DEPARTMENT OF MINES AND ENERGY SOUTH AUSTRALIA

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ORGANIC CARBON AND TRACE ELEMENT INVESTIGATIONS COOPER BASIN SEDIMENTS PROGRESS REPORT: MUNKARIE NO. 1

GEOLOGICAL SURVEY

BY

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> Rept.Bk.No. 79/32 G.S. No. 6151 D.M.

No. 225/78

CONTENTS	PAGE
ABSTRACT	1
INTRODUCTION	1
PREPARATION AND TREATMENT OF SAMPLES	2
DISCUSSION OF RESULTS	3
1. Raw Data	3
Carbonate carbon	.3
Organic and elemental carbon	.3
Elements determined by ES at AMDEL	4
Elements determined by AAS at SCAE	4
2. Manipulated Data	5
Carbonate carbon	5
Organic and elemental carbon	5
Zinc	6
Manganese	6
Iron	6
Combined element distribution	6 .
Correlation between elements	7
CONCLUSIONS AND RECOMMENDATIONS	8
ACKNOWLEDGEMENTS	9
APPENDICES	
I Munkarie Number 1 - Summary Lithologic L	og
II Munkarie Number 1 - Analytical Results	
FIGURES	
Fig. No. Title	Drawing No.
Munkarie No. 1, Geochemistry of Cuttings	79-146
Munkarie No. 1 Cuttings, Zinc Content of Shales, Emission Spectroscopy	79-147

Fig.	No.	<u>Title</u>	Drawing No.
3	•	Munkarie No. 1 Cuttings, Zinc Content of Shales, Atomic Absorption Spectroscopy	79-148
4		Munkarie No. 1 Cuttings, Carbon Content of Shales.	S-13888
5		Munkarie No. 1 Cuttings, Metal Content of Shales by Atomic Absorption Spectroscopy.	S-13889
6		Munkarie No. 1 Cuttings, Geochemistry of Shales showing Geochemically Indentifiable Unit Boundaries.	S-13890

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PROGRESS REPORT: MUNKARIE NO. 1

ABSTRACT

Preliminary investigations suggest that shales within conventionally-defined rock units in Munkarie No. 1 exhibit characteristic trace-element signatures. It appears moreover that the Toolachee Formation here can be subdivided into three chemostratigraphic units not otherwise recognisable from well logs.

There is no consistent correlation between trace element and organic carbon contents of the analysed samples; although exhaustive correlations are not yet completed, it seems therefore that a major initial aim of this investigation already has been achieved.

Potential stratigraphic applications of these geochemical data warrant further work.

INTRODUCTION

In April 1978 a joint project - "Organic carbon and trace element investigations" - was commenced by the S.A. Department of Mines and Energy and W.G. Shackleton of Salisbury College of Advanced Education (SCAE). The major purpose of the project is to identify possible relationships between the organic carbon (C_{org}) content and the trace metal content of sedimentary rocks.

Apart from contributing to the debate on the genesis of certain sedimentary mineral deposits, such an investigation may prove valuable to petroleum geology because:-

(a) if there is a significant relationship between metal and \mathbf{C}_{org} contents of sediments, then it may be simpler and cheaper to analyse sediments for a suite of elements rather than for organic carbon, to identify those sediments worthy of further investigation as potential petroleum source rocks; and

(b) lateral variations in the distributions of metals may indicate source areas for the sediments.

To determine the applicability of such an approach, a pilot project was undertaken whereby 77 ten-foot-interval well cuttings samples (including 7 duplicates) were taken from 5750 to 6450 feet depth in Munkarie No. 1 well, southeastern Cooper Basin (all Depth measurements are retained as 'feet' because this is standard practice in the Cooper Basin area). This interval includes the Permian Toolachee and Daralingie formations, from which petroleum is produced elsewhere in the basin and portion of the Lower-Middle Triassic Nappamerri Formation.

PREPARATION AND TREATMENT OF SAMPLES

Cuttings representative of ten-foot intervals were scoop sampled and split to provide a working sample of approximately 50 g. A lithological log for the interval sampled was compiled by the author from wire-line logs and binocular microscope examination of the cuttings (Appendix I) independently of Munkarie completion-report lithologs.

