group is to define a nomenclature and petrographic classification on heat-affected organic particles from self-heating coal seams and coal waste piles, which will permit an evaluation of the level and magnitude of changes experienced by the organic matter (as well as the mineral matter). The classification that is being developed within this active working group includes petrographic aspects of altered organic matter in coal and coal wastes and unaltered particles including: cracks and microfissures, oxidation rims, plasticized particles with development of special characteristics, coke structures, and newly formed particles such as pyrolytic carbon and natural chars (Misz-Kennan, 2010; Misz-Kennan and Fabianska, 2011; Misz-Kennan et al., 2010). Misz-Kennan (2010) applied this petrographic classification to thermally altered organic matter found in three coal wastes from the Upper Silesia Coal Basin (Poland) which had been subjected to self-heating and self-combustion processes. Some categories of the proposed classification already have been used in other studies (e.g., Misz et al., 2007; Misz-Kennan and Fabianska, 2010; Ribeiro et al., 2010a). Mineral matter also experiences modification during self-heating of coal and coal waste resulting in features similar to that found in fly ash from the combustion of coal in power plants (Ribeiro et al., 2010c).

The global dispersion of fly ash from the combustion of Siberian coals and organic rich sediments into oceans during the latest Permian times have been investigated by Grasby et al. (2011) as a potential mechanism contributing to extinction of about 90% of marine species due to the generation of toxic conditions. The authors found that a substantial amount of char (with similar petrographic characteristics to those shown by modern coal combustion fly ash) was deposited during the Permian in the Canadian high Arctic just before a documented global mass extinction event.

In summary, organic petrology, as demonstrated by the studies cited herein, contributes to an understanding of both the cause and effect of coal and coal waste fires and self coal combustion in the past and present times.

2.2.3. Environmental and anthropogenic impacts

In environmental sciences, the most significant application of organic petrology is related to anthropogenic activities. In conjunction with other analytical methods organic petrology has been used to investigate anthropogenic disruptions ranging from the introduction of changes in the type of vegetation in natural environments (invasive species) to pollution of rivers and estuaries by residues of the management and industrial utilization of coal. In the latter case the transportation, accumulation, lateral dissemination and finally the fate of

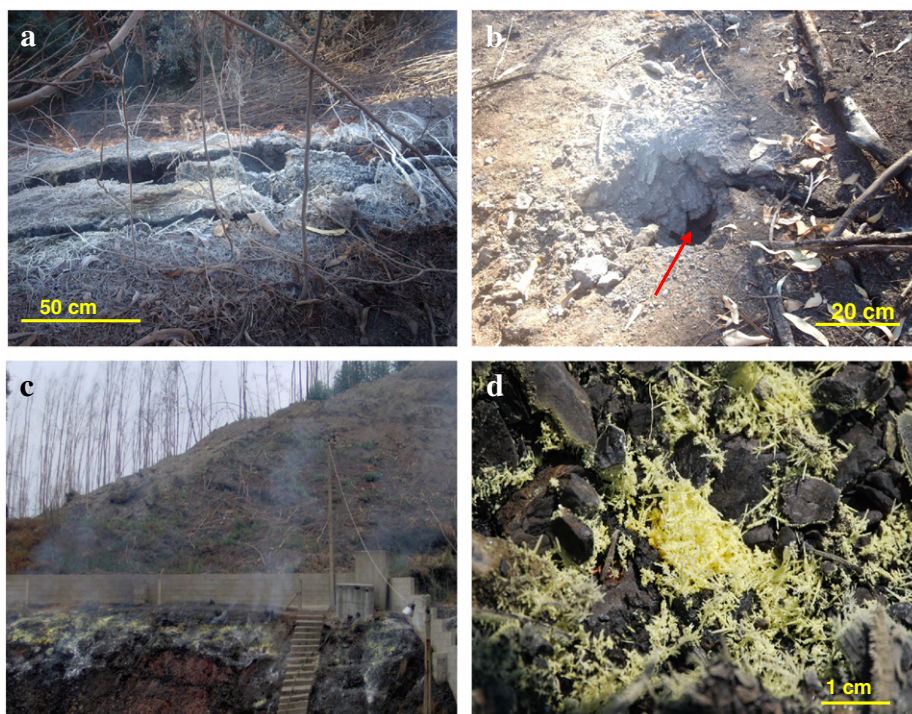


Fig. 5. Images showing fractures (a) and gas vents (arrow in b) with deposition of sal ammoniac (white color, NH_4Cl) nucleated from the exhaled coal-fire gas. San Pedro da Cova waste pile. (c) Sulfur and sal ammoniac (yellow and white colors, respectively; below the wall) nucleated from coal-fire gas exhaled from vents in the Lomba waste pile. Note the deformation in the stairway due to the reduction in rock volume from burning and hence subsidence. (d) Acicular sulfur crystals nucleated from the gas in San Pedro da Cova waste pile. Waste piles located in Portugal.

Photo credits: Joana Ribeiro (a, b), Francisco Soares (c) and Jorge Sousa (d).

solid organic particles extraneous to the natural environment are a significant aspect to be taken into account. Some early studies by Mukhopadhyay et al. (1995, 1996, 1997) used organic petrology and geochemistry methods to analyze the pollution derived from anthropogenic activities in recent sediments, particularly from the Halifax harbor in Nova Scotia, and the Ontario Lake, both in Canada. These authors brought attention to the role of organic petrology in environmental sciences by identification, characterization and quantification of the proportions of natural (both recent and ancient) and anthropogenic organic matter in recent sediments. For such investigations, a comprehensive knowledge of the petrology of all forms of coal, solid bitumen, crude oil, combustion residues, forest fire residues, kerogen, recent palynomorphs, and domestic combustion products of wood is necessary. Fig. 7 shows an example of organic contaminant particulates found in sediments of an estuary in North Spain.

Contemporaneous to Cohen et al. (1999a), Mukhopadhyay et al. (1995, 1996, 1997) carried out one of the first studies that combined organo-petrographic and palynologic methods for distinguishing natural from anthropogenic changes in plant communities in peat from the northern Everglades of Florida. They identified the presence of invasive plant species and used the distribution of pyrite in freshwater peat to document contamination of the study area from agricultural lands. Palynological analysis revealed the vectors of regional changes in the ecosystem, including the introduction of invasive species. Using the same approach Cohen et al. (1999b) also developed a similar study on peat deposits at the Savannah River site in South Carolina to assess the environmental impact of past nuclear weapons research in the area. The authors stressed the use of organic petrography as a means for assessing modes of adsorption and directions of transportation of waterborne contaminants within organic-rich wetlands. Stanley and Randazzo (2001) constructed a petrological database to obtain a record of sediment cover resulting from the interaction of natural transport processes and the rapid increase of human activities in the Rio Grande delta in Texas. This database comprised a set of

common petrologic parameters, including grain size, total organic matter and composition of sand-sized particles in the surficial sediment samples at numerous sites distributed across the delta.

Another example includes the study by Mastalerz et al. (2001) on anthropogenic organic matter in the Great Marsh of the Indiana Dunes National Lakeshore. These authors documented variations in concentration, type and size of anthropogenic organic matter (coal and coke, bitumen, fly ash) and related their occurrence to the concentration of trace elements including Pb, Zn, and Mn in the near-surface sediment section. Their results demonstrated that the first appearance of anthropogenic organic matter corresponded with the onset of local industrialization. Moreover, Mastalerz et al. (2001) established a general relationship between the occurrence of anthropogenic organic matter and Zn, Pb, and Mn and suggested that trace metals could have been transported from industrial sites to the area of their deposition as sulfur-bearing coatings on small anthropogenic particles. After deposition, those sulfur-bearing compounds reacted with organic matter within the marsh. The distance from the industrial complex upwind as well as local hydrologic conditions were seen as the major factors controlling distribution of organic anthropogenic particles and trace elements.

