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# Location and distribution of inorganic material in a low ash yield, subbituminous coal

Tennille E. Mares [a,*], Andrzej P. Radliński [b,c,d], Tim A. Moore [a,e], David Cookson [f,g], P. Thiyagarajan [h], Jan Ilavsky [i], Jürgen Klepp [j,k]

[a] Department of Geological Sciences, University of Canterbury, Private Bag 4800, Christchurch, New Zealand
[b] Geoscience Australia, Canberra, Australian Capital Territory 2609, Australia
[c] Cooperative Research Centre for Greenhouse Gas Technologies, Canberra, Australian Capital Territory2601, Australia
[d] Queensland Micro- and Nanotechnology Centre, Griffith University, Brisbane, Queensland 4111, Australia
[e] Solid Energy NZ Ltd., P.O. Box 1303, Christchurch, New Zealand
[f] Australian Synchrotron, 800 Blackburn Road, Clayton, VIC 3168, Australia
[g] School of Physics, University of Melbourne, VIC 3010, Australia
[h] Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL 60439, USA
[i] X-ray Operations Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA
[j] Institut Laue Langevin, Boîte Postale 156, F-38042 Grenoble Cedex 9, France
[k] TU Vienna, Atominstitut, Stadionallee 2, 1020 Vienna, Austria

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## ABSTRACT

Previous studies of mineral matter in low ash yield, low rank coals have suggested that much of the inorganic material is present as organically bound elements rather than as discrete minerals. This study investigates the location and occurrence of this inorganic material to the angstrom level using non-invasive small angle scattering techniques. Microstructural analysis conducted on matrix and vitrain samples, collected from the subbituminous coals of the Huntly coalfield, found that the inorganic material is located in the $12.5\ \text{Å} < r < 125\ \text{Å}$ size range. This was consistent for all samples, irrespective of seam or location. As there was greater influence on X-ray scattering curves seen in the vitrain samples than the matrix samples, it is suggested that the inorganic material is located within the structured vitrinite tissues, likely originating from the original plant material rather than being precipitated post deposition. The fitting of microstructural models to the scattering curves suggests that the inorganic material exists as inorganic shells or coatings.

## 1. Introduction

All coals contain some inorganic components, the quantity and distribution of which give considerable information on coal formation conditions. However these inorganic components can also limit coal utilization and, for coal seam gas, affect gas production. Mineral matter present in coals can originate in the following ways: (1) as syngenetic inorganic matter that was originally incorporated into the mire flora and persists through the progression to peat and coal, (2) as syngenetic inorganic/organic complexes and minerals that were introduced by wind or water into the mire or formed in situ during the early stages of peat formation, or (3) as epigenetic minerals that form post-coalification by crystallizing in cleats, fractures and pores in the coal from fluids moving through the system or from the alteration of original mineral matter (Taylor et al., 1998).

For low ash yield coals of lower than bituminous rank a significant part of the mineral matter may be contributed by inorganic elements being organically bound within the coal rather than being present as mineral phases (Newman et al., 1997). These organically associated elements can occur as inorganic elements dissolved in pore waters, as leachable salts, as cations held in exchangeable relationships with organic compounds, or as organometallic complexes within the organic matter (Newman, 1988; Ward, 1991, 1992, 2002). Microprobe mapping of the concentration of inorganic elements within visibly clean macerals of low-rank coals has found that a majority of these elements occur as non-mineral entities, possibly even as an inherent part of the organic structure of the macerals (Li et al., 2007; Ward et al., 2008).

The current study investigates the location and occurrence of inorganic elements in Tertiary subbituminous coals from the Huntly Coalfield, New Zealand, using small angle scattering techniques. It has been previously reported that the subbituminous ($R_{max}$ 0.42–0.45%) coal seams of the Huntly coalfield have very low ash yields of generally <5% (Edbrooke et al., 1994; Mares and Moore, 2008).

