

Geochemistry of marine and lacustrine bands in the Upper Carboniferous of the Netherlands

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Abstract

Geochemical studies on Upper Carboniferous marine bands showed that marked enrichment in redox-sensitive trace elements (uranium (U), vanadium (V), molybdenum (Mo)) mostly occur if they contain *Goniatites*. *Goniatites* indicate deposition in relatively distal and deep marine environments. In contrast, Westphalian marine bands found in the Netherlands predominantly show a *Lingula* facies, indicating deposition in a nearshore environment. These *Lingula* marine bands are mostly lacking significant trace element enrichments. The aim of this paper is to explain the mechanisms causing the differences in geochemical characteristics between distal (*Goniatites* facies) and proximal (*Lingula* facies) marine bands. Geochemical analyses (total organic carbon (TOC), sulfur (S), major and trace elements) were carried out on a selection of these marine bands. Furthermore, a comparison was made with some lacustrine bands which broadly show the same sedimentary development as the *Lingula* marine bands. The results show that the *Lingula* marine bands, in contrast to the *Goniatites* and lacustrine bands, are characterised by low organic carbon contents (1 - 2 wt.%). A relatively high input of siliciclastics probably prevented the accumulation of organic-rich layers (dilution effect). In turn, low organic carbon contents most likely prevented the effective scavenging of trace elements. Although the lacustrine bands are characterised by high TOC contents, here the limited availability of trace elements in fresh water forms the best explanation for low trace metal enrichments. Since marine bands form stratigraphically important horizons in the Upper Carboniferous, many attempts have been made to recognise marine bands using well logs (gamma-ray). The results from this study show that using gamma-ray devices (detecting U-enrichments), only marine bands in a *Goniatites* facies are clearly recognised while *Lingula* marine bands are not detected.

Keywords: Carboniferous, geochemistry, lacustrine bands, marine bands, the Netherlands

Introduction

The Upper Carboniferous of the Netherlands and surrounding areas consists of a fluvio-deltaic succession with a thickness of up to 5 km. In this succession, marine bands form important stratigraphic horizons since these are thought to be correlatable basinwide (Ramsbottom et al., 1979; Leeder, 1988; Leeder et al., 1990; Duser et al., 2000; Fig. 1). Marine bands are relatively thin layers (<1 - 30 m) of fine-grained sediment (clay to siltfraction; 1 - 50 µm) characterised by the presence of marine (micro)fossils. The origin of marine bands is commonly

attributed to (glacio-eustatic) sea-level rises (Holdsworth & Collinson, 1988; Martinsen et al., 1995). Based on fossil content, Calver (1969), Rabitz (1966) and Ramsbottom (1969) distinguished several faunal phases in marine bands, reflecting the relative position to the shoreline. The fossils indicating the deepest water and most distal conditions are *Goniatites* (ammonoids), whereas a *Lingula* (brachiopod) facies indicates deposition in nearshore or even brackish environments.

Attempts to identify the stratigraphically important marine bands in the Carboniferous succession using well logs or geochemical analyses have long been made. Hoogteijling (1948)

found the strongest enrichments in U (one of the 3 elements picked up by gamma-ray devices) in the finest sediments but he doubted the possibilities to identify marine bands using gamma-ray logs. However, De Magnée (1952) thought it is possible to distinguish marine bands using gamma-ray logs. More recently, several authors showed – using spectral gamma-ray (Archard & Trice, 1990; Hollywood & Whorlow, 1993; Davies & McLean, 1996) or geochemical analyses (Bloxham & Thomas, 1969; Spears, 1964; Fisher & Wignall, 2001) – that the *Goniatites* facies in marine bands often display enhanced U-concentrations. They concluded that an extremely slow sedimentation rate under anoxic and organic rich conditions favours enrichment in U. Indeed, the *Goniatites* facies in marine bands often shows enhanced organic matter contents (Calver, 1969; Ramsbottom, 1969). The term black shale has therefore often been used as a descriptive term for these U-enriched marine bands.

The marine bands found in the Netherlands mostly display a *Lingula* facies (Table 1) and (spectral) gamma-ray logs show weak or only faint peaks (Fig. 2). For instance, it can be seen that in the well Kemperkoul-1 (KPK-1) the marine band named Domina does not show a clear peak. Moreover, when a peak can be seen (for instance in the Aegir marine band in KPK-1), it turns out to be located in the coal underlying the marine band.

Most geochemical work has been performed on *Goniatites* marine bands. The availability of some continuously cored wells in the Netherlands, in which *Lingula* bands already are proven by fossil evidence, provides an excellent dataset to study the geochemical characteristics of these type of marine bands. The aims of this paper are to (1) explain the geochemical development of (proximal marine) *Lingula* marine bands and (2) put them into perspective using data from

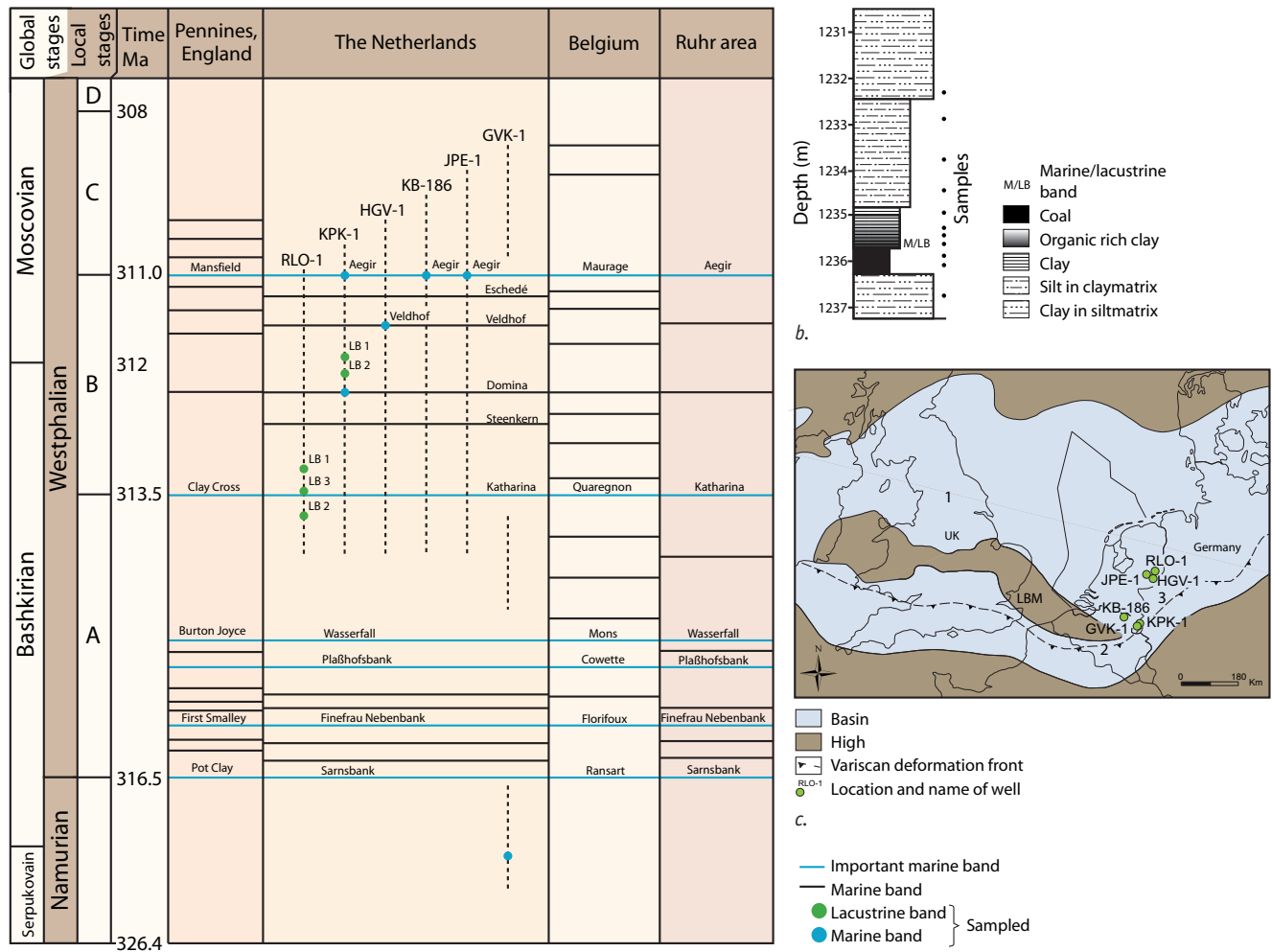


Fig. 1. a. Stratigraphic distribution of sampled sections, next to distribution of Westphalian marine bands recognised in the UK (Calver, 1967), Belgium (Paproth et al. 1983), the Netherlands (Thiadens (1963) and several biostratigraphy reports) and the Ruhr Basin (Drozdowski, 2005). Note that the number of marine bands mentioned in the text does not always exactly correspond with the number of marine bands showed in this diagram because some have been grouped for clarity. The large number of Namurian marine bands is not shown in this figure. RLO-1: Ruurlo-1; KPK-1: Kemperkoul-1; HGV-1: Hengevelde-1; KB-186: Kolen boring-186; JPE-1: Joppe-1; GVK-1: Geverik-1; LB: Lacustrine band; b. Generalised sedimentary log of a marine/lacustrine band; and c. Outlines of Northwest European Carboniferous Basin. 1: Pennines, UK, 2: Belgium, 3: Ruhr area, LBM: London Brabant Massif. Figure 1c modified after Ziegler (1990). Timescale after Gradstein et al. (2004).