Reyes et al. (2006) investigated the organic particulates present in stream sediments in the Trail area of British Columbia (Canada) to determine their source (natural/geogenic and/or anthropogenic), and Kalaitzidis et al. (2007) also traced the dispersed coal-derived fragments found in lake sediments from Finland, The Netherlands and Sweden in order to estimate the degree of pollution of these areas. Carrie et al. (2009) investigated anthropogenic environmental impact through organic petrology in the Mackenzie River basin, a major source of terrigenous organic carbon input to the Arctic Ocean and Beaufort Sea. The authors documented the spatial distribution and flux of different types of organic matter in the near-surface suspended sediments of the Mackenzie River and its main tributaries using organic geochemistry and petrological approaches. Carrie et

Table 4

Volatile organic compounds (VOCs) in gases sampled from vents close to burning zones of coal waste piles (from Ribeiro et al., 2010a, Table 3, page 370).

Source: Burning of coal waste piles from Douro Coalfield (Portugal); Petrological, geochemical and mineralogical characterization, by J. Ribeiro, E. Ferreira da Silva and D. Flores, International Journal of Coal Geology 81, 359–372, copyright 2010, reprinted with kind permission from Elsevier, www.elsevier.com.

Compound	Chemical formula	L1 ($\mu\text{g}/\text{m}^3$)	L2 ($\mu\text{g}/\text{m}^3$)	SP1 ($\mu\text{g}/\text{m}^3$)	SP2 ($\mu\text{g}/\text{m}^3$)
Aromatic hydrocarbons					
Benzene	C_6H_6	40.9		592.0	1257.0
Pyridine	$\text{C}_5\text{H}_5\text{N}$	50.6	22.3		23.4
Toluene	C_7H_8	78.3	27.8	236.0	505.0
Ethylbenzene	C_8H_{10}	18.1		23.7	51.6
m/p-Xylene	C_8H_{10}	36.8	17.6	39.5	69.1
o-Xylene	C_8H_{10}	10.5			27.3
1-Methyl-2-isopropylbenzene	$\text{C}_{10}\text{H}_{14}$	10.5			11.4
Triophene, 3-methyl	$\text{C}_5\text{H}_6\text{S}$			14.6	
Furan, 2,5-dimethyl	$\text{C}_6\text{H}_8\text{O}$			23.0	22.4
Benzoic acid	$\text{C}_7\text{H}_6\text{O}_2$			36.0	
Tetrahydrofuran	$\text{C}_4\text{H}_8\text{O}$				14.3
1,4-Dioxane	$\text{C}_4\text{H}_8\text{O}_2$				13.1
Pyrazine	$\text{C}_4\text{H}_4\text{N}_2$				12.8
3-Methyl-triophene	$\text{C}_5\text{H}_6\text{S}$				35.4
Styrene	C_8H_8				12.7
Aliphatic hydrocarbons					
Hexane	C_6H_{14}			89.3	229
Heptane	C_7H_{16}				38.5
Octane	C_8H_{18}				28.0
Nonane	C_9H_{20}				15.9
Decane	$\text{C}_{10}\text{H}_{22}$	12.5			
1-Hexanol, 2-ethyl-TXIB	$\text{C}_8\text{H}_{18}\text{O}$	20.9	29.9	12.5	
	$\text{C}_{16}\text{H}_{30}\text{O}_4$	19.2			
Ethane, isothiocyanate-Methyl-cyclopentane	$\text{C}_3\text{H}_5\text{NS}$	90.6	73.7	129.0	
	C_6H_{12}			15.4	25.8
Butanal, 3-methyl-	$\text{C}_5\text{H}_{10}\text{O}$			43.5	85.2
2-Butanone, 3-methyl-	$\text{C}_5\text{H}_{10}\text{O}$			11.7	25.2
2-Methylbutanal	$\text{C}_5\text{H}_{10}\text{O}$			24.1	45.9
Cyclohexane	C_6H_{12}			13.8	
4,7-Dimethyl-undecane	$\text{C}_{13}\text{H}_{28}$				11.8
2-Pentene, 3-methyl-	C_6H_{12}				18.9
Octane, 4-methyl	C_9H_{20}				13.4
Tetrachloroethylene	C_2Cl_4		30.8	18.8	12.1
Other compounds					
Dimethyl-disulfide	$\text{C}_2\text{H}_6\text{S}_2$			67.3	149.0
Trisulfide, dimethyl	$\text{C}_2\text{H}_6\text{S}_3$				53.9

L = Lomba waste pile; and SP = S. Pedro da Cova waste pile.

al. (2009) found that the organic matter was dominated by residual organic carbon, mainly terrigenous in nature, as indicated by abundant inertinite, vitrinite, and type III kerogen (terrigenous and reworked organic matter typical of riverine and deltaic systems). Sediments from the tributaries contained more algal-derived organic matter than the main channel of the river, highlighting the importance of low-energy lacustrine system dynamics which allowed for modest algal production, accumulation, and better preservation of the autochthonous organic matter in the tributaries. With this information the authors summarized major processes controlling distribution of organic matter types in the Mackenzie River basin as: the hydrodynamic energy level of the system; lacustrine input of autochthonous algal-derived organic matter; terrigenous input of organic matter; geogenic input of the organic matter; and particulate organic carbon fluxes.

Another effort to investigate environmental damage but using the same methodologies was documented by Hower et al. (2000) in their study of the source of a coal slurry spill in Virginia, USA, which precipitated a fish kill and pollution of streams leading to the Tennessee River. The authors investigated two slurries from coal mine portals and fines from a preparation plant. Maceral and microlithotype results were distinctive and concentrations of some trace elements, particularly Zr, Y,

and the lanthanide series also allowed for distinguishing between the slurries and to assign a source for the anthropogenic contaminant.

Over the past few decades, the development of environmental regulations, advances in analytical techniques, and increased rigor in industrial quality control procedures have combined to create a new discipline named environmental forensics. This field mainly uses chemical and geochemical analytical approaches (Wait, 2000), particularly in the case of pollution by compounds such as polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins and furans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs). Although not mentioned by Wait (2000), organic petrology also is playing a role in environmental pollution studies through e.g., identification of organic particulates derived from activities such as coal mining, preparation, transport, blending, management and shipment, storage and utilization, and by making of coke, coal-tar, pitches, manufactured gas plants and coal gas, among others. Some examples on contaminant organic particulates are shown in Figs. 8 and 9. The organic petrology approach is useful because relationships existing between concentrations of organic particulates and concentrations of PCBs, PAHs, and PCDD/Fs organic pollutants occur due to the sorption properties of organic particulates. Examples include the studies by Ghosh et al. (2000a,b, 2003) of the relationships between coal-derived particles and sorption/desorption of PAHs at the Milwaukee Harbor, USA. Karapanagioti et al. (2000) used petrographic techniques including white light and fluorescence microscopy to investigate the composition of organic matter in recent sediments of Canadian River alluvium and the sorption behavior of contaminants such as phenanthrene. They interpreted differences in sorption behavior as a result of the relative abundances of organic matter types and stressed the importance of identification and quantification of types of carbonaceous particles in sediments and/or soil samples as a prerequisite to understanding and predicting sorption behavior of organic pollutants. Ghosh et al. (2003) analyzed the partitioning of PCBs and PAHs among carbonaceous particle types including coke, charcoal, pitch, cenospheres, and wood in contaminated sediments (Fig. 10) from three harbors in the USA. They found that carbonaceous particles preferentially accumulated PCBs in the aqueous environments dependent on if the PCBs were released directly to the sediment or if they are deposited as airborne soot particles. PAHs were more bioavailable when present in semisolid coal tar pitch than when sorbed onto more inert carbonaceous particles such as coal, coke, charcoal, and cenospheres (Fig. 11).

