

Analysis and significance of mineral matter in coal seams

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Abstract

The material described as “mineral matter” in coal encompasses dissolved salts in the pore water and inorganic elements associated with the organic compounds, as well as discrete crystalline and non-crystalline mineral particles. A range of technologies, including but not restricted to low-temperature oxygen-plasma ashing, may be used to evaluate the total proportions of minerals and other inorganic constituents in a coal sample. The relative proportions of the individual minerals in the coal may be further determined by several different techniques, including Rietveld-based X-ray powder diffractometry, computer-controlled scanning electron microscopy (CCSEM), and normative interpretation of chemical analysis data. The mode of occurrence of particular minerals may be evaluated by optical or electron microscopy techniques.

The minerals in coal may represent transformed accumulations of biogenic constituents such as phytoliths and skeletal fragments, or they may be of detrital origin, introduced as epiclastic or pyroclastic particles into the peat bed. Other minerals are produced by authigenic precipitation, either syngenetically with peat accumulation or at a later stage in cleats and other pore spaces by epigenetic processes. They may represent solution and reprecipitation products of biogenic and detrital material, or they may be derived from solutions or decaying organic matter within the peat bed. Non-mineral inorganics may be derived from a range of subsurface waters, and possibly redistributed within low-rank seams by post-depositional ion migration effects. They may also be expelled in different ways from the organic matter with rank advance.

Quantitative analysis of minerals and other inorganics contributes significantly to defining coal quality. It may also be useful as an aid to stratigraphic correlation, either between seams in a coal-bearing sequence or between sub-sections within an individual coal bed. Mineralogical analysis may help in identifying the mode of occurrence and mobility of particular trace elements, including potentially toxic components such as arsenic and mercury. Knowledge of the mineral matter can also be used to evaluate the behaviour of particular coals in different utilization processes, including the processes that control the characteristics of fly ashes, slags and other combustion by-products.

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1. Introduction

Coal can be regarded for many purposes as consisting of two classes of material: organic components or macerals on one hand, and a range of minerals and other inorganic constituents, broadly referred to as “mineral matter”, on the other. The organic compo-

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nents are fundamental to defining the nature of coal (e.g. rank and type), and to its value in different utilization processes (e.g. Ward, 1984; Taylor et al., 1998). All of the benefits derived from coal, including its energy output on combustion, its role in metallurgical processing, its capacity for in-situ methane absorption, and its potential as an alternative hydrocarbon source, are derived essentially from the maceral constituents.

The inorganic fraction typically contributes little if anything to the value of the coal in utilization activities. At best it is a diluent, displacing more useful organic matter with a non-combustible component that leaves an ash residue when the coal is burned, or that needs to be removed as slag from the blast furnace during metallurgical processing. Mineral matter may also be a source of unwanted abrasion, stickiness, corrosion or pollution associated with coal handling and use. Most of the problems associated with coal utilization arise in some way from the incorporated mineral matter (e.g. Gupta et al., 1999b), rather than directly from the maceral components.

From the genetic point of view, the mineral matter in coal, like the organic matter, is a product of the processes associated with peat accumulation and rank advance, as well as changes in subsurface fluids and other aspects of sediment diagenesis. Although much is gained from petrographic or chemical study of the organic constituents, the mineral matter in the coal also provides information on the depositional conditions and geologic history of coal-bearing sequences and individual coal beds.

2. The nature of mineral matter in coal

As defined by Gary et al. (1972), “mineral matter” refers to “the inorganic material in coal”. “Mineral matter” is more specifically defined by Standards Australia (1995, 2000) as representing “the sum of the minerals and inorganic matter in and associated with coal”. Similar definitions are provided by Harvey and Ruch (1986), and by Finkelman (1994). Such definitions embrace three fundamentally different types of constituents, namely:

- Dissolved salts and other inorganic substances in the coal’s pore water;
- Inorganic elements incorporated within the organic compounds of the coal macerals; and
- Discrete inorganic particles (crystalline or non-crystalline) representing true mineral components.

The first two forms of mineral matter are perhaps best described as non-mineral inorganics. Such constituents are usually prominent in the mineral matter of lower-rank coals, such as brown coals, lignites, and sub-bituminous materials (Kiss and King, 1977, 1979; Given and Spackman, 1978; Miller and Given, 1978, 1986; Benson and Holm, 1985; Ward, 1991, 1992). They also contribute significantly to ash formation in lower-rank coal deposits. Kiss (1982), for example, indicates that up to one-third of the ash produced by combustion of Australian brown coals may be derived from fixation of organic sulphur by calcium, sodium, or magnesium originally present in non-crystalline form, rather than as direct residues of the coal’s mineral particles.

Expulsion of moisture (along with any associated materials in solution) and changes in the chemical structure of the organic matter usually combine to remove the non-mineral inorganics from coal with rank advance. Non-mineral inorganics are therefore typically present in relatively low proportions, if at all, in bituminous coals and anthracites. Discrete inorganic particles, or minerals, may occur in both lower-rank and higher-rank coals. In the absence of non-mineral inorganics they are the dominant if not the sole component of the mineral matter in higher-rank coal deposits.

Coals produced by operating mines typically contain additional mineral constituents derived from bands and other concentrations of non-coal material within the seam. They may also possibly contain some fragments of non-coal rock derived from contamination of the mined product by roof or floor strata. This portion of the mineral matter (sometimes referred to as extraneous mineral matter) may be at least partly removed by cleaning processes in coal preparation plants. There is, nevertheless, usually a significant level of mineral matter intimately associated with the macerals, sometimes referred to as inherent mineral matter, that cannot effectively be removed by coal preparation techniques. Inherent mineral matter is an unavoidable part of even the cleanest coal product, and must be taken into account along with the

macerals in assessing the coal's behaviour during handling, storage, and use.

3. Methods for mineral matter analysis

3.1. Determination of mineral matter content

A number of different techniques have been used to determine the percentage of mineral matter (as opposed to ash) in a coal sample. Data from mineral matter determinations are used, for example, to express other analytical results for the coal to a mineral-matter-free basis, such as might be needed for classification purposes.

3.1.1. Calculation from chemical analysis

One of the earliest approaches to mineral matter determination was to calculate the percentage of mineral matter from a combination of the ash yield of the coal and the proportions of other key inorganic constituents in the coal sample. Methods of this type include formulae proposed by Parr (1928) and King et al. (1936), both of which are summarized in Table 1. The formula of King et al. (1936), known as the King–Maries–Crossley or KMC formula, is the more comprehensive of these two computations, taking into account the carbonate carbon, chlorine, pyritic and sulphate sulphur contents of the coal and the proportion of sulphur

retained in the coal ash, as well as the percentage of ash itself. The Parr formula is simpler, and is based only on the coal's ash yield and total sulphur content. Given and Yarzab (1978), however, have suggested a modification to the traditional Parr formula, incorporating pyritic sulphur and chlorine rather than total sulphur, as indicated also in Table 1.

The use of such formulae in different contexts is reviewed by Rees (1966), Scholz (1980), and Hoefft et al. (1993). A similar approach has been taken by Pollack (1979), who used normative analysis methods to calculate the total mineral matter percentage from the proportions of the different inorganic elements found by chemical analysis in the coal sample. Such methods are, however, based on assumptions regarding the nature of the minerals in coals generally, and therefore do not necessarily give a precise estimate of the actual proportion of mineral material present.

Another method suggested for higher-rank coals involves digestion of the mineral components in hydrochloric and hydrofluoric acids (Radmacher and Mohrhauer, 1955), and regarding the proportional loss in mass as representing the mineral matter content. Sequential digestion of the coal in solutions including hydrochloric, nitric and hydrofluoric acids, combined with analysis of the respective leachates, has also been used by several workers (e.g. Finkelman et al., 1990; Dale et al., 1993; Palmer et al., 1993; Laban and Atkin, 1999) for selective extraction of the major and trace elements associated with different forms of mineral matter in coal samples.

3.1.2. Oxidation of the organic matter

Heating of the coal in air for a protracted period at around 370 °C has also been used by different authors (e.g. Hicks and Nagelschmidt, 1943; Nelson, 1953; Brown et al., 1959) to determine the percentage of minerals in the sample by destroying the organic matter. Although the temperature is not as high as that used for conventional ash determination (750 to 815 °C), it is still sufficiently high for many minerals, such as pyrite, siderite and some clay minerals, to undergo irreversible changes of mass and/or crystal structure (Ward et al., 2001a). Corrections can be applied to allow for some of these changes (Brown et al., 1959), but even so the mass percentage remaining after such heating is still not necessarily a reliable measure of the total mineral content.

Table 1

Formulae for calculating mineral matter percentages from other analytical data

King–Maries–Crossley (KMC) formula

$$MM = 1.13 A + 0.5 S_{\text{pyr}} + 0.8 \text{CO}_2 + 2.85 S_{\text{SO}_4} - 2.85 S_{\text{ash}} + 0.5 \text{Cl}$$

(King et al., 1936)

Parr formula

$$MM = 1.08A + 0.55 S \text{ (Parr, 1928)}$$

$$MM = 1.13A + 0.47 S_{\text{pyr}} + 0.5 \text{Cl (Given and Yarzab, 1978)}$$

Where: MM = percentage of mineral matter in coal; A = percentage ash yield from coal; CO₂ = percent carbonate carbon dioxide yield from coal; S_{pyr} = percent pyritic sulphur in coal; S_{SO₄} = percent sulphate sulphur in coal; S_{ash} = percent sulphur in coal ash; S = percent total sulphur in coal; Cl = percent chlorine in coal.

Several minor modifications to the KMC formula have also been published.

Isolation of the minerals from higher-rank coals without major alteration can be achieved by ashing the coal at low temperature (120–150 °C) in an electronically excited oxygen plasma (Gluskoter, 1965; Miller, 1984). This probably represents the most reliable method for determining the percentage of total mineral matter in higher-rank coals (Frazer and Belcher, 1973; Standards Australia, 2000). The use of hot, concentrated hydrogen peroxide to remove the organic matter and isolate an unaltered mineral fraction (Nawalk and Friedel, 1972; Ward, 1974) represents a useful substitute in some circumstances, but has more limited overall application. Any carbonate minerals, for example, may be dissolved in organic acids produced from the coal during its peroxide-induced oxidation (Ward, 1974). Pyrite in the coal, if present, may also cause spontaneous decomposition of the peroxide and cessation of the oxidation process.

Precise determination of the mineral matter percentage in coal by low-temperature ashing also involves correcting the oxygen-plasma ash yield for any un-oxidised organic carbon residues, and for any sulphur fixed in the LTA from the organic sulphur component (Standards Australia, 2000). These are often relatively small corrections, however, and for many purposes the proportion of low-temperature ash (LTA) gives an adequate indication of the percentage of mineral matter present.

3.1.3. *Separate determination of non-mineral inorganics*

Low-temperature ashing and computations from ash percentage are less useful for lower-rank coals, where non-mineral inorganics can form a significant part of the total mineral matter. Interaction may occur between the non-mineral inorganic elements and components such as organic sulphur in the course of the ashing process, producing solid residues, such as calcium, iron, or ammonium sulphates. These residues represent artifacts of the ashing, rather than constituents actually found in the coal in mineral form. Although the non-mineral inorganics are also part of the mineral matter, they occur within the coal in a different way to that suggested by the artifacts produced from the ashing technique.

Determination of the total percentage of mineral matter, especially in lower-rank coals, must therefore take into account the nature and relative abundance

of non-mineral inorganics, as well as the minerals in the coal sample. The non-mineral inorganics include exchangeable ions attached to carboxylates and metallic elements in organometallic complexes, as well as any dissolved salts in the (often abundant) pore water.

Selective leaching of the non-mineral inorganics may be combined with chemical analysis of the leachates to determine the abundance and form in which particular elements occur (e.g. Miller and Given, 1978, 1986; Benson and Holm, 1985; Ward, 1991, 1992). Low-temperature ashing of the leached coal residues provides a more definitive assessment of the minerals present, without contamination by mineral artifacts produced in the ashing process. Although non-mineral inorganics can also produce minor proportions of artifacts in ashing of higher-rank coals (e.g. Ward et al., 2001a), a combination of selective leaching with low-temperature ashing of the coal after leaching usually provides a better assessment of the mineral matter in lower-rank coals than the direct application of low-temperature ashing techniques.

3.2. *Megascopeic and microscopeic methods*

Some of the mineral matter in coal occurs as bands, lenticles, cleat infillings, and other megascopeic masses visible at a macroscopic or hand specimen scale. These may include permineralised wood fragments and peat masses in the coal, as well as mineral-rich laminae, concretions, and nodules within the organic matter (e.g. Beeston, 1981; Scott, 1990; Sykes and Lindqvist, 1993; Scott et al., 1996; Zodrow and Cleal, 1999; Greb et al., 1999). Other megascopeic occurrences of mineral matter can be seen with a hand lens, in X-radiographs of drill cores (Jones, 1970), or in more sophisticated images derived from X-ray tomography techniques (Simon et al., 1997; Van Geet et al., 2001). Mineral matter dissolved in the pore water (including water in cleats and other fractures) is also sometimes precipitated when the water evaporates from the coal in exposed outcrops, drill cores or mine faces. Ward (1991), for example, describes gypsum deposited on exposed coal surfaces in an open-cut lignite mine in northern Thailand, apparently from evaporation of Ca-bearing moisture in the coal seams.

