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Occurrence of non-mineral inorganic elements in low-rank coal macerals as shown by electron microprobe element mapping techniques

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Abstract

Significant proportions of inorganic elements (up to 1.5% Ca, up to 0.5% Al and up to 0.7% Fe) are consistently found in electron microprobe studies of such otherwise 'clean' coal macerals, especially vitrinite macerals, without any visible minerals or mineral inclusions in the macerals concerned. Detailed mapping of the concentration of these elements in visibly 'clean' macerals of several low-rank coals reveals that a majority of inorganic elements (Al, Ca and Fe) occur as non-mineral entities rather than discrete mineral particles, and are intimately distributed throughout the macerals; the distribution of the these elements is very similar to that of organic S, particularly in the collotelinite and fusinite of the same coal samples. The baseline concentrations seen in the inorganic element maps (Al, Ca, Fe and S) normally agree with the averaged concentrations derived from more general microprobe analysis of the same macerals in the coals, indicating that the elemental mapping technique provides a consistent basis and a powerful tool for evaluating the modes of inorganic element occurrence in coal macerals. The overall consistency in the baseline levels, instead of spike-like peaks expected from micron-sized mineral inclusions, suggests that these elements occur as an inherent part of the organic structure in the macerals concerned, possibly as a combination of exchangeable ions, carboxylates, chelates and other organometallic compounds; they may also be held by physical absorption and adsorption mechanisms. Better understanding the mode of occurrence of these non-mineral inorganic elements may provide important insights into a number of coal utilisation processes, such as catalyst reactions, slagging and fouling, and emission generation associated with combustion and carbonisation operations.

Keywords: Inorganic elements; Low-rank coals; Macerals; Microprobe; Element mapping; Leigh Creek

1. Introduction

Although only a minor constituent in most coals, inorganic elements are important because they affect the ways in which coal behaves when used, such as lowering the heating value in combustion, causing slagging and fouling (Vuthaluru and Zhang, 1999; Vuthaluru et al., 2000), or affecting the coking performance, and may provide a source of impurities through the coke, into the steel products. Inorganic elements occurring as minerals in coal have been well studied (e.g. Ward, 2002). However, details on the occurrence of non-mineral inorganic elements in individual macerals is still unclear.

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Apart from their well-known occurrence as discrete mineral phases, small but significant concentrations of inorganic elements are commonly found intimately associated with the organic matter of low-rank coals (e.g. Benson and Holm, 1985; Miller and Given, 1978, 1986; Given and Miller, 1987a,b; Ward, 1991, 1992; Li et al., 2001; Li, 2002). Such elements have also been identified from electron microprobe studies of the individual macerals of a number of low-rank coal samples (Gurba et al., 2003; Ward et al., 2003), but how these elements are distributed within the macerals concerned (e.g. as fine mineral inclusions or bound with organic molecules in macerals) has not previously been investigated.

Much of the previous research into non-mineral inorganic elements in coal is based on selective leaching tests, with the modes of occurrence for the inorganic elements inferred from the resulting element mobility data (e.g. Finkelman et al., 1990; Ward, 1991, 1992; Palmer et al., 1993; Li et al., 2001; Li, 2002). A significant proportion of some elements (especially Ca, Mg and Na) is typically leached from low-rank coals by ammonium acetate solutions (e.g. Ward, 1992, 2002; Li, 2002; Ward et al., 2003), and, although some carbonate components may also be soluble in the ammonium acetate, the elements concerned are mainly thought to be associated with organic matrix of the coals, possibly as exchangeable ions attached to carboxylate groups (e.g. Given and Miller, 1987a,b). Similarly, inorganic elements mobilised by treatment with HCl, after acetate extraction, are thought to include components of carbonates and any other acid-soluble mineral contaminants (e.g. Ward, 1992; Li, 2002).

However, this approach must be treated with caution, because it inevitably embraces some obvious uncertainties. It is virtually impossible to separate individual macerals from other intimately admixed components (other macerals or tiny mineral inclusions), so that selective leaching tests can only be applied to “whole coal” samples and not to the individual macerals involved. Any inferences regarding the modes of occurrence for these elements from selective leaching results is also made on a “whole-coal” basis, which inevitably combines all the potential sources of the various mobile components, including any acetate- or acid-soluble mineral inclusions also present in the coal sample. It is therefore difficult, if not impossible, to determine exactly how these elements occur in the coal, and how they are distributed among the different macerals and/or mineral phases in the coal concerned.

In-situ microanalysis techniques have great potential to overcome the above-mentioned problems, and to identify more precisely whether particular inorganic elements occur in the macerals of a particular coal sample, or in associated mineral phases. In particular, electron microprobe analysis of coal polished sections, using special techniques for light elements (Bustin et al., 1993, 1996; Ward and Gurba, 1999; Gurba and Ward, 2000; Mastalerz and Gurba, 2001; Ward et al., 2003, 2005), provides a direct basis for determining the abundance of different elements in the individual maceral components.

Previous studies of low-rank coals from Australia, Thailand and Indonesia using electron microprobe analysis (Ward et al., 2003), found that a significant concentration of inorganic elements was consistently present in otherwise clean maceral components. The mode of occurrence of these inorganic elements in the macerals, however, is not clear, even from those microprobe investigations.

The focus of the present study is to investigate further how these inorganic elements are distributed within the macerals in which they occur, by directly mapping their abundance using an extension of the electron microprobe technique. The objectives of the study are: (1) to gain a better understanding of where and how these inorganic elements are partitioned between the macerals in these coals; (2) to determine whether the main inorganic elements (Ca, Al and Fe) are homogeneously bound with the macerals, or present as discrete mineral phases (such as micron- or submicron-sized inclusions) within the macerals concerned, or both; and (3) to consider what possible mechanisms are responsible for the modes of occurrence identified by the study.

Such inorganic elements, especially if they are an inherent part of the organic compounds, can be expected to behave differently to equivalent elements in crystalline mineral phases, possibly being more reactive during combustion or remaining with the organic matter during coking processes (e.g. Raask, 1985; Filippidis et al., 1996; Ward, 2002). Improved knowledge of such organically associated elements, referred in this paper as non-mineral inorganic elements, may therefore provide some important insights into coal combustion and gasification processes (see Mühlen, 1990), including catalyst behaviour, slagging and fouling, and the reactions with other components during combustion or coking operations.

2. Sampling and methodology

A number of low-rank coals from the Leigh Creek coalfield, in the Telford Basin of South Australia (cf. Ward, 1992), the Cranky Corner Basin in New South Wales, and an Indonesian coal basin (Table 1), were selected for electron microprobe analysis and elemental mapping investigations.

Coarsely-crushed (<5 mm) samples of each coal were prepared as polished sections and coated with carbon for electron microprobe analysis as described by Bustin et al. (1993). Individual points on the various macerals in each