Environmental pollution related to the industrial utilization of coal is also well documented in many studies. Stout et al. (2002) cautioned that sediments suspected to contain coal must be carefully examined in order not to confuse coal-derived organic signals with those from hydrocarbons. Ponz (2002) attempted to distinguish coal ash from other debris at the site of Thomas Edison's laboratory in East Orange, New Jersey, USA, where difficulties were encountered in distinguishing coal-fired boiler slag deposits from metallurgical furnace slag. Emsbo-Mattingly et al. (2006) worked on the source of PAHs in sediments related to the activities of manufacture gas plants (MPGs). The authors discussed the use of geochemical approaches and stressed that the organic petrology provides evidence for resolving ambiguities about the physical manifestations of waste materials in soil samples through source identification. In a similar way Stout and Wasielewski (2004) studied an abandoned power station and MGP on a man-made island in Connecticut, USA. Petrographic studies of sediment samples confirmed the presence of coal and coke, bottom ash associated with combustion, and tars associated with the MGP. Coal and coke were associated with MGP tars in deeper soil horizons, confirming their common source as contaminants. Despite published investigations some questions on the true loading and association of PAHs in different particle types in industrially impacted sediments remain unclear. Thus Khalil and Ghosh (2006) investigated the role of weathered coal tar pitch in the partitioning of PAHs in MGP site

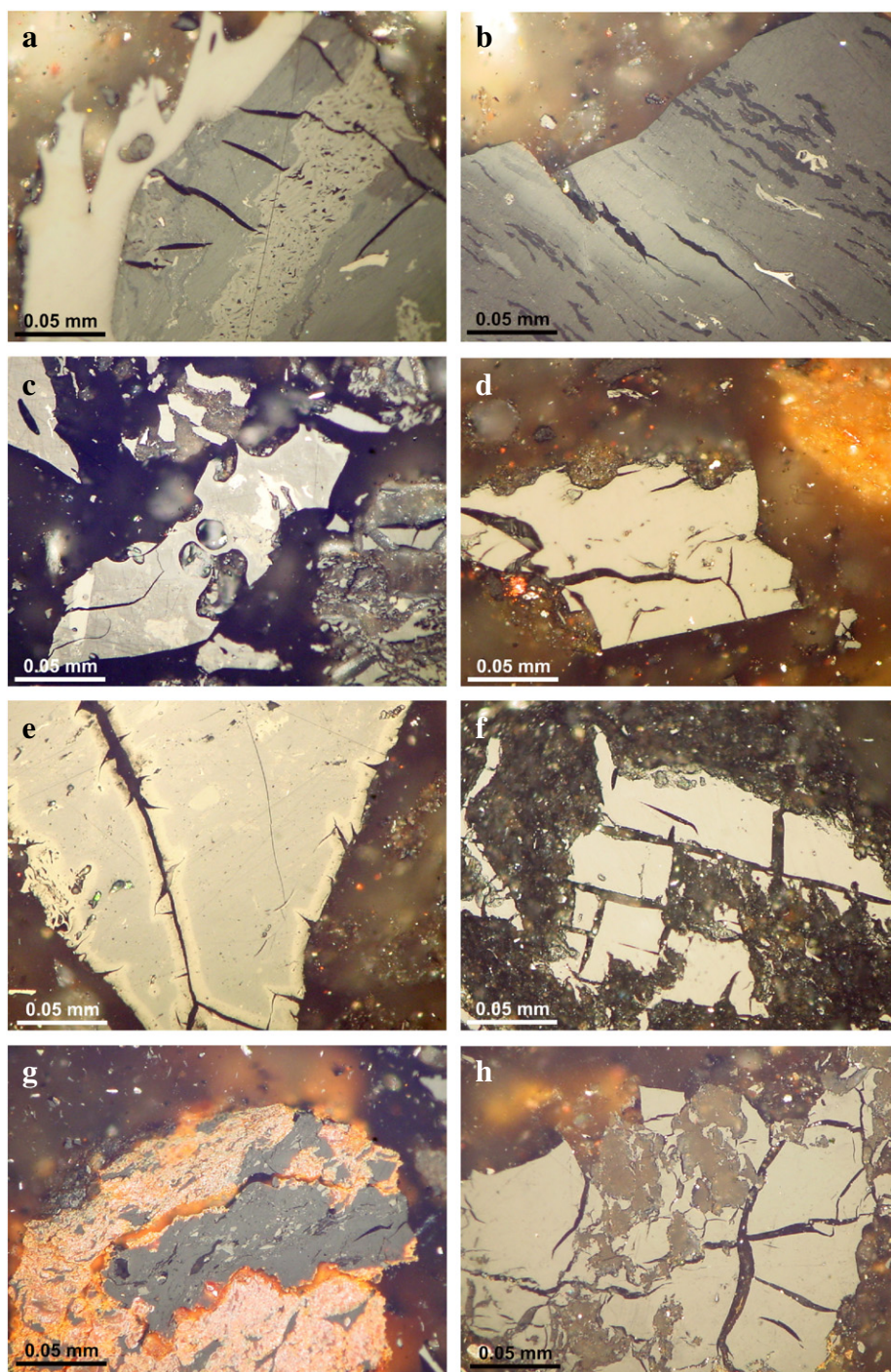


Fig. 6. Optical microscopy. Photomicrographs taken in reflected white light. Thermally altered organic and mineral matter in Starzykowice self-heated coal waste from Poland. a–e, h) organic particles strongly oxidized, f–h) mineral matter thermally affected. Photo credits: Magdalena Misz-Kennan

sediment in which petrographic analysis revealed that the organic particles (coal, coke, wood, and coal tar pitch, Fig. 12) comprised 10–20% of the total mass and hosted 70–95% of the PAHs (PAH concentrations determined via GC–MS). Among the different types of organic particles, coal tar pitch contributed the most to the bulk sediment PAH concentration. The particulate pitch residue in those sediments may have resulted from different types of MGP operations including coking operations, and may also have weathered differently in the environment

In contamination directly related to coal conversion, Ahn et al. (2005) characterized soil samples from a coke oven site to assess

particle associations and availability of PAHs because phytoremediation of the site had failed. Their petrographic analysis identified coal, coke, pitch, and tar decanter sludge in the soil as well as aggregates of tar sludge material adhering to mineral grains or to coal. Examples of the soil contaminants usually found in areas close to coking plants are shown in Figs. 8 and 9. In the work of Ahn et al. (2005) most PAHs were associated with tar sludge, hard pitch, and the coatings on soil mineral particles. Moreover, significant concentrations of PAHs were observed in the interiors of coarse tar decanter sludge-like aggregates. In the first case, PAH availability from the particles was very low due to hindered diffusive release from solid tar or pitch. In the second

