Available online at www.sciencedirect.com

ScienceDirect

International Journal of Coal Geology 69 (2007) 205–219

International Journal of COAL GEOLOGY

www.elsevier.com/locate/ijcoalgeo

Variations in elemental composition of macerals with vitrinite reflectance and organic sulphur in the Greta Coal Measures, New South Wales, Australia

Colin R. Ward *, Zhongsheng Li, Lila W. Gurba [1]

School of Biological, Earth and Environmental Sciences University of New South Wales, Sydney 2052, Australia

Received 4 January 2006; received in revised form 9 March 2006; accepted 9 March 2006
Available online 15 May 2006

Abstract

The elemental composition of the individual macerals in the Early Permian Greta Coal Measures of the northern Sydney Basin and adjoining Cranky Corner Basin, New South Wales, including some seams with high to very high organic sulphur contents, have been analysed in polished sections using light-element electron microprobe techniques, and the results evaluated in the light of vitrinite reflectance and other characteristics of the coals concerned. As with other Australian coals, the vitrinite macerals in each sample have the lowest proportions of carbon and highest proportions of oxygen, and the inertodetrinite and fusinite macerals the highest C and lowest O contents. Semifusinite and the liptinite macerals have intermediate C and O percentages. Organic sulphur and organic nitrogen are also highest in the vitrinite macerals of the individual samples, and lowest in the fusinite and inertodetrinite components.

The vitrinite macerals in the Puxtrees seam of the Greta Coal Measures on the Muswellbrook Anticline, in the upper Hunter Valley, have similar elemental compositions (78% C) and similar reflectance values (Rv_{max} around 0.7%) to vitrinites in the Late Permian bituminous coals in other parts of the Sydney-Bowen Basin. The vitrinites in the seams of the Cranky Corner Basin also have similar carbon contents to the Puxtrees seam material, suggesting a similar rank level, but have much lower vitrinite reflectance values ($Rv_{max}=0.4$–0.5%), probably due to marine influence associated with the depositional system. The vitrinites in the Greta seam on the Lochinvar Anticline, in the Lower Hunter region, have higher carbon contents (83%) than the Puxtrees material, suggesting a higher rank level, but similar to lower vitrinite reflectance values ($Rv_{max}=0.6$–0.7%). Vitrinite carbon is also constant through the seam profile, despite upwardly decreasing reflectance values in the seam due to progressive increases in marine influence.

The vitrinites in the upper Greta seam and the Cranky Corner Basin coals have high to very high organic sulphur contents, again probably due to marine influence on the depositional process. The vitrinites in the Cranky Corner Basin coals, which have particularly high organic sulphur contents, also have somewhat lower oxygen contents in relation to their carbon percentages than those of other Australian seams, suggesting that the additional organic sulphur has replaced oxygen in the macerals' molecular structure. The macerals, especially the vitrinites, in the coals with high organic sulphur and anomalously low vitrinite reflectance also have up to 0.5% Al and 1% Ca intimately associated with the organic matter. Similar organically associated inorganic elements are commonly found in lower-rank (e.g. sub-bituminous) coals, but are usually lost from the organic matter at higher rank levels. The coals of the Greta Coal Measures therefore have vitrinite carbon contents consistent with a high volatile bituminous rank, but

---

* Corresponding author. Fax: +61 2 9385 1558.
E-mail address: C.Ward@unsw.edu.au (C.R. Ward).

[1] Present address: Co-operative Research Centre for Coal in Sustainable Development, PO Box 883, Kenmore 4069, Australia.

doi:10.1016/j.coal.2006.03.003

those seams or parts of seams with high organic sulphur due to substantial marine influence appear to have preserved the vitrinite reflectance values and organically associated inorganic elements more typical of lower-rank, sub-bituminous materials.

Keywords: Coal chemistry; Organic sulphur; Electron microprobe; Vitrinite reflectance; Inorganic elements; Sydney Basin; Australia

1. Introduction

The Early Permian Greta Coal Measures are exposed and mined on the Lochinvar and Muswellbrook Anticlines in the northern part of the Sydney Basin, New South Wales (Fig. 1). The unit is also present in the Cranky Corner Basin, a small outlier basin a short distance to the north, located within the adjacent New England Fold Belt and separated from the Sydney Basin by the Hunter Thrust fault system. Details of the geology of the Greta Coal Measures in these areas are provided by several authors, including Van Heeswijck (2001), Agnew et al. (1995), Sniffin and Beckett (1995), Hamilton (1986) and Basden (1969). The principal stratigraphic subdivisions of the unit in each area, based on these studies, are summarised in Table 1.

The Greta Coal Measures is underlain and overlain by marine strata, the Dalwood Group and the Maitland Group, respectively (Table 1). Many of the coals in the unit also have unusually high sulphur contents for Australian seams (Maher et al., 1995). The upper part of the main seam of the Greta Coal Measures in the Lochinvar Anticline area, the Greta seam (Greta Coal Member of the Kitchener Formation), typically has visible pyrite, and also has a higher sulphur content (both pyritic and organic) than the lower 2–3-m section (Basden, 1969). Only the lower section is usually extracted in mining operations. The main seam in the Cranky Corner Basin, the Tangorin seam, has up to 6% total sulphur (Joint Coal Board and Queensland Coal Board, 1987; Maher et al., 1995), much of which occurs in organic form.

The marine origin of the overlying strata has also had a significant influence on the vitrinite reflectance in the seams of the Greta Coal Measures. Diessel (1992, p. 486) and Diessel and Gammidge (1998), for example, indicate that the mean random reflectance of

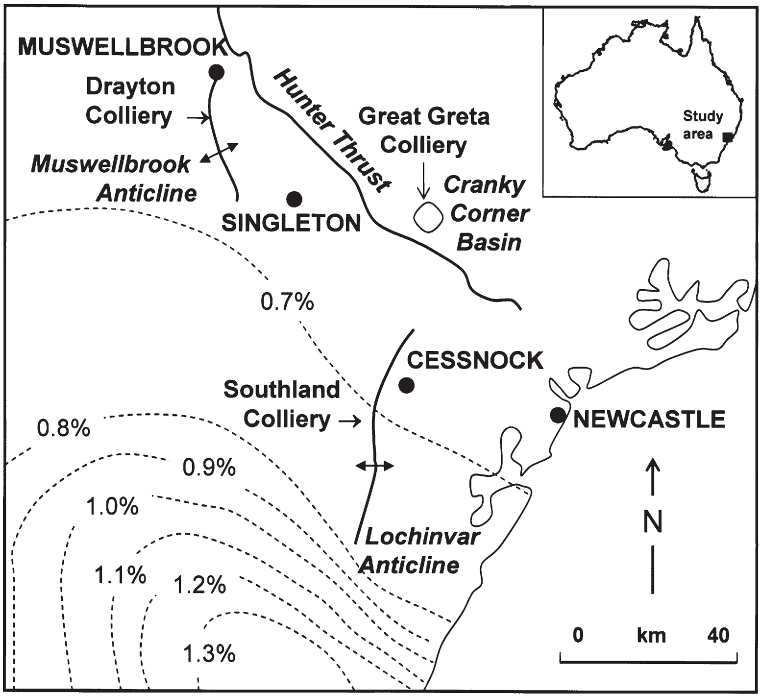

Fig. 1. Locality map of the northern Sydney Basin, showing major structures and sample locations. Contour lines represent mean maximum vitrinite reflectance in the Late Permian coal-bearing sequence (Wittingham Coal Measures and equivalents) after Brown et al. (1996).

