



The indigenous origin of Witwatersrand “carbon”

D.J. Mossman^{a,*}, W.E.L. Minter^b, A. Dutkiewicz^c, D.K. Hallbauer^d, S.C. George^e,
Q. Hennigh^f, T.O. Reimer^g, F.D. Horscroft^h

^a Department of Geography, Mount Allison University, Sackville, New Brunswick E4L 1A7, Canada

^b Department of Geological Sciences, University of Cape Town, Rondebosch 7700, South Africa

^c School of Geosciences, University of Sydney, Sydney, New South Wales 2006, Australia

^d Ortsstrasse 26, 07429 Doeschmitz, Germany

^e Department of Earth and Planetary Sciences, Macquarie University, Sydney, New South Wales 2109, Australia

^f Evolving Gold Corporation, Vancouver, British Columbia V6C 2X8, Canada

^g Bernhard May Str. 43, 65203 Wiesbaden, Germany

^h Hampton Wick, Surrey, KT1 4BA, United Kingdom

ARTICLE INFO

Article history:

Received 22 October 2007

Received in revised form 28 April 2008

Accepted 29 April 2008

Keywords:

Witwatersrand

Carbon

Indigenous

Spatial distribution

Kerogen

Bitumen

Fluid inclusion oil

ABSTRACT

In the Witwatersrand approximately 40% of the gold is intimately associated with so-called “carbon” in “carbon seam reefs”, which occur in over a dozen paleoplacers, many of them concentrated at two stratigraphic levels in the 7000-m-thick succession of Archean siliciclastic sedimentary rocks. This is reduced carbon, present as kerogen admixed in various proportions with derivative (now solid) bitumen(s). Oil generation and migration were active geological processes during Early Earth history. Numerous possible source rocks for oil generation, including the carbon seams themselves, occur within the Witwatersrand basin. In the Witwatersrand ore, oil-bearing fluid inclusions are also present, derived like the bitumen, by thermal maturation of the kerogen. The presence of kerogen and bitumen in the Witwatersrand sedimentary rocks, together with a wealth of observations on the spatial distribution of the carbon seams confirm that the carbon originated *in situ* from living organisms in microbial mat cover, as opposed to flowing in from elsewhere as liquid hydrocarbons as some researchers have suggested. Paleochannels, which truncated auriferous carbon seams early in the depositional history, are of widespread occurrence, and micro-synsedimentary faults offset carbon seams. The carbon seams are thus indigenous biogenic markers that grew contemporaneously with placer development. The various features highlighting the nature and spatial distribution of Witwatersrand carbon seams provide a classic case where field evidence trumps laboratory data in the reconstruction of geological processes.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The nature and origin of the so-called “carbon” in the Archean Witwatersrand gold deposits has long been a contentious issue. However, it is an important question because about 40% of the gold is intimately associated with the “carbon” (Nagy, 1993, p. 293). Thus, quite apart from the academic merit of correctly identifying the geologic origin of the carbon, this will help determine the location of much of the gold in so far as most of the paleoplacers containing carbon occur in distal facies. In short, more efficient mining will result.

The main concentration of carbon is in seams that occur at two stratigraphic horizons known as the Main Reef and the Bird Reef horizons. The high concentrations of gold associated with carbon

at these horizons led to their classification as “carbon seams reefs”. Their exploitation has provided the infrastructure for the entire gold mining industry and sustained the pre-eminent position of the Witwatersrand among gold producers. A high concentration of gold is widespread also in “quartz pebble reefs” with no carbon. These two types of reef are end members of different facies in the sedimentary environment of the Witwatersrand basin. Carbon seams are extensively but patchily developed on older paleosurfaces ranging from disconformities to unconformities (Jordaan et al., 1991; Minter, 1976, 1978), and all of the paleoplacers which contain carbon seams were deposited in braided-stream environments associated with pebbly-sand facies. According to a comprehensive review by Frimmel (2005), the atmosphere characteristic of the early Archean when those sedimentary rocks originated, is considered to have been reducing.

That “carbon” might be directly linked to once-living organisms was suggested by Sharpe (1949), and was first investigated in detail by Snyman (1965) using coal petrological techniques. It

* Corresponding author. Fax: +1 506 364 2625.

E-mail address: dmossm@mta.ca (D.J. Mossman).

was then thoroughly elaborated on by Hallbauer and co-workers in the mid-1970s (Hallbauer and van Warmelo, 1974; Hallbauer, 1975a,b). While the biogenic nature of Witwatersrand carbon is generally accepted (Spangenberg and Frimmel, 2001) the question whether it is indigenous remains a matter of debate. In contrast, “revisionists” (i.e., those supporting a hydrothermal origin of the gold) advocate a direct origin for the “carbon” from liquid hydrocarbons. In recent publications they show an inclination to cast all Witwatersrand carbon into the category of “bitumen” or “pyrobitumen” (Parnell, 1996, 2001; Gray et al., 1998; Barnicoat et al., 1997; Phillips and Law, 2000; England et al., 2001) with little regard for its possible syndeositional origins. However, Parnell (1999) has documented solid bitumen occupying minute fractures in quartz-pebbles from various goldfields across the Witwatersrand basin. Then, an example is reported by Gartz and Frimmel (1999) of bitumen nodules in veins which cross-cut pseudotachylite (attributable to the Vredefort impact event) in the Ventersdorp Contact Reef.

Concerning syndeositional origin of some Witwatersrand carbon there is one outstanding fact that cannot be ignored. This is that in numerous instances in the Witwatersrand goldfields there are carbon seams truncated by erosion channels present at two stratigraphic levels within the 7000-m-thick siliciclastic sedimentary succession. It might therefore reasonably be concluded that carbon seams comprised principally of protokerogen were present as part of the initial sedimentary package, and then erosion occurred. This is the only sequence that makes sense. Lest this fail to convince, our main purpose in this paper is to document more thoroughly the indigenous spatial distribution of Witwatersrand carbon seams.