Table 1. Fossil content of sampled sections. Fossils indicating marine conditions are: *Goniatites*, *Conodonts*, *Orbiculoidea* and marine ostracods. Brackish conditions are reflected by *Lingula* and *Foraminifers*. Fresh water conditions are interpreted when *Carbonita* and *Geisina* are found. When no fossils were found, a fresh water depositional environment is assumed because of the findings of fresh water fossils directly above and below the sections.

Section		Fossils
Marine bands	GVK-Goniatites MB	<i>Goniatites</i>
	KPK-Aegir	<i>Goniatites</i> , <i>Conodonts</i> , <i>Foraminifers</i> , Marine ostracods, <i>Lingula</i>
	KPK-Domina	<i>Foraminifers</i> , <i>Lingula</i> , <i>Orbiculoidea</i>
	JPE-Aegir	Marine ostracods, <i>Foraminifers</i>
	KB-Aegir	<i>Lingula</i> , <i>Trilobite</i> , <i>Conularia</i>
	HGV-Veldhof	<i>Foraminifers</i> , <i>Lingula</i>
Lacustrine bands	RLO-LB 1	-
	RLO-LB 2	<i>Geisina arcuata</i>
	RLO-LB 3	-
	KPK-LB 1	<i>Carbonita</i>
	KPK-LB 2	-

(distal marine) *Goniatites* marine bands and lacustrine bands (reflecting entirely fresh water conditions). In this way, a transect from lacustrine up to (deep) marine conditions will be investigated. Published geochemical data from the UK has been used to further illustrate the results.

Geological setting

During Namurian times, sedimentation in the Northwest European Carboniferous Basin (NWEBC, Fig. 2) mainly took place under deltaic conditions. In general, the lower part of the Namurian sequence is characterised by pro-delta basinal shale, giving way to typical coarsening and shallowing-upward cycles of pro-delta shale via fluvial silt/sandstone to a coal. The marine bands are intercalated between the basinal shale or overlie the coal, reflecting the peak of transgression where most distal conditions are reached. Glacio-eustatic sea-level fluctuations probably form the driving mechanism of the observed cyclicity and deposition of marine bands in the NWEBC. During the Westphalian these cycles are gradually replaced by continuous fluvial sedimentation characterised by the alternation of fluvial channel sands, floodplain mudstones and paralic coals. The Westphalian marine bands are mostly found on top a coal.

Marine bands were extensively studied in the UK (Calver, 1969; Ramsbottom, 1969), Belgium (Paproth et al., 1983; Duser et al., 2000) and the Ruhr area in Germany (Rabitz, 1966; Fig. 1). In the Namurian succession, numerous marine bands (>30) were found (not shown in figure 1). The UK Westphalian succession contains 19 marine bands (Calver, 1969), whereas in Germany, 15 marine bands occur (Rabitz, 1966). In the Netherlands, 14 marine bands are found in the Westphalian (Thiadens, 1963; Van Amerom & Meessen, 1985; Van Amerom et al., 1985). Most of the Namurian marine bands are developed in *Goniatites* facies, representing deep marine and distal conditions. However, most of the Westphalian marine bands have

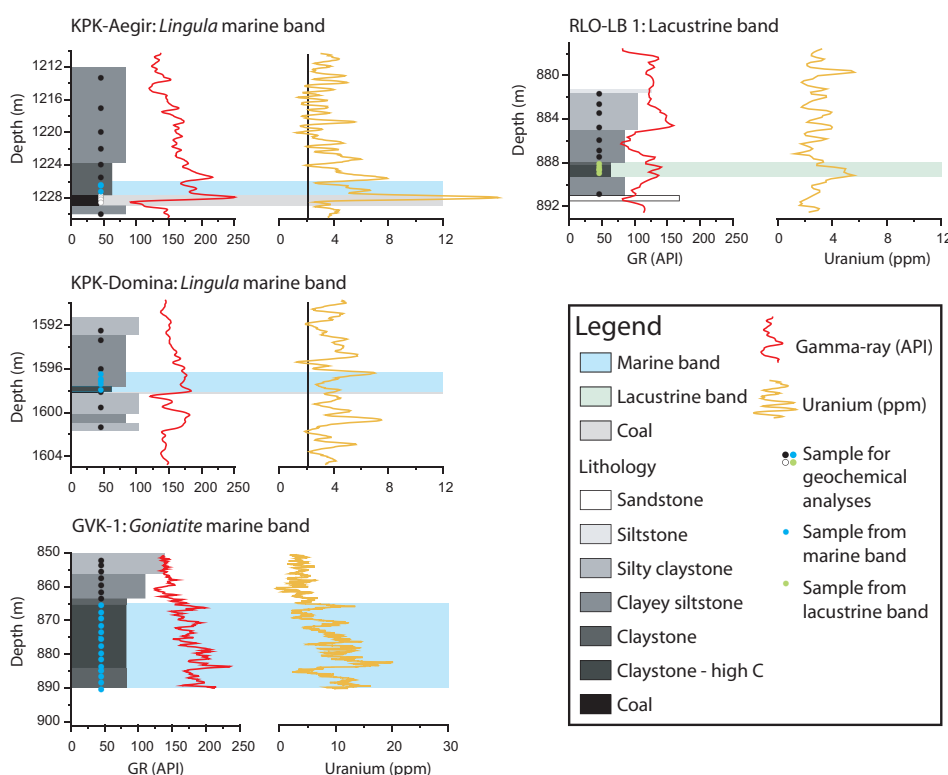


Fig. 2 Some examples of well log response (gamma-ray and spectral gamma-ray (uranium plotted here) and sonic) for marine and lacustrine bands. Sample locations are given. Note the scale change for the uranium-log in GVK-1.

a *Lingula* facies and only a limited number displays (Fig. 1) a *Goniatites* facies (Calver, 1969; Drozdowski, 2005). Extensive research on the fossil content of marine bands in the UK and Germany showed that one marine band can be developed in different faunal phases laterally and on one location. *Lingula* facies mainly occurs along basin margins and intervening highs such as the London Brabant Massif (Fig. 1), whereas the *Goniatites* marine bands are found in the basin centre (Calver, 1969; Ramsbottom, 1969). Moreover, the most complete record of marine bands is found in the basin centre as certain bands are lacking in the marginal areas (Calver, 1969). For example, marine bands change from *Lingula* to *Goniatites* facies across the Craven fault in the Pennines (Calver, 1969).

Data

In the 1980s, the Netherlands Geological Survey drilled five wells with complete core coverage of the Carboniferous (Fig. 1): Ruurlo-1 (RLO-1), Joppe-1 (JPE-1), Hengevelde-1 (HGV-1), Kemperkoul-1 (KPK-1) and Geverik-1 (GVK-1). 148 samples from 11 intervals (Fig. 1 and Table 2) were taken from these cores stored in the core-lab of TNO – Netherlands Geological Survey. The *Lingula* marine band KB-Aegir was sampled in the core-lab of the Geological Survey of Belgium in Brussels.

Table 2. Depth of sampled intervals, number of samples taken and thickness of investigated sections. The last column shows the maturity of the sections.

Section	Depth (m)	Number of samples	Interval thickness (m)	Thickness marine/lacustrine band (m)	Vitrinite reflectance (%RM)
GVK-Gon. MB	850-890	21	40	25	>3
KPK-Aegir	1226	17	30	0.8	0.82
KPK-LB 1	1495	11	4	0.9	1.08
KPK-LB 2	1571	10	4	0.2	1.16
KPK-Domina	1597	11	10	1.5	1.16
JPE-Aegir	1300	18	15	7.8	0.82
KB-Aegir	1130	9	5	1.4	1.07
HGV-Veldhof	1242	12	3	0.8	0.75
RLO-LB 1	888	13	9	0.9	1.01
RLO-LB 2	1184	11	4	0.5	1.15
RLO-LB 3	1235	15	6	0.8	1.29

Five lacustrine bands, five *Lingula* marine bands and one *Goniatites* marine band were sampled. The *Lingula* marine bands were selected on the basis of the fossil content derived from the cores. Sampling of the *Goniatites* marine band was performed on the basis of spectral gamma-ray and fossil content. The spectral gamma-ray log shows enhanced uranium contents (Fig. 2) whereas the findings of numerous *Goniatites* point to a marine depositional environment (Table 1). The thickness of this marine band is relatively high (25 m). The lacustrine bands

were selected on the basis of sedimentological criteria (parallel laminated, fine-grained and TOC-rich sediments). No fossils were found in three lacustrine sections (Table 1). However, a fresh water environment is assumed, based on the presence of fresh water fossils immediately below and above the sections (Van Amerom & Glerum, 1984; Meessen, 1985).

The investigated marine bands form a small subset of the total amount that has been recognised (Fig. 1). The stratigraphically lowest Westphalian marine band studied in this paper is Domina, which has a Middle Westphalian B age. In the Ruhr basin, Domina has only been found in the northwestern part, indicating a continuation of paralic sedimentation in the southeast (Drozdowski, 2005). The Veldhof marine band was discovered in the 1980's and has been tentatively correlated with German marine bands (Van Amerom & Meessen, 1985). The most important marine band that was sampled is the Aegir. It has a rich fauna in the Ruhr Basin (Rabitz, 1966), where it can attain a thickness of 30 m. This is the last fully marine flooding in this part of the NWECEB (in the UK the Top marine band is found in Middle Westphalian C sediments). In KPK-1 and JPE-1, the Aegir is characterised by some *Goniatites*-remains but these occur together with other fossils (Table 1).