Table 1
Stratigraphy of the Greta Coal Measures in different parts of the study area

	Lochinvar Anticline (Agnew et al., 1995; van Heeswijck, 2001)			Muswellbrook Anticline (Hamilton, 1986; Sniffin and Beckett, 1995)			Cranky Corner Basin (van Heeswijck, 2001)	
Early Permian	Maitland Group	Branxton Formation	Cessnock Sandstone Member	Maitland Group	Branxton Formation		Maitland Group	Big Table Top Formation
	Greta Coal Measures	Paxton Formation	Pelton Coal Member Bellbird Lens	Greta Coal Measures	Rowan Formation	Hilltop Coal Member	Greta Coal Measures	Tangorin seam
		Kitchener Formation	Greta Coal Member			Brougham Coal Member		
		Kurri Kurri Conglomerate	Homeville Coal Member			Grasstrees Coal Member		Stanhope seam
		Neath Sandstone				Puxtrees Coal Member		
					Skeletar Formation	Ayrdale Sandstone Member		
						Balmoral Coal Member		
	Dalwood Group	Farley Formation		Dalwood Group	Gyarran Volcanics		Dalwood Group	Billy Brook Formation

telocollinite (collotelinite) in the Greta Coal Member in two different vertical sections on the Lochinvar Anticline decreases from between 0.6% and 0.7% at the base of the seam to around 0.5% at the top, where the coal is overlain by the lacustrine to brackish sediments of the Bellbird Lens (Table 1) as a result of marine transgression. In the overlying Pelton Coal Member, which is in turn overlain by the marine sediments of the Maitland Group, Diessel (1992) further indicates that the random reflectance of telocollinite drops from 0.55% at the base of the seam to around 0.4% at the top. The fluorescence of the vitrinite also increases in both seams, in conjunction with the decreases in reflectance values.

Diessel and Gammidge (2003), who investigated the variations in vitrinite reflectance through the lower part of the Cranky Corner Basin succession, indicate that the mean random vitrinite (telocollinite or collotelinite) reflectance decreases from around 0.77% at the base of the Greta Coal Measures to 0.42% just above the top of the Stanhope seam. Although the pattern elsewhere in the section is influenced by a number of factors, this particular contrast, which occurs over only a short stratigraphic distance (around 120 m), is suggested to be due to marine influence on the coal, taking place especially above a conglomerate band that divides the seam into two separate splits.

Although only limited data are available, the vitrinite reflectance values in the seams of the Greta Coal Measures on the Muswellbrook Anticline are typically around 0.65% to 0.7% (Joint Coal Board and Queensland Coal Board, 1987), with no published reports of anomalously low reflectance values either within or between the individual coal beds.

The purpose of the present study was to investigate further the nature of the coals in the Greta Coal Measures, focusing on the elemental chemistry of the individual macerals using light-element electron microprobe techniques (Bustin et al., 1993, 1996; Gurba and Ward, 2000; Ward et al., 2005). A particular objective was to investigate the relation between maceral chemistry and vitrinite reflectance in coals showing the effects of marine influence, especially in cases, such as the Greta Coal Member (Greta seam) on the Lochinvar Anticline, where significant changes of reflectance appear to occur within a single coal bed. Another objective was to investigate the partitioning of organic sulphur among the individual macerals within the high-sulphur coals of this Early Permian succession, especially those of the Cranky Corner Basin, in relation to partitioning established for lower-sulphur coals in the Sydney, Gunnedah and Bowen Basins (Ward and Gurba, 1998, 1999; Ward et al., 2005).

2. Coal samples

A total of 15 coal samples were analysed for the present study (Tables 2 and 3), representing the Greta Coal Measures and some of the overlying Late Permian coal seams from the Lochinvar and Muswellbrook Anticlines and the Cranky Corner Basin.

A series of three coal samples was provided for the study from the Greta seam at Southland Colliery, an underground mine located around 10 km west of Cessnock in the Lochinvar Anticline area (Fig. 1). The

Table 2
Properties of coal samples from the Lochinvar Anticline (Southland Colliery) and Cranky Corner Basin

	Lochinvar Anticline			Cranky Corner Basin			
	Greta seam			Tangorin seam			Stanhope seam
	Top	Middle	Bottom	Ply 1	Ply 4	Composite	Ply 2
Ply thickness	2.2 m	1.0 m	2.0 m	0.46 m	1.72 m	4.10 m	0.47 m
Proximate analysis (% ad)							
Moisture	1.9	2.4	2.4	1.6	1.5	1.9	2.4
Ash	8.6	3.9	4.4	10.5	8.4	13.6	17.4
VM	43.3	41.3	41.0	50.8	49.2	46.4	38.2
FC	46.2	52.4	52.2	37.1	40.9	38.1	42.0
Rv_{max} (%)	0.62	0.69	0.70	0.40	0.48	0.45	0.54
Sulphur forms (% ad)							
Total sulphur	3.87	1.55	1.06	6.18	5.94	5.55	7.58
Pyritic sulphur	1.18	0.2	0.14			1.00	5.74
Sulphate sulphur	0.02	0.02	<0.01			0.01	0.12
Organic sulphur	2.68	1.33	0.92			4.54	1.72
Ultimate analysis (% daf)							
Carbon	83.8	85.3	84.8			78.5	
Hydrogen	6.35	6.16	6.23			6.44	
Nitrogen	1.77	1.98	2.00			1.20	
Sulphur	4.32	1.65	1.14			5.57[a]	
Oxygen	3.8	4.9	5.8			8.3	

[a] Organic sulphur only.

Table 3
Location and properties of other coal samples studied

Sample identification	Location and stratigraphy	Rv_{max} (%)
Greta A	Southland Colliery, Lochinvar Anticline, 1 m above seam floor, grab sample	0.66
Greta B	Southland Colliery, Lochinvar Anticline, 1 m below seam roof, grab sample	0.64
Greta C	Southland Colliery, Lochinvar Anticline, 1.5 m above seam floor, grab sample	0.66
Greta seam torbanite	Pelton Colliery, Lochinvar Anticline, 1.5 m above seam floor, grab sample	
Puxtrees seam	Greta Coal Measures, Drayton Colliery, Muswellbrook Anticline, Ply 2	0.67
Lower Pikes Gully seam	Wittingham Coal Measures, Howick Colliery, Muswellbrook area, grab sample	0.63
Upper Liddell seam	Wittingham Coal Measures, Howick Colliery, Muswellbrook area, grab sample	0.65
Woodlands Hill seam	Wittingham Coal Measures, Saxonvale Colliery, Singleton area, grab sample	0.75

samples were taken by the colliery operators to represent the upper, middle and lower sections of the Greta seam (Greta Coal Member), and key properties of the sub-sections sampled are listed in Table 2. The three parts of the seam have broadly similar whole-coal chemical properties, especially with respect to carbon, hydrogen and nitrogen (dry, ash-free basis). However, the total sulphur content of the coal (daf basis) increases significantly through the section, from around 1% in the lower part of the seam to a little over 4% in the upper part. Part of this variation is due to an increase in pyritic sulphur and part due to a substantial increase in the (whole-coal) organic sulphur content.

Several additional coal samples were provided for the study from other parts of the Greta seam in and around the mine area. Three grab samples of coal were taken from different horizons within the seam at Southland (Table 3), to supplement the three ply samples referred to above. A grab sample of boghead coal (torbanite) from a horizon around 0.5 m thick within the lower part of the Greta seam at Pelton Colliery, a few kilometres north of the Southland operation, was also used in the study, to provide data on a contrasting coal type, rich in alginite, within the same coal bed.

A second series of samples was provided from an exploration borehole near Great Greta Colliery in the Cranky Corner Basin. Samples from two of the plies within the Tangorin seam and of one ply within the Stanhope seam from this borehole (Table 2) were used in the study, along with a composite sample representing the full section of the Tangorin seam. The Stanhope and Tangorin seams both have relatively high total sulphur (Table 2), with around 7.5% total sulphur (air-dried) indicated for the Stanhope ply studied and around 6% for the Tangorin seam samples. Most of the sulphur in the Stanhope seam (5.75%) appears to be pyritic in nature; the whole-coal organic sulphur in the sample studied was only 1.75%. Most of the sulphur in the Tangorin seam (4.5% air-dried), however, is organic; pyritic sulphur only makes up 1% (air-dried) of the composite section studied.