Considerable contamination by bit shavings was removed by passing a bar magnet through the samples.

The samples were then numbered randomly and forwarded to the Australian Mineral Development Laboratories (AMDEL). After pulverising to pass 150 mesh BSS, 10 to 15 g were split from each sample for analytical work.

The following were determined at AMDEL:

- (a) Carbonate carbon content
- (b) Organic and elemental carbon content
- (c) 32 elements by emission spectroscopic (ES) scan.

The results (initially reported as AMDEL Job AC3910/78) are presented as Appendix II. Note that with the exception of

one value for Mo, the following elements were not detected: Mo, As, Bi, Cd, Ge, In, Sb, Ta, Th, W and Yb. Results from this analytical method are precise only to \pm 50%.

On completion of the work at AMDEL, the remainder of the pulverised samples was sent to the Department of Earth Science, SCAE. 0.5 g of each sample was boiled in 2 ml of Aqua Regia for one hour. After cooling and dilution to 10 ml with distilled water, copper, lead, zinc, manganese and iron were determined on a Pye Unicam SP 191 atomic absorption spectrophotometer (AAS). The machine was recalibrated at frequent intervals, averaging once per ten samples. The results, precise to ± 5 percent at the 95 percent confidence level, also are included in Appendix II.

The results of the analytical work carried out at both AMDEL and SCAE are plotted against depth in Figure 1, which also includes two stratigraphic (lithological) columns: one compiled by the author's interpretation of wireline BHC-GR logs, using formation boundaries given in the well completion report, and the other compiled from the author's cuttings descriptions in conjunction with wireline logs.

DISCUSSION OF RESULTS

1. Raw Data - Refer to Figure 1

Carbonate carbon (C_{CO3}) There is little variation with lithology, except for slight decreases in sandy units. The lower portion of the Toolachee Formation contains significantly less carbonate carbon than the intervals above and below, and highest concentrations occur in the middle portion of the Toolachee Formation.

Organic and elemental carbon (C_{org}) Content varies markedly with lithology, the coaly units naturally exhibiting very high values. There is a sharp contrast in C_{org} concentrations

between the Nappamerri Formation and the Toolachee Formation: these obviously formed in different environments. Although C_{org} content remains high through the Permian interval sampled, the lower portion of the Toolachee Formation contains slightly higher concentrations than the upper.

The carbon content decreases by about 50 percent from the lower Toolachee Formation to the Daralingie Beds.

Elements determined by ES at AMDEL These generally show variation in concentrations with lithology, especially evident by element concentrations in the basal sandstone unit of the Toolachee Formation and shales of the upper Daralingie Beds.

Some elements also vary in concentration within shales of different stratigraphic units. Zinc, for example, is "high and variable" in the Nappamerri Formation; "moderate and variable" in the upper Toolachee Formation; "very low" in the lower Toolachee Formation and "variable but high" in the Daralingie Beds.

To a lesser extent, but still significantly, lead and manganese also show this tendency.

Elements determined by AAS at SCAE The five elements, Cu, Pb, Zn, Mn and Fe, all show variation with lithology similar to those elements determined by ES. However, largely because of the higher precision of the AAS determinations, there is less apparent variation in element concentrations within a lithological unit.

The main difference between the results of the two analytical methods is that AAS shows no marked contrast in concentrations of any of the five elements between the lower Nappamerri Formation and the upper portion of the Toolachee Formation.

However Fe, as the other metals, tends to occur at relatively lower concentrations in the lower portion of the Toolachee Formation.

2. Manipulated Data

Variations in element concentrations are due mainly to lithological variations. To minimise that influence upon the data, only analytical results from samples principally composed of shale, the most common lithology, were considered.

Because of the variation within lithological units, particularly as apparent by the imprecise ES method, results were evaluated by a rolling-mean technique. Zinc concentrations, which on initial inspection of the data appeared to show significant variation, were subjected to a range of averaging calculations from the raw data to the rolling mean calculated on seven consecutive values (n=7). Both ES and AAS results for Zn were treated in this manner (Figs 2 & 3)*.

