

# Origin and occurrence of selenium in some Australian coals

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## Abstract

The analyses are reported of six Australian coals for mineral type and content, B, Se speciation (by selective leaching) and S speciation (by selective leaching and XANES) together with XANES data for Se in one coal (from a marine sequence). The results of these analyses and of thermodynamic calculations of thiophenes and Se analogues are used to suggest that selenoprotein structures in coal's precursors (bacteria and algae and possibly higher plants) make Se bonding in coal unique from that of the other trace elements.

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## 1. Introduction

The occurrence of trace elements in coal has been extensively studied (see Swaine, 1990, 1995). Finkelman (1994, 1995) reports studies into the modes of occurrence and ranks the confidence (from one to a maximum of ten) in the assignment of the likely mode. There is a general consensus that Se is present in or associated with the organic matter, pyrite and accessory sulfides in most coals as well as occurring as selenides. Finkelman (1994, 1995) gives a rating of eight out of ten for the confidence in the speciation of Se in coal. Hower and Robertson (2003) tentatively identified clausthalite (PbSe) in coal. In a recent review (Yudovich and Ketris,

2006), the occurrence of Se and mineralogical associations in coals worldwide are discussed and relationships to S identified. Geochemically, it is to be expected that Se will behave like S as these elements share similar chemical behaviour.

The determination of the occurrence of trace elements in coal is difficult and there are significant differences in the techniques used by researchers. For a review of analytical techniques including those used for modes of occurrence, see Huggins (2002). In a report on the results of an international interlaboratory study, Davidson (2000) comments on the often poor agreement between techniques such as gravity separation and sequential leaching and the need for confirmation from techniques such as X-ray absorption near edge structure (XANES) spectrometry. Part of the problem is the very low concentrations at which many of the trace elements occur. This is a particular difficulty when analysing for

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Se as it occurs at very low levels in most coals. In Australian coals, pyrite contents are commonly low and Se is generally present at <1 mg/kg.

Even with these analytical difficulties, there is strong evidence for the occurrence of Se bound to or associated with the organic matter of most coals. [Dreher and Finkelman \(1992\)](#) report that Se in Powder River Basin coal occurs predominantly in the organic fraction with lesser amounts associated with pyrite and also in accessory sulfides (and selenides) as well as water soluble or exchangeable forms. [Huggins and Huffman \(1996\)](#) in a XANES study of two US coals (Lewiston–Stockton, West Virginia and Illinois #6, Illinois) from the Argonne Premium coal sample set, ([Vorres, 1990](#)) postulated that the Se was organically associated; this was based upon the position of the main absorption peak with respect to that of elemental Se. [Dale et al. \(1999\)](#) used selective leach techniques to estimate mineralogical associations of trace elements in six Australian coals; Se was reported as being present in pyritic (HNO<sub>3</sub> soluble) and organic (residual) phases.

The presence of Se in an “organic association” or occurrence as a species that is bonded within the organic matrix of coal poses interesting questions as to the origin of the Se. The probability is high that Se occurs in the coaly material (organic polymeric structures) in a similar manner to the organic S. The chemical forms and suggested origins of S in coal are reviewed by [Calkins \(1994\)](#). It is possible that organic S occurs in coals as sulfide linkages and thiols although [Davidson \(1993\)](#) suggests that thiophenic forms are the only species for which there is substantive evidence. Although there is no direct evidence for the nature of the organic Se in coal, it is possible that it would be present as analogues of standard S heterocyclic compounds ([Nishioka et al., 1986](#)), such as thiophenes.

[Casagrande et al. \(1979\)](#) report that the organic S is likely present (at least in part) as a consequence of the incorporation of the S amino acids present in the precursors of the coal. The very same origins and processes that lead to the incorporation of S into the organic matrix of coal may also be responsible for the incorporation of Se. Selenoproteins exist in bacteria and algae (see for example: [Stolz and Oremland, 1999](#); [Köhrle et al., 2000](#); [Fu et al., 2002](#); [Novoselov et al., 2002](#); [Jacob et al., 2003](#); [Foster, 2005](#); [Obata and Shiraiwa, 2005](#)) and it is possible that these could be incorporated into the matrix of coal in a similar manner to S-containing proteins. There is much debate on the occurrence of Se in and its essentiality to higher plants ([Terry et al., 2000](#); [Minorsky, 2003](#)). However, the possibility that selenoproteins in higher plants may also

be a source of organoselenium in coal should be considered.