A ply sample from the Puxtrees seam (Table 1) in the Greta Coal Measures at Drayton Colliery, an open-cut mine on the Muswellbrook Anticline (Fig. 1), was also used as part of the sampling program. Grab samples from two seams in the lower part of the Late Permian Wittingham Coal Measures at Howick Colliery, 10 km SE of Drayton, and the upper part of the Wittingham Coal Measures at Saxonvale (now Bulga) Colliery, 15 km south of Singleton (Fig. 1), were also studied, to provide a basis for comparison to other seams in the Hunter Valley succession.

3. Analytical methods

Coarsely crushed (<5 mm) samples of each coal were prepared as polished sections in the same way as grain mount 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, using conditions and calibration standards as described by Ward et al. (2005). The accelerating voltage for the electron beam was 10 kV and the filament current 20 nA, with a magnification of 20,000× giving an 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. A range of mineral standards (Ward et al., 2005) was used for the other elements.

The percentages of carbon, oxygen, nitrogen, sulphur, silicon, aluminium, calcium and iron were measured for each point, with a note on the type of maceral represented in each case. The results of the individual analyses were tabulated in spreadsheet format. Although care was taken to analyse only “clean” macerals and avoid areas where visible minerals were also present, the area analysed for some points unavoidably included mineral components (e.g. quartz, clay, pyrite) as well as the organic matter. Points that apparently included mineral contaminants (e.g. points with high Si or points with particularly high percentages of both Fe and S) were excluded from consideration; so, too, were points that included some of the mounting epoxy resin (e.g. epoxy filling empty cell structures), indicated by unusual oxygen and high nitrogen contents.

Other polished sections of the coals were subjected to conventional petrographic studies using optical microscopy, including measurement of the mean maximum vitrinite (telocollinte) reflectance.

4. Maceral chemistry in the Greta seam

4.1. Carbon, oxygen and nitrogen

Microprobe and vitrinite reflectance data for the three Greta seam samples from the Southland seam section (Table 2), and also for the three grab samples from the same colliery (Table 3), are summarised in Table 4. As with coals from other areas (Ward and Gurba, 1999; Ward et al., 2005), the vitrinite macerals of each sample have the lowest proportions of carbon and highest proportions of oxygen, and the inertodetrinite and fusinite particles have the highest C and lowest O contents. Semifusinite and the liptinite macerals have intermediate C and O percentages. Organic nitrogen is also highest in the vitrinites and lowest in the fusinite and inertodetrinite components (cf. Gurba, 2001).

The two main vitrinite macerals, telocollinite (collotelinite) and desmocollinite, have similar proportions of carbon and oxygen in the samples from the seam section, but in the grab samples the desmocollinite tends to have a slightly higher proportion of C and a lower proportion of O than the telocollinite in the same coal samples. The inertodetrinite in all of the Greta seam samples appears to have slightly more C and less O than the fusinite in the same coals. Similar contrasts in C and O content were noted by Ward et al. (2005) for a series of coals from the Bowen Basin of Queensland.

Although only a few particles were able to be studied without overlap of the measuring spot by other macerals, the liptinites in the coals appear to have slightly higher carbon and significantly lower oxygen contents than the respective vitrinite components (Table 4). Most of the liptinite macerals studied under the microprobe were sporinites, but the torbanite sample provided an opportunity also to evaluate the elemental composition of the alginite component. This appears to be similar to the elemental composition of alginites reported by Mastalerz and Hower (1996) from Carboniferous coals of comparable rank, such as the Skyline

Table 4
Elemental composition of macerals in Greta seam samples from the Lochinvar Anticline

	Rv_{max} (%)	Maceral	No	C%	O%	N%	S%	Al%	Si%	Ca%	Fe%
Southland top section, 2.2 m	0.62	TC	24	83.66	8.35	1.82	2.44	0.20	0.04	0.12	0.04
		DSC	13	83.60	8.46	1.86	2.56	0.20	0.06	0.17	0.01
		SP	3	89.49	4.77	1.30	2.03	0.07	0.08	0.04	0.04
		SF	9	86.74	6.66	1.80	1.16	0.14	0.03	0.13	0.04
		FUS	15	90.21	4.01	1.40	0.74	0.04	0.02	0.19	0.04
		IND	3	92.95	2.58	0.92	0.50	0.03	0.09	0.19	0.09
Southland middle section, 1.0 m	0.69	TC	18	83.25	8.91	1.97	1.39	0.14	0.03	0.06	0.02
		DSC	16	83.75	8.56	1.99	1.40	0.16	0.03	0.05	0.03
		SP	3	89.03	4.88	1.42	1.12	0.02	0.01	0.01	0.04
		SF	19	86.68	6.81	1.37	0.86	0.01	0.02	0.10	0.03
		FUS	18	90.65	4.10	0.94	0.49	0.02	0.04	0.09	0.04
		IND	4	93.49	2.65	0.33	0.42	0.00	0.01	0.19	0.06
Southland bottom section, 2.0 m	0.70	TC	17	83.64	8.59	1.71	1.08	0.14	0.03	0.05	0.03
		DSC	10	83.33	8.84	1.95	1.09	0.18	0.08	0.18	0.04
		CUT	3	88.58	5.48	0.84	0.77	0.06	0.04	0.05	0.00
		SF	6	84.87	8.20	1.08	0.86	0.01	0.02	0.09	0.00
		FUS	18	90.78	4.24	0.95	0.51	0.08	0.12	0.13	0.04
		IND	4	93.86	2.31	0.75	0.35	0.03	0.02	0.05	0.06
Southland Greta B, 1 m below roof	0.64	TC	21	83.83	8.48	1.39	2.41	0.31	0.03	0.15	0.03
		DSC	23	85.43	8.28	1.48	2.62	0.21	0.07	0.15	0.04
		SP	4	87.93	5.25	1.35	2.55	0.08	0.06	0.05	0.01
		SF	7	89.09	4.80	1.70	1.27	0.09	0.03	0.09	0.04
		FUS	14	92.45	3.03	1.18	0.59	0.05	0.03	0.29	0.02
Southland Greta A, 1.5 m above floor	0.66	TC	25	83.99	7.50	1.66	0.94	0.12	0.05	0.08	0.03
		DSC	18	87.51	6.81	1.93	1.09	0.08	0.03	0.06	0.05
		SF	8	88.57	3.79	1.41	0.53	0.02	0.02	0.13	0.01
		FUS	7	90.46	3.46	0.62	0.45	0.08	0.05	0.35	0.02
		IND	7	91.42	2.89	0.55	0.38	0.04	0.02	0.38	0.02
Southland Greta C, 1 m above floor	0.66	TC	14	83.25	8.91	1.81	0.79	0.01	0.01	0.01	0.03
		DSC	12	83.86	8.25	1.88	0.81	0.03	0.03	0.03	0.09
		SP	3	93.54	2.14	0.60	0.50	0.00	0.02	0.03	0.04
		SF	8	89.74	4.77	1.20	0.41	0.04	0.04	0.08	0.02
		FUS	14	87.07	3.87	3.13	0.24	0.05	0.05	0.09	0.10
		IND	8	94.95	1.73	0.67	0.23	0.00	0.02	0.03	0.01
Pelton Greta torbanite		TC	16	81.24	10.32	1.85	0.65	0.01	0.02	0.02	0.02
		DSC	5	82.03	9.81	1.78	0.67	0.03	0.05	0.02	0.04
		SP	1	85.10	6.82	2.12	0.46	0.00	0.00	0.02	0.00
		ALG	12	89.22	4.75	1.04	0.53	0.00	0.01	0.04	0.03

seam of eastern Kentucky. The alginite in the Greta coal has a higher proportion of C and a lower proportion of O than the sporinites in the same sample suite (Table 4). The vitrinite in the torbanite has lower carbon and higher oxygen contents than the vitrinites in the other Greta seam samples (Table 4); however, the sample is from a different location and the difference suggests that the coal in that particular area may be at a slightly lower rank level.

