

**ECONOMIC GEOLOGY
RESEARCH UNIT**

University of the Witwatersrand
Johannesburg

**PETROGRAPHIC, CHEMICAL AND SPECTROSCOPIC
STUDIES OF CARBONACEOUS MATTER
IN THE WITWATERSRAND BASIN,
SOUTH AFRICA**

**L.J. ROBB, P. LANDAIS, G.R. DRENNAN
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— • INFORMATION CIRCULAR No. 312

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SOUTH AFRICA**

by

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ABSTRACT

Although the nature and origin of carbonaceous matter in the Witwatersrand Basin has long been contentious, there is now agreement that it represents the solidified or bituminous residue of a liquid hydrocarbon phase that circulated along suitable pathways during burial and thermal maturation of the basin. Petrographic studies suggest that most of the bitumen formed in response to radiation-induced polymerization and was deposited in and around conglomerate-hosted concentrations of uraninite that for the most part are texturally akin to detrital lags. The circulation of aquo-carbonic fluids took place as one event among several other fluid circulation events that define a post-depositional paragenetic sequence which is superimposed onto an original, placer-derived heavy mineral suite. Well-preserved evidence in fluid inclusions identifies the nature of the post-depositional fluids and points to the pathways along which they have passed. Bitumens are described not only from conglomerate layers of the Witwatersrand Basin, but also from Archaean basement granitoids adjacent to the basin, from fault-filling quartz veins that cut through the basin, and as trapped nodules within fluid inclusions from such quartz veins. The different types of hydrocarbons are identifiable in terms of variations in their structural characteristics, which in turn relate to variables such as extent of migration, degree of maturation and the process which resulted in fixation of the hydrocarbon. Bitumen appears to have been formed subsequent to accumulation of uraninite as well as certain episodes of authigenic sulphide phases, but prior to the deposition of the principal stage of authigenic gold deposition. The compositional and structural maturity of the bitumen is consistent with a formation that is prior to the peak metamorphic overprint on the basin margins at circa 300-350°C and 2-3 kbars. The origin of the hydrocarbons and the exact timing of its maturation and fixation are still uncertain, although there are indications that the event might be related to deposition of the upper portions of the Transvaal Sequence at circa 2350 Ma.

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INTRODUCTION

The presence of carbonaceous matter in the gold- and uranium-bearing conglomerates of the Witwatersrand Basin is one of the more intriguing and controversial aspects of the genesis of these deposits. Its occurrence is particularly relevant to mining operations since it is usually an indication of high grades of both gold and uranium. Values of up to 4,7% gold and 11,5% uranium have been reported from analyses of separated carbonaceous matter (Hallbauer, 1986; Landais et al., 1990) and, consequently an understanding of its origins, distribution, and relationship to gold and uranium is pertinent to the economic evaluation of individual reef horizons. Unfortunately, widely differing opinions exist in the literature as to the origin of the carbonaceous material in the Witwatersrand Basin and few attempts have, therefore, been made to utilize its occurrence in a predictive capacity during exploration, both within and outside the basin.

The first detailed description of Witwatersrand carbonaceous matter was made by Young (1917) who recognized three different modes of occurrence, namely, nodular granules, massive, compact veins and columnar or fibrous veins. He suggested that the carbonaceous matter was unlikely to represent the *in situ* residue of animal or vegetable matter, but a deposit from a liquid that had pervaded the sediments sometime after their deposition. Witwatersrand carbonaceous matter was subsequently referred to as "thucholite", an outdated term used to describe what was thought to be an authigenic Th-U-C-H-O bearing mineral (Ellsworth, 1928).

The detailed ore-microscopic studies of Ramdohr (1955) and Liebenberg (1955) favoured a detrital origin for uraninite grains in the conglomerates and recognized that carbonaceous matter was intimately associated with uraninite, and was observed to surround, fragment and, in some cases replace, the latter. It was also noted that carbonaceous matter and gold often occurred together but that this relationship was not as extensive as that between carbonaceous matter and uraninite.

Early stable isotope analyses of Witwatersrand carbonaceous matter indicated depleted $\delta^{13}\text{C}$ values typical of sedimentary organic carbon, suggesting that the material had a biogenic origin (Hoefs and Schidlowski, 1967). Support for the presence of primitive life-forms in the Witwatersrand Basin also came from the observation of circular and annular micro-structures of bacterial or algal morphology preserved, ironically not in carbonaceous matter, but in pyrite grains (Schidlowski, 1965). Coal petrographers likewise recognized the presence of circular and filamentous shapes within the carbonaceous matter itself and suggested that the Witwatersrand hydrocarbons contained *in situ* remnants of algal and fungal organisms similar to those seen in sapropelic coals (Snyman, 1965). The *in situ* biogenic origin of Witwatersrand material gained popularity when Hallbauer and van Warmelo (1974) and Hallbauer (1975) published high-resolution photographs supposedly representing well-differentiated organic remains that included bacteria, algae, fungi and lichens. This hypotheses was metallogenically relevant since it was suggested that the presence of biogenic material growing in low-energy sedimentary environments could have physically trapped detrital gold and uraninite particles.

Schidlowski (1981) persistently rejected the *in situ* biogenic hypotheses and regarded the Witwatersrand carbonaceous matter as the solidified product of mobile hydrocarbons that had undergone radiolytic polymerization in the vicinity of detrital uraninite. He argued that *in situ* preservation of delicate fossil life-forms in compacted and metamorphosed sediments was unlikely and also pointed to the biological problems of having relatively advanced life-forms in existence in rocks as old as 2,7-2,9 Ga. The hypothesis of a radiolytically-polymerized origin for the Witwatersrand hydrocarbons was also supported by Zumberge et al (1981) who suggested that the aromaticity and high concentration of free radicals was consistent with a hydrocarbon structure that had been subjected to intense radiation. Nevertheless, they stated that the kerogen seams contained preserved remnants of coccoid and filamentous micro-structures consistent with an originally biogenic (algal or bacterial) origin. A more recent study by Ebert et al (1990) utilized a variety of analytical techniques (NMR and ESR) to conclude that the carbonaceous matter had not been subjected to temperatures in excess of 300°C, but that palynological observations suggested that biogenic shapes, although indeterminate, were present. Finally, in a detailed study of the optical properties of organic matter in the Witwatersrand Basin, Gray et al. (1997) regarded the material as pyrobitumen, and concluded that the filamentous shapes were characteristic of 'carbonaceous mesophase' that formed bed perpendicular and indicated opening, or extension, of fractures during organic maturation.

The contrasting viewpoints that exist for the origin of carbonaceous matter in the Witwatersrand Basin are largely based on data obtained for the conglomerate hosted material. This study presents the results of new petrographic, chemical and spectroscopic data for carbonaceous matter that is now known to be texturally more variable than was previously thought, and is contained in different host environments both within and external to the basin. These observations shed new light on the nature and origin of Witwatersrand carbonaceous matter and also contribute to an improved understanding of its relationship to gold and uranium, both within and outside the basin.

TERMINOLOGY

The terminology applied to carbonaceous matter is largely dependent on the extent to which its origin is understood. Mossman (1993) and Nagy (1994) have simplified usage to two terms: **kerogen** refers to a solid, polymer-like organic substance which has remained *in situ* since deposition, while **bitumen** is a macromolecular organic compound which was once mobile as a viscous fluid but has since solidified. Kerogen is normally the most abundant organic substance in a sedimentary sequence and represents the residue after a normal cycle of organic evolution. In ore deposits, bitumens are the products of organic maturation and have been solidified by processes such as biodegradation, oxidation, thermal stress or radiation induced polymerization (Landais, 1993). Witwatersrand terminology over the past 20 years has been dominated by usage of the term kerogen because of widely held support for the *in situ* biogenic origin of the carbonaceous matter. Recently, however, the terms bitumen and pyrobitumen have been applied to the carbonaceous matter in the Witwatersrand Basin (Barnicoat et al., 1997; Gray et al., 1997; Nagy, 1994; Robb et al., 1994). The present study will attempt to shed light on usage of the two terms in a Witwatersrand context.

METAMORPHIC EVOLUTION

Any study of organic matter in a sedimentary basin must be made in the context of its thermal and burial history. Phillips and Law (1994) reviewed the metamorphic history of the Witwatersrand goldfields and confirmed that a regional P-T climax of $350 \pm 50^\circ\text{C}$ and 1.5-3 kbars applied throughout the basin. Metamorphic grades are considered to have been fairly consistent around the edge of the basin, although pressures and temperatures increase inwards towards the Vredefort Dome where conditions of up to 600°C and 4.5 kbars prevailed (Gibson and Wallmach, 1995). Although the timing of metamorphism is difficult to constrain, a review of isotopic age determinations in and around the basin suggests that metamorphism may have been episodic, occurring mainly in response to increments of progressive burial at ca. 2550 and 2350 Ma, and then to a major thermo-tectonic perturbation at 2060 - 2025 Ma related to intrusion of the Bushveld Complex and the Vredefort catastrophism (Robb and Meyer, 1995; Robb et al., 1997; Stevens et al., 1997). It is during the latter episode that the basin is believed to have been subjected to its metamorphic climax (Gibson and Wallmach, 1995).

Organic maturation in the Witwatersrand Basin will have been controlled by the successive increments of post-depositional burial and thermal evolution of the host rocks. Kerogen that is Archaean in age is derived from the biodegraded products of prokaryotic micro-organisms. With diagenesis the latter substances progressively lose oxygen, nitrogen and sulphur which are substituted by cyclic aromatic compounds. Mature kerogen largely comprises condensed aromatic compounds arranged in partially ordered sheets. Subsequent metamorphism of the host rocks eventually results in the mobilization of all volatile constituents and the formation of graphite. As in modern environments, the production of liquid and gaseous hydrocarbons from maturing kerogen occurs progressively, with maxima occurring during and subsequent to the "oil-window", which is typically between $100-150^\circ\text{C}$ and 1-1.5 kbars/3-6 km (Tissot and Welte, 1978). The duration of hydrocarbon production and the period of time subsequent to sediment deposition when the oil window is attained are also highly variable and depend largely on subsidence rates. Oil production can be ongoing for anything between 5 to 100 Ma, while the elapsed time between sedimentation and petroleum generation may vary from a few million years to more than 300 million years (Tissot and Welte, 1978). Organic material in the Witwatersrand Basin is characterized by reflectance (in oil) measurements typically in the range 4-8%, which equates to a short term thermal overprint of about 400°C , or a long-lived burial temperatures of around 280°C (Gray et al., 1997).

The Witwatersrand Basin was deposited on what had, by 2700 Ma, become a relatively stable proto-continent and was subjected to slow and protracted subsidence over the following 700 Ma. The period of maximum oil generation would, in all likelihood, have been a long lived event (perhaps 10^1-10^2 million years), while a considerable period of time might also have elapsed between the end of sedimentation and the onset of hydrocarbon generation. U-Pb isotopic analyses of carbonaceous matter from Witwatersrand conglomerates yields an apparent upper intercept concordia age of ca. 2330 Ma (Allsopp et al., 1986), a figure that is similar, statistically, to an upper intercept age of 2380 Ma for bituminous nodules from granitoids surrounding the basin (Robb et al., 1994). This 2380-2330 Ma age span approximately coincides with the deposition of the upper part of the

Transvaal Sequence (i.e the Pretoria Group), and it is this event which may be causatively linked to oil production and migration in the Witwatersrand Basin.

There does not seem to be a systematic pattern in the distribution of carbonaceous matter as a function of metamorphic grade. The most voluminous occurrences of carbonaceous matter occur in conglomerates such as the very rich "Carbon Leader" in the Carletonville Goldfield, and the uraniferous Beisa Reef in the Welkom Goldfield. The eastern extremity of the basin (the Evander Goldfield), on the other hand, records only sporadic development of mainly nodular carbonaceous matter. It should be emphasized that the high degree of maturity of carbonaceous matter in the Witwatersrand Basin precludes the use of bio-markers to provide a definitive statement on its original nature.

SAMPLING

In order to obtain representative samples of carbonaceous matter, a total of 7 mines across the entire basin were visited (Figure 1). Samples of carbonaceous matter from the 'B' and Basal Reefs of the Welkom Goldfield, the Ventersdorp Contact and Vaal Reefs of the Klerksdorp Goldfield, the Carbon Leader, Ventersdorp Contact, Elsburg and White Reefs from the Carletonville and West Rand Goldfields, and the Kimberley Reef of the Evander Goldfield, were collected and then slabbed, polish sectioned and separated for a variety of chemical and spectroscopic analyses. In addition, bitumen nodules were separated from quartz veins cutting through the Witwatersrand sequence and samples also obtained of rare, granitoid-hosted bitumens from a number of peraluminous granites beneath and adjacent to the Witwatersrand sediments (Robb et al., 1994).

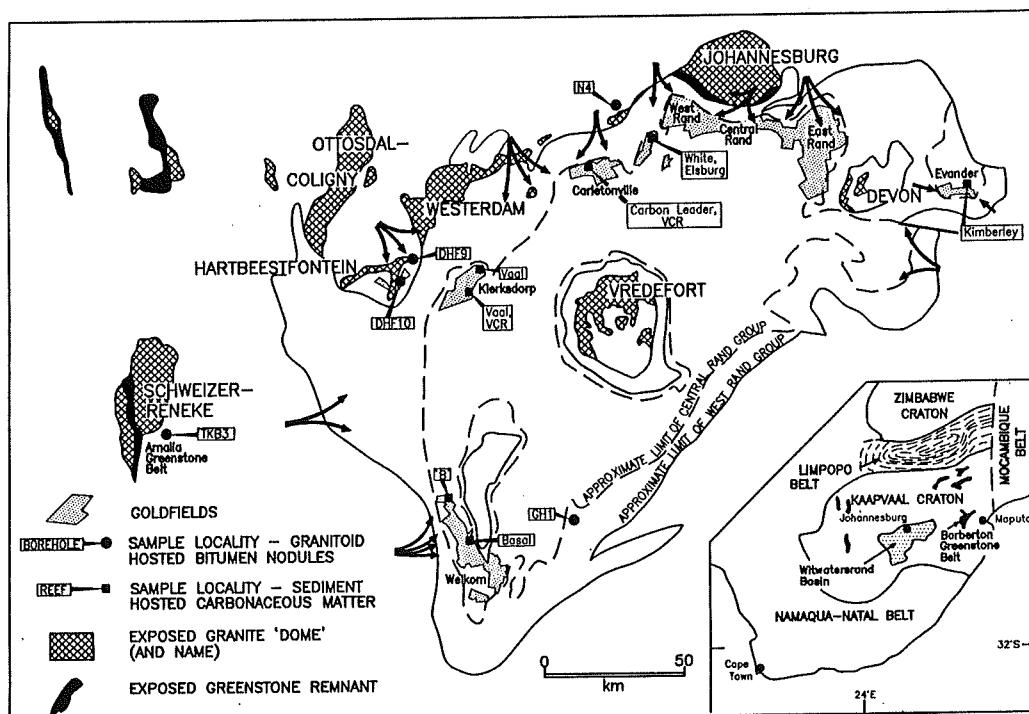


Figure 1: Simplified outline of the Witwatersrand Basin and the location of samples described in the present study.