[Casagrande et al. \(1979\)](#) also report that the organic S concentration in peat is also increased by reaction with H<sub>2</sub>S during the early stages of coalification. In the coal-forming environment, ubiquitous sulfate-reducing bacteria ([Postgate, 1979](#)) are a source of this H<sub>2</sub>S. A similar process may also be responsible for the incorporation of some Se in the organic matrix of coal. Biogeochemical processes in anoxic environments can lead to the production of H<sub>2</sub>Se ([Oremland, 1994](#); [White and Dubrovsky, 1994](#)). Presumably, the H<sub>2</sub>Se could react with peat in a similar manner to that of H<sub>2</sub>S.

[Casagrande and Ng \(1979\)](#) suggest that elemental S reacting with humic acids in peat may also be a source of organic S in coal. The laboratory experiment required refluxing of humic acids with chloroform containing dissolved elemental S. If such a process is considered to mimic or indicate possible reactions in nature, then one question that must also be considered is whether elemental Se can be incorporated into the organic matrix of coal. It is well established that species of anaerobic bacteria produce elemental Se (see for example: [Oremland, 1994](#); [Stolz and Oremland, 1999](#); [Stolz et al., 2002](#)) and that they would be present during coalification.

In this paper we report the concentration and forms of S and Se in six Australian coals. Data are also reported on the concentration and identification of the mineral matter in the same coals as well as the concentrations of B. The B concentrations provide an indication of marine influences i.e. high B concentrations are indicative of marine conditions ([Goodarzi and Swaine, 1994](#)). Also reported are the relative thermodynamic properties of S and Se analogues of compounds considered to be present in coal.

## 2. Experimental

### 2.1. Description of the Australian coal samples

Six coals from Permian and Triassic deposits in Australia (“Gondwana coals”) were analysed (see [Table 1](#)). Four of these were from the collection of the Cooperative Research Centre for Coal in Sustainable Development (CCSD). The two other coals were feed coals from Queensland power stations (see [Narukawa et al., 2003](#)).

The sample from the Great Greta Colliery is of the early Permian Tangorin seam, occurring within the Greta Coal measures. The Tangorin Seam is unusual in its high organic S content and has a marine influence unlike the

Table 1  
Description of coal samples

| Coal (location)           | Description                                                                          |
|---------------------------|--------------------------------------------------------------------------------------|
| Blair Athol (ROM)         | Permian, bituminous, Blair Athol Basin, Queensland                                   |
| Warkworth (ROM)           | Permian, bituminous, Sydney Basin, Hunter Valley, NSW                                |
| Great Greta (single seam) | Permian, bituminous, marine sequence, Sydney Basin, Hunter Valley, NSW               |
| Curragh (ROM)             | Permian, bituminous, Bowen Basin, Queensland                                         |
| Callide feed coal (ROM)   | Triassic, subbituminous, cool climatic non-marine deposit, Callide Basin, Queensland |
| Tarong feed coal (ROM)    | Triassic, bituminous, wet palaeo-environment, Meandu, Queensland                     |

Note: For more details on the geology of Australian coal basins refer to Ward et al. (1995).

coals described below which are of terrestrial origin. The Warkworth mine sample is a blend of six seams (Vaux, Mt. Arthur, Piercefield, Glen Munro, Woodlands Hill and Blakefield seams) occurring within the upper Permian Wittingham coal measures of the Sydney Basin. The sample from the Blair Athol mine is of a low-ash export thermal coal produced from a blend of the Nos 1, 3 and 4 seams. The coal is a medium volatile coal of Early Permian age deposited within the Blair Athol Basin, a structural outlier of the larger Bowen Basin. The Curragh coal is a steaming coal for domestic power generation and is produced from the Cancer, Aries, Castor, Pollux and Pisces seams within the Late Permian terrestrial Rangal Coal measures of the Bowen Basin. The Callide power station feed coal is a subbituminous high ash coal and is a blend of several seams within the Late Triassic coal measures of the Callide Basin in central Queensland. The sample of Tarong feed coal is from the Tarong mine and is a blend of three mined seams within the Upper Triassic Tarong Basin.

Apart from the Great Greta sample which is of a single seam, all samples are of run-of-mine (ROM) coals and are blends of working sections from an individual mine. Although the coals are blends rather than spot or individual ply samples from single seam sections, each of the coal samples represents a limited stratigraphic interval from a broadly similar depositional environment.