2. Kerogen vs. bitumen in Witwatersrand rocks

Kerogen and bitumen are two of the most common forms of reduced carbon on Earth. However, their distinction is not always straightforward. Ambiguity stems from, among other things, the early assignation of “kerogen” as a term equivalent to oil shale (synonymous with so-called “pyrobitumen”) from which petroleum can be extracted by distillation (Tissot and Welte, 1984). Kerogen is now understood to be the remains of former living organisms (organic carbon); specifically, it is a solid polymer-like organic substance which has remained *in situ* since deposition (Mossman and Thompson-Rizer, 1993). As a chemical term it is the organic fraction insoluble in organic solvents, whereas “macerals” – a term describing the shape, texture, and optical nature of petrographically identifiable entities in kerogen – can contain both kerogen and bitumen fractions. Most macerals contain less than 10% bitumen. Another term requiring definition is “vitrinite”. Vitrinite is one of three major groups (*vitrinite*, *liptinite* and *inertinite*) into which macerals are divided according to their petrographic and chemical properties (Stach et al., 1982). *Vitrinite*, *sensu stricto*, is that component which derives mainly from ligno-cellulose components of plants. Derived in part from plant and animal lipids, *liptinite* is an exception to most macerals in that it can contain slightly more than 10% bitumen. *Inertinite* is a component derived from oxidation of plant/animal material (for details see Stach et al., 1982).

The terms kerogen and maceral are in practice used interchangeably for isolated organic matter (Mukhopadhyay, 1992). Kerogen can thus be considered as a complex mixture of high molecular weight organic materials (depending on the source and environment of the organic matter) formed by the diagenetic transformation of organic matter. Kerogen is a precursor to hydrocarbons but is not itself a hydrocarbon (Stach et al., 1982). In contrast, solid bitumen (hereafter sometimes simply referred to as “bitumen”) is a macromolecular organic compound which was once mobile as a viscous fluid but which has since solidified (Mossman

and Thompson-Rizer, 1993). A complication is the term “bitumen” used by organic geochemists (e.g., Tissot and Welte, 1984, p. 123), which is the fraction extractable with organic solvents (i.e., extractable organic matter) and which is quite different from solid bitumen. Unquestionably some solid bitumens enriched in heavy polar molecules such as asphaltenes, are insoluble, one example being albertite. Note that according to the definitions, neither kerogen nor bitumen consists solely of carbon, although with high grade metamorphism both are converted to graphite (Mossman and Nagy, 1996).

In some Phanerozoic source rocks, reduced carbon occurs as kerogen together with traces of bitumen where the latter evidently has either been generated, or has been arrested during migration through the rock (Thompson-Rizer, 1987). This holds true for kerogen-bearing rocks of any geological age, which have attained the oil window, given the numerous factors which can complicate the tracing of the evolutionary pathways of bitumen (Mossman and Nagy, 1996). Examples include the oil shales of the 2.1 Ga Franceville Series of Gabon (Bros, 1993; Mossman et al., 1993), the Karelian shungite [described by (Mastalerz et al., 2001, p. 117) as “. . . *in situ* organic matter, with solid bitumen occurring as small veins.”], and the 2.7 Ga Pilbara black shales (Rasmussen, 2005). Stupp (1984) recognized the phenomenon in the occurrences of kerogen as both seams and granules in Pongola Supergroup and Moodies Group sedimentary rocks. In all these cases, both kerogen and bitumen are recorded. Likewise for the 2.7–2.9 Ga siliciclastic rocks of the Witwatersrand there are many reports of a mixture of kerogen and bitumen (Zumberge et al., 1978; Smits, 1984; Mossman, 1987; Jordaan et al., 1991). Thus, while we agree that bitumen occurs in Witwatersrand clastic sedimentary rocks, it clearly is not present to the exclusion of kerogen, and certainly not for the reason given by England et al. (2001, p. 1907) who, simply (and erroneously), state that “Because the *Witwatersrand* (our italics) carbonaceous matter is not exclusively carbon, it should more strictly be referred to as bitumen.”

Standard methodologies, which rely heavily on experience, are used to distinguish kerogen from bitumen (e.g., Stach et al., 1982; Bustin et al., 1983; Mukhopadhyay, 1992; Mossman and Nagy, 1996). One of the main problems in this procedure is maturation. If the reflectance (R_o) is <2%, the distinction is readily made; however, if $R_o > 2\%$, then it may be very difficult (at least optically) to distinguish bitumen from kerogen. Nevertheless, some macerals are recognizable even through to the development of meta-anthracite (Tissot and Welte, 1984). Fortunately, low-grade metamorphism characterizes several important Precambrian sedimentary successions (see below), among them the Witwatersrand. This condition facilitates recognition of primary features in sedimentary rocks of all ages, including the precursor(s) of constituent kerogen and bitumen (Mossman and Thompson-Rizer, 1993). In Witwatersrand rocks, organic matter of uncertain affinity, as distinct from bitumen on the basis of texture and morphology, is referred to as kerogen or to a specific maceral group (e.g., vitrinite-like, etc.). Using standard procedures (Bustin et al., 1983; Mukhopadhyay, 1992) the distinction between kerogen and bitumen is illustrated by petrographic examination of carbon from the Vaal Reef in the Klerksdorp Goldfield.

