



Occurrence of non-mineral inorganic elements in macerals of low-rank coals

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ABSTRACT

Electron microprobe study of individual macerals in low-rank coals of Permian to Tertiary age from Australia, New Zealand, Indonesia and Thailand has shown that measurable proportions of inorganic elements are consistently found in organic components, especially the vitrinite macerals, in which no minerals or mineral inclusions are visible under the microscope. The vitrinites of such coals have been found to contain up to around 0.5% Al, 1.5% Ca, 0.1% Mg, 0.7% Fe and 0.2% Ti. The Al occurs without measurable proportions of Si, and hence does not represent sub-micron clay minerals within the maceral components. Inertinite macerals in the coals, such as fusinite, typically contain lesser proportions of these elements, and often have no more than background (<0.05%) concentration levels.

Except where soluble minerals such as carbonates are also present, the proportion of Ca, Al and Fe indicated from microprobe analysis in the macerals, especially in the vitrinites, is very close to the mobile proportion of the same elements indicated in previous studies from selective leaching techniques. This suggests that the elements occur as an inherent part of the organic structure in the macerals, possibly as a combination of exchangeable ions, carboxylates, chelates and other organometallic compounds; they may also be held by physical absorption and adsorption mechanisms, or may possibly represent inorganic nanoparticles. The proportions of Al, Ca and Fe in the vitrinites of the samples studied decrease with coal rank. Although there are exceptions, these and other non-mineral inorganic elements (Mg, Ti) are also not usually detected by the microprobe in higher rank coals (above 75% carbon in vitrinite or around 0.6% vitrinite reflectance). Their absence is probably a consequence of expulsion from the maceral structures during the progressive aromatization associated with rank advance, by processes such as dehydration, decarboxylation and dehydroxylation.

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1. Introduction

As indicated by Ward (2002), the mineral matter of coal, especially low-rank coal, typically includes inorganic elements (other than sulphur and nitrogen) that occur as minor constituents of the organic matter. These non-mineral inorganic elements are generally thought to represent exchangeable ions attached to carboxylates and metallic elements in organometallic complexes, as well as any dissolved salts in the pore water of the coal concerned (Kiss and King, 1977; Given and Spackman, 1978; Given and Yarzab, 1978; Kiss and King, 1979; Benson and Holm, 1985; Miller and Given, 1986). Unlike the same elements in crystalline mineral particles, which form oxides and similar compounds during combustion, the non-mineral inorganics are typically released in a reactive atomic form, allowing them to participate more readily, for example, in slagging and fouling processes (Falcone and Schobert, 1986).

Selective leaching tests are commonly used to assess the relative abundance and modes of occurrence for particular non-mineral inorganic elements and soluble minerals (such as salts) in lower-rank coals (e.g. Benson and Holm, 1985; Finkelman et al., 1990; Ward, 1991, 1992; Matsuoka et al., 2002). This approach, however, considers only the occurrence of such elements on a “whole-coal” basis, and does not indicate how the elements are distributed among the different maceral or mineral components. Although some success has been achieved with density-gradient centrifugation (e.g. Dyrkacz et al., 1981; Kars et al., 1985; Dyrkacz et al., 1991; Bensley and Crelling, 1992; Crelling et al., 1993), separation of individual macerals for analysis by conventional means is difficult and time-consuming, since the small particle size (a few μm to tens of μm) and intimate mixing of the different components in the coal limits the effectiveness and reliability of any concentration process. With low-rank coals the separation process might also affect the nature of the non-mineral inorganics in the maceral structures.

Studies of coal polished sections under the electron microprobe, using special techniques for light element investigations (Bustin et al., 1993, 1996; Mastalerz and Bustin, 1997; Ward and Gurba, 1999; Gurba and Ward, 2000; Mastalerz and Gurba 2001; Ward et al., 2005, 2008),

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allow the proportions of carbon, oxygen, nitrogen and sulphur to be evaluated in the individual macerals at a scale consistent with optical microscopy data. Such an approach overcomes the uncertainties associated with maceral concentration/separation, including the possibility that the composition of particular macerals might be altered by reactions with the separating media used.

As well as studying light elements such as C, O and N, electron microprobe analysis techniques can also be used to determine directly the concentrations of a range of other elements in the maceral components. It is common in such studies, for example, to determine the concentration of Si, Al, Fe and Ca in the macerals, in addition to C, O, N and S, to check if any otherwise unseen mineral particles may occur as contaminants of the areas being analysed. Previous studies of low-rank coals, including detailed element mapping with the electron microprobe (Li et al., 2007), have confirmed the presence of such elements in the macerals, and also shown that the inorganic elements are typically uniformly distributed within those macerals. The spatial distributions of Ca and Al, for example, were found by Li et al. (2007) to be similar to those of organic S in the same macerals, suggesting that the elements may be incorporated into the chemical structure of the macerals concerned.

The present study represents an attempt to evaluate the proportions of key non-mineral inorganic elements in coals of different rank levels, based on a suite of samples from New Zealand, Thailand and Indonesia as well as a number of different Australian lower-rank deposits. It also includes, for a few samples, data on the abundance of a wider range of inorganic elements in the macerals, namely Mg, K and Ti, the concentration of which has not previously been investigated by electron microprobe techniques. A particular focus of the study is to evaluate the changes in concentration of such inorganic elements with rank advance, based on samples covering a wide range of ages and geologic settings, and for this purpose several higher-rank coals were also included in the sample suite.