### 1.1. Small angle scattering

Various methods have been used to investigate coal microstructure, the most common techniques being mercury injection and nitrogen adsorption. Techniques involving fluids are affected by accessibility, the connectivity of the pore network, as well as sorption

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* Corresponding author at: School of Earth Sciences, University of Queensland, St Lucia, QLD 4072, Australia. Tel.: +61 412298292.
*E-mail address:* t.mares@uq.edu.au (T.E. Mares).

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phenomena and modification of the coal microstructure depending on the sorbate used (Levine, 1993). Small angle scattering (SAS) is a relatively inexpensive, noninvasive technique requiring little material and sample preparation, with both open and closed porosity being measured. As such it is an attractive alternative to using fluid for probing pore space (Radlinski, 2006; Radlinski et al., 2001, 2004a).

In several branches of science, SAS of neutrons and X-rays is widely used as a diffraction method for studying the structure of matter on many scales, from near-molecular size particles to microscopic objects (Feigin and Svergun, 1987). Small angle neutron (SANS) and small angle X-ray scattering (SAXS) have been used for decades to study the geometry of supra-molecular objects in both the suspended or solid phase (Radlinski, 2006). The application to rocks was considerably enhanced by the discovery of the fractality of rock microstructure by Bale and Schmidt (1984). In the last decade small angle scattering techniques have been integrated into main stream petroleum, coal and engineering geology (Mares et al., 2009b; Melnichenko et al., 2009; Prinz et al., 2004; Radlinski and Hinde, 2001, 2002; Radlinski and Radlinska, 1999; Radlinski et al., 1996, 2000, 2001, 2004a, 2004b, 2009; Winans et al., 2006).

Coals are chemically heterogeneous materials at every scale level. However, the scattering contrast between the coal matrix and the pore (void) space is considerably larger than the contrast variations within the coal matrix itself (Radlinski et al., 2004b). Neutron scattering perceives sedimentary rocks as a two-phase system, rock material and pore space, irrespective of the organic/inorganic composition, as there is little contrast between the solid organic and inorganic components of rock (Radlinski, 2006). For X-rays, the matrix–void contrast for organic material is about 25% of that for inorganic material. Hence, if the rock is composed purely of organic material or inorganic material the system remains two-phase and the information obtained using X-ray scattering will be the same as that for neutron scattering. However, where there are contributions of both organic and inorganic matter in the rock, the system will be three-phase for X-ray scattering and the data obtained will differ from that obtained by neutron scattering (Mares et al., 2009b; Radlinski, 2006; Radlinski et al., 1996).

## 2. Methods

### 2.1. Sample selection and preparation

The coal samples analyzed for this study were selected from cores collected as part of a coal seam gas exploration program. As such, coal properties have been analyzed on the 0.5 m intervals of the desorption samples. After macroscopic description of the coal core, block samples were collected from each desorption canister interval. From this suite, suitable samples of matrix coal (Moore and Shearer, 1999) and pure vitrain were selected for small angle scattering (SAS) analyses. These two types of samples were chosen as the coal from the Huntly coalfield, like most New Zealand coals, is mostly bright in luster (Beamish et al., 1998; Edbrooke et al., 1994; Ferm et al., 2000; Mares and Moore, 2008; Sherwood et al., 1992) and the major macroscopic difference between the identified coal types is the proportion of vitrain banding (Mares and Moore, 2008; Newman et al., 1997). Further discussion of the properties of the Huntly coals and the methods of analysis have been reported elsewhere (Mares, 2009; Mares and Moore, 2008; Mares et al., 2009a, 2009b), with the results pertaining to the current suite of samples presented in Tables 1 and 2.

