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Application of electron microscopy TEM and SEM for analysis of coals, organic-rich shales and carbonaceous matter

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ABSTRACT

This paper provides a brief summary of the history, development and variety of applications of electron microscopy techniques to analyze coals, organic-rich shales, and carbonaceous materials. General construction and principles of operation of transmitted (TEM) and scanning electron microscope (SEM) are outlined, along with guidance on specimen preparation, and a brief overview of published TEM and SEM applications related to coal, shales, and carbonaceous materials. This work was accepted as the chapter 18.2 of International Committee for Coal and Organic Petrology Methods Handbook at the ICCP Plenary Session on September 27, 2018 in Brisbane (Australia).

1. Introduction

This paper outlines the principles and methods for expanding our understanding of coals, organic-rich shales and carbonaceous matter using transmitted (TEM) and scanning (SEM) electron microscopy. The International Committee for Coal and Organic Petrology's (ICCP) primary goal is the investigation and study of carbonaceous material and organic matter (*i.e.,* coals, organic-rich shales), and associated carbon products (i.e. coke, chars and ash). For such studies electron microscopy provides an important and useful tool for expanding our understanding of these materials by 1) examining morphology and chemical composition of coals, source and reservoir rocks petrographic components; 2) the study of coals or carbonaceous matter structures and textures (*i.e.,* arrangement and dimensions of aromatic layers, interlayer spacing, etc.) and their transformation in various physical and chemical conditions, 3) the investigations of micro and nano fossil structures in palynology, paleobotany and micropaleontology, and 4) physical and chemical properties of *in situ* minerals and other inorganic components in coals, shales, and associated carbonaceous products.

An overview of the history of electron microscopy, procedures/considerations required in specimen preparation, and examples of TEM/SEM applications for the analysis of coals, organic-rich shales, and carbonaceous matter are provided. The methods/applications presented were developed in collaboration with the ICCP as a part of the ICCP Methods Handbook (www.iccop.org/publications/iccp-handbook/).

2. Electron microscopy

Electron microscopes were developed due to the resolution limitations of light microscopes of around 300 nm, which is imposed by the wavelength of visible light (Williams and Carter, 2009). An electron microscope uses a particle beam of electrons instead of visible light to illuminate the specimen and produce a magnified image. Because electrons have de Broglie wavelengths about 100,000 times shorter than visible light, electron microscopy can achieve 0.05 nm resolution and magnifications of up to about 10,000,000x. There are two main types of electron microscopes: scanning electron microscope (SEM) and transmission electron microscope (TEM); and, more recently, a combined scanning transmission electron microscope (STEM). Similar to reflected light and transmitted light microscopes, SEM's collect the response of reflected electrons and photons to generate an image, while TEM's mainly rely on the collection of transmitted electrons through the sample, although some TEM's can have detectors to collect the same signals that SEM generate (Goldstein et al., 2007; Williams and Carter, 2009). Each type of electron microscope is discussed in more detail below.

As the beam of electrons, generated by an electron gun penetrates the sample, it causes the emission of electrons with different energy spectra as well as other radiations (Fig. 1). The emission contains information about the sample's surface topography, crystallographic structure, chemical composition, and other properties (*e.g.* electrical

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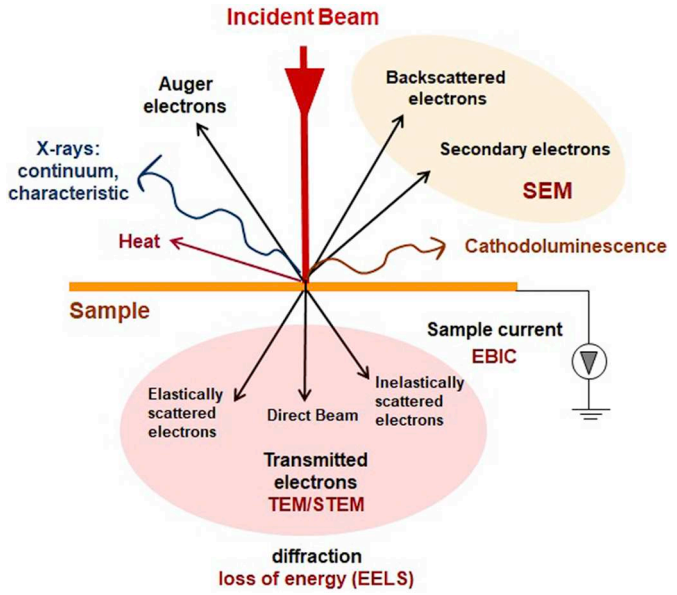

Fig. 1. Signals generated when a high-energy beam of electrons interacts with a thin sample (by S. Pusz).

conductivity). Each emission mode is potentially a signal, from which various images of the sample can be formed (Goldstein et al., 2007).

There are some limitations and considerations that must be made in the application of electron microscopy methods for studying various kinds of samples, including coals and carbonaceous matter. The samples need to meet specific requirements, namely they have to be vacuum tolerant, vacuum friendly and electrically conductive. Few samples in the field of organic petrology meet all of these criteria, but this problem can be overcome by special sample preparation or by using features found in the new generation of electron microscopes (Goodhew et al., 2001; Williams and Carter, 2009).

Electron microscopy methods for carbonaceous samples vary slightly from other solid materials in that the low atomic number of carbon results in low contrast when compared to higher atomic weight elements in electron microscopic images. Carbonaceous samples are sensitive and react poorly to the effects of the electron beam if not properly prepared, which has the potential to cause surface damage and possibly destruction of sample structures, especially during TEM analysis. Reducing the electron beam power can be beneficial but the image resolution will decrease. For the above reasons, analysis of carbonaceous samples by electron microscopy is not easy and therefore requires, not only a good quality microscope, but an experienced operator as well (Harris, 2018).

2.1. Transmission electron microscopy (TEM)

The first type of electron microscope was a TEM constructed by Max Knoll and Ernst Ruska in 1931. It was patterned exactly on the design of a light transmission microscope except that a parallel beam of electrons was used instead of light to “image” the specimen and gain information. Currently, a 400 kV TEM can provide resolutions below 0.2 nm and allows for the observation of relatively thick samples, about 500 nm. Advanced STEM instruments can achieve 0.05 nm resolution (Williams and Carter, 2009).

Each TEM consists of the following basic elements (Fig. 2): the electron gun (tungsten filament, LaB6 or field emission) producing a stream of electrons, which is focused into a small, thin, parallel electron beam using condenser lenses (C1 and C2) and the condenser aperture. The beam strikes the prepared specimen (required thickness from about 500 to less than 100 nm) and part of the electron beam is transmitted. The transmitted portion is focused by the objective lens creating the