From a sedimentological point of view, the *Lingula* bands are comparable to the lacustrine bands (Figs 2 and 3). Both are characterised by the following sedimentary succession: at the base a grey and mostly mottled clayey siltstone occurs, deposited in a floodplain where bioturbation caused mixing of the sediments. This floodplain was drowned and peat formation started, resulting in a coal of variable thickness (usually <1 m). In case of the *Lingula* bands, seawater flooded the swamps and shallow marine conditions were established. A lacustrine setting developed because subsidence probably exceeded peat-growth. In both cases parallel laminated clay, (slightly) enriched in organic matter was subsequently deposited. Organic carbon contents decrease upwards and parallel lamination gives way to ripple lamination while bioturbation increases. In turn, the shallow marine and lacustrine sediments are overlain by fluvial mouthbar or channel sandstones and fine grained sediments deposited in floodplains. The Namurian *Goniatites* marine band of the Geverik well entirely consists of a claystone, deposited under relatively deep marine conditions. The sediments are well laminated and dark coloured because of the high organic matter content. Going upwards, the first pro-delta coarsening upward sequence marks the onset of the Namurian basin fill.

Methods

All samples were ground to small particle size using a Tungsten-carbide mill in an automated grinding machine (Herzog HSM-HTP). X-ray fluorescence spectrometry (XRF) was carried out on glass beads to obtain major element concentrations (see Table 3 for precision). The glass beads were analysed using an ARL9400 spectrometer with an Rh tube with full matrix correction for



Fig. 3. Core-photograph of a lacustrine band (RLO-LB 2). The mottled sediment (1) below the coal is well developed, as well as the organic-rich section (2) on top of the coal (lacustrine band). The white labels indicate the sample locations.

major elements. However, before XRF analysis could be carried out, TGA (thermo-gravimetric analysis) was performed on 3 - 4 g of grounded samples, using a LECO® TGA 601. The TGA results were used for the determination of the moisture (105° C), organic matter (450 - 550° C) and carbonate content (800 - 1100° C).

Total carbon content (TC) and total sulphur content (TS) were obtained using a LECO® SC 144DR C/S analyzer. Determination of the total organic carbon content (TOC) was carried out by subtracting the carbon content attributed to CaO (obtained by XRF) from the TC content. This corresponds well with the determination of TOC using carbonate from the TGA-results (not shown). Due to maturation, some loss of organic matter took place. However, except for GVK-1 the original TOC values have not been restored. There are two reasons for this: 1) the maturities of these sections are well comparable and not very high and 2) probably most of the organic matter is of terrestrial origin, implying only moderate loss of organic matter. Using the method published by Raiswell & Berner (1987), the original TOC for GVK-1 will fall within a range of 8 - 10 wt%.

It is assumed, based on Leeder et al. (1990), that the total sulphur concentrations obtained from the siliciclastic sediments are present in the form of pyrite. When plotted against Fe (Fig. 4), most of the samples with clear enrichment in sulphur are situated near the pyrite line, which indeed suggests the dominant residence of sulphur in pyrite. Based on studies by Diessel (1992) and Spears et al. (1999) it is also assumed that enrichments in sulphur (>1.5 wt%) in the coals analysed in this study are caused by pyrite.

HF-based destruction of 125 mg of pulverised sample was carried out to measure trace elements by ICP-MS. The solutions were analyzed by an Agilent 7500 ICP-MS with a low uptake nebulizer. The analytical quality of the XRF, C/S and ICP-MS analyses was determined by calculation of the precision of duplicate sample pairs. Accuracy was calculated with the mean

Table 3. Precision and accuracy of C/S (LECO), XRF (only precision) and ICP-MS analyses for elements used in this paper. Concentrations for C/S and XRF: wt%, for ICP-MS: mg/kg (nd = not determined).

Element	Method	Precision			Accuracy		
		Mean	Precision (σ)	2 σ (%)	Mean	Standard	Accuracy (%)
TS (wt%)	LECO	1.52	0.02	2.64	0.51	0.50	2.40
TC (wt%)	LECO	2.00	0.06	5.99	3.91	3.60	8.60
Al (wt%)	XRF	18.57	0.11	1.18	nd	nd	nd
Fe (wt%)	XRF	6.31	0.03	0.95	nd	nd	nd
K (wt%)	XRF	3.69	0.04	2.17	nd	nd	nd
Ca (wt%)	XRF	0.28	0.01	7.05	nd	nd	nd
Mo (mg/kg)	ICP-MS	2.91	0.11	7.57	1.20	1.14	5.22
U (mg/kg)	ICP-MS	3.98	0.16	8.04	2.28	2.31	-1.18
V (mg/kg)	ICP-MS	126.16	8.51	13.49	87.41	92.00	-4.99
Zn (mg/kg)	ICP-MS	105.67	6.61	12.52	622.31	528.00	17.86
Pb (mg/kg)	ICP-MS	256.03	3.04	2.38	164.39	167.00	-1.56
Ni (mg/kg)	ICP-MS	63.82	5.01	15.71	42.85	43.60	-1.72
Cu (mg/kg)	ICP-MS	46.58	2.72	11.68	90.16	95.00	-5.10
Th (mg/kg)	ICP-MS	10.29	0.76	14.77	9.28	9.74	-4.72

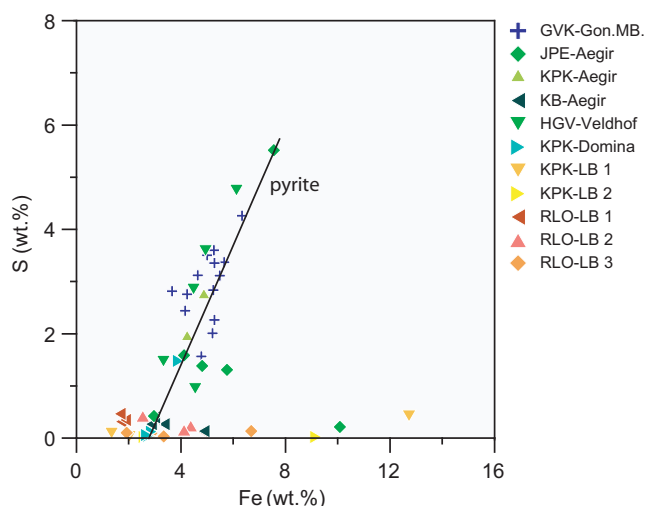


Fig. 4. Cross-plot displaying the Fe/S ratio for the marine and lacustrine bands. The samples enriched in pyrite plot relatively well on the pyrite line. PAAS: Post Archean Average Shale.

values of the standard measurements and the reported mean element concentrations of these standards (Table 3).

Trace elements enrichment factors (EF) were calculated for a number of elements. The mean EF for a particular marine/lacustrine band or overlying sediment layer is based on the following formula:

$$EF = \frac{\sum_{i=1}^N (El/Al)_{\text{sample}} / (El/Al)_{\text{av. shale}}}{N}$$

where *El* and *Al* are the trace element and aluminium concentrations (ppm) respectively for the average shale (*av.shale*) and *sample* (Taylor & McLennan, 1985) whilst *N* refers to the number of samples taken from the marine band or overlying sediments. Normalisation on *Al* has been carried out to remove the effect of the changing clay-percentages per sample. The EF for coal has been calculated in a different way because *Al* concentrations are very low in coal (Dellwig, 1999). Moreover, some trace elements may have an association with organic matter (Goodarzi & Swaine, 1993) which causes normalisation on *Al* alone to overestimate the enrichment. Therefore, world mean trace elemental concentrations in coal were used (Swaine, 1990; Gayer et al., 1999) to calculate the EF. The following formula was used:

$$EF = \frac{\sum_{i=1}^N (El_{\text{sample}} / El_{\text{mean}})}{N}$$

The following parameters were used to characterise the geochemistry of the marine and lacustrine bands:

1. *TOC*. Marine bands are often associated with enhanced TOC contents (Bloxham & Thomas, 1969; Spears & Sezgin, 1985; Wignall, 1994; Fisher & Wignall, 2001). The analysis of the sampled sections therefore starts with a description of TOC.

2. *Pyrite*. Pyrite is often used as an indicator of marine sulphate-reducing conditions (Berner & Raiswell, 1984). However, clear enrichment of pyrite only occurs under high TOC conditions (when degradable organic matter is present) because under low TOC conditions reduction of sulphate is limited (Lyons et al., 2003).
3. *Trace elements*. It is widely recognised that marine bands often display enrichment in U (Davies & McLean, 1996; Leeder et al., 1990; Fisher & Wignall, 2001) next to other trace elements like Molybdenum (Mo), Vanadium (V), Nickel (Ni), Zinc (Zn), Lead (Pb) and Copper (Cu) (Coveney et al., 1991; Algeo & Maynard, 2004; Algeo et al., 2004; Schultz, 2004). Enrichment of uranium and other trace elements in marine sediments will only occur if anoxic conditions prevail in the sediments and if there is a source. As the main source for trace elements like U, Mo and V is seawater (Taylor & McLennan, 1985), these elements will be investigated in particular.