2. Samples studied

A total of 18 coal samples were studied for the present paper (Table 1, Fig. 1) from beds of Permian to Tertiary age. Based on vitrinite reflectance criteria used by ISO (2005), the coals range from sub-bituminous (low-rank A) to low-volatile bituminous (medium rank A) materials. The Permian coals include a sub-bituminous coal from the Collie Basin in Western Australia, a sub-bituminous and a bituminous (medium rank C) coal from the German Creek Coal Measures of the Bowen Basin in Queensland, and two bituminous coals (medium rank C and D) from the Wittingham Coal Measures of the Sydney Basin in New South Wales. Other Australian coals include three different samples of Triassic sub-bituminous coal from the Callide Basin and a sample of Jurassic sub-bituminous coal from the Surat Basin, both in Queensland, as well as three Triassic sub-bituminous coal samples from the Leigh Creek coalfield in the Telford Basin of South Australia. Details of the geological setting for these deposits are given by several different authors in a compilation by Ward et al. (1995). Additional data on the Bowen Basin samples included in the study are given by Ward et al. (2005) and on the samples from the Telford Basin by Ward (1992).

Two samples of coal from New Zealand were also included in the study, a bituminous coal (medium rank C) of Cretaceous age from the Greymouth Coalfield in the South Island and another of Tertiary age (medium rank D) from the Huntly Coalfield in the North Island. Further details of the setting of these deposits are given by Newman (1985), Nathan et al. (1986), Newman, 1987, Moore (1995), Ward (1997), Li et al. (2001) and Li (2002), among others.

Two samples of Tertiary sub-bituminous coal from Indonesia were included in the study: one from a deposit in South Kalimantan and one from the Bukit Asam coalfield in south-east Sumatra. A low-volatile bituminous coal (medium rank A) was also included from an area in

Table 1
Location, age and vitrinite reflectance of coal samples studied.

Coalfield area	Age	Samples	R _{v,rand} %	Notes
Bowen Basin, Australia	Permian	PS 2302	0.54	German Creek
		PS 1035	0.66	Coal Measures (Ward et al., 2005)
Sydney Basin, Australia	Permian	Whybrow	0.74	Whybrow seam, Saxonvale Colliery
		LPGUL	0.58	Lower Pikes Gully seam, Howick Colliery
Collie Basin, Australia	Permian	Collie	0.50	Typical coal sample, Premier mine
Leigh Creek Coalfield (Telford Basin), Australia	Triassic	LCK M 6	0.46	Middle Series coal (Ward, 1992)
		LCK M 10	0.42	Middle Series coal (Ward, 1992)
		LCK U 26	0.50	Upper Series coal (Ward, 1992)
Callide Basin, Australia	Triassic	Callide 1	0.47	Typical coal, main pit
		Callide 2	0.60	Dull coal, main pit
		Callide 3	0.51	Typical coal, Boundary Hill deposit
Surat Basin, Australia	Jurassic	Wandoan	0.41	Typical coal sample, Wandoan deposit
Greymouth Coalfield, New Zealand	Cretaceous	Greymouth	0.60	Main Upper Series (Li, 2002)
Huntly Coalfield, New Zealand	Tertiary	Huntley	0.52	Typical coal sample
Bukit Asam Coalfield, Indonesia	Tertiary	BAS 1	0.44	B2 seam, sub-bituminous coal (Susilawati and Ward, 2006)
		BAS 2	1.58	B2 seam, low-volatile bituminous coal (Susilawati and Ward, 2006)
South Kalimantan, Indonesia	Tertiary	Kalimantan	0.40	Typical coal sample, Arutmin mine
Mae Moh Basin, Thailand	Tertiary	Mae Moh	0.47	Typical coal sample, K seam (Ward, 1991)

the Bukit Asam deposit where the rank had been significantly increased by igneous intrusion processes (Pujobroto, 1997; Susilawati and Ward, 2006). This allowed study of lower-rank and higher-rank coals taken from close proximity to each other within the same coal seam. A sample of sub-bituminous coal from the Mae Moh Basin in northern Thailand (Corsiri and Crouch, 1985; Ward, 1991) was also included in the sample suite.

3. Analytical methods

Representative samples of each coal were prepared as polished sections in the same way as samples for optical microscopy, and coated with carbon for electron microprobe analysis as described by Bustin et al. (1993). Individual points on the various macerals in each coal were analysed using a Cameca SX-50 electron microprobe equipped with the Windows-based SAMx operating system and interface software. The accelerating voltage for the electron beam was 10 kV and the filament current 20 nA, with a magnification of 20,000× giving a beam spot size on the sample of around 5 to 10 μm in diameter. As discussed by Bustin et al. (1993), an independently analysed anthracite sample was used as the standard for carbon in the analysis process. Mineral samples supplied with the instrument were used as standards for the other elements. Calibration data for the various elements, including spectral lines and analysing crystals, are given in Table 2. Other details of microprobe procedures for coal macerals are given by Bustin et al. (1993, 1996), Mastalerz and Gurba (2001), and Ward et al. (2005, 2007, 2008).

The percentages of C, O, N, S, Si, Al, Ca and Fe were measured for a number of points on each sample, with a note on the type of maceral represented at that point in each case. For some samples the study was

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