After examination of these vertical "shale-only" profiles it was decided to adopt a five-consecutive-value rolling mean (n=5) in subsequent manipulations, since this mean appears to smooth variations in the raw data to a satisfactory level without rendering unrecognisable the main contrasts seen in Raw values and rolling means (n=5) also were plotted for C_{CO3} and C_{org} (Fig. 4), manganese and iron (Fig. 5). Carbonate carbon (C_{CO3}) The averaging technique emphasises consistent concentrations from Nappamerri Formation levels to the middle portion of the Toolachee Formation, where markedly higher values occur. The lower portion of the Toolachee Formation contains consistently lower concentrations, that increase slightly on entering the Daralingie Beds. Organic and elemental carbon (Corg) As is apparent from the raw data, the most marked change in concentrations occurs at the Nappamerri - Toolachee formation boundary.

^{*} On Figures 2 and 3, and on subsequent figures, are shown three subdivisions of the Toolachee Formation interval. Bases for these subdivisions are explained in the ensuing discussion.

Concentrations within Toolachee Formation shales identify three units: an upper unit, containing lower concentrations than a lower unit, with an intervening "transitional zone". The Daralingie Beds exhibit $C_{\hbox{org}}$ concentrations similar to the upper Toolachee unit.

Zinc Values for the Nappamerri Formation appear to depend on the efficiency of the analytical extraction technique. Emission spectroscopy produces much higher values than the aqua regia extraction for AAS, thus enabling a distinction to be made between the Nappamerri and Toolachee formations that is not apparent by the AAS results alone. Both sets of results however enable the Toolachee Formation to be subdivided into upper (with higher zinc content) and lower units. The boundary between these two units, at about 6030 feet depth, approximates a boundary recognised by both CCO3 and Corg data.

Zn values by both ES and AAS are significantly higher in the Daralingie Beds than in the Toolachee Formation. Concentrations of this element show little variation through most of the sampled interval, although a "lower Toolachee" unit can be identified where concentrations are only about 50% of those apparent elsewhere. The boundaries of this unit are seen also in $C_{\rm org}$ and $C_{\rm CO3}$ data. Iron Values show variations similar to those for AAS zinc. Combined element distribution All the above results suggest that element concentrations may be used to define major stratigraphic units, and more particularly to subdivide the Toolachee Formation. Unit boundaries are shown in Table 1, the intra-Toolachee boundaries being chosen from both the raw and rolling-mean plots (Figures 1 to 5). The element concentrations shown in this table are means (not rolling means) of <u>all</u> predominantly-shale samples from each of the chosen subdivisions.

TABLE 1

ROCK UNIT, Established	SUBDIVISI Proposed			EAN ASSA	AY VALU	ES (SHAI	E-ONLY	BASIS)
terminology	here		Corg %	C _{CO3}	Zn _{ES} ppm	Zn AAS ppm	Mn AAS ppm	Fe AAS ppm
Nappamerri Fm.	***	-5860		0.85	297	86	641	38,640
Toolachee Fm.	Upper Midd1e	5860-6030 6030-?615	0 4.44	0.83 1.28	108 40	81 49	578 475	37,140 36,430
Daralingie Beds	Lower	?6150-6370 6370-	6.75 3.51	0.53 0.84	32 257	51 106	263 579	21,800 35,290

The boundary between the middle and lower Toolachee Formation units is problematic, since it may be placed above or below a coaly unit occurring near that depth.

To make clearer the variations in element concentrations summarised in Table 1, the above means are expressed in Table 2 as percentages of the https://doi.org/10.1001/journal.org/

TABLE 2

ROCK UNIT	DEPTH (Feet		MEAN ASSAY VALUES (SHALE-ONLY BASIS), AS PERCENT OF HIGHEST VALUE											
				Corg	C _{CO3}	Zn _{ES}	Zn AAS	Mn AAS	Fe _{AAS}					
Nappamerri Fm.	Upper	586	-5860 0-6030	7.85 80.44		100.00 36.36	81.13 76.42	100.00	100.00 96.12					
Toolachee Fm.	Middle Lower	603	0-?6150 0-6370		100.00	13.47 10.77	46.23 48.11	74.10 41.03	94.28 56.42					
Daralingie Bed	S	637		52.00		86.53	100.00	90.33	91.33					

These data are plotted as Figure 6.