4.2. Carbon content and vitrinite reflectance

Mean maximum telocollinite (collotelinite) reflectance for the samples studied decreases from 0.7% in the lower part of the seam to a little over 0.6% in the upper part (Table 4). The grab samples, Greta A, B and C, also show reflectance values within this range. The variation is slightly greater than the upward decrease from around 0.7% to a little over 0.5% in mean random reflectance indicated by Diessel and Gammidge (1998) for another section within the Greta seam in the same area, and similar in magnitude but higher in absolute terms than the decrease from 0.6% to 0.5% indicated for a different section in the same seam by Diessel (1992). The difference between the latter section and the present data may be due in part to the fact that maximum, not random reflectance was measured in the present study, and in part due to lateral variations in overall rank levels within the coalfield area. The profiles shown by Diessel (1992) and Diessel and Gammidge (1998) were also based on a larger number of coal samples, each representing a relatively thin subsection of the seam. The relatively large stratigraphic intervals (1–2 m) represented by the samples taken for the present study may therefore have smoothed out some of the smaller-scale variations in reflectance within the coal bed.

Despite the marked upward decrease in vitrinite reflectance, Table 4 indicates that the C and O contents of the vitrinites, and also for most of the other macerals, remain essentially the same throughout the seam section. This is consistent with the observations of Gurba and Ward (2000) for coals of the Gunnedah Basin, where the vertical trends in C and O within the vitrinites, as determined by electron microprobe, respectively show a steady increase and decrease with depth, and hence with increasing rank, despite the appearance at different levels of anomalously low vitrinite reflectance values associated with marine influence on the coal seams.

The proportion of carbon within the vitrinites in the Greta seam at Southland, including both the seam section and the grab samples, is a little over 83% (Table 4). The whole-coal carbon content (Table 2) is of a similar magnitude, especially for the upper part of the seam. The whole-coal values, however, are also influenced by the abundance of other macerals, such as liptinites and inertinites, within the coal samples. Diessel and Gammidge (1998) suggest that the maceral assemblage in the Greta seam is relatively constant from top to bottom, with around 70% vitrinite, 20% inertinite and 10% liptinite. Vitrinite is slightly more abundant in the upper part of the seam in the section studied by Diessel and Gammidge (1998), and liptinite slightly more abundant in the lower section.

Microprobe data from a series of coals in the Bowen Basin (Ward et al., 2005) suggest that a carbon content of around 83% occurs in the vitrinites of Australian Permian coals with mean maximum reflectance values, unaffected by marine influence, of around 1.0%. Such a value is higher than the reflectance of 0.7% measured at the base of the Greta seam in the present study and higher still than the reflectance of 0.6% measured near the top. It is also higher than the reflectance values of 0.6–0.7% reported for the working section of the Greta seam in other parts of the Lochinvar Anticline (Joint Coal Board and Queensland Coal Board, 1987; Diessel and Gammidge, 1998).

The vitrinite reflectance in the Greta seam thus appears to be anomalously low throughout the entire seam section, with the magnitude of the anomaly increasing from bottom to top of the coal bed. Vitrinite reflectance values, even in the lower part of the seam, may therefore provide a significant underestimate of the coal's overall rank level, and, by extension, an inadequate indication of its thermal history, compared to other coals in the Sydney-Bowen Basin sequence.

4.3. Organic sulphur

The organic sulphur content of the vitrinite macerals in the Greta seam increases from around 1% in the lower part of the section studied to around 2.5% in the upper part (Table 4). A similar trend is shown by the grab samples, with a range from 0.8% in the Greta C sample to 2.4% in Greta A. The vitrinite in the torbanite sample has even lower sulphur (0.65%).

The organic sulphur content of the inertinite macerals in the lower part of the seam, especially the fusinite, is around 0.5%, approximately half that of the vitrinite in the same coal samples. The semifusinites and, where present, the liptinites (including the alginite in the torbanite sample) have intermediate organic sulphur contents. The inertinites in the upper portion of the seam, however, have only slightly higher proportions of organic sulphur than those in the lower part (Table 4), despite the significantly higher proportions of organic sulphur in the vitrinites and liptinites of the upper seam section. This greater contrast in organic sulphur in the upper part of the seam (Fig. 2), in conjunction with the lower vitrinite reflectance, may indicate preferential fixation of S by the vitrinite in association with increased marine influence during or shortly after peat formation.

4.4. Inorganic elements in coal macerals

With the exception of the torbanite and the Greta C grab sample, both of which have low organic sulphur

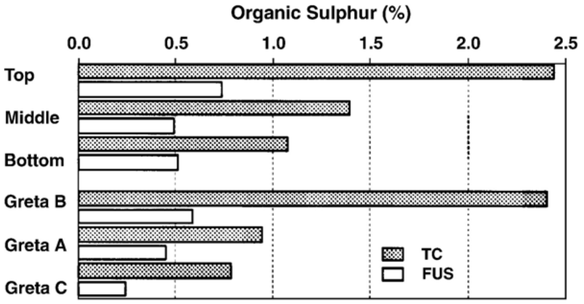

Fig. 2. Organic sulphur of telocollinite (shaded) and fusinite (open), as determined by electron microprobe, in samples from the Greta seam at Southland Colliery, showing increasing contrast up the seam section.

contents (0.65–0.8%), small but significant proportions of aluminium occur in the vitrinites of the Greta seam coal samples (Table 4), especially in the high-sulphur vitrinites from the upper part of the seam (Fig. 3). Significant concentrations of aluminium are not present in the other macerals of the same coal samples (Table 4), except for the semifusinite in the uppermost part of the seam section.

The Al detected by the microprobe may represent sub-microscopic particles of Al minerals such as bauxite incorporated into the maceral's pore spaces, or it may represent Al incorporated directly into the organic structure. The individual points analysed tend to have relatively consistent Al concentrations, especially in the vitrinite components. Aluminium is suggested as a component of the organic matter in lower-rank coals by Miller and Given (1986), possibly in the form of Al-bearing complexes, and the relatively even distribution of Al in the macerals may be consistent with such a mode of occurrence. Although the bauxite minerals have been reported in a few overseas coal samples (Ward, 2002), such minerals have not been detected in the coals of the present study. The absence of significant concentrations of Si in the same macerals (Table 4) rules out the possible inclusion in the analysis field of clay minerals such as kaolinite, which are common components of this and other Australian coal seams. Contamination of the samples by Al from polished section preparation is also ruled out; alumina was not used as a polishing medium at any stage in section preparation for the electron microprobe study and colloidal silica was used for the final polishing process.

Fig. 3. Plots showing the percentages of organic sulphur (A) and Al and Ca (B) in telocollinite for samples from different levels in the Greta seam, Southland Colliery. For details of samples, see Tables 2–4.

Small but significant proportions of calcium also occur in most of the maceral groups in the Greta seam, especially the vitrinites in the upper part of the seam section (Table 4). Ca is more abundant and also more consistently distributed in the vitrinites than in most other macerals, although some fusinite and inertodetrinite samples also have relatively high Ca contents. Ca is not, however, present to a significant extent in the macerals of the low-sulphur Greta C or torbanite samples.

As with Al, the Ca may represent either very fine mineral particles (e.g. calcite) within the macerals, or it may represent Ca incorporated in some way into the organic structure. Several workers, including Miller and Given (1986) and Ward (1992), report the incorporation of Ca in the organic matter of lower-rank coals, either dissolved in the pore water or attached as exchangeable ions to carboxylate groups. Ca is less abundant than Al in the vitrinites (Fig. 3), but its consistent occurrence in the high-sulphur vitrinite in the upper part of the seam suggests that it is possibly associated with the organic matter. Care was taken to avoid testing particles with visible minerals in the microprobe study. While the vitrinites studied, especially the telocollintes, were relatively large, homogeneous particles free of visible mineral impurities, traces of minerals such as calcite may have been incorporated into some of the inertinite particles tested, due to the smaller sizes and more complex textures involved.