PETROGRAPHY

There are two principal modes of occurrence of carbonaceous matter in the Witwatersrand conglomerates. These are "seams", which occur as 1-15mm thick fibrous or massive layers usually at the base of a conglomerate, but also occasionally occur as stacked and anastomosing layers cutting through the conglomerates, and "nodules" which are 0,2-1mm diameter aggregates with irregular, bulbous outlines. Nodules, which are referred to colloquially as "fly-speck" carbon, occur disseminated throughout the conglomerate matrix with other heavy minerals, or at the extremities of seams where a continuous layer of carbonaceous matter eventually breaks down into progressively dismembered aggregates and globules. Nodules are often seen scattered throughout conglomerate reefs where there is no carbonaceous seam evident, and may also occur as rare specks in hanging wall quartzites. In addition, bituminous nodules have now also been recovered from quartz veins cutting through the Witwatersrand sediments (Drennan et al., in prep.), in fluid inclusions within the same quartz veins (Drennan, 1995) and in granites adjacent to the basin (Robb et al., 1994). These occurrences are described below.

Carbonaceous seams

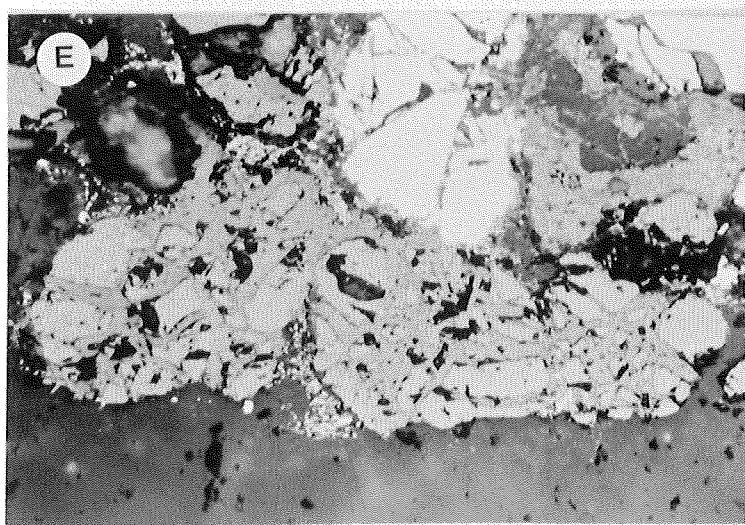
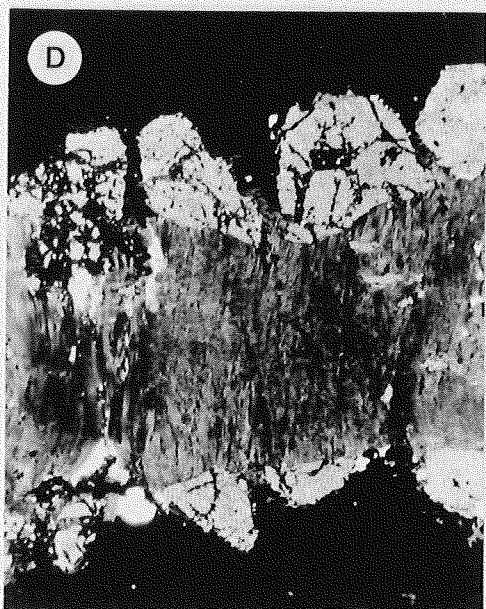
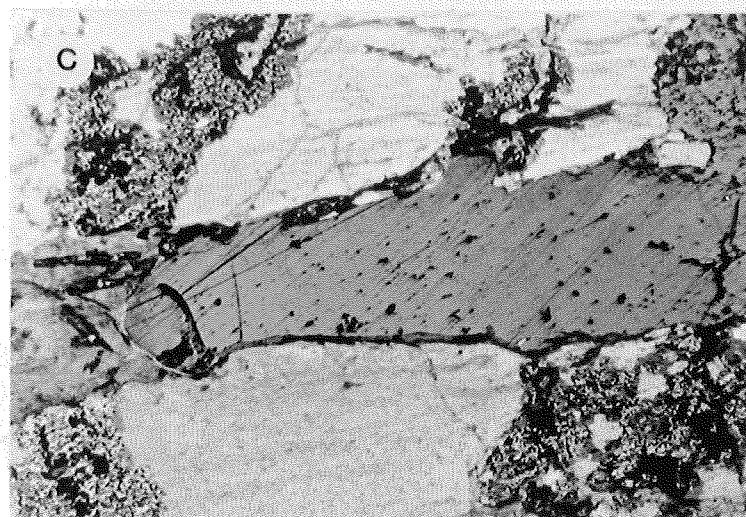
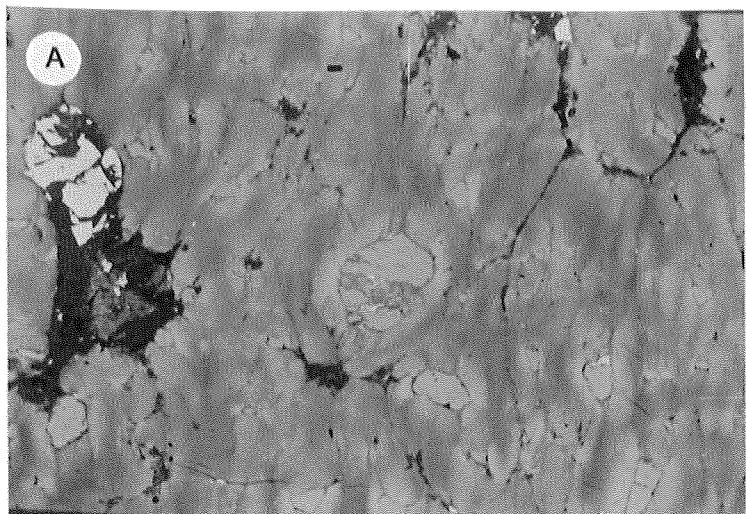
Although carbonaceous seams most often occur at the base of a conglomeratic unit and may be underlain by shale, they are also seen to anastomose through the conglomerate, bifurcate around pebbles and gradually disaggregate. Seams incorporate most of the alloigenic mineral constituents of the conglomerate, including uraninite, pyrite, quartz, chromite, zircon, uraninite and gold. Uraninite is, however, undoubtedly the most common constituent associated with the seams, and its abundance varies from \pm 20% of the volume of the seam to a virtually undetectable presence. Figure 2a shows part of a carbonaceous seam containing numerous fragmented and partially replaced uraninite grains. Figure 2b is a view under high magnification of a single grain of uraninite that has apparently been partially replaced by carbonaceous matter. The original outline of the now partially replaced uraninite grain is demarcated by the halo of enhanced reflectance which is believed to be the result of - radiation.

Well-developed seams, particularly at the base of a conglomerate, may exhibit a fibrous aspect which, in the past, has been attributed either to algal (or fungal) symbionts preserved as micro-fossils (Hallbauer, 1975) or to "fibre-vein" growths formed by precipitation of solid hydrocarbons in an extensional fracture environment (Schidlowski, 1981). Evidence from the present study clearly favours the latter suggestion. Carbonaceous seams are observed to have been precipitated along fractures representing pre-existing fluid pathways. Figure 2c shows a veinlet containing sericitic material and migrated carbonaceous matter transecting a quartz pebble and merging eventually with a thicker carbonaceous seam. Evidence for the development of fibrous or columnar-textured bitumen is presented in Figure 2d which shows a thin seam of carbonaceous matter deposited in a fracture which transects a row of en echelon uraninite grains. The fracture has bisected several of the uraninite grains such that they are now located on each side of the dislocation. These observations are interpreted to suggest that carbonaceous matter was precipitated in a tensional fracture during passage of a hydrocarbon-bearing fluid. As the vein continued to open under extension the fibrous texture developed at right angles to the vein walls. Solidification of the bitumen was

Figure 2: Photomicrographs of carbonaceous material in conglomerates from the Witwatersrand Basin;

- a. Typical appearance of a carbonaceous seam in plane reflected light, showing the occurrence of numerous included uraninite grains, each identified by a rim of higher reflectance material. Large uraninite grain in the centre of the field of view has been dis-aggregated during solidification of the hydrocarbon. Width of field of view (WOF) = 1,5mm.*
- b. Single grain of uraninite that appears to have been partially replaced by carbonaceous material. The original outline of the uraninite grain is indicated by the annulus of higher reflectance carbonaceous material surrounding the grain. The bitumen which replaces uraninite is also characterized by higher reflectance. WOF = 0,05mm.*
- c. Bituminous seamlet deposited along a pre-existing bedding-parallel fracture. WOF = 2,5mm.*
- d. Fibrous bituminous seam deposited along a bedding-parallel fracture which dislocates a layer of uraninite grains. WOF = 0,3mm. [Photomicrograph courtesy of Dr. Thomas Oberthür, BGR, Germany].*
- e. Several uraninite grains fragmented and cemented by bitumen to form a large, elongate nodule. WOF = 0,6mm.*
- f. Three discrete uraninite grains illustrating a progression of fragmentation and replacement by bitumen. WOF = 0,2mm. The sequence of photomicrographs in e and f suggests that nodules form largely as a result of the precipitation of bitumen around single, discrete uraninite grains, whereas seams represent the solidification of more substantial amounts of bitumen around a lag of uraninite grains.*

FIGURE 2



caused by the radiation flux emanating from the uraninite grains, whose deposition must have preceded the formation of the fracture. It is suggested that the uraninites represent a detrital lag that was concentrated towards the base of the conglomeratic host. The sequence of events recorded here contradict previous suggestions that the bitumen and uraninite represent coeval precipitates from a single fluid (Barnicoat et al., 1997; Gray et al., 1997).

The fibrous elements developed in many carbonaceous seams are unlikely, therefore, to represent the fossilized remnants of primitive organic life-forms. Components of carbonaceous seams which exhibit clear evidence for having replaced pre-existing detrital uraninite grains, or for having migrated along fractures or veins, qualify texturally for designation as bitumen. The question of whether all the carbon seams can, on this basis, be inferred to be bitumen, or whether some might still preserve kerogen, is, however, debatable and requires further observations.

Carbonaceous nodules

Carbonaceous nodules are usually distributed in the matrix of the same conglomeratic units that contain well developed carbonaceous seams, but may also occur as isolated aggregates in hangingwall and footwall quartzitic sequences. The larger carbonaceous nodules are spatially related to seams and merely represent small-scale versions of the latter. Such nodules (2-3 mm diameter), may have irregular outlines with a large length to width aspect, and are usually associated with numerous uraninite particles (Fig. 2e). Nodules which are not obviously related to a carbonaceous seam tend to be smaller, more circular to globular in aspect, and may not enclose visually-detectable uraninite particles. This may be due to, either the complete replacement of uraninite by kerogen, or to a hydrocarbon fixation mechanism that is unrelated to the presence of a radiation-emitting phase. Occasionally, small nodules (circa 100 μm diameter) form around individual uraninite particles and represent discrete aggregates of carbonaceous matter that occur where there is little or no seam developed. In Figure 2f three discrete uraninite grains reflect progressive increments of fragmentation and replacement by bitumen; this observation lends support to the notion that some nodules might represent the products of complete replacement of a pre-existing uraniferous phases, a feature also observed in granitoid hosted bitumen nodules adjacent to the basin (Robb et al., 1994).

The textures described above indicate that carbonaceous nodules are not the *in situ* remnants of micro-biota, but more likely the products of migrating hydrocarbons that were solidified around or replaced individual uraninite grains, as a result of radiolytically induced polymerization. As such they should be referred to as bituminous nodules. The formation of seams as opposed to nodules appears to be related to the amount of uraninite present at any point in the conglomerate and the extent to which the bitumen has invaded and replaced the uraninite.

Granitoid-hosted carbonaceous nodules

Several workers have now recorded the presence of bituminous nodules in granitoids surrounding the Witwatersrand Basin (Hallbauer, 1984; Klemd and Hallbauer, 1987; Robb et al., 1990; 1994). A detailed account of their distribution and petrographic characteristics is provided in Robb et al. (1994). In summary, nodules or nodular stringers ranging in

diameter between 0.2-0.8mm (Fig. 3a), commonly occur in peraluminous granitoids that contain primary uranium-thorium bearing accessory minerals. Nodules may not be associated in every case with visually-detectable uranium-bearing minerals, but are always associated with high concentrations of uranium, as evident from detailed fission-track micro-mapping (Robb et al., 1994). In other cases, however, bitumen is observed to progressively fragment and replace primary grains of uraninite or uranothorite in the peraluminous granitoid host (Fig. 3b) in exactly the same way as within the Witwatersrand conglomerates. It has been suggested that the same hydrocarbon-bearing fluids that permeated the Witwatersrand sediments also passed through granitoids adjacent and subjacent to the basin (Robb et al., 1994). It would appear that bitumens were precipitated in these granitoids by radiolytic polymerization in much the same way as hydrocarbons were fixed within the Witwatersrand Basin.

Quartz vein- and fluid inclusion-hosted carbonaceous matter

A recent, detailed study of post-depositional fluids in the Witwatersrand Basin has revealed the presence of, *inter alia*, a hydrocarbon bearing fluid population comprising CO₂ and variable proportions of CH₄, C₂H₆, H₂ and N₂ (Drennan, 1995; Drennan et al., in prep.; Robb et al., 1989). Inclusions bearing these fluids are occasionally coated by a thin film of solid hydrocarbon, or actually contain bituminous nodules up to 10 microns in diameter (Fig 3c). In addition, small bituminous nodules are occasionally observed along the sites of annealed micro-fractures within quartz pebbles in the conglomerates (Oberthür, 1983; Fig 3d). Nodules have also recently been discovered in association with pyrite and gold from quartz veins that cut the conglomerates and are associated with late stage faulting in the basin (Drennan et al., in prep.). Quartz vein hosted bitumen nodules either occur as discrete warty aggregates of hydrocarbon (Fig. 3e), or intimately intergrown with pyrite and occasionally gold (Fig. 3f). The presence of these bitumens clearly demonstrates that hydrocarbon circulation in the basin was not restricted to the conglomeratic horizons, but also involved aquo-carbonic solutions migrating along other conduits such as faults and shears.