Vaal Reef carbon shows a textural maturity well below the onset of metamorphism (~4.5% R_o), although there are of course striking differences between the maximum (>3% R_o) and minimum (1.22–1.58% R_o) maturity (Fig. 1). These values are similar to those reported by Gray et al. (1998) for Vaal Reef carbon, except we record that minor amounts of kerogen accompany the dominant bitumen in these samples. The local dominance of solid bitumen over kerogen can account for the presence of “carbonaceous mesophase” elaborated on by Gray et al. (1998) as a characteristic of bitumen

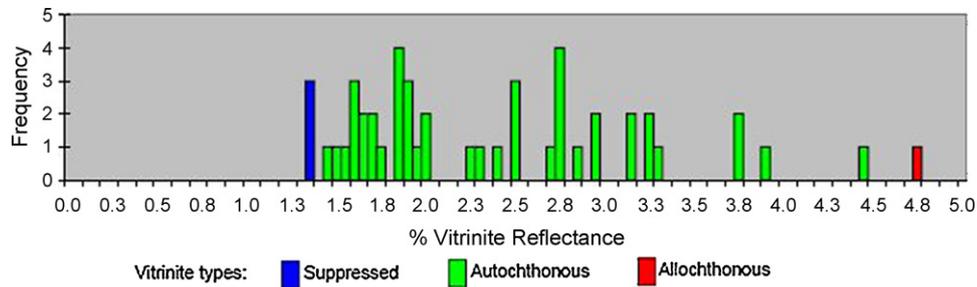


Fig. 1. Random reflectance data (R_0) for 44 vitrinite-like grains measured in a typical Vaal Reef sample show a maturity (mean of all autochthonous vitrinite-like grains = 2.42% R_0) less than early metamorphism stage. Vitrinite (i.e., vitrinite-like maceral and vitrinite-like solid bitumen) types include: suppressed (lower than normal R_0 , attributable to such features as type of hydrocarbon within bituminous material, amount of organic sulfur, manner of original deposition, etc.); autochthonous (normal R_0); and allochthonous (recycled or heat-affected vitrinite-like grains or solid bitumen). See text for details.

“mesophased” by hydrothermal fluids; Gray et al. (1998) assume a late-stage hydrothermal flux event to account for the occurrence of bedding-perpendicular anisotropy. The fact that both bedding-parallel and bedding-perpendicular anisotropy occur in the carbon is accounted for by the existence of both bitumen and kerogen in the Witwatersrand carbon seams.

Unlike carbon of hydrothermal origin, which always has the same R_0 , the reflectance values of autochthonous vitrinite grains in the Vaal Reef samples are characterized by quite a wide range of R_0 values due to the progressive development of anisotropy and homogenization (Mukhopadhyay, 1992). Specifically, the kerogen component consists of inertinite-like macerals (incipient or broken cell structures similar to semifusinite) (Fig. 2) and vitrinite-like macerals including gelified remains of cell-like tissues (see Fig. 3). That several different macerals are observed in Vaal Reef carbon is precisely a characteristic of oil source rocks in that no one maceral (and certainly not bitumen) occurs to the exclusion of all others.

Kerogen from Archean rocks such as those in the Witwatersrand, is most likely of cyanobacterial origin because cyanobacteria are one of the main life forms understood to have been on the planet over 2.7 Ga ago (e.g., Brocks et al., 1999). Cyanobacterial biomarkers such as 2α -methylhopane hydrocarbons, have been identified in Archean metasedimentary rocks from the Pilbara (Brocks et al., 1999, 2003) and in Paleoproterozoic fluid inclusion oils in the 2.45 Ga Elliot Lake Matinenda Formation (Dutkiewicz et al., 2006)

and the 2.1 Ga Franceville Series at Oklo (Dutkiewicz et al., 2007).

3. Liquid oil and possible source rocks

Dutkiewicz et al. (1998) first identified oil-bearing fluid inclusions in authigenic cements in Witwatersrand ores. Drennan et al. (1999) and Frimmel et al. (1999) focused on the aqueous and gaseous components, including hydrocarbon gases, of fluid inclusions associated with gold mineralization. England et al. (2002) have elegantly confirmed that “... processes of oil generation and migration, and their timing relative to burial history, have not changed since the Archean.” We are currently investigating more precisely the nature of the liquid hydrocarbons.

Fluorescent oil-bearing fluid inclusions are common within quartz arenites and conglomerates from the Vaal and Steyn Reefs. They are usually between 5 and 10 μm in diameter, and display irregular, spherical, oval and negative crystal shapes. They occur as trails within intragranular microfractures (Fig. 4A and B) and within transgranular microfractures cutting sutured framework quartz grains and quartz cement as shown in Fig. 4C and D (see also Dutkiewicz et al., 1998).

The oil-bearing fluid inclusions usually comprise three or four phases, most commonly as H_2O –oil–gas mixtures (Fig. 4E–H). Gas-rich inclusions comprising 50–95 vol.% gas with a thin rim of oil and in some cases an aqueous phase at the contact between the inclusion cavity and its mineral host are a relatively minor com-

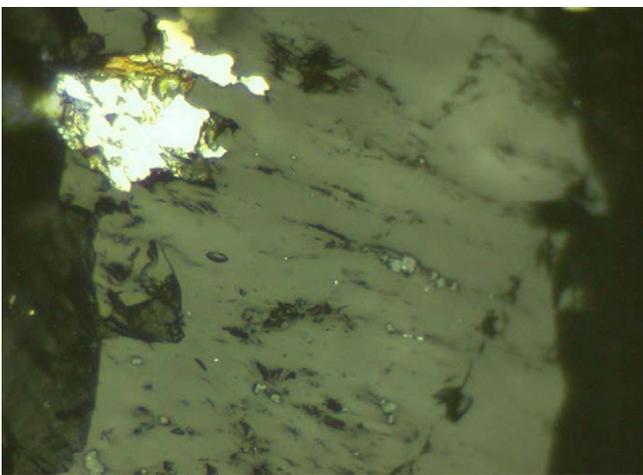


Fig. 2. Reflected light photomicrograph, showing organic remains in a Vaal Reef carbon seam (Anglo American Corporation specimen No. 304, Klerksdorp Gold-field). Inertinite-like structures (most likely oxidized cellular components) have void spaces partially filled with uraninite and sulfides (pyrite and radiogenic galena). The highly reflecting white patch is galena. Field of view is approximately 100 μm . Specimen housed in Department of Geography, Mount Allison University. Photomicrograph by P.K. Mukhopadhyay. See text for details.