5. Macerals in the Cranky Corner Basin

Samples were examined from two seams in the Greta Coal Measures of the Cranky Corner Basin, the Tangorin seam near the top of the sequence (Table 2) and the Stanhope seam further down the section. As with the coal from the Lochinvar Anticline, the vitrinite macerals in the coals have significantly lower carbon and higher oxygen and nitrogen contents than the inertinite macerals (Table 5), with semifusinite and the

Table 5
Elemental composition of macerals in coals from the Cranky Corner Basin

	Rv_{max} (%)	Maceral	No	C%	O%	N%	S%	Al%	Si%	Ca%	Fe%
Tangorin seam, Ply 1	0.40	TC	15	78.37	10.87	1.62	6.23	0.28	0.04	1.05	0.01
		DSC	6	78.91	10.06	0.96	6.15	0.33	0.15	1.08	0.05
		SF	9	84.41	7.07	1.31	2.97	0.09	0.10	0.93	0.01
		FUS	9	90.82	4.01	0.70	1.66	0.07	0.03	0.21	0.02
		IND	2	93.38	2.62	0.23	1.33	0.01	0.02	0.22	0.00
Tangorin seam, Ply 4	0.48	TC	17	78.12	10.77	1.33	6.46	0.49	0.08	0.66	0.01
		DSC	3	84.56	7.69	1.30	4.00	0.15	0.12	0.21	0.00
		SP	6	84.06	6.34	0.62	6.77	0.15	0.11	0.31	0.02
		SF	11	85.43	7.36	0.96	2.75	0.03	0.03	0.29	0.03
		FUS	8	89.71	4.91	0.54	2.00	0.01	0.02	0.19	0.02
		IND	2	91.59	3.61	0.54	1.65	0.00	0.02	0.13	0.06
Tangorin seam, composite	0.45	TC	17	77.73	11.04	1.04	5.59	0.29	0.06	0.83	0.04
		DSC	5	78.34	11.09	1.16	5.21	0.31	0.06	0.74	0.00
		SF	15	87.41	5.90	1.27	1.59	0.02	0.06	0.18	0.02
		FUS	4	89.93	3.06	0.83	2.08	0.18	0.05	0.31	0.00
Stanhope seam, Ply 2	0.54	TC	11	79.90	10.32	1.48	2.93	0.29	0.07	0.57	0.02
		DSC	8	79.56	10.21	1.65	3.25	0.28	0.06	0.67	0.04
		SF	6	84.95	7.47	1.07	1.28	0.02	0.04	0.30	0.03
		FUS	4	87.45	6.00	0.82	0.95	0.01	0.08	0.26	0.00
		IND	4	91.71	3.25	0.51	0.98	0.01	0.01	0.22	0.04

few liptinite macerals that could be analysed having intermediate C, O and N contents. The desmocollinite also appears to have slightly more carbon and slightly less oxygen than the telocollinite (collotelinite) components, with nitrogen evenly partitioned (within the precision of measurement) between the two.

5.1. Vitrinite carbon and reflectance

The vitrinite in all three Tangorin seam samples contains around 78% carbon, consistent with a coal of high volatile bituminous rank. Comparison with similarly analysed coals from the Bowen Basin (Ward et al., 2005) suggests that the carbon content of the Tangorin material resembles other coals with vitrinite reflectance (Rv_{max}) values of around 0.8%. Vitrinite (telocollinite) reflectance of the Tangorin samples, however, is between 0.45% and 0.5%, a value more consistent with sub-bituminous material. This appears to indicate a high level of reflectance suppression for the Tangorin materials, probably due to marine influence associated with deposition of the coal-bearing strata.

The vitrinite in the Stanhope seam has a slightly higher carbon content (79%), consistent with deeper burial in the sequence. Vitrinites with similar carbon contents from the Bowen Basin have reflectance values of around 0.9% (Ward et al., 2005). The Stanhope seam has a slightly higher reflectance value than the Tangorin coal, but the reflectance is still anomalously low at a little over 0.5%. Again, as indicated by Diessel and Gammidge (2003), the anomalously low value is probably due to marine influence on coal deposition.

5.2. Organic sulphur, calcium and aluminium

Organic sulphur is up to 6.5% in the vitrinite of the Tangorin seam samples and around 3% in the vitrinite of the Stanhope seam ply (Table 5). As with the Greta seam, sulphur is much less abundant (1% to 2%) in the inertinites of the same coal samples. The contrast between the sulphur contents of vitrinite and inertinite macerals, expressed as the ratio of S in vitrinite to S in inertinite, varies from 2.8:1 (Stanhope seam sample) to around 4:1 (Tangorin seam, Ply 1), which is significantly higher than the typical ratio of 2:1 observed by Ward and Gurba (1998, 1999) for lower-sulphur Australian coal seams.

Although pyrite is relatively abundant in the polished sections studied, no significant Fe was noted in the actual maceral components. This, together with the absence of visible minerals at the sites analysed, suggests that the sulphur in the macerals is all in organic form. Allowing for the occurrence of both vitrinite and inertinite in the coals (although vitirinite is the dominant component), the levels are also consistent with the proportions of (whole-coal) organic sulphur (Table 2), especially on a daf basis, indicated by traditional analysis techniques.

The macerals in the Cranky Corner coals also contain up to 1% Ca and 0.5% Al (Table 5). Ca and Al are also more abundant in the vitrinites than in the other maceral components. Although significant proportions of Ca are present in the inertinite and liptinite macerals of all the coals, Al appears to be only present to a significant extent in the inertinite macerals of the Cranky Corner samples.

6. Greta coals on the Muswellbrook Anticline

The vitrinite in the Puxtrees seam on the Muswellbrook Anticline has a similar carbon content (78%, Table 6) to the vitrinite in the Tangorin seam of the Cranky Corner Basin. Vitrinite reflectance in the Puxtrees seam, however, is significantly higher (0.67%) than that of the Tangorin and more consistent with the reflectance of other Australian vitrinites having similar carbon contents (Ward et al., 2005). The vitrinites in the coals from the upper and lower Wittingham Coal Measures, sampled at points away from the anticlinal axis, have slightly higher carbon contents (79%) and broadly similar reflectance values. The sample from the upper Wittingham Coal Measures has a slightly higher (0.75%) vitrinite reflectance than the Puxtrees material, while those from the lower Wittingham Coal Measures have slightly lower (0.65%) reflectance values. This may suggest a somewhat low level of reflectance in the lower Wittingham materials relative to the coal rank (i.e. a slight reflectance suppression), but does not indicate any significant reflectance anomaly in the Puxtrees seam sample.

The fusinites and inertodetrinites in the Puxtrees seam and the Wittingham samples are markedly richer in carbon and lower in oxygen than the vitrinite components. As with the other coals, the semifusinites and the liptinites have intermediate carbon and oxygen contents.

Despite the similarity in carbon content, the proportion of organic sulphur in the Puxtrees seam vitrinites is much lower than in those of the Cranky Corner Basin. The Puxtrees inertinites have even lower organic sulphur contents, a little under half the vitrinite sulphur values (giving a sulphur ratio, as defined above, of 2:1). The sporinites tend to have somewhat higher sulphur contents than the inertinites but less S than the vitrinites; the limited number of cutinite particles analysed, however, appear to have only slightly higher S levels than the inertinite components.