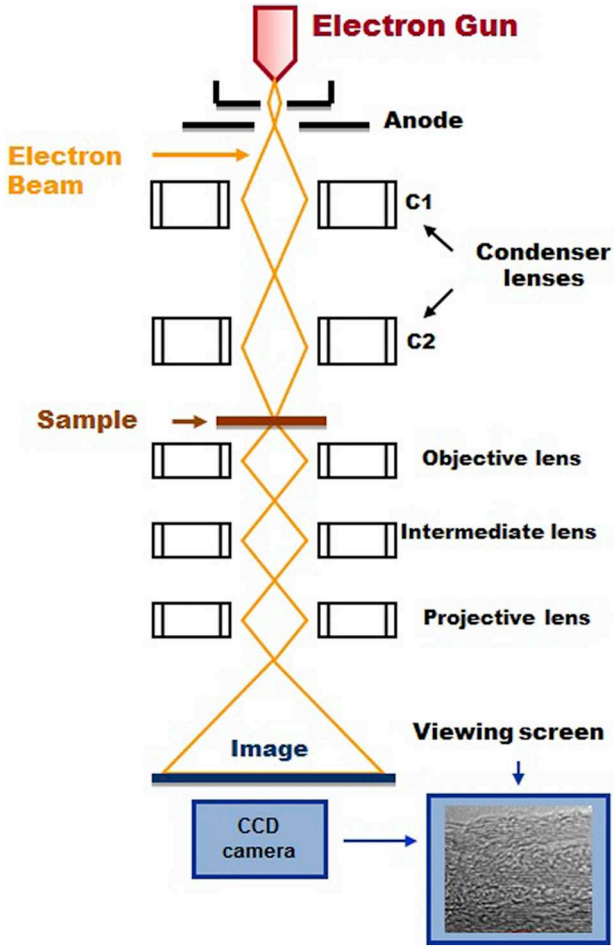

Fig. 2. Schematic drawing of transmission electron microscope (TEM) (by S. Pusz).

image. The image is passed down the column through the intermediate and projector lenses, which are enlarged through each of the lens. The strength of the lens can be adjusted, and, in a consequence, the magnification can be varied smoothly. Magnetic lenses, similar to glass lenses, have different types of aberration: spherical aberration; chromatic aberration; and astigmatism, which must be corrected to obtain a good image. If the specimen is crystalline, there will be a diffraction pattern at a different point in the lens, known as the back focal plane (Goodhew et al., 2001).

TEM images are then projected onto a fluorescent screen where they can be recorded on negative film, imaging plates or most often on modern TEMs slow-scan CCD cameras. Further post processing and analysis of images can then be completed. Modern electron microscopes employ fast and powerful computers to control and record the operating conditions of the microscope and to support extended data acquisition for analytical applications.

The development of new technologies enables modern TEMs to include a wide range of different techniques that use various signals arising from the interaction of the electron beam with the sample (Fig. 1). The most common are:

- Bright Field (BF)/Dark Field (DF) image – basic mode of TEM observation,
- High Resolution Transmission Electron Microscopy (HRTEM) - image obtained from the interference in the image plane of the electron wave with itself allowing direct imaging of the atomic structure of a sample,
- Electron Diffraction (ED)/Selected Area Electron Diffraction (SAED)

– a method to obtain information on crystal structures from diffraction patterns, acquired by the electron-beam illumination on a specimen,
- Scanning Transmission Electron Microscopy (STEM) – a technique, in which a small, convergent electron beam obtained in the condenser lenses scans a defined area of the sample,
- Energy-dispersive X-ray Spectroscopy (EDS) – a method to obtain elemental composition (point analysis, elemental mapping) of a sample by collecting and analyzing the X-ray spectra produced from the interaction of electron beam and sample surface,
- Energy Filtered Transmission Electron Microscopy (EFTEM) - a technique, in which only electrons of particular kinetic energies are used to form the image or diffraction pattern, useful in chemical analysis of a sample,
- Electron Energy Loss Spectroscopy (EELS) – a method to perform qualitative and quantitative analysis of elements from micro- or nano-areas of a sample based on the energy spectra of the inelastically scattered electrons. It has significantly better spatial and energy resolution compared to EDS.

Application of a combination of the above techniques allows researchers to obtain very detailed information about the structure, texture, morphology and composition of materials studied. Extensive, theoretical and practical background of TEM techniques was published by Goodhew et al. (2001) and Williams and Carter (2009).

TEM is an appropriate technique to examine structural units in all kinds of carbonaceous material, including graphite. Examination can yield information about topography, morphology, composition and crystallographic features (Oberlin, 1989; Rouzaud, 1990). TEM can be a complementary tool to conventional crystallographic methods such as X-ray diffraction (XRD). Electron diffraction has the unique advantage over XRD in that properties like morphological, crystallographic and chemical information can be collected simultaneously using a single instrument. Electron diffraction patterns can be obtained from relatively small volumes of material compared with X-rays and neutrons. Electron diffraction of amorphous materials has a number of advantages over X-rays as amorphous materials are not crystalline, but have some short-range order (Hammond, 1997; Jurkiewicz et al., 2018).

An extension of traditional TEM is STEM and electron tomography. In STEM, the condenser lenses of the microscope demagnifies the electron probe to form a small electron beam, which scans a defined area of the sample. Such a convergent beam can be used to gain a highly localized signal from the specimen in analytical TEM (e.g. EDXS, EELS) and thus the combination of STEM with other analytical methods is a valuable technique for analytical work. Electron tomography allows creating a 3D image of a sample using a sequence of TEM images taken at different tilt angles of the specimen around a single axis (Weyland and Midgley, 2004). Thus, it can be an interesting technique in paleontology for reconstruction of internal structures of microorganisms.

TEM is a very powerful tool for qualitative and quantitative characterization of material's micro- and nanostructures and their local chemical composition. However, it should be used rather as a complementary method than in isolation when assessing organic or carbonaceous samples (Hower et al., 2018; Jurkiewicz et al., 2018; Ward, 2016).

2.1.1. TEM specimen preparation techniques

The quality of TEM results strongly depends on the quality of the specimen. In general, the specimen must be sufficiently thin, approximately 500 to less than 100 nm, to be transparent to electron beam. Every branch of research has its own specific methods of preparing samples for electron microscopy. The selection of a proper preparation method depends on the material itself and on the kind of information that is desired. Presented below are various preparation techniques suitable for coal/carbon specimens.

- *Powdered samples*
  Typically, powdered samples are fine-ground in an organic solvent, most often ethanol, then dispersed and dropped on an amorphous carbon or collodion film which is deposited on a copper grid. A sample is ready after evaporation of the solvent in a desiccator. Variations in the procedure may be needed depending on the study. A few examples of powdered sample preparation methods can be found in: Henning and Storr (1986), Jehlicka and Rouzaud (1993), Oberlin (1989), Rantitsch et al. (2016), Rouzaud (1990), Silva et al. (2009), Taylor et al. (1998), Walters et al. (2014), Wang et al. (2018) and others.
- *Ultra-microtome*
  For solid specimens that have strong electron scattering, thin-cut sections can be made for direct transmission, using an ultra-microtome equipped with a glass or diamond knife. Examples of ultra-microtome methods are outlined by Glickson and Taylor (1986), Taylor et al. (1991), Taylor and Teichmüller (1993). Special application of this method are also described by Uwins et al. (2000).
- *Focused Ion Beam*
  Focused Ion Beam (FIB) is the most modern technique of sample preparation for TEM. A Ga^{+} beam is used for selective removal of material to obtain a sufficiently thin sample. The process of cutting of the specimen can be controlled by operator at any time. Extensive description of the FIB technique was published by Giannuzzi and Stevie (1999).
- *Ion milling, electropolishing and lithography*
  These methods are used to finish TEM specimen preparation by non-mechanically thinning previously dimpled specimens until they become properly smooth and electron transparent. The most modern and advanced ion milling method uses broad ion beam (BIB) where a controlled Ar+ beam is used to reduce the thickness of the sample, exposing very fine details of the surface or structure (Goodhew et al., 2001; Langford and Petford-Long, 2001).
- *Replicas*
  This technique allows for the extraction of small fragments/particles from the surface followed by examinationby other techniques including diffraction pattern if they are crystalline and transparent to the electron beam. For close observation of surface textures, different replica techniques can be used. There are one-stage (negative) and multi-stage (positive) replicas. For the investigation of organic matter one-stage replicas with Pt-shadowing and carbon backing are most commonly used. The replicas are taken from natural specimen surfaces or cleavage faces (Goodhew et al., 2001; Koehler and Mattern, 1965; Kwiecinska, 1980).
  Before the development of ultra-microtomes, FIB and BIB, the replica techniques were very popular. Presently they are only applied occasionally.