Much of the crystalline mineral matter in higher-rank coals occurs in masses too small to be seen with

the naked eye, but in a form that can be seen under the optical or electron microscope. Microscopically visible mineral matter includes fine layers and other concentrations intimately intergrown with the maceral components, as well as discrete mineral fragments or crystals and a range of nodules, lenticles, veins, pore infillings and cell replacement structures (Kemezys and Taylor, 1964; Diessel, 1992; Taylor et al., 1998). Although some assistance might be provided by staining methods (Warne, 1962), the identity of the minerals is not always apparent from optical studies, especially for quartz, carbonates and clay minerals. However, the textural relationships revealed by microscopy often indicate how the mineral material may have formed, or how it might respond to coal preparation and utilization processes.

The proportions of microscopically visible minerals in a coal sample may be evaluated in conjunction with microscopic point count analysis used to determine the relative percentages of the different maceral components (Taylor et al., 1998; Standards Australia, 1998). Comparative studies (e.g. Ward et al., 1996) suggest that the total mineral percentage determined by point counting may be around half the total percentage of mineral matter in the same coals indicated by low-temperature ashing (Fig. 1). This may in part reflect the difficulty of distinguishing small mineral particles as separate entities in point-count studies. However, the mineral percentages determined

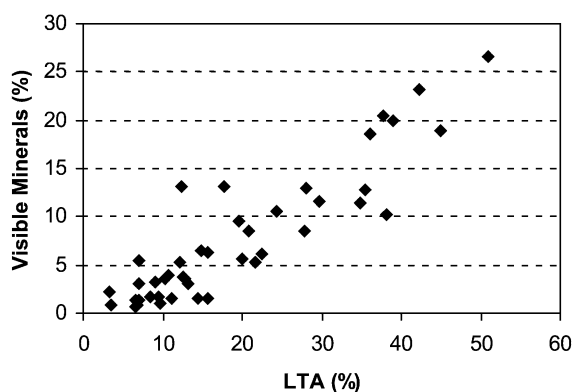


Fig. 1. Correlation between volumetric percentage of microscopically visible minerals identified in point counting and mass percentage of low-temperature ash (LTA) for a range of Australian coal samples (after Ward et al., 1996).

by point counting are volumetric percentages, whereas the mineral matter determined from low-temperature ashing is measured as a mass percentage. The density of the minerals in coal is typically around twice that of the organic particles, and even higher for sulphides such as pyrite. Conversion of the volumetric percentages of mineral matter in the point count data to mass percentages for silicate-rich materials therefore involves approximately doubling the volumetric percentage values (Davis, 1984). At least for the samples in Fig. 1, such multiplication of the microscopic mineral percentages suggests that point counting provides a basis for assessing the overall proportion of minerals in polished sections that is broadly consistent with independent LTA determinations.

The difference between point count mineral abundance and the corresponding LTA percentage, even after adjustment of the point count values for density effects, is greater in Fig. 1 for coals with relatively low LTA and visible mineral percentages. Many samples with less than 5 vol.% visible minerals, for example, have more than 10 wt.% low-temperature ash yields. This may reflect the occurrence of small mineral particles within the coal macerals, which may be overlooked as part of the point counting process. Such particles are likely to represent a significant proportion of the total mineral matter in relatively clean coals, appearing in the LTA but not among the minerals identified by point-count techniques. Unless the LTA percentage is increased due to the production of mineral artifacts from organically associated inorganic elements, low-temperature ashing thus probably provides a more complete assessment of the total mineral percentage in low-ash coal samples than point counting.

3.3. Scanning electron microscopy

Mineral particles in coal can be investigated by scanning electron microscope and similar techniques (e.g. Stanton and Finkelman, 1979; Russell and Rimmer, 1979; Allen and Vander Sande, 1984; Corcoran, 1989; Martinez-Tarazona et al., 1992; Kwiecinska et al., 1992; Hower et al., 1994, 2000; Ward et al., 1996; Finkelman et al., 1998). Electron microscopy may be used either on polished sections or on broken coal surfaces. Identification of the minerals in coal can be aided by accessory X-ray fluorescence analysers to

identify the elements in particular mineral masses. Automatic collection of elemental data from coal sections using scanning electron microscopy (SEM) techniques, combined in some cases with image analysis methods, can also be used to evaluate the nature and distribution of minerals in coal using computer-controlled scanning electron microscopy (CCSEM) and related techniques (Straszheim and Markuszewski, 1990; Galbreath et al., 1996; Gupta et al., 1999a).

CCSEM is a widely used technique for determining the size, association, composition and abundance of minerals in coal, particularly for purposes associated with coal utilization (e.g. Wigley et al., 1997; Wigley and Williamson, 1998; Gupta et al., 1998; Virtanen et al., 1999). Details of the principal methods used are given by Galbreath et al. (1996). In the most common configuration the electron beam is stepped across a polished coal surface in an SEM operating in backscattered electron (BSE) mode, and mineral grains (as distinct from organic matter) identified at points where the BSE response rises above a predetermined threshold. The particle size is measured from the geometry of the area with the elevated BSE signal, after which an energy-dispersive X-ray spectrum is acquired from the centre of that area. The intensity of the X-ray emissions from key mineral-forming elements is measured, and the particles classified into several mineral categories based on the indicated chemical composition. The volumetric and hence weight proportions of the different minerals are measured to give an estimate of the various mineral percentages.

A special variety of the CCSEM technique is QEM*SEM (quantitative evaluation of materials by scanning electron microscopy), described by Creelman et al. (1993) and Creelman and Ward (1996). This technique determines the association of chemical elements at individual points on a coal polished section from the output of several X-ray analysers directed at each point in a controlled scan under the SEM. The element association at each point is then processed through a species identification program to determine, from the elements present, the mineral or mineral group represented at that particular data point. Data from numerous such points in the scan are integrated to give a volumetric assessment of the relative proportions of the different minerals or ele-

ment-associations present in the coal sample. Other image analysis functions, such as determination of size and shape distributions, can also be applied to the mineral particles in the coal using the QEM*SEM technique.

An international comparison of several different CCSEM techniques, including QEM*SEM, as a basis for determining mineral percentages in coal, is discussed by Galbreath et al. (1996). A generally low level of inter-laboratory reproducibility was indicated by this study, particularly for clay minerals such as kaolinite, highlighting the need for development of standardized calibration procedures for the CCSEM technique.

3.4. *Electron microprobe analysis*

More precise determination of the composition of particular minerals may also be obtained from electron microprobe analysis of polished coal sections, using methods outlined by Reed (1996). Electron microprobe techniques have been applied to the study of minerals in coal by authors such as Minkin et al. (1979), Raymond and Gooley (1979), Patterson et al. (1994, 1995), and Zodrow and Cleal (1999). Kolker and Chou (1994) used an X-ray fluorescence synchrotron microprobe, which offers better detection limits than the more conventional electron microprobe technique, to investigate trace elements in carbonate veins of Illinois Basin coal seams.

Patterson et al. (1994, 1995) used electron microprobe techniques to determine the composition of the different carbonate mineral phases in a range of Australian coal seams. Three main types of carbonate material were found: early-formed siderite nodules varying from essentially pure FeCO_3 to siderite with significant proportions of Mg and/or Ca; later-stage veins of essentially pure calcite; and veins of dolomite–ankerite, ranging from essentially pure dolomite ($\text{CaMg}(\text{CO}_3)_2$) to an iron-rich ankerite with a composition of $\text{Ca}(\text{Mg}_{0.4}\text{Fe}_{0.54}\text{Ca}_{0.06})(\text{CO}_3)_2$.

Zodrow and Cleal (1999) found that an essentially pure siderite, with only minor Mg and/or Ca, was the initial mineral deposited during plant permineralization associated with the Foord seam in Canada. This was followed by deposition of ferroan dolomite and ankerite in various modes of occurrence, each with a wide range of Ca, Mg and Fe contents.

3.5. X-ray diffraction analysis

The identity of the crystalline minerals in coal can also be investigated by subjecting powdered coal samples or minerals isolated from the coal (e.g. LTA residues) to study by X-ray diffraction (XRD) techniques. Indeed, XRD was one of the first techniques to be applied for definitive identification of the minerals in coal samples (e.g. Mitra, 1954; Rekus and Haberkorn, 1966; Gluskoter, 1967; O’Gorman and Walker, 1971).

Although long established as a definitive tool for mineral identification, XRD has generally been regarded as having a limited value for quantitative determination of mineral proportions. Variations in mineral crystallinity, preferred orientation in the sample mount, and differential absorption of X-rays by the minerals in the mixture, for example, may affect the XRD pattern produced (Moore and Reynolds, 1997). Several methods have nevertheless been developed over the years, mainly on a semi-quantitative basis, to study the minerals in coal samples (e.g. Rao and Gluskoter, 1973; Ward, 1977, 1978, 1989; Russell and Rimmer, 1979; Renton, 1986). These have mainly been based on powder diffraction patterns obtained after adding a known mass of mineral spike to an LTA sample, and evaluating the intensity of key peaks for each mineral in relation to the intensity of a key peak from the mineral spike added (e.g. Klug and Alexander, 1974).

Rao and Gluskoter (1973), Ward (1977), and Harvey and Ruch (1986) used interpretations based on XRD data from spiked LTA samples, supplemented by quantitative evaluation of clay mineral proportions based on XRD analysis of clay-fraction concentrates subjected to glycol and heat treatment, to study the distribution of major minerals in individual coal seams of the Illinois Basin, USA. The number of minerals that can be incorporated in such a study, however, is limited, due to the need to prepare calibration curves for each individual mineral component prior to evaluation of the spiked sample traces. There are, moreover, a number of different methods that may be used in XRD analysis based on peak intensity (Renton et al., 1984), and variations in methodology may give rise to substantial variations in estimated mineral percentages. Such variations were noted, for example, in an interna-

tional study of duplicate samples subjected to mineral matter analysis by different laboratory groups (Finkelman et al., 1984), suggesting a need for more reliable quantitative XRD procedures in LTA analysis.

3.5.1. Rietveld XRD analysis techniques

The full profile of an XRD pattern provides considerably more information for mineral quantification than the intensities of particular diffractogram peaks. Rietveld (1969) has developed a formula to give the intensity at any point in the diffraction trace of a single mineral, with information on how to refine relevant crystal structure and instrumental parameters by least-squares analysis of the profile. A total of 14 different parameters were identified, including the mineral scaling factor, asymmetry, preferred orientation, half-width, instrument zero, line shape, and unit-cell parameters.

Although originally used to facilitate refinement of XRD patterns to allow for crystallographic variations, Rietveld methodology has been used more recently to quantify the proportions of individual minerals in powdered mineral mixtures (e.g. O’Connor and Raven, 1988; Taylor, 1991; Bish and Post, 1993). Such an approach allows a calculated XRD profile of each mineral (or phase) to be generated from its known crystal structure. The sum of the calculated patterns for each mineral can then itself be calculated, and fitted to the observed XRD profile of a multi-mineral sample by iterative least-squares analysis to find the optimum individual phase scales for best overall fit. The optimum phase scales are then used to determine the percentages of the different minerals present in the sample.

One of the more comprehensive methods for using X-ray diffractometry in this way is SIROQUANT, a personal computer software system described by Taylor (1991). In its present form, SIROQUANT allows the proportions of up to 25 different minerals in a mixture to be quantified from a conventional X-ray powder diffractometry pattern using Rietveld techniques. The different crystallographic parameters for each mineral can be adjusted interactively, to allow for variations due to atomic substitution, layer disordering, preferred orientation and other factors in the standard patterns used. Ward et al. (1999b) give additional details of SIROQUANT operation.

The SIROQUANT technique has been applied to analysis of the minerals in both LTA and whole-coal samples by authors such as Mandile and Hutton (1995), Ward and Taylor (1996), and Ward et al. (1999a, 2001a). Independent checks against other analytical data, including comparison of the inferred chemical composition of the mineral assemblage indicated by the SIROQUANT analysis to the actual chemical composition of the ash for the same coal samples (Ward et al., 1999a, 2001a), have confirmed the consistency of the SIROQUANT evaluations. The inferred mineral compositions were adjusted in these studies to allow for loss of CO₂, H₂O and S from relevant minerals at the high temperatures associated with ash formation, after which the inferred ash compositions gave good agreement to the actual ash analyses of the coals concerned.

Specific examples of such evaluations include a study of the Argonne Premium Coals (Ward et al., 2001a), where XRD analysis based on SIROQUANT determinations was applied to low-temperature (oxygen-plasma) ash (LTA), to ash prepared by heating the coal in air at 370 °C, and to the raw coal itself. In the raw coal analysis the high level of background radiation due to the organic matter was removed from the XRD trace using SIROQUANT functions, and the percentages of the different components determined as fractions of the total crystalline mineral matter. Background was also removed from the diffractograms of the two different types of ash samples, but this was less difficult than for the whole coals due to the higher peak-to-background ratios involved.

Analysis of raw coals avoids the need for a preliminary ashing process, but is less sensitive than analysis of mineral concentrates, such as LTA residues, to minerals present in low proportions in the coal samples. It may also be difficult to distinguish irregularly interstratified clay minerals from the organic background in some instances. The results for analysis of the different types of material were nevertheless found by Ward et al. (2001a) to be broadly consistent with each other, allowing for mineralogical changes induced by the different sample preparation processes. They were also found to be consistent with the chemistry of the coal ash, and with other values such as pyritic sulphur content, published in the relevant data set (Vorres, 1989).

