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THE GEOCHEMISTRY OF BLACK SHALES
FROM THE CHUNIESPOORT GROUP,
TRANSVAAL SEQUENCE,
EASTERN TRANSVAAL, SOUTH AFRICA

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by

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July, 1993

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ABSTRACT

Geochemical and mineralogical data have been obtained from black carbonaceous shales interbedded with dolomite in the Chuniespoort Group of the late Archaean-early Proterozoic Transvaal Sequence. The black shales are fine-grained, generally argillaceous and contain on average 1.2 % total organic C, 0.7% S, 7.5 ppb Au, 60 ppm Cu, 330 ppm Cr and 125 ppm Ni. These metal concentrations are similar to or slightly higher than the values given for the USGS black shale standard SDO-1. All other heavy and transition metals, however, are depleted in the Chuniespoort shales relative to SDO-1. It is well known that high concentrations of Cr and Ni occur in Archaean shales. The enhanced Cr and Ni values found in the Chuniespoort shales is a reflection of their antiquity and their provenance, and are not linked to preferential uptake of these metals during sedimentation and/or diagenesis. The Chuniespoort shales are characterized by excess Fe with respect to pyrite formation and extremely variable C/S ratios. This, together with the wide ranging S-isotope ratios, is taken as an indication that biogenically produced sulphide was augmented by sulphide introduced from an extraneous source. Whole rock S-isotopes further indicate that S could have been derived from both biogenic and inorganic reduction of sulphate as well as possibly from hydrothermal fluids. Inter-element correlations suggest that organic carbon does not play a role in hosting significant concentrations of base and transition metals. Element associations rather indicate that V and Cr are preferentially contained in illite/hydromuscovite while Ni, Co, Zn, Cu, Fe, Pb and Mo probably occur in pyrite and/or chalcopyrite. Gold is only weakly correlated with other elements which may indicate that its distribution is not solely controlled by sulphide minerals. The fact that Au, Cu and S/C ratios show a tendency to be enriched in samples with $\delta^{34}S$ ratios around 0‰, suggests that these elements are likely to have an epigenetic hydrothermal origin. The limited syngenetic metal accumulation can be explained by the stable cratonic environment in which the sediments were deposited and the absence of submarine hydrothermal springs venting metalliferous fluids into the basin. Other factors, such as the low metal potential of the provenance, the rate of sedimentation and the degree of oxygenation of the bottom-waters of the basin, may have been additional factors limiting the concentration in and extraction of metals from seawater. The fact that the Chuniespoort shales host significant epigenetic gold occurrences is, inter alia related to their chemical characteristics, which promoted permeability and high absorption capacities for metals in hydrothermal fluids. Because of their low metal concentrations they cannot, however, be considered the source rocks for the Pilgrim's Rest gold mineralization.

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THE GEOCHEMISTRY OF BLACK SHALES FROM THE CHUNIESPOORT GROUP, TRANSVAAL SEQUENCE, EASTERN TRANSVAAL, SOUTH AFRICA

CONTENTS

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THE GEOCHEMISTRY OF BLACK SHALES FROM THE CHUNIESPOORT GROUP, TRANSVAAL SEQUENCE, EASTERN TRANSVAAL, SOUTH AFRICA

INTRODUCTION

Many major gold deposits worldwide are associated with black shales, among them the Getchell Trend deposits in Nevada, Bendigo-Ballarat in Australia, several deposits in the C.I.S. and eastern Europe, and the Sabie-Pilgrim's Rest Goldfield in South Africa. These deposits invariably have an epigenetic character and in the Sabie-Pilgrim's Rest Goldfield, for example, there exist clearly defined chemical and structural controls on the localization of mineralization within carbonaceous shale beds (e.g. Harley and Charlesworth, 1993; Tyler, 1989; Meyer et al., 1986). On the other hand, significant accumulations of base and transition metals in black shales can also be explained by processes active at their time of deposition. Many black shale units of Lower Palaeozoic and Mesozoic age stand out as being particularly metalliferous and this can be linked to the cycling of biogeochemical elements such as C, N, P and S as well as of transition and heavy metals, most notably Cu, Ni, Zn, V, Mo, Pb, and U. Although metalliferous black shales represent potential mineral and energy resources, most of them are not ores, but they are important for the understanding of processes of metal enrichment in sedimentary rocks. Goodfellow (1990) discussed a number of possible processes responsible for metal enrichment in black shales and these include:

(1) episodic venting of metalliferous hydrothermal fluids;
(2) accelerated accumulation of metals by organic matter during times of rapid organic sedimentation;
(3) metal precipitation at the interface between an oxidized and reduced water column;
(4) turn-over of an anoxic water column with the migration of reduced waters on to adjacent platforms and the formation of metalliferous layers;
(5) the trapping of metals by diagenetic H_2S generated in organic-rich units and;
(6) the preservation of Ni-PGE-rich ejecta from major meteoritic impact events.

The discharge of hydrothermal fluids in rift-related basins is regarded as the most important process of syngenetic metal-enrichment (Goodfellow, 1990). Many metal-rich black shales, however, were deposited on stable continental platforms far from active margins and with no associated volcanic/hydrothermal activity (Schultz, 1991). In this setting metal accumulation was probably controlled by the degree of anoxia and the rate of deposition, with very slow sedimentation favouring extraction of metals from seawater (Schultz, 1991). This paper concerns the mineralogy and geochemistry of black shales from the late Archaean-early Proterozoic Transvaal Sequence. These shales are the main host of epigenetic, stratabound quartz-carbonate-gold-sulphide mineralization in the Sabie-Pilgrim's Rest Goldfield. Thus, the distribution, mineralogical siting and origin of gold and other transition metals in the Transvaal black shales is of particular interest, and relevant to ore-genesis studies.

GEOLOGIC FRAMEWORK

The Transvaal Sequence preserves a record of chemical and terrigenous sedimentation in a stable, intracratonic basin. The original depository probably covered an area of more than 500 000 km^2 on the Kaapvaal Craton and is now preserved in two structural basins, the Griqualand West sub-basin in the northwestern Cape Province and the Transvaal sub-basin in the Transvaal

Province (Figure 1). The Transvaal sub-basin comprises up to 15000 m of relatively undeformed clastic and chemical sediments and volcanics (Figure 2). Basin-infilling commenced in a small
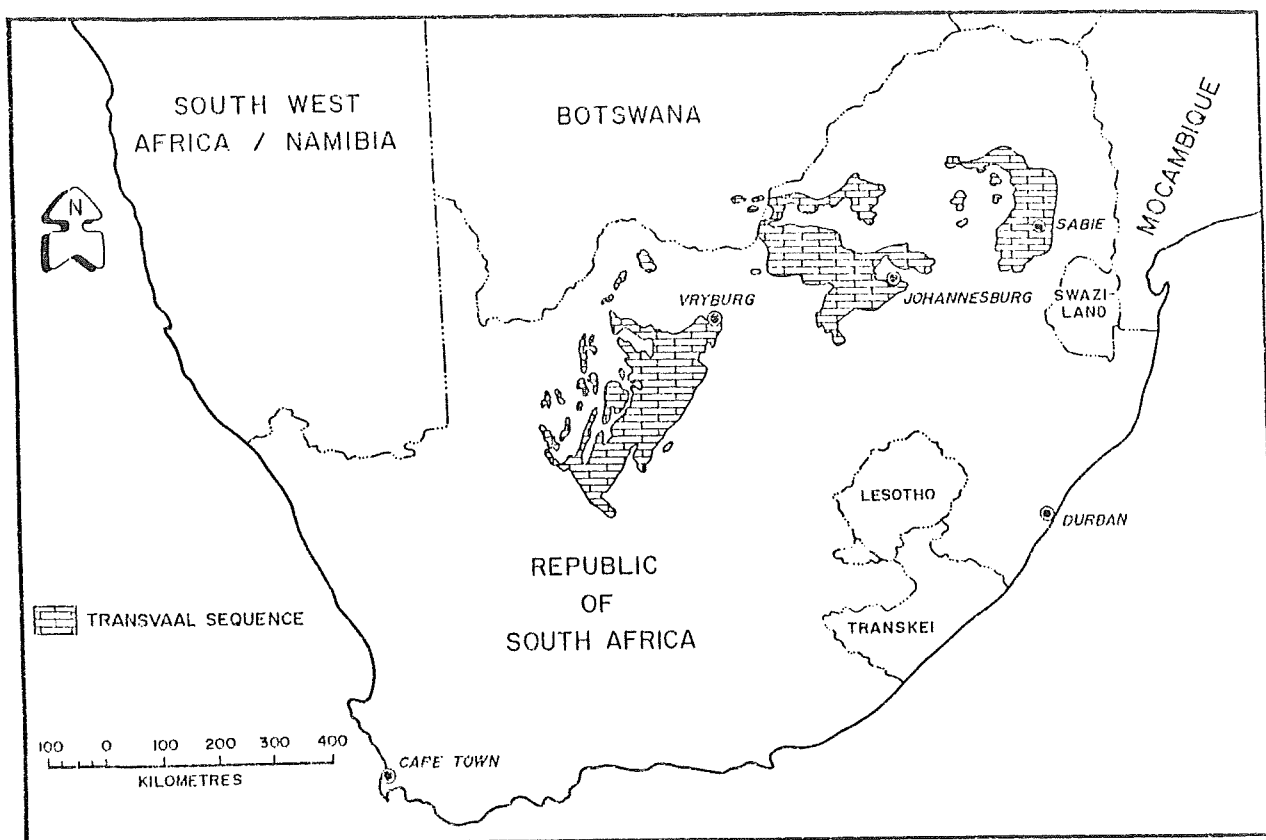