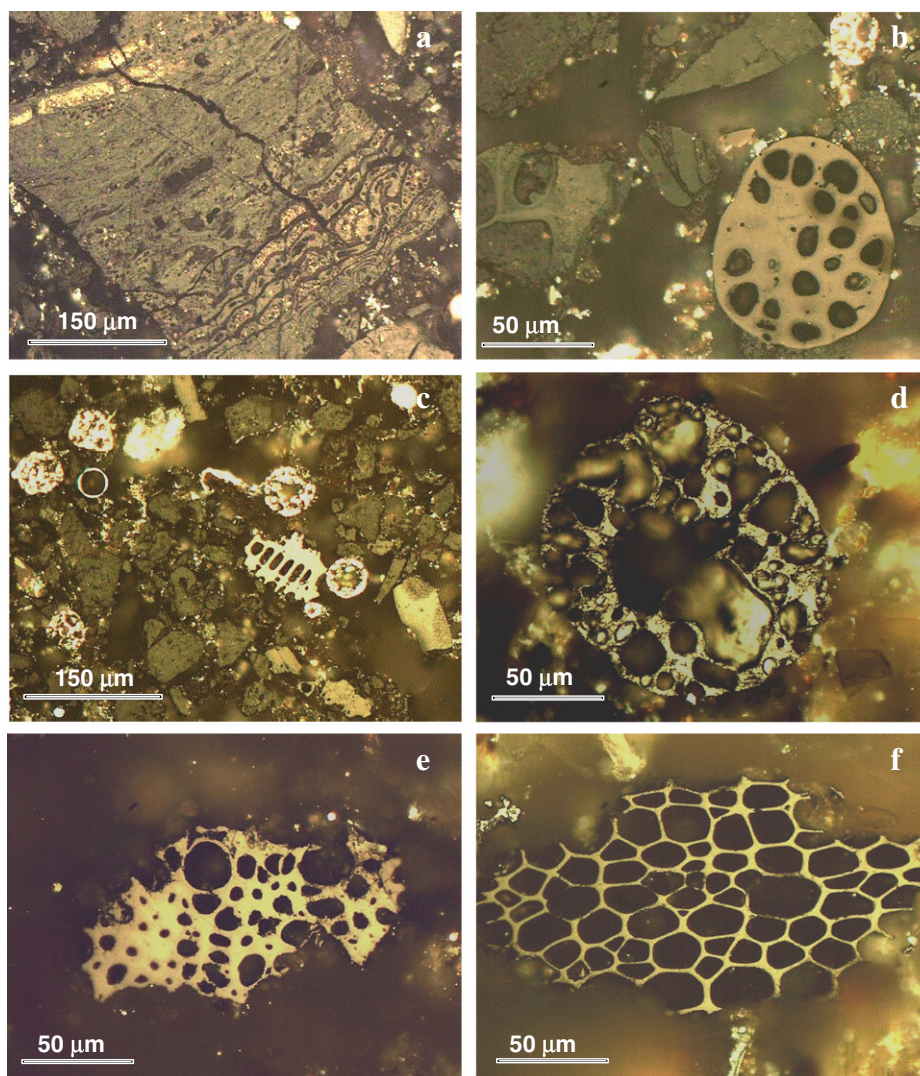


Fig. 7. Optical microscopy. Photomicrographs taken in reflected white light. Natural (recent and ancient) and anthropogenic organic particulates found in sediments of an estuary in North Spain. This estuary is close to an urban area, a coal deposit and a power plant. a): lignite; b): recent organic matter, heated altered coal particle, lignite, inertinite and char (anthropogenic light particle at the upper right); c): lignite, chars, charcoal with well-preserved cellular structure; d): char (cenosphere), recent organics (transparent brown particles at the bottom right); e): charcoal, and f): inertinite particle (fusinite) probably from forest fires or domestic wood burning.

case, the release of PAHs from the interior of aggregate particles required diffusion over a substantial distance across the aggregates. These findings were proposed as the main causes by which phytoremediation of the site soil did not produce significant decrease in total PAH concentrations.

Ligouis et al. (2005) reported a classification of carbonaceous airborne contaminants in soils and sediments. These authors distinguished three major groups of organic particles that usually are found in natural environments such as i) the recent organic matter mainly consisting in translucent phytoclasts, fungal phytoclasts, pollen, spores, and recent charcoal; ii) the fossil organic matter composed of primarily of algae, spores, pollen, amorphous organic matter (AOM), xylite, coal (eroded and resedimented coal particles), vitrite, and charcoal, and iii) airborne contaminants that are composed of particles of raw brown coal, hard coal, charcoal, brown-coal coke, hard-coal coke, char, and asphalt. The importance of a clear identification of anthropogenic organic particulates for proper assessment and to trace their origin and source led Crelling et al. (2006) to publish an atlas of anthropogenic particles that can be identified by using petrographic methods. The atlas grouped anthropogenic particles according to their morphology and optical properties following two concepts: i) anthropogenic particles grouped according to their source:

combustion, carbonization, and manufacture-derived; and ii) anthropogenic particles grouped according to their site of occurrence: atmospheric, soil (peat), and water sediments.

Yang et al. (2008a,b) studied the floodplain soils of the Mosel River (a tributary of the Rhine River in Germany) with three purposes: i) to identify and quantify (vol.%) the various types of black particles with high levels of PAHs by petrographic methods; ii) to characterize the distribution of PAHs in the soil; and iii) to elucidate the dominant geosorbents for the PAHs. Based on concentrations of three identified groups of particles (recent organic matter, fossil organic matter from ancient sediments, and anthropogenic organic particles), considered with PAHs concentrations and distribution, the authors showed that anthropogenic particles probably were the most important source for PAHs. Secondly, they showed that anthropogenic particles acted as sinks for PAH contaminants and so were the dominant geosorbents for PAHs. The identification and characterization of organic materials that control hydrophobic organic chemical sorption was essential in predicting the fate and transport of those chemicals in soils and sediments.

Jeong et al. (2008) investigated the role of condensed carbonaceous materials on the sorption of trichloroethene (TCE), a common groundwater pollutant, in the oxidized and reduced zones of a

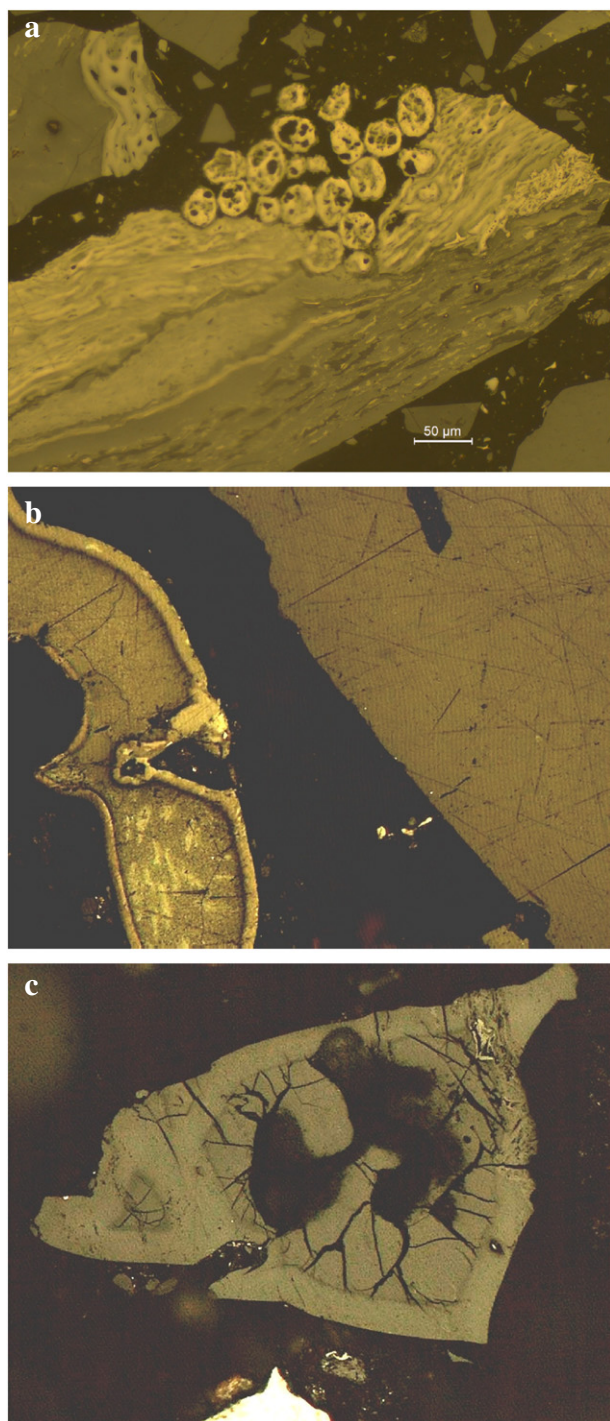


Fig. 8. Optical microscopy. Photomicrographs taken in reflected white light. Particles of unaltered coal (a) and of coal with different degree of thermal alteration (b, c) typical in soils surrounding areas of coal management and conversion (coking plant in North Spain). (Same scale for all the images).

glacially deposited groundwater sediment in central Illinois. In the presence of oxygen, carbonaceous particles were subject to weathering which produces less condensed and less aromatic materials with more hydrophilic functional groups. Their results indicated that carbonaceous particles were concentrated in the heavy fractions of the samples and dominated sorption because of their greater mass. In the reduced sediments, black carbon may sequester as much as 32% of the sorbed TCE mass, but kerogen and humin were the dominant sorbents.

In Europe, [Sýkorová et al. \(2009\)](#) characterized organic matter (modern organic matter, incompletely combusted particles from power plants, local heating installations, traffic and plant remnants) in several areas of Prague (Czech Republic) by using optical microscopy and SEM as well as chemical techniques, to understand the distribution of natural and anthropogenic organic matter in relation to depositional environments. Coal soot and wood ash also were examined to reveal their possible contribution to the environmental samples and in relation to their content and distribution of PAHs.