## 2.2. Analysis of the Australian coals

The minerals present in the coals were determined by X-ray diffraction (XRD) with quantification using SIROQUANT software after ashing at approximately 100 °C–150 °C in an oxygen plasma asher to obtain a low-temperature ash (LTA).

Moisture in the coals was determined by drying at 110 °C in a nitrogen-purged oven (Standards Australia, 1995).

Total S was determined using a sinter with Eschka's mixture and extraction with hydrochloric acid (Stan-

dards Australia, 1997) with final measurement by inductively coupled plasma atomic emission spectrometry (ICP-AES). The sulfate S and pyritic S were determined using a sequential acid leach procedure with hydrochloric and nitric acids (Standards Australia, 2002) and subsequent measurement of soluble Fe and S using ICP-AES.

Four of the coals were also analysed for forms of S using XANES spectroscopy at beam-line X-19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, New York. The S XANES spectra were collected in fluorescence mode using a PIPS detector. The spectra appear to contain varying amounts of the same S forms, with thiophenic S (peak at 2473.5 eV) and sulfate S (peak at 2482 eV) being dominant in all four spectra (Fig. 2). A least-squares fitting procedure was applied to the data to quantify the different S forms (Taghiei et al., 1992; Huggins et al., 1993). This least-squares fitting procedure fits the data to a model that employs peaks of Lorentzian–Gaussian shape and an edge function based on a double arctangent function. Small peaks representing minor S forms had to be added in order to obtain a reasonable fit. The area percentages were then converted to percentage S in the different forms according to the procedure described elsewhere (Taghiei et al., 1992; Huggins et al., 1993). As a consequence of sulfur's association with Fe and other heavy metals, FeS<sub>2</sub> and other metal sulfides are not normally observable in the S XANES spectra until pyritic S represents more than about 30% of the total S. Hence, the S XANES analysis is best suited for analysis of organic S and oxidised S forms, including elemental S.

B was determined by ICP-AES following ashing in the presence of Eschka's mixture and extraction with hydrochloric acid (Standards Australia, 1998a).

Total Se was determined using a standard procedure that requires sintering with Eschka's mixture, extraction with HCl, reduction of the Se to selenite and measurement using hydride/atomic fluorescence spectrometry (Standards Australia, 1998b).

Table 2

Thermodynamic data of elements in gaseous phase

| Element (spin state) | $\Delta H_f^\circ$ (298 K)<br>kJ mol <sup>-1</sup> | $\Delta G_f^\circ$ (298 K)<br>kJ mol <sup>-1</sup> | $S^\circ$ (298 K)<br>J mol <sup>-1</sup> K <sup>-1</sup> | $\Delta H_f^\circ$ (400 K)<br>kJ mol <sup>-1</sup> | $\Delta G_f^\circ$ (400 K)<br>kJ mol <sup>-1</sup> | $S^\circ$ (400 K)<br>J mol <sup>-1</sup> K <sup>-1</sup> |
|----------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------------|
| H ( <sup>2</sup> S)  | 217.999                                            | 203.278                                            | 114.716                                                  | 218.636                                            | 198.150                                            | 120.824                                                  |
| C ( <sup>3</sup> P)  | 716.652                                            | 671.228                                            | 158.093                                                  | 717.716                                            | 655.537                                            | 164.202                                                  |
| S ( <sup>3</sup> P)  | 276.980                                            | 236.500                                            | 167.828                                                  | 274.712                                            | 222.761                                            | 174.629                                                  |
| Se ( <sup>3</sup> P) | 235.350                                            | 195.261                                            | 176.716                                                  | 234.796                                            | 181.647                                            | 182.947                                                  |

The modes of occurrence of Se in the coals were determined by sequential extraction (and subsequent measurement using hydride reduction/atomic fluorescence spectrometry with standards prepared in matrices matched to the extractants). The sequential extraction procedures are described below:

- Soluble: 10 g coal was extracted with 200 mL MilliQ water in a closed polypropylene bottle; this was placed in an ultrasonic bath for 10 min to mix the contents; the bottle was then rolled for 18 h at ambient temperature. The extract was recovered by filtration; this was acidified prior to the determinations of the soluble Se.
- Exchangeable species: the washed residue was extracted (by rolling) with 200 mL of 1 M ammonium acetate for 18 h at ambient temperature to release “exchangeable” Se.
- Carbonate, oxide and monosulfide associated: the washed residue was extracted (by rolling) with 150 mL of 6 M HCl for 18 h at ambient temperature to dissolve the Se associated with the carbonates, oxides and monosulfides.
- Pyritic: the washed residue was extracted (by rolling) with 150 mL of 2 M HNO<sub>3</sub> to dissolve pyrite; again this was done for 18 h at ambient temperature.
- Silica bound: the silicate minerals in the washed residue were extracted with 25 mL conc. HF and 2.5 mL conc. HCl at 50 °C in a heated ultrasonic bath for 2 h; the extract was diluted to 150 mL with MilliQ water.
- Residual: determined by difference (total–sum of extractable phases) indicative of an organic association or occurrence in a resistate mineral phase.

X-ray absorption fine structure (XAFS) spectroscopy was also used to determine Se speciation in the Great Greta coal. This sample was selected as it had a concentration of Se high enough to obtain a reasonable spectrum. This coal was examined by Se K-edge XAFS spectroscopy using a 12-element germanium detector at beam-line X-18B of the National Synchrotron Light

Source (NSLS), Brookhaven National Laboratory, NY. Six scans were recorded, for a total of 72 individual spectra; these spectra were averaged to obtain the final overall spectrum.

### 2.3. Calculation of thermodynamic properties of possible organoselenium species

Statistical thermodynamics techniques and *ab initio* calculations were used to provide data for a comparison of the thermodynamic properties of possible organoselenium compounds with organosulfur compounds present in coal.

Statistical thermodynamics, appropriately summarised by Irikura (1998), includes methods used to convert molecular energy levels into macroscopic properties, especially enthalpies, entropies, and heat capacities. These energy levels arise from molecular translation (i.e., motion through space), rotation, vibration, and electronic excitation. Such information constitutes the spectroscopy of the molecule of interest

Table 3

Percentages of mineral phases in low temperature ashes of coals

|           | BA    | W     | GG    | C    | Callide pf | Tarong pf |
|-----------|-------|-------|-------|------|------------|-----------|
| LTA wt.%  | 8.9   | 13.9  | 18.5  | 21.8 | 28.3       | 36.6      |
| %         |       |       |       |      |            |           |
| Quartz    | 29.0  | 33.6  | 5.4   | 27.2 | 14.9       | 48.9      |
| Kaolinite | 63.2  | 37.9  | 32.7  | 21.9 | 68.1       | 50.0      |
| Illite    | 1.7   | 21.3  |       | 6.3  |            |           |
| Smectite  | 0.6   | 1.2   | 1.0   | 0.6  |            |           |
| Chamosite |       |       |       | 18.7 |            |           |
| Anatase   |       |       |       |      | 0.8        | 1.0       |
| Brookite  |       |       |       | 1.3  |            |           |
| Boehmite  |       |       |       |      | 0.5        |           |
| Hematite  | 1.9   | 0.3   |       |      | 3.0        |           |
| Calcite   |       |       | 18.9  | 10.4 |            |           |
| Ankerite  |       |       |       | 2.7  |            |           |
| Siderite  | 1.2   | 5.7   |       |      | 9.6        |           |
| Bassanite |       |       | 10.4  | 8.2  | 3.2        |           |
| Gypsum    |       |       | 11.8  |      |            |           |
| Anhydrite |       |       | 14.1  |      |            |           |
| Pyrite    | 2.5   |       | 5.7   | 2.6  |            |           |
| Total     | 100.1 | 100.0 | 100.0 | 99.9 | 100.1      | 99.9      |

Table 4  
Calculated percentages of mineral phases in coals

|           | BA   | W    | GG   | C    | Callide pf | Tarong pf |
|-----------|------|------|------|------|------------|-----------|
| %         |      |      |      |      |            |           |
| Quartz    | 2.58 | 4.67 | 1.00 | 5.93 | 4.22       | 17.90     |
| Kaolinite | 5.62 | 5.27 | 6.05 | 4.77 | 19.27      | 18.30     |
| Illite    | 0.15 | 2.96 |      | 1.37 |            |           |
| Smectite  | 0.05 | 0.17 | 0.19 | 0.13 |            |           |
| Chamosite |      |      |      | 4.08 |            |           |
| Anatase   |      |      |      |      | 0.23       | 0.37      |
| Brookite  |      |      |      | 0.28 |            |           |
| Boehmite  |      |      |      |      | 0.14       |           |
| Hematite  | 0.17 | 0.04 |      |      | 0.85       |           |
| Calcite   |      |      | 3.50 | 2.27 |            |           |
| Ankerite  |      |      |      | 0.59 |            |           |
| Siderite  | 0.11 | 0.79 |      |      | 2.72       |           |
| Bassanite |      |      | 1.92 | 1.79 | 0.91       |           |
| Gypsum    |      |      | 2.18 |      |            |           |
| Anhydrite |      |      | 2.61 |      |            |           |
| Pyrite    | 0.22 |      | 1.05 | 0.57 |            |           |
| Total     | 8.91 | 13.9 | 18.5 | 21.8 | 28.3       | 36.6      |