French et al. (2001b) have used the same Rietveld-based technique to determine both the overall percentage of crystalline mineral matter and the relative proportions of each mineral by direct XRD powder analysis of whole-coal samples. Based on XRD traces derived from chemically demineralised coals, structure models were separately developed for the organic matter of coals at different rank levels. Incorporation of an appropriate coal structure model into the Rietveld analysis process allowed the proportion of organic matter to be quantified as if it was another, albeit poorly crystalline, “mineral” phase. Processing of whole-coal XRD patterns in this way was found to give a percentage of organic matter, and hence of mineral matter in the samples studied, consistent with independent LTA evaluations. The relative proportions of the different minerals indicated by the whole-coal analysis using SIROQUANT were also found to be consistent with SIROQUANT analysis of LTA from the same coal samples.

3.6. *Other analytical methods*

A wide range of other techniques have been used to identify the minerals in coal, and in some cases also to estimate the relative proportions of each mineral present. Thermal analysis techniques have been used by authors such as Warne (1964, 1975), O’Gorman and Walker (1973), Mukherjee et al. (1992), and Vassilev et al. (1995) to identify minerals in whole-coal and LTA samples. Although subject to some difficulties in obtaining appropriate reference standards (Finkelman et al., 1981), Fourier-transform infrared (FTIR) spectrometry has been used by Painter et al. (1978, 1981) to help assess mineral percentages on a quantitative basis.

Computation of mineral percentages from ash or whole-coal chemical analysis data, using normative procedures (Pollack, 1979; Cohen and Ward, 1991), may also be used to estimate both mineral percentages and the total proportion of mineral matter in coal samples. Such techniques are inherently based on assumptions concerning the mode of occurrence of the different inorganic elements, and are improved if the nature of the mineral matter is known from independent sources such as microscopic observation, SEM studies, chemical leaching, or qualitative XRD interpretation. Normative methods provide a basis for

quantitative interpretation of ash analysis records in mineralogical terms, and, given the wide availability of ash analyses from many exploration programs and coal quality studies, normative evaluations of chemical data may provide a useful alternative for some purposes to direct mineralogical investigation.

4. Minerals in coal and LTA residues

The most common minerals in coal are quartz, clay minerals (especially kaolinite, illite and interstratified illite/smectite), feldspars, carbonates such as siderite, calcite and dolomite, and sulphide minerals such as pyrite (Mackowsky, 1968; Ward, 1978; Harvey and

Ruch, 1986; Palmer and Lyons, 1996). These and other minerals are summarized in Table 2. Minor but sometimes significant accessories include phosphate minerals, such as apatite or aluminophosphates of the crandallite group (Ward, 1974; Finkelman and Stanton, 1978; Cressey and Cressey, 1988; Ward et al., 1996; Rao and Walsh, 1997, 1999), titanium minerals such as anatase (Dewison, 1989), and aluminocarbonates such as dawsonite (Loughnan and Goldbery, 1972). Other carbonate minerals, such as strontianite (SrCO_3), witherite (BaCO_3) and alstonite ($\text{BaCa}(\text{CO}_3)_2$) have been found in coals of the Hunter Valley of Australia by Tarriba et al. (1995). The zeolite mineral analcime has been noted in a low-rank coal from the western USA (Triplehorn et al., 1991; Ward

Table 2
Principal minerals found in coal and LTA (compiled from various sources)

Silicates		Carbonates	
Quartz	SiO_2	Calcite	CaCO_3
Chalcedony	SiO_2	Aragonite	CaCO_3
Clay minerals:		Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Ankerite	$(\text{Fe,Ca,Mg})\text{CO}_3$
Illite	$\text{K}_{1.5}\text{Al}_4(\text{Si}_{6.5}\text{Al}_{1.5})\text{O}_{20}(\text{OH})_4$	Siderite	FeCO_3
Smectite	$\text{Na}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$	Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$
Chlorite	$(\text{MgFeAl})_6(\text{AlSi})_4\text{O}_{10}(\text{OH})_8$	Strontianite	SrCO_3
Interstratified		Witherite	BaCO_3
Clay minerals		Alstonite	$\text{BaCa}(\text{CO}_3)_2$
Feldspar	KAlSi_3O_8 $\text{NaAlSi}_3\text{O}_8$ $\text{CaAl}_2\text{Si}_2\text{O}_8$	Sulphates	
Tourmaline	$\text{Na}(\text{MgFeMn})_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{OH})_4$	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	Bassanite	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
Clinoptilolite	$(\text{NaK})_6(\text{SiAl})_{36}\text{O}_{72} \cdot 20\text{H}_2\text{O}$	Anhydrite	CaSO_4
Heulandite	$\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O}$	Barite	BaSO_4
Sulphides		Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
Pyrite	FeS_2	Rozenite	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
Marcasite	FeS_2	Szomolnokite	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
Pyrrhotite	$\text{Fe}_{(1-x)}\text{S}$	Natrojarosite	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$
Sphalerite	ZnS	Thenardite	Na_2SO_4
Galena	PbS	Glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$
Stibnite	SbS	Hexahydrite	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
Millerite	NiS	Tschermigite	$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
Phosphates		Others	
Apatite	$\text{Ca}_5\text{F}(\text{PO}_4)_3$	Anatase	TiO_2
Crandallite	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$	Rutile	TiO_2
Gorceixite	$\text{BaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$	Boehmite	Al-O-OH
Goyazite	$\text{SrAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$	Goethite	$\text{Fe}(\text{OH})_3$
Monazite	$(\text{Ce,L a,Th,Nd})\text{PO}_4$	Crocoite	PbCrO_4
Xenotime	$(\text{Y,Er})\text{PO}_4$	Chromite	$(\text{Fe,Mg})\text{Cr}_2\text{O}_4$
		Clausthalite	PbSe
		Zircon	ZrSiO_4

et al., 2001a), and another zeolite, clinoptilolite, in a Turkish lignite (Querol et al., 1997) and a Canadian coal seam (Pollock et al., 2000).

Other accessories, usually only at trace levels or in localised concentrations, include sulphides such as sphalerite (Hatch et al., 1976; Hower et al., 2001), stibnite (Karayigit et al., 2000), millerite (Lawrence et al., 1960), marcasite, chalcopyrite and galena (Kemezs and Taylor, 1964), as well as the lead selenide clausthalite (Hower et al., 2001), and the lead chromate mineral crocoite (Li et al., 2001). Chromite (Ruppert et al., 1996; Pollock et al., 2000), and rare-earth phosphates such as monazite and xenotime (Finkelman and Stanton, 1978), are also reported in some coal samples. Vassilev et al. (1994) list a number of other minerals found in high-ash coals of Bulgaria, with notes on their mode of occurrence. Many of the more unusual minerals reported in coal, however, are noted only from optical or electron microscope studies; they are not always sufficiently abundant to be identified from XRD analysis of whole coal or isolated mineral fractions.

Iron sulphate minerals such as (natro)jarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$) and coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) may also be found in coal and LTA. These minerals are usually thought to represent oxidation of sulphide components, such as pyrite, during coal exposure or storage (Rao and Gluskoter, 1973).

Calcium and other sulphates, including bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), and tschermigite ($\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), may be found in the LTA residues produced from some coals, particularly lower-rank materials such as lignites (e.g. Foscolos et al., 1989; Ward, 1991, 1992). The bassanite may represent partly dehydrated gypsum, with the gypsum being produced by reactions between calcite and sulphuric acid and the acid being produced by oxidation of pyrite in the coal with storage (Rao and Gluskoter, 1973; Pearson and Kwong, 1979). However, many bassanite-yielding coals are low in pyrite and also devoid of calcite. The bassanite in such cases may possibly be formed by precipitation and dehydration of gypsum, following evaporation of the pore water during sample drying. Alternatively, and perhaps more commonly, bassanite and other sulphates may represent artifacts produced in the plasma ashing process, formed by interaction between the organic sulphur in the coal and Ca, Mg or other

elements occurring as inorganic components of the organic matter.

Calcium oxalates such as whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), found in the residues of some coals after oxidation by hydrogen peroxide (Ward, 1974), may be produced in a similar way. The whewellite in peroxide residues may be either a product of interaction between calcite in the coal and oxalic acids formed during the peroxide oxidation process, or a product of interaction between the oxalic acid and organically associated Ca in the maceral constituents.

Although mineral artifacts derived from the non-mineral inorganics are common components of some LTA residues, especially those derived from low-rank coals, they are generally not detected by XRD analysis of equivalent raw coal samples (e.g. Ward et al., 2001a). The only exception could be any crystalline materials precipitated from the pore water of the coal during drying of the samples prior to XRD analysis. Gypsum formed by evaporation of pore water in fractures and on other surfaces of some exposed low-rank coals (Kemezs and Taylor, 1964; Ward, 1991) provides an example of a crystalline mineral apparently produced in this way.

5. Processes of mineral formation

Apart from artifacts produced by oxidation of the organic matter in the course of low-temperature ashing, or by drying out of coals with high moisture contents, the minerals occurring in coal may form by a range of different processes (Davis et al., 1984). These include input of fragmental sediment into the original peat-forming environment by epiclastic and pyroclastic processes (e.g. Triplehorn, 1990; Ruppert et al., 1991), accumulation of skeletal particles and other biogenic components within the peat deposit (Raymond and Andrejeko, 1983), and precipitation of material from solution in the peat swamp or in the pores of the peat bed. They also include precipitation of minerals in pores, cleats and other fractures of the coal by post-depositional processes (Cobb, 1985). Non-mineral inorganics, which are also part of the mineral matter, may be concentrated in different parts of low-rank, water-filled coal seams by post-depositional ion migration effects (Brockway and Borsaru, 1985).

5.1. Detrital minerals

Some of the mineral matter in coal represents material washed or blown as detrital fragments into the accumulating peat deposit (Davis et al., 1984). This includes components from river water and flood inputs, airborne dust, etc., introduced by epiclastic processes, and volcanic debris introduced to the peat from pyroclastic activity.

5.1.1. Epiclastic sediment

The vegetation in and around the peat swamp is thought to act as a filter, preventing some of the sediment carried in rivers and other water bodies from penetrating beyond the margins of the peat bed, or

from clastic sources within the peat-forming environment such as intra-seam channel-fill bodies (Ruppert et al., 1991). Acid or saline waters in the swamp may also cause flocculation of clays and other suspended mineral particles, further reducing clastic dispersal. The relative elevation of raised mire environments (McCabe, 1984) is another factor that may prevent water-borne sediment from penetrating very far into some areas of peat accumulation.

Minerals of epiclastic origin may include silt to sand-sized fragments of quartz and sometimes feldspar (Kemezys and Taylor, 1964; Ruppert et al., 1991), along with fine, often irregular bands made up mainly of clay minerals (Fig. 2A). Ruppert et al. (1991) indicate that detrital quartz in the Upper

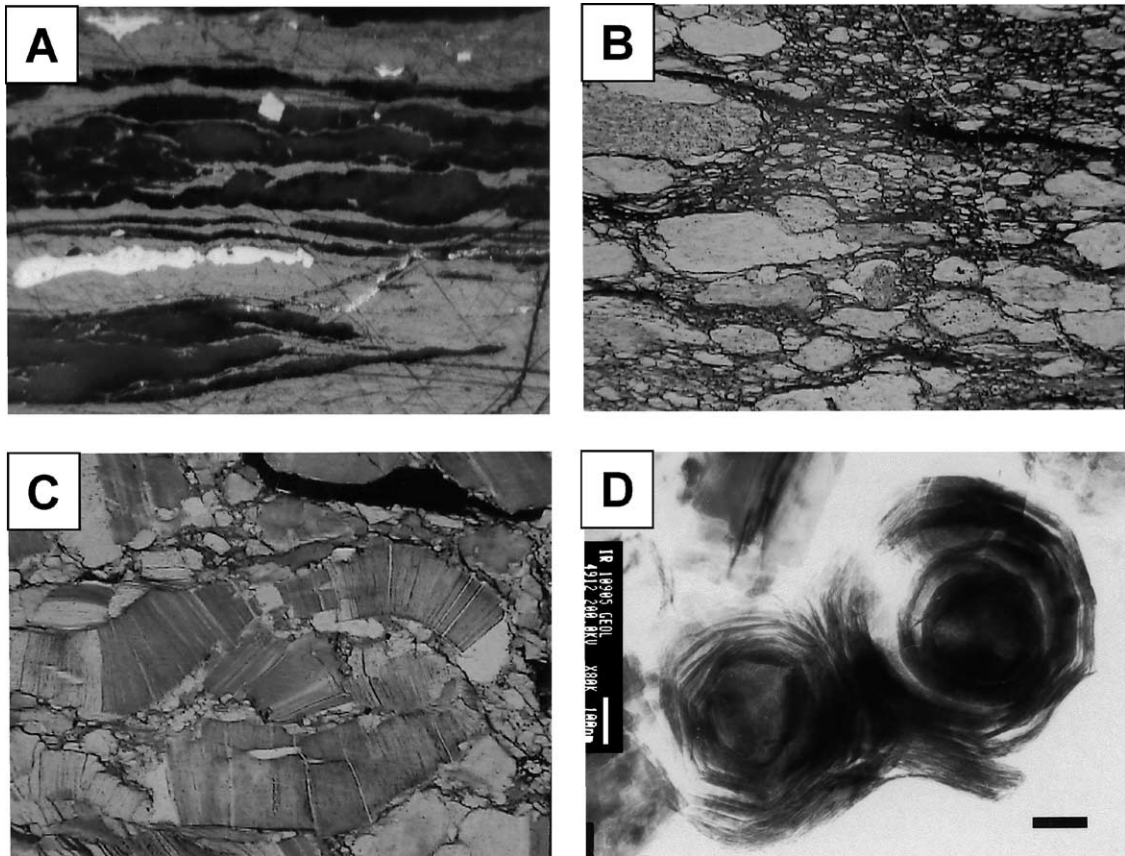


Fig. 2. Mode of occurrence of detrital and authigenic minerals in coal and tonstein, as seen using optical and electron microscopy. (A) Clay-rich laminae (dark colour) of probable detrital origin in coal polished section (field width 1.4 mm). (B) Pelletal texture in a tonstein associated with coal, Bowen Basin, Australia (field width 1.4 mm). (C) Vermicular kaolinite aggregates in a tonstein, Bowen Basin, Australia (field with 1.4 mm). (D) Spherical halloysite aggregates isolated from coal of the northern Sydney Basin (Australia) and viewed under TEM (after Ward and Roberts, 1990); scale bar represents 100 nm (0.1 μm).