[Yang et al. \(2010\)](#) studied the distribution of asphalt- and bitumen-like substances, and coal-tar pitch identified by petrographic analysis (incident, polarized light and fluorescence) in the urban Lake Como watershed in Fort Worth, Texas, USA, to determine the dominant sources of PAHs in soils, parking lot and street dust, and streambed and lake sediment. The carbonaceous particles identified in their study included hard coal, coke, char, soot, and coal- and petroleum-derived materials such as coal-tar pitch and asphalt resulting from anthropogenic contamination. Fractions of soot were higher in lake sediments and unsealed parking lot dust. Asphalt dominated samples from unsealed parking lot dust and it was found to be a major component of residential street dust, along with recent organic matter. The fraction of asphalt decreased progressively from unsealed parking lot and residential street dust, to streambed sediment, to lake sediments and this result was interpreted to indicate asphalt transportation via surface runoff, dilution by other carbonaceous particles, and removal/degradation with time in buried sediments. The significant correlation between PAH concentrations and organic carbon in coal tar, asphalt, and soot indicated that these were the major sources of PAHs in the watershed. Particularly, the coal-tar pitch used in some pavement sealcoats, was the dominant source of PAHs in the watershed, and contributed to the anthropogenic organic matter in sealed parking lot dust, unsealed parking lot dust, soil from commercial areas, streambed sediment, and lake sediment. A similar study on PAH concentrations was presented by [Sullivan et al. \(2011\)](#) on natural fire-impacted sediments from Oriole Lake in California (USA).

Coal waste piles resulting from coal mining activities also have caused environmental impacts in abandoned mines and adjacent areas. Pollution of waters, sediments and soils from the acidic coal waste drainage system occurs due to leaching of heavy metals ([Ribeiro et al., 2010d, 2011a](#)) and distribution of other compounds such as PAHs ([Ribeiro et al., 2011b](#)).

Other workers have presented investigations concerned with the relationship between various types of organic matter and mercury concentration in natural environments such as lakes (e.g., [Carrie et al., 2010](#); [Sanei and Goodarzi, 2006](#); [Stern et al., 2009](#)). These authors used organic petrography to confirm a strong association between mercury and the so-called refractory organic carbon (including coal particles and by-products of forest fires and domestic wood burnings such as char, ash and soot). However, recent increases in algal productivity due to warming climate also promotes increase in Hg concentration in the Arctic Lakes.

Information obtained from the studies such as those cited above provide government agencies and other concerned organizations with important tools and information to aid in environmental restoration efforts. In addition, organic petrology may also help in the investigation of materials for production of soil amendments and organic fertilizers. An example was reported by [Giannouli et al. \(2009\)](#) wherein Greek peat and low rank coal were evaluated for application in the agricultural /horticultural sector as a potential soil conditioner and for use as raw materials in the manufacture of fertilizer.

2.2.4. Archeology and related applications

2.2.4.1. Organic gemstones: jet and amber. For more than 60 years coal petrography has been a tool for the archeologists to ascertain the

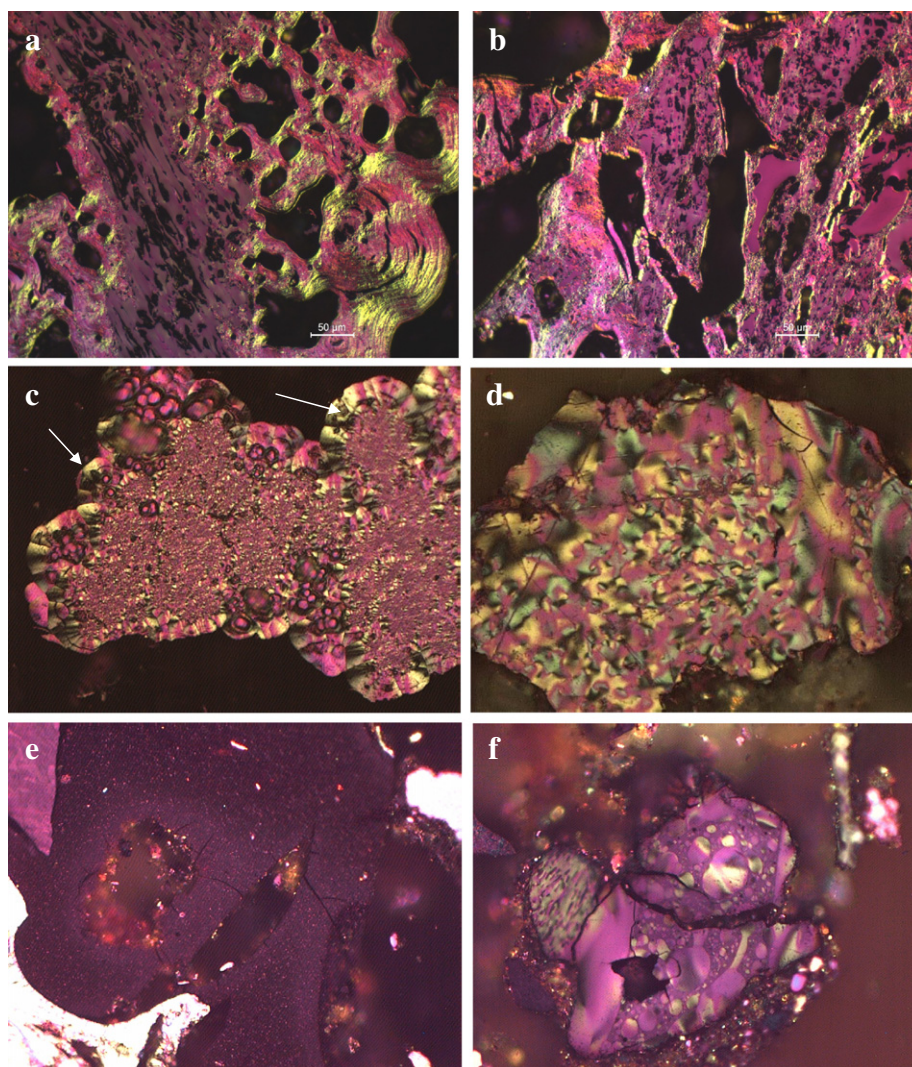


Fig. 9. Optical microscopy. Photomicrographs taken in polarized light and with a 1λ retarder plate. Typical particles contaminating soils surrounding coking and tar distillation plants. a–b) metallurgical coke, c) pyrolytic carbon (arrows), d) anisotropic solid tar, e) isotropic solid tar, and f) mesophase pitch. (Same scale for all the images).

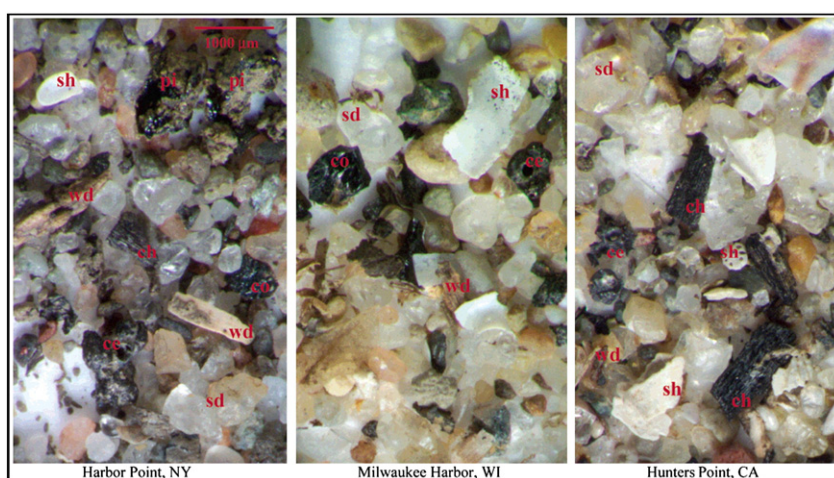


Fig. 10. Images of particles showing various contaminant organic fragments of variable size in sediments from three urban locations (Harbor Point, New York; Milwaukee Harbor, Wisconsin; and Hunters Point, California) investigated for determining polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbon (PAH) distribution. The particle types are: sd, sand; sh, shell; co, coal; ch, charcoal; pi, coal tar pitch; and ce, cenosphere.

From Ghosh et al. (2003, Fig. 2, page 2212). Source: PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability, by U., Ghosh, J.R., Zimmerman and R.G., Luthy. Environmental Science and Technology 37, 2209–2217, copyright 2003, with kind permission from American Chemical Society, www.acs.org.

