

MINERAL MATTER IN COAL
MINERAL MATTER DALAM BATUBARA**Rita Susilawati**Center for Geological Resources, Geological Agency of Indonesia
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Email : winkwinkproud@gmail.com*Diterima : 10 Maret 2015**Direvisi : 6 April 2015**Disetujui : 20 Mei 2015***ABSTRACT**

The term "mineral matter" in coal is defined as all inorganic, non-combustible material that is in or associated with coal which include discrete crystalline mineral particles, dissolved ions and other inorganic components in the pore water or surface water of the coal, and inorganic elements combined within the organic compounds of the coal macerals. The minerals existing in coal are a result of processes that occur throughout the entire history of coal formation. Its distribution is influenced by biological, hydrological and geochemical factors. Quartz and the clay minerals are the most widespread and abundant mineral found in coal. Another common minerals are feldspars and carbonate in the form of siderite, calcite and dolomite and sulfide minerals such as pyrite. Coal mineral matter analysis and characterization are useful for various reasons, particularly to take as much as benefit from coal utilization and to avoid any negative influence of coal inorganic components to the environment.

Keywords: coal, mineral matter, coal utilization.**ABSTRAK**

Istilah mineral matter dalam batubara didefinisikan sebagai semua komponen inorganik yang tidak mudah terbakar yang terkandung dalam batubara maupun yang berhubungan dengan batubara. Termasuk dalam definisi ini adalah partikel-partikel kristal mineral, ion-ion terlarut dan komponen anorganik yang terkandung dalam air pori atau air permukaan batubara serta senyawa anorganik yang bersatu dengan komponen organik dalam maseral batubara. Mineral dalam batubara terbentuk sepanjang sejarah pembentukan lapisan batubara. Distribusi mineral tersebut dipengaruhi oleh faktor biologi, hidrologi dan geokimia. Kuarsa dan mineral lempung adalah kristal dan mineral yang paling banyak ditemukan dalam batubara diikuti oleh felspar dan mineral karbonat dalam bentuk siderit, kalsit dan dolomit serta mineral sulfida seperti pirit. Analisis dan karakterisasi mineral dalam batubara menjadi penting terutama karena kandungan mineral berpengaruh dalam proses pemanfaatan batubara, termasuk juga untuk menghindari pengaruh negatif mineral tersebut terhadap lingkungan.

Kata Kunci: batubara, mineral matter, pemanfaatan batubara.**INTRODUCTION**

Coal is a combustible sedimentary material that is composed of two major constituents. The first constituent is organically derived material (macerals), which makes up the majority of coal composition and makes a significant contribution in the use of the coal for many purposes. The second constituent is inorganically sourced material (mineral matter), which although commonly present in coal as only a minor component can exert an important influence on the

performance and value of the coal in different utilization processes.

There are several significant reasons why the study of mineral matter in coal is a necessary complement to studies of the organic matter. The amount and composition of mineral matter can influence the exploitation and modification of coal during resource development, mining, preparation, storage and utilization (Finkelman, 1994; Harvey and Ruch, 1986; Saxby, 2000; Vassilev and Vassileva, 1996; Ward, 2002). Many problems, such as boiler fouling, slagging,

corrosion, erosion and agglomeration, arise during coal utilization as a result of the mineral matter in coal (Chang *et al.*, 2004; Gurba *et al.*, 2001; Keller *et al.*, 2014; Kolker and Finkelman, 1998; Kolker *et al.*, 2009; Maldonado-Hódar *et al.*, 1995; Saxby, 2000; Vassilev and Vassileva, 1996; Ward, 2002).

From an academic point of view, quantitative analysis of the minerals and other inorganics contributes significantly to defining coal quality, and may be useful as an aid to stratigraphic correlation (Bohor and Triplehorn, 1993; Hill, 1988; Ward *et al.*, 2001a; Zhou *et al.*, 2000). The mode of occurrence and mobility of some trace elements in coal, including toxic elements, can also be identified by coal mineralogical analysis (Finkelman, 1995; Li, 2002; Vejehati *et al.*, 2010). The occurrence of particular minerals in coal may also indicate nearby mineralization (Ward, 2002). Minerals in cleat and other fractures may influence coal bed methane production and mining, as the minerals may block the drainage of gas from coal seams (Gurba *et al.*, 2001). In addition, the abundance and composition of the minerals emplaced within the coal during coalification represent the sedimentological and geochemical history of the early peat deposit, the post-depositional and coal-forming environment (Renton, 1982).

This paper provides a literature review of the important concepts related to the nature, origin and significance of the mineral matter in coal.