Figure 1: General reference map showing preserved strata of the Transvaal Sequence on the Kaapvaal Craton. The location of the town of Sabie in the eastern Transvaal Province is also indicated.
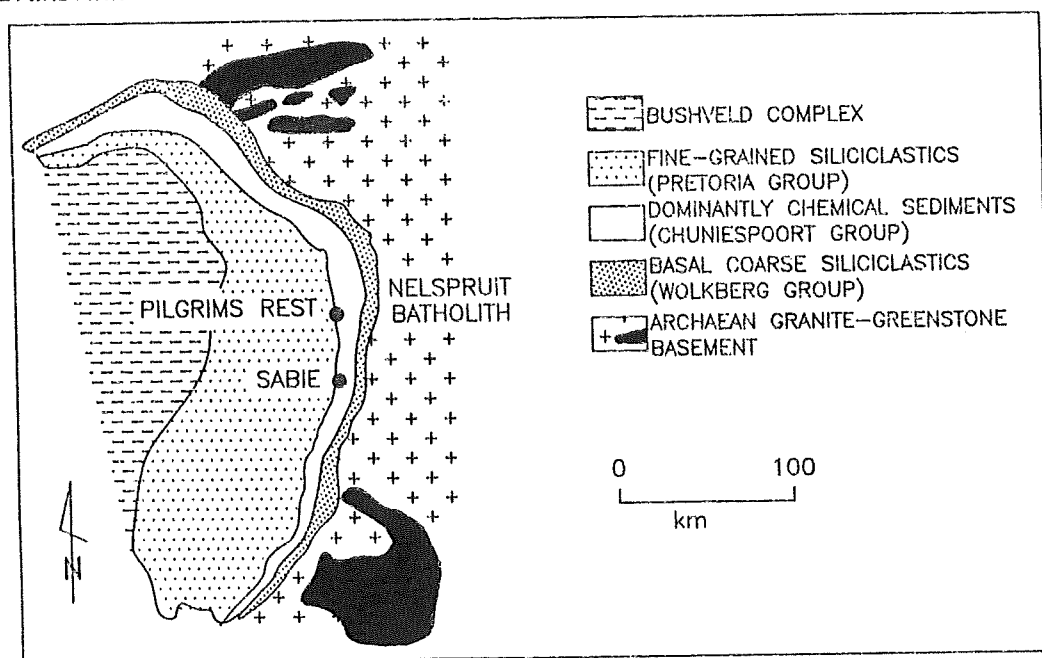

Figure 2: Map showing the generalized geology of the Sabie-Pilgrim's Rest area.

proto-basin with the deposition of predominantly fluvial and deltaic sediments and volcanic rocks of the Wolkberg Group. Continental rifting and periods of reactivated subsidence resulted in the extension and deepening of the basin which also controlled the deposition of the high-energy, fluvial and deltaic conglomerates and sandstones of the Black Reef Quartzite Formation, which are immediately followed by the deposition of the supratidal to shelf-edge carbonates, iron formations and clastics of the overlying Chuniespoort Group (Clendenin et al., 1991). The cyclic shore-zone and shelf clastic sediments and volcanics of the Pretoria Group are separated by a regional unconformity from the underlying Chuniespoort Group. More detailed accounts relating to the depositional history of the Transvaal Sequence are presented by Clendenin (1989), Eriksson et al. (1976) and Button (1973, 1986). Radiometric age constraints for the Transvaal Sequence are discussed by Jahn et al. (1990) who concluded that the Chuniespoort Group is of late Archaean age (2500-2600 Ma) separated by a hiatus of about 300 Ma from the Pretoria Group which is of early Proterozoic age (2000-2230 Ma).

The Transvaal Basin is the repository of a wide range of mineral commodities such as iron, manganese, asbestos, fluorspar, lead and zinc and also constitutes the third largest gold source in South Africa. Economic gold deposits are found throughout the Transvaal Sequence, but they are best developed in the carbonates of the Malmani Subgroup of the Chuniespoort Group (Figure 2). Geographically, the main gold production from the Transvaal Sequence is confined to the eastern basin edge centred on the Sabie-Pilgrim's Rest Goldfield (Figure 3). The principal ore bodies are tabular, stratiform quartz-gold lodes which commonly occur in close association with carbonaceous shales. Cross-cutting veins (vertical reefs) are most abundant in the granitic basement but also intrude into the overlying sediments. The deposits show many characteristics of mesothermal systems and the vein mineralogy comprises pyrite, chalcopyrite, arsenopyrite, tetrahedrite, bismuthinite, gold, quartz and carbonate. More detailed descriptions of the ore deposits have been provided by Boer et al. (1993), Harley and Charlesworth (1993), Anderson et al. (1992), N. Tyler (1986), R. Tyler (1989), Meyer et al. (1986), Zietsman (1967) and Swiegers (1949).

REGIONAL GEOLOGY AND SAMPLING

A total of 87 shale samples, including shales from the Black Reef Quartzite Formation and the Malmani Dolomite Subgroup of the Chuniespoort Group (Figure 2), were selected for analysis from borehole core drilled in the Sabie-Pilgrim's Rest Goldfield (Figure 3). The Black Reef Quartzite Formation (Figure 4), which is approximately 40 m thick and comprises mainly sandstones, with minor conglomerates and shales, can be separated into a lower upward-fining sequence and an upper coarsening-upward sequence. The formation is capped by a transgressive carbonaceous shale horizon marking the transition from predominantly siliciclastic to chemical sedimentation (Clendenin, 1989; Clendenin et al., 1991; Henry et al., 1990). The conformably overlying Malmani Dolomite Subgroup is divided into the Oaktree, Monte Christo, Lyttelton and Eccles Formations and attains a thickness of ca. 1000m in the area. Facies arrangements indicate sedimentation under supratidal to subtidal conditions on a wide, shallow marine platform (Clendenin, 1989; R. Tyler, 1989; Button, 1986; N. Tyler, 1986). Five principal transgressive-regressive cycles of deposition were recognized by R. Tyler (1989), ranging from supratidal siliciclastic tidal flats to subtidal carbonates in the Oaktree, Monte Christo and Eccles Formations and from supratidal carbonates to shelf-edge carbonates in the Lyttleton Formation. The interbedded carbonaceous shales were interpreted as forming part of the regressive components of these cycles
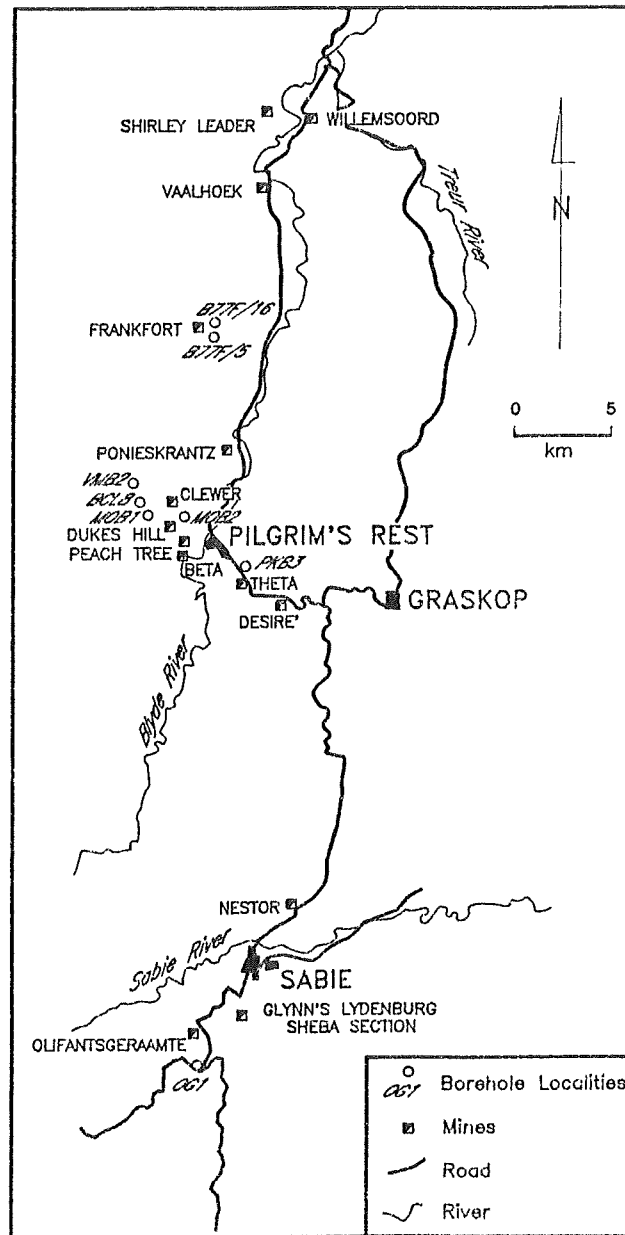
Figure 3: Map of the Sabie-Pilgrim's Rest area showing the location of gold mines as well as boreholes sampled for this study.