Freeport coal of the USA commonly has a positive spectral response to cathodoluminescence study, probably due to impurities or lattice defects, which is not found in quartz of authigenic origin. Davis et al. (1984) and Rimmer (1991) report a distinctive illite polymorph in several eastern US coals, which is also thought from its crystal structure to be of detrital origin.

X-ray diffraction studies of seam profiles commonly show mineral matter assemblages in the basal parts of seams that are similar to those found in the lutites underlying the coal bed, rather than the typically more simple mineral assemblages found higher within the seam section. Illite and interstratified clays, for example, along with small proportions of poorly ordered kaolinite, are commonly found in the basal parts of Sydney Basin coal seams (Ward, 1989), whereas well ordered authigenic kaolinite, with minimal proportions of illite and other clays, makes up most of the mineral matter over the remainder of the seam thickness. The clay mineral distribution in such cases is interpreted as representing admixture of detrital sediment with the organic debris as peat was beginning to accumulate, but exclusion of detrital material after the swamp had become more fully established. Alternatively, it may represent greater opportunities for alteration of the detrital input, if any, as peat-forming conditions became dominant and more widespread in the overall depositional system.

Davis et al. (1984) indicate that significant proportions of detrital minerals are found in the basal parts and near the margins of peat beds in the Okefenokee swamp-marsh complex, occurring mainly as well-rounded grains from 10 μm to over 300 μm in size. Some of the quartz is thought to have been transported by water flow from the swamp margin, and some introduced to the peat by mixing with the sediment of the swamp floor. Mixing of peat and swamp floor sediment is thought to have arisen from a combination of bioturbation and contemporaneous clastic deposition early in the history of peat accumulation.

5.1.2. Tonsteins

Sedimentary particles blown by winds into the swamp, including air-borne material of pyroclastic origin, may penetrate more extensively into the peat-forming environment than other fragmental sedi-

ment. Such materials include the extensive deposits of altered volcanic ash found in some coal seams, referred to as tonstein deposits (Loughnan, 1971, 1978; Burger et al., 1990; Bohor and Triplehorn, 1993; Spears and Lyons, 1995; Hower et al., 1999). Tonsteins typically occur as thin but persistent bands in the host coal seams, and have been used in some areas to provide a basis for stratigraphic correlation (e.g. Burger and Damberger, 1985; Hill, 1988; Bohor and Triplehorn, 1993; Knight et al., 2000).

Although there is some controversy as to the actual definition of tonstein (Senkayi et al., 1984; Bohor and Triplehorn, 1993), these materials often consist almost entirely of well-ordered kaolinite (Loughnan, 1978). Remnant volcanic textures are sometimes preserved in tonsteins, indicating a pyroclastic origin. Kaolinite-rich materials may grade into or be associated with smectite-dominated claystones, referred to by some authors (e.g. Senkayi et al., 1984) as bentonite deposits. Bohor and Triplehorn (1993) distinguish these two types of material in non-marine strata, including coal measures, as kaolinitic tonsteins and smectitic tonsteins, respectively, and restrict the term bentonite to deposits formed in more marine settings. Spears et al. (1999a,b) regard tonsteins as equivalent to kaolinitic bentonites. Whether kaolinite or smectite occurs as the dominant component may reflect contrasts in the nature of the original volcanic ash material, or it may represent different interactions of the tuffaceous sediment with the final depositional environment. Bohor and Triplehorn (1993), among others, suggest that the thickness of the individual ash bed may also play a part; thin beds and the margins of thicker beds are commonly kaolinised, whereas thicker ash layers are often richer in smectitic clay minerals.

An extensive literature exists on tonsteins in coal-bearing sequences, much of which is summarized by Bohor and Triplehorn (1993). As well as the different clay minerals (kaolinite, smectite, or in some cases interstratified illite/smectite), they may also contain bipyramidal crystals of β quartz, euhedral zircons, and phosphate minerals such as crandallite, xenotime and monazite. A range of textures is also developed, including tonsteins dominated by rounded clay pellets (Fig. 2B) or more angular intraclast-like brecciated fragments, by euhedral or vermicular crystals (Fig.

2C), by infillings of plant tissues, and by fine grained and massive, apparently featureless, sediment. They may occur as separate beds within coal-bearing sequences, or they may occur as thin but often persistent bands within individual coal seams.

Intra-seam tonstein bands may be incorporated with mined coal products, and if not removed in the preparation plant, become part of the coal when it is used. Similar volcanic debris to that which forms tonstein bands may also be more intimately admixed with the peat, and with burial the originally pyroclastic sediment will become part of the inherent mineral matter in the coal seam. Crowley et al. (1993), for example, describe the interplay of epiclastic and pyroclastic inputs in the formation of a Powder River Basin coal seam. Indeed, in the absence of sediment influx from rivers and other sources, contemporaneous volcanic sediment may represent the dominant source of clastic mineral matter in thick and extensive coal beds.

As another example of volcanic input, Ward and Roberts (1990) have noted the presence of small aggregates of spherical halloysite (Fig. 2D) in a TEM study of a number of coal seams from the Sydney Basin (Australia). The aggregates are found mainly in coals from the northern part of the basin, close to the contemporaneous and then volcanically active New England Orogen, and are thought to represent fine particles of volcanic glass altered by contact with the waters of the peat swamp.

Not all thin but persistent bands of clay and similar non-coal material, however, necessarily represent pyroclastic deposits. Other processes that may form intra-seam bands of non-coal material include input of clastic sediment from river floods or alluvial fan outwash in upland environments, and from washover processes or sea level changes in coastal settings. Bands produced by these processes may more closely resemble the epiclastic sediment of the associated roof and/or floor strata, and be able to be distinguished from horizons of volcanic origin by mineralogical or textural features (e.g. Ward, 1989). Residual concentrations of mineral matter, including material originally formed by biogenic processes or authigenic precipitation (see below), as well as minerals of epiclastic or pyroclastic origin, may also be developed with degradation of the peat bed (e.g. exposure at low water levels), and removal of the organic matter by oxidation or fire activity (Davis et al., 1984).

5.2. Biogenic minerals

Many of the minerals in coal, or at least in modern-day peat deposits, result directly from biological activity in the peat swamp (Raymond and Andrejeko, 1983; Davis et al., 1984). These include skeletal fragments from diatoms, molluscs and other organisms, minerals formed within living plant tissues (phytoliths), and possibly minerals deposited in the peat swamp as faecal pellets.

The siliceous skeletons (frustules) of diatoms, and also possibly siliceous sponge spicules, are abundant in a number of modern-day peat deposits (Raymond and Andrejeko, 1983; Davis et al., 1984). However, these biogenic particles are composed essentially of amorphous silica, rather than crystalline quartz, and are relatively soluble in water. They commonly show signs of degradation with time, and may be corroded and partly dissolved in older peat accumulations. Although sponge spicules have been reported in coals in some instances (e.g. Warwick et al., 1997), siliceous biogenic remains are not readily recognised as separate entities in the mineral matter of coal seams.

Calcareous shells may also be present within or closely associated with coal beds (e.g. Ward, 1991; Kortenski, 1992). Ward (1991), for example, has noted thin fossiliferous limestone bands, composed almost entirely of mollusc fragments (Fig. 3A), within the Tertiary coal seams of the Mae Moh basin in Thailand. As well as calcite, these contain aragonite, a metastable CaCO_3 polymorph commonly found in modern day mollusc shells that reverts to calcite over geological time. The coals in question were formed in an intermontane basin, probably in a lacustrine environment; the shell-rich bands are therefore thought to represent deepening of the swamp water, which drowned the accumulating peat and replaced its floral ecosystem with a deeper-water faunal accumulation.

Many of the plants forming modern-day peats contain accumulations of silica as phytoliths within the vascular structure (Raymond and Andrejeko, 1983). These mineral accumulations may remain within the plant tissue as it forms the peat deposit. However, they may also be released in solution with plant decay (Davis et al., 1984), and either be lost from the depositional system or reprecipitated as authigenic silica in other parts of the peat deposit.

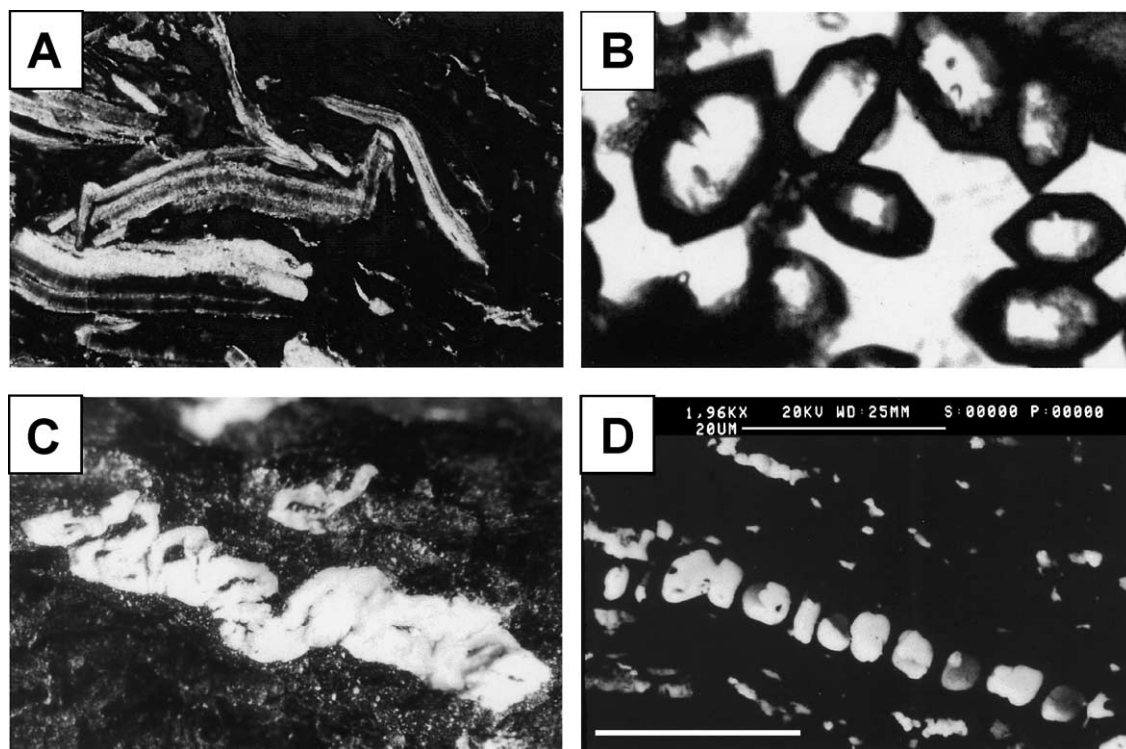


Fig. 3. Mode of occurrence of biogenic and authigenic minerals in coal, as seen by optical and electron microscopy: (A) Shell fragments in thin section of coal from Mae Moh Basin, Thailand (after Ward, 1991); field width 1.5 mm. (B) Bipyramidal quartz crystals isolated from a South Australian lignite (after Ward, 1992); field width 0.6 mm. (C) Vermicular aggregate of kaolinite crystals in the bedding plane of a coal from the Surat Basin, Australia (after Ward, 1989); field width 3.5 mm. (D) Apatite cell infillings in a polished section of a Queensland coal under SEM examination (after Ward et al., 1996); scale bar represents 20 μm .

5.3. Syngenetic mineral precipitates

Minerals formed by crystallization in place (i.e. authigenic minerals), either within the peat deposit at or shortly after its formation (primary or syngenetic precipitates), or in the cleats and fractures of the coal after compaction and probably rank advance (secondary or epigenetic precipitates), are a very common component of coal seams. Primary precipitates include siderite nodules, microcrystalline pyrite framboids, and a range of cell and pore infillings (typically kaolinite, quartz, phosphate minerals, and pyrite). Cleat infillings can include calcite, dolomite, ankerite and siderite, as well as pyrite, marcasite, apatite, dawsonite, illite, and chlorite.

5.3.1. Syngenetic quartz accumulations

In addition to fragments that are clearly of detrital origin, quartz is commonly found as cell and pore infillings in the organic matter of coal, a mode of occurrence that clearly indicates an authigenic precipitation process (Sykes and Lindqvist, 1993). Fine-grained quartz, thought from its lack of response to cathodoluminescence to be of authigenic origin, is also common in the interior parts of the Upper Freeport coal seam, in areas devoid of more luminescent detrital quartz grains (Ruppert et al., 1985, 1991).

Detailed accounts of authigenically precipitated quartz in New Zealand coals are given by Lindqvist and Isaac (1991) and Sykes and Lindqvist (1993), where quartz has filled the cell cavities of plant tissues

at an early stage of peat development. The origin of the silica that formed the quartz is uncertain, but it may have been derived from leaching of the basement rocks or released from siliceous phytoliths within the peat-forming plant tissues.