2.1.2. Examples of application of TEM for coals and carbonaceous matter studies

Transmission electron microscopy has made breakthroughs in the study of natural organic matter as well as carbon materials. It allows for direct observation of carbon structures predicted previously by other methods, *e.g.* light microscopy, XRD or different spectroscopic methods.

High resolution transmission electron microscopy (HRTEM) has proved to be an excellent method for examination of all varieties of organic matter, including coals of different rank derived from different sources (Taylor, 1966; Taylor et al., 1991; Taylor et al., 1998; Taylor and Teichmüller, 1993). It has provided new information on the ultrafine structure of coals, coal compositions and coaly kerogen and their structural development during coalification (Bustin et al., 1995; Oberlin et al., 1980; Wang et al., 2018). Many scientists have focused on the application of various TEM techniques to study internal structures and textures. Examples include lattice fringes derived from aromatic layers dimensions and arrangement, structural homo- or heterogeneity and degree of maturation of carbonaceous matter of high molecular

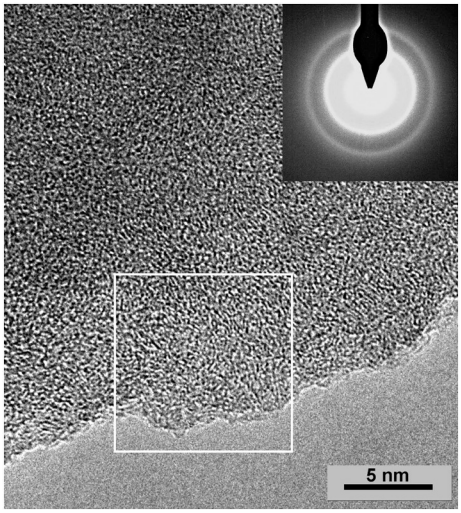

Fig. 3. HRTEM image of turbostratic structure and diffraction pattern of semi-anthracite. [Duber, 2011]

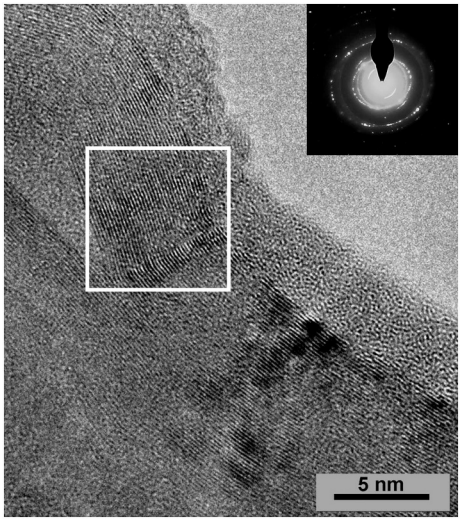

Fig. 4. HRTEM image of ordered structure and diffraction pattern of meta-anthracite. [Duber, 2011]

ordering of anthracite, meta-anthracite, semi-graphite and graphite as seen in Fig. 3-5 (Duber, 2011; Kwiecińska, 1980; Kwiecińska and Petersen, 2004; Pusz et al., 2014; Rantitsch et al., 2016). TEM studies have helped to identify specific structures of rare types of natural carbon matter like shungite, thucholite or anthraxolite (Jehlicka and Rouzaud, 1993). HRTEM accompanied with EDS spectrometry has revealed sub-micron minerals dispersed in coals (Glikson et al., 2000). Using this technique, Hower et al. (2018) showed that some inorganic elements previously considered as chemically associated with organics proved to be related to mineral matter. TEM supported by electron diffraction or by SAED as well as STEM were used to identify ultrafine particles in fly ashes (Ribeiro et al., 2013; Saikia et al., 2015; Silva et al., 2009), coal cleaning rejects (Cutruneo et al., 2014; Oliveira et al., 2018) and coal wastes (Ribeiro et al., 2010). Organic matter dispersed in inorganic rocks not distinguishable in light microscopy have been also detected by HRTEM combined with EDS (Morga and Pawlyta, 2018; Smieja-Król et al., 2009; Walters et al., 2014).

The results obtained improve our knowledge on nano-sized minerals and organic matter that can help in determining paleodeposition conditions, and the changes that occur during coalification/catagenesis and diagenesis. It also allows make a prediction about potential influence of

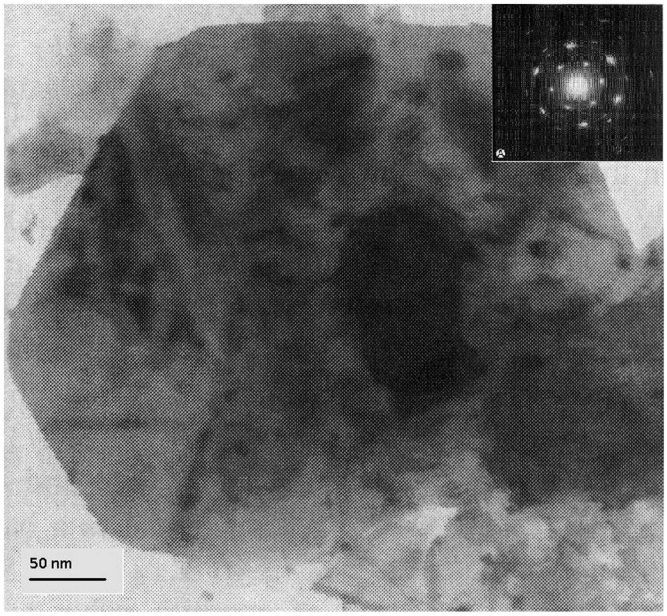

Fig. 5. HRTEM image of ordered structure and diffraction pattern of natural graphite. (by B. Kwiecińska)

these nano-sized particles on environment and to develop the methods of their neutralization or sourcing.

HRTEM, often combined with electron tomography, was applied to the investigation of ultrafine structures of carbon materials like nanofoams, fullerenes, nanofibres, nanotubes (Fig. 6) (Bourrat, 2000; Crawford and Marsh, 1977; Groopman and Nittler, 2018; Pawlyta, 2013; Pawlyta and Hercman, 2016), and graphene structures (Bachmatiuk et al., 2015). Based on profound HRTEM studies, Pawlyta et al. (2015) have shown complex structure of carbon blacks and its transformation during heat treatment.