by R. Tyler (1989) who further suggested that they were deposited in a shallow-water (lagoonal) environment. Clendenin (1989), recognized three shallowing-upward grandcycles from the Black Reef Quartzite Formation through to the Eccles Formation and related the deposition of the carbonaceous shales to the shallow basinal environment. According to Clendenin (1989) the black shales provide evidence of marine transgressions and record successive drownings of the basin with periodic cessation of carbonate production.
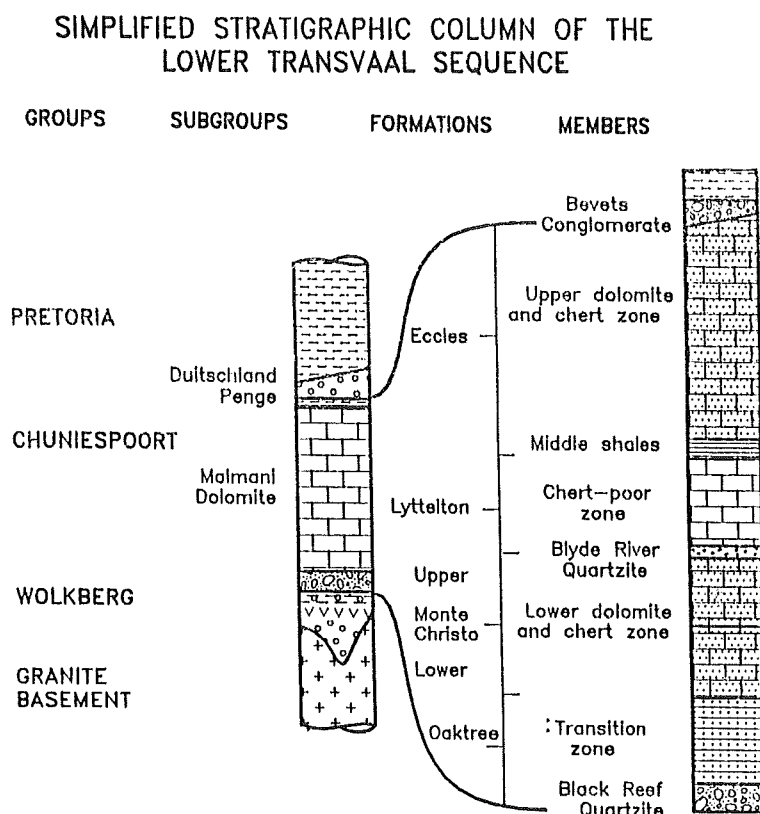
SIMPLIFIED STRATIGRAPHIC COLUMN OF THE
LOWER TRANSVAAL SEQUENCE

Figure 4: *Simplified stratigraphic column of the lower Transvaal Sequence in the Sabie-Pilgrim's Rest area.*

MINERALOGY

The sample suite studied comprises mainly convolute-laminated, dark-grey to black shale, the latter often interstratified with layers of carbonate mudstone. Polished thin sections revealed that most of the samples are also well laminated on a fine scale. Laminations are defined either by differences in composition (i.e. variation in carbonate content) or by thin layers of opaque organic material. In places silt-size and clay-size layers are interlaminated. The silt-size fraction comprises quartz, microcline, very rare plagioclase and chert together with interstitial dolomite and clay minerals. Pyrite is the most abundant sulphide and occurs mainly in the form of discrete isometric crystals. Chalcopyrite was detected in a few samples. Powder X-ray diffraction analysis revealed that illite and hydromuscovite are the principal sheet silicates. Mg-Fe chlorite occurs to a much lesser extent.

GEOCHEMISTRY

Analytical Procedure

Major elements and a number of trace elements were analyzed by X-ray fluorescence using fused glass disks and pressed powder pellets, respectively. Other trace elements such as REE, U,

Th, Hf, Ta, Sc, Ba and Cs were determined by instrumental neutron activation analysis. A dual gamma-counting method was employed by using both planar and coaxial Ge detectors simultaneously. LECO analyzers were used to determine CO_2, total organic carbon (TOC), S and H_2O. Sulphur isotope analyses were performed on whole rock samples using the Cu_2O oxidation method of Coleman and Moore (1987). The isotope ratio of the purified SO_2-gas was measured with a Micromass MM602 dual inlet mass spectrometer. The precision of the method is 0.2 ‰. S-isotope values are reported in δ-notation in per mil units relative to Canyon Diablo troilite (CDT).

Major Elements

Arithmetic and geometric mean values, standard deviations, as well as maximum and minimum values are summarized in Table 1. Many elements show distinct differences between arithmetic and geometric mean values which is an indication of the non-normal distribution of the data. The high variations in element contents reflect variable degrees of carbonate and quartz dilution. SiO_2, for example, varies between 10 and 81 % and CO_2 ranges from less than 1 to more than 36 %. Arithmetic mean SiO_2, TiO_2, Fe_2O_3 and P_2O_5 contents of the Chuniespoort shales are comparable with those of the USGS black shale standard SDO-1 (Figure 5a). MnO and Na_2O, however, are markedly depleted in the Chuniespoort samples while the MgO, CaO, K_2O and CO_2 contents are significantly enriched relative to SDO-1. High CaO, MgO and CO_2 is indicative of the presence of carbonate mineral phases while K_2O reflects the abundance of microcline in some of the silt-size layers.

Table 1: Average chemical composition of black shales of the Chuniespoort Group

N = 87	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	CO_2	LOI
X	60.43	0.57	14.69	3.15	0.08	3.86	2.49	0.05	7.07	0.10	3.34	7.34
G	58.90	0.51	13.82	2.38	0.04	3.11	0.47	0.03	6.18	0.07	0.53	5.64
STD	10.9	0.30	4.3	3.1	0.10	2.90	4.60	0.05	2.70	0.10	6.70	6.70
MAX	81.57	2.26	27.08	23.99	0.76	17.65	24.39	0.31	11.58	0.67	36.64	38.31
MIN	10.01	0.06	2.05	0.69	0.01	0.38	0.01	0.01	0.30	0.01	0.01	1.90

	Sc	Cr	Co	Ni	Y	Zr	Nb	Hf	Ta	Th	U
X	13	328	17	125	18	123	10	3.0	0.8	7.5	2.1
G	12	290	13	110	15	110	9	2.7	0.8	6.6	1.8
STD	5.0	140	12	72	12	73	5.2	1.3	0.2	3.8	1.3
MAX	34	617	65	417	64	568	36	7.6	1.6	25	9.3
MIN	0.8	22	3	21	2	9	1	0.2	0.1	0.8	0.2