Results

Organic matter

The TOC content of the *Goniatites* marine band varies from 1 to 4.9 wt%, which is an underestimation regarding the very high maturity (see above). In the grey shale on top of the marine band, a mean TOC content of 1 wt% is common. In general, the *Lingula* marine bands are characterised by lower TOC contents compared to the *Goniatites* marine band. A maximum of 4.6 wt% occurs in HGV-Veldhof whereas in KPK-Aegir and JPE-Aegir maxima around 2 wt% were obtained. In KPK-Domina and KB-186, the TOC content is only slightly higher than 1 wt%. The maxima mostly occur in the interval just above the coal and rapidly decrease upward (Fig. 5). The TOC contents in the 'normal' shale on top of the *Lingula* marine bands vary around 1 wt%, comparable to the values obtained in GVK-1.

In the lacustrine bands, higher TOC contents occur than in both types of marine bands (Fig. 5 & Appendix 1). A maximum of 40 wt% was obtained in RLO-LB 1 whereas in KPK-LB 1, RLO-LB 2 and RLO-LB 3 maxima of 17, 7 and 6.6 wt% occur respectively. Only in KPK-LB 2, TOC contents are comparable to those in the *Lingula* marine bands; the maximum percentage amounts to 2.4 wt%. The TOC maxima of the lacustrine sections also occur in the interval just on top of the coal and decrease upwards (Fig. 5). The TOC contents of the normal shale overlying the lacustrine bands are comparable to those found in the sections on top of the *Lingula* marine bands (appr. 1 wt%).

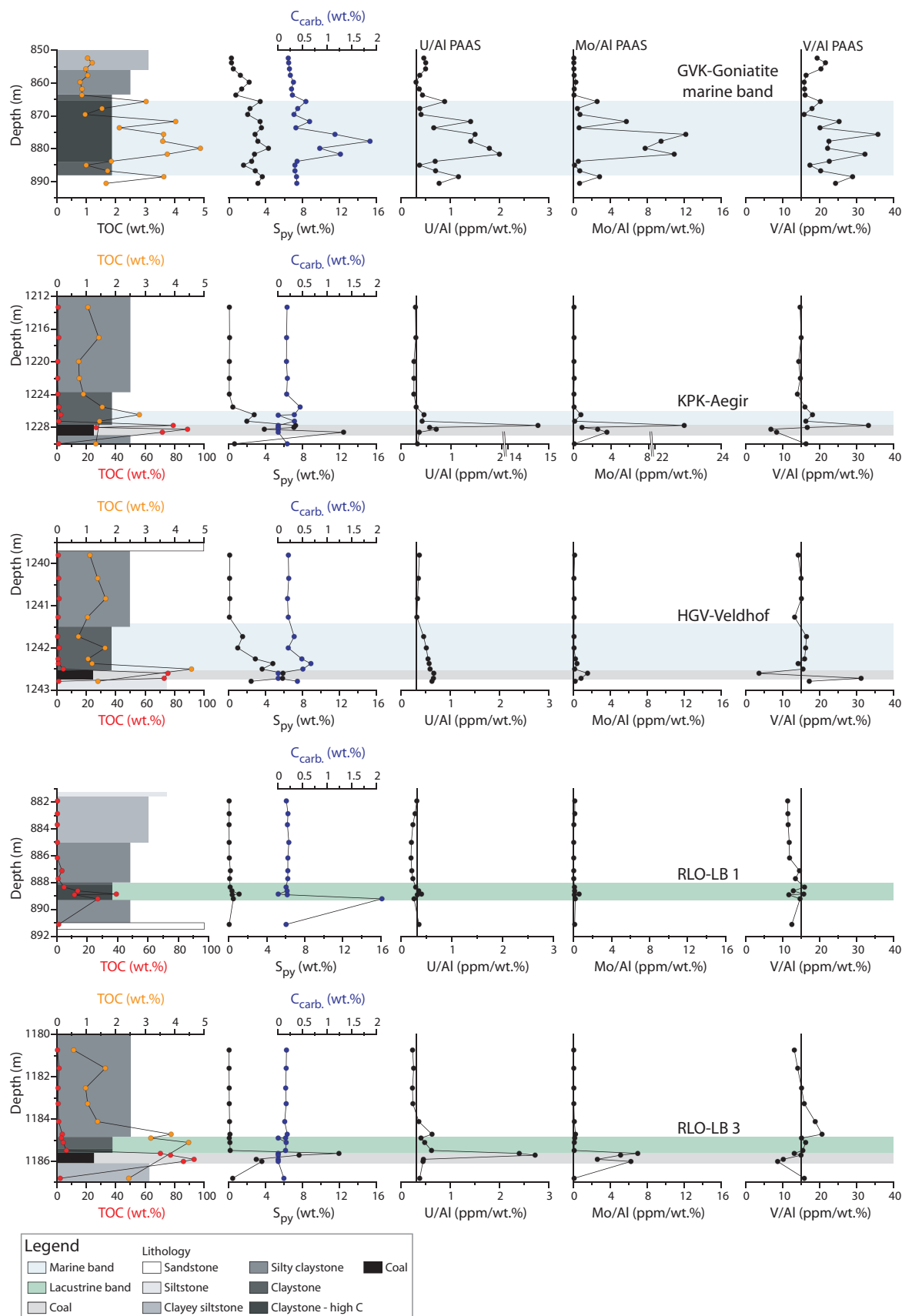


Fig. 5. Plots of two *Lingula* marine bands, two lacustrine bands and the *Goniatites* marine band to show the distribution of TOC, S, $C_{\text{carbonate}}$ and a selection of trace metals. Note the different scales used for TOC. In this figure the Al-normalised values for coal are shown. Note that the enrichment factors for coal displayed in figure 6 has been calculated in a different way. The coal-values in this figure are probably slightly over-estimated (see Methods).

Pyrite

In the *Lingula* marine bands KPK-Aegir, JPE-Aegir, HGV-Veldhof, enhanced S contents (up to 5.52 wt% in JPE-Aegir) occur in the basal part overlying the coal. In KPK-Domina only one sample shows an enrichment of >1 wt% S, whereas in KB-186 none of the samples from the marine band is >1 wt%. An upward decrease in pyrite content can in most cases be observed within the marine band (Fig. 5 and Appendix 1), leading to a 'background' value of ≤ 0.1 wt% in the normal shale overlying the *Lingula* marine bands. The only exception is JPE-Aegir in which pyrite contents remain relatively high ($S \geq 1.5$ wt%) throughout the marine band. The *Goniatites* marine band shows marked enrichments in pyrite (Fig. 5 and Appendix 1). The lacustrine bands are characterised by low S contents without exception. In RLO-LB 2 a maximum of 0.42 wt% (of all lacustrine bands) has been measured, which is significantly lower than the S contents in the *Lingula* marine bands.

The coals located below the *Lingula* marine bands show even higher sulphur contents than the overlying shale (Fig. 5 and Appendix 1). At the base of the coal below KPK-Aegir, a maximum of 12.4 wt% S has been measured. These sulphur contents are probably related to percolating seawater after the marine flooding, a process well-known from literature (Chou, 1984; Spears et al., 1999). In contrast, the coals below the lacustrine bands does not have strong enrichments in sulphur. The only exception is the RLO-LB 3 coal in which S is present up to 12 wt%. This coal is probably directly influenced by seawater, regarding the lack of S enrichments in the overlying lacustrine shale.

Trace elements

The *Goniatites* marine band shows a relatively high mean EF for U and Mo, whereas V is only moderately enriched (Fig. 6). None of the *Lingula* marine and lacustrine bands shows a mean EF higher than 2 for U, Mo and V; KPK-Aegir and RLO-LB 1 for Mo excluded. Apart from Pb/Zn and Zn in RLO-LB 1 and RLO-LB 2 respectively, in general the EFs for Cu, Ni, Pb and Zn are very low to insignificant for both the marine and the lacustrine bands (Fig. 6). Some sections do not show enrichments and even depletions relative to the average shale can be seen. The highest EF of U, Mo and V do not occur in the *Lingula* marine bands but in some of the underlying coals instead. This is also applies to some coals underlying the lacustrine bands (Fig. 6). An example is the coal located below the Aegir marine band in KPK-1. In the topmost sample in the coal a 30 ppm concentration for U was obtained, which clearly corresponds with the peak in the spectral gamma-ray at that depth (Fig. 1).