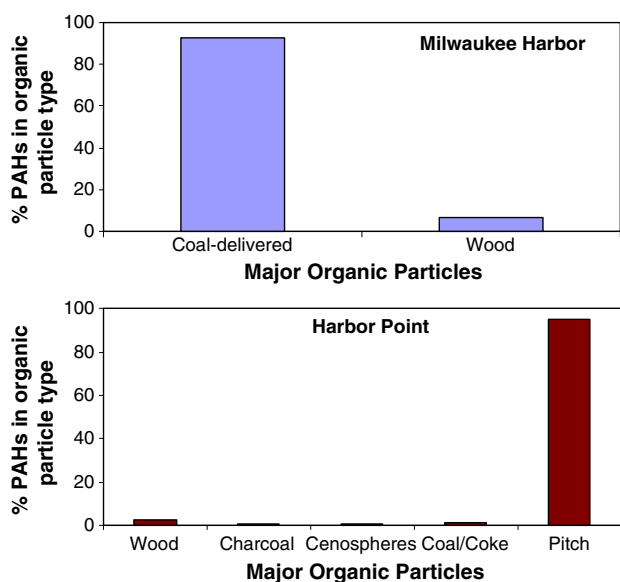


Fig. 11. Example of concentration of PAHs in major organic particles identified in sediments from two urban areas affected by anthropogenic activities. Predominance of PAH association with coal-derived particles in Milwaukee Harbor (Wisconsin) and coal tar pitch particles in Harbor Point (New York).

From Ghosh et al. (2003, Fig. 10, page 2216). Source: PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability, by U., Ghosh, J.R., Zimmerman and R.G., Luthy. Environmental Science and Technology 37, 2209–2217, copyright 2003, reprinted with kind permission from American Chemical Society, www.acs.org.

nature, origin and provenance of some organic materials. For example, organic relics from the Bronze age were sculpted from the Kimmeridgian oil shale, carboniferous cannel coal and Jurassic jet (see Smith, 1996 and references therein). The application of organic petrology in investigations of organic archeological objects such as jet and amber was recently reviewed by Crelling and Suárez-Ruiz (2008). One of the earliest studies was carried out by Teichmüller (1992) on a set of Celtic-through-to-Roman ornaments of jet, bituminous coals, and oil shales, in order to determine their nature and geographical provenance. Jet can be found in many places of the world although the pieces of highest quality come mainly from European mines. Most of the scientific research into the occurrences of jet (mainly of Jurassic and Cretaceous age) from different countries, including its nature, origin, properties and quality were carried out in

the last three decades by e.g., Costa et al. (2010), Heflik et al. (2001), Iglesias et al. (2002, 2006), Laggoun-Defarge et al. (2003), Lambert et al. (1992), Markova et al. (1988, 1989), Markova (1991), Petrova et al. (1985), Pollard et al. (1981), Sales et al. (1987), Suárez-Ruiz et al. (1994), Suárez-Ruiz and Iglesias (2007), Traverse and Kolvoord (1968), Watts et al. (1997), Weller and Wert (1994), and Wert and Weller (1991). Organic petrography in combination with organic geochemistry has demonstrated that some jet is perhydrous coal, with suppressed reflectance, high H/C atomic ratio and, therefore, high oil yield. Because of its scarcity, jet ornaments are highly valued and organic petrography has become the preferred technique to differentiate jet from similar natural materials (cannel coals, solid bitumens, lignite, anthracite, oltu stone from Turkey, horn, bog oak, black onyx, black glass), and from synthetic products of similar macroscopic appearance (vulcanite/ebonite, bakelite, epoxy resin) (Fig. 13). Petrographic observations may also permit differentiation among jets from various origins by identification of specific characteristics that permit discrimination and the assignment of provenance to a specific geographical area. Lambert et al. (1992) noted that organic petrography was useful in determination of provenance of jet pieces found at North American archeological sites as previously shown more generally by Teichmüller (1992). Determination of provenance also provides information regarding the history and customs surrounding exploitation and trading of jet. However, Crelling and Suárez-Ruiz (2008) noted that determination of provenance can be difficult or impossible in some cases, either because of the lack of complete jet descriptions and/or lack of information about geographical sources. An example of a recent successful determination of jet provenance includes a petrographic study using incident light and fluorescence microscopy to characterize jet pieces from Pannonian (ancient province of the Roman Empire) graves by Hámor-Vidó (2010). The petrographic results allowed this author to propose an origin from locations in Austria and Balkan Peninsula region.

Organic petrology has also been sporadically used in the characterization of amber. Fossilized amber is found worldwide with two main commercial sources located in the Baltic region and in the Dominican Republic. Because amber is a fossilized resin it often contains material trapped inside, such as insects, leaves, pine cones and other seeds, spores and pollen, hairs, feathers, and even the occasional amphibian. All of these inclusions are best studied by petrographic methods examining for example, the nature, geological age of included insects; the presence of associated dust, dirt and trapped bubbles, and the presence of anthropomorphic artifacts such as hairs, pencil marks, drill borings and glue. As in the case of jet, one of the main

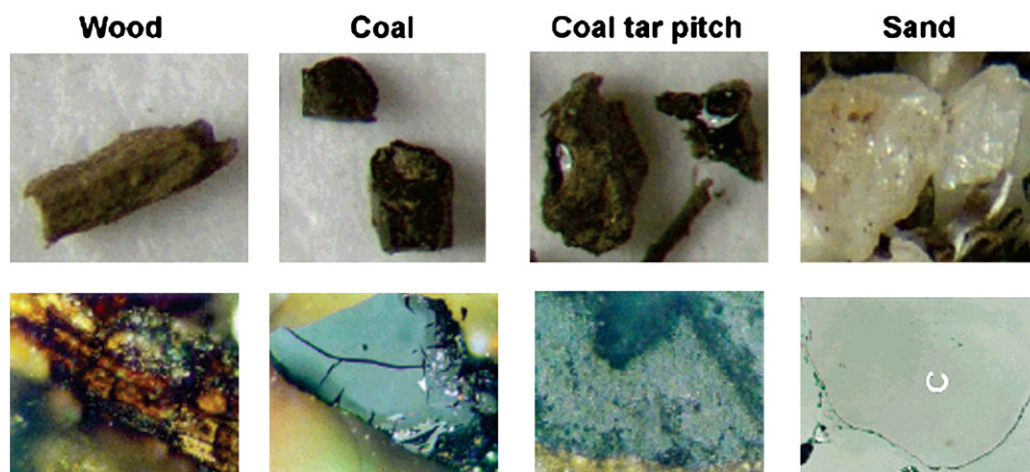


Fig. 12. Light microscopy (top) and optical microscopy in reflected white light (bottom) of the four most abundant organic particle types present in manufactured gas plant (MGP) site sediments as described by Khalil and Ghosh (2006), Fig. 2, page 5683, in their work on the partitioning of PAHs at MPG sites.

Source: Role of weathered coal tar pitch in the partitioning of polycyclic aromatic hydrocarbons in manufactured gas plant site sediments, by M.F., Khalil and U., Ghosh. Environmental Science and Technology 40, 5681–5687, copyright 2006, with kind permission from American Chemical Society, www.acs.org.