Oberlin and others, using HRTEM combined with electron diffraction techniques, were able to provide evidence of the mechanisms of carbonization, graphitization and as well as other changes during coking processes (Oberlin and Terriere, 1975; Oberlin, 1984, 1989; Rouzaud and Oberlin, 1983, 1985; Rouzaud, 1990). TEM images (BF

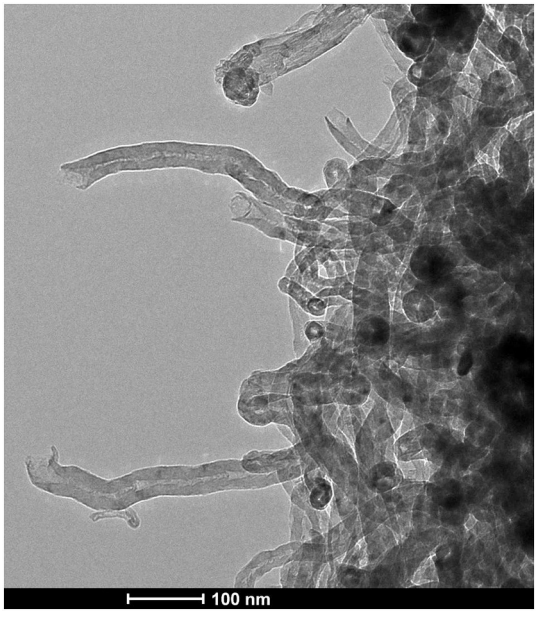

Fig. 6. TEM image of carbon nanotubes. (by S. Pusz)

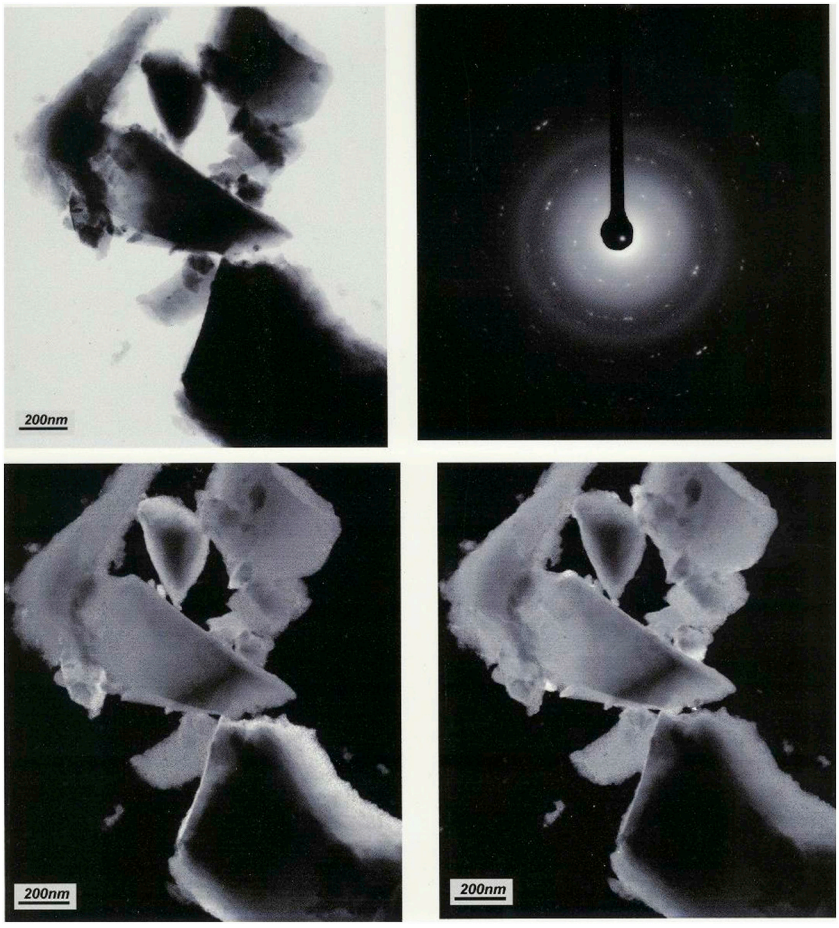

Fig. 7. TEM images of anthracite grains: (a) Bright Field, (b) electron diffraction pattern, (c, d) Dark Field, white dots – ordered areas [Duber, 2011].

and DF modes, Fig. 7) were used to develop the method for quantification of coking textures (Bourrat et al., 1986; Bourrat, 2000). This method was further advanced allowing for the determination of average size of molecular oriented domains (SMOD), which reflects the structure of the solid phase of porous carbon materials, e.g. cokes (Krzesinska et al., 2009; Pusz et al., 2010; Smędowski and Krzesińska, 2013).

Recently, most advanced TEM systems can be applied to *in situ* synthesis of new carbon or inorganic-carbon structures (Rummeli et al., 2018; Zhao et al., 2017). TEM techniques have also allowed for the study of micro-nano- fossil structures in the field of palynology, paleobotany and micropaleontology (Glasspool et al., 2009; Hemsley and Scott, 1991; Okoli and Nyananyo, 1988; Van Campo and Lugardon, 1973), which are very useful in paleoenvironmental and paleofacial studies of sedimentary basins.

2.2. Scanning electron microscopy (SEM)

SEM is an instrument that produces a largely magnified image by using electrons instead of light waves. Pioneering work on the physical principles of SEM and beam-specimen interactions was performed by Manfred von Ardenne in 1937. The first SEM was constructed in 1942 by three researchers at RCA Labs in New Jersey, USA, Drs. Zworykin, Hillier and Snyder, and had a resolving power of 50 nm and a magnification of 8,000x. The first commercial SEM was built in 1965 by Cambridge Scientific Instruments (UK) after the work by the Charles Oatley team (1948-1963). Nowadays SEMs can have a resolving power of less than 1 nm and can magnify over 400,000x (Goldstein et al., 2007).

The benefits of SEM over conventional light microscopy include very high resolution and a dynamic magnification range (better than 10x to 400,000x), greater depth of field (ability to image rough sample surfaces), and microanalysis – the ability to analyze the chemical composition of samples in detail when connected to an x-ray analyzer (EDS or WDS) (Goldstein et al., 2007; Goodhew et al., 2001).

All SEMs consist of a column where a beam of electrons is generated; a sample chamber, where the electron beam interacts with the sample; detectors monitoring a variety of signals that result from beam-sample interaction, and a viewing system that constructs an image from the signal. The electron column consists of an electron gun (tungsten, LaB6 or field emission), a series of magnetic lenses, beam-defining apertures and a set of scanning coils (Fig. 8). An electron gun generates the electron beam. Magnetic lenses form a fine convergent beam of electrons that scans the surface of the specimen row by row. The collected signals are properly amplified and digitized while keeping a strict correspondence between sample scanned point and image point, to generate a real-time image viewed in a display screen that can be stored in a computer (Goldstein et al., 2003).

The beam of electrons affecting the sample causes the emission of electrons with various energies and other kinds of radiation, which provide information about the sample's surface morphology, composition, crystallographic structure and other properties. The recorded signals are created not only on the surface of the sample, but also the beam penetrates the sample to a certain depth depending on certain beam/sample conditions. The area where various kinds of signals are created, as a result of interaction between electron beam and a sample, is called the area of interaction (excitation). The size and shape of the excitation volume is defined mainly by the composition of the sample and the accelerating voltage. The accelerating voltage determines the amount of energy transmitted by the electrons of the beam and the

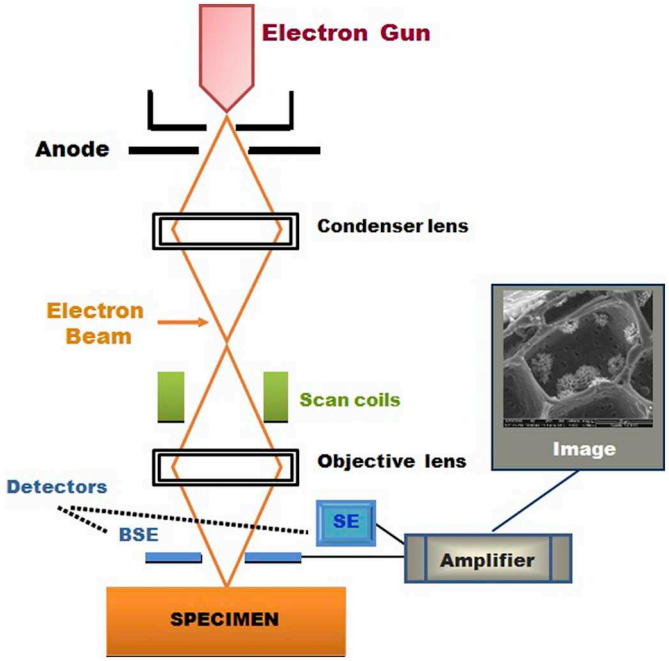

Fig. 8. Schematic drawing of scanning electron microscope (SEM) (by S. Pusz).

higher the electrons' energy, the deeper the excitation area. In a sample of greater density, i.e. containing elements of higher atomic number (Z), the excitation volume is smaller than in a sample composed of the elements of a lower atomic number (Fig. 9) (Goldstein et al., 2003).