MINERAL MATTER DEFINITION

Coal is a complex heterogeneous mixture of organic and inorganic material. The term “mineral matter” in coal is defined as all inorganic, non-combustible material that is in or associated with coal (Finkelman, 1995; Gary *et al.*, 1972; Richard and Rodney, 1986). This definition includes all of the elements in the coal, except for the organically combined carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S). However, inorganic combinations involving C, H, O

and S that are found in coal, such as C in carbonates, H in absorbed water and hydroxides in clay minerals; O in water, silicates, carbonates, sulphates or other minerals; and S in sulphide and sulphates, are also considered part of the mineral matter (Harvey and Ruch, 1986).

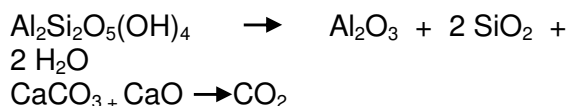
The term “mineral matter” in such definitions covers three types of inorganic material present in coal (Ward, 2002), which are: (i) discrete crystalline mineral particles, (ii) dissolved ions and other inorganic components in the pore water or surface water of the coal, and (iii) inorganic elements combined within the organic compounds of the coal macerals.

From a geological perspective, only the first type can be considered as a true mineral component. Discrete crystalline particles are the major form of non-organic material in higher rank coals (Kiss and King, 1977; Vassilev and Vassileva, 1996). However, non-mineral inorganics in the form of dissolved salts, exchangeable ions and organometallic complexes, are usually abundant in the mineral matter of lower rank coals (brown coal, lignite and sub-bituminous coal), and also make a significant contribution to ash formation in such coal deposits (Benson and Holm, 1985; Miller and Given, 1986; Ward, 2002).

Kiss and King (1979) has suggested the term “mineral” for the discrete inorganic grains and the term “inorganics” for dissolved ions and other inorganic components in the pore water and organically combined inorganic material (except for N and S). Similarly, Ward (2002) has used the term non-mineral inorganics to describe the inorganics in coal other than the discrete mineral particles.

It is also important to make a careful distinction between the term “mineral matters” and “ash” in coal, as these two materials are quite different. Ash represents the residue of the mineral matter after combustion of the coal, while mineral matter is the material present before the combustion process begins (Saxby, 2000; Vassilev and Vassileva, 1996; Ward, 2002; Ward and Ferm, 1984).

Ash can also be considered as the non-combustible fraction of the mineral matter (Harvey and Ruch, 1986; Karl, 1986; Saxby, 2000). Many of coal's minerals react during combustion, by processes such as:



MODES OF MINERAL OCCURRENCE

The mineral matter occurring in coal is perhaps best described as a combination of megascopic and microscopic mineral matter. The megascopic minerals are typically present as discrete bands, layers or partings of clay or carbonate, as nodules including lenticular and concretionary bodies of sulfide, carbonate or silica, and in fissures, including cleat and other fracture or void fillings (Ward, 2002). On the other hand, the microscopic minerals, may occur as thin bands, fill cracks or fissures, or be intimately associated with the coal's organic constituents. It has been recognized that cell lumens are often infilled by minerals (Ward, 2002). Mineral such as pyrite or siderite, may also replace the coal cell structure (Zodrow and Cleal, 1999). The mode of occurrence of inorganic constituents in coal defines as the way in which the elements are chemically bound in the coal (Finkelman, 1994). It has been noted that many of the elements present in coal may occur in a range of forms (Finkelman, 1994). For example, about six forms of selenium have been identified selenium bearing pyrite, organically bound selenium, selenium bearing sphalerite, lead selenide, water soluble selenium and ion-exchangeable selenium (Dreher and Finkelman, 1992). Study has noted that elements in coal can also be present in just one form, such as zirconium, which is present entirely in coal as the mineral zircon (Dreher and Finkelman, 1992). However in lignites, zirconium may also be incorporated with the organic material (Miller and Given, 1986).

More than one hundred species of minerals have been identified as occurring in coal, although of this number, only around twenty are common (Finkelman, 1994; Harvey and Ruch, 1986; Miller and Given, 1986; Ward, 2002).

ORIGIN AND DISTRIBUTION OF MINERAL MATTER

Based on its origin, mineral matter in coal has been grouped by numerous authors into several different classes. These include a "syngenetic" class for minerals that were introduced during coal formation and an "epigenetic" class for minerals that were introduced after coal formation (Mackowsky, 1968). Another widely used classification is based on dividing mineral matter into two categories (Ward, 2002): the "inherent mineral matter" for the inorganic material present in the coal-forming plants and "adventitious mineral matter" for the inorganic constituents added to the coal forming deposit after the death of the plants. The inherent mineral matter is very closely associated with the macerals, and it difficult to remove by physical methods (Ward, 2002). In contrast, adventitious mineral matter can be more easily separated from the coal material (Ward, 2002). However, there has been a controversy concerning the use of this classification. Some authors believe to use this classification based on the process of formation while other on the ease of separation, such as by coal preparation processes.