Th/U ratios, which are used to distinguish marine bands from normal shale, were obtained for all marine and lacustrine bands (Fig. 7). Davies & McLean (1996) considered Th/U ratios lower than 3.8 diagnostic for marine bands whereas Adams &

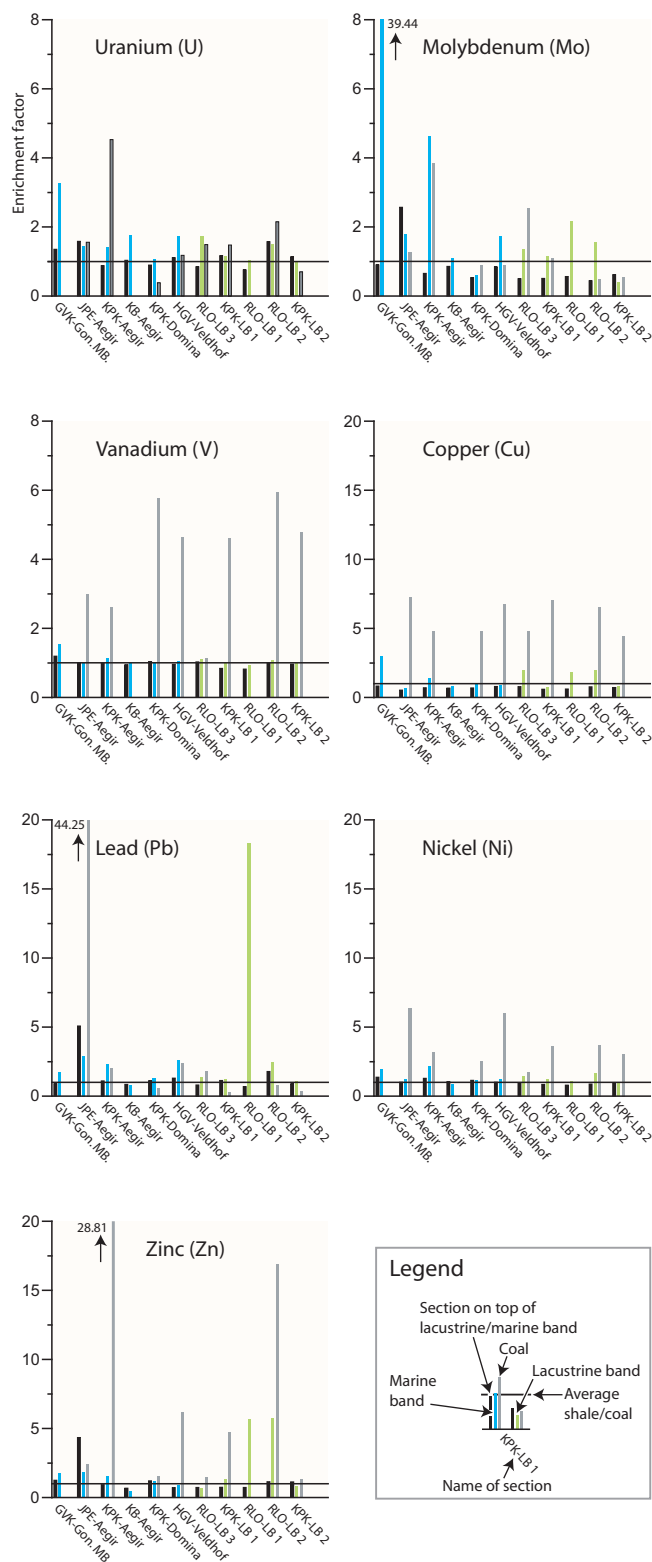


Fig. 6. Bar charts displaying the enrichment factors for the marine/lacustrine bands, the underlying coal and the overlying sediments. It is important to realise that the enrichment factors for the coals have been calculated differently (see text). Therefore, an enrichment of a certain element in a coal (for instance vanadium) does not necessarily mean that the absolute concentrations are higher in the coal than in the underlying and overlying sediments (see Appendix 1).

Weaver (1958), used by Hollywood & Whorlow (1993), thought a ratio lower than 2 representative for fully marine conditions. This figure again shows that the *Lingula* marine bands display the same order of U enrichments as the lacustrine bands whereas the *Goniatites* marine band is the only one clearly enriched.

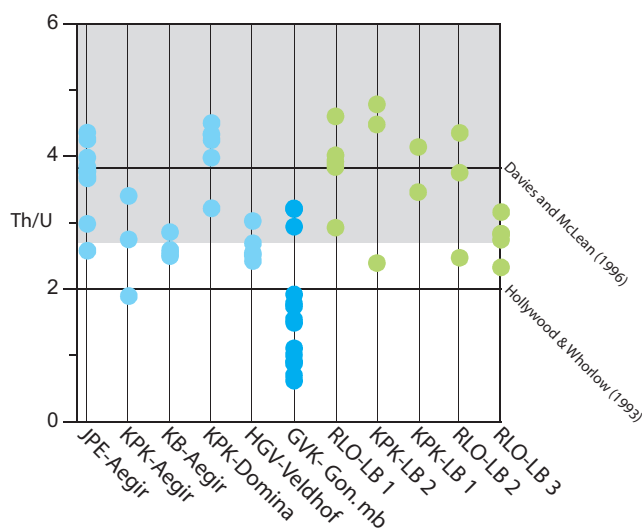


Fig. 7. Th/U ratios for marine and lacustrine bands. The grey box indicates the area where the Th/U ratios plot derived from the sediments overlying the marine and lacustrine bands. It can be seen that only the *Goniatites* marine band (dark blue) clearly displays an enrichment in U. The *Lingula* marine (light blue) and lacustrine bands (green) display minor or no enrichment in U compared to the overlying sediments.

Discussion

The data suggest that the *Lingula* marine bands have a low organic carbon content compared to the *Goniatites* marine band and the lacustrine bands. Pyrite contents are, however, clearly enriched in most *Lingula* bands which set them apart from the lacustrine bands. Trace element enrichment in the *Lingula* and lacustrine bands is low and often absent, in contrast to the *Goniatites* marine band investigated here and reported in literature (Bloxxham & Thomas, 1969; Fisher & Wignall, 2001). Although it has to be realised that the enrichment factors in Fig. 6 are mean values and that individual samples sometimes have higher enrichment factors, the mean EFs for the *Lingula* marine bands are considered to be insignificant. They are comparable to the EFs obtained for the sediments overlying the marine bands. Moreover, in general EFs are far higher (3.5 - 200 times) in marine bands/black shale reported in literature (Coveney et al., 1991; Fisher & Wignall, 2001, their table 1; Algeo & Maynard, 2004; Cruse & Lyons, 2004). Therefore, the *Lingula* marine bands can not be easily distinguished using the Th/U ratio alone. To effectively find marine bands on the basis of the Th/U ratios the ratio defined by Hollywood & Whorlow (1993) should be used. The ratio defined by Davies & McLean (1996) is not diagnostic because numerous samples derived from floodplain sediments fall into the marine bands-field.

Based on the results obtained here and those reported in literature, i.e. the clear enrichment of U in *Goniatites* marine bands and the absence in *Lingula* marine bands, recognition of marine bands using the gamma-ray log is only promising when they are found in *Goniatites* facies. Since the *Lingula* marine bands mainly occur along the basin margins, in these areas recognition of marine bands using gamma-ray only would be complicated. Although the dataset is limited, it might be concluded that the southern part of the Netherlands and Belgium did not belong to the main depocentre during Westphalian B/C.

In addition, the following questions remain to be answered: 1) what determines the TOC in the *Lingula*/*Goniatites* marine bands and the lacustrine bands; 2) why such poor trace element EFs in the *Lingula* marine and 3) lacustrine bands; 4) why are the trace element EFs in the coals mostly higher than in the overlying marine/lacustrine bands and 5) are the EFs syn-sedimentary or diagenetic?

Ad 1. Ramsbottom (1969) observed that although the total succession (of, for instance the Westphalian A) thins towards the basin margins, the individual marine horizons are thicker when benthonic fossils are present (like the *Lingula* marine bands) than when they only contain *Goniatites*. Therefore, the siliciclastic sedimentation rate in the *Goniatites*-bearing intervals is probably lower than in the *Lingula* marine bands. A relatively high siliciclastic sedimentation rate, together with the absence of anoxic bottom water conditions (thus causing enhanced oxidation and dilution of organic matter) probably lead to lower TOC in the *Lingula* bands. A comparable situation was observed in Mediterranean sapropels, which tend to become thicker and therefore show 'diluted' TOC towards the Nile delta (ten Haven et al., 1987). The higher TOC of the lacustrine bands probably has to be explained by a combination of a rather slow sedimentation rate plus a high influx of (non-degradable) organic matter.

Ad 2. Algeo & Maynard (2004) found that the trace elements U, Mo, V, Zn and Pb show strong enrichments under euxinic (>10 wt% TOC) circumstances, forming complexes with sulphides preferentially. During anoxic (TOC <10 wt%, non-sulphidic) conditions these TEs show a strong correlation with TOC, but the EF remain rather limited. In this light, the original TOC values of the *Goniatites* marine band (up to 10%) are in accordance with the higher trace element EFs. In the *Lingula* marine bands, TOC concentrations do not even exceed 5 wt%. This suggests that at the most, anoxic and no euxinic conditions prevailed during deposition of the marine bands, which forms an explanation for the small enrichment of trace elements in the sections studied here. The presence of *Lingulas* (brachiopods) already suggests that the oxygen concentration in the bottom waters is not too low to prevent these animals to live there. In addition, Bloxxham & Thomas (1969) and Fisher & Wignall (2001)

concluded that U is concentrated in the most organic rich parts of marine bands. Another explanation for the poor trace element enrichment may be a brief period of oxygenation which leads to the dissolution of scavenged elements (Anderson et al., 1989).

Ad 3. Trace elements can also be enriched in organic-rich fresh water sediments (Elbaz-Poulichet et al., 1997; Fisher & Wignall, 2001). However, it has to be realised that the concentrations of U and Mo in fresh water are much lower than in seawater (Taylor & McLennan, 1985) which probably means that anoxic conditions have to be more prolonged than in marine anoxic environments. Although the TOC contents of the lacustrine bands are in general much higher than the *Lingula* marine bands, the strongly limited availability of these trace elements prevents a significant enrichment.