	Sr	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
X	22	166	9.5	726	26.0	56.6	26.1	4.50	0.88	0.49	1.63	0.24
G	19	150	7.7	430	22.8	50.1	23.4	3.77	0.72	0.42	1.43	0.24
STD	15	56	6.0	1100	11.9	25.2	11.2	3.90	0.54	0.30	0.87	0.12
MAX	93	281	27	5753	63.5	141	60.3	35.0	2.63	1.51	4.50	0.65
MIN	8	12	0.5	28	1.55	3.48	2.00	0.30	0.01	0.06	0.10	0.01

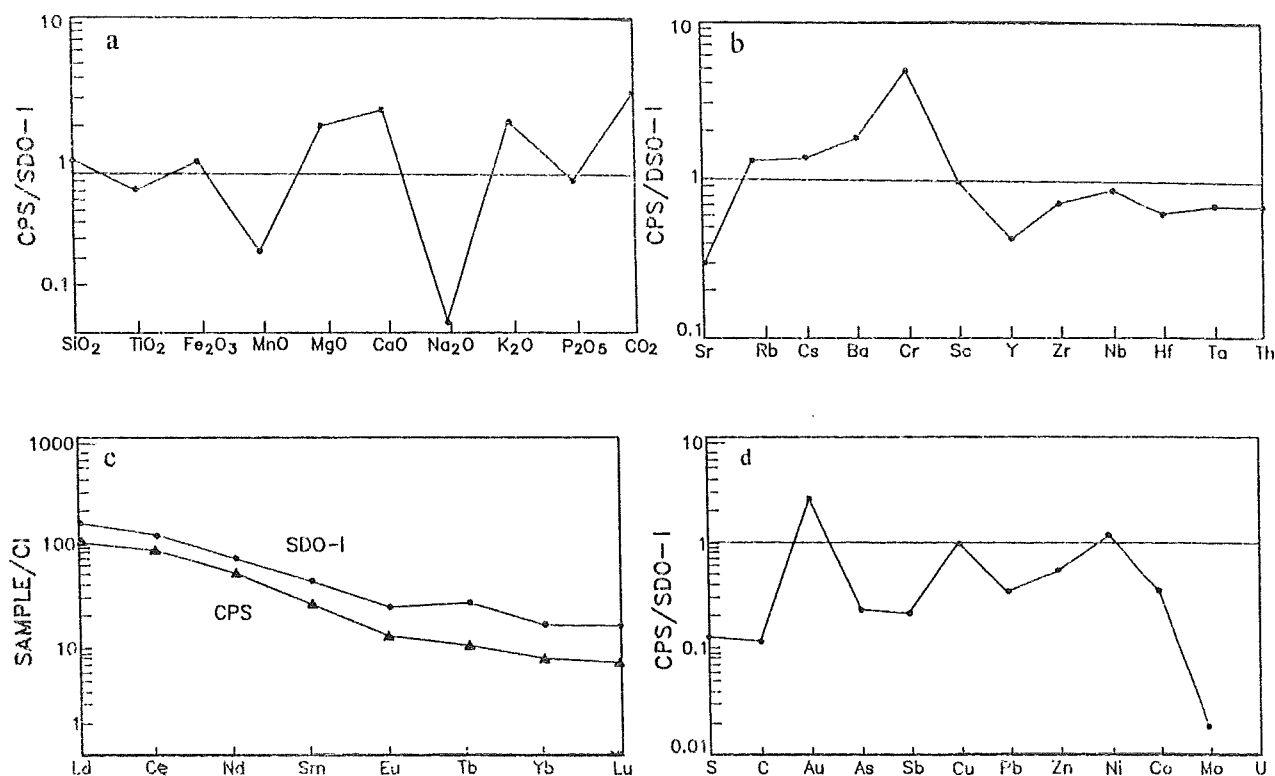|	S %	C %	As	Sb	Au ppb	Cu	Pb	Zn	Mo	V
X	0.70	1.20	15.8	1.0	7.5	61	10	36	3	105
G	0.20	0.75	3.65	0.65	3.2	24	5.5	22	2.5	96
STD	1.5	1.4	45	1.5	14	96	16	40	4	45
MAX	10.9	9.1	304	12	122	633	87	155	23	319
MIN	0.01	0.05	0.2	0.1	0.2	3	2	2	2	13

Figure 5: Plot of USGS SDO-1 normalized distributions of major and trace elements in Chuniespoort shales (CPS) (4 a,b,d) as well as chondrite normalized REE distributions in SDO-1 and CPS (4c).

Trace Elements

Trace element distributions are also controlled by shale mineralogy and mirror the trend indicated by the major elements. The alkalies and alkaline earths Rb, Cs and Ba are enriched in the Chuniespoort shales relative to SDO-1, but, Sr is significantly depleted (Figure 5b). The high field strength elements (Y, Zr, Nb, Hf, Ta) as well as Th and Sc have concentrations equal to or slightly less than SDO-1. It is well known that Archaean shales are significantly enriched in Cr (Taylor and McLennan, 1985) and it is obvious from Figure 5b that the Chuniespoort shales possess Cr abundances more than 5 times higher than SDO-1. Absolute concentrations of REE are consistently higher in SDO-1, the La/Yb ratio is higher in the Chuniespoort shales and both chondrite-normalized patterns show only minor negative Eu anomalies (Figure 5c). The abundance, relative to SDO-1, of a number of chalcophile elements and transition metals is shown in Figure 5d. The only element enriched in the Chuniespoort shales is Au, while Cu and Ni have concentrations similar to SDO-1. All other elements, particularly Mo and U, clearly have lower abundances in the Chuniespoort shales. Archaean shales, generally, are significantly enriched in Ni relative to younger shales (Taylor and McLennan, 1985). Thus, the relatively high abundance of Ni in the Chuniespoort samples probably reflects the high proportion of greenstone material in the provenance. The distribution of Au values is distinctly positively skewed (Figure 6). The arithmetic mean value is 7.5 ppb, almost 3 times higher than the Au content of SDO-1 (i.e. 2.8 ppb). However, more than 50% of the Au values are below 3 ppb, and the geometric mean value,
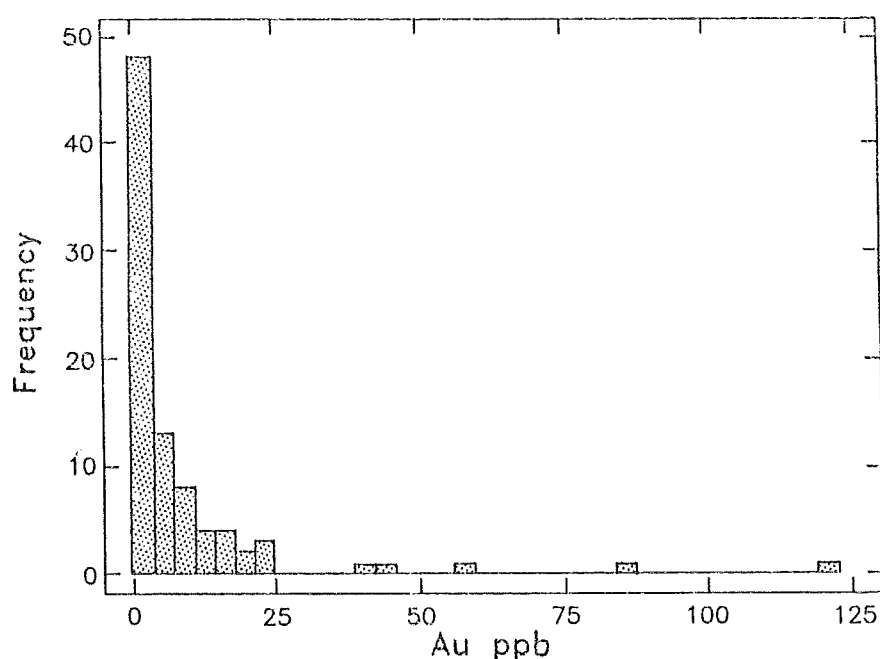
Figure 6: Frequency histogram of Au values.

which in this case must be regarded as the best measure of central tendency, is 3.2 ppb. If this value reflects the average Au content then the Chuniespoort shales are not abnormally enriched relative to SDO-1. The Cu values also follow a positively skewed distribution with an arithmetic mean value of 61 ppm and a much lower geometric mean of 24 ppm. It appears, therefore, that Cu is also depleted in the Chuniespoort shales compared to SDO-1.