The minerals existing in coal are a result of processes that occur throughout the entire history of coal formation. The first source of mineral matter in coal is the plants that form the peat swamp. Examples here include siliceous phytoliths in peat and also diatoms shells and sponge spicules derived from other swamp-dwelling organisms (Andrejko *et al.*, 1983). Three distinct processes thought to be responsible for mineral formation in coal (Ward, 2002). Detrital processes are responsible for solid particles washed or blown into the peat

swamp by wind or water. Tonstein, made up of altered volcanic ash found in some coal seams, provides a thick and distinctive example of wind-borne detrital (or pyroclastic) material. Direct chemical precipitation from solution or by biogenic processes involving inorganic or organic materials may introduce new minerals to the peat or coal formation. This can be described as formation by "authigenic" or "neof ormation" processes. "Diagenetic alteration" is another process, involving the interaction of minerals with peat or swamp waters or interactions during the rank advance to form new mineral phases. In addition, post-depositional migration effects associated with groundwater movement in coal seams may cause non-mineral inorganics to be concentrated in various parts of low-rank coal beds (Ward 2002).

The distribution of mineral matter in coal is influenced by biological, hydrological and geochemical factors. A large variation can exist in the mineral matter abundance in coal, and this variation can be as significant across micrometers as it is across kilometers (Finkelman, 1994).

The syngenetic phase of mineral emplacement begins during the peatification stage (Harvey and Ruch, 1986; Renton, 1982). At this stage, microbial activity decomposes the less resistant plant tissues into various gasses and water. Amorphous silica and alumina materials are released into the peat during primary decomposition of the plant debris, and these apparently become precursors to the silicate mineral assemblage that dominates the inorganic elements of most coals (Renton, 1982). In addition, syngenetic minerals may form by crystallization of inorganic elements that are incorporated with the inherent mineral matter (Harvey and Ruch, 1986). Minerals in coal may also be formed by bacterial reduction, or crystallize around nuclei or

other centers to form nodules (Ward, 2002).

After the syngenetic phase and with continued coalification, a further three episodes of mineral emplacement may occur which represent early diagenetic, late diagenetic and epigenetic processes (Ward, 2002). The "early diagenetic" phase introduces minerals to the peat or coal formation shortly after the initial burial of the plant debris by more peat or other sediment. A great variety of authigenic minerals may form during this phase, which is facilitated by the relative ease with which ground water containing solutions of mineral-forming ions can move through the coal (Renton, 1982). The "late diagenetic" phase of mineral formation takes place during deeper burial and rank advance. The final "epigenetic" phase represents mineral formation after the coal has essentially reached its present rank. At this stage, the development of major fractures throughout the coal bed allows the movement of groundwater with solutions of mineral-forming ions through the coal bed.

During the epigenetic phase, mineral formation processes may continue without any involvement of the organic constituents, as the organic material has become relatively inert during the process of coalification (Renton, 1982). The lateral distribution of mineral matter in coal is influenced by this epigenetic phase of mineralization (Finkelman, 1994). Minerals formed in this stage are found as fillings of fissures (e.g, pyrite, calcite and kaolinite) and voids, and as products of weathering or oxidation (Harvey and Ruch, 1986). Variations in the concentration of particles inorganic constituents in coal can occur over very short distances, and give rise to an irregular distribution of minerals in cleat and fractures (Finkelman, 1994).

The processes of mineral formation in relation to coalification can be found in figure 1.