Ward et al. (1997) describe quartz-rich phases in some Australian coal seams, which may give rise to frictional ignition of methane in underground mining operations. In at least one such case the quartz has infilled the cells and other spaces of the plant tissue prior to compaction, and has produced a locally permineralised peat accumulation. The quartz-rich coal in this instance occurs immediately beneath intra-seam claystone bands apparently of pyroclastic origin, and it is possible that the infilling quartz represents silica released by alteration of volcanic glass, feldspars, and other minerals in the pyroclastic sediment, due to interaction of the tuff with the waters of the peat swamp environment. The silica would then have been re-precipitated in the pores of the peat, immediately below the introduced pyroclastic material.

Euhedral crystals of quartz have also been isolated from coal by low-temperature ashing and similar processes. Described in different coal deposits by Baker (1946), Sykes and Lindqvist (1993), and Ward (1992), the crystals commonly have a doubly terminated bipyramidal form (Fig. 3B). Similar euhedral quartz crystals, 10–80 μm in size, are noted by Vassilev et al. (1994) in a Bulgarian coal. Although they may possibly represent crystals introduced to the peat from volcanic sources, the absence of volcanic material in some of the associated sequences (e.g. Ward, 1992), together with the development of prism faces on the quartz crystals as well as the bipyramids, suggests that they represent authigenically precipitated material, grown from solution in the pores of the peat deposit. Quartz crystals in tonsteins, which are regarded as being of direct volcanic origin (β quartz), typically have only a bipyramidal form (Bohor and Triplehorn, 1993), without the additional prism face development.

5.3.2. Syngenetic clay minerals

X-ray diffraction studies show that kaolinite is a very common constituent of many coal seams (e.g. Gluskoter, 1967; Rao and Gluskoter, 1973); indeed, along in some cases with quartz, it may make up

almost all of the mineral matter (e.g. Ward, 1978). As with much of the quartz in some coals, the kaolinite may also occur in the pores and cell cavities of the coal macerals (e.g. Balme and Brooks, 1953; Kemezys and Taylor, 1964). Kaolinite in coal may also occur as vermicular aggregates of individual crystals, deposited within the peat bed (Fig. 3C). Authigenic kaolinite may also occur in tonstein beds, as vermicular aggregates and as replacements of plant tissue (Bohor and Triplehorn, 1993). While poorly ordered kaolinite may be the dominant kaolinite type in the lutites forming the roof and floor of individual seams, the kaolinite in the coal itself, as well as in many associated tonstein bands (if present), typically has a well ordered crystal structure (Ward, 1978, 1989; Dewison, 1989).

Following suggestions made by Spears (1987), precipitation of kaolinite in the pores of coal macerals may be explained by changes in pH conditions within the peat bed. Low pH conditions ($\text{pH} < 3$) may develop in parts of the peat subject to oxidation. Although normally insoluble over the natural pH range, Al is soluble under such low pH conditions (Loughnan, 1969). The higher solubility would allow the Al to be leached from any detrital mineral material (including volcanic ash) and transferred with the acidified swamp water to other parts of the peat deposit. Development of organometallic complexes by interaction of partly degraded aluminosilicates with the swamp environment could also assist the Al mobilization process.

Movement of leachates formed in this way to areas with a higher pH would cause the Al to be precipitated, initially forming bauxite-group minerals such as gibbsite and boehmite. Although small proportions of boehmite are found in the LTA of some coal samples (Ward, unpublished data), gibbsite is unstable in the presence of silica (Loughnan, 1969). Interaction of the precipitated alumina with any silica in solution would therefore result in the formation of authigenic kaolinite. The well-ordered structure probably developed in the kaolinite as a result of the precipitation conditions.

In the absence of significant detrital input, and where low proportions of pyrite or carbonate minerals (see below) are present, quartz and well-ordered kaolinite may represent the dominant form of mineral matter in the coal, a situation not uncommon in Australian coal beds (e.g. Ward, 1978, 1989; Ward

and Taylor, 1996). Despite being dominated by silicates in both instances, the mineral matter of the coal in such seams provides a marked contrast to the quartz-rich sediments, with a greater diversity of clay minerals, which form the non-coal lutites in the immediately overlying and underlying sedimentary successions.

The increased abundance of certain trace elements associated with kaolinite in a British coal seam (Dewison, 1989) suggests that the kaolinite, although ultimately precipitated by authigenic processes, may have been sourced from volcanic material input to the original peat deposit. The abundance of kaolinite in coal may thus be linked in some instances to contamination of the peat-forming environment by the same type of volcanic material responsible for tonstein formation, accompanied by remobilization and reprecipitation in the pores of the peat deposit.

5.3.3. *Syngenetic phosphate minerals*

A range of phosphate minerals can also occur in coals, including apatite as well as aluminophosphates of the crandallite group (e.g. Ward, 1974, 1978; Finkelman and Stanton, 1978; Cressey and Cressey, 1988; Crowley et al., 1993; Ward et al., 1996; Rao and Walsh, 1997, 1999). Although skeletal fragments and possibly coprolite particles rich in phosphate may be present in some cases (Diessel, 1992), optical and electron microscope studies (Cook, 1962; Ward et al., 1996; Rao and Walsh, 1999) indicate that the phosphates and aluminophosphates in many coals occur as cell and pore infillings (Fig. 3D), and thus represent mineral deposits syngenetically precipitated in the peat bed. High phosphorus concentrations, moreover, are commonly found only at particular horizons in individual coal seams (Ward et al., 1996; Rao and Walsh, 1999).

Crandallite-group minerals are also found in a number of different tonstein bands associated with coal (e.g. Wilson et al., 1966; Loughnan, 1971; Hill, 1988; Spears et al., 1988; Bohor and Triplehorn, 1993), suggesting a direct association with volcanic input to the coal seam. Phosphorus-rich horizons in some coal seams may, for example, represent intervals during which particular abundances of phosphorus-enriched volcanic material were deposited. However, Spears et al. (1988) indicate that volcanic sources alone may be inadequate to supply the phosphorus

required, and suggest derivation of much of the phosphorus from other materials, possibly the organic matter of the peat bed.

Phosphorus is an abundant element in many present-day plants (Francis, 1961), but is released from the plant structure, remobilized and in many cases reprecipitated elsewhere in the peat bed by processes associated with organic decay (Swain, 1970). Ward et al. (1996) also suggest that phosphorus occurring in plant tissues is released into the swamp or peat waters by decay processes associated with peat formation. Additional P release may be associated with alteration of any volcanic ash that is introduced to the peat deposit. Movement of the dissolved P through the swamp or the peat bed, followed by precipitation in places with appropriate peat-water chemistry, may then give rise to re-concentration within the coal seam. Rao and Walsh (1999) suggest, on the basis of the associated coal type, that thin but persistent layers with a high phosphorus (crandallite) content in Alaskan coal seams represent horizons where the peat was oxidized by drying out in response to periods of lowered water table. Aluminophosphate minerals would be expected from intra-seam precipitation if Al was also available in reactive form at the site of phosphate deposition (Ward et al., 1996), and apatite if Al was not available to react with the precipitated phosphatic material.

5.3.4. *Syngenetic pyrite and marcasite*

Pyrite is a common mineral in many coal seams, especially those of Carboniferous age in Europe and North America (e.g. Gluskoter et al., 1977; Harvey and Ruch, 1986; Spears, 1987). Much of this pyrite occurs in intimate association with the organic matter, and clearly represents sulphide mineralization formed during or very shortly after peat accumulation. Other sulphides also occur as epigenetic veins that formed later in the coal's burial history. Although there may be a gradation between syngenetic and epigenetic sulphides, the epigenetic processes are discussed separately elsewhere in this paper.

Pyrite and other sulphide minerals (marcasite, pyrrhotite, sphalerite, etc.) have been the focus of many studies of coal mineral matter, including the works of Rao and Gluskoter (1973), Ward (1977), Frankie and Hower (1987), Querol et al. (1989), Hower and Pollock (1989), Renton and Bird (1991), and Korten-

ski and Kostova (1996). Syngenetic pyrite can occur as framboids, as euhedral crystals, as anhedral crystals infilling or replacing coal macerals, and as more massive pyrite accumulations. Marcasite, where present, can also occur in radiating crystalline masses, isolated or aggregated crystals, or in massive form (Querol et al., 1989).

Framboids are small, polycrystalline aggregates of pyrite, spherical in shape, ranging from 1 to 100 μm across. They are usually intimately associated with the macerals of the coal deposit, occurring for example within individual vitrinite bands (Fig. 4A). SEM study shows the framboids to be made up of small euhedral crystals, with the crystals aggregated into an overall spherical form. As discussed by Kortenski and Kostova (1996), they may represent pyritised bacteria, algal cells or fungal spores, or they may represent inorganic precipitates from mineral solutions.

Pyrite may also occur as a cell and pore infilling (Fig. 4B), or a replacement of the maceral components. Other forms include individual and clustered euhedral crystals, isolated anhedral, and massive but internally crystalline accumulations. Special terms, such as “specular pyrite” (Hower and Pollock, 1989) and “fibrous pyrite” (Querol et al., 1989), are also used to describe particular modes of pyrite occurrence.

Syngenetic pyrite in coal is thought mainly to represent sulphide material precipitated by interaction of dissolved iron with H_2S , the H_2S having been produced by bacterial reduction of sulphate ions in the reducing environment of the peat deposit (Williams and Keith, 1963; Querol et al., 1989). The sulphate may be introduced from the water filling the swamp itself, or from waters that permeate the peat bed after its deposition. Influxes of fresh water during peat formation, such as around contemporaneous channel-fill deposits, may be associated with lower proportions of pyrite in the mineral matter than areas of the seam in which marine conditions have had a more intense influence (e.g. Rao and Gluskoter, 1973). Renton and Bird (1991) suggest that sulphide precipitation is favoured by high pH (>4.5) in the peat swamp, whereas at lower pH bacterial reduction is suppressed and lesser proportions of sulphide minerals are formed.

The water in which the sulphate occurs may be sea water, and the presence of syngenetic pyrite is often taken as an indicator of coal formation under the

influence of marine conditions. However, syngenetic pyrite may also be abundant in coals formed in lacustrine and similar environments having no obvious connection to the sea (e.g. Ward, 1991), suggesting that sulphate-rich lake waters or sulphate-rich groundwaters, as well as marine influxes, may be involved in the pyrite production process.

Although of the same chemical composition, marcasite is distinguished from pyrite by its crystal structure (and XRD pattern), and by its optical properties. Querol et al. (1989) describe marcasite of apparently syngenetic origin in a series of Spanish coal samples, occurring as radiating crystals grown on and often also coated by pyrite, as replacements and cementing materials of pyrite framboids, as isolated euhedra, and as massive cell infillings. The factors controlling precipitation of marcasite rather than pyrite are not well defined, but Querol et al. (1989) suggest that lower pH in the micro-environment of precipitation may play a significant part. Other possible factors, discussed by Querol et al. (1989), include the presence of particular trace elements (e.g. Mn, As, Pb), and a deficit of sulphur in the aqueous precipitation system.

5.3.5. Syngenetic siderite and other carbonates

Syngenetically formed accumulations of siderite may also be found in coal, intimately admixed with the organic matter. Siderite occurrences include nodules with a typical radiating crystal structure (Fig. 4C), as well as infillings and replacements of the maceral components (Kortenski, 1992; Zodrow and Cleal, 1999).

Siderite, if present, is commonly found in the mineral matter of coals that have minimal proportions of syngenetic pyrite, such as many of the coal seams of the Sydney–Bowen Basin in eastern Australia (Ward, 1989; Ward et al., 1999a). In some cases, however, the siderite may be associated with syngenetic pyrite crystals as well (e.g. Kortenski, 1992). An abundance of syngenetic siderite is usually thought to indicate deposition of the coal mainly under non-marine conditions, or at least under the influence of swamp or formation waters with a low sulphate content. Iron in solution that would otherwise combine with bacterially produced H_2S appears instead to combine with dissolved CO_2 , released by fermentation of the organic matter (Gould and Smith, 1979).