Sulphur Isotopes

Sulphur isotope analyses were performed on 9 whole rock samples (Table 2). The isotopic ratios vary between -23.4 and +3.53‰. Seven of the nine samples have ratios between -3.35 and 3.53‰ while two samples are strongly depleted in $\delta^{34}S$ with values of -12.3 and -23.4‰. Cameron (1982) also reported a wide, though somewhat smaller $\delta^{34}S$ range, from ca -10 to 0 ‰ for shales

Table 2: Sulphur isotope ratios and metal contents of selected shale samples

SAMPLE	$\delta^{34}S$‰	S/C	Au ppb	Cu %	S %	As ppm	Sb ppm
7F/36	-23.4	0.7	0.6	7.0	0.85	2.8	0.3
7F5/37	-12.3	0.7	0.4	8.0	0.90	4.7	0.3
PKB3/586	-3.35	1.8	2.1	8.0	1.75	6.0	0.5
7F5/162	-2.72	9.5	19.3	85	2.85	78	3.5
PKB3/121	-2.48	1.7	5.0	80	2.45	12.5	1.7
PKB3/279	-0.65	1.8	0.7	55	2.95	22.1	0.8
PKB3/749	-0.34	5.3	15.4	75	1.91	17.6	1.51
B77F/16	+0.78	4.3	5.9	65	3.42	12.2	1.60
BCL8/19	+3.53	8.5	12.8	220	10.8	305	12.0

from the Chuniespoort Group. The $\delta^{34}S$ ratios in hypogene pyrite from the Sabie-Pilgrim's Rest gold deposits vary between -3.16 and +4.13‰ (Meyer et al., 1990).

DISCUSSION

Total Organic Carbon (TOC) and Total Sulphur (TS)

According to Huyck (1991) a black shale is defined as a dark-coloured, fine-grained, laminated sedimentary rock that is generally argillaceous and contains >0.5 % carbon. The distribution of TOC values shown in Figure 7 demonstrates that almost 70% of the Chuniespoort samples analyzed have TOC in excess of 0.5 %. The arithmetic and geometric mean values are 1.2 and 0.75 %, respectively. Limited analyses (Clay, 1981) indicated that the organic carbon consists of approximately 88 % n-alkane homologs in the range $n\text{-}C_{12}$ to $n\text{-}C_{25}$, which is typical of modern marine organisms (Clark and Blumer, 1967). The relationship between TOC and pyrite sulphur in marine shales has recently been discussed by Whittaker and Kyser (1990), Raiswell and Al-Biatty (1989) and Raiswell and Berner (1986). In anoxic marine sediments pyrite is formed by the reaction of iron with H_2S produced by sulphate-reducing bacteria, while in modern normal marine sediments overlain by oxygenated water, the amount of bacterially metabolizable organic matter is the main controlling factor in pyrite formation (Berner, 1984). However, low Fe contents can also be a limiting factor in the formation of pyrite (Gibson, 1985). Generally, there is a good positive correlation between TOC and pyrite sulphur in normal marine shales and total sulphur (TS) is essentially equal to pyrite sulphur (Raiswell and Berner, 1986). The ratio of TS over TOC (S/C ratio) is around 0.4 for modern normal marine sediments, and this reflects the process stoichiometry of bacterial sulphate reduction and concomitant pyrite formation if Fe is not a limiting factor (Dean and Arthur, 1989). Raiswell and Berner (1986) suggested that early Proterozoic normal marine sediments typically have a mean S/C ratio of 2 while Donnelly et al. (1987) reported a value of 0.65 for Cambrian sediments. High S/C ratios (i.e. > 1) are known from euxinic marine environments and from black shales where sulphides were deposited from hydrothermal fluids or where organic C was lost relative to S during burial. The Chuniespoort samples cover a large range in TS values from 0.01 to 10.9 %. The arithmetic mean is 0.70 and the geometric mean is 0.20 %. Total sulphur and TOC are moderately well correlated (R=0.72) if the one aberrant point in Figure 8 is excluded. Raiswell and Berner (1986) recommended two parameters, namely the slope of the regression curve in a TOC versus TS scatterplot and the ratio of the mean TS to TOC, as the preferred measures of central tendency for S/C ratios. The slope of the best fit line in Figure 8 is 0.51 and the ratio of the mean values is 0.58. The Chuniespoort shales, therefore, have a mean S/C value somewhere in between that of Cambrian and modern marine sediments. Individual S/C values, are extremely variable, however, with the data ranging over 4 orders of magnitude from 0.003 to 5.
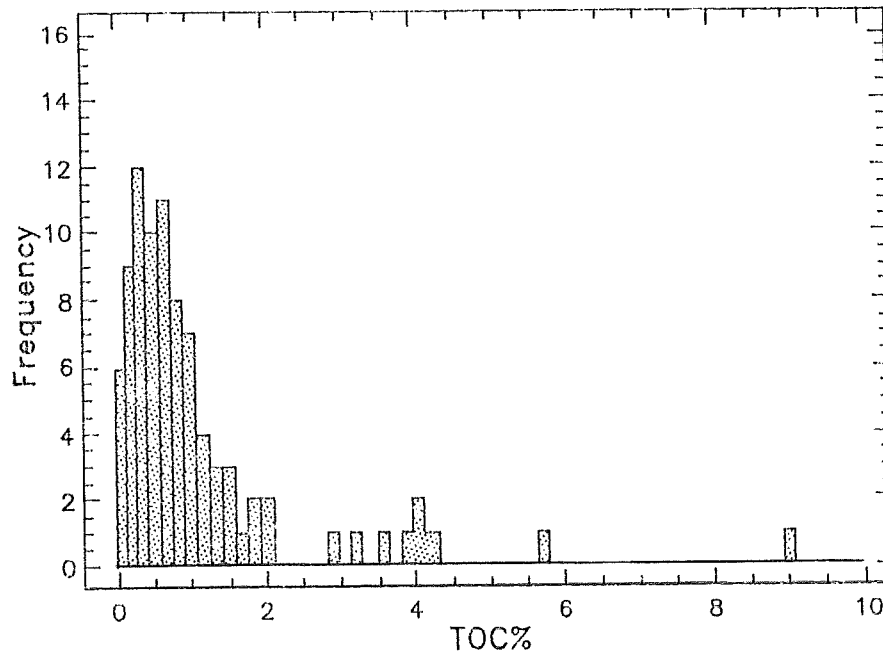
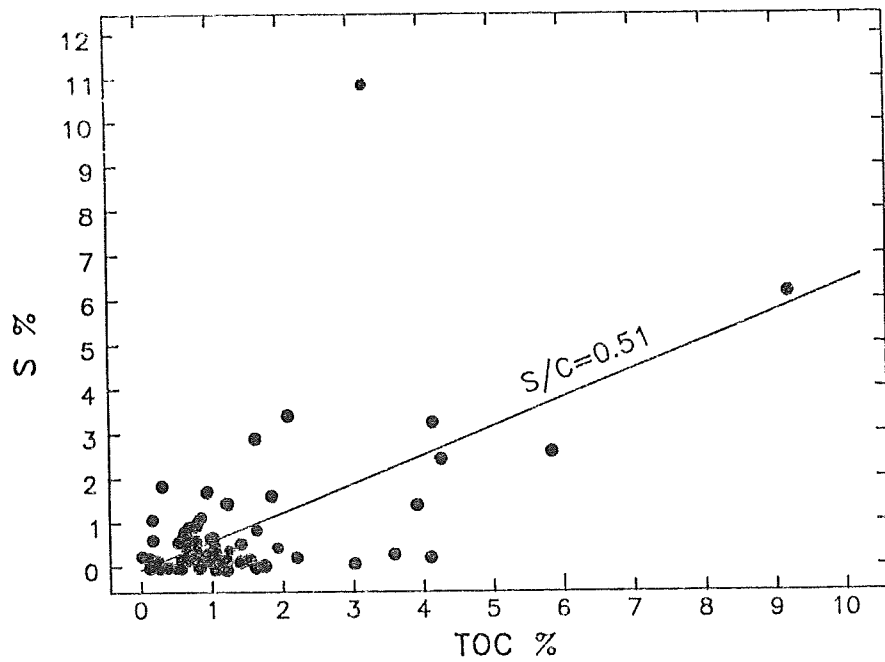*Figure 7: Frequency histogram of total organic carbon (TOC) values.*