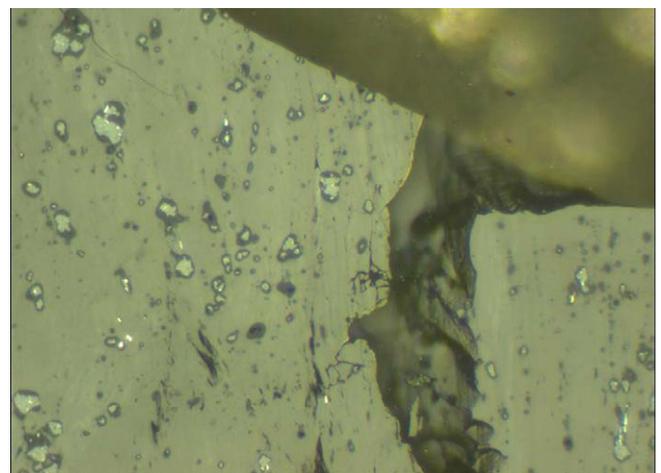


Fig. 3. Reflected light photomicrograph, showing organic remains in a Vaal Reef carbon seam (Anglo American Corporation specimen No. 304). Vitrinite-like (similar to collogelinite) contains grains of uraninite (grey) and lesser sulfides (pyrite and radiogenic galena, light grey and white). Specimen housed in Department of Geography, Mount Allison University. Field of view approximately 100 μm . Photograph by P.K. Mukhopadhyay.

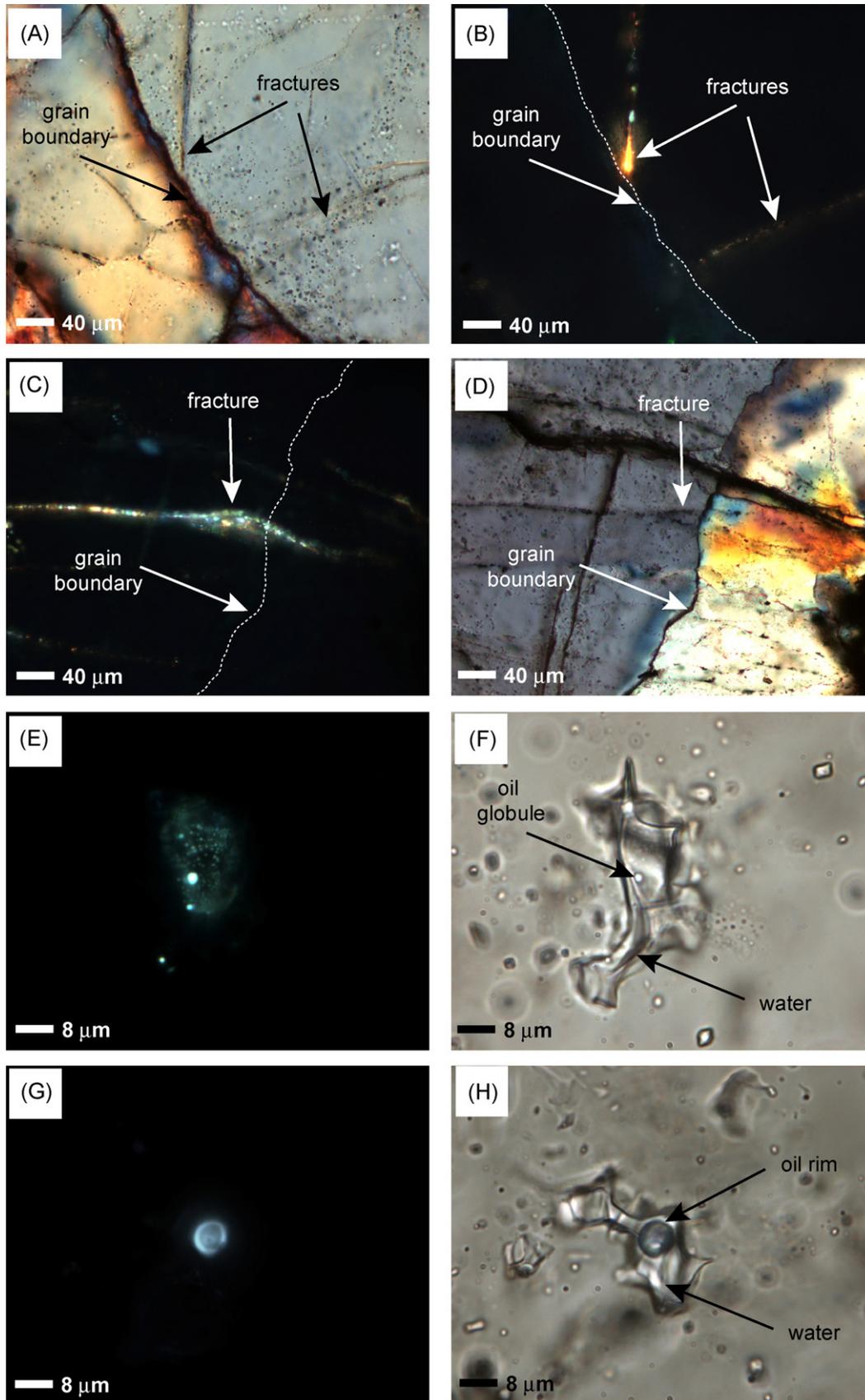


Fig. 4. Oil-bearing fluid inclusions and their textural contexts in samples Vaal Reef 304 (A–D) and WRV64 (E–H). Photomicrographs (A, D, F, and H), transmitted light; (B, C, E, and G) UV-epifluorescence. A and B show trails of oil-bearing fluid inclusions within intragranular microfractures terminating at the boundary between two detrital quartz grains. C and D show trails of oil-bearing fluid inclusions within a transgranular microfracture cutting the boundary between two detrital quartz grains. E and F show a large aqueous fluid inclusion containing globules of oil. The inclusion occurs within a microfracture in a detrital quartz grain. G and H show a three-phase fluid inclusion comprising a gas bubble, an oil rim and water within a microfracture in a detrital quartz grain.