Ad 4. Mo and U show higher EFs in the coals located below two of the *Lingula* marine bands than observed in the coals below the lacustrine bands (Fig. 6). Although it does not apply to all coals below the *Lingula* marine bands, it is suggested here that the influence of percolating seawater may lead to enhanced enrichments of U and Mo in the underlying coal. An example of this phenomenon is the U peak in the coal located below the Aegir marine band in the well KPK-1. The same process is probably responsible for the enrichment of Mo in the RLO-LB 3 coal, which also showed marine influence through its high sulphur contents. This is in accordance with the study of Gayer et al. (1999) who also found higher U and Mo contents in marine influenced coal than in coal overlain by lacustrine deposits. However, independent of the composition of the overlying sediment, coal tends to act as traps for migrating trace elements (Laznicka, 1985). It is therefore suggested that the enrichment of Ni, Pb, Zn and Cu as observed in the coals is mainly due to diagenetic processes because there is no preferential enrichment of these metals for marine or lacustrine influenced coal (Fig. 6). Late diagenetic enrichment of these metals was also interpreted by Dill & Pöhlmann (2002) in their study on Carboniferous coals in the Ruhr Basin. Uranium can also be diagenetically enriched. Jedwab (1966) reported a late-diagenetic enrichment of

uranium in coal intercalated in a sequence of lacustrine black shale whereas Davidson & Ponsford (1954) concluded that uranium enrichments in coal were caused by percolating meteoric waters. Nekrasova (1957) also concluded that the permeability and reducing conditions in Jurassic coal caused the diagenetic enrichment of U. The observation (in this study) that U mainly occurs in coal that experienced marine influence, does not prove that this is the only way to get enrichment but rather the absence of other mechanisms or sources.

Ad 5. Most authors imply that enrichment of trace elements in marine bands/black shale took place syn-genetically by scavenging of trace elements by organic matter or Fe-sulphides (Bloxham & Thomas, 1969; Fisher & Wignall, 2001; Algeo & Maynard, 2004). However, Laznicka (1985) attributed enrichment of trace elements on top of coals (where the marine bands are found) to late diagenetic processes. Realising that iron ore formation together with the associated enrichment in trace elements frequently took place above coal seams in the Carboniferous (Laznicka, 1985), this clearly leaves the possibility for a diagenetic enrichment of iron-sulfide and associated trace elements. Although the EFs in the lacustrine and *Lingula* marine bands are very low, such a process cannot be ruled out as the highest enrichments consequently takes place just on top of the coal seam.

Conclusions

Lingula and *Goniatites* marine bands can be distinguished in the Upper Carboniferous fluvio-lacustrine sedimentary sequence of the Netherlands and surrounding areas (Calver, 1969; Ramsbottom, 1969). *Lingula* bands formed in a nearshore environment whereas *Goniatites* marine bands are characterised by a deeper marine setting. The marine bands show a marked difference in enrichment of redox-sensitive trace elements such as U and Mo. The geochemical characteristics of both marine band types were analysed. Lacustrine bands were also investigated because these show the same sedimentological characteristics as the *Lingula* marine bands. These depositional environments show a typical set of geochemical characteristics (Fig. 8), which will be explained shortly.

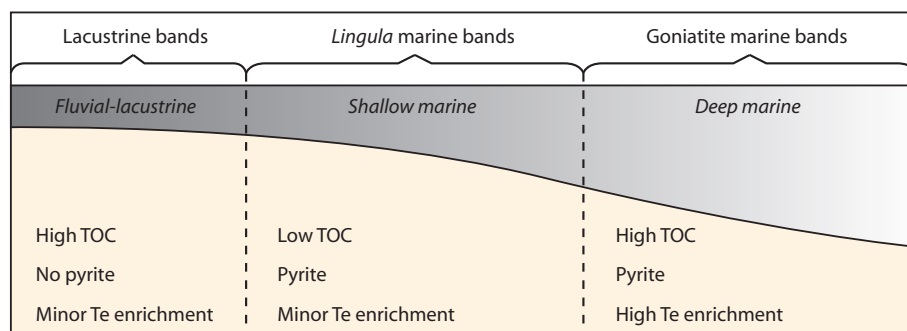


Fig. 8. Schematic cross-section displaying the areal distribution and geochemical characteristics of the intervals studied in this paper. TOC: total organic carbon; Te: trace elements.

The *Goniatis* marine band displays high TOC (up to 10 wt%), sulphur and redox sensitive trace element contents. Therefore, *Goniatis* marine bands can typically be characterised as marine black shale. Condensed sedimentation under marine and anoxic bottom water conditions lead to the effective scavenging of redox-sensitive trace elements. An important difference between the *Goniatis* and *Lingula* marine bands is the much lower TOC contents in the latter (1 - 2 wt%). This is attributed to a relatively high siliciclastic sedimentation rate during marine flooding, leading to dilution. It is proposed that the absence of high TOC concentrations (and possibly the absence of anoxic bottom water conditions) prevented the effective scavenging of trace elements during deposition of *Lingula* bands. Next to this explanation, a diagenetic process like the migration of an oxidation front or late-diagenetic enrichment cannot be ruled out. The lacustrine bands are characterised by high TOC contents but low sulphur and trace element concentrations. The high TOC contents can be explained by a combination of a slow siliciclastic sedimentation rate and a high influx of (non-degradable) organic matter. Enrichment of trace elements and sulphur in the lacustrine bands is absent or moderate. The limited availability of elements like S, U, Mo and V in fresh water is the most likely explanation.

Based on the results obtained during this study it is proposed that detection of marine bands with a gamma-ray device is only promising when they are developed in *Goniatis* facies. Along the margins of the basin, where marine bands occur in shallow marine *Lingula* facies, this method will probably fail.