Excitation volume as well as the spot size (electron beam diameter at the sample) determine the resolution of microscopic image. There is a mutual relationship between the electron beam energy and the size of the spot. An increase of one of these parameters causes other to increase as well. Some applications, such as EDS and WDS analyzes, require high beam energy, whereas for the production of high-resolution images the smallest possible size of the spot is needed. Thus, in order to obtain an image of good quality and, concurrently, to make chemical microanalysis of a sample, a compromise between sufficiently high accelerating voltage and appropriately small size of the spot is necessary (Goodhew et al., 2001).

SEM imaging and analysis can be classified as follows:

- *secondary electron (SE) image* – generally the most useful type of image for studying surface topography. The secondary electron image is similar in appearance to a light optical image, except the-image is only in grayscale contrast, but both the resolution and the depth of focus are greatly improved,
- *backscattered electron (BSE) image* – obtained by collecting high-energy electrons that leave the specimen with more than 50 eV energy, as the result of elastic collision with the nuclei of sample atoms. The contrast in BSE image originates from differences in the average atomic number of the atoms being excited, thus it can provide critical information about sample composition. With specialized detectors (EBSD) and properly prepared samples, the backscattered electrons can be used to study the local crystallographic structure (electron backscattered diffraction) and generate phase and grain orientation images,
- *X-ray microanalysis: energy- (EDS) or wavelength- (WDS) dispersive spectroscopy* – obtained by collecting characteristic X-rays that can be used to display qualitative, quantitative and spatial distribution of chemical elements in a specimen,
- *cathodoluminescence (CL) imaging/analysis* - obtained by collecting the light emission due to cathodoluminescent phases in a sample, with information related to trace element composition and structural defects,

Although standard SEMs have great advantages compared to light microscopy (*i.e.,* superior resolution, depth of field and microanalytical capabilities) they also can have a number of limitations, mainly derived from the high vacuum that must be maintained in the specimen chamber. Thus, samples must be able to tolerate high vacuum conditions and be electrically conductive. In practice, many samples do not meet these criteria and either need special preparation (basically, removing all water, solvents or gases that could vaporize while in under a vacuum and coating with electrically conductive layers to avoid charging artifacts) or cannot be investigated by SEM. The above problems have been resolved by the new generation of environmental SEM (ESEM) or low/variable pressure SEMs (Goldstein et al., 2003). In these instruments, multiple Pressure Limiting Apertures (PLAs) separate the column from the sample chamber; the column remains at high vacuum, whereas the chamber may sustain pressure up to 200 Pa (low pressure SEM) and to 4000 Pa (ESEM). The balance of gas flow into and out of

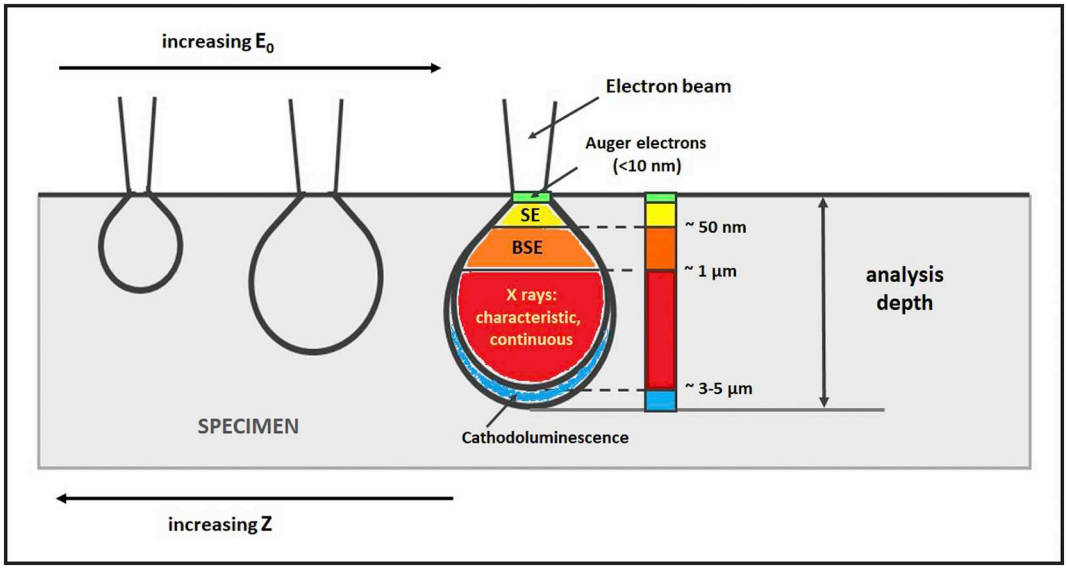

Fig. 9. Beam/sample interaction: types of signals and the area of their emission; excitation volume dependence on electron beam energy (E_0) and atomic number (Z) of sample components (by S. Pusz).

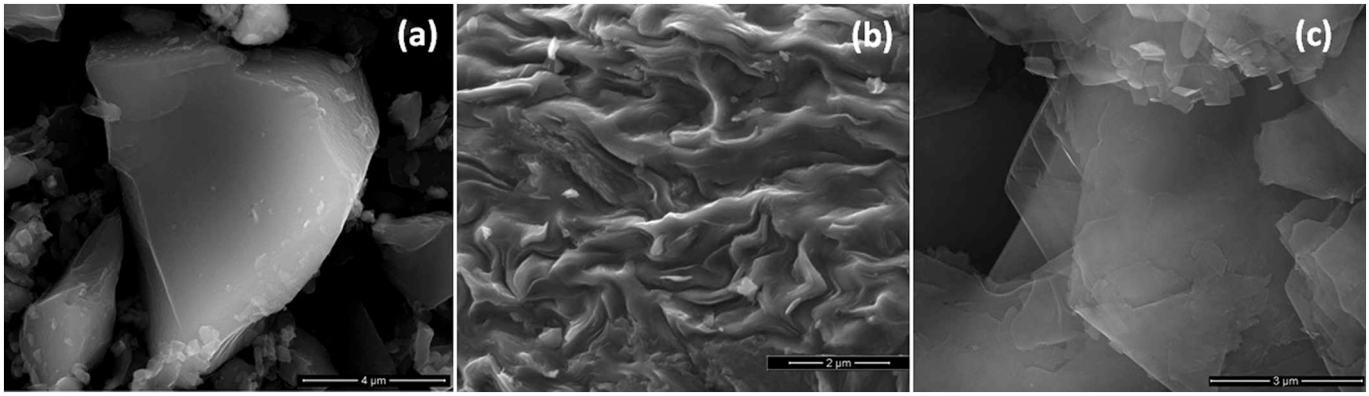

Fig. 10. SEM images (SE) of: (a) raw anthracite; (b) natural coke; (c) natural graphite. (by B. Kwiecinska, S. Pusz)

the sample chamber determines its pressure. In low vacuum SEM high resolution imaging is still possible. Low vacuum SEMs allow for the examination of specimens without restrictions concerning conductivity (nonconductive-uncoated specimens) and strict high vacuum compatibility, while retaining high resolution. The ESEM, in turn, allows for the examination of practically any specimen under a broad range of gaseous conditions (nonconductive-uncoated specimens, hydrated or contaminating samples) and the observation of *in-situ* dynamic experiments taking place in the SEM chamber (phase transition, hydration, oxidation, corrosion and other thermal, mechanical and chemical processes) (Johnson, 1996). Modern SEMs also employ a fast, powerful computer enabling extended automation for imaging applications and for analytical operation modes, e.g. X-ray microanalysis and electron backscattered diffraction.