Figure 8: Plot of total organic carbon (TOC) versus S. The solid line indicates an average S/C ratio of 0.51.
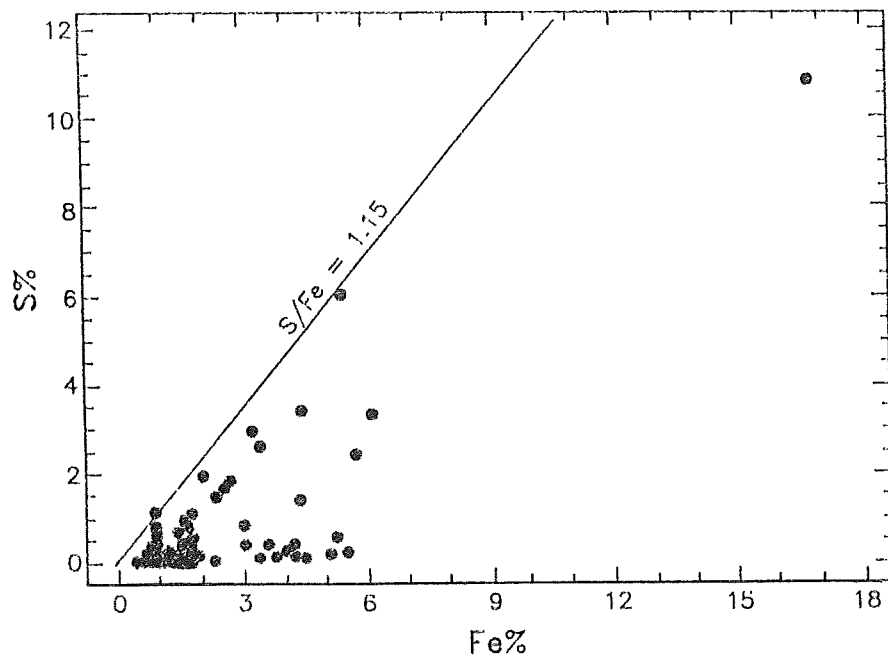
Figure 9: Plot of Fe versus S. The solid line represents the stoichiometric pyrite line with a S/Fe ratio of 1.15.
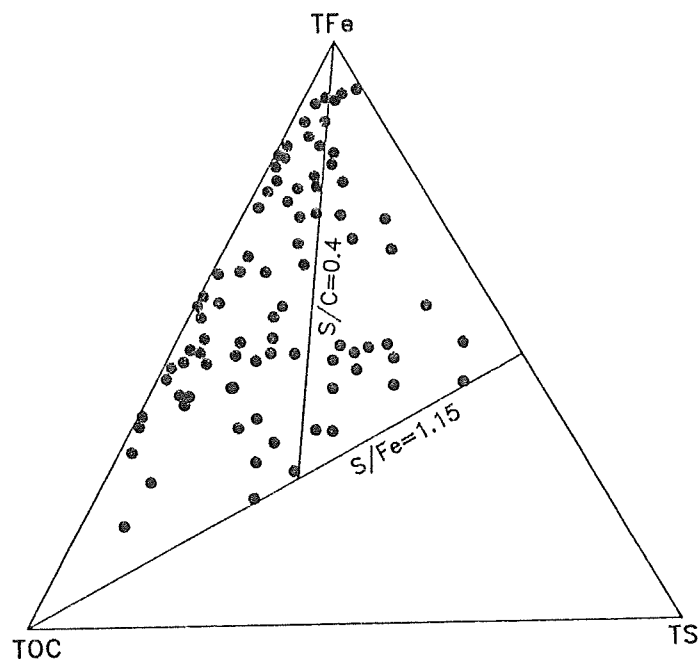

Figure 10: Triangular diagram of total iron (TFe), total organic carbon (TOC) and total sulphur (TS).

The other parameter which controls biogenic pyrite formation is iron. The relationship between total Fe (TFe) and TS is shown in Figure 9. The plot clearly demonstrates that the TFe content of the Chuniespoort shales is in excess of that bound in pyrite, as almost all the data plots well below the line. Also, if pyrite formation was Fe-limited a significant correlation should exist between S and Fe. A summary of the S-C-Fe relationship is provided in a ternary diagram (Figure 10), a detailed discussion of the systematics of which is given by Dean and Arthur (1989). The data in Figure 10 indicate excess Fe with respect to pyrite formation and a wide scatter of S/C ratios. Data that plot to the left of the line of constant S/C ratios and close to the TFe-TOC axis suggest that pyrite formation was limited by the availability of metabolizable organic C. Those data that plot to the right of the constant C/S line and close to the TFe-TS axis either indicate that almost all of the original organic matter was reactive and variably utilized, or that S was added to the system from an extraneous source. Raiswell et al. (1988) defined the DOP parameter (degree of pyritization of iron = $Fe_{pyrite}/Fe_{pyrite} + Fe_{HCl-soluble}$) as a palaeoenvironmental indicator of bottom-water oxygenation. Since the present samples were not analyzed for HCl-soluble iron only the ratio of Fe_{pyrite}/Fe_{total} could be calculated. This ratio assumes that all iron is HCl-soluble and reflects, therefore, minimum DOP values. More than 80 % of the values thus calculated are below 0.45, which would suggest aerobic bottom-water conditions according to Raiswell et al. (1988). However, S-isotope systematics point to the prevalence of anoxic conditions.

