Inorganic matter in Victorian brown coals

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ABSTRACT

A common method to quantify the mineral matter in coals is to remove the carbonaceous matter by low-temperature oxygen plasma ashing (LTA) followed by X-Ray Diffraction (XRD) analysis. However, some low-rank coals, such as Victorian brown coals (lignites), have low levels of mineral matter and contain significant amounts of non-mineral inorganics (organically associated elements and salts dissolved in the coal pore's water), which form artifact phases during low-temperature ashing. The presence of these phases also lowers the concentration of the low abundant mineral species in the ash below the detection limit of the XRD. Some of the non-mineral-matter components can be removed by leaching of the coal prior to ashing, but the leaching conditions have to be chosen so that the mineral matter is not removed. In this study, sequential leaching was performed on three Victorian brown coals (Hazelwood, Yallourn and Loy Yang) in order to increase the concentration of the mineral species in the low-temperature ashes by removing the non-mineral inorganics. We introduced diammonium ethylenediaminetetraacetate (NH_4-EDTA) solution into the leaching process, because of its potential to extract ion-exchangeable cations without dissolving acid-sensitive mineral matter or contaminating the extract solution with introduced metal cations. The leaching protocol was stepwise extraction by water, ammonium acetate, NH_4-EDTA, hydrochloric acid and nitric acid. Sequential leaching enabled quantification of the minerals that occur in very small amounts in the coals. K-feldspar, pyrite, augite and kaolinite were the additional minerals quantified in the leached coals beside quartz, plagioclase (calcian albite), marcasite and calcite, which were found in the original coals. Most non-mineral inorganics, which produce large amounts of artifact phases in the low-temperature ashes, were removed by water, ammonium acetate and NH_4-EDTA. NH_4-EDTA effectively removed significant amounts of inorganic elements, which most likely occur in coordination complexes and would be extracted in conventional leaching studies only by strong acids. This procedure makes it possible to discriminate between inorganic elements that occur organically associated and mineral matter that is dissolved by strong acids.

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1. Introduction

The mineral matter in a coal determines its utility in nearly all of its commercial uses, so its quantification is important. X-Ray Diffraction (XRD) has been used in many studies for identification and quantification of mineral matter in coals (Hower et al., 2015; Huggins, 2002; Koukouzas et al., 2009; Liu et al., 2015; Martinez-Alonso et al., 1992; Miller and Given, 1987; Morgan et al., 1981; Ward, 2002). The analysis of the mineral matter in coals is performed on the coal ashes prepared at low temperatures (100–120 °C) in a radio-frequency oxygen plasma asher (Gluskoter, 1965). This way the organic matter is removed from the mineral matter with minimal alteration of the mineral species. However, low-rank coals contain significant amounts of non-mineral inorganics, which form artifact phases during low-temperature ashing and these interfere in the quantification of the inherent mineral matter.

For instance, inorganic elements associated with the organic matter react with organic sulfur to form sulfates (Dai et al., 2015; Ward, 2002; Ward et al., 2001). The formation of these artifact phases diminish the concentration of the true minerals in the ash to a level where the low abundant minerals cannot be detected by XRD. In Victorian brown coals, which commonly have less than 2% inherent mineral matter (Gloe and Holdgate, 1991), this problem is particularly severe.

The inorganic matter in the low rank coals, brown coals in particular, consists of inorganic elements associated with the organic matter, dissolved salts and other inorganic substances in the pore water (Brockway et al., 1991; Dai et al., 2015; Li et al., 2010; Ward, 2002), minerals that occur as crystalline discrete particles (true mineral components) and mineraloids. The inorganic elements associated with the organic matter occur as exchangeable cations attached to carboxylic acids (carboxylate salts), phenols, chelates and other organometallic complexes such as metalloporphyrins (Bonnett et al., 1987; Branthaver, 1987; Filby and Vanberkel, 1987; Given and Miller, 1987; Schafer, 1991; Ward, 2002).