ponent of the fluid inclusion population. Drennan et al. (1999) established the presence of CH_4 , C_2H_6 and C_3H_8 gases within some of the CO_2 -rich aqueous fluid inclusions, which were trapped with 8–10 wt.% $\text{NaCl}_{\text{equiv}}$ aqueous fluid at temperatures between 230 and 280 °C in late-stage quartz veins. Carbonic oil-bearing fluid inclusions reported in Dutkiewicz et al. (1998) may be related to early inclusion populations trapped in vein quartz described by Drennan et al. (1999). Textural evidence thus indicates multiple phases of oil migration and entrapment of oil, water and gas inside fluid inclusions. Preliminary microthermometry of aqueous oil-bearing fluid inclusions trapped in intragranular fractures indicates homogenisation temperatures around 160 °C consistent with burial digenesis, and the presence of hypersaline brines with salinities around 20 wt.% $\text{NaCl}_{\text{equiv}}$. These salinities are considerably higher than those determined by Frimmel et al. (1999) and Drennan et al. (1999) and indicate that hydrocarbon migration in the Witwatersrand Basin involved fluids of highly variable chemistries that may not necessarily have been associated with gold mineralization.

While the source of the inclusion oil is the subject of on-going work involving gas chromatography–mass spectrometry of inclusion oil and source rock extracts, some of the oil and its related bitumen will have been locally derived from the carbon seams such as the Vaal Reef during burial maturation or from a source within the Witwatersrand Basin as suggested by Barnicoat et al. (1997), Gray et al. (1998) and Spangenberg and Frimmel (2001). The Booyens Shale with up to 0.42% reduced carbon (Boice et al., 2007) and shales of the Jeppetown Subgroup with up to 0.34% reduced carbon (Danchin, 1970) must be numbered among possible sources.

4. Nature and spatial distribution of Witwatersrand carbon seams

The argument that the carbon associated with the Witwatersrand gold deposits originated in terrestrial microbial mats is not new (Spilisbury, 1908; Pretorius, 1976). What is new is an increased

recognition of the evidence for extensive microbial activity in Precambrian siliciclastic sedimentary rocks, especially in continental settings. Microbial mats influence physical and chemical processes in siliciclastic sedimentary environments by (1) stabilizing depositional surfaces, (2) trapping and binding sediment and generally enhancing sediment accumulation, (3) prompting photosynthesis and consequent local oxygen build-up, (4) stimulating biomineralization either directly, or upon decomposition of mat material by heterotrophic bacteria resulting in the growth of minerals such as marcasite, pyrite, and siderite along distinct surfaces outlining former mat boundaries. This was probably a function of prevailing pH associated with pyritiferous concentrations within placer sediments, the detrital pyrite, for example, owing its preservation to low oxygen levels. Widespread development of microbial mats on the Precambrian landscape, like vascular plants in later times, helped stabilize loose sediment thus facilitating weathering, contributing to the production of first cycle quartz sandstones and quartz-pebble conglomerates (Dott, 2003). Opportunities doubtless existed for organic development throughout the stacked fluvial deposits, though it is chiefly those within the Witwatersrand placers that are preserved.

The following observations bear directly on the origin and distribution of the Witwatersrand carbon seams. Given the direct biogenic origin of the kerogen component of the common kerogen and bitumen mix in the carbon seams, they are testimony to diverse indigenous (syndimentary) features.

4.1. Carbon seams are in numerous instances truncated by paleoerosion channels

The truncation of carbon seams by erosion channel deposits is irrefutable support for the concept of their primary sedimentary deposition. The Carbon Leader, one of the richest gold-bearing carbon seams in the Central Rand Group, is a prime example. It occurs intermittently upon a paleoerosion surface over hundreds

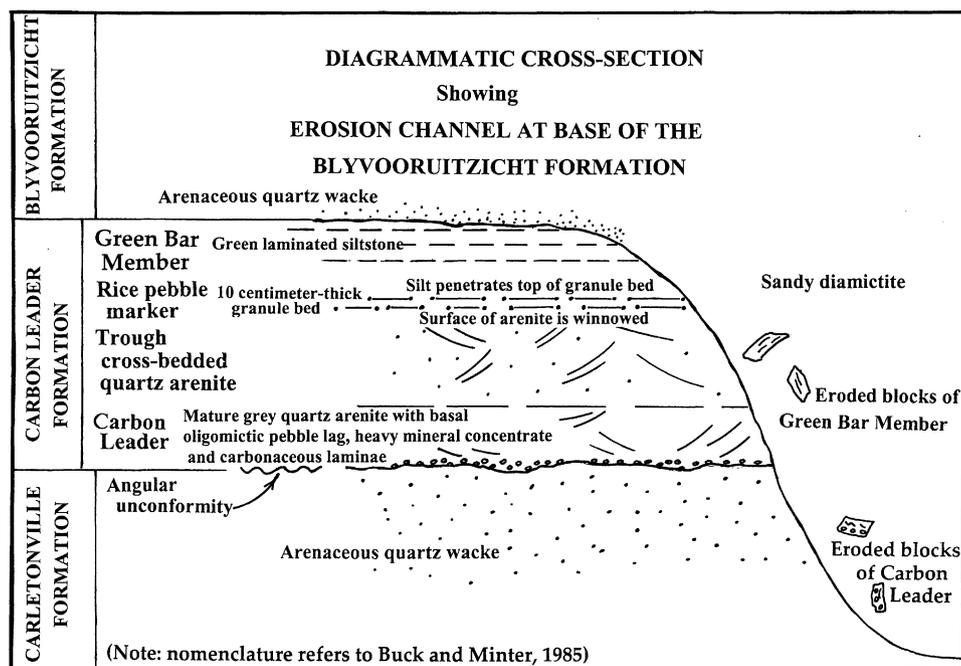


Fig. 5. Diagrammatic section of an erosion channel which has truncated the Carbon Leader Reef at the base of the Blyvooruitzicht Formation, East Driefontein Mine. This channel is up to 2.2 km wide; maximum depth is 100 m. Note the presence of eroded blocks of Carbon Leader and Greenbar Shale within the channel. Nomenclature refers to Buck and Minter (1985). (cf. Engelbrecht et al., 1986, p. 604).