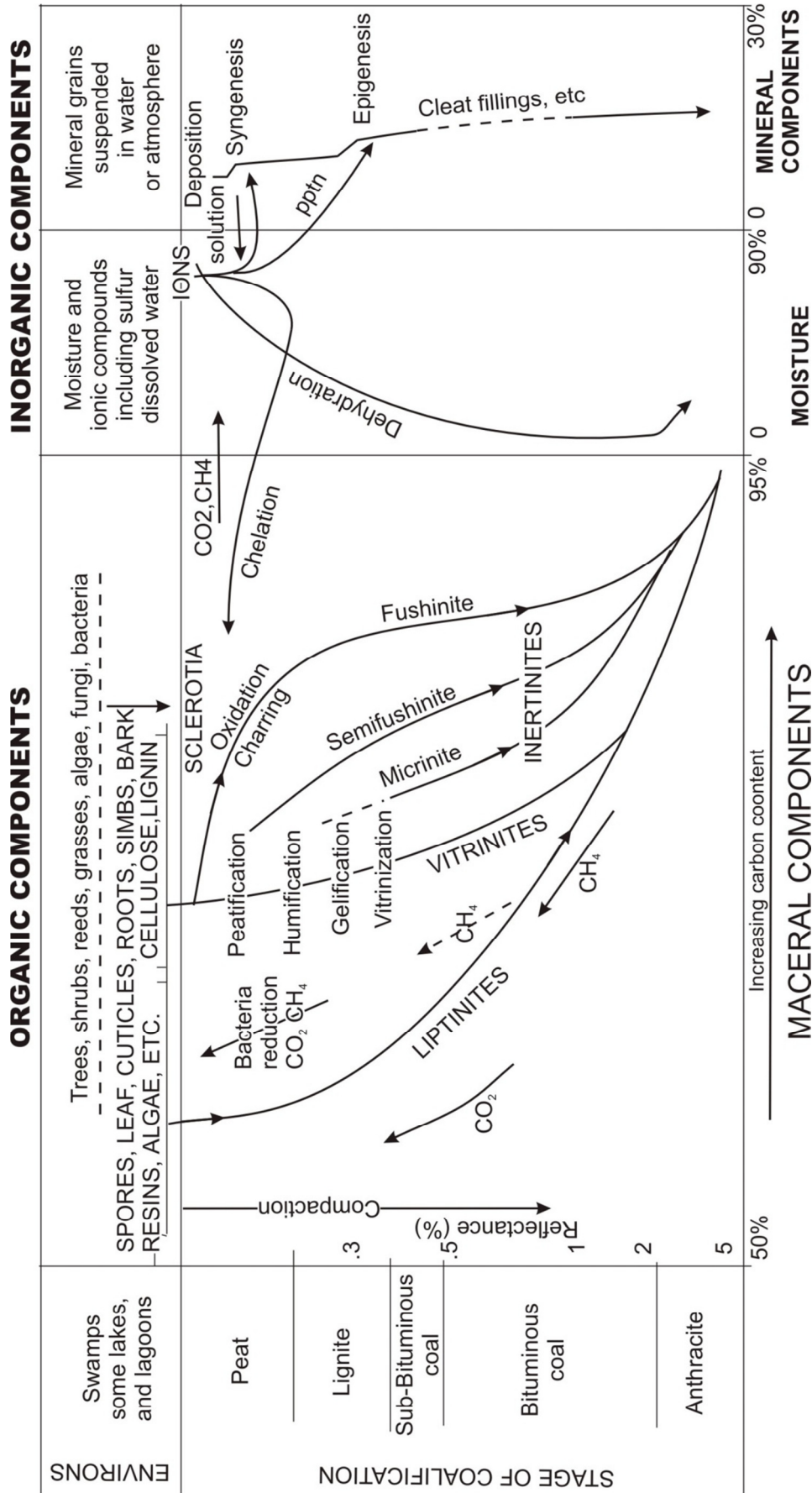


Figure 1 Diagrammatic representation of coalification processes involving the conversion of plant debris to various macerals, and those involving moisture and genetic processes of mineral matter (from Harvey and Ruch 1986)

MINERALS IN COAL

The minerals commonly found in coal are listed in table 1. Among them, quartz and the clay minerals are the most widespread and abundant. Feldspars, carbonate in the form of siderite, calcite and dolomite, and sulfide minerals such as pyrite, are other common minerals in

coal(Finkelman, 1994; Renton, 1982; Ward, 2002).

A brief explanation is given below of the common minerals present in coal. This includes a discussion of the non-mineral inorganics, which are also included in the broad term “mineral matter” used in this review (see section 2).

Table 1. Common minerals in coal
Compiled from Harvey & Ruch (1986) and Ward (2002)