Note: The mineral phases, bassanite, gypsum and anhydrite may have formed during ashing.

and can be obtained experimentally or from calculations. The enthalpy of formation and free energy of a species may be derived by using both predictive methods via quantum mechanical *ab initio* techniques and utilisation of experimental enthalpies of formation at standard conditions for each constituent element.

*Ab initio* techniques produce detailed structure-oriented molecular energy information although no or limited thermodynamic information is directly available. Furthermore, the raw results do not correspond to properties at absolute zero temperature and must always be corrected. Post-processing of results is therefore needed to generate familiar, ideal-gas quantities such as the standard molar entropy ( $S^\circ$ ), heat capacity ( $C_p^\circ$ ), and enthalpy change [ $H^\circ(T) - H^\circ(0)$ ]. From an *ab initio* approach, electronic, thermal enthalpies, free energies as well as incorporation of zero-point vibrational energy (ZPE) corrections (i.e. corrections for the small residual motion at absolute zero temperature), all contribute inclusively to relate structure to thermal stability and activity.

Density functional theory (DFT) calculations were used to predictively calculate the enthalpy of formation ( $\Delta H_f$ ) and free energy ( $\Delta G_f$ ) of S and Se compounds possibly present in coal. DFT methods have been widely used in the calculation of molecular geometries and vibrational frequencies provided that suitably large basis sets are utilised to ensure an acceptable level of accuracy when comparing to experimental published data. DFT methods account for electron correlations accounting for the instantaneous interactions of pairs of electrons. All vibrational frequencies were calculated from ground state optimised structures *in vacuo* at a B3LYP level of theory incorporating the cc-pvtz basis set for H, C, S and Se elements (Dunning, 1989; Woon and Dunning, 1993; Wilson et al., 1999).

In order to calculate enthalpic and formation energies of compounds, it is necessary to calculate accurate geometries for the formation products, corresponding vibrational frequencies and electronic energies. Thermodynamic data at standard state of the elements present in the compounds of interest were drawn from published data (Barin et al., 1989) and are summarised in Table 2 along with the appropriate spin states.

In calculating the vibrational frequencies, appropriate scaling factors were incorporated to counter the effect of overestimation of vibrational energies inherent with the use of DFT. (Scott and Radom, 1996; Sinha et al., 2004). All calculations were done with the Gaussian 03 code (Frisch, 2004).

### 3. Results and discussion

The LTA yields and the percentages of the mineral phases present in the ash are listed in Table 3. The mineral phase percentages were calculated to a coal basis and are reported in Table 4. These LTA yields (Table 4) provide an approximation of the mineral matter content of the coals.

It is apparent from the data in Tables 4 and 5 that there is no simple relationship between the mineral matter contents and Se concentrations nor between the pyrite concentration and the Se concentration. The

Table 5  
Forms of Se in coals

| Coal    | MilliQ | Acetate | HCl   | HNO <sub>3</sub> mg/kg | HF   | Sum  | Total | Organic % of total |
|---------|--------|---------|-------|------------------------|------|------|-------|--------------------|
| BA      | 0.02   | <0.01   | 0.02  | 0.10                   | 0.07 | 0.21 | 0.81  | 74                 |
| W       | 0.03   | <0.01   | 0.01  | 0.03                   | 0.02 | 0.08 | 0.50  | 84                 |
| GG      | 0.19   | <0.01   | 0.03  | 0.47                   | 0.01 | 0.70 | 3.45  | 80                 |
| C       | 0.04   | <0.01   | <0.01 | 0.07                   | 0.06 | 0.18 | 0.38  | 53                 |
| Callide | 0.02   | <0.01   | <0.01 | 0.03                   | 0.04 | 0.09 | 0.38  | 77                 |
| Tarong  | 0.10   | 0.01    | 0.02  | 0.03                   | 0.03 | 0.18 | 0.57  | 69                 |