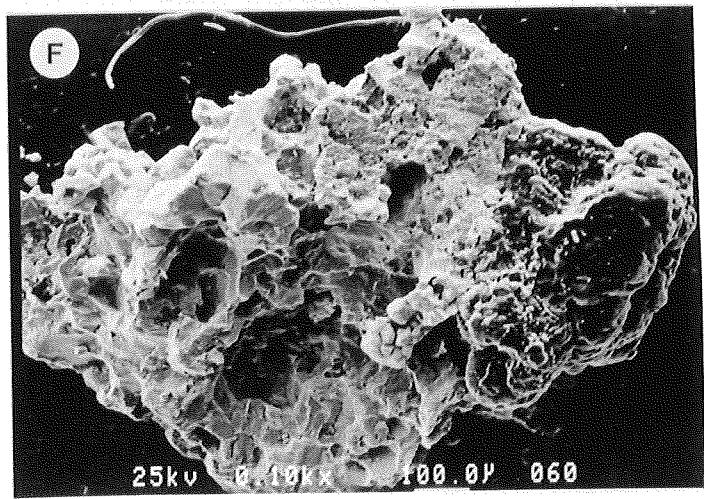
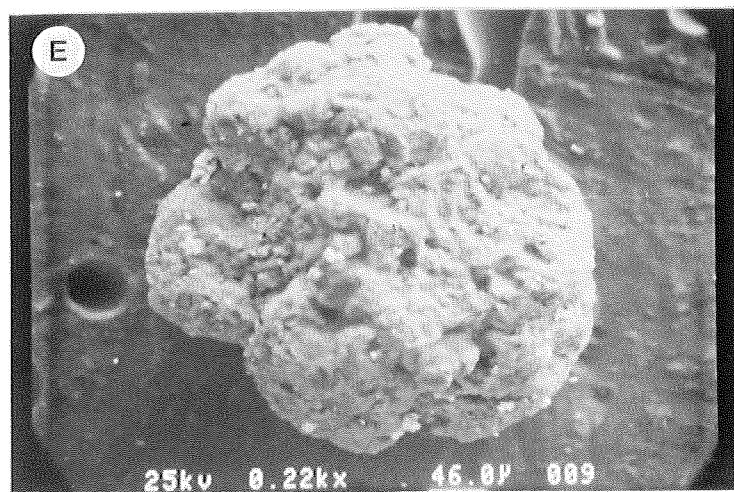
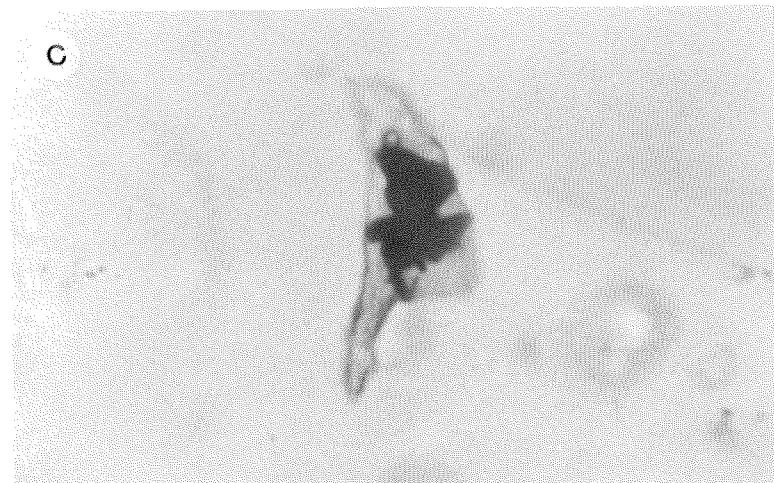
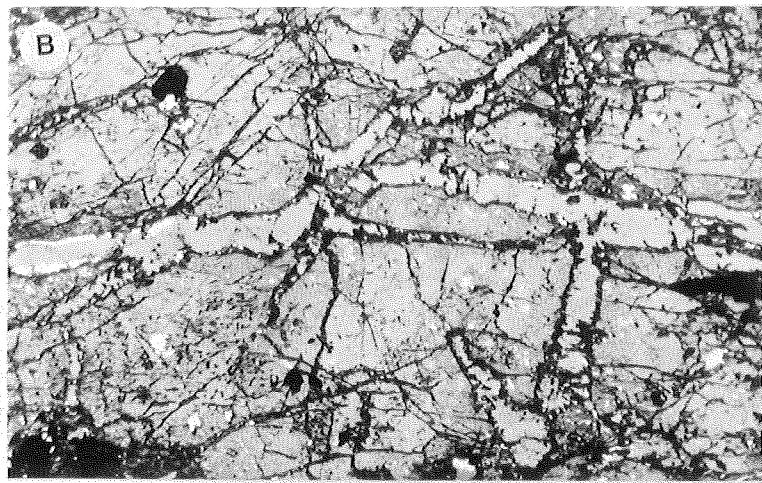
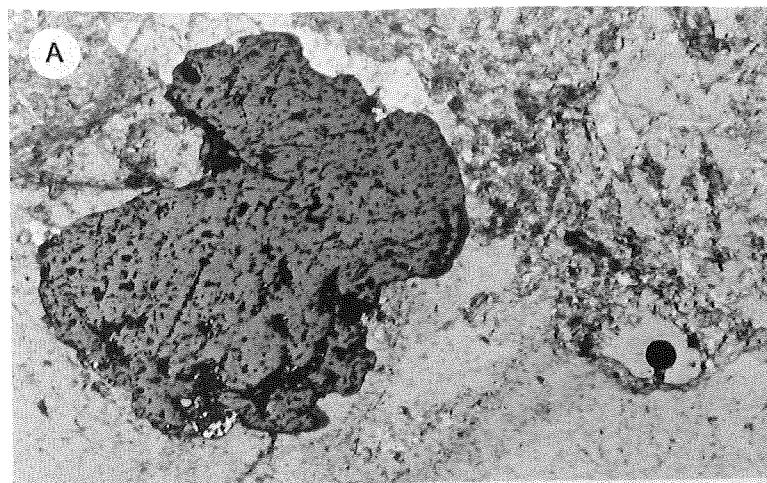
PARAGENETIC SEQUENCE |

The paragenetic sequence of ore formation in the Witwatersrand Basin is relatively well known although its relationship to the burial history and metamorphic evolution of the basin is still poorly constrained. Robb and Meyer (1995) and Robb et al. (1997) suggested a three-fold post-depositional paragenetic sequence comprising (i) early sulphide remobilization at ca. 2550 Ma, related to an increment of burial associated with deposition of the lower portion of the overlying Transvaal Sequence, (ii) circulation of hydrocarbon-bearing fluids at ca. 2350 Ma related to a further increment of burial associated with deposition of the upper portion of the Transvaal Sequence and, (iii) late quartz-sulphide veining and gold remobilization between 2060 and 2025 Ma, related to the peak metamorphic overprint in the basin during intrusion of the Bushveld Complex and the Vredefort catastrophism.

Figure 3: Photomicrographs of bituminous nodules from granites surrounding the Witwatersrand Basin, as well as from quartz veins and fluid inclusions within quartz veins cutting through sediments of the Witwatersrand Basin;

- a. Bituminous nodule within altered granite. WOF = 2mm.*
- b. Uranothorite grain from a granite adjacent to the basin margin showing fragmentation by veinlets of bituminous material. WOF = 1mm.*
- c. Bituminous nodule trapped within an aquo-carbonic fluid inclusion in a quartz vein cutting through conglomerate. WOF = 50 microns.*
- d. Bituminous nodule deposited along an annealed microfracture in a quartz pebble from a Witwatersrand conglomerate. WOF = 0,1mm.
[Photomicrograph courtesy of Dr. Thomas Oberthür, BGR, Germany].*
- e. SEM photomicrograph of a bituminous nodule extracted by acid dissolution of quartz vein material cutting through conglomerate. Small crystals on the surface of the nodular bitumen are sulphides. Scale bar = 46 microns.*
- f. SEM photomicrograph of a bituminous nodule intergrown with pyrite and minor gold extracted by acid dissolution of quartz vein material cutting through conglomerate. Scale bar = 100 microns.*

FIGURE 3



The present study supports the above scheme in providing evidence for hydrocarbon migration subsequent to the development of early authigenic sulphides such as pyrite and pyrrhotite. Figure 4a shows a discontinuous carbonaceous seam, precipitated along two parallel bedding plane fractures, which cuts across a veinlet of pyrrhotite orientated at right angles to the bedding. Figure 4b demonstrates a large bituminous nodule that has overgrown early authigenic pyrite in a conglomerate matrix. In both cases the precipitation of bitumen appears to post-date the formation of authigenic sulphide phases, with hydrocarbon-filled fracture sets forming after the conduits along which earlier sulphide phases have developed.

With respect to a significant proportion of the authigenic gold that occurs within the Witwatersrand Basin, however, a different situation prevails. Much of the gold that occurs within hydrocarbon-bearing conglomerate horizons appears to have been precipitated subsequent to fixation of bitumens since authigenic grains and filaments of the metal commonly occur within, and alongside, carbonaceous seams. In Figure 4c a veinlet of gold cuts across a bituminous seam typically characterized by numerous fragmented uraninite inclusions. Whilst it might be argued that the gold and bitumen in the latter photomicrograph were co-precipitated, this is unlikely to be the case in Figure 4d where distinct fluid pathways cutting across a bitumen seam are clearly identified by linear zones along which small grains of sulphides and gold have formed. Gold appears to have been precipitated, possibly by reduction of auriferous fluids circulating through, or alongside, bitumen seams, as suggested by Robb and Meyer (1995).

It is also evident that on rare occasions at least two generations of hydrocarbon may be observed in juxtaposition. Figure 4e shows an early carbonaceous seam containing numerous uraninite inclusions cross-cut by a fracture-controlled, bitumen veinlet which is devoid of uraninite inclusions; Figure 4f illustrates the corresponding fission track micromap confirming the high content of uranium in the early seam and the complete absence of any fission producing isotopes in the later vein. Since this type of occurrence is relatively infrequent it is unlikely that the Witwatersrand basin was subjected to two major episodes of hydrocarbon fluid circulation and the two events recorded here are probably closely linked in time. The sequence does, however, suggest that there were other precipitation mechanisms for bitumen in the Witwatersrand Basin besides radiolytic polymerization.

ANALYTICAL TECHNIQUES

Elemental analysis

Standard pyrolysis analysis was undertaken on all samples in which an excess of approximately 2g of pure organic material could be recovered. This provided the bulk composition of the organic material in terms of carbon, hydrogen, oxygen and percentage ash. Atomic H/C and O/C ratios (Table 1) were calculated from this information. The same samples were then also subjected to standard atomic absorption analysis for their U, Au, Fe, Pb, Zn and Cu contents (Table 2).

Figure 4: Photomicrographs showing the paragenetic relationships between bitumens and other phases of mineralization in the Witwatersrand Basin;

- a. Elongate bituminous nodules deposited along two sub-parallel fractures which define a discontinuous seam, cutting at right angles through a pyrrhotite veinlet. WOF = 2mm.*
- b. Bituminous nodule overgrowing, and partially replacing, authigenic pyrite.*
Photomicrographs in a and b suggest that bitumen formation post-dated the early generation of sulphide remobilization in the Basin. WOF = 1,5mm.
- c. Carbonaceous seam containing numerous inclusions of uraninite cut by a veinlet of gold. WOF = 0,2mm. [Photomicrograph reproduced with permission of the Geological Society of Australia].*
- d. Carbonaceous seam illustrating linear zones of altered hydrocarbon which appear to represent micro-conduits along which later fluids have transgressed the bitumen. The same zones also represent the sites along which gold and sulphides have been precipitated. The photomicrographs in c and d suggest that bitumen formation was post-dated by a fluid migration event that was associated with the mobilization of gold. WOF = 1mm.*
- e. Two generations of hydrocarbon; an early bedding-parallel seam associated with numerous fragments of uraninite, cut by a later seam which is devoid of any uranium-bearing phase. WOF = 2mm.*
- f. Accompanying fission track micromap of the same field of view as e, showing the contrasting incidence of radiation-emitting phases in the two generations of hydrocarbon.*