Concentration	Mineral	Formula	Occurrence	Mode of Occurrence	
				Physical	Genetic
MAJOR	Silicate				
	Clay Mineral				
	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	Common-dominant	L,F	d,e,s
	Illite	K _{1.5} Al ₄ (Si _{8.5} Al _{1.5})O ₂₀ OH ₄	Abundant-dominant	D,L	d,s
	Smectite	Na _{0.33} (Al _{1.67} Mg _{0.33})Si ₄ O ₁₀ (OH) ₂	Rare-common	D,L	d,s
	Chlorite	(MgFeAl) ₆ (AlSi) ₄ O ₁₀ (OH) ₈	Rare	L	d
	Mix-layer clay	Variable	Rare-very common	D,L	d,s
Quartz	SiO ₂	Common	D,L,N	d,s	
MINOR	Sulfides				
	Pyrite	FeS ₂	Rare-common	D,N,F	s,e
	Marcasite	FeS ₂	Rare-moderate	D(?)	s
	Sphalerite	ZnS	Rare	F	e
	Galena	PbS	Rare	F	e
	Chalcopyrite	CuFeS ₂	Rare	F	e
	Carbonate				
	Calcite	CaCO ₃	Rare-common	N,F	e,s
	Dolomite	CaMg(CO ₃) ₂	Rare-moderate	N,L	s,e
	Ankerite	(Fe,Ca,Mg)CO ₃	Rare	N,L	s,e
	Siderite	FeCO ₃	Rare	N,F	s,e
	Sulfates				
	Gypsum	CaSO ₄ ·2H ₂ O	Rare	D,F	w
	Bassanite	CaSO ₄ ·1/2 H ₂ O	Rare	A	w
	Anhydrite	CaSO ₄	Rare	D	w
	Coquimbite	Fe ₂ (SO ₄) ₃ ·9H ₂ O	Very rare	D	w
	Szomolnokite	Fe(SO ₄) ₃ ·9H ₂ O	Very rare	D	w
	Natrojarosite	NaFe ₃ (SO ₄) ₂ (OH) _R	Very rare	D	w
	Hexahydrate	MgSO ₄ ·6H ₂ O	Very rare	A	w
	Feldspars				
	Plagioclase	(NaCa)Al(AlSi)Si ₂ O ₈	Very rare	D,L	d
	Orthoclase	KAlSi ₃ O ₈	Rare	D,L	d
	Phosphates				
	Apatite	Ca ₅ F(PO ₄) ₃	Rare	D	d,s
	Crandalite	CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	Very rare	F,L	s,e
	Goyazite	SrAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	Very rare	F,L	s,e
	Monazite	(Ce,La,Th,Nd)PO ₄	Very rare	F	s,e
	Xenotime	(Y,Er)PO ₄	Very rare	F	s,e
	Others				
	Anatase	TiO ₂	Rare	D	d
	Rutile	TiO ₂	Rare	D	d
	Boehmite	Al ₂ O ₃ ·OH	Rare	A	w
	Zircon	ZrSiO ₄	Rare	D	d
Hematite	Fe ₂ O ₃	Rare	N	s	

D-disseminated, L-layers (partings), N-nodules, F-fissures (cleat), A-artifacts
d-detrital, s-syngenetic, e-epigenetic, w-weathering.

Clay Minerals

Clay minerals including kaolinite, illite, chlorite and a range of interstratified clay minerals account for some 60-80% of the total mineral matter present in most coals (Renton, 1982; Taylor *et al.*, 1998; Ward, 1984). Clay minerals are commonly present in the pores and cell cavities, or as finely dispersed inclusions in the coal macerals.

Among the clay minerals, kaolinite is the most common constituent of many coal seams. In some cases a combination of this mineral and quartz make up for nearly all of the mineral matter in the coal (Ward, 2002; Renton, 1982). Kaolinite may occur as a syngenetic clay mineral in the pores and cell cavities of the organic constituents, as vermicular aggregates of individual crystals, as an authigenic or detrital mineral concentrated at particular horizons, such as in tonstein beds, or as a replacement of plant tissue (Renton, 1982; Ward, 2002).

Illite, along with kaolinite is another common clay mineral in coal. It is rare, however, to find illite as a discrete mineral constituent in coal. This mineral is commonly found interstratified with other clay minerals (Renton, 1982; Ward, 2002). Renton (1982) noted that occurrences of illite within coal are commonly concentrated along bedding planes. Most illite is probably of detrital origin. Ward (2002) noted that low concentrations of illite in coal may simply reflect a low proportion of detrital input into the peat swamps.

However, it may also indicate that the mineral in its pure form is susceptible to alteration by the swamp waters to form mixed-layer clays or other mineral species. On the other hand, high concentrations of illite in some coals may be related to authigenesis under more marine conditions or be influenced by the detritus supplied to the coal basin.

Another common component is a range of interstratified clay minerals. According to Renton (1982), most coal contains at least some mixed-layered clay minerals. Mixed-layered or interstratified clay minerals are clay minerals in which

the crystal is built up of several different kinds of layers, rather than just one type as normally occurs in a "pure" clay component (Ward, 2002). This circumstance happens because the different clay minerals, especially montmorillonite, vermiculite and chlorite, all have essentially the same basic crystal structure. The nature of the ions and water between the aluminosilicate layers can be altered as a result of subtle ion exchange processes in some of those layers. The most common mixed-layer clay minerals are illite-montmorillonite, montmorillonite-chlorite and chlorite-vermiculite. Other common interstratifications include illite-chlorite, illite-vermiculite and montmorillonite-vermiculite (Ward, 2002).

Quartz

Quartz is another widespread and common mineral in coal. Syngenetic quartz can occur as a result of several processes: 1) detrital grains introduced by wind or water, which is typically shown by the presence of angular or rounded grains, 2) re-precipitation of dissolved silica derived from the alteration of silicate minerals, and 3) remnants of plant derived silica, such as phytoclasts and diatoms (Renton, 1982; Ward, 1984, 2002). The combination of these processes determines the total silica content in the coal. Ward (2002) noted that the silica that forms quartz in coal may also come from leaching of the basement rocks. It is also noticed that diagenetic quartz, in some circumstances can be dominant rather than detrital quartz grains (Saxby, 2000).