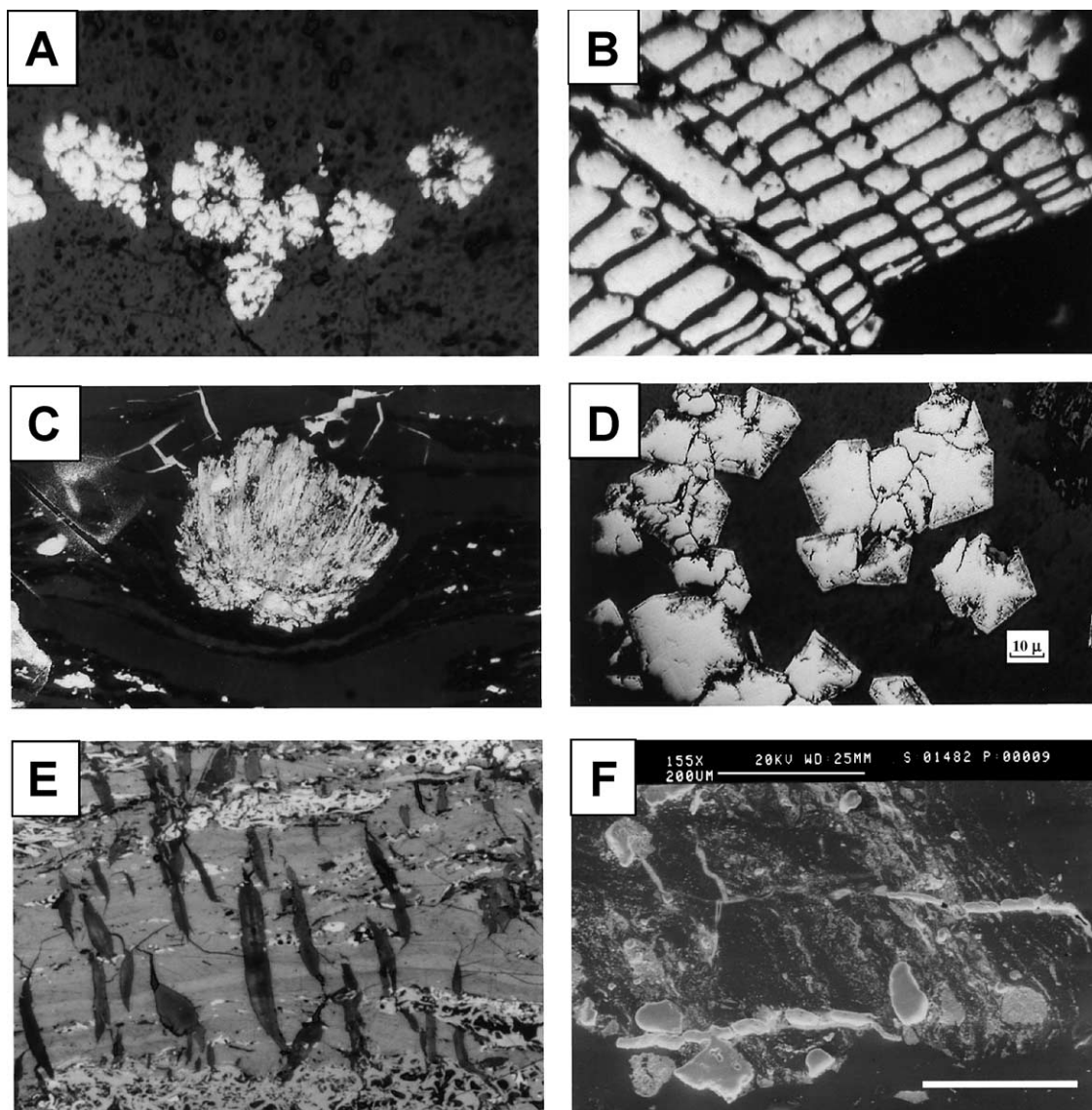


Fig. 4. Mode of occurrence of authigenic and epigenetic minerals in coal, as seen using optical and electron microscopy. (A) Spheroidal nodules of pyrite in polished section of a coal from the Gunnedah Basin, Australia (photo L.W. Gurba); field width 0.2 mm. (B) Cell-cavity infillings of pyrite in polished section of a Gunnedah Basin coal (photo L.W. Gurba); field width 0.2 mm. (C) Thin section of a siderite nodule in a coal, Moreton Basin, Australia; field width 1 mm. (D) Euhedral crystals of epigenetic marcasite in polished section cut parallel to a cleat infilling, showing individual crystals grading to pyrite and/or intergrown with quartz, Sydney Basin, Australia (photo M. Drazovic); scale bar represents 10 μ m. (E) Polished section of calcite veins in vitrinite bands of a coal from the Sydney Basin, Australia, showing en-echelon, sigmoidal form of veins and fibrous pattern of crystal growth; field width 1 mm. (F) Scanning electron micrograph showing apatite veins in a polished section of a coal from the Bowen Basin, Australia (after Ward et al., 1996); scale bar represents 200 μ m.

Larger, spheroidal to irregular masses of syngenetic minerals, mainly calcite but also including siderite, dolomite, pyrite and quartz, occur in some seams

as coal balls (Scott, 1990; Scott et al., 1996; Greb et al., 1999). Ranging up to 300 mm or so in diameter, these mineral accumulations are generally regarded as

representing concretions formed in the peat bed, either during plant deposition or after early diagenesis (Scott et al., 1996). The majority of coal balls appear to form in paralic basins, with carbonate precipitation probably arising from mixing of different peat waters (Greb et al., 1999). Zodrow and Cleal (1999) describe the mineralogy of a concretion formed by dolomitization of early-formed siderite plant infillings, associated with a Canadian coal seam.

5.3.6. Syngenetic to epigenetic zeolites

Querol et al. (1997) have described the extensive development of zeolite minerals, analcime, clinoptilolite and heulandite (see Table 2 for chemical compositions), in a Turkish lignite deposit. The analcime occurs in vitrinite (detrohuminites), associated with syngenetic pyrite, as large round crystals 50–150 µm in diameter, typically with a hollow nucleus, and the clinoptilolite as smaller lath-shaped crystals 5–15 µm long. Both appear to be syngenetic minerals, possibly derived from interaction of Na or Ca-rich volcanic ash in the original peat with Na-rich formation waters under alkaline conditions. Triplehorn et al. (1991) and Ward et al. (2001a) also note the presence of analcime in low-rank coal from the western USA. Pollock et al. (2000) describe the presence of clinoptilolite in a Canadian coal seam, again apparently derived from alteration of volcanic ash material.

Veins, fracture fillings and root replacements of clinoptilolite, along with marcasite, are reported in a Texas lignite by Senkayi et al. (1987). The lignite is associated with tonstein beds, one of which, overlying the lignite, is also partly altered to clinoptilolite. Movement of siliceous groundwater from the tuff into the lignite is thought to have been responsible for clinoptilolite precipitation in the coal seam.

5.4. Epigenetic mineralization

A number of different minerals, including sulphides, carbonates, quartz and clay components, are found as post-depositional fracture infillings in coal seams. Most of the infillings are quite persistent, following the different cleat fractures within the coal. Such infillings represent minerals deposited in the cleat and other fractures after the coal had been almost fully compacted (Cobb, 1985), generated by fluids of different compositions and/or at different temperatures

moving through the cleated coal bed (Faraj et al., 1996; Hower et al., 2001).

5.4.1. Epigenetic sulphides

In addition to syngenetic precipitates, sulphide minerals may occur as epigenetic cleat and fracture infillings in coal seams (e.g. Querol et al., 1989; Demchuk, 1992; Kortenski and Kostova, 1996). The dominant sulphide mineral in these veins is usually pyrite, although marcasite (Fig. 4D), millerite (Lawrence et al., 1960), and sphalerite (Hatch et al., 1976) may be present in some instances instead.

Some epigenetic sulphide occurrences may represent remobilization of organic sulphur or syngenetic sulphides within the coal (Demchuk, 1992). Others may be the result of factors outside the original depositional system, such as nearby igneous intrusions, or caused by post-depositional fluid movement through the coal-bearing succession. Querol et al. (1989), Hower and Pollock (1989) and Hower et al. (2000) describe coals with multiple phases of sulphide mineralization, ranging from syngenetic framboids and euhedral crystals to syngenetic and/or epigenetic overgrowths, emplacements and fracture fillings. Querol et al. (1989), for example, have identified five stages in the syngenetic to epigenetic precipitation of pyrite and marcasite in a Spanish coal deposit.

Unlike most syngenetic pyrite, post-depositional sulphides are not necessarily an indication of marine influence on the formation of the coal seam. Karayigit et al. (2000), for example, describe stibnite (SbS), in addition to pyrite, calcite and quartz, occurring as epigenetic veins in a Turkish coal seam. The veins apparently formed as a result of hydrothermal processes that also gave rise to antimony deposits in the associated basement rocks.

5.4.2. Epigenetic carbonates

Carbonate minerals, such as calcite, dolomite, ankerite, and siderite, are common cleat infilling materials in coal seams (Kortenski, 1992; Patterson et al., 1994; Kolker and Chou, 1994). In some cases, the cleat fillings may show chemical variation, revealed using SEM or electron microprobe techniques. Shields (1994), for example, describes the presence of two separate carbonate phases in cleat fillings for coals of the central Sydney Basin, Australia; the main infilling consists of ankerite, but the

ankerite is bordered on both sides in some instances by calcite. Cathodoluminescence studies by Kolker and Chou (1994) indicate up to five separate stages in the formation of calcite veins in Illinois Basin coals, from early-formed material with a low to moderate Fe content to later-stage high-Fe calcite deposits. Isotope and fluid inclusion data, discussed by Kolker and Chou (1994), suggest formation temperatures of between 15 and 70 °C for the cleat-filling calcite in these Illinois Basin coal samples.

Other carbonate minerals that have been found to occur as cleat infillings include the sodium aluminocarbonate dawsonite (Loughnan and Goldbery, 1972), and Sr and Ba carbonates such as alstonite and witherite (Tarriba et al., 1995). Dawsonite is a widespread epigenetic mineral in the coal-bearing and marine strata of the Sydney–Bowen Basin, and is suggested by Baker et al. (1995) to have been deposited from an influx of magmatic CO₂ in the latter stages of the basin's burial history. The alstonite and witherite appear to have a more localized mineral source.

Hower et al. (2001) describe the formation of carbonate veins, with minor epigenetic pyrite, sphalerite and clausenthalite, cementing a brecciated coal from western Kentucky. The coal in this area has a higher vitrinite reflectance than the surrounding coals in the region, suggesting that hot fluid injection from the subsurface was responsible for emplacing the carbonates and other epigenetic minerals.

Carbonate vein infillings of a slightly different type occur in a coal seam of the northern Sydney Basin, Australia. These are represented by short, elliptical-shaped fracture fillings, often sigmoidal in shape, confined essentially to the vitrinite (especially telocollinite) bands (Fig. 4E). Further information on their form is given by Hutton and Doyle (1999).

The shape and orientation of these fractures suggest that they were formed by brittle failure of the vitrinite under a post-depositional stress pattern. The other macerals and microlithotypes seem to have behaved in a more ductile manner, and not fractured under the stress involved. The fractures are wider, but much less persistent than the cleat fractures in the coal, and are filled with calcite showing a fibrous crystal structure.

The individual fractures appear to be isolated, and it is difficult to visualise how the infilling carbonate could have migrated into them from an outside source.

One possibility is that the infillings were formed by expulsion of inorganically associated calcium from the organic components of the coal (see below), during the transition from low rank (e.g. lignite) to higher-rank (bituminous) material.

5.4.3. *Other epigenetic minerals*

Faraj et al. (1996) report the occurrence of authigenic illite, with some kaolinite and chlorite, in face cleats of coals from the Bowen Basin of Australia. Isotopic and other evidence indicates that epigenetic illite formation in this area took place in several discrete pulses, at temperatures ranging from 70–80 to 100–170 °C, and suggest the influence of hot post-depositional fluids on this particular phase of mineral formation. A range of carbonate minerals, including calcite, ankerite, siderite and ferroan calcite, also occurs in the butt cleats of the same coal seams. The carbonate minerals were apparently formed at lower temperatures than the silicates, with fluid inclusions suggesting deposition at temperatures of around 80 °C.

Several authors, including Juster et al. (1987), Daniels and Altaner (1993), and Ward and Christie (1994), have noted the presence of ammonium illite in or associated with coals of anthracitic to semi-anthracitic rank. Ammonium illite formation in such cases may be a result of interaction between nitrogen in the coal macerals and more normal potassium-bearing illite, or possibly between nitrogen and kaolinite, at the high temperatures associated with development of anthracite rank.

Phosphate minerals, including apatite, and in some cases crandallite-group minerals, can also occur as cleat and fracture fillings (Fig. 4F). These may represent local remobilization of phosphate formed earlier within the coal seam or associated strata (Ward et al., 1996). Hower et al. (1999) also note rare earth phosphate minerals, tentatively identified as monazite, in cracks and cell infillings beneath a tonstein in a Kentucky coal seam.

5.4.4. *Igneous intrusion effects*

Although the effects of igneous intrusions on the organic matter have been extensively studied (e.g. Taylor et al., 1998), only a few authors have investigated the effects of igneous intrusions on the inorganic matter of coal seams. Carbonate minerals, such

as calcite and dolomite, are often abundant in the coal around intrusive bodies, introduced as epigenetic minerals mainly from hydrothermal alteration of the igneous material (Kisch and Taylor, 1966; Ward et al., 1989; Querol et al., 1997; Finkelman et al., 1998). It is generally believed that CO and CO₂ derived from carbonization of the coal interact with fluids derived from the magma to produce this carbonate mineralization. Epigenetic pyrite is also developed adjacent to some intrusive bodies (e.g. Querol et al., 1997).

The minerals already present in the original coal may also be affected by the heat of such intrusions, as the organic matter is carbonized and converted into natural coke or “cinder”. Ward et al. (1989), for example, describe the formation of illite from epiclastic or pyroclastic smectite in an Australian coal at the contact with an igneous intrusive body. Although vitrinite reflectance studies indicate that temperatures in the coal further away from the contact were also high enough to have had an impact on the smectite, it appears that the actual formation of illite in this particular case occurred only when the thermally altered smectite could take up potassium from direct contact with the intrusive rock material. Although abundant well-ordered kaolinite also occurs in the unaffected parts of the seam, the kaolinite in the heat-affected coal is poorly ordered, possibly reflecting disruption of the kaolinite structure by heat from the intrusion, followed by rehydration under conditions that allowed only poorly ordered material to form.

Kwiecinska et al. (1992) also report the development of illite close to an igneous dyke in a Polish coal seam. The illite in this coal occurs as fibrous crystals, the form of which suggests a maximum temperature of 550–650 °C for the mineralization process. The additional occurrence of kaolinite platelets in the carbonized coal is further suggested to indicate a maximum formation temperature of around 575 °C. Querol et al. (1997), on the other hand, note an absence of crystalline kaolinite or illite in carbonized coal near an intrusive contact in a Chinese occurrence, and suggest that the collapse of clay mineral structures found in a normal state elsewhere in the coal indicates formation temperatures of at least 950 °C.