2.2.1. SEM specimen preparation techniques

The results of SEM studies strongly depend on the specimen's quality thus the type of preparation procedures that are used are critical. In general, the specimens should meet the following criteria, similar for both coal/carbon specimens and other solid samples:

- if using typical high vacuum conditions, they must be vacuum tolerant, electrically conductive, void of free particles and releasing no volatile matter,
- the specimen face/surface should be perpendicular to the beam direction (as much as possible) to reduce focus issues across the examination surface,
- in the case of bedded specimens, such as coals and shales, samples should be sectioned parallel as well as vertical to the layers, especially when textures are to be investigated,
- the specimen should be fixed to the holder using a conductive, vacuum-proof adhesive, to facilitate the discharge of any electric charge that can cumulate on the specimen's surface,
- non-conductive and low-conductive specimens should be covered by a carbon or metal coat using a vacuum evaporation technique (e.g. sputter coating). The main purpose of the coating is to increase the yield of secondary electrons to enhance image resolution, and to avoid the charge build-up on the specimen surface. A carbon coat is especially recommended for samples intended for EDS analysis in order to minimize the influence of a conductive layer on obtained X-ray spectra,
- conductive coatings are not necessary when using low pressure SEM or ESEM techniques,
- to enhance contrast or expose structural details, additional treatment of the specimen surface can be necessary. The most common treatment types are: etching: chemical, by low temperature ashing or in plasma cleaner, electrolysis and decoration.

Recently, as in the case of TEM, focused ion beam (FIB) and broad ion beam (BIB) techniques are increasingly used to prepare high quality specimens for SEM analysis (Goodhew et al., 2001). Both these methods allow for the exposure of previously invisible or hardly visible details of the surface or structure of sample. Since the ion polishing process is rather slow, it is necessary to make the sample pre-thinned by using mechanical grinding and polishing. It should be noted that ion milling (BIB and FIB) has been found to increase organic matter reflectance (R_o) under reflected light conditions, which have been attributed to: 1) possible thermal alteration of organic material (Katz and Arango, 2018; Mastalerz and Schieber, 2017; Sanei and Ardakani, 2016) or 2) due to increased surface flatness (Grobe et al., 2017; Valentine et al., 2019). The possible effects of ion milling are still being investigated as any possible changes to organic material could potentially be altering properties such as porosity (Schieber et al., 2016).

Many specific procedures of sample preparation for SEM studies are presented in the Echlin handbook (Echlin, 2009) as well as in scientific papers, e.g. Giffin et al. (2013), Mastalerz and Schieber (2017), Zhou et al. (2017).

2.2.2. Examples of application of SEM for coals, organic-rich shales and carbonaceous matter studies

The introduction of various SEM techniques has greatly benefited the study of micro-nanoscale properties of coals, organic-rich shales and carbonaceous materials. The SEM is commonly used for structural investigation of highly metamorphosed organic matter, *e.g.* high rank coals, anthracites, natural cokes and graphite (Fig. 9; Kwiecińska, 1980; Kwiecińska et al., 1992, 1995; Kwiecińska and Petersen, 2004). It is also a very good complementary method to study the structure of various carbonaceous matter and its transformation during processing, e.g. pyrolysis, coking, oxidation or weathering (Fig. 10; Gornostayev and Harkki, 2006; Kumanek et al., 2018; Legin-Kolar et al., 1999; Pusz et al., 2014; Xia et al., 2014). Fracture analysis of various carbon materials observed with SEM reveals detailed information on their structure, which allow for improved predictions of their behavior during processing. (Fig. 11; Kwiecińska and Pusz, 2016; Pusz et al., 2015; Szeluga et al., 2015).

One problem that has hindered SEM applications for organic petrology studies is the inability to adequately identify/distinguish macerals (Hackley and Cardott, 2016). Traditional organic petrology techniques use optical microscopy to identify macerals based on reflectance, form/shape, relief, and fluorescence, while SEM exhibits contrast in relief (SE), atomic number (BSE), and in most cases the form/shape of organic material (Stanton and Finkelman, 1979). Cardott and Curtis (2016, 2018) found that examining coal samples using low accelerating voltages (1-2kV) resulted in low grey scale contrast (BSE) between macerals making identification difficult, whereas higher accelerating voltages (10kV) yielded higher contrast between maceral groups (vitrinite, inertinite and liptinite), with some ability to distinguish maceral subgroups (telovitrinite *vs.* detrovitrinite) or even macerals (sporinite

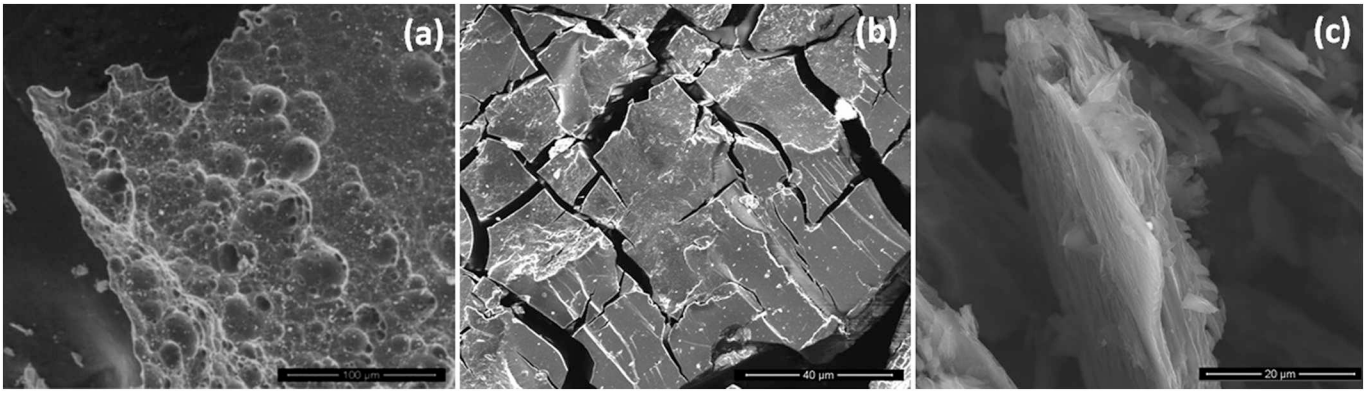

Fig. 11. SEM images (SE) of: (a) meta-anthracite treated with oxygen plasma; (b) anthracite oxidized in air, at 420 °C; (c) anthracite thermally treated at 1700 °C, in N_2. (by S. Pusz)