Table 6

Elemental composition of macerals in coals from the Muswellbrook Anticline and the Singleton area

Sample	Rv_{max} (%)	Maceral	Points	C%	O%	N%	S%	Al%	Si%	Ca%	Fe%
Puxtrees seam	0.67	TC	8	77.85	15.65	2.06	0.76	0.04	0.05	0.01	0.03
Greta Coal Measures		DSC	11	79.32	14.36	1.76	0.75	0.05	0.06	0.01	0.02
Drayton Colliery		SP+DSC	6	81.51	13.56	1.57	1.00	0.07	0.08	0.01	0.01
		SP	5	86.19	8.34	1.10	0.56	0.02	0.09	0.02	0.03
		CUT	4	88.57	6.18	0.68	0.38	0.01	0.01	0.01	0.05
		SF	9	81.35	12.89	1.36	0.26	0.04	0.05	0.03	0.06
		FUS	7	86.62	7.73	0.77	0.28	0.02	0.01	0.14	0.02
		IND	4	89.91	4.61	1.03	0.27	0.01	0.01	0.10	0.00
Lower Pikes Gully seam	0.63	TC	17	79.11	13.92	1.74	0.50	0.02	0.05	0.01	0.02
Wittingham Coal Measures		DSC	8	81.12	11.62	1.96	0.50	0.00	0.01	0.01	0.02
Howick Colliery		SP	10	83.58	10.01	1.13	0.78	0.03	0.06	0.01	0.03
		SF	9	85.09	8.69	1.03	0.31	0.01	0.03	0.04	0.04
		FUS	5	87.28	7.50	0.95	0.22	0.01	0.01	0.06	0.09
		IND	7	87.71	7.21	0.75	0.23	0.01	0.01	0.14	0.07
Upper Liddell seam	0.65	TC	6	78.71	13.44	1.61	0.45	0.03	0.01	0.01	0.02
Wittingham Coal Measures		DSC	5	79.08	13.46	1.71	0.49	0.04	0.05	0.01	0.04
Howick Colliery		CUT+DSC	4	80.87	11.48	1.90	0.43	0.01	0.02	0.02	0.05
		SP	3	83.73	9.90	0.52	0.33	0.03	0.06	0.01	0.01
		SF	4	88.11	6.23	1.30	0.25	0.04	0.04	0.20	0.00
		FUS	8	90.33	4.52	0.33	0.20	0.01	0.02	0.11	0.06
		IND	2	91.62	3.90	1.13	0.17	0.01	0.01	0.00	0.13
Woodlands Hill seam	0.75	TC	10	80.00	12.88	1.91	0.48	0.02	0.03	0.01	0.12
Wittingham Coal Measures		DSC	4	79.75	12.49	1.58	0.35	0.02	0.02	0.01	0.03
Saxonvale Colliery		SF	9	85.12	7.96	1.77	0.29	0.02	0.04	0.06	0.02
		FUS	11	90.33	4.94	0.77	0.31	0.05	0.05	0.14	0.04
		IND	2	91.11	3.92	0.79	0.27	0.01	0.01	0.07	0.00

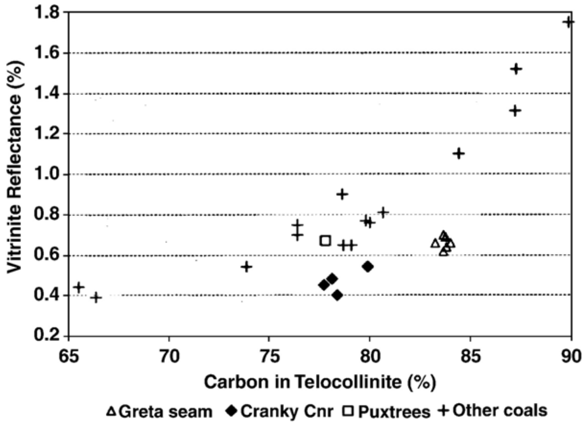

Fig. 4. Relation between mean maximum vitrinite (telocollinite) reflectance and carbon content of telocollinite for samples studied, in comparison to similar data from other Australian coal seams. Data for other Australian coals from Ward et al. (2003a,b, 2005). The vitrinites in the Greta seam and Cranky Corner Basin materials clearly have lower reflectance values than others with equivalent carbon contents, including the Puxtrees seam material.

More significantly, the vitrinites and other macerals of the Puxtrees seam, and also those in the samples from the Wittingham Coal Measures (Table 6), generally have quite low proportions of aluminium or calcium, again contrasting with the Cranky Corner Basin coals and with the Greta seam materials. A few of the individual data points for some of the inertinite macerals in the samples do have relatively high Ca contents (up to around 0.2%), whereas other data points on the same macerals have almost no Ca, resulting in a small but significant average percentage of Ca for some of the inertinites detailed in Table 6. The scattered distribution, however, suggests that the Ca that is indicated for these macerals may represent inclusion of mineral particles in the individual fields analysed. Low proportions of Al and Ca, especially in the vitrinites, are also consistent with observations on the bituminous coals of the Bowen Basin (Ward et al., 2005), where no significant Al or Ca appear to be present in the organic matter of coals containing vitrinite with more than 75% carbon.

7. Maceral chemistry, reflectance and rank

Fig. 4 shows the relation between the carbon content of the telocollinite and the mean maximum telocollinte reflectance for the samples studied, and also for a number of other Australian coals based on previous studies (Ward et al., 2003a,b, 2005). The relationship between vitrinite composition and vitrinite reflectance for the Puxtrees seam is consistent with that of other coals in different Australian basins, and thus the vitrinite reflectance of the Puxtrees coal appears to provide a reasonable basis for rank evaluation. The vitrinites in the seams of the Cranky Corner Basin (Fig. 4) have similar carbon contents, suggesting a similar rank level (i.e. equivalent to around 0.7% Rv_{max}), but have much lower vitrinite reflectance values. As indicated above, these low reflectance values are due to marine influence on coal formation, often described as reflectance suppression effects. If used as a rank indicator, the vitrinite reflectance of the Cranky Corner Basin coals would therefore significantly underestimate the extent of the coals' thermal maturation.

The vitrinites in the Greta seam samples from Southland Colliery all have similar carbon contents. Despite the variation in reflectance outlined in Table 4, this suggests a similar rank level throughout the seam section. The vitrinite carbon content for these coals is higher than for the Puxtrees or Cranky Corner materials (Fig. 4), indicating a higher rank for the Greta Coal Measures on at least this part of the Lochinvar Anticline than on the Muswellbrook Anticline or in the Cranky Corner Basin. This suggests that the vitrinite reflectance value, even in the lower part of the seam, again provides an underestimate of the actual thermal maturity level for the Greta seam section.

The lateral variation in vitrinite carbon content across the three areas (Fig. 5) provides a general indication of the direction of rank increase in this part of the basin. This diagram suggests that the Greta seam at Southland is of a significantly higher rank than the coal of the same unit in the other two localities. Although there may have

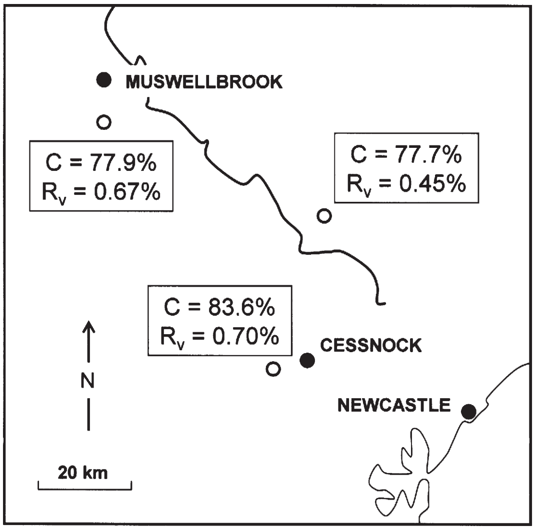

Fig. 5. Lateral variation in telocollinite carbon content and mean maximum telocollinite reflectance for key samples from different parts of the study area.

been a higher heat flow over the axis of the Lochinvar Anticline that also affected the rank level, the overall direction of rank increase towards the south-west is consistent with deeper burial of the Greta Coal Measures on the southern end of the Lochinvar Anticline, away from the Hunter Thrust and towards the structural axis of the basin, following trends mapped by Brown et al. (1996) and shown in Fig. 1. Uplift on the anticline has subsequently brought the higher-rank Greta seam coals closer to the present-day ground surface. The seams of the overlying Wittingham Coal Measures, although not exposed in this part of the Lochinvar Anticline, are of a lower rank where they are exposed further to the NW, and apparently have a similar burial history to the Muswellbrook Anticline and Cranky Corner Basin materials.