FIGURE 4

-11-

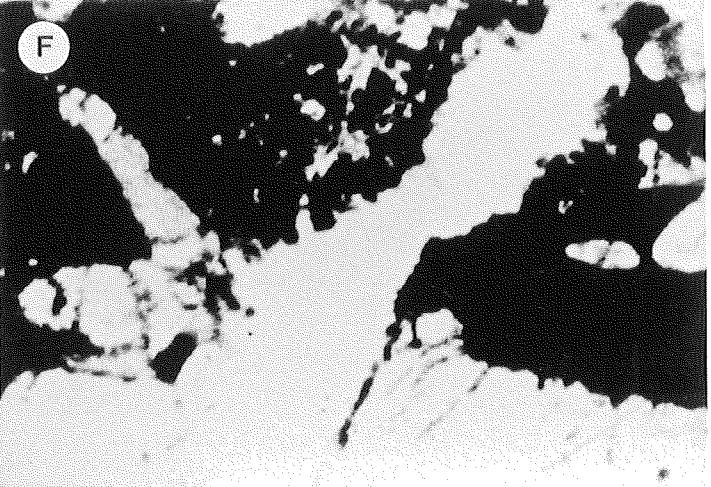
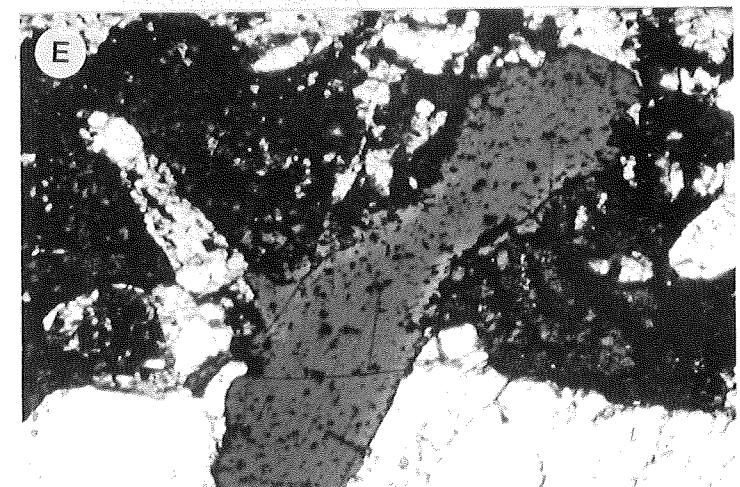
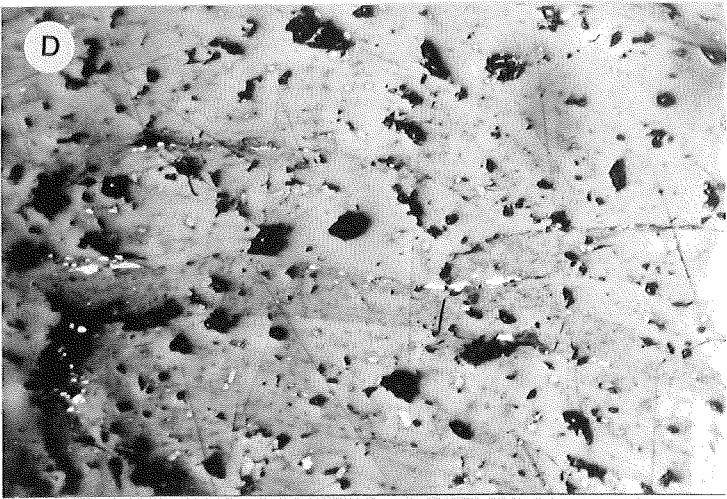
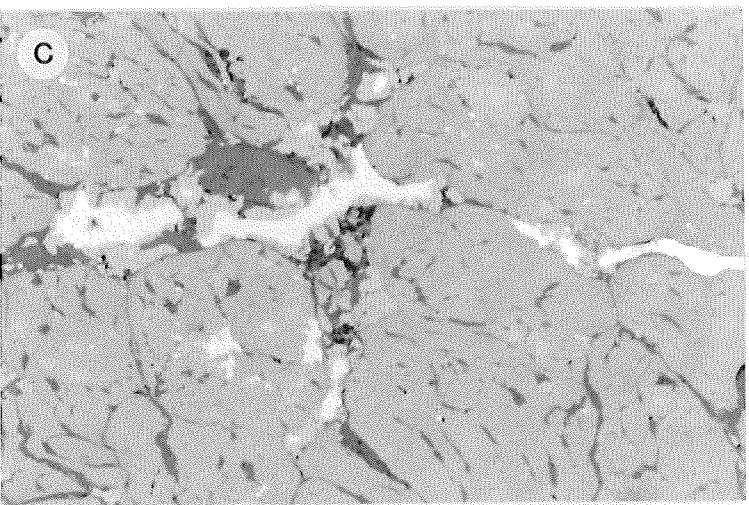
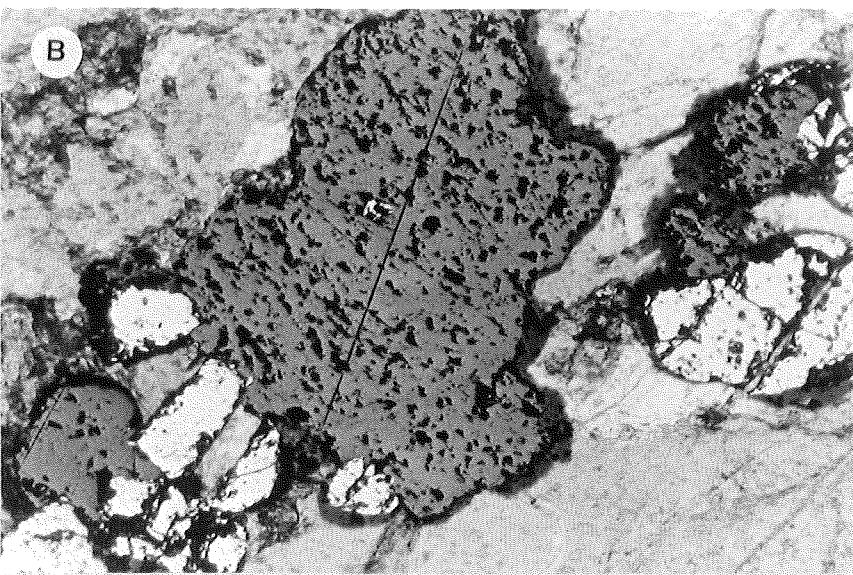
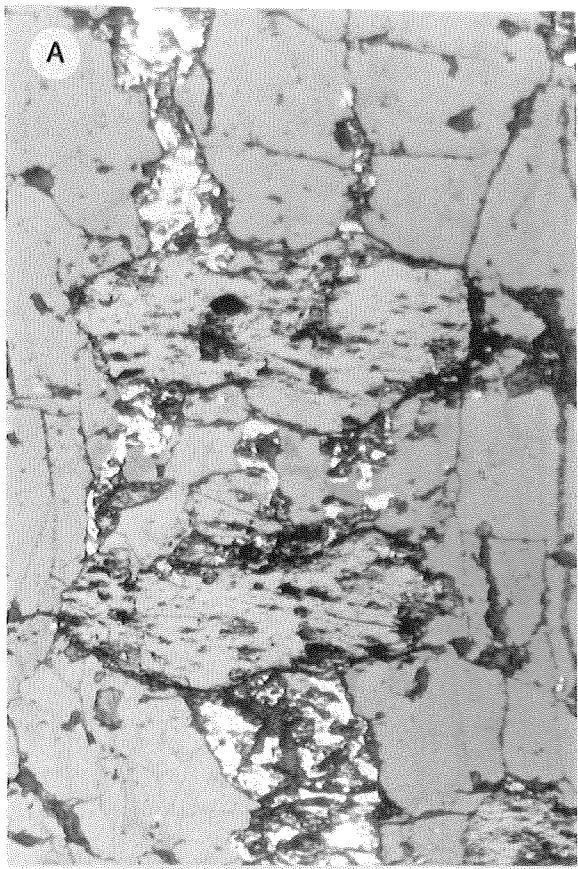


TABLE 1
ORGANIC CHEMISTRY OF WITWATERSRAND CARBONACEOUS MATTER

SAMPLE	H/C (at.)	O/C (at.)	C (%)	T _{max} (°C)	Fa (%)	HI mg/g TOC	methyl/ methylene	aromatic substit.
1 VR	0.499	0.051	54.1	466	-	51	-	-
2 VR1	0.464	0.074	53.0	474	68.6	36	0.68	0.45
3 VR1a	0.423	0.070	52.0	476	62.0	42	0.63	0.43
4 Miller	0.423	0.074	52.2	465	70.5	26	0.66	0.48
5 DN D1	0.488	0.065	75.2	464	69.6	53	0.58	0.40
6 DN3531	0.550	0.030	80.8	458	61.9	87	0.58	0.37
7 HB3	0.491	0.054	43.5	475	66.4	36	0.64	0.46
8 HB4	0.525	0.054	50.6	457	64.4	50	0.68	0.42
9 FSG	0.462	0.067	77.8	469	70.7	43	0.52	0.32
10 BP7735	0.490	0.054	59.3	476	66.1	36	0.64	0.36
11 BP7743	0.550	0.057	78.7	459	66.0	55	0.55	0.37
12 COOK	-	-	36.6	456	69.2	21	0.71	0.49
13 LOR3	-	-	27.8	447	63.3	92	0.64	0.41
14 LEADER	-	-	40.2	444	71.9	35	0.70	0.40
15 WHITE	-	-	55.2	490	69.8	15	0.63	0.47
16 TKB3/1	0.470	0.074	79.5	-	-	-	-	-
17 TKB3/2	0.460	0.085	73.2	-	-	-	-	-

H/C, O/C and C by pyrolysis

T_{max} - Temperature of maximal hydrocarbon generation by Rock-Eval pyrolysis

Fa - Aromaticity factor by ¹³C NMR

HI - Hydrogen Index (S2 pyrolysis peak/total organic carbon)

methyl/methylene by ¹³C NMR

degree of aromatic substitution by ¹³C NMR

[VR-Vaal Reef, Miller-Miller Reef; Vaal Reefs Mine: DN-Carbon Leader; Doornfontein Mine: HB-Vaal Reef; Hartebeestfontein Mine: FSG-Basal Reef; Free Gold: BP-Carbon Leader; Carletonville: Cook; Elsburg Reef; Randfontein Estates: LOR- B Reef; Loraine Mine: LEADER-Leader Reef; Free Gold: WHITE- White Reef; Randfontein Estates: TKB3- granite west of the basin.]

TABLE 2

CHEMICAL CHARACTERISTICS OF WITWATERSRAND CARBONACEOUS MATTER

SAMPLE	U (%)	Au (%)	Fe (%)	Pb (%)	Zn (ppm)	Cu (ppm)
1 VR	7.5	1.8	3.5	2.2	175	250
2 VR1	10.4	0.73	2.4	2.7	1700	630
3 VR1a	8.8	0.31	4.0	2.2	82	250
4 Miller	11.5	0.0085	2.0	4.7	10500	490
5 DN D1	2.0	0.42	0.4	0.3	32	250
6 DN3531	2.2	0.27	1.4	0.5	32	880
7 HB3	7.7	1.47	5.0	2.3	107	270
8 HB4	5.3	1.1	5.2	1.6	100	310
9 FSG	4.0	0.46	0.23	1.4	62	100
10 BP7735	8.5	-	-	-	-	-
11 BP7743	3.1	-	-	-	-	-
12 COOK	8.2	4.7	6.6	10.2	12000	950
13 LOR3	7.1	0.67	7.6	2.4	150	320
14 LEADER	8.8	0.03	3.0	3.5	375	80
15 WHITE	5.8	0.026	2.3	1.8	325	80
16 TKB3(1)	0.6	0.89ppm	-	-	-	-
17 QVNOD	2.5	25ppm	-	-	-	-

ROWS 1-15: Carbonaceous seams in various Witwatersrand conglomerates (see Table 1)

16: Bituminous nodule in granite TKB3

17: Bituminous nodule in quartz vein cutting conglomerate

Rock-Eval pyrolysis

This is an open-medium pyrolysis technique (Monin et al., 1980) in which samples were heated in a medium swept by inert gas at 550°C and syphoned off at a constant rate. Free hydrocarbons released up to 250 °C were trapped and analysed by a Flame Ionization Detector (FID) as a first peak S1. Hydrocarbons liberated between 250°C and 550°C were formed by cracking of bitumen/kerogen and analysed by FID as a second peak S2. The ratio of S2 to the carbon content provides the Hydrogen Index (HI), while the temperature of maximum hydrocarbon generation is referred to as T_{max} (Table 1).

¹³C Nuclear Magnetic Resonance (NMR) spectroscopy

NMR spectroscopy was carried out on a Brucker CXP100 spectrometer using techniques and methodology described by Dereppe et al. (1983). Quantification of organic parameters from NMR spectra is somewhat controversial and is carried out in terms of a scheme which recognizes the presence of oxygen-bearing, aromatic and saturated carbon bands (Landais et al., 1988). Organic parameters such as the aromaticity factor (F_a = percentage of organic carbon), methyl/methylene ratio and degree of substitution of aromatic rings are calculated from these data (Table 1).

Raman spectroscopy

The systematics of Raman spectroscopy as applied to the characterization of organic material is now relatively well established (Wang et al., 1989). Analyses were carried out on a X-Y Dilor multichannel Raman spectrometer using the excitation radiation of the 514.5nm line of an Ar laser set at low power to minimize alteration of the carbonaceous matter. A microscope attached to the spectrometer facilitated selection of the precise spot for analysis. Integration times of 20 seconds were used to collect data which was then plotted and identified, with emphasis being placed on the 1600 cm⁻¹ (E_{2g2} C=C) and 1350 cm⁻¹ (defect) vibrational bands (Tuinstra and Koenig, 1971).

Fourier transformed infrared (FTIR) spectroscopy

Infrared spectra were recorded with a Bruker IFS88 Fourier transform spectrometer also equipped with a dedicated microscope for spot selection. The microscope contains its own MCT detector cooled to 77K. In this study reflected energy spectra were recorded in absorbance as a function of wavenumber in the range 600-4000 cm⁻¹. The assignment of absorbance infrared bands to recognizable organic compounds is summarized from several sources in Rochdi and Landais (1990).

CHEMICAL CHARACTERISTICS

Carbonaceous matter in the Witwatersrand Basin has a bulk composition similar to that of a semi-anthracite (i.e 0,4 < H/C < 0,6). It exhibits generally lower O/C ratios (0,03 < O/C < 0,08) than uraniferous bitumens from, for example, the Oklo deposits (Fig. 5 inset), and other epigenetic, unconformity-related deposits in the Athabasca Basin such as Cluff Lake and Cigar Lake . Py-GC analyses of carbonaceous matter from the Vaal Reef

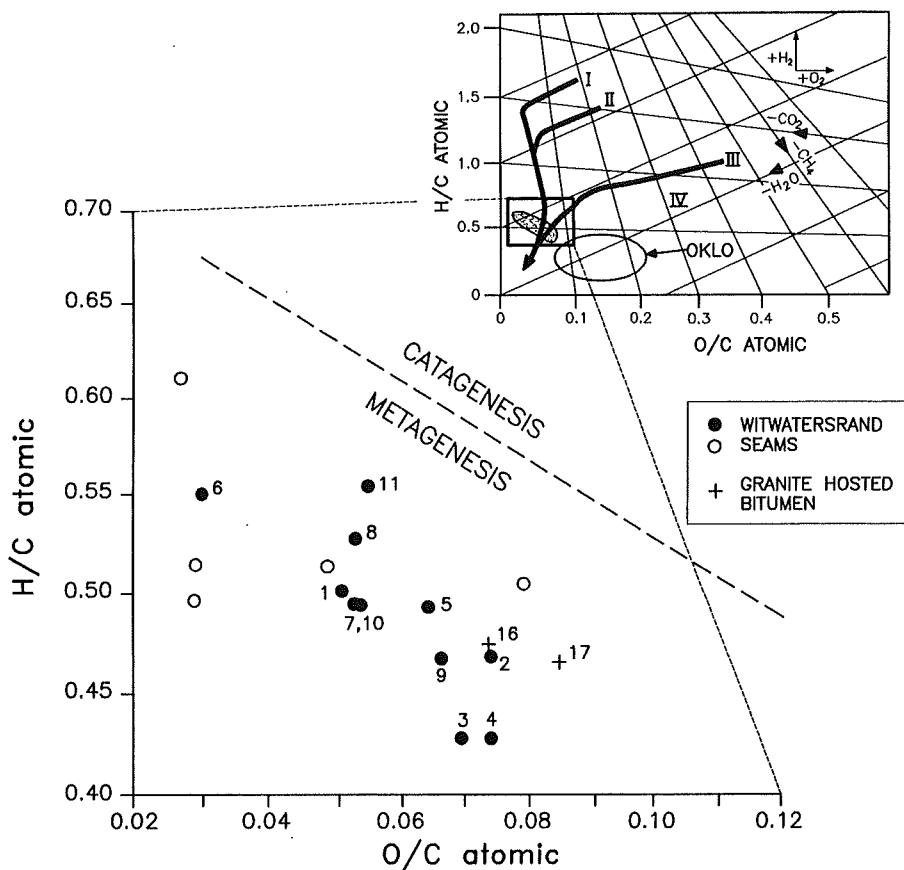


Figure 5: Van Krevelen diagram plotting atomic H/C versus O/C - filled circles and crosses represent data from Table 1; data for open circles are from Hallbauer, 1986. Inset is the hydrocarbon maturation diagram for Type I, II and III kerogens in relation to the fields for the Witwatersrand data (present study) and Oklo (P. Landais, unpublished data).

identified numerous organic compounds, summarized as mainly alkyl-substituted aromatic hydrocarbons and low molecular weight aliphatic hydrocarbons, together with lesser amounts of aromatic sulphur and aliphatic oxygen compounds (Zumberge et al., 1978).