Most of the sodium, calcium and magnesium in these coals are present as carboxylates (Brockway et al., 1991; Schafer, 1991). Some sodium

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may occur as sodium chloride (Perry et al., 1982). Iron and aluminum could be present as complex ions bound by a single valency to carboxylate groups (Brockway et al., 1991). The exchangeable iron is usually present in the ferrous form but it tends to be readily oxidized to the ferric state on exposure to air. Cook and Cashion (1987) identified three non-pyritic iron species in the Victorian brown coals using Mössbauer spectroscopy. A poorly-ordered ferric oxyhydroxide as a dominant phase, a ferrous humate that can precipitate as ferric oxyhydroxide and a third species whose nature could not be confirmed, but believed to be a Fe^{+2} compound. Aluminum hydroxide is also found in the brown coals. The minerals identified in the Latrobe Valley coals are quartz, clays (mainly kaolinite associated with illite, montmorillonite, muscovite), silica, pyrite and/or marcasite (Perry et al., 1982).

Some of these species can be removed by selective leaching of the brown coal. Selective leaching is commonly used to determine the relative abundance and modes of occurrence of the non-mineral inorganic components and mineral matter (Dai et al., 2004; Davidson, 2000; Finkelman et al., 1990; Grasset et al., 2010; Li et al., 2010; Liu et al., 2015; Riley et al., 2012; Spears, 2013; Ward, 1992; Wijaya et al., 2011; Zhang et al., 2008a,b). The most common reagents used in the leaching protocols are water, ammonium acetate, HCl, HNO₃ and HF. The soluble species and the inorganic elements associated with carboxylic acids are removed by water and ammonium acetate, respectively. However, Matsuoka et al. (2002) found that ammonium acetate also dissolved calcite. HCl extracts cations from chelates and clays, but also dissolves carbonates, and Fe and Al hydroxides (Davidson, 2000; Miller and Given, 1987). Sulfides, such as pyrite and marcasite, and silicates are dissolved by HNO₃ and HF, respectively.

Chelates such as EDTA and citric acid are used for extraction of metal cations (transitional/heavy elements) from contaminated soils (Peters, 1999; Ritchie and Sposito, 1995). The pH of the solution and the concentration of the chelant are two of the factors controlling the metal cation uptake (Peters, 1999; Ritchie and Sposito, 1995). Borggaard (1981, 1982) observed that amorphous iron oxide was extracted by 0.01–0.2 M EDTA at pH 8–10 with negligible effect on the crystalline iron-bearing minerals. He dissolved EDTA and ammonium acetate in ammonia solution to obtain the selected pH. Disodium ethylenediaminetetraacetate (Na-EDTA) 0.1 M was used by Wijaya et al. (2011, 2012) for advanced removal of organically associated inorganic elements in Victorian brown coals. However, the addition of sodium can affect the mineral matter; Wijaya et al. (2011) reported the formation of a Na-silicate believed to occur due to interaction of Na from EDTA with aluminosilicates.

The aims of this study are to identify and quantify the mineral matter and the nature of the inorganic elements that are organically associated in three Victorian brown coals. Sequential leaching was carried out on the coals to make possible quantification of the low abundance mineral species and to improve discrimination between inorganic elements associated with different functional groups in coal. The leaching protocol was water, ammonium acetate, diammonium ethylenediaminetetraacetate, hydrochloric acid and nitric acid. We introduced diammonium ethylenediaminetetraacetate solution into the leaching process, because of its potential to extract ion-exchangeable cations without dissolving acid-sensitive mineral matter or contaminating the extract solution and sample with introduced metal cations. The strong acid leaching steps were included to enable quantification of the very low abundance minerals that are not dissolved by HCl and HNO₃.