Carbonates

Carbonate minerals, particularly siderite, calcite and dolomite, are another frequently occurring group of minerals in coal. They can be formed during the syngenetic or epigenetic phases of mineral emplacement (Renton, 1982; Saxby 2000), and different members of the group may form by precipitation during each diagenetic phase (Renton, 1982).

Calcite is possibly the most widespread carbonate mineral, and can be

found in coal deposited either in freshwater or marine conditions (Renton, 1982). Syngenetic calcite is usually present in coal as cavity fillings while epigenetic calcite is common as a cleat filling. Thin section examination of some coal samples of Mae Moh Basin, Thailand shows the fibrous internal structure in the shell fragments, suggesting the presence of aragonite (Ward, 1991) which was also identified by XRD analysis.

Syngenetic siderite in the form of nodules, infillings or replacements of the organic matter may also be found in coal (Kemezys and Taylor, 1964; Ward, 2002). The presence of this mineral in coal is commonly related to low concentrations of syngenetic pyrite, but in some cases the siderite may also be associated with syngenetic pyrite crystals. The occurrence of syngenetic siderite in coal is usually thought to indicate an acid, freshwater environment for peat accumulation (Renton, 1982; Ward, 2002). Epigenetic siderite is also found as a cleat infilling material in coal and related strata. Other carbonates, such as dolomite and ankerite, are also common as cleat filling materials, suggesting an epigenetic nature. In some cases, two different carbonate minerals can be found filling the same cleat, such as in coals of the Sydney Basin, Australia, where ankerite is found as the main infilling but calcite in some instances is also present as a border (Ward, 1986).

Sulfides

Sulfide minerals occurring in coal may be either syngenetic or epigenetic in nature. Pyrite is the most common sulfide mineral in coal. Syngenetic pyrite can present as framboids, isolated euhedral crystals, infilling or replacing coal macerals, and as more massive pyrite accumulations (Ward, 2002). The occurrence of this mineral often indicates the influence of marine conditions. Syngenetic pyrite is also abundant in coals formed in non-marine environments, such as the intermontane lacustrine basins of Thailand, indicating that the process of pyrite formation may also be influenced by

sulfate-rich lake waters or sulfate-rich groundwater (Ward, 1991).

Syngenetic marcasite can be found in coal as radiating crystalline masses, isolated or aggregated crystals, or in massive form (Ward, 2002). Epigenetic sulfide minerals, including pyrite, marcasite, millerite and sphalerite, are present as infilling of the cleat and other fractures in coal-bearing strata (Ward, 2002). There are several processes that may result in the presence of epigenetic sulfides in coal: remobilization of organic sulfur or syngenetic sulfides within the coal, influence of igneous intrusions, and post-depositional fluid movement through the coal-bearing succession (Ward, 2002).

Feldspar

Feldspar minerals are also commonly found in coal and associated strata, although they are usually present only in small concentrations (Renton, 1982). However, feldspar may also present in abundance as can be found in the Theodore district of Bowen Basin, Australia (Ward, 1986). Feldspar in the form of plagioclase is more common than orthoclase (Renton, 1982). Microscopic observation on Australian bituminous coal specimen showed the occurrence of unaltered grains of feldspar suggesting that feldspar mineral in the samples is a detrital or pyroclastic in origin (Kemezys and Taylor, 1964)

Sulphates

A range of sulphates may form as a result of oxidation of sulfide minerals during prolonged storage or exposure of the coal, or even during the oxygen plasma ashing process. Some sulfate minerals may be present in their own right as inherent mineral components of unaltered coal (Ward, 1986). For instance, gypsum veins in coal from Leigh Creek, South Australia possibly formed as groundwater deposits due to the arid climate of the area (Kemezys and Taylor, 1964). Gypsum is also formed on the surface of low-rank coals exposed in open cut mines in Thailand, possibly due to evaporation of the inherent moisture

seeping from the coal seams (Ward, 1991).

The oxidation of pyrite during plasma ashing can form sulfate minerals such as coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$), szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$). However pyrite oxidation before ashing can also form these materials. Sulfuric acid, produced by pyrite oxidation, may also react with any calcite in the coal to form gypsum. Later, during low-temperature ashing, the gypsum may dehydrate and form minerals such as bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) or even anhydrite (CaSO_4). However, bassanite and anhydrite may also form directly from the macerals of coal during the LTA process. At temperatures more than 200°C , this mineral may be altered to anhydrite (Ward, 1986).