Pyrite in the coal may be altered to pyrrhotite by intrusive effects. Kwiecinska et al. (1992) describe a steady decrease in the S/Fe ratio for iron sulphides in a

Polish coal with increasing proximity to the intrusive body, consistent with progressive replacement of pyrite by a pyrrhotite material. Based on textural features of the sulphides and on experimental data from other studies, Kwiecinska et al. (1992) suggest that the conversion of pyrite to pyrrhotite took place, possibly in localized hot-spots, at a minimum temperature of around 750 °C.

Querol et al. (1997) also note the development of pyrrhotite, together with the calcium sulphide mineral oldhamite (CaS), in laboratory coal pyrolysis processes. Some well-crystallized CaSO₄ is noted by Kwiecinska et al. (1992) in the carbonized coal from Poland, suggesting that sulphur released by pyrrhotite formation may have been taken up by Ca and precipitated as part of the alteration process.

5.5. *Non-mineral inorganics*

Particularly in lower-rank coals (sub-bituminous coals and lignites), a significant part of the mineral matter may be represented by inorganic elements associated with the organic constituents. Such occurrences include inorganic components dissolved in the pore water of the coal, elements held in exchangeable relationships with particular organic compounds (e.g. carboxylates), and inorganic elements forming chelates and other organometallic complexes within the organic matter (Miller and Given, 1978).

The elements occurring in different ways within the non-mineral inorganic fraction may be removed from the coal by a series of selective leaching processes (Miller and Given, 1978; Benson and Holm, 1985; Ward, 1991, 1992), and determined by analysis of the different leachate fractions. Soaking in water, for example, might be used to remove constituents dissolved or potentially soluble in the pore water, soaking in ammonium acetate to remove exchangeable ions from components such as carboxylates, and treatment with hydrochloric acid to remove any acid-soluble organometallic complexes from the organic matter. The results may be evaluated by calculating, as a percentage, the concentration of each element in the respective leachates, in relation to the total concentration of the same element in the coal, with the latter being determined from ash analysis of the untreated coal sample. Low-temperature ashing can also be applied to the coal remaining after the leaching

process, to identify the (acid-insoluble) minerals also present.

An example of the results obtained from such a selective leaching process is given in Fig. 5. A large proportion of the sodium in this particular instance, as well as a significant proportion of the sulphur, appears to be dissolved or potentially soluble in the pore water. Much of the Ca, Mg and Mn, together with all but a small proportion of the remaining Na, appears to be held in an exchangeable relationship, and removed by acetate treatment. Large proportions of the Fe and Al in the coal, as well as much of the remaining Ca, Mg and Mn, appear to be in acid-soluble organometallic components. Phosphorus shows a variable distribution in this particular

deposit, being mainly in the pore water and exchangeable fraction in some coals and in an acid soluble form (including possibly phosphate minerals) in others.

The non-mineral inorganics contribute significantly to the formation of ash in combustion of low-rank coals (Kiss, 1982). As discussed above, they may also form a range of mineral artifacts (e.g. bassanite) in residues left by low-temperature ashing, as a result of interaction with organic sulphur in the ashing process. Analysis of data from selective leaching may indicate a greater overall abundance of some elements in the coal, such as the total Na for the samples in Fig. 5, than is indicated by (high-temperature) ash analysis (Ward, 1991, 1992). This is prob-

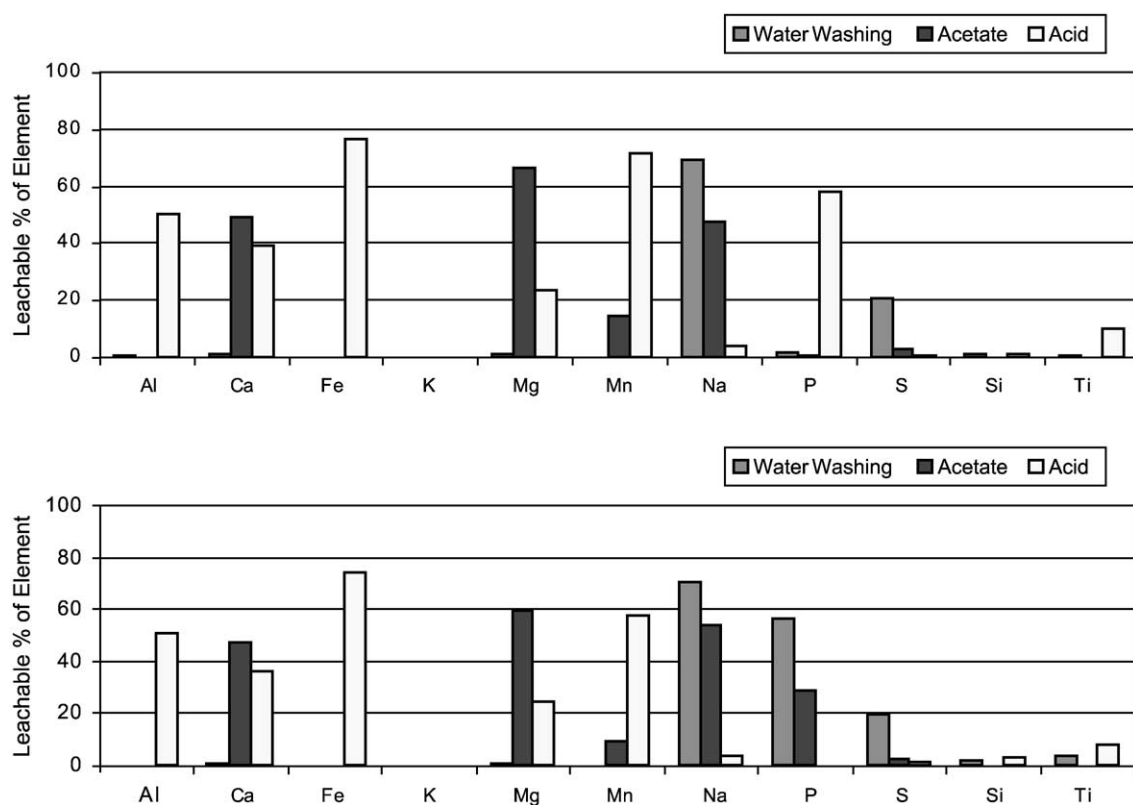


Fig. 5. Proportions of inorganic elements in sub-bituminous coals from Leigh Creek area, South Australia, removed by water washing, ammonium acetate and hydrochloric acid during selective leaching experiments. The values shown represent the total amount of each element leached from each coal sample as a proportion of the total amount of that element in the same sample determined by raw (untreated) coal ash analysis.

ably because some of the element in question is volatile, and is lost during ashing but retained in the more aqueous leaching environment.

The distribution of non-mineral inorganics within the seam may be controlled by post-depositional factors unrelated to the environments that formed the different lithotype units of the coal bed. Studies of the brown coals in the Latrobe Valley of Australia, for example (Kiss et al., 1985; Brockway and Borsaru, 1985), suggest that Na, Mg, Ca, Al, Fe and Cl ions migrate with upward movement of water through the thick, porous, coal seams. The water movement in the seams apparently occurs in response to a combination of hydrostatic pressure from the underlying aquifers and loss by surface evaporation. The coal acts in part as an ion exchange medium as the water moves through it; ions that are held more strongly to the organic matter are thought to move more slowly, giving rise to different concentrations of the mobile ions at different levels in the coal bed.

6. Some applications of mineral matter studies

Mineral matter is significant to a number of different aspects of coal exploration, mining, preparation and use. These include provision of geological markers for stratigraphic correlation, development of abrasion and stickiness in coal handling, dispersion of clays in preparation plants, formation of acids from pyrite, and release of soluble or suspended materials in runoff water from stockpiles and refuse emplacements (Ward, 1984, 2001). Minerals in cleats and other fractures may impede the drainage of gas from coal seams (Gurba et al., 2001), with implications for both coal mining and coal-bed methane production. The forms in which potentially toxic trace elements are held in coal (Swaine, 1990; Finkelman, 1995), and the extent to which those elements might be released with coal exposure or use, are also related in many cases to the mineral matter.

The mineral matter in coal is very significant to many different coal utilization processes. Phosphorus-bearing minerals, for example, can be transferred from coal to coke, and interact with iron ore to provide difficulties in steel production (Ward et al., 1996). A range of mineral-related factors is also involved in

coal combustion (Raask, 1985; Gupta et al., 1999a,b), including abrasion, erosion, corrosion, fouling and slag development.

6.1. Inter-seam and intra-seam correlation

Particularly in areas where complex sedimentology or structure obscures the relevant relationships, the relative proportions of different minerals in coal can provide a basis for stratigraphic correlation of individual coal beds. Ward et al. (2001b), for example, have used the relative proportions of pyrite, kaolinite, feldspar and quartz as criteria for identification of individual coal seams, assisting stratigraphic correlation in the folded and faulted succession of the Gloucester Basin, New South Wales. Many other authors (e.g. Burger and Damberger, 1985; Hill, 1988; Bohor and Triplehorn, 1993; Knight et al., 2000; Zhou et al., 2000; Kramer et al., 2001) have also used the mineralogy or trace element geochemistry of tonsteins, and similar clayrocks associated with coal seams, as a basis for stratigraphic correlation.

Mineralogical data can also be of use in correlating the various subsections within seams, indicating the persistence of particular plies or benches across a basin or a mining area. Fig. 6, based on data from Sakulpitakphon et al. (in preparation), shows mineralogical variations in different subsections of the Manchester coal seam of western Kentucky, USA. Although subject to some variation in thickness, these intervals can be traced in the seam across the relevant coalfield, providing a basis for better understanding the variation in particular geochemical components.

Several other authors have made similar use of mineralogical markers. Crowley et al. (1993), for example, have used mineral matter composition to correlate individual beds within a thick sub-bituminous coal seam in the Powder River Basin, and Rao and Walsh (1999) have used horizons based on phosphate mineral abundance as a basis for correlation within an Alaskan coal seam. Dewison (1989) has also described the occurrence of kaolinite-rich coal at particular horizons within a UK coal bed. Such variations in mineralogy may be used to delineate or explain changes in the overall quality of individual coal beds, making them significant in understanding the three-dimensional distribution of product parameters for mining operations.

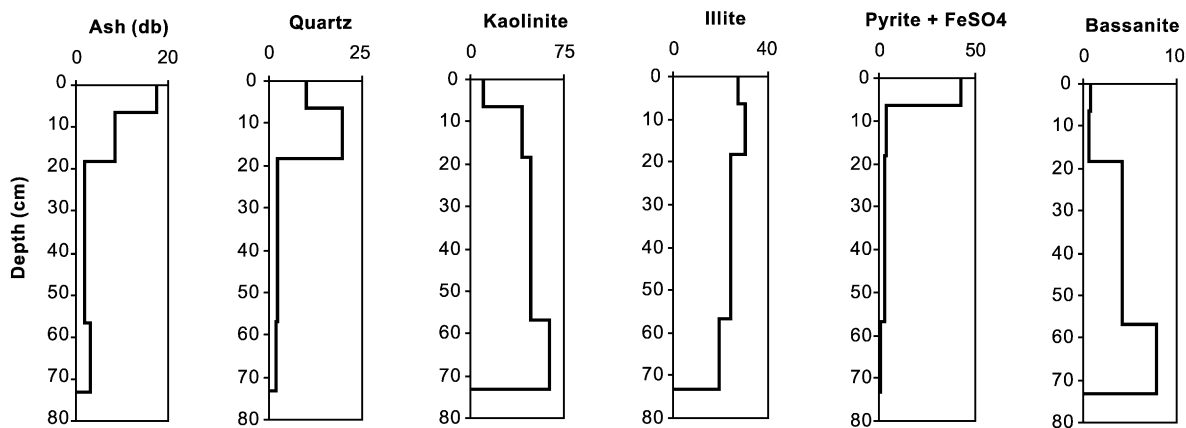


Fig. 6. Relative proportions of ash (dry basis) and of selected minerals in total mineral matter for sub-sections of a coal seam from the Illinois Basin, western Kentucky, showing mineralogical variation through the seam section. Data from Sakulpitakphon et al. (in preparation).

6.2. Trace element occurrence

Many authors (e.g. Gluskoter et al., 1977; Finkelman, 1982, 1994; Swaine, 1990; Spears and Zheng, 1999; Ward et al., 1999a; Alastuey et al., 2001) have indicated links between the minerals in coal and the concentration of particular trace elements. Complete discussion of this extensively researched topic is beyond the scope of the present paper. However, examples of relationships identified by these and other authors include the association of As, Cd, Se, Tl, Hg, Pb, Sb and Zn with sulphide minerals, Rb, Ti, Cr, Zr, Hf and a number of other elements with aluminosilicate components, and Sr and Ba with carbonates or aluminophosphate minerals. A wide range of other associations is also reported in the literature, depending in part on the techniques used to investigate the association, and in part on the geological setting of the coal or coals concerned. Several trace elements, including Ge, Ga, Cl and B, appear in some coals to lack any association with the minerals, and possibly occur in such cases as part of the organic matter.

As an example of an association between mineral and trace element percentages, Fig. 7 shows the correlation between arsenic and pyrite in coals of the Gunnedah Basin, Australia, based mainly on quantitative assessment of the relevant mineral percentages by X-ray diffractometry (Ward et al., 1999a). Other relationships highlighted by that particular study include associations of Tl also with pyrite, Ti

with kaolinite, Ba and Sr with dolomite, and Rb with a range of K-bearing minerals including illite, mica and orthoclase. A number of other authors, including Dewison (1989), Weise et al. (1990), Rimmer (1991), Palmer and Lyons (1996), Querol et al. (1997), Hower et al. (1999), Spears et al. (1999a,b), and Pollock et al. (2000), have also related abundances of different trace elements in the coals of various regions to particular mineral components.