The absence of graphite in the Witwatersrand carbonaceous matter has been confirmed in numerous petrographic and XRD studies, and more recently by ¹³C-NMR spectra which reveal that some 20% of carbon atoms are sp³ hybridized (Ebert et al., 1990). Quantitative NMR analysis of an unidentified carbonaceous seam from the St. Helena gold mine (Welkom Goldfield) in the latter study yielded 74% aromatic carbon, 22% paraffinic carbon and 4% oxidized carbon. The results of elemental analyses, ¹³C-NMR and Rock-Eval pyrolysis in the present study are shown in Tables 1 and 2. The abundances of non-organic constituents in the carbonaceous matter are highly variable. Uranium contents in seams are generally very high (values up to 11.5% in a sample from the Vaal Reef Mine), but are much lower in the granite- and vein-hosted bituminous nodules (Table 2). Very high concentrations of gold (up to 4.7%), usually reflected as visible gold, occur in many of the carbonaceous seams, while

granite nodules again record lower, but nevertheless anomalous (0.89 ppm), gold contents. Abundances of Fe, Cu, Pb and Zn are also very variable and reflect the content of pyrite and other authigenic sulphide phases associated with the carbonaceous matter. A positive correlation between U and Pb (Table 2) suggests that the latter element is mainly a product of the radiogenic decay of uranium in uraninite contained within the carbonaceous matter.

Carbon contents vary between 28% and 81% (Table 1) although typically the seams contain 50-70% carbon with 1-5% hydrogen and 2-6% oxygen. Nitrogen contents are typically low (<0.3%; Ebert et al., 1990; Hallbauer, 1986). Sulphur contents are variable (1-10%; Hallbauer, 1986), but this mainly reflects variations in the amount of contained pyrite and other sulphide phases and not the organic sulphur content. A Van Krevelen-type plot of atomic H/C versus atomic O/C shows that Witwatersrand carbonaceous matter is highly mature with compositions corresponding to the metagenetic stage of maturation (Fig. 5). This is consistent with other features such as reflectance (in oil) which ranges between 1.5-4% (Eakin, 1989), relatively high Rock-Eval T_{max} values (444-490°C) and low hydrocarbon potential ($15 < HI < 92$ mg/g TOC; Table 2). Atomic ratios are fairly restricted in terms of the total range exhibited by natural kerogens (Fig. 5, inset). The variability exhibited in terms of H/C and O/C cannot simply be related to the geological setting of the samples, but rather to redox and radiolytic processes as discussed later.

Compositional variations of Witwatersrand carbonaceous matter are also evident in a plot of Hydrogen Index (HI) versus T_{max} (Fig. 6). The negative correlation observed here reflects the decrease in hydrocarbon potential associated with the increasing thermo-stability of the organic structure and points to the importance of redox reactions (or removal of hydrogen/protons) in the compositional variations observed in Witwatersrand material. ^{13}C -NMR aromaticity factor (F_a) plotted against H/C (Fig. 7) also shows a well-defined inverse relationship with Witwatersrand material occupying an intermediate position between the Oklo and Athabaskan uranium deposits. F_a in Witwatersrand organic matter falls between 62-72% which corresponds with the mature, catagenetic nature of the material evident in the Van Krevelen plot (Fig. 5).

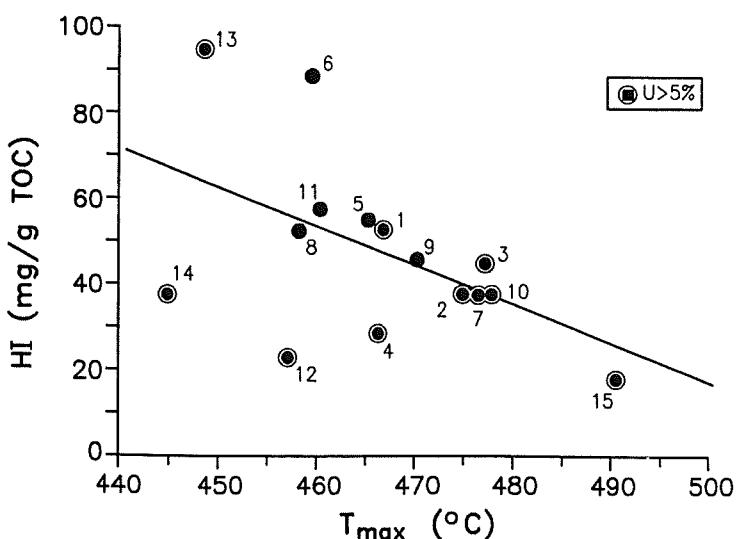


Figure 6: Plot illustrating the inverse correlation that exists between Hydrogen Index (HI) and T_{max} for Witwatersrand carbonaceous matter, data is from Table 1.

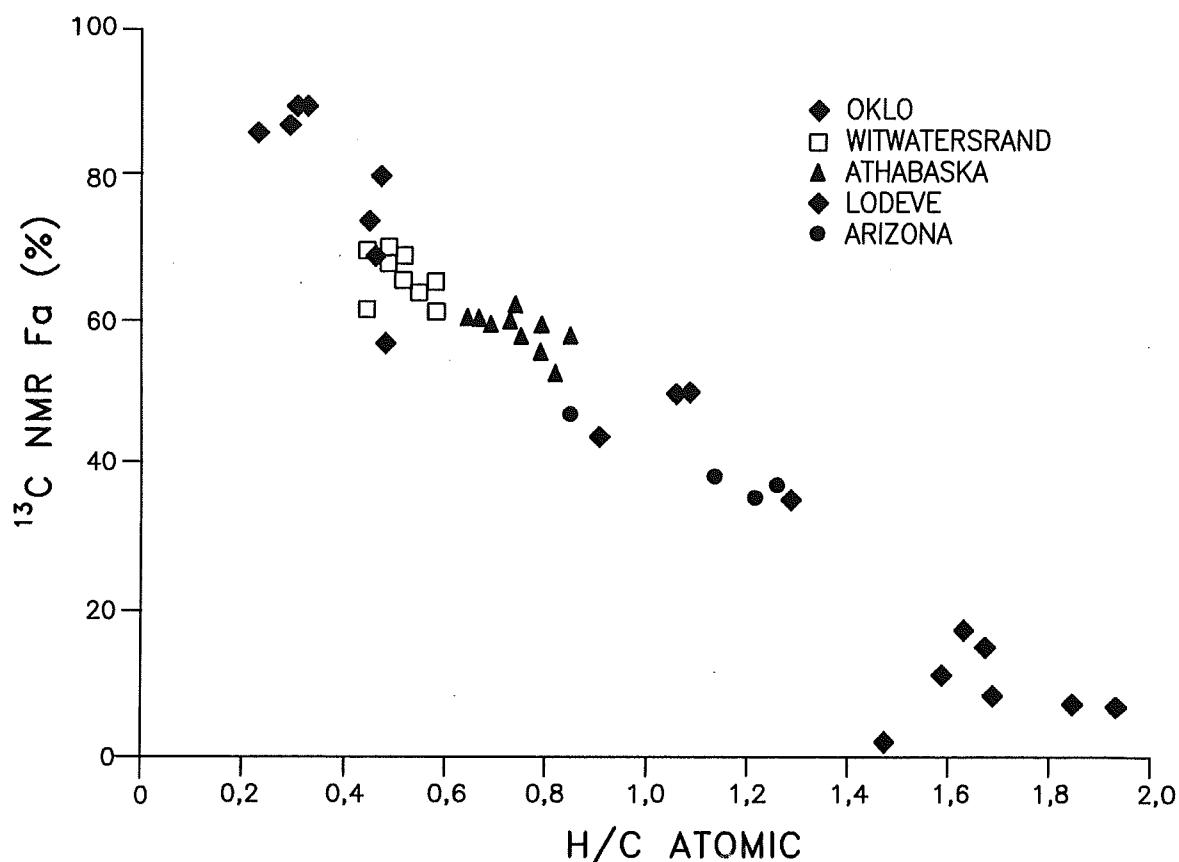


Figure 7: Plot of ^{13}C NMR aromaticity factor (F_a) versus atomic H/C showing the marked inverse correlation that exists for the Witwatersrand carbonaceous matter, as well as bitumens from a variety of other uranium deposits. The Witwatersrand data (from Table 1) fall in a position intermediate between the Oklo and Athabaska Basin deposits (P. Landais, unpublished data).

Other organic parameters derived by ^{13}C -NMR spectroscopy, for example, reveal a positive correlation between the methyl/methylene ratio and the degree of aromatic substitution (Fig 8a). A similar correlation was observed in mineralized and barren bitumens from the unconformity-related uranium deposits of the Athabaska Basin in Canada (Landais et al., 1989). Mineralized bitumens are characterized by a lower methyl/methylene ratio and a higher proportion of unsubstituted aromatic rings than barren equivalents. This again implies that both composition and structure of Witwatersrand carbonaceous matter are affected by uranium content. Long-chain alkyl substituents are more likely to be present in high-uranium organic material, whereas bitumens subjected to lower radiation doses tend to be typified by aromatic ring/methyl substitution. Hydrogen index, on the other hand, is negatively correlated with the aromaticity factor (Fig 8b) indicating that the proportion of aromatic constituents in the Witwatersrand carbonaceous matter is reduced during progressive thermal and/or radiogenic maturation.

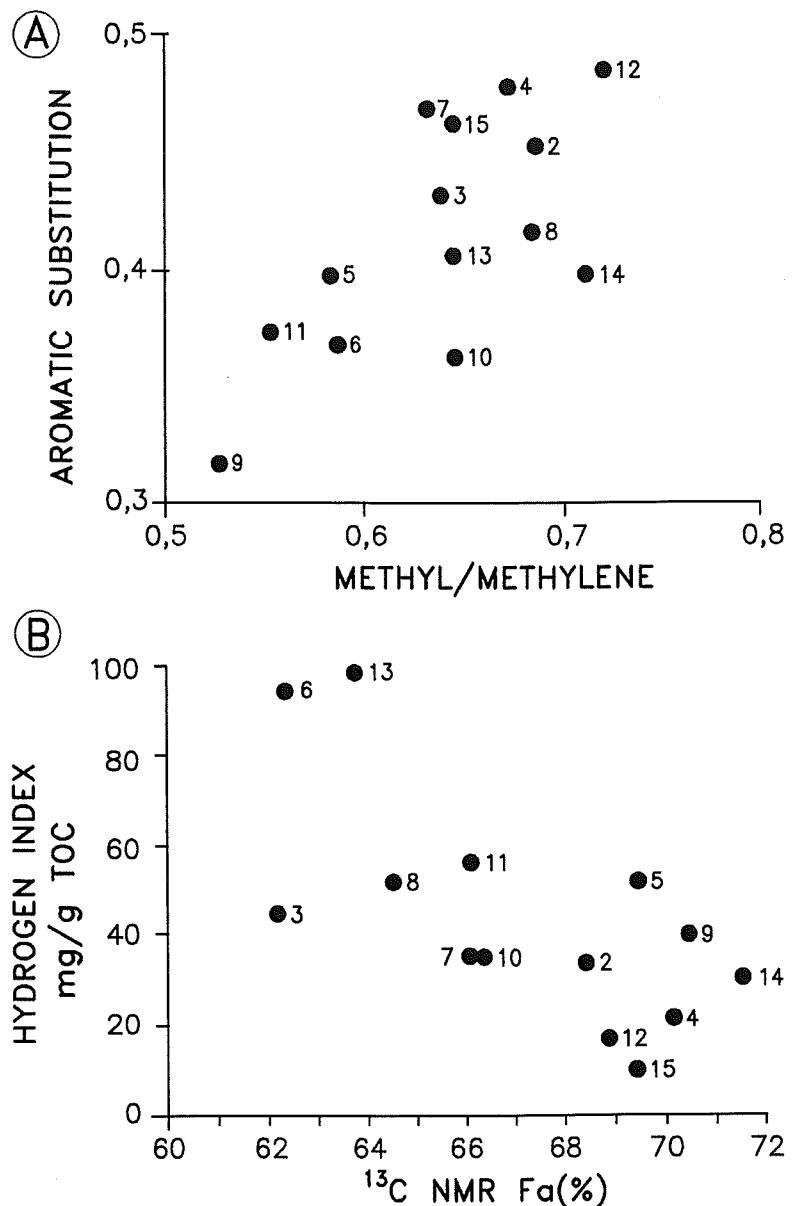


Figure 8: Plots of: a. ¹³C NMR generated methyl/methylene ratio versus degree of aromatic substitution; and b. ¹³C NMR aromaticity factor (F_a) versus Hydrogen Index; for Witwatersrand carbonaceous matter. Data is from Table 1.

ORGANIC PARAMETERS AS A FUNCTION OF Au AND U CONTENTS

Zumberge et al. (1978) first pointed out that the chemical characteristics of Witwatersrand carbonaceous matter varied as a function of its uranium content (or radiation dose). By contrast they could detect little or no correlation between pyrolysis product ratios and gold contents. The abundance of dimethylnaphthalenes (relative to other alkyl naphthalenes) was shown to be positively correlated with uranium content, a feature attributed to increasing aromaticity in the hydrocarbon during prolonged irradiation.

In the present study a correlation is observed between factors such as H/C, methyl/methylene and the uranium content (Fig. 9a and b). The relationships observed suggest that hydrogen is lost and aliphatic chains are shortened during radiolytic degradation. There appears to be little or no correlation between gold content of carbonaceous matter and most organic parameters. The one possible exception is the O/C ratio which apparently exhibits, except for a single aberrant and unexplainable point, a negative correlation with gold content (Fig. 9c). This relationship suggests that gold contents may be somewhat higher in more reduced carbonaceous matter, a feature that possibly reflects the low oxygen fugacities of post-depositional fluids circulating and re-distributing gold around the basin (Robb and Meyer, 1995).