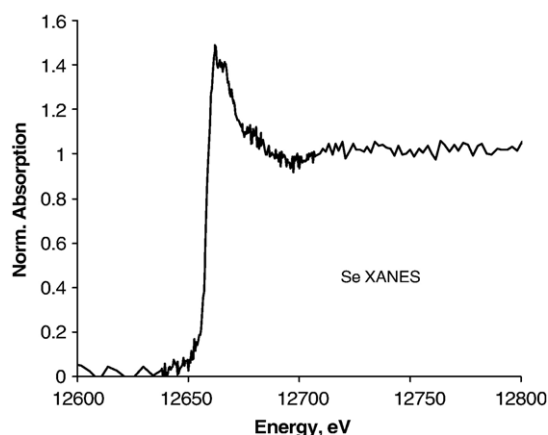


Fig. 1. XANES spectrum of Se in Great Greta coal.

analyses of the extractant solutions used to estimate the amounts of Se associated with each phase in the coal are given in Table 5. The difference between the sum of the extracted Se and the total Se is defined as the organic or organically associated Se. This is expressed as a percentage of the total Se present in each of the coals.

From the data in Table 5, it is obvious that most of the Se is present in the residual matter (organic or resistate minerals) in the coals. There does not appear to be any reports of the occurrence of acid-resistate minerals containing Se, commonly occurring in coal (Wedepohl, 1969). Although it is possible that fine-grained sulfides (e.g. pyrite) maybe protected from acid attack, the assumption of an organic association for Se is strong for all of these coals. This observation that Se is organically associated is similar to the findings generally of researchers worldwide (see Finkelman, 1994, 1995; Yudovich and Ketris, 2006). Lesser amounts are present in an HCl-soluble form, most probably in monosulfides or as selenides (e.g. Hower and Robertson, 2003) or bonded to Fe oxides (see also Swaine, 1990). These findings that Se in Australian coals is present primarily in the organic matter and also associated with pyrite are consistent with those of Dale et al. (1999).

Table 6  
Concentrations of S species and B in the coals

| Coal        | S Species (%) |         |         |         | B<br>mg/kg |
|-------------|---------------|---------|---------|---------|------------|
|             | Total         | Pyritic | Sulfate | Organic |            |
| Blair Athol | 0.29          | 0.12    | 0.02    | 0.15    | 20         |
| Warkworth   | 0.40          | 0.07    | <0.01   | 0.33    | 15         |
| Great Greta | 5.32          | 0.53    | 0.12    | 4.67    | 86         |
| Curragh     | 0.71          | 0.36    | 0.08    | 0.27    | 6          |
| Callide     | 0.19          | 0.02    | 0.02    | 0.15    | 18         |
| Tarong      | 0.23          | 0.06    | 0.02    | 0.15    | 12         |

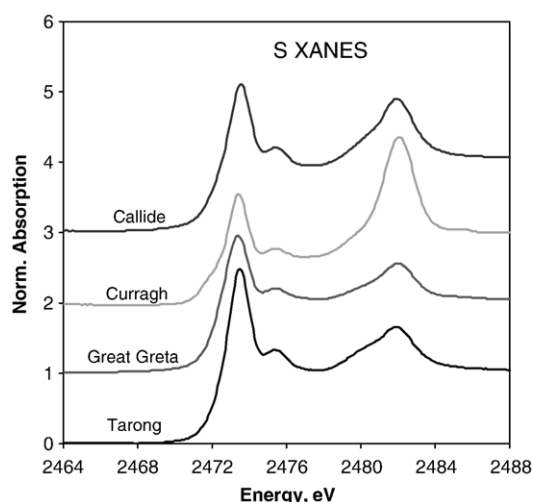


Fig. 2. XANES spectra of S in four of the Australian coals.

There are some low amounts of water soluble Se present in some coals; in particular Tarong and Great Greta. It is possible that the presence of soluble Se is a consequence of some oxidation and selenite or selenate salts are present.