Table 1
Gold mine ownership changes and renaming of Witwatersrand gold mines and goldfields in recent years

Previous name	New name
Western Holdings	Harmony Welkom Operations
Loraine	President Steyn
West Driefontein	Driefontein
East Driefontein	Driefontein
Blyvooruitzicht	Blyvooruitzicht Operations
Vaal Reefs South	Great Nologwa
Welkom	Harmony Welkom Operations
Western Reefs	Harmony Orkney Operations
Saaiplaas	Harmony Free State operations
Klerksdorp Goldfield	Klerksdorp Area
Welkom Goldfield	Free State Area
Orange Free State Goldfield	Free State Area
Carletonville Goldfield	West Wits Line

of square kilometers and has been mined sporadically for over about 120 km² (Buck and Minter, 1985). It is laterally continuous for tens of square kilometers. As shown in Fig. 5, the Carbon Leader Reef is clearly truncated by an erosion channel. The erosion event reflects a low stand of sea level that occurred throughout the Witwatersrand Basin following deposition of the Main Reef, and was repeated after the Kimberley Reef deposition (Minter, 1982, p. 135). The indigenous nature of this carbon seam is emphasized by the fact that fragments of the disrupted seam were redeposited in the channel itself. This is compelling evidence, proof positive of the contemporaneity of carbon seams and conglomerates. Flynn (1991) notes, that in the West Driefontein Mine, about 15–20% of the Carbon Leader has been eliminated by erosion in a broad 2200-m-wide zone extending southeastwards into the East Driefontein Mine (see Engelbrecht et al., 1986, p. 606). [Table 1 lists the ownership changes and renaming of various Witwatersrand mines and goldfields which have occurred in recent years; for simplicity the original names are here retained].

The truncation of the Carbon Leader is not an isolated instance. Another example, supplied by Cheatle (1991, p. 55), shows the truncation of the “C” (Cristalkop) Reef against a paleochannel (Fig. 6). This reef contains a continuous basal carbon seam, and is the youngest of the Johannesburg Subgroup in the Central Rand Group.

The presence of carbon seams at different stratigraphic levels in the ~7000-m-thick Witwatersrand succession of siliciclastic rocks has precedents in the earliest known microbial mats in siliciclastic rocks of the 2.9 Ga Pongola Supergroup (Noffke et al., 2003a, 2003b). Stupp (1984, p. 90–91) recognized the phenomenon in the

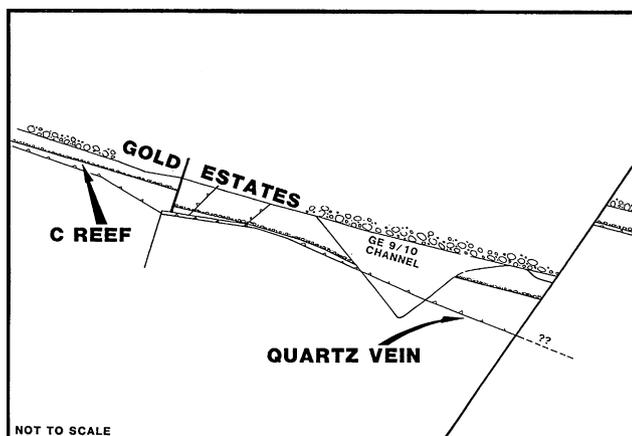


Fig. 6. Diagram shows basal carbon seam of the “C” Reef, Vaal Reefs, Vaal Reefs South Mine, truncated by an erosion channel (after Cheatle, 1991, p. 55, Fig. 3.2).

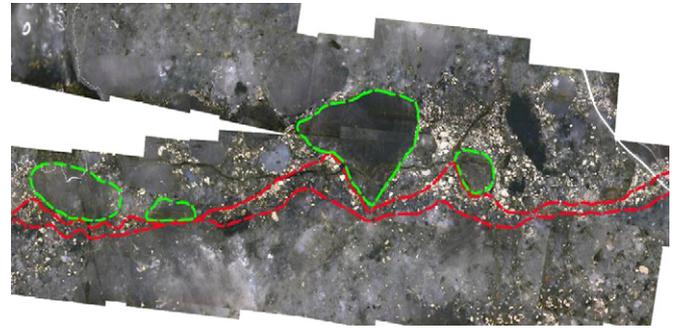


Fig. 7. Basal contact of the Carbon Leader, here less than 0.5 cm thick (outlined in red), Blyvooruitzicht Mine, Carletonville. Quartz-pebbles (outlined in green) appear to have deformed the carbon seam, although the effect might be partly the result of imbrication (current flow from the right). Note that the carbon seam thickens and protrudes upward on the left hand side of pebbles in the hanging wall (due to soft-sediment deformation). It does not transect the large pebble as would be expected if the Carbon Leader were occupying a structure, although a small crack (black) exists at the top of the pebble. Large pebble is 1.5 cm in diameter. Photograph and specimen, QH.

occurrence of seams and granules of kerogen in Pongola Group and Moodies Group metasedimentary rocks, which considerably pre-date the Witwatersrand. Carbon is also present in the Dominion Reef in the approximately 3.074 Ga Dominion Group directly underlying the Witwatersrand Supergroup in the northwestern part of the basin, as first mentioned by Liebenberg (1955). C. Kingsley, former group sedimentologist at Klerksdorp with Anglo American Corporation, confirms (personal communication to DKH, January, 2008) that carbon seams exist in the Upper Reef of the Dominion Reef system. One of us (DKH) has observed these seams in the Afrikander Leases Mine, which is located about 30 km northwest of the Klerksdorp Goldfield and scheduled for reopening shortly as a uranium producer.