Controls on Metal Distributions

Black shales are known to concentrate a wide variety of metals and are termed metalliferous black shales if they are enriched in any given metal by a factor of 2 relative to SDO-1 (with the exception of Be, Co, Mo, and U for which concentrations equal to SDO-1 are sufficient, Huyck, 1991). According to this definition the Chuniespoort shales cannot be classified as metalliferous (Figure 5 a,b,c,d). The preferential association of many metals such as Fe, Cu, Zn, Cr, Ni, Mo, U and V with metabolizable organic matter is related to the production of H_2S by sulphate reducing bacteria. Hydrogen sulphide reacts with certain elements to form sulphides, or reduces others to less soluble species (Desborough et al., 1991). The present data do not, however, show any significant correlation between TOC and transition metals or high field strength elements (HFSE). Vanadium is highly correlated with TiO_2 (Figure 11, R = 0.90), and moderately correlated with Al_2O_3 (R = 0.67) and K (R = 0.61). This element association suggests that V is hosted in mica and not in organic carbon. Coveney et al. (1987) reported a similar vanadium-illite association for black shales from the Middle Pennsylvanian Mecca Quary Shale Member. The fact that a moderate correlation exists between Cr and Al_2O_3 (Figure 12, R = 0.75) and K_2O (R = 0.56) suggests that Cr is also concentrated in mica. Uranium is correlated with Th (R = 0.82), while Th and La are moderately correlated (R = 0.63) supporting the findings of McLennan et al. (1980) that these elements show similar geochemical behaviour during weathering and erosion. The majority of the base and transition metals (i.e. Ni, Co, Zn, Cu, Fe, Pb, Mo) analyzed for this study are correlated with S, As and Sb, which are themselves inter-correlated. The correlation coefficient between Cu and As is 0.90 for samples with Cu concentrations in excess of 100 ppm (Figure 13) while Cu-S and Cu-Sb correlations are 0.70 and 0.68, respectively. The lack of correlation between Au and all other elements investigated suggests that no single mineral controls Au distribution. The highest correlation coefficient (R = 0.60) was found between Au and As but the scatterplot (Figure 14) clearly indicates very little systematic variation between the two variables.
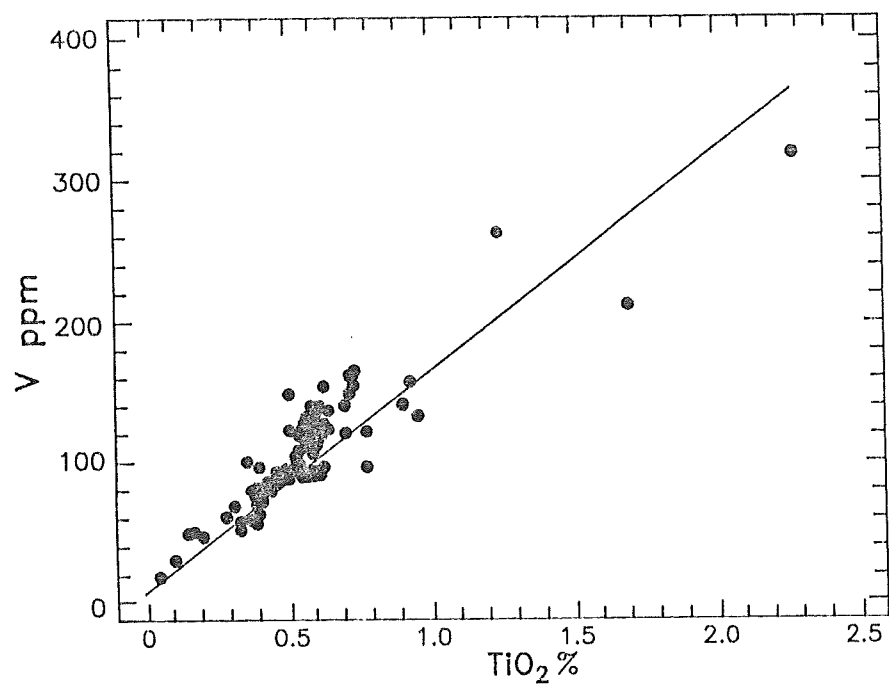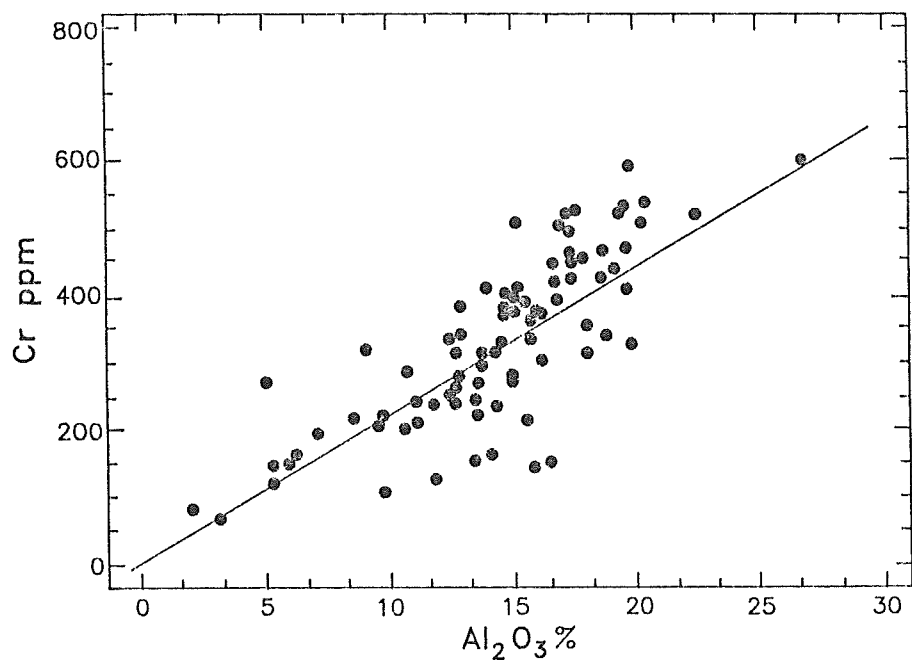
Figure 11: Plot of TiO$_2$ versus V.
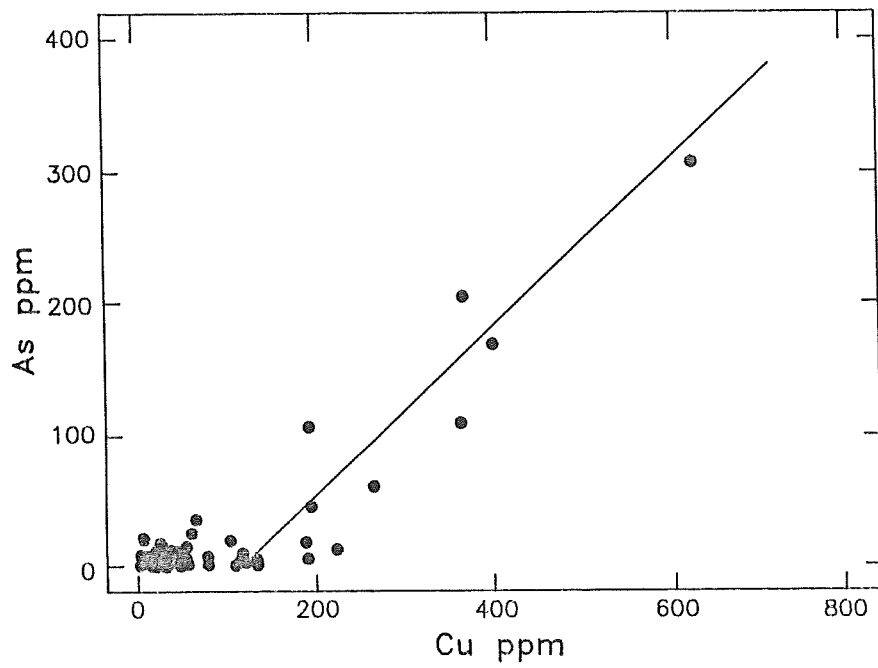

Figure 12: Plot of Al$_2$O$_3$.

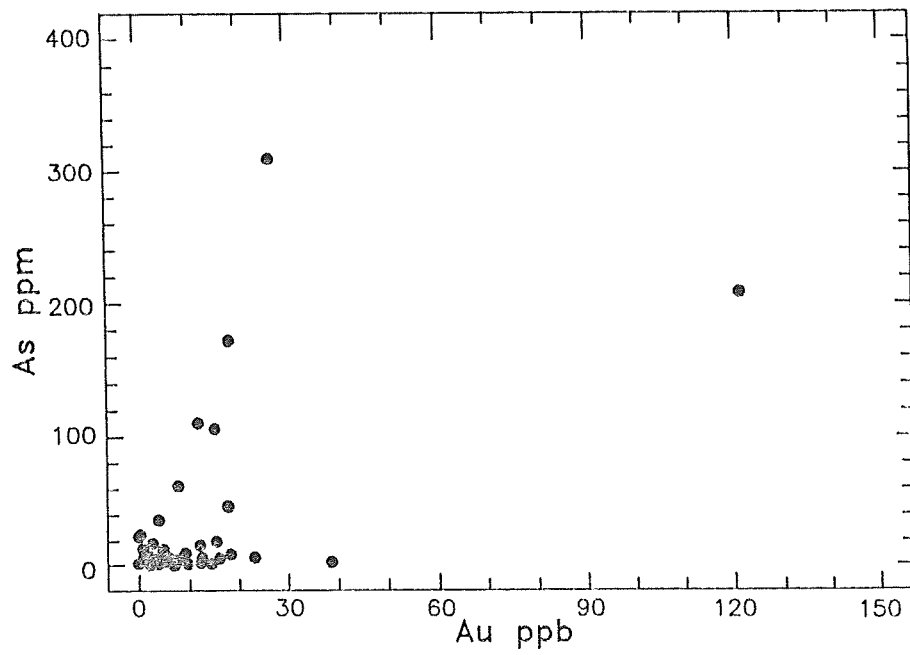*Figure 13: Plot of Cu versus As*

Figure 14: Plot of Au versus As.

Sulphur Isotopes

Cameron (1982) identified a S-isotopic excursion in the transition zone at the base of the Chuniespoort Group. This was interpreted as marking an increase in sulphate concentration in seawater to a level sufficient for biogenic and inorganic reduction to cause significant isotopic fractionation. Below this isotopic transition zone, in the lowermost part of the Oaktree Formation, $\delta^{34}S$ values are close to 0‰, reflecting a magmatic source of sulphur. Above the isotopic transition the $\delta^{34}S$ values are significantly negative and whole rock values of -30.6‰ occur in the Pretoria Group shales. Cameron (1982) suggested that the sulphides in the Chuniespoort Group above the isotopic transition were derived from two sources, one related to the biogenic and inorganic reduction of sulphate, and the other to a hydrothermal source. The distinctly negative values in the Pretoria Group shales were considered to reflect chiefly biogenic processes. Hence, two of the three possible sources of sulphur in the Chuniespoort shales are independent of the presence of metabolizable organic carbon and this may explain the large range in S/C ratios observed in the present sample set (Figure 10). In this study S-isotope ratios were determined in shales collected stratigraphically above the isotopic transition zone. The ratios vary from -23.4 to +3.53‰ with the majority of the data falling in the range from -3.35 to +3.53‰ (Table 2). Hypogene pyrites from the Sabie-Pilgrim's Rest gold deposits occupy the same range in $\delta^{34}S$ values (Meyer et al., 1990). Scatter diagrams of $\delta^{34}S$ versus S/C, Cu and Au are shown in Figure 15 a,b,c. The plots indicate that the samples with $\delta^{34}S$ values close to 0‰ have higher C/S ratios and higher Cu and Au contents than the two samples characterized by distinctly negative $\delta^{34}S$ values. In keeping with Cameron's (1982) interpretation the sulphide in the samples containing the light S-isotope ratios is considered to have been derived by biogenic reduction of sulphate. The samples with $\delta^{34}S$ ratios around 0‰, however, acquired additional S, Cu and Au, most probably from hydrothermal fluids which were also responsible for the Sabie-Pilgrim's Rest gold mineralization. The assumed hydrothermal contamination of some of the Chuniespoort samples suggests that the uptake of Au by the shales during sedimentation was negligible. The mean Au content of the uncontaminated samples is probably around 1 ppb, a value very similar to the mean Au content of the Archaean granitic basement in the eastern Transvaal (e.g. Saager and Meyer, 1982).