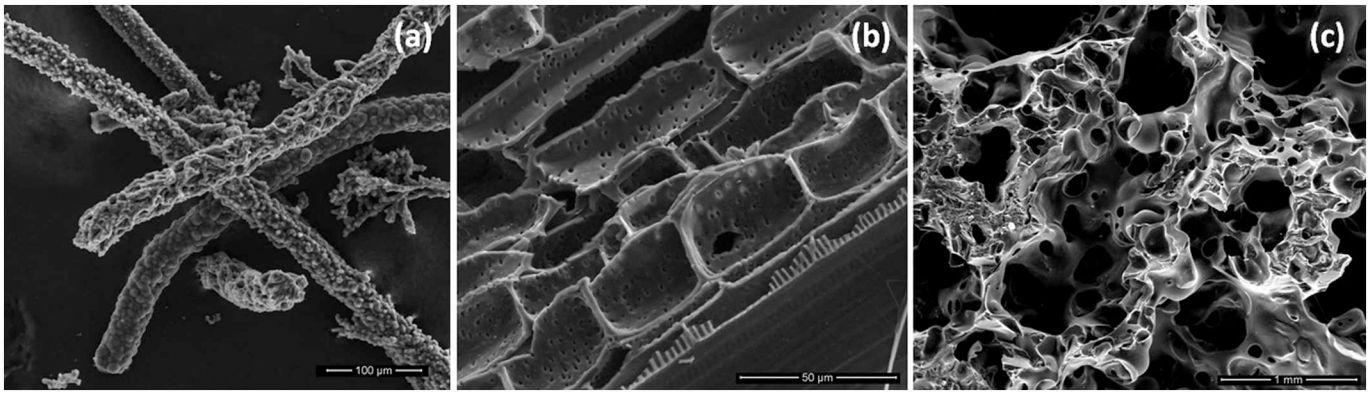

Fig. 12. SEM images (SE) of carbon materials: (a) fibrous pyrolytic carbon; (b) carbonized bamboo tissue; (c) carbon foam. (by S. Pusz)

vs. cutinite). Their study also found that the identification based solely on contrast between the different inertinite macerals (semifusinite, fusinite, macrinite) was difficult unless the maceral had bogen structure (fusinite *vs.* semifusinite). This also extended to the identification of inertinite *vs.* vitrinite in shale samples, where little to no grey-scale contrast can be used to distinguish between the maceral groups. Evaluation of samples with reflected light microscopy before SEM analysis is highly recommended where distinctions between maceral types is needed (*e.g.* Liu et al., 2017; O'Brien et al., 2011). Valentine and Hackley (2019) compared correlative reflected light (white and blue light) with SE and BSE (5kV, low current intensity, 5 mm WD) and found that in a low maturity Bakken Formation (solid bitumen R_o 0.3%) sample, no grey scale distinctions could be made between adjacent amorphous organic material, solid bitumen and inertinite with the exception of inertinites with high R_o (3.25% R_o) and arch structures (Fig. 12). Hackley et al. (2017) used an integrated correlative light microscope system integrated with an SEM (iCLEM) which allowed for simultaneous analysis using low magnification (500x) fluorescence microscopy and high resolution (> 10,000x) evaluation with SEM (Fig. 13).

Further distinction between organic matter (OM) types by Bernard et al. (2012a and b) used the C-XANES spectra from synchrotron-based scanning transmission X-ray microscopy (STXM) with STEM images on shale samples to identify different organic matter types (kerogen, bitumen, and pyrobitumen). Efforts by Loucks and Reed (2014) focused on the processing of SEM photomicrographs to distinguish organic matter types as depositional (kerogen, solid bitumen, pyrobitumen) or migrated (solid bitumen, pyrobitumen) using the form/shape of the organic material, pore size/textures/shape, and the examination of adjacent mineral cementation to determine depositional origin. Their distinction between depositional *vs.* migrated organic material could help to understand the pore networks present in organic rich shales, as depositional organics tend to have a limited pore network compared to migrated organic material.

With the increased interest in unconventional oil and gas petroleum systems worldwide, electron microscopy plays a vital role in characterizing microstructures of source rocks and reservoirs (Cardott et al., 2015; Chalmers et al., 2012; Curtis et al., 2012; Lu et al., 2015; Milliken and Curtis, 2016). The high resolution achieved with modern SEMs with field emission guns (FE-SEM) coupled with ion milling have made it possible to determine the dimensions, morphology and distribution of nano- to macropores and their quantitative analysis in coals of different rank (Giffin et al., 2013; Klaver et al., 2012; Li et al., 2017; Loucks et al., 2009; Zhou et al., 2017) as well as in organic-rich shales (Jiao et al., 2014; Mastalerz and Schieber, 2017). Most studies indicate that as the thermal maturity of organic-rich shales increases, generating hydrocarbons, the development of secondary pores in organic matter also increases (Bernard et al., 2012a and b; Chalmers et al., 2012; Jarvie et al., 2007; Modica and Lapierre, 2012). However, some studies have not been able to document this trend (Fishman et al., 2012; Milliken et al., 2013), supporting the idea that development of organic porosity could be affected by several factors (*i.e.*, organic matter/maceral type, burial history, mineral interactions, TOC content). In particular, the mineral matrix may exert an influential control for organic porosity preservation. For example, the study by Fishman et al. (2012) did not reveal any organic porosity preserved in samples from the mature organic-rich Kimmeridge Clay Formation, a lack which they suggested was due to plasticity and deformation of the clay-rich inorganic matrix. The conflicting results found in the literature suggests that the factors contributing to the development of porosity are still not well

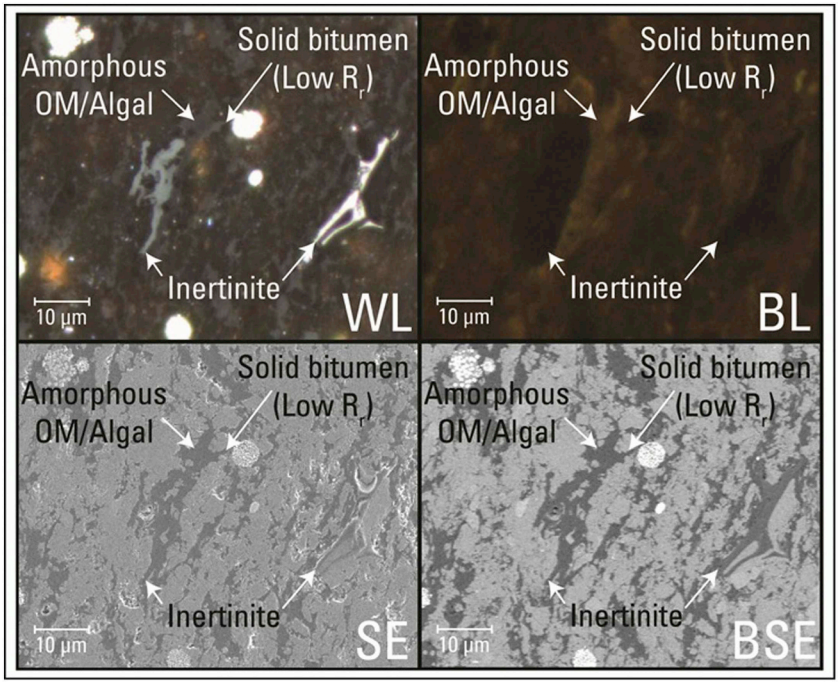

Fig. 13. Correlative images of the same field of view using optical (white and blue light) microscopy and SEM (SE and BSE modes, 5 kV, spot intensity 10, 5mm working distance) to compare different maceral types [Valentine and Hackley, 2016].