4.2. Carbon seams depressed by pebbles: (an artefact of imbrication?)

Like several other carbon seams, the Carbon Leader in many instances is depressed by clasts (usually quartz) [e.g., Plumstead, 1969; Minter, 1975a, 1991]. Fig. 7 shows the Carbon Leader (in Blyvooruitzicht Mine) ranging from about 2 mm to 1 cm thick, apparently depressed by several small clasts. It is possible that the “depressions” are in part an artefact of imbrication, with current flow from the right (see also Minter, 2006, Fig. 6, p. 109). An additional interesting feature occurs in the form of a small grain of porous, concentrically-banded pyrite (Fig. 8) directly above the carbon seam. Relevant to this observation is what currently seems to be a centerpiece of revisionist argument, namely the concept that fractures allowed penetration of liquid hydrocarbons to form the carbon seams. Fracturing due to low-angle thrusting is

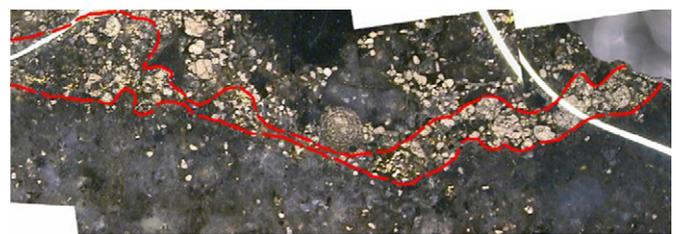


Fig. 8. Porous, concentrically zoned pyrite grain (center of photo) ~2 mm diameter (possibly diagenetic in original source area?), occurring directly above the Carbon Leader basal contact (outlined in red), Blyvooruitzicht Mine. Photograph and specimen, QH.

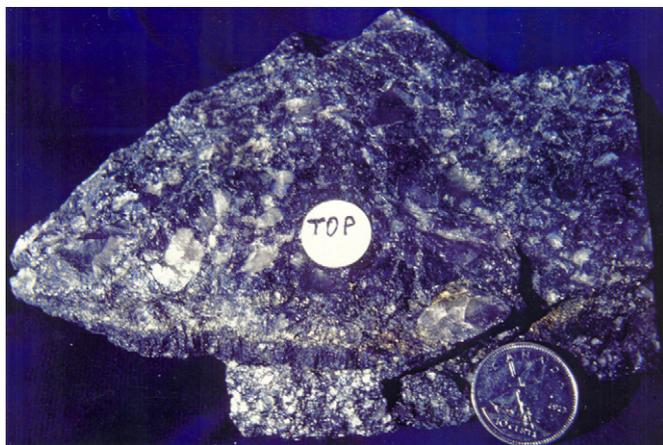


Fig. 9. Rough hand specimen of conglomerate shows small ventifact (~1.5 cm diameter) located (immediately to top left of coin) on top of the 3-mm-thick basal contact of the Carbon Leader, Blyvooruitzicht Mine. Coin is 1.8 cm in diameter. Photograph and specimen, DJM.

purported to have allowed ingress of liquid bitumen along flat low-angle shear-induced fractures (Barnicoat et al., 1997; Parnell, 2001; Jolley et al., 2004). Such a mechanism might be called upon to account for instances of fracture fillings by bitumen extending across quartz clasts and/or primary structures. However, it cannot reasonably account for the hundreds of square kilometers of paleoerosion surfaces commonly manifest by thin pebble lags and occupied by thin carbon seams. Note that the concentrically-banded pyrite grain (Fig. 8) has not been affected by shearing. Its pristine condition makes it patently impossible that liquid bitumen can have been emplaced along shear-induced fractures under near surficial conditions over hundreds of square kilometers, only to have been dissected by erosion channels shortly following emplacement.

Ventifacts figure prominently among clasts that are spatially associated with carbon seams (e.g., see Figs. 9 and 10). Minter (1991, p. 37) refers to numerous exposures in the Cristalkop Placer at No. 8 Shaft on Vaal Reefs South gold mine where ventifacts are recorded overlying centimeter-thick carbon seams, a situation impossible if the carbon seam originated as liquid bitumen.

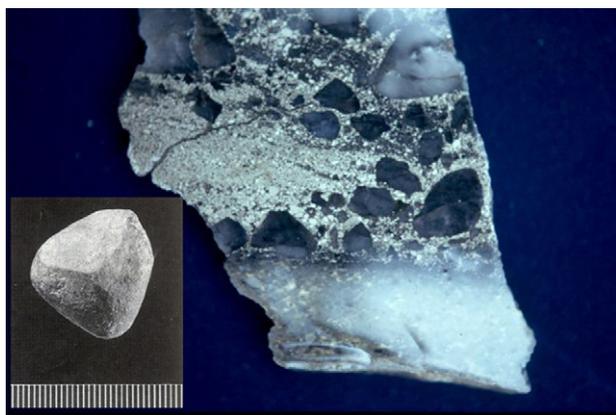


Fig. 10. Saw section through sample from Vaal Reef, Klerksdorp goldfield, showing several small ventifacts (the largest is 2.5 cm in diameter) lying directly upon the unconformity above a thin, apparently double set of carbon seams totalling about 0.4 cm thickness. Inset shows the morphology of a ~2.2 cm diameter ventifact liberated from the reef. (see also Minter, 1999, Fig. 6A, p. 668). A dense concentration of nodular pyrite grains accompanies various other heavy minerals, including gold. Specimens housed at Department of Geological Sciences, University of Cape Town. Photographs by WELM and Harry Taylor.