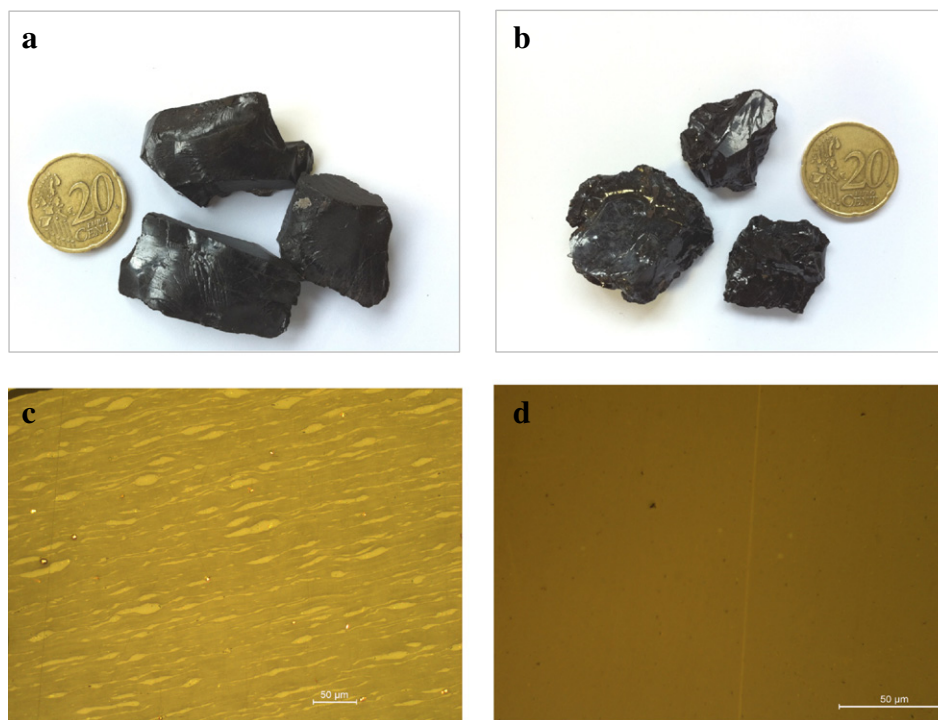


Fig. 13. Images of jet from North Spain (a) and solid bitumen (b) albertite (from Canada). (c, d): Optical microscopy. Photomicrographs taken in reflected white light. Jet (c) composed by ulminite and phlobaphite macerals, and bitumen (d).

concerns is to be able to differentiate true amber from other fossil resins of different origins and from good imitations. Petrographic techniques and chemical investigations can be used to detect the fake ambers. Gold et al. (1999) used optical microscopy and SEM with a series of spectroscopic and geochemical techniques to study the nature of fossilized amber from various geographical locations, as well as copal and modern tree resins. Using petrographic methods combined with other analytical techniques Teodor et al. (2009) investigated Baltic and Romanian amber to establish definitive criteria to certify origin. Their study showed that Baltic amber contained many fluid inclusions while Romanian amber displayed small surface cracks and that the influence of diagenetic processes had induced an internal organization with development of a weak optical anisotropy in Romanian amber. The authors considered the presence of cracks in Romanian amber a consequence of its lower proportion of free water. The cracks and fluid inclusions were considered as definitive criteria to differentiate the source of the Romanian and Baltic amber gemstones.

2.2.4.2. Provenance of organic artifacts and coal from archeological and related sites. In addition to investigations of jet and amber described above, there are a few studies that used organic petrography approaches to investigate the provenance of organic objects and artifacts from archeological and related sites. In particular, by combining the methods of palynology and organic petrology it is possible to obtain precise information to determine the provenance of specific organic materials. Almost thirteen years ago Smith and Owens (1983) investigated the composition, geological source and archeological significance of the Caergwrle bowl from Wales, a votive object dating to the Middle Bronze Age, originally manufactured from shale, tin and gold. The examination of a small chip of this object using incident white light and fluorescence microscopy suggested the Kimmeridgian oil shale in England as a tentative source. Smith (1996) also determined the provenance of coals from 15 Roman archeological sites throughout the UK by using two criteria, the geological age obtained from the microscopic study of spore assemblages and the coal rank from vitrinite reflectance measurements. By

matching these coal characteristics with those of the coal seams outcropping in the exposed British coalfields the sources of those pieces of coals from the archeological sites were assessed. Kalkreuth et al. (1993) analyzed the varied geological, archeological, and historical occurrences of coal in Ellesmere Island (Canada) to determine its origin and characteristics by means of coal petrology. Later Kalkreuth and Sutherland (1998) investigated in a similar way coal artifacts excavated by archeologists from the Thule culture settlements in the Canadian Arctic and Alaska. Smith (2005) reviewed the use of organic petrology and palynology in the study of coal and related jewelry artifacts (made from jet, cannel coal, boghead, and oil shales) in pre-Roman and Roman periods, and throughout Medieval to Modern times and remarked that this approach provided evidence of usage patterns and trading routes of original materials.

Petrologic studies also may help in investigations of the trading patterns of coals during the nineteenth and early twentieth centuries through the study of shipwrecks. For example, Smith (2005) reported three different investigations with a maritime connection: the Isle of Skye, RMS Titanic, and HSM Bounty shipwrecks. In the first case the barque contained 200 tons of coal of cannel like appearance. This observation and the subsequent petrographic study of the material showed it was a torbanite of 0.3% of reflectance, identical to the coal from Torbane Hill, the type site of Scottish Torbanite. In the second case Palmer et al. (2003) investigated some pieces of coal recovered from the wreck of the RMS Titanic to determine the source and alteration during its 75 years residency at 3780 m depth in the Atlantic Ocean. The authors used a set of different analytical techniques including optical microscopy (palynological studies) to determine the age of the coal. Spore assemblages were indicative of a Langsettian age (Westphalian A) and in the early 1900s the British coalfields that were being mined contained coal seams of that age. However coals of that age were rare in the USA at that time and therefore the authors concluded that most of the Titanic coals originated in England. In addition, geochemical studies on some trace elements indicated that the coals were unaltered by their submersion with the Titanic and therefore had a minimal environmental impact due to

leaching of trace elements. As for the HSM Bounty shipwreck [Smith \(2005\)](#) reported that coals found with it were of bituminous rank (1.05% vitrinite reflectance) and Westphalian B age. Although the characteristics of the coal samples were similar to those of coals from three different mining area in UK, after consultation of historical records the author suggested Durham Coalfield as the most likely source. More recently [Erskine et al. \(2008\)](#) investigated the provenance of coal samples recovered from another shipwreck, at the HMAV Bounty. Petrographical and palynological evidences suggested that the coals were Westphalian B in age, with a bituminous coal rank (1.07% vitrinite reflectance) and the Durham Coalfield in UK, (Hutton and Low Main coal seams) also was suggested as the most likely source of the HMAV Bounty coals.

2.2.5. Forensic applications

Forensic geology ([Murray and Tedrow, 1992](#)) 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; Petraco et al., 2008; Ruffell, 2010](#)). Therefore forensic geology (Fig. 14) includes geological methods of analysis such as geophysics, petrography, geochemistry, microscopy and micropaleontology ([Ruffell, 2010; Ruffell and McKinley, 2005](#)). Palynological analysis (spore/pollens and other microscopic acid-resistant materials) from ropes, soil samples, and other materials, have been used for years in New Zealand to solve crimes. [Mindelhall \(1990\)](#) reported five cases in which palynological studies have been useful. Also in New Zealand [Horrocks and Walsh \(1998\)](#) described three cases (car chase, alleged sexual violation, and cannabis cultivation) in which palynological data provided evidences that strongly supported the accusation. Later [Horrocks et al. \(1999\)](#) presented a study on the variation of the pollen content of soil on shoes and in shoeprints in soil to demonstrate the forensic

value of using such samples to determine whether or not there was an association between people and crime scenes. By using palynological analysis the authors demonstrated that pollen analysis of soil samples from shoes provided a valuable forensic tool in forensic investigations. Forensic geology was used by [Lombardi \(1999\)](#) in the investigation of the death of the Italian Prime Minister Aldo Moro who was murdered by the Red Brigades and whose body was found in a car parked in the center of Rome. The main material collected from his clothes, shoes and the car included beach sand, volcanic soil, bitumen (in the form of smears and pellets), road asphalt (as small aggregates and minor fragments), vegetal fragments, and anthropogenic material (such as building materials, polyester, paints and fibers among others). These materials were investigated through a multi-disciplinary approach that included petrographic microscopy of thin sections for the initial identification of the morphology, surface characteristics and details of the various items, and for discrimination of the various materials. A point counter coupled to the microscope was used to determine the percentage of components in the analyzed samples. Palynological analyses were also performed on pollen from soil adhered to the car fender in order to trace back the period of adhesion. SEM analyses were also included.