Phosphates

Apatite is the most common phosphate mineral in coal, typically occurring as small crystals intimately associated with the maceral constituents (eg. Inertinite) or with other minerals, such as kaolinite or quartz (Saxby, 2000). Some Australian bituminous coals have found to contain goyazite and related aluminophosphate minerals indicating an authigenic origin (Ward, 1989). Those minerals have been thought to be formed as a result of the interaction of calcium ions and aluminous complexes with phosphatic components derived from the decomposition of the organic matter (Ward, 1989).

Non Mineral Inorganics

An important part of the mineral matter in lower rank coal appears as inorganic elements associated with the organic material (Kiss and King, 1977; Miller and Given, 1986; Ward, 2002). Non-mineral inorganics in coal can occur as inorganic components dissolved in the pore water of the coal, elements held in an exchangeable relationship with particular organic compounds, and inorganic elements forming chelates and other organometallic complexes within the organic matter (Ward, 2002).

Decomposition of metal-organic compounds at higher rank may lead to crystalline mineral phases (Saxby, 2000).

A series of selective leaching processes combined with analysis of the leachate fractions has been used to examine the elements occurring in different ways within the non-mineral inorganic components (Li *et al.*, 2010; Ward, 1991, 1992). Material dissolved or potentially soluble in the pore water can be removed from the coal by water soaking, while exchangeable ions attached to components such as carboxylates can be removed by treatment with ammonium acetate. Soaking the coal in hydrochloric acid can be used to extract any acid soluble organometallic complexes from the maceral components. The concentration of each element in the individual leachates can be calculated, as a fraction of the original coal and compared with the total concentration of the same element in the coal as determined by ash analysis, in order to evaluate the modes of occurrence of the different non-mineral inorganics in coal samples. In addition, the minerals present in coal can also be determined by low-temperature ashing of the leached coal (Ward, 2002). It has been suggested that post-depositional factors, unrelated to the environments that produced different lithotype units of the coal seam, are the main processes that control the distribution of non-mineral inorganics within individual coal seams (Brockway and Borsaru, 1985).

TRACE ELEMENT IN COAL

Almost all of the elements in the periodic table are reported to be present in coal, although most are only at very low or trace concentrations (Finkelman, 1982). Elements occurring in coal at concentrations of less than 0.1% or less than 1000 ppm in general are categorized as trace elements (Finkelman, 1982).

The study of trace elements in coal has increased with increasing public awareness to the environmental impact of coal mining and combustion. Some trace elements in coal have been identified as

toxic materials. Information on the form in which particular elements are present is therefore significant in assessing the possible release of any toxic material to the environment during coal mining, preparation, storage or utilization (Finkelman, 1995; Vejahati *et al.*, 2010). There is a relationship between the minerals in coal and the concentration of its trace elements (Finkelman, 1995; Vejahati *et al.*, 2010; Ward, 2002). Some elements, for example Cr, F and Ga, are thought to be associated with clay minerals (Finkelman, 1995; Ward, 2002). Sulfide minerals are the likely site of As, Cd, Se, Ti, Hg, Pb, Sb and Zn, while the presence of Mn and Sr appears to be associated with carbonate minerals (Finkelman, 1995). Despite their inorganic affinity, the trace elements in coal may also possibly have an organic affinity. Organically combined trace elements are usually significant for coal with ash less than 5% (Finkelman, 1995). The organic affinity decreases with rank advance, while the abundance of many trace elements associated with the mineral matter increases as the coal rank increases (Finkelman, 1995).

METHODS FOR MINERAL MATTER ANALYSIS AND CHARACTERIZATION

Various analytical methods are available to characterize and determine the mineral matter in coal. A detailed overview of the methods used for coal mineral matter analysis can be found in Huggins (2002); Vassilev and Tascon (2003) and Ward (2002).

The first step of coal mineral matter characterization can be done using macroscopic observation. Information on color, hardness, visible texture, massive inclusion, partings, weathering or type of mineralization of coal sample studied can be examined using this type of observation. The result could be used to determine the type of method for further investigations. In general, analytical methods for mineral matter identification can be divided into three categories: (1) methods to measure elemental

concentrations in coal or ash (e.g.: X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA), inductively coupled plasma atomic emission spectrometry (ICP/AES), atomic absorption spectrometry (AAS) or mass spectrometry methods, (2) methods to determine mineralogical components (e.g.: X-ray diffraction (XRD), infra-red spectroscopy, low temperature ashing (LTA), coal petrography or scanning electron microscopy), and (3) methods to determine modes of elemental occurrence (e.g.: leaching schemes, electron microprobes or float sink analysis).

WORK ON MINERAL MATTER ON COAL

In the literatures there are several comprehensive reviews of the nature, occurrence, analysis and significance of mineral matter in coal (Finkelman, 1994; Huggins, 2002; Saxby, 2000; Vassilev and Tascon, 2003; Vassilev and Vassileva, 1996; Vejahati *et al.*, 2010; Ward, 2002).