The spectrum obtained via XANES spectroscopy for Se in the Great Greta coal is shown in Fig. 1. One broad, poorly structured peak is observed at the Se absorption edge; indicating the presence of more than one Se form. Based on the position at mid-peak, the selenite oxidation state ( $\text{SeO}_3^{2-}$ ) is definitely present. Other Se forms, involving both higher and lower oxidation states, are also likely to be present. The lower oxidation state could be either Se associated with pyrite or organically associated Se or a mixture of the two. However, it can be noted that the characteristic spectrum associated with Se in pyrite (Huggins and Huffman, 1996) does not appear to be significant, suggesting that this is not a major form. In view of the fact that much (~80%) of the Se in this coal is not leached by any of the reagents, there is strong evidence that such Se is associated with the organic matter, possibly in substitution for S in thiophene or other organosulfur forms. The XANES

Table 7  
Distribution of sulfur among major sulfur forms (excluding metal sulfides) in four of the coals (XANES data)

| Coal    | %S as   |              |            |         |         |
|---------|---------|--------------|------------|---------|---------|
|         | Elem. S | Org. sulfide | Thiophenic | Sulfone | Sulfate |
| Callide | 29      | <5           | 48         | 2       | 21      |
| Curragh | 10      | <5           | 49         | 3       | 38      |
| G Greta | <3      | 21           | 73         | <2      | 6       |
| Tarong  | 5       | 7            | 74         | <2      | 14      |

Table 8  
Comparisons of S and Se forms in coals

|             | Total S | Total Se | Py S | Py Se | Org S | Org Se |
|-------------|---------|----------|------|-------|-------|--------|
|             | %       | mg/kg    | %    | mg/kg | %     | mg/kg  |
| Blair Athol | 0.29    | 0.81     | 0.12 | 0.10  | 0.15  | 0.60   |
| Warkworth   | 0.40    | 0.50     | 0.07 | 0.03  | 0.33  | 0.42   |
| G Greta     | 5.32    | 3.45     | 0.53 | 0.47  | 4.67  | 2.75   |
| Curragh     | 0.71    | 0.38     | 0.36 | 0.07  | 0.27  | 0.20   |
| Callide     | 0.19    | 0.38     | 0.02 | 0.03  | 0.15  | 0.29   |
| Tarong      | 0.23    | 0.57     | 0.06 | 0.03  | 0.15  | 0.39   |

spectrum would appear to confirm this observation; in addition it provides evidence for more oxidised Se forms, i.e. the existence of water-soluble selenite and/or selenate salts.

The concentrations of total, pyritic and organic S together with the concentration of B in each coal are listed in Table 6.

B concentrations in five of the six coals are in the range of 6–20 mg/kg (Table 6). The exception is the Great Greta coal; this coal contains B at a concentration of 86 mg/kg. This is consistent with some marine influence (Goodarzi and Swaine, 1994). Most of the Australian Gondwana coals are overlain by Permian and Triassic rocks of freshwater origin (Taylor et al., 1998). One of the exceptions is the Greta seam that is overlain by marine sediments (Taylor et al., 1998, p 323).

The XANES spectra of the forms of S in four of the six coals are shown in Fig. 2. The two major peaks arise from thiophenic S (at 2473.5 eV) and from sulfate S (at 2482 eV). The results of the XANES data for S are listed in Table 7.

The most surprising result is the relatively low %S as sulfate for the Great Greta coal. Based on the XRD analysis of the low temperature ash (Tables 3 and 4), this coal appears to contain significant amounts of anhydrite, bassanite and gypsum, but the percentage S as sulfate for this coal is the lowest of the four coals. The high levels recorded in the XRD mineralogical analysis are due to the reaction of the oxides of the organically bound S with Ca compounds during the ashing process.

Table 9  
Heats of formation and free energies at 298 K (1 atm) and 400 K (150 atm) of S and Se model compounds

| Molecule           | 298 K (1 atm)      |                    | 400 K (150 atm)    |                    |
|--------------------|--------------------|--------------------|--------------------|--------------------|
|                    | $\Delta H_f^\circ$ | $\Delta G_f^\circ$ | $\Delta H_f^\circ$ | $\Delta G_f^\circ$ |
| Thiophene          | 473                | 564                | 463                | 130                |
| Selenophene        | 518                | 609                | 509                | 175                |
| Dibenzothiophene   | 330                | 372                | 321                | 54                 |
| Dibenzoselenophene | 366                | 409                | 360                | 91                 |

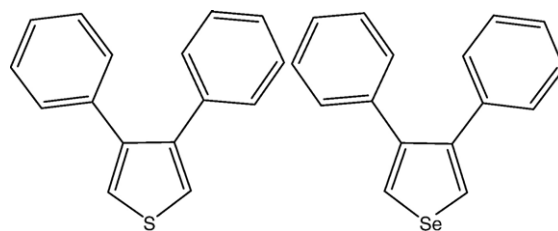


Fig. 3. Thiophene and the Se analogue.