Correlations between elements Table 3 illustrates correlation coefficients between each of (Mn, Fe, Zn) and ($^{\rm C}_{\rm org}$, $^{\rm C}_{\rm CO3}$) pairs. Correlation of the metals with $^{\rm C}_{\rm org}$ content is shown to be highly variable and although correlation with $^{\rm C}_{\rm CO3}$ is marginally better, it is too variable to be of practical value.

TABLE 3

Elemental Pairs-		C _{or}	y with			C _{CO3}	with	Vi iv
Rock Unit (shale samples only)	^{Mn} AAS	Fe _{AAS}	^{Zn} ES	^{Zn} AAS	^{Mn} AAS	^{Fe} AAS	^{Zn} ES	^{Zn} AAS
All shales	-0.23	-0.12	-0.55	-0.43	0.52	0.64	-0.03	-0.01
Nappamerri Fm.	-0.34	-0.57	-0.29	-0.56	0.79	0.82	0.46	0.43
''Upper'' Toolachee	e 0.25	0.34	-0.38	-0.52	0.47	0.51	-0.39	-0.52
''Middle'' Toolache	ee 0.36	0.20	-0.73	0.04	0.39	0.51	-0.07	-0.01
"Lower" Toolachee	e -0.15	-0.11	-0.74	-0.73	0.91	0.82	0.29	0.43
Daralingie Beds	0.63	0.72	-0.42	-0.15	0.94	0.95	-0.55	0.10

CONCLUSIONS & RECOMMENDATIONS

There is no consistent correlation of trace metals with organic and elemental carbon in the cuttings samples analysed. It is unlikely therefore that any estimation of organic carbon contents by correlation with trace metal analyses would be a success in this area, or probably in the Cooper Basin.

A potential value of this preliminary work is the possibility of recognising and defining rock units by their trace-element content. To further investigate these aspects, Munkarie cuttings from intervals above and below that discussed here will be analysed by ES and AAS, and results will be integrated in a subsequent review report.

It is proposed that cuttings from another Cooper Basin well be similarly analysed, to establish the potential for wider application of this chemostratigraphic tool within the basin. Big Lake No. 23 lies in a different province of the basin from Munkarie No. 1, but penetrated a comparable stratigraphic sequence with adequate well control, and cuttings from this well should be analysed for their trace-elements.

ACKNOWLEDGEMENTS

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Mr. P.M. Austin, of the same Department, contributed stimulating discussion, constructive criticism and valuable advice throughout this investigation.

Mr. L.P. Dorsett and Mrs. L. Halfpenny of S.C.A.E. provided valuable assistance during the preparation and analysis of the samples by AAS.

Salisbury C.A.E. is thanked for making available College research facilities, particularly the Pye-Unicam Spectrophotometer.