Samples for SAS analyses were prepared at the Sedimentology Laboratory of Geoscience Australia. For each coal, samples were prepared as a solid platelet cut perpendicular to the bedding plane (called “perpendicular sample” for short) and a solid platelet cut parallel to the bedding plane (called “parallel sample” for short). Platelet size (typically 20 × 30 mm) was designed to suit the largest neutron beam size required, and samples were cut as thin as possible; in most cases thickness was less than 1 mm, to avoid the effects of multiple scattering (Radlinski et al., 1999). As the coals are of low rank and the platelets are brittle, the orientated blocks of coal (trimmed to create platelets) were encapsulated with a low viscosity epoxy resin and then sliced using a low-speed precision diamond saw lubricated with a minimal amount of water. Eight matrix sets and four vitrain sets (from two seams across five locations) were prepared, as there was a distinct lack of suitable vitrain bands in the collected block samples.

### 2.2. Equipment and data processing

In this study, four separate instruments were used: SAXS (Small Angle X-ray Scattering), USAXS (Ultra-small Angle X-ray Scattering), SANS (Small Angle Neutron Scattering) and USANS (Ultra-small Angle Neutron Scattering). The pinhole-geometry SAXS instrument at ChemMatCARS, sector 15 of the Advanced Photon Source (APS), Argonne National Laboratory, was used to obtain information in the Q-range from $1.1\ \text{Å}^{-1}$ to $2.9 \times 10^{-2}\ \text{Å}^{-1}$ (Cookson et al., 2006). The Q-range of the SAXS data was then extended into the small-Q region using the APS UNICAT USAXS instrument with 1-D collimated Bonse–Hart geometry (Q-range from $0.66\ \text{Å}^{-1}$ to $1.2 \times 10^{-4}\ \text{Å}^{-1}$; (Long et al., 2000)). For neutron analysis a time-of-flight instrument, Small-Angle Neutron Diffractometer (SAND), at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory was used to acquire SANS data in the Q range from $1.0\ \text{Å}^{-1}$ to $3.6 \times 10^{-3}\ \text{Å}^{-1}$ (Thiyagarayan et al., 1998), while neutron scattering in the small-Q region (from $2.0 \times 10^{-3}\ \text{Å}^{-1}$ to $1.55 \times 10^{-5}\ \text{Å}^{-1}$) was measured using the Bonse–Hart geometry USANS instrument S18 at the Austrian Beam Line, Grenoble Research Reactor, France (Hainbuchner et al., 2000). Both SAXS and SANS data were acquired and processed in a way that yields the scattering intensity in absolute units of $\text{cm}^{-1}$, corresponding to the absolute scattering cross section. Further details of the experimental and modeling procedures, as well as references to previous work, can be found in Radlinski et al. (2004b), Radlinski (2006) and Mares et al. (2009b).

Knowledge of scattering contrast for the analyzed material is essential for quantitatively interpreting absolutely calibrated neutron and X-ray scattering data (Radlinski, 2006). Using the bulk coal composition data for each canister interval (Table 1), the X-ray coherent scattering contrast term and the neutron scattering length density term can be calculated for each sample using Eqs. (1) and (2) respectively (Radlinski, 2006).

$$\rho_n = (\mathtt{N}_\mathtt{A}.d)/\mathtt{M}.\sum_j \mathtt{p}_j\left(\sum_i \mathtt{s}_i.\mathtt{b}_i\right)_j \tag{1}$$

where: $N_A$ is Avogadro's number $6.022 \times 10^{23}$

$d$ is density in $\text{g/cm}^3$

M is the pseudo-molar mass

$s_i$ is the proportion by number of nucleus $i$ in the compound $j$

$p_j$ is the proportion by molecular number of the compound $j$ in the mixture

$b_i$ is the coherent scattering amplitude for nucleus $i$

$$\rho_{el} = \mathtt{I}_e.\rho_e = (\mathtt{N}_\mathtt{A}.\mathtt{d})/\mathtt{M}.\mathtt{N}_e.\mathtt{I}_e \tag{2}$$

where: $\rho_e$ is the electron density (i.e. the number of electrons per unit volume)

$I_e = e^2/(mc^2) = 2.82 \times 10^{-13}$ cm is the scattering amplitude of a single electron

$N_e$ is the number of electrons per one supra-molecule

M is the molecular weight of one supra-molecule

$d$ is the bulk density in $\text{g/cm}^3$