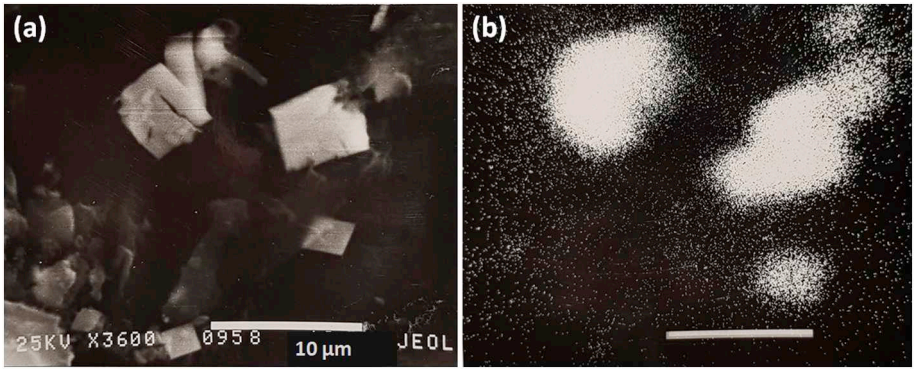

Fig. 14. SEM image (SE) of barite crystals in coal (a) and the map of Ba distribution (b). (by S. Pusz)

understood but will continue to be a crucial research topic, and electron microscopy will play an essential role in characterizing nanostructures (Katz and Arango, 2018).

Due to specific technical capabilities, SEMs have contributed to the development of micropaleontology, including paleobotany and palynology (House and Balkwill, 2013; Taylor, 1968; Taylor et al., 2009; Traverse, 2009). Anatomical details of previously termed paleoorganisms are revealed, and new ones discovered, especially those with ultrafine dimensions (Glasspool et al., 2009; Villanueva-Amadoz et al., 2012; Hemsley and Scott, 1991).

The research capability of scanning electron microscopy was broaden significantly by the combination of SEM with an X-ray analyzer (EDS or WDS). This technique allows for the study of morphological characteristics with the added benefit of geochemistry that has proved to be particularly important for the study of mineral matter and non-mineral inorganic elements in coals, organic-rich shales and coal utilization products (Ward, 2016). SEM-EDS method, besides identification of minerals or mineral mixtures, can provide information on the chemical composition of a sample for elements with atomic number (Z) > 3. It enables the detection of particular elements and mapping their spatial distribution within the studied area (Fig. 14). No special sample preparation, other than that typically used for SE imaging is required for qualitative analysis, but for quantitative analysis the sample must be bulk, flat, polished, and needs to be evaluated using analytical standards if necessary. Typical detection limit (minimum amount of element one can measure) of EDS analyser is 0.1 wt% (Goodhew et al., 2001). It should be noted that the spectra generated by an EDS system do require some evaluation by an experienced microscopist to identify possible collection artifacts and the misidentification of spectral peaks.

The seminal figure for the application of SEM-EDS method in the study of mineral matter in coal was R.B. Finkelman. Since the end of 1970s, he used this technique to study types, distribution and modes of occurrence of mineral matter in coals (Finkelman et al., 1976, 1984; Finkelman and Stanton, 1978; Minkin et al., 1984; Stanton and Finkelman, 1979). He also pioneered the application of SEM-EDS technique to study trace elements in coals (Finkelman, 1978, 1981, 1988, 1995). Based on the previous work by Finkelman other researchers have continued to develop the use of SEM-EDS to analyze coals and shales (Belkin and Luo, 2008; Dai et al., 2002, 2008, 2012,

2015a, Dai et al., 2015b, 2015c, Dai et al., 2017a; Kalaitzidis and Christanis, 2003; Permana et al., 2013; Saikia et al., 2014; Silva et al., 2012; Seredin and Finkelman, 2008; Seredin and Dai, 2012; Straszheim et al., 1988; Straszheim and Markuszewski, 1990; Sutku and Karayigit, 2015; Wang et al., 2012; Ward, 2002, 2016; Yossifova, 2014; Yu et al., 2007), and coal processing products (Creelman et al., 2013; Cutruneo et al., 2014; Kolker et al., 2017; Kutchko and Kim, 2006; Ribeiro et al., 2013; Saikia et al., 2015; Sanei et al., 2010; Zeng et al., 2016; Oliveira et al., 2018).

The Australian CSIRO developed over a period of 20 years an automated quantified image analysis system called initially QEM*SEM (Quantitative Evaluation of Materials by Scanning Electron Microscope) and later changed to QEMScan. This system was mainly designed for metallurgy applications, but in 1994 programs applying the system to the study of coal mineral matter and the products of coal combustion were initiated. With QEMScan the configuration was significantly altered by employing up to four light-element EDS detectors, computer control of the stage, and rapid data acquisition. At first detectors were unable to fully differentiate C and O elements, but improvements in solid state detectors have now overcome these limitations. Combination with image analysis techniques allows for mineral names to be ascribed to the images and, in a consequence, strongly facilitates evaluation of the nature, distribution and elemental composition of mineral matter in coals and other carbonaceous materials (Creelman and Ward, 1996). The system has proven particularly useful for not only the minerals in coal, but for the products of coal combustion such as furnace deposits and fly ash (Creelman et al., 2013; Liu et al., 2005).

Application of SEM and SEM-EDS methods plays an important role in the study of tonsteins. Detailed knowledge on tonsteins' mineralogical and chemical components and textural features obtained by these techniques facilitates identification of tonsteins origin and investigation the nature and periodicity of the volcanic activity, and also improves correlating coal seams and coalbearing strata (Arbuzov et al., 2016; Bohor and Tripplehorn, 1993; Dai et al., 2003, 2011, 2014a; Dai et al., 2017a, 2017b; Huff and Spears, 1989; Kramer et al., 2001). Determination of the concentration of some elements occurring in tonsteins, especially rare metals and specific trace elements may allow, from one side, evaluation of potential risk to the environment, and from the other side, estimation potential value of the deposit as a resource (Dai et al., 2003, 2010, 2014b; Hower et al., 1999; Zou et al., 2016).

A specific variation of a SEM equipped with X-ray analyzers is an electron probe micro-analyzer (EPMA). Both instruments have the same basic principle of operation and similar construction. However, SEMs are optimized mainly for imaging, whereas the EPMA is designed primarily for quantitative analysis. As in the case of SEM-EDS studies, EPMA allows to identify minerals and elements dispersed within the coal, and also allows for mapping the distribution of particular elements in the area studied. The EPMA, besides EDS, usually has several WDS detectors that make the results of microanalysis more accurate, especially for light elements and elements at low concentrations (minor and trace elements). Microanalyses by electron probe are always performed on polished surfaces (Reed, 2005).

EPMA techniques have made significant progress in the study of maceral chemistry by documenting diversity of C, H, N, O and S element composition within particular macerals (Mastalerz and Gurba, 2001; Ward and Gurba, 1998; Ward et al., 2005) and revealed the dependence between macerals' chemistry and coal rank (Gurba and Ward, 2000; Walker and Mastalerz, 2004; Ward et al., 2005; Ward et al., 2008). This method plays an important role in detailed study of minerals distributed in coals (Ward et al., 1996; Ward, 2002; Ward, 2016). and is used to evaluate minor and trace elements dispersed both in various mineral phases (Diehl et al., 2012; Patterson et al., 1994) and in organic matter (Ding et al., 2001; Li et al., 2007; Zodrow and Cleal, 1999). Overall, an application of EPMA technique has improved the knowledge on origin, associations and modes of occurrence of inorganic matter occurs in coals, both minerals and individual elements.

3. Summary

SEM and TEM techniques have been used as complementary methods to other prominent techniques such as light microscopy, XRD, Raman spectroscopy, etc. With the improvements made on the current generation of electron microscopes, SEM and TEM will continue to improve our understanding of micro-nanoscale physical and chemical characteristics of coal, organic-rich shales, and carbonaceous materials. Modern techniques of specimen preparation combined with various electron microscopy methods and analytical techniques can be sufficient to conduct full characterization of a wide variety of carbonaceous matter, thus providing an important complement to organic petrology.

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