APPENDIX 1

Munkarie No. 1

Summary Lithologic Log

APPENDIX I

Munkarie Number 1

Summary Lithologic Log

From -	To	Description
5750 '	5860'	Shale - silty. Fine to medium grained, quartz and lesser feldspar; traces organic matter. Traces of very fine pyrite in silty fraction Grey.
5860'	58701	Shale - silty. Similar to above but frequent black coal fragments. Grey.
5870°	58801	Coal - black, lustrous. Some silty shale as above.
5880'	6000'	Shale - silty. Similar to shales above but abundant organic material gives dark brown to black colour.
6000'	6020'	Coal - black, lustrous.
6020'	6080'	Shale - silty and sandy in parts some coal fragments. Grey to brown depending on amount of organic material. Coarser towards bottom.
6080	6090'	Sandstone - coarse, angular - subangular clear quartz grains.
6090 '	6130'	<u>Shale</u> - silty, as for 5880'-6000'.
6130'	6150'	$\frac{\text{Coal}}{6080' - 6090'}$.
6150'	6180'	Shale - silty, as for 5880'-6000'.
6180'	62001	<u>Coal</u> - as before.
6200'	6210'	Shale - silty, dark grey, organic rick.
6210'	6230'	Coal - black, less lustrous than above. Larger silty shale component.
6230'	6270'	<u>Shale</u> - silty, as for 6200'-6210'.
62701	6280'	Coal - black, lustrous.
6280'	6300'	Shale - as above, 50% organic silty shale.
63001	6310'	Coal - as above, 50% organic silty shale.
6310'	6370 '	Sandstone - 1-2 mm dia. angular quartz grains. Traces organic silty shale and coal fragments.

From -	To	Description
6370 '	6430'	Shale - dark grey, highly organic, suggestion of bedding in other section.
6430'	6440'	Coal - black, lustrous.
6440'	6450'	Shale - as for 6370'-6430'.

APPENDIX II

MUNKARIE NUMBER 1

TABULATED ANALYTICAL RESULTS

The following tables present the results of analysis of well cuttings from Munkarie Number 1.

Determinations of carbonate carbon, organic carbon and the multi element scan by emission spectroscopy for 32 elements were all carried out by the Australian Mineral Development Laboratories, South Australia.

Determinations of copper, lead, zinc, manganese and iron by atomic absorption spectroscopy were carried out by W. G. Shackleton, P. Dorsett and L. Halfpenny at Salisbury College of Advanced Education, South Australia, on a Pye Unicam atomic absorption spectrophotometer.

N.B.

- 1. X = not detected at the limits quoted.
- Results are in ppm unless otherwise stated.
- 3. Detection limits in brackets.
- * Duplicate sample.

MUNKARIE NO.1

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				- 6 Ze C	6.71	61.10	×	2	x	10	8.0	x	666	×	¥	8.0	7	¥	****
4				- 6290	0.85	7,45	7.0	3.	, ¥	5	100	×	1005	x	X	80	10	Ÿ	
				- 6368	0.66	b.70	563	2	x	13	100	50	900	×	x	100	10	50	A
war and the same	_			- 6 31 0	0.31	27.90	300	1	¥	5	100	X	500	X	x	7.0	- 5	50	
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			6320	- 6331	0.14	4,16	705	2	x	20	200	73	300	Ÿ	20	100	15		
			6330	- 6 J-P	0.23	1.35	250	1	X	10	100		200	Ŷ	٧.	30	13	- 0-	
			6340	- p35 f		2.13	×	1	. X	10	106	¥	300	ŷ	Ç	70	7		
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a title to a superior	* 5780 - 5790	X 10030	150	X 75		300	0.30	💸		X	100	50	<u> </u>	<u>X</u> -	100	-,-
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العباد والمراز الفيد يكن العامله لعالمك بعدد يعالم المتعاجم	5818 - 582C	<u>x 3000</u>	100	X_ 5.0	. , _ X	100	0.20	K	X	×	100	15	x	x	100	
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	5860 - 589C	× 3000	100	X 50	X	106	0.40	X	X	X	60 50	2.0 25	X	<u> ¥</u>	7 <u>1</u>	-
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	6100 - 6110	X 3000	150	X 30	×	100	0.30	×	X	X	100	30	X	X	30	4.1
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MUNKARIE NO.1

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		- 6250	X	10000	100	x	73	x	200	0.30	X	x	<u> </u>	70	40			50
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	6280	- 6290	X_	10000	150	X	. 5 u	. X	2.0 C	0.30	X	×	x	70	30	Ŷ	Ŷ	60
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	6313	- 6320	×	10000	150	X	5.0	X	500	0.30	X	X	Y	100	20	D	Ç-	70
	6320	- 6336	X_	10000	200	X	76	X	560	0.30	X	¥	. ¥	100	30	Ŷ	Ç	
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MUNKARIE NO.1

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