The use of soil characteristics (as determined through organic petrology) in conjunction with pollen analysis was strongly endorsed by [Brown et al. \(2002\)](#) as forensic evidence in a search for the bodies of a retired couple in a murder investigation. Soil characteristics allowed redefinition and pinpointing of the search area. Although soil type is not unique to specific locations, its constituents (mineral content, fossil, plant debris), considered in conjunction with pollen evidence (an independent analysis of vegetation type) may provide an association that can be rare or unique. And this was the case in this investigation where soil petrography and palynology provided a link between the car, the murder and grave site and supplementary evidence of the car positioning at the crime scene. Since then [Pye and Croft \(2004\)](#) recognized that soil and geological evidence has been increasingly used in investigations and in both criminal and civil law trials in the UK, although its acceptance in the courts varies from country to country. These authors (and previously [Horrocks et al., 1999](#)) indicated that there are two key questions to be solved in forensic geology (or palynology) when samples are analyzed and compared: i) to determine if there is a 'match' between the studied samples (usually samples from the crime scene and from the suspect or issue investigated), and ii) the evidential value of such a 'match'. However, [Morgan et al. \(2006\)](#) indicated that when samples are analyzed, the resultant interpretation may be to exclude and not to match samples. In any case the two questions are usually answered; such occurred in a murder investigation that took place in the English Midlands reported by [Bull et al. \(2006\)](#). In this case forensic analysis of soils and sediments from the cast of a footprint was developed. Samples investigated were taken from the field, the cast, and two pairs of shoes belonging to the suspect and the 19 exclusion samples were analyzed by binocular microscopy which identified the presence of a large number of different fibers, cut animal hair, and a series of common minerals associated with river terrace deposits overlying limestone and shale substrate. An accord was found between soil particulates taken from a pair of shoes with those of the cast and field samples. Palynological analyses were also carried out on the pollens found in the samples. Results obtained provided evidence of a two-way transfer of material between the sole of a boot and the soil. Lumps of soil, which had dried on a boot, were deposited on the field as the footprints were made. Pollen analysis of the soil lumps indicated that the perpetrator of the imprint had been recently standing in a nearby stream. Fiber analysis together with physical and chemical characteristics of the soil suggested a provenance for this mud contamination prior to deposition of the footprint. Therefore, it was possible to reconstruct three phases of previous activity of the wearer of the boot prior to leaving the footprint in the field after the murder had taken place.

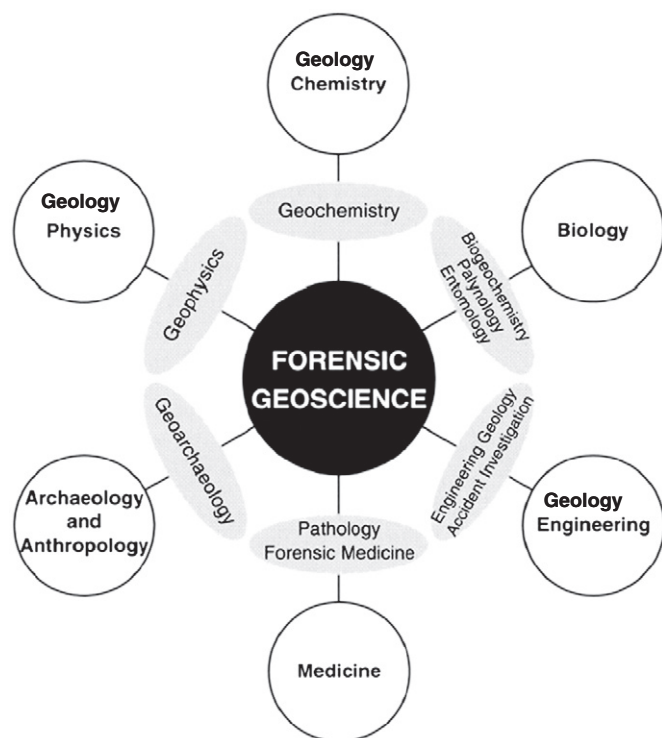


Fig. 14. Interrelationships of forensic geoscience with other disciplines and subdisciplines, including geology. Modified from [Pye and Croft \(2004\)](#), Fig. 1, page 2. Source: Forensic geoscience: introduction and overview, by K., Pye and D.J., Croft, Geological Society, London, Special Publications 232, 1–5, copyright 2004, with kind permission from Geological Society of London, www.geolsoc.org.uk.

Pollen and spore analysis in combination with mineralogical studies of soils via XRD were used by Brown (2006) in his investigation of the war crimes in northeastern Bosnia. The increasing analysis of soils as one of the evidences in forensics has been also extended to investigation of wildlife crime, such as those reported by Morgan et al (2006). Two of the cases involved analysis of soils recovered after incidents of badger baiting in the UK and the third involved the illegal importation of falcons into UK from the Mediterranean (Mallorca Island). In each of the three cases a large set of analytical techniques was applied to the soil samples, including microscopy for mineralogical composition and identification of plant debris, palynology and SEM analysis. From the two first cases the authors concluded that there was a significant similarity between soils taken at both badger baiting sites with soils recovered from spades, shovels and clothing belonging to the suspects. In the last case the results of the analysis of soil associated with the rope of a climbing kit (for removal of the falcons) were compared with four samples taken from the cliffs in Mallorca Island where it is known that the falcons breed in the wild. Three of the four breeding sites were excluded as the source of the soil found on the rope. A recent paper by Dawson and Hillier (2010) emphasized the value of analyzing the inorganic and organic components of soils by using all the available automatic techniques (a controversial subject discussed by Bull et al., 2008) in forensic applications. Although Dawson and Hillier (2010) mentioned the organic matter in soils, they only cited polarized light microscopy for mineralogical analysis without taking into account information that this technique provides when applied to the study of organic matter. The value of the petrographic analysis has been shown by Crelling and Suárez-Ruiz (2008) in a review of the specific contributions that coal petrology discipline has made to the forensic investigations. They included summaries of several cases reported by Armstrong and Springs (1989), Hower et al. (2000), and Murray (2004) in relation to criminal and civil law issues in which coal petrography was the key tool that provided forensic evidence to solve the questioned cases. As was indicated a long time ago by Lombardi (1999), the petrographic techniques integrated with other disciplines may help to realize the potential of a geologist's work in forensic science.

3. Summary and conclusions

The role of organic petrology in areas other than geology (discussed in part 1 of this review) and industry (reviewed by Suárez-Ruiz and Crelling, 2008) was addressed herein. The scope of organic petrology in unconventional applications and its importance for ore genesis and other multidisciplinary investigations such as coal fires (self-heating and self-combustion), and environmental, archeological and forensic sciences, was discussed.

Some ore deposits of economic interest as hosts of metals (uranium, gold, zinc, lead, copper, among others) are associated with organic matter. The nature of involvement of the organic matter in issues related to ore formation and interaction of organic matter with metals was discussed with special reference to the most exploited and larger ore bodies from all over the world.

Other applications of organic petrology are less well known but are of increasing societal relevance. Coal fires in un-mined outcrops, abandoned mines and coal waste piles constitute a serious safety and environmental hazard. Petrologic studies of organic matter and mineralogical changes contribute to evaluation of factors responsible for spontaneous combustion and also to assess the changes that are taking place in coal and coal waste material as a result of coal fires. In the same way organic petrology, together with other analytical methods, has been widely used in investigations of anthropogenic disruption and the pollution of natural environments and ecosystems by residues of the management and industrial utilization of coal.

Organic petrography has been a tool for archeologists to ascertain the nature and origin of organic materials such as jet and amber and an important way to link artifacts and coal from archeological sites to the geographical areas of their provenance. Some examples were presented to illustrate the application of the discipline in this archeology field.

Palynological analysis is one of the traditional methods used in forensic geology. However some examples are described in the literature and herein where the incident light organic petrology techniques together with other microscopic and geochemical methodologies were successfully used in forensic investigation.

In the light of what has been described, it is anticipated that the application of organic petrology techniques will remain strong in the traditional areas of investigation, including depositional environments and basin analysis, fossil fuel exploration (conventional and unconventional systems), ore deposits and in coal utilization. However, the future of this field will grow as the techniques are increasingly incorporated into multidisciplinary environmental and forensic science investigations with pressing societal relevance.

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