CARBON ISOTOPE CHARACTERISTICS

Biogenic carbon is known to be enriched in ^{12}C relative to sedimentary carbonate and atmospheric CO_2 and, therefore, characterized by light $\delta^{13}\text{C}$ values. Analyses of the carbon isotope composition of Witwatersrand carbonaceous matter (Hoefs and Schidlowski, 1967; Förster, 1986) reveals that $\delta^{13}\text{C}$ varies between -20 and -38 permil. Carbon isotope variations in organic matter either reflect the character and environment of formation of the original living organisms (eg. marine organisms tend to have heavier $\delta^{13}\text{C}$ than terrestrial ones), or the thermodynamic isotope exchange properties of the compounds making up the organic matter (Galimov, 1980). In addition, however, kinetic isotope fractionation effects may be very important, particularly during the maturation of organic material where lighter or gaseous hydrocarbons are separated from heavier residues. Kinetic fractionation is caused by the greater mobility of ^{12}C - ^{13}C relative to ^{13}C - ^{12}C linkages and the fact that products of kerogen maturation preferentially incorporate ^{12}C over ^{13}C , and therefore have lighter $\delta^{13}\text{C}$ signatures (Galimov, 1980).

The light $\delta^{13}\text{C}$ signature of Witwatersrand carbonaceous matter clearly indicates that it is biogenic in origin. The large, up to 20 permil, variation in the isotopic signature is, however, problematical and cannot simply be the result of original biogenic heterogeneities or thermodynamic fractionation. There is some indication that carbonaceous matter in the Carbon Leader Reef has a more depleted $\delta^{13}\text{C}$ signature than that in the Vaal Reef (Förster, 1986), although the distinction is not entirely convincing since a great deal of overlap exists. It is more likely that the variations reflect kinetic fractionation associated with organic maturation and the separation of bitumens and gaseous hydrocarbons from their source material. Kerogen-bitumen isotope fractionation of -10 permil, and kerogen-methane fractionation of up to -40 permil, have been recorded (Galimov, 1980) and clearly indicate that organic maturation can give rise to significant $\delta^{13}\text{C}$ variations. The Huronian Basin deposits exhibit $\delta^{13}\text{C}$ values of -15 to -25 permil for uranium rich kerogen seams, with much lighter values of -25 to -33 permil for globular bitumens (Nagy and Mossman, 1992). The variations in Witwatersrand carbonaceous material probably also, therefore, indicate fractionation associated with separation of light gaseous and bituminous products from its source material. This is supported by the fact that granitoid-hosted bitumen nodules have $\delta^{13}\text{C}$ ranging between -35 and -41 permil and are, therefore, significantly lighter than sediment-hosted material (Robb et al., 1994).

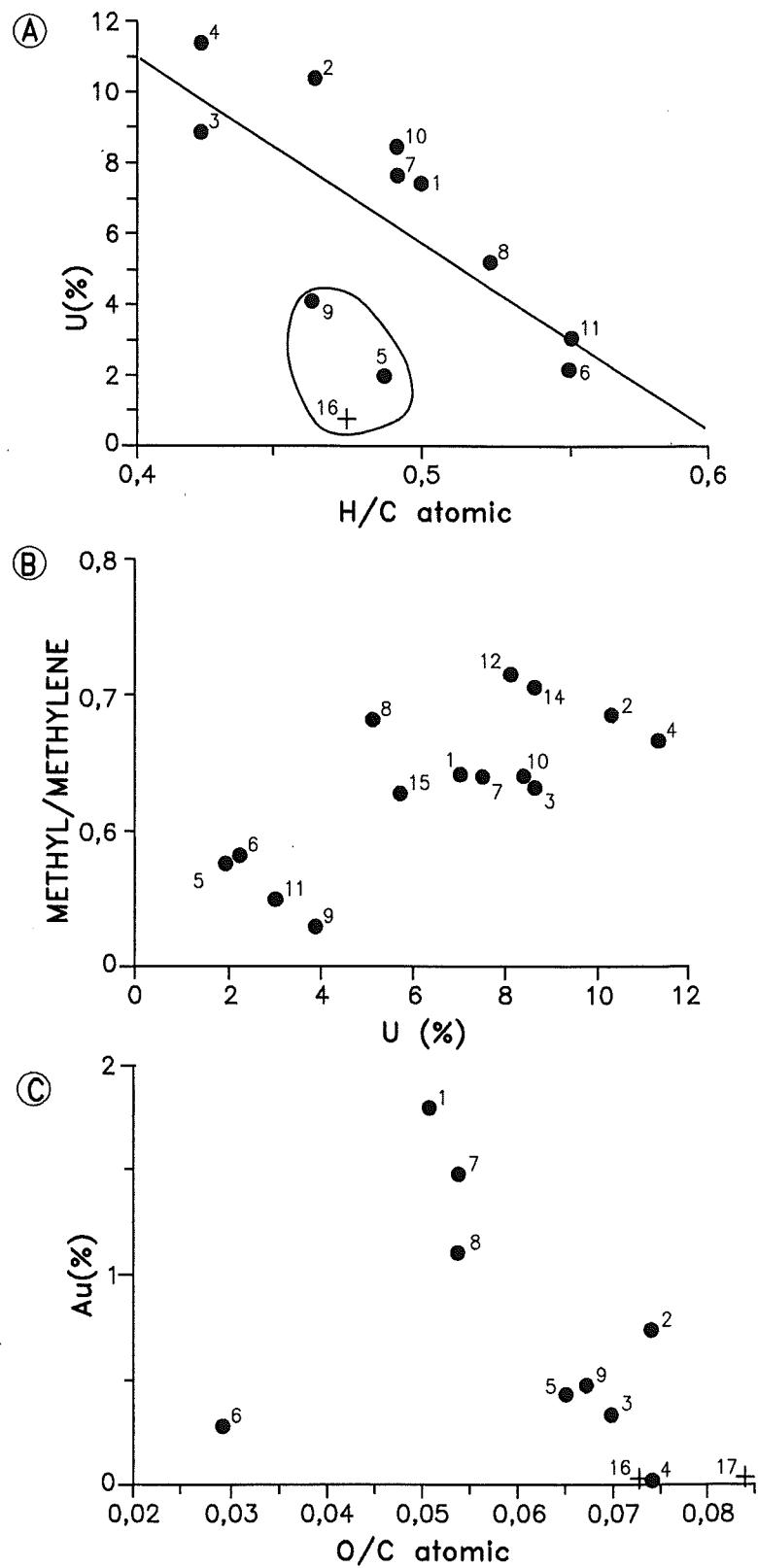


Figure 9: The relationship between various organic parameters and the U and Au contents of Witwatersrand carbonaceous matter: a. U content versus atomic H/C; b. U content versus methyl/methylene; c. Au content versus atomic O/C. Data is from Tables 1 and 2.

MICRO-SPECTROSCOPIC CHARACTERIZATION OF CARBONACEOUS MATTER

Micro-Raman and -FTIR spectroscopy has been applied to the various types of carbonaceous matter described above. These techniques are particularly useful where bulk analytical techniques were not possible because of the limited size of many of the samples, such as the nodular bitumens in granitoids and quartz veins. The spectroscopic techniques were instructive in facilitating comparisons between nodules and the more voluminous seam material and also in extracting additional compositional and structural information not normally available from more routine analytical techniques.

Micro-Raman spectroscopy has been utilized to obtain structural and compositional information on carbonaceous matter, particularly where it occurs in association with uranium mineralization (Landais et al. 1990a, b). Pure graphite exhibits a dominant peak at 1575 cm^{-1} which is an E_{2g2} Raman mode attributed to $\text{C}=\text{C}$ vibrations (Wang et al. 1989). Witwatersrand hydrocarbons and other mature organic matter, on the other hand, reveal two prominent spectral bands, one at 1600 cm^{-1} (which is akin to the graphite peak but somewhat shifted) and the other at 1350 cm^{-1} (a defect band related to lattice distortion, which becomes more pronounced with progressive disorganization-alteration; Oh 1987; Lespade 1982). The intensity ratio (I_{1600}/I_{1350}) of these two peaks can be determined as a measure of structural organization of the organic matter, and compared to the half-height width (L_{1600}) of the predominant (1600 cm^{-1}) peak (see Figure 10a for a definition of terms).

Micro FTIR spectroscopy of organic matter has proved to be a useful technique in assessing the *in situ* functional and chemical variations in organic matter (Rochdi and Landais, 1990). FTIR spectra of Witwatersrand carbonaceous matter reveal the presence of infrared absorbances which indicate the presence of aliphatic CH , CH_2 , aromatic CH , and minor hydroxyl functions as well as $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds (Rochdi and Landais, 1990).

MICRO-RAMAN SPECTROSCOPY

A summary of Raman spectral characteristics (i.e. peak intensity ratios and half-height widths) is presented in Table 3. Typical examples of Raman spectra for each of the modes of occurrence of carbonaceous matter in and around the basin are provided in Figure 10. In all cases the carbonaceous matter exhibits two well defined peaks, one at around 1600 cm^{-1} and the other at about 1350 cm^{-1} , although subtle variations in peak characteristics do occur. The presence of a substantial defect peak indicates that Witwatersrand carbonaceous material is poorly organized and in no way resembles the ordered structure of pure graphite. Sediment hosted seams and nodules are very similar in character (Fig. 10 a and b) with the 1600 cm^{-1} peak intensity only slightly exceeding that at 1350 cm^{-1} . Granite hosted nodules are similar although the 1350 cm^{-1} peak tends to be broader and less well defined (Fig. 10c). In addition, the E_{2g2} peak maximum is shifted towards lower wave numbers (i.e. $1592-1593\text{ cm}^{-1}$). The width of the 1350 cm^{-1} peak is even more pronounced in the quartz vein hosted nodules, where an incipient peak of unknown significance is also present at $1450-1500\text{ cm}^{-1}$. Carbonaceous linings in fluid inclusions exhibit a small, narrow 1600 cm^{-1} peak (i.e. reduced half height width relative to quartz vein- and granitoid-hosted nodules) but similarly enhanced peak intensity ratios as the other migrated bitumens (Fig 10e).

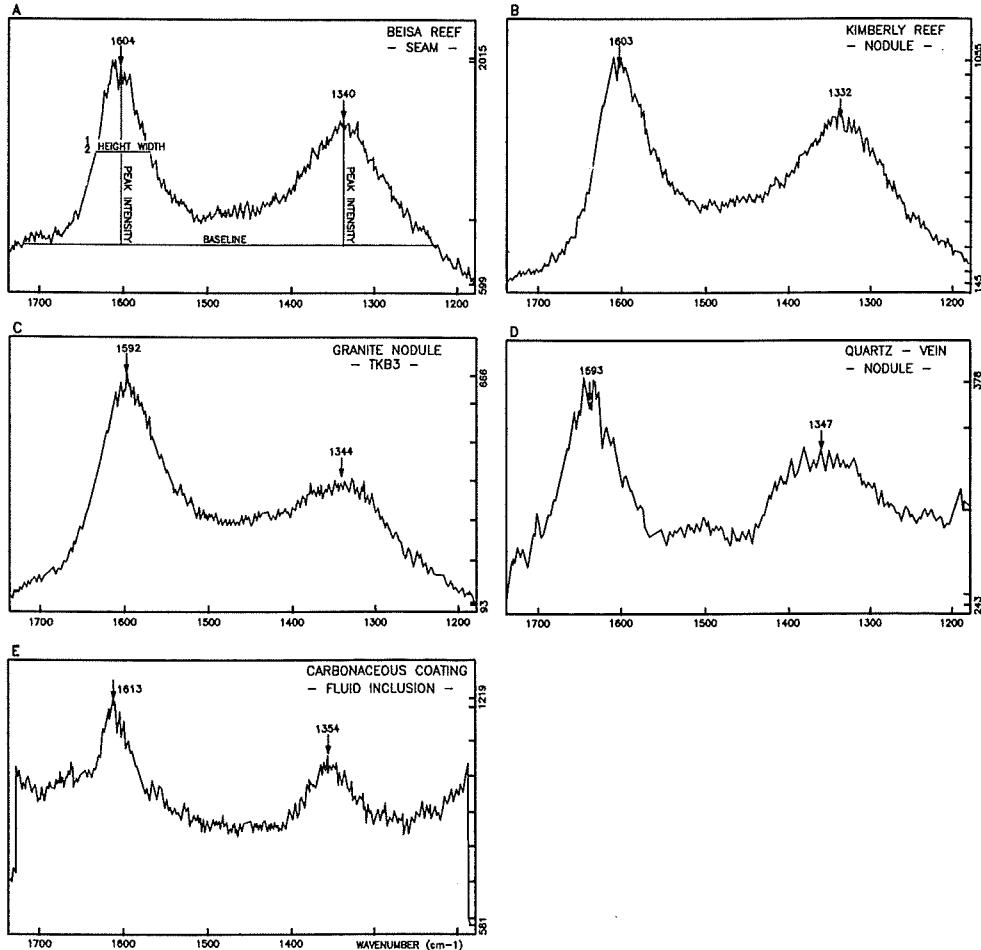


Figure 10: Typical micro-Raman spectra for the various modes of occurrence of carbonaceous material described in the present study; a. carbonaceous seam from the Beisa Reef; b. bituminous nodule from the Kimberley Reef; c. bituminous nodule from granite TKB3; d. bituminous nodule from a quartz vein cutting the Vaal Reef; e. carbonaceous material coating the edge of a fluid inclusion. The dimensions used to calculate the peak intensity ratio ($1600/1350$) and the half-height width ($L1600$) are shown in Figure 10a.