8. Organic sulphur and other elements

The coals with anomalously low vitrinite reflectance values also tend to have relatively high total sulphur and organic sulphur contents, with organic sulphur being especially abundant in the vitrinite components. A plot of carbon against oxygen for the individual macerals in these and other coal samples (Fig. 6) suggests that the vitrinites in the coals from the Cranky Corner Basin, which have particularly high organic sulphur contents, also have anomalously low proportions of oxygen in relation to their carbon content. The magnitude of the anomaly is close to the additional percentage of organic sulphur in the vitrinites of these coals, relative to the other Sydney-Bowen Basin materials plotted in the figure (see Ward et al., 2003b, 2005 for further discussion of the other coal samples). This suggests that the additional sulphur in the Cranky Corner coals has replaced oxygen in the molecular structure of the macerals concerned. The contrast is less marked for the Greta seam materials (Fig. 6), especially the Greta seam vitrinites with relatively low organic sulphur contents.

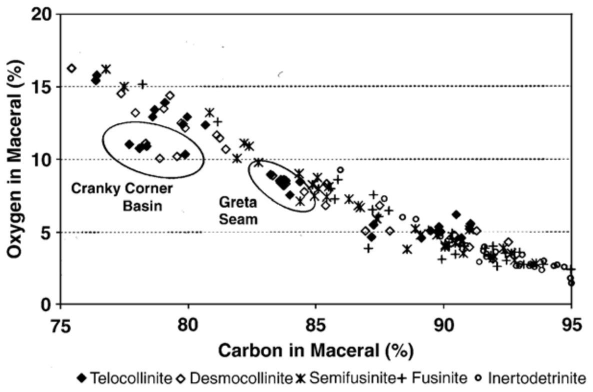

Fig. 6. Carbon–oxygen plot for macerals in Greta Coal Measures and other Australian coal samples. Note the low oxygen content of the high-sulphur vitrinites in the Cranky Corner Basin coals, relative to other vitrinites with equivalent carbon contents, including the Greta seam.

As indicated in the earlier discussion, the vitrinite macerals containing high levels of organic sulphur also have significant percentages of Al and Ca, apparently occurring within the organic structure. Such organically associated inorganic elements are common in lower-rank coals (Miller and Given, 1986; Ward, 1992), but in other coals are typically lost at higher rank levels (Ward et al., 2003a, 2005). The coals containing these elements, the Cranky Corner and upper Greta seam samples, therefore have elemental compositions (especially vitrinite carbon contents) consistent with a high-volatile bituminous rank, but the vitrinite reflectance and organically associated inorganic elements of lower-rank materials.

Based mainly on studies in the Illinois Basin, Chou (1990) suggests that the sulphur in low-sulphur coals (<1% S) is mainly derived from the parent plant debris. However, in medium-sulphur (1–3% S) and high-sulphur coals (>3% S), there are two major sources of sulphur: (a) the parent plant materials and (b) sulphate ions from seawater that flooded the peat swamps.

Chou (1990) further suggests that, when seawater is infiltrated into the peat swamps, the sulphate is first reduced to H_2S by anaerobic bacteria and the H_2S in the interstitial waters then reacts with organic matter (pre-maceral humic substances) to form organo-sulphur compounds, as well as forming pyrite and other sulphide minerals by reactions between H_2S and Fe. The extent of partitioning between these two sulphur forms, represented by organic and pyritic sulphur, may depend on the availability of iron in the peat-forming system, with the proportion of organic sulphur increasing relative to pyritic sulphur where the proportion of available Fe is low.

This is consistent with the fact that, although the total sulphur is high in both seams of the Cranky Corner Basin (Table 2), the sulphur in the Tangorin seam, whether measured by conventional means or microprobe techniques, is mainly organic in nature (especially in the vitrinites), whereas that in the higher-sulphur Stanhope seam is mainly pyritic in form. Similarly, although pyritic sulphur also increases in abundance up the Greta seam section, the level of organic sulphur, especially in the vitrinite macerals, increases substantially, in the section studied, with increasing marine influence.

The vitrinites in coals of the present study with relatively low (<1%) organic sulphur, measured either on a whole-coal basis (Table 2) or within the vitrinites themselves (Tables 4–6), do not appear to have significant concentrations of Al or Ca. This is possibly consistent with the suggestion of Chou (1990) that the sulphur in such coals is derived mainly from the plant tissue. It also suggests that any additional sulphur introduced by marine influence on the peat may also have been accompanied by other elements, such as Al and Ca, which were similarly fixed into the organic structure of the vitrinite macerals.

The proportions of Al and Ca in the vitrinite macerals of the coals from the present study are plotted in Fig. 7 against the organic sulphur content of the vitrinites in the same coal samples. The plot suggests that, although the individual concentrations of Al and Ca are somewhat variable, the proportions of these elements in the vitrinite both tend to increase with increasing organic sulphur content. The total proportion of these two elements (i.e. Al+Ca), moreover, shows an essentially linear increase with the vitrinite's organic sulphur content, with a relatively high correlation coefficient ($R^2=0.93$). The slope of the regression line (0.21) further suggests that the Ca and Al consistently make up a combined total representing around 20% of the organic sulphur in the vitrinite components.

It is also significant to note that the Al and Ca remain in the vitrinite, and possibly to a lesser extent in the other macerals, even though the rank of the coal, based on the vitrinite carbon content, is higher than that at which organically associated inorganic elements appear to be expelled from other coal seams. The reflectance of the vitrinites retaining these elements, however, is still within the range over which they seem to be preserved in lower-rank coal beds (Ward et al., 2003a). It is therefore possible that the processes associated with anomalously low vitrinite reflectance (reflectance suppression) in marine-influenced strata have in some way preserved some of the chemical characteristics of the original lower-rank coal, including the organically associated inorganic elements, but not the overall carbon and oxygen contents. As discussed elsewhere (e.g. Gurba and Ward, 2000), the anomalously low reflectance values may represent at least some preservation of aliphatic structures in the vitrinite despite an increasing carbon content.

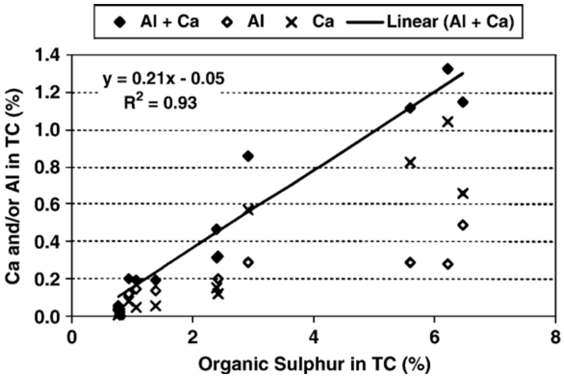

Fig. 7. Abundance of Al, Ca and total Al+Ca in telocollinite in relation to (organic) sulphur content of telocollinite for all samples from the Greta Coal Measures. Linear regression correlation line and equation for Al+Ca against sulphur in telocollinite is also shown.

9. Conclusions

The Early Permian coals of the Greta Coal Measures on the Lochinvar Anticline and in the Cranky Corner Basin are significantly higher in rank than suggested by their mean maximum vitrinite reflectance values. This indicates not only that the coals have anomalously low reflectance values due to marine influence, but that the magnitude of the anomaly is significantly greater than that indicated by the intra-seam reflectance profile, at least in the case of the Greta seam. The pattern of rank variation across the study area, based on the carbon content of the vitrinite as determined by electron microprobe, is also consistent with broader elements of the basin structure, and the rank variation in the other coal-bearing sequences.