2. Experimental

Three run-of-mine brown coals from the open-cut mines Hazelwood, Yallourn and Loy Yang in the Latrobe valley, Victoria, Australia, were selected for sequential leaching. These coals are low-rank Tertiary coals (Gloe and Holdgate, 1991; Holdgate, 2005). Gloe and Holdgate (1991) and Holdgate (2005) published detailed geology of the Victorian brown coals. The coals were ground to less

than 212 μm. The leaching solutions used in this work were ultra pure water (Milli-Q), 1 M ammonium acetate, 0.1 M NH₄-EDTA buffered by NH₄OH to pH 9, 1 M hydrochloric acid and 2 M nitric acid. The NH₄-EDTA step was included between the ammonium acetate and HCl steps to extract iron and other elements held in chelate complexes or associated with functional groups other than carboxylic groups. Also, the high pH of the NH₄-EDTA solution is expected to minimize the effect of NH₄-EDTA on the crystalline mineral matter. Using NH₄-EDTA instead of Na-EDTA eliminates the contamination of the supernatant liquor with Na from the reagent. Although HCl and HNO₃ dissolve some of the mineral matter, they may also extract some of the inorganic elements organically associated if they were not removed by NH₄-EDTA leaching.

The ultimate and proximate analyses of the coals are shown in Table 1. The moisture levels in the coals were determined according to the Australian Standard AS 2434.1-1999 (Australia, 1999) in order to calculate the coal mass on a dry basis. Inductively Couple Plasma-Atomic Emission Spectroscopy (ICP-AES) was used for chemical analyses of the coals and the supernatant liquids derived from each leaching steps. The preparation method of coals for ICP-AES analysis consists of two steps. The coals were oxidized at 815 °C then the resulting ashes were dissolved with a mixture of hydrochloric, nitric and hydrofluoric acids in 60 mL polypropylene bottles (Riley et al., 2012). The excess fluoride was complexed with boric acid. The ash yields and ash analyses are shown in Table 2.

The coals and the leaching solutions were loaded into 2 L Nalgene polyethylene bottles and shaken at room temperature for 24 h. The ratio of leaching solution to coal (dry basis) was 3.7. The leached coal was washed three times with Milli-Q water after each filtration to remove the remaining supernatant solution from the coal. After every leaching step aliquots of filtrate were taken for both pH determination and chemical analysis, and a coal sub-sample was taken for mineralogical and chemical analyses. The pH values of the filtrates and blank solutions are shown in Table 3.

The mineralogical compositions of the coals were determined by XRD analyses of the low-temperature ashes of the coals. The coals were oxidized at approximately 120 °C using a radio-frequency oxygen plasma asher (Gluskoter, 1965). Samples were oxidized until a constant weight was reached. The time taken ranged from two months (original brown coal) to less than one week for strong acid (HCl and HNO₃) leached brown coals. We believe that coal oxidation by oxygen plasma was hindered by the presence of ion-exchangeable cations. The XRD patterns were used for identification and quantification of the mineral phases using Bruker Eva search/match software and SIROQUANT™ (Taylor, 1991). The proportion of the amorphous matter was determined by spiking the ashes with known amounts of corundum. The method has been described elsewhere (Ward and French, 2006).

Scanning Electron Microscopy in conjunction with Electron Dispersive Spectroscopy (SEM–EDS) was used for analysis of mineral matter and elements associated with organic matter in coals, and mineral phases in the low-temperature ashes.

Table 1
Proximate and ultimate analyses of the original coals.

	Hazelwood	Yallourn	Loy Yang
Proximate analysis (wt%, db)			
Ash	2.9	2.0	0.80
Volatile matter	49.0	52.1	49.6
Fixed carbon	48.1	45.9	49.6
Ultimate analysis (wt%, db)			
Carbon	67.8	64.4	69.4
Hydrogen	4.52	4.27	4.8
Nitrogen	0.74	0.74	0.71
Sulfur (total)	0.28	0.30	0.31
Oxygen (by difference)	24.1	27.8	24.2