Raman spectral characteristics are summarized in a plot of I_{1600}/I_{1350} versus L_{1600} in Figure 11. It is clear that granitoid-, quartz vein- and fluid inclusion-hosted bitumens show higher peak intensity ratios than both seams and nodules from the Witwatersrand reefs, but that half-height widths are similar with the exception of the carbonaceous linings in fluid inclusions. The higher peak intensity ratios in the bitumens could be related to enhanced thermal maturation or a graphitization trend as this is normally indicated by increasing I_{1600}/I_{1350} ratios (due to the elimination of the 1350 cm^{-1} peak) accompanied by decreasing L_{1600} (Oh, 1987). This is not the case for the quartz vein- and granitoid-hosted bitumen nodules, but could explain the spectral characteristics of the carbonaceous fluid inclusion linings. The peak intensity shifts might, on the other hand, reflect a migration factor related

TABLE 3

RAMAN SPECTRAL CHARACTERISTICS OF WITWATERSRAND CARBONACEOUS MATTER

	Sediment hosted seams/ nODULES	L1600 (cm ⁻¹)	1600/1350	Granite hosted nodules	L1600 (cm ⁻¹)	1600/1350	Quartz vein nODULES	L1600 (cm ⁻¹)	1600/1350
1	76	1.3		78	2.07		69	1.65	
2	77	1.29		67	2.20		72	1.52	
3	78	1.21		76	2.00		71	1.62	
4	62	1.45		88	2.07		72	1.83	
5	85	1.60		83	1.81		79	1.87	
6	97	1.61		88	1.95		42	1.69	
7	62	1.33		80	1.70		56	1.76	
8	62	1.22		73	1.55		44	2.16	
9	67	1.12		65	1.72				
10	70	1.18		72	1.76				
11	70	1.31		75	1.80				
12	68	1.24		95	1.89				
13	66	1.28		97	1.90				
14	77	1.36							
15	71	1.22							
16	74	1.35							
17	65	1.71							

NOTE: Instrument precision in the calculation of L1600 estimated to be $\pm 1\%$
Graphic estimation of 1600/1350 peak ratio estimated to be $\pm 5\%$

Sediment hosted seams/nODULES:	Rows 1-3 Vaal Reef Rows 4-6 Beisa Reef Rows 7-11 Carbon Leader Row 12 Basal Reef Rows 13-16 Bituminous nodules from various locations Row 17 Bituminous veinlet cutting earlier seam, Beisa Reef
Granite-hosted nODULES:	Rows 1-2 DHF9 Rows 3-7 TKB3 Row 8 DRH10
Quartz vein-hosted nODULES:	Rows 1-5 Quartz-pyrite vein in Vaal Reef Rows 6-8 Carbonaceous material within fluid inclusions

to the tendency for lighter hydrocarbon compositions to be more labile and migrate further in the rock medium. This is possibly the case for the late, uranium deficient, bitumen veinlet from the Beisa Reef (Fig. 4e and f) which cuts through a carbonaceous seam and has been emplaced along an existing micro-fracture. The relative intensities of 1600 and 1350 cm⁻¹ peaks may, therefore, reflect compositional differences related to differential migration, in much the same way as bitumens (for example, from the Huronian deposits) exhibit lighter ¹³C values than in situ kerogen. This assertion still, however, requires testing in environments where bitumen migration distances are well constrained.

Values attributed to L1600 show wide variations for both the migrated bitumens and the sediment hosted carbonaceous matter (Fig.11). Landais et al. (1990a) have suggested that

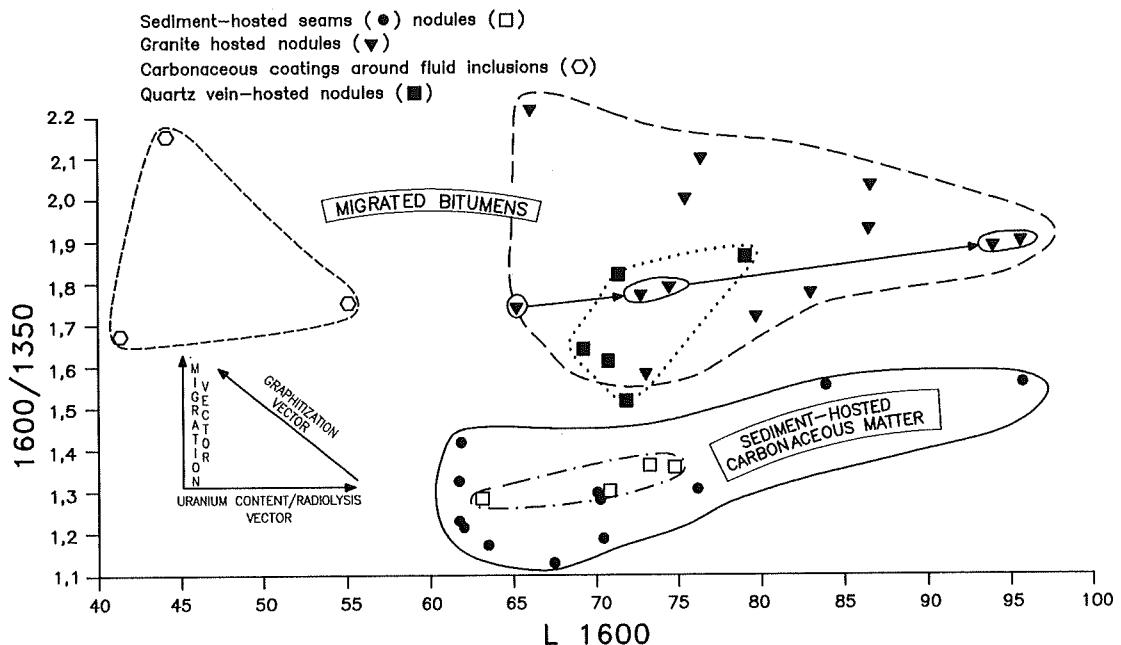


Figure 11: Plot of the peak intensity ratio (1600/1350) versus half-height width (L1600) for Raman spectra from the various modes of occurrence of carbonaceous material described in the present study; data is from Table 3.

L1600 is broadly correlatable with the uranium content of Witwatersrand carbonaceous matter, with $L1600 < 68$ for carbonaceous matter with $U < 5\%$ and vice versa. The present, more extensive data set, is consistent with this observation and explains, for example, the low L1600 values attributed to the carbonaceous linings in fluid inclusions which, although not analysed, are likely to have low or insignificant uranium contents. However, the range of L1600 (Fig. 11) is as variable for the carbonaceous seams (with up to 11.5% uranium) as it is for the quartz vein- and granitoid-hosted bitumen nodules which typically have much lower uranium contents (Table 2). Consequently, the compositional and structural modifications that are reflected in the Raman spectral characteristics are not simply related to bulk uranium content, but also the distribution of uranium-bearing minerals within the carbonaceous matter and the volume proportions of bitumen relative to the radiation-emitting phase which it surrounds or replaces. In order to explain the variation in L1600 in granitoid-hosted bitumen, where isolated uranium-bearing accessory minerals are selectively replaced by bitumen, three nodules exhibiting a progressive sequence of replacement, were analysed (Robb et al., 1994). A systematic increase in L1600 occurs as the proportion of bitumen within the host radiation-emitting phase decreases (refer to the arrowed points shown in Figure 11). This suggests that the structural parameter reflected in the half height width varies in relation to the intensity of radiation, but that the latter does not significantly shift the peak intensity ratios.

In summary, therefore, a number of variables appear to affect the Raman spectral characteristics of Witwatersrand carbonaceous matter and these are indicated as trend or displacement vectors in Figure 11. Thermal maturation and graphitization result in reduced I1600/I1350 and L1600 which might explain the characteristics of carbonaceous linings in

fluid inclusions which are themselves hosted in quartz veins cutting through the sedimentary sequence. In general, however, increases in I1600/I1350 appear to reflect a migration trend perhaps related to compositional differences arising from the fact that lighter hydrocarbons tend to migrate further. Variations in L1600 reflect structural changes in the organic matter which are correlatable with uranium content or the relative proportions of bitumen and associated radiation-emitting phase.

MICRO-FTIR SPECTROSCOPY

Comparative spectra for sediment-hosted seams and nodules exhibit very similar characteristics (Fig. 12 a and b). A spectrum from a granitoid-hosted nodule, however, reveals a higher aliphatic CH absorbance, a higher aliphatic CH/aromatic C=C peak ratio and a shift of the aromatic C=C band towards higher wavenumbers (Fig. 12c). The overall composition of the granite nodule is clearly very similar to the sediment-hosted material, but the structure of the former is less aromatic and less condensed. These features are again consistent with the notion that the granite nodules formed from hydrocarbons that had migrated some distance from their source.

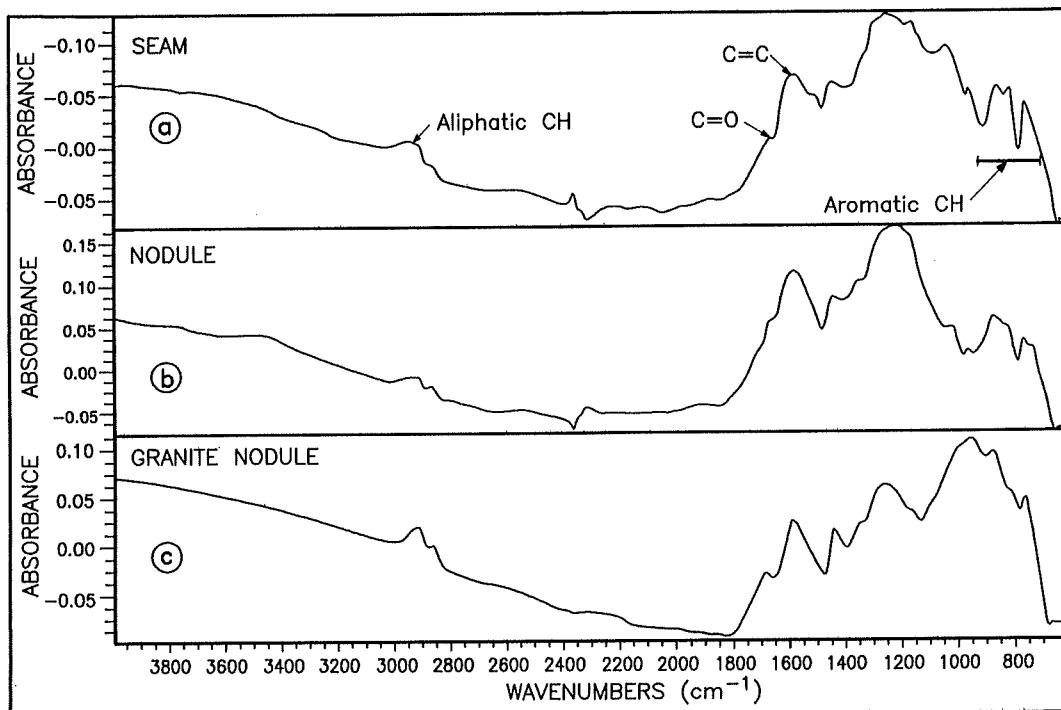


Figure 12: Selected micro-FTIR spectra for the various modes of occurrence of carbonaceous material described in the present study; a. and b. represent seams and nodules from within the conglomerates; c. represents a granite-hosted nodule.

Interesting structural and compositional changes are also evident in FTIR spectra of seam related organic material as a function of proximity to individual uraninite particles within the seams (Landais et al., 1989). Spectra well removed from a uraninite grain exhibit all the functional groups described above (Fig 13a). However, spectra obtained at the limit and within the high reflectance, pleochroic halo which often surrounds the larger uraninite

grains in seams are characterized by a loss in both aliphatic and aromatic CH and an increase in the concentration of C=C and C=O functions. The diameter of the halo surrounding the uraninite grain approximately coincides with the travel distance of an α particle emitted from the edge of the uraninite grain and appears to provide evidence for the fact that severe compositional and structural changes result from α -radiation. The presence of α -radiation halos does not militate against the possibility that different or diminished radiolytic changes also accrue in carbonaceous matter that is further removed from a source of irradiation, and subject only to γ and β radiation.

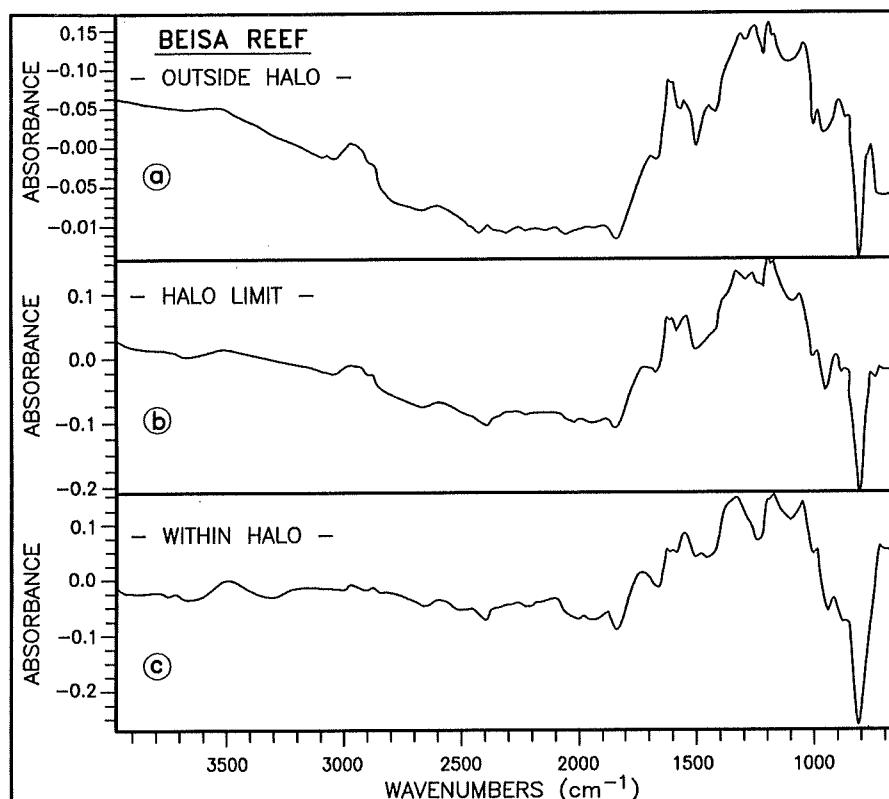


Figure 13: Contrasting micro-FTIR spectral characteristics in a carbonaceous seam from the Beisa Reef as a function of the proximity of the incident beam to the halo of enhanced reflection pleochroism adjacent to a uraninite grain within the seam.