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


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Appendix 1

	Depth	C/S			Major elements (wt%)				Trace elements (ppm)						
		TC (%)	TS (%)	TOC (%)	Al	Fe	Ca	K	U	Mo	V	Cu	Ni	Pb	Zn
GVK-Gon.mb.	852.39	1.1	0.3	1.0	10.1	4.0	0.2	3.0	4.7	0.5	195.4	37.8	77.5	9.4	89.7
	853.81	1.3	0.3	1.2	9.0	4.8	0.3	2.5	4.5	0.4	194.0	43.2	87.5	12.8	134.0
	855.67	1.1	0.5	1.0	9.7	4.2	0.2	2.8	4.8	0.5	197.2	45.0	79.6	10.5	127.0
	857.63	1.1	1.2	1.1	9.8	4.8	0.2	2.9	3.7	0.8	159.4	35.2	62.5	15.9	80.1
	859.72	0.8	2.2	0.8	9.8	5.1	0.2	3.0	3.0	2.6	155.7	48.2	69.9	38.8	97.5
	861.80	0.9	1.4	0.9	9.1	4.7	0.3	2.7	3.3	0.8	144.6	33.2	69.3	21.8	94.8
	863.66	1.0	0.7	0.9	10.3	4.6	0.3	3.1	4.5	0.6	165.4	38.5	63.6	11.2	89.8
	865.62	3.5	3.4	3.0	8.9	5.7	1.5	2.8	7.9	22.9	180.1	135.7	94.5	61.8	79.8
	867.76	1.7	2.3	1.5	10.0	5.3	0.6	3.1	3.8	4.3	179.5	61.7	75.2	32.3	107.1
	869.56	1.1	2.0	1.0	10.8	5.2	0.3	3.3	4.4	7.7	171.3	42.1	74.7	20.3	92.6
	871.72	4.7	3.4	4.0	8.1	5.3	2.1	2.5	11.4	46.4	204.7	172.5	103.6	27.2	108.9
	873.63	2.3	3.5	2.1	9.3	5.0	0.7	2.9	6.1	5.7	186.2	112.9	84.8	25.4	119.3
	875.63	5.0	2.8	3.6	4.8	3.7	4.5	1.5	7.3	59.0	173.6	138.5	91.5	18.0	105.9
	877.73	5.3	3.1	3.6	6.6	5.5	5.8	1.9	9.4	63.0	149.6	146.6	77.5	19.7	115.8
	879.88	5.8	4.3	4.9	7.6	6.3	3.2	2.2	13.6	59.0	168.4	170.5	89.3	27.1	126.4
	881.67	5.0	2.8	3.7	5.0	4.2	4.0	1.5	10.1	55.0	162.7	134.2	87.9	22.1	114.7
	883.84	2.0	2.5	1.8	10.0	4.2	0.6	3.1	6.9	5.3	225.7	76.6	78.8	19.8	129.1
	885.02	1.3	1.6	1.0	11.4	4.8	0.9	3.4	4.2	1.3	198.1	48.8	74.7	21.6	122.0
	886.74	1.8	2.9	1.7	10.6	5.2	0.3	3.2	7.4	7.2	214.6	74.8	79.4	22.7	138.8
	888.54	4.1	3.6	3.6	8.2	5.3	1.5	2.4	9.6	23.3	238.3	183.6	85.4	42.3	190.1
	890.55	1.8	3.1	1.7	10.0	4.6	0.3	3.1	7.7	6.6	243.3	100.8	83.4	39.5	156.4
JPE-Aegir	1118.93	1.0	1.2	0.9	5.4	3.5	0.3	1.8	2.8	1.5	82.1	22.1	34.6	70.8	178.7
	1120.26	1.8	1.2	1.7	6.9	4.8	0.4	2.4	3.2	1.7	104.2	8.4	32.7	49.8	283.8
	1121.59	nd	nd	nd	nd	nd	nd	nd	3.3	1.6	117.7	21.7	54.2	61.2	159.5
	1123.04	1.9	1.3	1.8	8.0	5.8	0.4	2.9	3.0	1.2	128.4	18.4	49.0	64.9	224.0
	1124.32	nd	nd	nd	nd	nd	nd	nd	4.1	1.2	127.7	22.6	42.6	79.3	221.9
	1124.73	nd	nd	nd	nd	nd	nd	nd	4.3	1.3	129.1	21.5	49.8	54.4	286.6
	1125.24	nd	nd	nd	nd	nd	nd	nd	4.3	1.5	140.2	27.5	56.1	59.4	221.1
	1126.03	1.7	1.4	1.7	10.4	4.8	0.3	3.4	4.3	2.3	147.0	30.9	59.4	50.7	291.5
	1126.56	nd	nd	nd	nd	nd	nd	nd	4.0	1.1	133.9	23.7	58.3	48.5	226.4
	1127.23	nd	nd	nd	nd	nd	nd	nd	4.0	1.2	146.5	26.7	49.0	66.0	210.7
	1129.10	2.6	0.2	2.4	9.6	10.1	0.5	3.1	3.1	1.3	178.8	23.2	40.1	31.2	83.0
	1129.86	0.3	0.4	0.2	12.1	3.0	0.2	4.1	4.7	0.8	180.5	39.5	51.6	56.0	97.7
	1130.31	1.6	1.6	1.6	10.1	4.1	0.2	3.1	6.5	3.9	132.4	34.8	69.1	53.9	159.7
	1130.79	1.7	5.5	1.6	9.9	7.6	0.2	3.0	4.9	1.1	128.7	54.3	131.0	86.7	50.8
	1130.99	80.5	6.5	80.5					3.1	5.1	57.3	51.3	82.7	2611.3	47.7
	1131.05	0.6	2.5	0.6	11.4	4.9	0.1	3.6	5.0	2.0	135.6	25.1	59.7	58.0	48.1
	1131.50	0.9	0.9	0.6	10.9	4.0	0.9	3.8	5.6	0.8	166.7	29.0	52.6	228.6	166.9
	1131.90	83.2	1.2	83.2	3.6	nd	nd	nd	10.2	0.9	49.6	45.1	67.5	891.7	80.8
	1192.41	nd	nd	nd	nd	nd	nd	nd	2.7	0.6	145.6	26.6	63.2	15.8	99.9
	1203.18	nd	nd	nd	nd	nd	nd	nd	3.0	0.5	154.2	34.4	53.7	23.2	142.9
KPK-Aegir	1213.33	1.1	0.1	1.1	11.0	3.5	0.3	3.5	3.1	0.7	162.2	32.1	73.4	23.4	120.5
	1217.04	1.6	0.1	1.4	9.9	4.4	0.4	3.0	2.9	0.6	147.9	29.7	64.2	17.3	87.6
	1219.95	0.8	0.1	0.7	11.9	2.8	0.2	3.7	3.0	0.7	170.9	34.9	81.4	27.9	91.4
	1222.00	0.8	0.0	0.8	11.9	2.8	0.2	3.9	3.0	1.0	176.4	35.8	91.7	22.3	88.7
	1223.93	1.0	0.0	0.9	12.6	3.0	0.2	4.2	3.2	0.7	176.7	40.2	60.4	34.0	66.1
	1225.50	1.9	0.4	1.5	11.6	3.7	1.3	3.7	3.5	0.8	185.8	72.7	115.7	29.2	83.0
	1226.44	2.9	2.7	2.8	11.2	4.9	0.3	3.6	5.1	8.8	202.4	94.0	134.7	48.2	133.4
	1226.5	nd	nd	nd	nd	nd	nd	nd	6.8	4.4	225.7	86.7	128.5	44.7	159.8
	1227.23	1.9	1.9	1.5	10.9	4.2	1.4	3.3	4.6	1.5	178.2	58.0	125.4	55.1	160.3
	1227.75	79.0	7.2	79.0	nd	nd	nd	nd	31.1	48.3	70.1	34.0	26.0	35.2	182.2
	1227.99	26.8	7.0	26.8	nd	nd	nd	nd	3.7	6.0	109.9	52.3	78.6	188.2	706.6
	1228.21	88.7	3.8	88.7	nd	nd	nd	nd	1.1	3.9	10.4	18.9	18.6	31.6	120.1
	1228.57	71.6	12.4	71.6	nd	nd	nd	nd	0.3	3.1	7.2	30.2	42.1	223.3	1295.8
	1229.99	1.4	0.6	1.3	9.9	3.2	0.4	2.8	3.2	0.9	161.9	33.3	62.9	25.1	181.9
	1250.28	nd	nd	nd	nd	nd	nd	nd	2.7	0.3	145.6	29.1	43.8	17.1	83.1
KB-Aegir	1296.5	1.1	0.1	1.0	9.9	4.3	0.2	3.3	2.8	1.0	156.4	40.9	68.6	15.9	91.5
	1297.7	1.2	0.1	1.1	9.9	4.6	0.2	3.3	2.8	0.6	147.5	33.8	58.8	16.3	55.6
	1298.7	0.9	0.0	0.8	11.2	3.8	0.2	3.8	3.1	0.8	161.5	36.5	70.1	31.9	50.9
	1299.9	1.2	0.1	1.2	11.0	3.4	0.2	3.1	4.2	1.0	139.9	36.2	55.7	10.7	57.5
	1300.7	0.9	0.1	0.9	11.5	3.4	0.2	3.5	4.5	1.2	153.0	35.3	55.6	17.7	52.7
	1301.1	1.3	0.1	1.3	12.0	4.9	0.3	3.7	6.0	0.9	186.6	45.4	53.9	16.0	46.1
	1301.8	0.9	0.3	0.8	11.9	3.4	0.3	3.6	6.6	0.9	162.3	35.5	47.4	15.3	49.1
	1302.1	0.9	0.3	0.8	11.7	2.9	0.1	3.9	6.5	1.5	173.5	50.2	53.8	17.4	47.1
	1302.5	0.9	0.4	0.8	11.6	3.0	0.1	4.0	6.6	1.9	180.8	61.3	60.7	23.0	45.5
	1302.5	0.9	0.4	0.8	11.6	3.0	0.1	4.0	6.6	1.9	180.8	61.3	60.7	23.0	45.5
HGV-Veldhof	1239.80	1.2	0.1	1.1	12.6	2.5	0.3	4.3	4.6	1.7	178.8	46.7	96.3	28.8	67.1
	1240.35	1.5	0.1	1.4	11.7	3.4	0.2	3.9	4.1	0.7	175.2	49.6	47.7	27.8	58.2
	1240.83	1.7	0.1	1.7	11.1	3.7	0.2	3.9	3.7	0.9	168.1	48.2	72.9	29.6	79.0
	1241.27	1.1	0.1	1.0	12.7	2.7	0.2	3.9	4.1	0.9	167.9	47.2	49.6	40.3	90.4
	1241.73	0.8	1.5	0.7	11.5	3.3	0.1	3.5	5.3	0.7	189.7	51.4	60.6	64.3	145.9
	1242.00	1.7	1.0	1.6	11.0	4.5	0.2	3.3	5.6	0.8	179.2	49.9	53.6	42.5	155.8
	1242.26	1.1	2.9	1.1	11.6	4.5	0.1	3.5	6.3	2.5	184.8	47.6	80.4	45.5	51.6
	1242.37	1.2	4.8	1.2	11.5	6.1	0.2	3.4	6.5	4.5	163.3	47.7	99.1	65.4	44.9
	1242.50	4.6	3.6	4.6	11.0	4.9	0.2	3.2	6.4	1.5	170.3	57.9	93.0	78.0	48.5
	1242.60	75.4	5.9	75.4	nd	nd	nd	nd	1.2	2.7	6.2	26.0	55.0	103.9	42.7
	1242.72	72.9	5.8	72.9	nd	nd	nd	nd	3.6	4.5	169.9	68.2	100.5	174.4	205.0
	1242.79	1.5	2.4	1.4	11.1	4.2	0.2	3.6	6.9	2.1	190.9	52.0	87.6	44.5	93.9