SUMMARY AND CONCLUSIONS

Black carbonaceous shales are mainly interbedded with dolomite in the Chuniespoort Group of the late Archaean-early Proterozoic Transvaal Sequence. The sediments were deposited on a wide, shallow marine platform with the carbonaceous shales accumulating in the shallow basinal depositional environment during marine transgressions (Clendenin, 1989). The Chuniespoort shales are fine-grained, generally argillaceous and contain on average 1.2 % carbon and can, therefore, be classified as black shales according to the criteria proposed by Huyck (1991). Comparison of mean metal concentrations with the USGS black shale standard (SDO-1) shows, however, that with the exception of Cr, Ni, Cu and Au all other metals are depleted in the Chuniespoort shales. The enrichment of Cr and Ni in the Chuniespoort shales is a reflection of their antiquity and is not linked to preferential cycling of these metals. Gold and Cu distributions are strongly positively skewed with geometric mean values being ca 2.5 times lower than corresponding arithmetic means. If the geometric mean values are considered as the better measure of central tendencies, it is apparent that the mean Au content of the Chuniespoort shales is similar to that of SDO-1, while Cu is depleted by a factor of two. Accordingly, the Chuniespoort shales cannot be regarded as metalliferous.
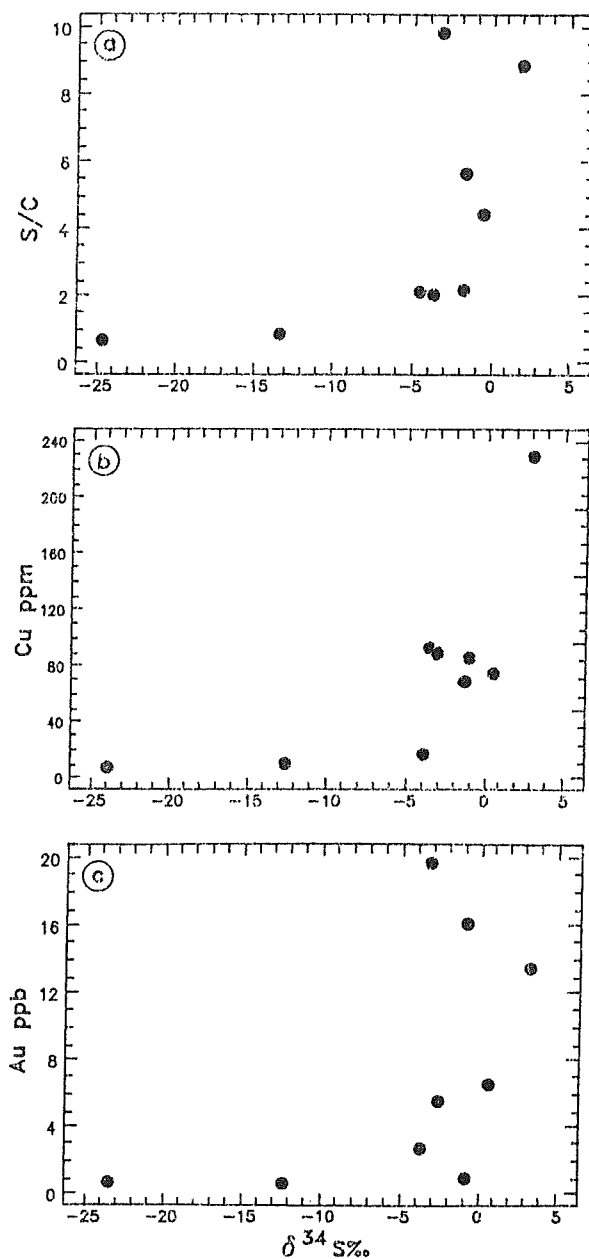
Figure 15: Plot of $\delta^{34}S$ versus S/C (a), Cu (b) and Au (c).

Normal marine shales show systematic relationships between total S (TS), total organic C (TOC) and total Fe (TFe). The Chuniespoort shales are characterized by excess Fe with respect to pyrite formation and extremely variable C/S ratios. This suggests that not all the S was of biogenic origin, but that S was also added to the system from an extraneous source. Whole-rock S-isotopes confirm this suggestion and indicate that S could have been derived from both biogenic and inorganic reduction of sulphate, as well as from input by hydrothermal fluids.

Inter-element correlations provide information about probable element residence in minerals and/or organic matter. The fact that no significant correlations exist between TOC and base and

transition metals suggests that organic carbon is not a major host for these elements. Element associations rather indicate that V and Cr are preferentially housed in illite/hydromuscovite while Ni, Co, Zn, Cu, Fe, Pb and Mo are correlated with S, As and Sb and, thus, are probably contained in pyrite and/or chalcopyrite. Gold is only weakly associated with S, As and Sb which indicates that its distribution is not solely controlled by sulphide minerals.

Gold, Cu and S/C show a tendency to be enriched in samples with $\delta^{34}S$ ratios around 0‰. Because hypogene pyrites from the Sabie-Pilgrim's Rest gold deposits also have S-isotope ratios around 0, it must be concluded that Au, Cu and S (as well as As and Sb) are, to a certain extent, also of epigenetic hydrothermal origin. Consequently, it follows that there was only limited sedimentary and/or diagenetic accumulation of metals in the Chuniespoort shales. Goodfellow (1990) suggested that venting of hydrothermal fluids is the most important process responsible for metal enrichment in black shales deposited in rift-related basins. However, in metalliferous shales which occur in cratonic basins, the most important control on metal accumulation is probably the degree of oxygenation of the bottom waters. Rate of deposition may be a contributing factor since very slow sedimentation favours the extraction of metals from seawater (Schultz, 1991). The Chuniespoort shales were deposited in an epeiric sea, on a stable continental platform where chemical and terrigenous sedimentation was largely uninterrupted by igneous and/or hydrothermal activity. Clendenin (1989) suggested that the 'Pilgrim's Rest Line' (Figure 1) episodically acted as the eastern margin of the Transvaal basin when sediments were supplied from an easterly provenance now underlain by the Archaean Nelspruit Batholith, as well as small greenstone remnants (Figure 2). Saager and Meyer (1982), who studied the distribution of gold in samples from the Barberton granite-greenstone terrane, found that granitoids such as the Nelspruit Batholith have a mean Au content of 1 ppb while volcanic rocks from the greenstone assemblage average around 2.4 ppb Au. The fact that no submarine hydrothermal springs were active during Chuniespoort sedimentation and that the provenance area was not enriched in Au or base metals is considered to be the main reason for the non-metalliferous nature of the Chuniespoort black shales. It is considered unlikely that synsedimentary metal accumulation was hampered by aerobic bottom-water conditions.

Bloomstein and Clark (1991) found that certain geochemical features contribute to the suitability of black shales as host rocks for epigenetic gold mineralization. These features include the presence of significant amounts of carbonate (which facilitates decalcification, and, therefore, enhanced permeability), a relatively low (1-5%) organic C content (which enhances permeability by comparison C > 10% which inhibits permeability), and advanced thermal maturation of organic C (which provides a high sorption capacity for precipitating gold from hydrothermal solution). The Chuniespoort shales have high Ca, Mg, and CO_2 and relatively low C contents, and, therefore, satisfy all the geochemical prerequisites for suitable host rocks for epigenetic gold mineralization. However, because of the low metal contents in the shales, their suitablility as source rocks for the adjacent Pilgrim's Rest mineralization is rather limited and Boer et al. (1993) concluded that Au, sulphur and other metals were derived from a magmatic source and not by leaching from the host rocks.

ACKNOWLEDGEMENTS

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