COMPARISONS WITH THE HURONIAN DEPOSITS

The conglomerate-hosted uranium deposits of the Elliot Lake-Blind River region of the late-Proterozoic Huronian Basin in Ontario, Canada, have many similarities with those of the Witwatersrand Basin and these are relevant to the present study. Detrital accumulations of mainly uraninite, which co-exist with carbonaceous matter, were deposited in fining-upward sedimentary cycles. Conglomerates represent the initiation of a cycle which is terminated by finer sediment and layers of uraninite (Nagy, 1993). The organic substances which are associated with the uraninite are believed to have been derived from cyanobacterial mats which grew during the low energy period of the sedimentary cycle and helped to trap

the uraninite particles (Nagy and Mossman, 1992; Willingham et al., 1985). Carbonaceous matter now occurs in two forms: first as thin stratiform layers of kerogen which contains 20-30% uranium (mainly as dispersed uraninite fragments within the seam), and second as bituminous globules or fracture/vein fillings which have <5ppm uranium. Kerogen and bitumen are clearly identifiable in terms of mode of occurrence, texture, reflectance, uranium content and carbon isotope signature. Bitumen has apparently been derived almost *in situ* from its syngenetic parental kerogen and the two substances have been noted in juxtaposition, suggesting that migration has been fairly restricted (in the order of metres; Nagy, 1993). H/C versus O/C plots for the Huronian Basin straddle the catagenic to metagenic transition and indicate that organic matter was not as mature as in the Witwatersrand Basin. The differences that exist between Witwatersrand and Huronian carbonaceous matter, appear to be related, not so much to origin, but to degree of maturation and the factors affecting migration and alteration of bitumen.

DISCUSSION AND CONCLUSIONS

Origin and evolution of Witwatersrand organic matter

The carbon isotopic signature of carbonaceous matter in the Witwatersrand Basin indicates that it is biogenic in origin. In most previous studies this material is referred to as kerogen, implying that the organic source rocks occur within the basin. Since it is now clear that much of the organic matter in and around the basin has been mobilized some distance from its site of generation, the location of the organic source rock becomes a pertinent problem. It is, for example, conceivable that the source rocks were not within the Witwatersrand Basin at all, but in an overlying sequence such as the ca. 2550 Ma dolomites of the Transvaal Supergroup, which contained abundant organic material now preserved as algal stromatolites. This suggestion appears to receive support from the 2330-2380 Ma age bracket suggested for the deposition of the Witwatersrand bitumens (Allsopp et al., 1986; Robb et al., 1994), which coincides with the time when the Transvaal dolomites underwent substantial burial by the overlying Pretoria Group sediments. The notion of a Transvaal source of the hydrocarbons implies that the latter would have had to migrate laterally and downwards in the crust, through the extensive, blanketing cover of the Ventersdorp flood basalts, in order to percolate into the underlying Witwatersrand sequences, an encumbrance that effectively eliminates this sequence as a likely source rock. Since it is also unlikely that an organic source rock could have existed beneath the Witwatersrand Basin (i.e. the subjacent Dominion Group comprises little or no organic material), the most expedient source rocks are, therefore, most likely to be found within the basin itself. Gray et al. (1997) have suggested that shales, which occur mainly in the lower part of the Witwatersrand Supergroup (i.e. the West Rand Group), might have had considerably higher total organic carbon contents in the past and most likely represent the rocks from which the bitumen, which now occurs predominantly in the uraniferous conglomerates of the upper portion of the sequence, was derived. It is also possible that the distal portions of major unconformity surfaces might also have represented sites where colonies of prokaryotic micro-organisms flourished, and that hydrocarbons simply migrated up-dip during compaction and biodegradation.

If, as seems likely, the Witwatersrand organic material was derived *in situ*, then both kerogen and bitumen are likely to exist in the sequence. Whereas bitumens are easily

recognized as migrated products, the *in situ* residues of biodegradation may be more difficult to identify. The carbonaceous seams, for example, present a problem with respect to descriptive nomenclature. Features such as the dis-aggregation and replacement of uraninite by carbonaceous matter suggest that the seams are bituminous, although this may be inadequate proof if the original micro-organisms had a predilection for uraninite (Hallbauer, 1975). Although uranium and other metals may be absorbed by microbiota, it is unlikely that primitive prokaryotic organisms could have digested and then reconstituted uranium to form the types of textures observed in Figure 2. It also seems unlikely that hydrocarbon and uranium bearing fluids were co-precipitated, as suggested by Gray et al. (1997), since the bitumen seams and nodules have consolidated around uraninite grains that typically bear every resemblance of detrital particles (Figure 2 F). The observations that relate to the paragenetic sequence of ore deposition in the Witwatersrand Basin are consistent with the view that most of the bitumen in the Witwatersrand Basin has polymerized around uraninite grains at a late stage in the post-depositional history of the sediments.

The distinction between kerogen and bitumen in the Witwatersrand sediments is unclear and perhaps masked by the extreme age and degree of maturation of the organic material. As in the Huronian Basin, bitumen and kerogen may be spatially juxtaposed indicating limited migration distances. On the basis of the present study, however, it is suggested that most of the carbonaceous seams in the Witwatersrand deposits comprise bitumen which has been solidified by the effects of radiolysis. Most of the organic material in the Witwatersrand Basin, with the exception of occasional bitumen veins such as those in Figure 4e, is associated with substantial amounts of uranium (Table 2). By contrast, other uranium deposits associated with carbonaceous material, such as those at Oklo, Saskatchewan, the Huronian, Lodeve and Arizona, contain bitumens which are both mineralized and barren with respect to uranium (Corsial et al., 1990; Landais et al., 1990; Landais 1993). Radiolytic polymerization appears, therefore, to have been the main precipitation mechanism for Witwatersrand bitumens, a feature which is not always the case in other uranium deposits.

Petrographic studies reveal that carbonaceous matter in and around the Witwatersrand Basin occurs in a variety of settings and is texturally variable. In addition, it is heterogeneous in terms of chemical composition and degree of structural organization. Although highly mature, the carbonaceous matter exhibits a wider range in bulk composition than expected of unaltered, algal-derived kerogen, and this reflects modification related either to demethanation or oxidation/reduction. Many of the organic factors described above vary systematically as a function of the uranium content of the carbonaceous matter and this is also consistent with the notion that radiolysis, rather than the more typical manifestations of hydrous pyrolysis, played the major role in compositional and structural modifications.

Organic maturation and paragenetic sequence

Many ores, especially uranium and base metal sediment-hosted types, are associated with carbonaceous matter (Landais, 1993; Parnell, 1988; 1993). The timing of bitumen formation in relation to ore deposition is variable and examples of pre-, syn and post-ore hydrocarbons in different deposit types have been documented. In certain cases bitumens are genetically unrelated to the process of ore formation, while in others organic matter has

played a role in the precipitation of metals through redox reactions or absorption. In a few cases, a close genetic link suggests that organo-metallic complexes appear to have been associated with the aqueous solutions responsible for concentration of ore components. In the Witwatersrand deposits the latter two scenarios may both have applied since carbonaceous matter is intimately associated with gold and uranium, the deposition of which is reflected in a complex and long-lived paragenetic sequence (Robb et al., 1997).

A scheme illustrating the paragenetic sequence of ore formation in the Witwatersrand Basin is shown in Figure 14. The initial concentration of alloigenic ore constituents, including uraninite, took place during sedimentation which, for the upper auriferous part of the sequence, took place between 2900 and 2700 Ma. This would also, therefore, be the period when prokaryotic microbiota flourished in suitable environments within the basin. Post-depositional ore modification took place for at least 700 Ma after termination of

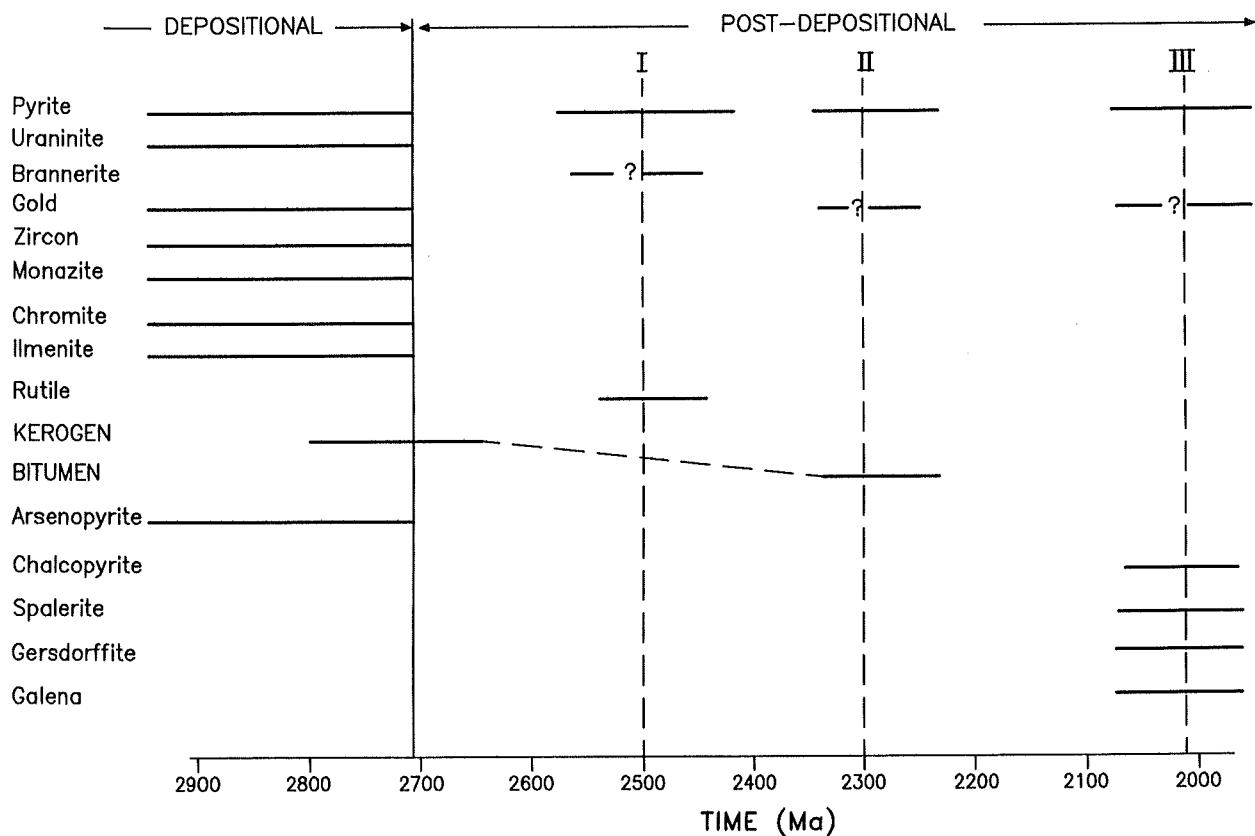


Figure 14: Simplified scheme showing the appearance of bitumen in relation to the paragenetic sequence of ore deposition in the Witwatersrand Basin.

sedimentation and probably occurred during three main events, at circa 2500 Ma, 2300 Ma and 2000 Ma (Robb and Meyer, 1995; Robb et al, 1997). Pb-Pb isotopic data from authigenic pyrite suggests that a major event of sulphide remobilization took place at around 2500 Ma (Robb et al., 1996); this apparently preceded bitumen formation according to both petrographic evidence (Fig 4 a,b) and U- Pb dating of carbonaceous matter (Robb et al., 1994). Hydrocarbon production and fixation of bitumens around uraninite grains appears to

have taken place somewhere around 2380-2330 Ma according to the dating of both sediment- and granitoid-hosted carbonaceous material (Robb et al., 1994). Bitumen appears, therefore, to have formed subsequent to early sulphide remobilization at 2500 Ma, but prior to the final major authigenic mineral forming event at ca. 2000 Ma. The latter event is associated with the attainment of peak metamorphic conditions in the basin (Stevens et al., 1997) and also the remobilization of late sulphides and gold (Robb and Meyer, 1995). The presence of abundant gold associated with, but *post-dating* carbonaceous matter (Fig. 4C,D), indicates that a substantial amount of the metal was precipitated late in the paragenetic sequence. The estimates of peak metamorphic conditions in the Witwatersrand gold fields are not inconsistent with the degree of maturation exhibited by the organic matter presently observed along the basin margins. These constraints need to be more rigorously tested, however, as the relationship between the metamorphic grade of organic material and that of the host sediments in deeper portions of the basin have obvious implications for the timing of bitumen precipitation relative to the peak metamorphic event (E. L. Tongu, personal communication, 1996).

Role of carbonaceous matter in the mineralization process

The role of organic matter in the genesis of ore deposits is multi-faceted and complex (Saxby, 1976; Parnell et al., 1993). At low temperatures micro-organisms such as bacteria and fungi are able to concentrate uranium and other metals from solution (Milodowski et al., 1990). Mature organic matter is also often associated with metal concentrations by virtue of its ability to act as a powerful redox barrier to the passage of metal-charged hydrothermal solutions. In addition, however, hydrothermal solutions themselves often contain substantial amounts of organic ligands, which enhances their metal carrying capacity by leaching and metal complexation along the fluid pathway.

It is now considered unlikely that colonies of prokaryotic micro-organisms would have been capable of physically trapping uraninite, gold and other heavy mineral detritus and concentrating it during sedimentation. The reasons are twofold; first, it is difficult to conceive a mechanism whereby heavy particles could remain trapped in algal mats, and whether the latter would have been preserved in the high energy depositional environments that characterized the Witwatersrand conglomerates in the first place. Second, uraninite is almost always the principal mineral phase that occurs within the carbonaceous seams, and there is a notable paucity of other heavy mineral detritus (i.e. pyrite, zircon and chromite) which is far more abundant in the conglomerates. The association between uranium and carbonaceous matter in the Witwatersrand Basin is rather one where primary concentrations of detrital uraninite represent the sites where bitumens were precipitated and solidified by the effects of ionizing radiation and radiolytic polymerization. By contrast the association between gold and carbonaceous matter is probably related to the likelihood that bituminous seams acted as redox barriers that caused the precipitation of gold associated with the circulation of the late, peak metamorphic hydrothermal fluid. Robb and Meyer (1995) have suggested that, irrespective of whether gold was in solution as a chloride- or thio-complex, a decrease in local fO_2 would have the effect of precipitating gold out of solution. The gold-carbon association appears, therefore, to be chemical, and points to the paragenetically late mobilization of gold in the Witwatersrand deposits.

In addition to these relatively obvious paragenetic associations, there is now increasing evidence that organo-metal complexation occurred during the migration of hydrocarbon-bearing fluids in the Witwatersrand Basin. Petrographic evidence exists indicating that bituminous nodules in quartz veins are intimately associated with pyrite and gold (Drennan et al., 1995). In addition PIXE metal distribution maps of the same bituminous nodules show that a variety of metals, including gold, uranium , thorium, aresenic and copper, are distributed elementally throughout the bitumen, and not as discrete mineral inclusions (Robb et al., 1997). This supports the view that some form of organo-metallic complexation was taking place during the circulation of hydrocarbons in the basin and that this may have been a pertinent process in the post-depositional redistribution of ores (Robb et al., 1997). The mechanics of this process, and its significance in terms of exploration in the Witwatersrand Basin and surrounds, are topics that still require study and evaluation.

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