Elemental analysis of the macerals, using electron microprobe techniques, therefore appears to provide a better indicator of rank for such coals than the vitrinite reflectance values. This is significant in explaining the overall coal chemistry in relation to the coals' petrography and in interpreting the post-depositional history of the basins. It may also help to elucidate the behaviour of the coals in different utilisation processes, such as gasification and coking operations.

The vitrinites in the coals with the more extreme anomalies in reflectance (i.e. those with more strongly suppressed reflectance values) due to marine influence also have high proportions of organic sulphur. The sulphur in these coals appears to occur as a replacement for oxygen in the molecular structure of the vitrinite components, especially in the Cranky Corner Basin materials. The additional organic sulphur may have been derived from the same marine source that produced the anomalously low reflectance values, with the S being incorporated into the organic matter (vitrinite precursors) in environments where insufficient Fe was available to form pyrite.

The vitrinites with high proportions of organic S and anomalously low reflectance also contain significant proportions of Al and Ca, incorporated very intimately into the organic material. The Al and Ca in the vitrinite combine to represent a total of around 20% of the vitrinite's organic sulphur, especially where the organic sulphur content of the vitrinite is greater than around 1%.

Although Ca, Al and other elements may occur in the organic matter of many lower-rank coals, they are typically lost from those coals as the rank increases, especially at ranks where there is more than 75% carbon in the vitrinite macerals. The vitrinites in the coals of the present study, especially the Greta seam, have higher carbon contents (and therefore higher rank), but still retain the Al and Ca within the maceral structure. The coals of the Greta Coal Measures with particularly strong marine influence therefore have many of the properties of lower-rank coals (low vitrinite reflectance, inherent inorganic elements) despite being metamorphosed to a higher rank level.

Acknowledgements

Financial support for the study was provided under the Large Grants Scheme of the Australian Research Council. Thanks are expressed to Rad Flossman for polished section preparation, Maria Mastalerz for provision of the carbon standard used in the microprobe study and Barry Searle for assistance with the electron microprobe analyses. Thanks are also expressed to the relevant mining and exploration companies, and to Guy Palese, Ron Slocombe, Luc Daigle and Anton Crouch for provision of the coal samples.

References

Agnew, D., Bocking, M., Brown, K., Ives, M., Johnson, D., Howes, M., Preston, B., Rigby, R., Warbrooke, P., Weber, C.R., 1995. Sydney Basin, Newcastle Coalfield. In: Ward, C.R., Harrington, H. J., Mallett, C.W., Beeston, J.W. (Eds.), Geology of Australian Coal Basins. Geological Society of Australia Coal Geology Group Special Publication, vol. 1, pp. 197–212.

Basden, H., 1969. Greta coal measures. In: Packham, G.H. (Ed.), Geology of New South Wales. Journal of the Geological Society of Australia, vol. 16(1), pp. 323–329.

Brown, K., Casey, D.A., Enever, J.R., Facer, R.A., Wright, K., 1996. New South Wales Coal Seam Methane Potential. . New South Wales Department of Mineral Resources Petroleum Bulletin, vol. 2. 96 pp.

Bustin, R.M., Mastalerz, M., Wilks, K.R., 1993. Direct determination of carbon, oxygen and nitrogen content in coal using the electron microprobe. Fuel 72, 181–185.

Bustin, R.M., Mastalerz, M., Raudsepp, M., 1996. Electron-probe microanalysis of light elements in coal and other kerogen. International Journal of Coal Geology 32, 5–30.

Chou, C.L., 1990. Geochemistry of sulfur in coal. In: Orr, W.L., White, C.M. (Eds.), Geochemistry of Sulfur in Fossil Fuels. American Chemical Society, Washington, DC, pp. 30–52.

Diessel, C.F.K., 1992. Coal-Bearing Depositional Systems. Springer Verlag, Berlin. 721 pp.

Diessel, C.F.K., Gammidge, L., 1998. Isometamorphic variations in the reflectance and fluorescence of vitrinite—a key to depositional environment. International Journal of Coal Geology 36, 167–222.

Diessel, C.F.K., Gammidge, L.C., 2003. Downhole vitrinite reflectance in DM Tangorin DDH 1. In: Facer, R.A., Foster, C.B. (Eds.), Geology of the Cranky Corner Basin. New South Wales Department of Mineral Resources, Coal and Petroleum Bulletin, vol. 4, pp. 107–114.

Gurba, L.W., 2001. Distribution of organic nitrogen in Australian coals. Proceedings of 18th Pittsburgh International Coal Conference, Newcastle, NSW, Australia, 13 pp (CD-ROM Publication).

Gurba, L.W., Ward, C.R., 2000. Elemental composition of coal macerals in relation to vitrinite reflectance, Gunnedah Basin, Australia, as determined by electron microprobe analysis. International Journal of Coal Geology 44, 127–147.

Hamilton, D.S., 1986. Depositional systems and coal seam correlation in the Greta Coal Measures of the Muswellbrook Anticline. Australian Coal Geology 6, 1–18.

Joint Coal Board, Queensland Coal Board, 1987. Australian Black Coals. Joint Coal Board, Sydney. 48 pp.

Maher, T.P., Bosio, M., Lindner, E.R., Brockway, D.J., Galligan, A.G., Moran, V.J., Peck, C., Walker, M.P., Bennett, P.A., Coxhead, B.A., 1995. Coal resources, quality and utilisation. In: Ward, C.R., Harrington, H.J., Mallett, C.W., Beeston, J.W. (Eds.), Geology of Australian Coal Basins. Geological Society of Australia Coal Geology Group Special Publication, vol. 1, pp. 133–159.

Mastalerz, M., Hower, J.C., 1996. Elemental composition and molecular structure of Botryococcus alginite in Westphalian cannel coals from Kentucky. Organic Geochemistry 24, 301–308.

Miller, R.N., Given, P.H., 1986. The association of major, minor and trace inorganic elements with lignites: I. Experimental approach and study of a North Dakota lignite. Geochimica et Cosmochimica Acta 50, 2033–2043.

Sniffin, M.J., Beckett, J., 1995. Sydney Basin, Hunter Coalfield. In: Ward, C.R., Harrington, H.J., Mallett, C.W., Beeston, J.W. (Eds.), Geology of Australian Coal Basins. Geological Society of Australia Coal Geology Group Special Publication, vol. 1, pp. 177–195.

Van Heeswijck, A., 2001. Sequence stratigraphy of coal-bearing, high-energy clastic units: the Maitland-Cessnock-Greta Coalfield and Cranky Corner Basin. Australian Journal of Earth Sciences 48, 417–426.

Ward, C.R., 1992. Mineral matter in Triassic and Tertiary low-rank coals from South Australia. International Journal of Coal Geology 20, 185–208.

Ward, C.R., 2002. Analysis and significance of mineral matter in coal seams. International Journal of Coal Geology 50, 135–168.

Ward, C.R., Gurba, L.W., 1998. Occurrence and distribution of organic sulphur in macerals of Australian coals using electron microprobe techniques. Organic Geochemistry 28, 635–647.

Ward, C.R., Gurba, L.W., 1999. Chemical composition of macerals in bituminous coals of the Gunnedah Basin, Australia, using electron microprobe techniques. International Journal of Coal Geology 39, 279–300.

Ward, C.R., Gurba, L.W., Li, Z.S., Susilawati, R., 2003a. Distribution of inorganic elements in lower-rank coal macerals as indicated by electron microprobe techniques. Proceedings of 12th International Conference on Coal Science, Cairns, Queensland, 2–6 November. 10 pp. (CD publication).

Ward, C.R., Li, Z.S., Gurba, L.W., 2003b. Elemental composition of macerals in coals from the Sydney and Cranky Corner Basins. Proceedings of Sydney Basin Symposium. University of Wollongong, New South Wales, pp. 181–187.

Ward, C.R., Li, Z.S., Gurba, L.W., 2005. Variations in coal maceral chemistry with rank advance in the German Creek and Moranbah Coal Measures of the Bowen Basin, Australia, using electron microprobe techniques. International Journal of Coal Geology 63, 117–129.