The presence of elemental S is also a little unusual. It may be an oxidation product and there is possibly an error in estimating the relative amounts of elemental S in the low S coals. Elemental S would report as organic S in the chemical separation approach (Table 6). A comparison of the data in Tables 6 and 7 indicates that the relative amounts of sulfate S and organic S (assuming elemental reports as organic) are in reasonable agreement.

The concentrations of pyrite, total Se and “pyritic” Se, calculated from the chemical extractions are listed in Table 8.

Pyrite, although common in the Gondwana coals, occurs at low concentrations. Pyrite has been identified in three of the coal samples (see Tables 3 and 4). Chemical analysis indicates that pyrite is present at low levels in all of the coals; this is confirmed by XRD on the low temperature ashes but was not identified in the other three samples as the concentrations are below the detection limit of the technique. The coals are low in S and most of this is organic S. Again, the only coal in this suite of samples that has a high organic S content is the marine influenced coal from Great Greta. This coal also contains the greatest concentration of total Se, organic Se and also of pyritic Se (Tables 4–6).

There is some evidence of a relationship between the various forms of S and Se (Table 8). Although there is no simple direct correlation, the concentrations of Se are approximately four orders of magnitude lower than that of S in each of the forms. This is consistent with the observation of Jacob et al. (2003) that “Se in the earth’s crust is about four orders of magnitude lower than that of sulfur, and this is also reflected in the natural abundance of these elements in biological systems”. Similarly, Adriano (2001) reports the concentration of

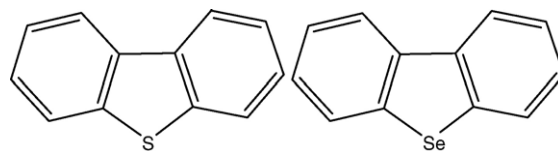


Fig. 4. Dibenzothiophene and the Se analogue.

Se in the earth's crust to be in the range 0.05–0.09 mg/kg; about 1/6000 of the abundance of S.

The fundamental thermodynamic properties (Heats of Formation and Gibb's Free Energies) of possible S compounds and the corresponding Se analogues are listed in Table 9. The molecular structures of the compounds are shown in Figs. 3 and 4.

The possibility that organic Se compounds analogous to those of S exist in coal has been discussed above. Thermodynamic calculations indicate that there are thermodynamic constraints to the replacement of S with Se to form selenophene moieties in the polyaromatic structures of coal and this is evident at both STP and at higher pressure and temperature (in the coalification range). Thus there is some thermodynamic inhibition to the formation of selenophenes. Biological activity may overcome this thermodynamic disadvantage. The major limiting factor in the incorporation of Se into the coal matrix may simply be related to its availability in comparison to that of S in the precursor material and in the environment during coalification.

#### 4. Concluding remarks

The mode of occurrence designated "organic association" is where the majority of Se occurs in the six Gondwana coals from Australia. There is little direct evidence for organic bonding of Se in maceral structures. The determination of this mode of occurrence is the most uncertain being based on the presence of the analyte in the residual organic matter following acid extraction. However, in the absence of any acid resistate minerals containing Se and the low concentrations of pyrite in the coals (with the exception of Great Greta), it is likely that much of the Se is organically bonded in the coal structure. Confirmatory data were obtained by XANES on the Great Greta coal; the spectrum is consistent with an organic bonding of the greater proportion of the Se.

Whether the bonding is analogous to that of S has yet to be determined but considering their similar chemistry, it is possible. In absence of direct evidence, there is certainly strong circumstantial evidence for organic bonding of Se in the coaly material. Of course, Se will also coprecipitate with sulfides in reducing environments. The presence of Se in sulfides or as selenides is to be expected in coals. Bacterial reduction is obviously a factor. Anaerobic bacteria including the ubiquitous sulfate-reducing bacteria would be present in coal-forming swamps or mires. Interestingly, Se is the only metal/metalloid element that forms amino acids and thus selenoproteins. It is the presence of selenoprotein structures in coal's precursors (bacteria and algae and

possibly higher plants) that potentially makes Se bonding in coal unique from that of other trace elements.

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