Several studies provide information about the occurrence and abundance of minerals in coal, including how these minerals were incorporated into the coal forming system (Finkelman, 1994; Harvey and Ruch, 1986; O'Gorman and Walker, 1971; Renton, 1982; Ward, 1984). Some works also discussed the relative timing of coal mineralization in relation to the coalification process, and the genetic processes that are responsible for the occurrence of particular minerals in coal and coal seams (Harvey and Ruch, 1986; Renton, 1982; Ward, 1984, 1991, 1992; Ward *et al.*, 1999).

The influence of igneous intrusions on the mineral matter in coal has become a subject of particular study (Finkelman *et al.*, 1998; Susilawati and Ward, 2006; Ward *et al.*, 1989) as well as the mineralogy of tonsteins and the influence of pyroclastic activity on the coal forming environment (Burger *et al.*, 1990; Hill, 1988; Knight *et al.*, 2000; Simas *et al.*, 2013; Spears, 2011). Many studies also focused on understanding mineral matter in lower rank coals (Benson and Holm,

1985; Kiss and King, 1979; Miller and Given, 1986; Ward, 1991, 1992). It has been noted that the different types of non-mineral inorganics, including the nature and concentration of metal cations contained in the organic components of the coal may potentially provide a source of cations for later mineral precipitation (Ward, 1991, 1992). The geochemistry of the inorganic constituents of some lower rank coals in the USA are provided by Miller and Given (1986) while Li *et al.* (2001); Li *et al.* (2010) have also examined the process of leaching associated with coal formation, which is believed to be responsible for the unusually low ash yield of the thick coals in New Zealand. Many studies also put attention to the mode of occurrence of mineral and trace elements in coal as well its significance related to coal utilization (Finkelman, 1982; Li, 2002; Meij and te Winkel, 2009; Shaver *et al.*, 2006; Vejehati *et al.*, 2010; Wang *et al.*, 2008; Ward *et al.*, 1999).

The most widely used method for coal mineral matter characterization is XRD. Many studies have used XRD method and combine it with mineral quantification using specific software (Susilawati and Ward, 2006; Ward, 1992; Ward *et al.*, 1999; Ward *et al.*, 2001b). LTA is one of the techniques that have been used to characterize and analyze mineral matter in coal (Li *et al.*, 2010; Miller and Given, 1986; Pietrzak and Wachowska, 2003; Soong and Gluskoter, 1977; Ward, 1991). Selective leaching of the non-mineral inorganics combined with chemical analysis of the leachates has been used to examine the abundance and form of particular non-mineral inorganic elements (Benson and Holm, 1985; Li *et al.*, 2001). The mineral matter in peat and coal has also been characterized using the scanning electron microscope (Creelman and Ward, 1996; Singh *et al.*, 2015). Along with the scanning electron microscope, electron microprobe methods have also been employed to determine the composition of particular minerals in coal polished sections (Patterson *et al.*, 1994; Zodrow and Cleal, 1999) as well as to

investigate the relationship between the organic constituents and the mineral matter in coal (Ward and Gurba, 1999; Ward *et al.*, 2006). Many studies also explored the influence of mineral matter to coal utilization (Chang *et al.*, 2004; Keller *et al.*, 2014; Maldonado-Hódar *et al.*, 1995) and examined the effect of trace element present in coal to the environment (Cabon *et al.*, 2007; Clemens *et al.*, 2000; Finkelman, 1995; Hwang *et al.*, 2001; Kolker and Finkelman, 1998; Kolker *et al.*, 2009).

CONCLUSION

The term “mineral matter” was widely used to describe all of the inorganic non-combustible material that is in or associated with coal. This definition includes all the elements in coal, except the *organically combined* carbon, hydrogen, oxygen, nitrogen and sulfur. However, the *inorganic combinations* of C, H, O and S that are found in coal are also considered to be part of the mineral matter. The terms “minerals” and “non-mineral inorganics” are also used by researchers. The first is used to describe the discrete inorganic grains and the second is used to describe dissolved ions, inorganic components in the pore water and organically combined inorganic material.

The minerals exist in coal as a result of processes that occurred throughout the entire history of coal formation. Water and wind can introduce solid particles to the peat swamp or coal seam to produce “detrital” mineral matter. On the other hand, chemical, physical, biochemical and physicochemical processes may form “authigenic” minerals. In terms of when it is formed, mineral matter in coal can be classified into “syngenetic” mineral matter, which formed at the same time as coal formation and may have some relationship to rank advance, and “epigenetic” minerals, which were introduced to the coal seam after the formation of the coal.

Better knowledge of the mineral matter in coal is important in order to

maximize the use of coal for many purposes, from scientific studies through commercial applications.

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