	Depth	C/S			Major elements (wt%)				Trace elements (ppm)						
		TC (%)	TS (%)	TOC (%)	Al	Fe	Ca	K	U	Mo	V	Cu	Ni	Pb	Zn
KPK-Domina	1592.49	2.2	0.1	2.0	9.3	7.0	0.4	2.5	2.8	0.7	144.3	31.5	62.0	16.3	97.4
	1593.37	1.0	0.0	1.0	11.9	3.8	0.2	3.6	3.1	0.5	178.5	41.5	69.8	26.0	121.0
	1596.00	1.1	0.0	1.1	11.8	3.9	0.2	3.6	3.2	0.5	189.0	42.0	74.0	32.6	122.0
	1596.47	1.1	0.1	1.1	12.8	2.9	0.2	3.9	4.1	0.7	200.6	56.6	81.1	42.0	95.2
	1596.93	1.5	0.1	1.4	12.9	2.8	0.2	3.8	4.0	0.8	180.1	49.3	93.5	35.6	130.2
	1597.1	nd	nd	nd	nd	nd	nd	nd	3.5	0.4	191.5	53.7	59.8	18.9	110.1
	1597.39	1.3	0.1	1.2	12.6	2.7	0.2	3.7	3.6	0.5	190.1	83.1	56.4	18.8	128.9
	1597.93	1.3	1.5	1.3	12.5	3.9	0.1	3.6	4.9	1.1	195.4	60.9	86.9	32.5	153.3
	1598.12	82.8	7.5	82.8	nd	nd	nd	nd	0.8	3.6	109.6	33.4	32.4	31.7	31.3
	1599.53	0.3	0.4	0.3	11.7	1.8	0.1	3.3	3.9	0.7	160.9	27.1	257.8	40.1	75.2
1601.34	1.5	0.0	1.5	9.6	4.2	0.2	2.8	2.8	0.8	137.8	32.3	58.0	16.7	98.6	
RLO-LB 3	1180.73	0.6	0.0	0.6	12.1	2.9	0.1	3.4	2.8	0.4	159.1	32.0	52.3	11.6	67.6
	1181.59	1.7	0.0	1.6	10.7	6.2	0.3	3.0	2.7	0.4	151.3	35.7	70.9	20.3	122.4
	1182.53	1.0	0.0	1.0	12.7	3.5	0.2	3.7	2.9	0.5	192.0	40.1	72.7	17.4	76.7
	1183.27	1.1	0.0	1.1	13.2	2.7	0.2	3.9	3.1	0.6	209.4	47.6	68.0	23.0	61.0
	1184.12	1.5	0.1	1.4	13.2	2.6	0.3	3.9	4.7	1.3	248.3	92.0	65.9	29.3	43.9
	1184.72	3.9	0.1	3.9	12.0	1.9	0.1	3.4	7.5	2.7	248.1	163.2	98.0	47.5	59.5
	1184.90	3.2	0.0	3.2	12.0	3.3	0.2	3.4	4.8	1.7	181.7	93.7	77.3	27.0	60.7
	1184.9	nd	nd	nd	nd	nd	nd	nd	4.9	1.6	210.2	118.0	68.5	23.8	54.8
	1185.11	4.5	0.1	4.5	12.0	2.9	0.2	3.3	5.7	1.1	194.6	116.6	83.5	30.0	57.8
	1185.49	6.8	0.1	6.6	9.7	6.7	0.4	2.3	6.0	0.8	150.2	86.4	94.2	19.8	75.6
	1185.63	70.3	11.9	70.3	2.9	nd	nd	nd	7.1	20.5	38.7	52.4	44.8	99.8	29.9
	1185.71	77.2	7.6	77.2	1.3	nd	nd	nd	3.4	6.4	18.9	26.2	10.6	220.2	30.1
	1185.91	93.1	3.0	93.1	1.6	nd	nd	nd	0.7	4.1	16.2	19.0	10.4	40.5	28.6
	1186.01	85.9	3.6	85.9	1.5	nd	nd	nd	0.7	9.4	13.1	36.1	22.7	59.2	33.0
1186.81	2.5	0.4	2.4	7.6	2.0	0.1	2.0	2.9	0.6	120.5	33.5	43.4	17.5	47.5	
KPK-LB 1	1491.65	1.6	0.0	1.5	11.3	3.8	0.2	3.0	3.9	0.5	134.2	28.9	40.5	24.1	94.0
	1492.24	1.8	0.1	1.7	10.1	3.8	0.2	2.6	4.4	0.7	130.2	31.2	46.9	21.2	73.0
	1493.16	0.8	0.0	0.8	12.1	2.2	0.1	3.4	4.2	0.5	142.9	27.2	50.5	22.6	75.1
	1493.98	1.8	0.0	1.7	13.0	3.7	0.2	4.1	4.2	0.7	182.2	54.4	81.6	38.6	48.5
	1495.05	6.6	0.1	6.5	13.3	1.3	0.2	4.2	3.5	0.8	177.8	17.2	60.9	29.3	51.3
	1495.48	1.0	0.0	0.9	10.5	2.0	0.3	3.2	2.9	0.7	137.7	28.0	35.9	15.9	64.4
	1495.90	17.8	0.4	17.4	7.7	12.7	1.1	1.9	4.1	1.7	144.0	59.6	95.6	29.1	193.1
	1496.10	71.1	1.1	71.1	nd	nd	nd	nd	2.9	4.7	80.7	51.8	43.2	15.5	95.2
	1496.10	75.9	1.5	75.9	nd	nd	nd	nd	2.8	5.3	75.8	51.8	42.8	15.8	100.8
	1496.52	40.9	0.6	40.9	nd	nd	nd	nd	3.2	2.9	106.4	44.4	54.1	17.9	87.9
	1496.72	7.1	0.2	7.1	9.3	2.2	0.1	2.6	3.5	1.1	124.1	34.3	61.4	23.0	113.7
	1569.14	1.4	0.1	1.3	8.1	3.4	0.2	1.9	3.7	0.6	113.9	32.2	44.6	17.1	95.9
KPK-LB 2	1569.76	0.8	0.1	0.7	10.9	2.5	0.1	2.9	3.5	0.8	153.9	35.9	55.5	18.2	116.4
	1570.48	0.6	0.1	0.6	11.9	2.3	0.1	3.4	4.2	0.7	175.6	40.8	66.1	19.8	92.5
	1571.11	0.7	0.0	0.7	11.6	2.4	0.1	3.4	3.3	0.5	175.6	42.3	63.8	19.2	94.3
	1571.44	1.1	0.0	1.0	12.6	2.6	0.1	3.8	4.0	0.6	204.1	60.9	69.0	25.2	68.2
	1571.58	2.5	0.0	2.4	9.9	9.2	0.2	2.6	3.1	0.4	137.8	31.4	48.0	21.7	91.9
	1571.70	93.2	0.8	93.2	nd	nd	nd	nd	1.0	2.5	189.3	31.5	69.5	23.5	37.5
	1572.04	99.4	0.7	99.4	nd	nd	nd	nd	0.2	1.8	6.6	19.7	21.4	7.8	12.5
	1572.52	75.8	0.5	75.8	nd	nd	nd	nd	3.0	2.0	77.3	42.8	27.6	28.8	28.4
	1573.19	0.6	0.0	0.6	10.0	2.6	0.1	2.7	3.5	0.2	127.5	30.2	58.0	21.2	93.8
	RLO-LB 1	881.92	0.6	0.0	0.5	9.1	2.8	0.2	2.5	2.8	1.2	103.3	30.0	42.6	15.3
882.87		0.5	0.0	0.5	10.6	3.1	0.2	3.1	2.9	1.4	120.5	26.9	43.3	14.2	74.0
883.69		0.4	0.0	0.4	12.0	2.9	0.1	3.7	2.8	0.4	137.7	31.3	50.2	16.8	61.0
885.01		0.5	0.0	0.5	12.6	3.0	0.1	4.0	2.5	0.3	148.7	60.7	44.1	11.0	59.5
886.17		0.5	0.0	0.4	13.1	3.1	0.1	4.2	2.5	0.3	155.9	32.7	50.8	9.1	61.0
887.12		3.7	0.2	3.5	9.3	14.2	0.7	2.8	1.9	0.2	134.9	24.6	51.7	17.0	44.0
887.71		1.0	0.1	1.0	12.7	4.0	0.1	4.2	2.9	0.3	171.3	41.1	62.9	23.4	92.6
888.34		4.9	0.1	4.8	11.8	4.8	0.2	3.9	3.4	1.2	188.1	84.3	74.6	44.8	92.9
888.62		13.9	0.3	13.9	9.7	1.7	0.0	2.4	3.3	1.1	124.5	41.8	50.2	84.0	311.7
888.86		39.3	1.1	39.3	nd	nd	nd	nd	3.2	4.6	124.2	63.6	66.6	330.7	271.9
888.91		11.7	0.4	11.7	9.8	1.9	0.0	2.5	3.1	0.9	114.8	40.2	49.1	59.0	124.9
889.21		29.5	0.5	27.0	6.3	1.7	8.3	1.5	1.6	1.2	93.0	140.6	35.5	776.0	979.3
891.12		1.4	0.0	1.3	8.7	4.3	0.2	2.3	3.1	1.1	108.8	22.8	43.7	13.5	69.5
RLO-LB 2		1232.39	1.1	0.1	1.0	12.2	3.6	0.2	3.7	5.2	0.6	142.6	37.8	60.9	31.2
	1232.86	2.5	0.0	2.4	11.4	8.6	0.5	3.5	5.9	0.4	188.7	46.1	51.1	48.4	104.1
	1233.80	2.1	0.0	2.0	11.6	6.9	0.3	3.6	5.9	0.5	190.7	46.6	57.9	46.3	120.7
	1234.47	1.0	0.0	0.9	12.5	3.5	0.2	3.9	6.2	0.6	188.9	52.6	62.0	42.9	107.7
	1234.99	4.3	0.2	4.2	11.7	4.4	0.2	3.5	7.3	1.9	179.5	118.1	107.0	60.0	141.0
	1235.31	3.6	0.2	3.5	11.9	4.1	0.2	4.2	4.0	1.8	207.6	92.0	99.5	54.8	129.4
	1235.51	7.0	0.4	7.0	11.7	2.5	0.0	3.7	5.0	1.8	183.9	137.3	111.9	60.7	1454.7
	1235.55	66.7	0.6	66.7	nd	nd	nd	nd	4.6	1.5	236.7	38.3	77.2	51.0	899.7
	1235.72	79.6	0.6	79.6	nd	nd	nd	nd	1.4	2.0	55.1	34.6	36.7	30.9	79.1
	1236.15	87.2	1.0	87.2	nd	nd	nd	nd	6.9	2.4	47.9	64.6	30.3	62.6	34.6
1236.71	1.2	0.0	1.2	12.6	1.4	0.0	2.1	4.4	0.4	215.6	48.3	99.0	30.3	32.2	

 Marine band
 Lacustrine band
 Coal
 nd not determined