Knowledge of the form in which particular trace elements occur is important in assessing the likely release of any toxic material to the environment when the coal is mined, stored or used (Swaine, 1990; Finkelman, 1995). It may also be significant in assessing the potential to reduce the concentration of

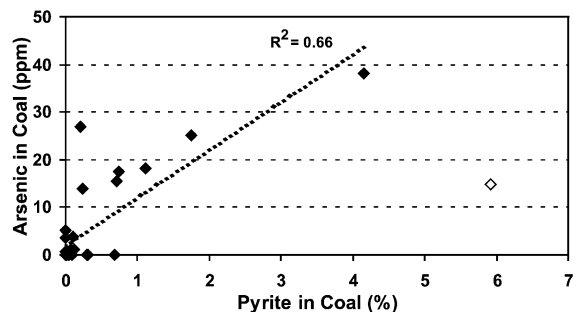


Fig. 7. Correlation between percentage of pyrite and proportion of arsenic in coals of the Gunnedah Basin, NSW (after Ward et al., 1999a). The outlier point (open symbol) is not included in the correlation line.

particular elements in coal products by selective mining and/or preparation processes (e.g. Harvey and DeMaris, 1987; Garcia and Martinez-Tarazona, 1993; Partridge et al., 1992; Sakulpitakphon et al., in preparation), or the incorporation of particular trace elements in fly ashes and other combustion products (e.g. Hower et al., 1996; Sakordafa et al., 1996).

6.3. Mineral matter behaviour in coal combustion

The minerals and other inorganic constituents in coal react, along with the organic particles, when the coal is used in technological applications, such as combustion and coking processes. Processes involving mineral matter include transformation to fly ash and bottom ash, fusion and crystallization to form slag deposits, vaporization and condensation associated with fouling of furnace systems, interaction with internal boiler components to produce corrosion, and abrasion of exposed materials by minerals or mineral-derived particles (e.g. Raask, 1985; Gupta et al., 1999b). The resistivity of the individual ash particles, derived from the mineral matter, may also be significant in controlling the collection of fly ashes in electrostatic precipitator systems.

Changes in the mineral matter of coal at the high temperatures associated with coal combustion have been discussed by authors such as O’Gorman and Walker (1973), Nankervis and Furlong (1980), Vassilev et al. (1995), Filippidis et al. (1996), Reifenstein et al. (1999), and French et al. (2001a). As well as alteration of individual minerals brought about by exposure to high temperatures, such as loss of CO₂ from carbonates, S from sulphides, and crystal lattice OH from clay minerals, they may also include interaction of the minerals with each other, interaction of minerals with carbon to form products such as silicon carbide, and, especially in low-rank coals, interaction of minerals with the non-mineral inorganic components. Many of the minerals or their high-temperature products fuse at still higher temperatures to form a liquid phase, which then cools in other parts of the furnace to become a non-crystalline glass in the ash or slag residues. Some inorganic components may vaporize, with the vapor condensing in cooler regions to form different types of fouling accumulations.

The mineralogical analysis techniques used for coal can also be applied to studying the products of

mineral reactions at high temperatures, including fly ashes, slags and other residues derived from combustion processes. While amorphous materials such as glass may also be present, the crystalline mineral components can be identified, and their proportions evaluated, by X-ray diffraction and CCSEM techniques.

A list of mineral species reported in different high-temperature materials associated with coal utilization is given in Table 3. Knowledge of these minerals, in relation to the mineral matter characteristics of the original coal, provides a basis for understanding the interactions that take place among the different mineral matter components at the high temperatures associated with coal utilization.

Table 3
Principal minerals identified in high-temperature phases associated with coal utilization (compiled from various sources)

Mineral	Composition
Quartz	SiO ₂
Cristobalite	SiO ₂
Tridymite	SiO ₂
Metakaolin	Al ₂ O ₃ ·2SiO ₂
Mullite	Al ₆ Si ₂ O ₁₃
Albite	NaAlSi ₃ O ₈
Anorthite	CaAl ₂ Si ₂ O ₈
Sanidine	KAlSi ₃ O ₈
Corundum	Al ₂ O ₃
Pyrrhotite	Fe _(1-x) S
Oldhamite	CaS
Anhydrite	CaSO ₄
Aragonite	CaCO ₃
Vaterite	CaCO ₃
Portlandite	Ca(OH) ₂
Lime	CaO
Periclase	MgO
Wuestite	FeO
Hematite	Fe ₂ O ₃
Maghemite	Fe ₂ O ₃
Magnetite	Fe ₃ O ₄
Spinel	MgAl ₂ O ₄
Magnesioferrite	MgFe ₂ O ₄
Calcium ferrite	CaFe ₂ O ₄
Srebrodolskite	Ca ₂ Fe ₂ O ₅
Brownmillerite	Ca ₄ Al ₂ Fe ₂ O ₁₀
Wollastonite	CaSiO ₃
Gehlenite	Ca ₂ Al ₂ SiO ₇
Merwinite	Ca ₃ Mg(SiO ₄) ₂
Melilite	Ca ₄ Al ₁₂ MgSi ₃ O ₁₄
Whitlockite	Ca ₃ (PO ₄) ₂

Due to its high fusion temperature (around 1800 °C), quartz is often regarded as essentially non-reactive in combustion processes, at least if it is present as relatively large monomineralic particles. High-temperature phases such as tridymite and cristobalite may be formed by solid-state reactions (Reifenstein et al., 1999), but the slow rate at which these reactions occur often allows much of the original quartz to persist through the combustion process. Since it is inherently a hard mineral, coarse-grained quartz may thus represent an abrasion or erosion hazard in furnace operation (Raask, 1985). Finer-grained quartz and other silica occurrences within the coal, however, left as residues from burnout of the enclosing organic particles, may become incorporated in coatings on the furnace tubes (ten Brink et al., 1997), and build up to reduce the heat transfer capacity of the combustion system.

Kaolinite loses the OH units in its crystal structure at around 450 °C, forming an almost amorphous material known as metakaolin (Moore and Reynolds, 1997). This is transformed to gamma-alumina, mullite and cristobalite at 950–1000 °C (O’Gorman and Walker, 1973). The mullite and other products appear to persist as solid phases to at least 1600 °C (Reifenstein et al., 1999), and provide the basis for a refractory ash material. After losing the OH from their lattice, illite and smectite-group minerals similarly form spinel and mullite at around 950–1050 °C. Unlike kaolinite, however, illite and other clays typically fuse to form glassy components at around 1200 to 1350 °C (Reifenstein et al., 1999), resulting in relatively low ash fusion temperatures and possible slag development.

Calcite may be transformed to its polymorphs aragonite and vaterite with increasing temperature (Reifenstein et al., 1999), and decomposes to form lime (CaO) at around 900 °C. The lime may, however, interact with atmospheric water on cooling to form portlandite (Ca(OH)₂). Dolomite decomposes in a two-stage process to form lime and periclase (MgO). Calcium in either mineral or inorganic form can also react with sulphur to form anhydrite (Filippidis et al., 1996), in a similar way to the formation of bassanite, discussed above, in low-temperature ashing processes. Calcium may also interact with aluminosilicate materials at the high temperatures associated with coal combustion. French et al. (2001a), for example,

describe the formation of gehlenite (Ca₂Al₂SiO₇) and anorthite (CaAl₂Si₂O₈) in hot-stage XRD experiments by interaction of lime with metakaolin, followed by fusion of the mineral mixture at 1400 to 1500 °C. Sakordafa et al. (1996) also describe the occurrence of gehlenite and lime in fly ash from some Greek lignite deposits.

Depending on the nature of the furnace atmosphere, pyrite and siderite break down to form iron oxide minerals such as hematite, maghemite and magnetite during coal combustion. Each mineral, however, reacts differently; siderite undergoes an endothermic reaction to expel its CO₂, whereas pyrite undergoes an exothermic reaction, and burns due to interaction of its sulphur with oxygen, before producing an iron oxide residue. The iron released from both minerals, together with any iron in illite and other clays, and, in many cases, Ca and Mg from different mineral and/or inorganic sources, may then react to form a range of minerals, including spinel, magnesioferrite, calcium ferrite, srebrodolskite and brownmillerite (Table 3). The chemistry of these interactions is complex, however (Huffman et al., 1981; Raask, 1985; Reifenstein et al., 1999), and beyond the scope of the present discussion.

A key factor in determining the types of reactions and reaction products in an operating coal utilization plant is the extent to which the different minerals in the coal, and in some cases also the non-mineral inorganics, have the opportunity to interact with each other in the combustion system. Calcite particles, for example, may decompose independently to produce lime; the lime may in turn react with particles of clay residue (e.g. metakaolin) to form calcium aluminosilicates, such as gehlenite or feldspar, but only if the lime and clay residue particles are brought into contact for long enough at an appropriate temperature to allow the reaction to take place. Ca occurring in the organic matter, on the other hand, may be released into the furnace atmosphere in a more reactive and dispersed elemental form, and thus have a greater opportunity to interact with the same clay residues and produce a low-melting gehlenite or feldspar-rich material during furnace operation.

The nature of the minerals and other inorganics in the coal is therefore of critical importance in understanding the mineral reactions at high temperature in different utilization processes. The knowledge re-

quired for such applications includes not only the relative abundance of the different mineral and inorganic components, but also the composition of the minerals, the nature of any intimately associated impurities such as fluid inclusions or alteration products, and the ways in which the different minerals and inorganics occur in the coal itself. Such an understanding is best based on the application of geological principles, together with geologically based analytical techniques.

7. Conclusions

Along with the organic constituents, the mineral matter in coal, which embraces both the discrete mineral particles and the inorganic elements associated with the organic matter, is fundamental in the understanding of coal and the evaluation of coal quality for a variety of purposes. Inorganic elements dissolved in the pore water or occurring as inorganic components of the organic compounds are a common part of the mineral matter in lower-rank coals (brown coals, lignites and sub-bituminous materials). However, they are less abundant, and may not even be present at all, in higher-rank bituminous coals and anthracites. Mineral particles can occur in coals at all rank levels, and, in the absence of other inorganics, are usually the dominant form of mineral matter in higher-rank coal deposits.

Evaluation of the total proportion of mineral matter may be based on direct analysis methods such as low-temperature oxygen-plasma ashing, or on indirect methods, such as calculation from ash percentage and other chemical data. Additional procedures, such as selective leaching, may be necessary to allow for any non-mineral inorganic constituents, especially in lower-rank coal samples. A correlation may be identified between the volumetric percentage of mineral particles indicated by point counting and the weight percentage of mineral matter indicated by low-temperature ashing. However, small mineral occurrences may be overlooked in microscopic observations, giving rise to under-estimation of mineral content in petrographic analysis of coals with low mineral concentrations.

A range of techniques, including X-ray diffraction, electron microscopy, thermal analysis, and selective

leaching processes, may be used to evaluate the nature of the mineral matter. Quantitative information on mineral abundance can be provided by some of these techniques, including Rietveld-based processing of XRD data and possibly use of computer-controlled scanning electron microscopy. Although there is still scope for standardization in different aspects of the procedures, checks in a number of cases show that the chemistry implied by the mineralogical data obtained from these methods is consistent with the chemical composition of the coal ash, obtained from the same samples by direct analytical methods.

The minerals in coal include quartz, pyrite and other sulphides, calcite, dolomite, siderite and other carbonates, and kaolinite and a range of other clay minerals. Phosphate and alumino-phosphate minerals, feldspar minerals, and also zeolites, may be present in some coal samples. Additional mineral materials, such as bassanite and other sulphates, may be formed as artifacts, especially in low-rank coals, by interaction of organically associated elements with organic sulphur during different ashing processes.

Some of the minerals in coal represent the remains of biogenic constituents, such as skeletal fragments and phytoliths, within the original peat deposit. Other minerals are introduced as fragmental sediment, either by epiclastic processes associated with non-coal sedimentation (e.g. river floods) or by input of pyroclastic debris, into the peat deposit. Much of the mineral matter, however, including syngenetic material occurring as a range of nodules and replacement features, is formed by fluid migration and/or authigenic precipitation during or shortly after peat accumulation. Fluid migration may also control the distribution of non-mineral inorganics in lower-rank coal beds. Epigenetic processes, such as development of cleat and fracture infillings, may be responsible for authigenic mineral formation at later stages in the burial history of many coal seams, sometimes without perceptible break from similar syngenetic processes. Non-mineral inorganics, released from the organic matter during rank advance, may also be reprecipitated as epigenetic mineral deposits.

Knowledge of the mineral matter in coal is an essential complement to studies of the organic matter in developing a complete understanding of the processes of coal formation. It is also important in coal classification, such as in correcting analytical data to

a mineral-matter-free basis. The minerals and other inorganics in coal are significant in a range of practical applications of coal geology, including correlating coal seams and seam sub-sections, identifying the mode of occurrence and potential mobility of particular trace elements, understanding potential barriers to gas drainage, and evaluating the behaviour of different coals in preparation and utilization processes.

Recent advances in technology have provided a more definitive basis for evaluating the mineral matter in coal, including reliable assessment of the abundance of the different minerals in quantitative terms. Because of the importance of mineral matter, especially in different types of utilization problems, such studies need to be incorporated more fully into advanced coal characterization programs. They also need to be integrated more closely with organic petrology and coal chemistry, as well as with wider-ranging geological and engineering studies, to allow optimum and environmentally sustainable use to be made of the world's extensive coal resources.

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