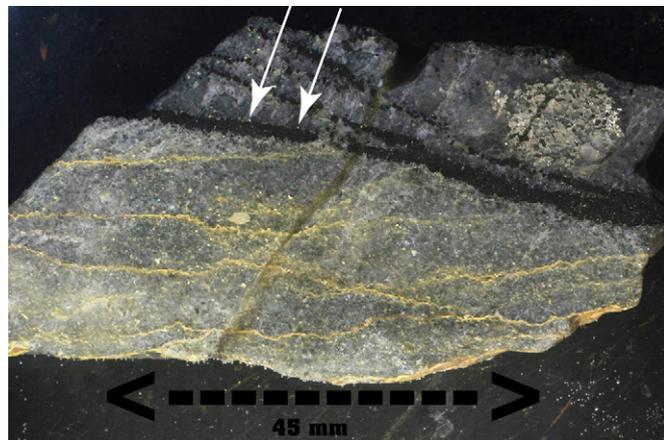


Fig. 11. Partial cross-section of a specimen of Carbon Leader Reef (Blyvooruitzicht Mine, Carletonville) showing cross-bedded footwall quartzite (with thin yellow clay drapes slightly stylolitized) followed above by the Reef deposit, which consists of coarse quartz arenite with interbedded layers of carbon. At upper right is a rounded aggregate of coarse quartz grains and pyrite. The carbon is on cross-bedded foresets, supporting its sedimentary association with the arenite. Small gold grains (arrows) occur on top of the carbon layers. Within the carbon the gold is of filamentous structure and arranged mostly in line with the columnar structure of the carbon (A surface crack across the specimen, middle right to lower left, is filled with epoxy resin. Scale as indicated. Photograph DKH.

4.3. Carbon-draped foreset beds occur in planar cross-beds

Numerous carbon-covered bedforms have been recorded in the Witwatersrand, particularly in the Welkom Goldfield. The Steyn placer provides abundant evidence for contemporaneous deposition of sediment and carbon. According to Minter (1991), one exposure in a relatively distal location shows a sequence of carbon-covered foreset beds in a planar cross-bed that also displays carbon on the bottomset (see Fig. 11). In the more distal parts of the Steyn placer, Minter (1978) has documented primary structures in the dominantly sandbody reefs (in contrast to the conglomeratic, so-called “banket” reefs) which clearly illustrate the process of heavy mineral concentration. Specifically, in this setting hydraulic processes result in the concentration of heavy minerals tangentially on the toes of foreset beds, merging along the scoured base of each foreset (see also Minter, 2006). According to Minter (1978, p. 817) “When the migration of sediment dominated and preservation was low, only the bottom well-mineralized part of each set was preserved. The operation of this process over a long period produced a layer of apparently small-scale trough remnants which was very mature and contained a heavy mineral concentrate at its base. These concentrations were generally held there by small-pebble accumulations and by algal mats . . .”. This description aptly applies to his Fig. 11, which provides a small elegant window upon approximately 200 km² of “ . . . the longest, most extensively accessible paleoslope exposure available in the Witwatersrand Basin . . .” (Minter, 1978, p. 808).

One of the most instructive carbon bedforms in the Witwatersrand occurs in the Leader Reef at Welkom gold mine in the Welkom Goldfield. The bedform in question is a thin (~0.25 m thick) wedge-shaped cross-bedded pebbly sandbar which is extremely well-mineralized with gold and uranium (Smith and Minter, 1980, Fig. 19, p. 12). The pebbly sandbar consists of multiple alternating 1–3-mm-thick foreset laminae of carbon and pyrite-enriched quartz arenite (Fig. 12). According to Smith and Minter (1980) the sandbar, bounded top and bottom by carbon-free quartz-pebble conglomerates, advanced by foreset accretion over the surface of what was originally a gravel bar. Highest

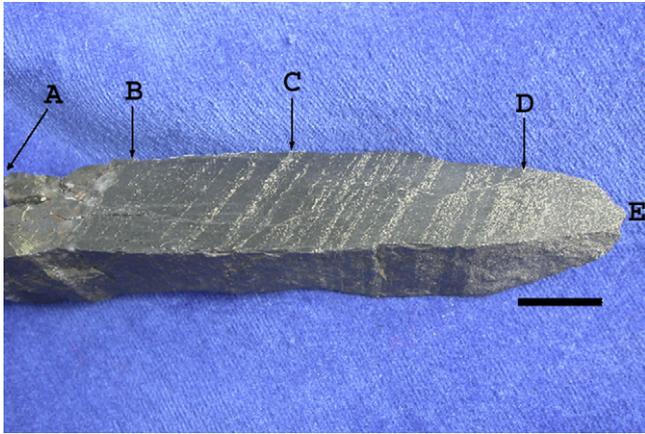


Fig. 12. Quartz-pebble conglomerate (A–B) overlies thin-bedded pyritic and carbonaceous quartz arenite from the Leader Reef, Welkom Goldfield, No. 3 Shaft. Carbon-dominant foreset beds (B–C) overlie carbon, silicate and pyrite laminae (C–D) and pyrite-dominant laminae at the base (D–E). Note that near the base, some laminae are offset by syndimentary micro-faults. No gold or sulfide mineralization is present. Specimen housed in the Department of Geological Sciences, University of Cape Town. Length of specimen is 7.5 cm. Photograph WELM. Scale bar is 1 cm.

values of gold (16.2 ppm) and uranium (870 ppm) occur in the sandstone; gold and uranium in the sandbar correlate strongly with carbon in the Leader Reef. Close examination reveals that some of the carbonaceous laminae comprising the cross-beds are offset along micro-synsedimentary faults (Fig. 12). This is significant supporting evidence for the indigenous origin of some of the Witwatersrand carbon. Synsedimentary faulting of carbon seams/laminae is totally incompatible with the revisionist concept of Witwatersrand carbon having been emplaced as liquid bitumen.

4.4. Pebbles in some cases occur between multiple carbon seams, and heavy mineral grains can be interstitial to columns of carbon

Multiple carbon seams are commonly encountered at the base of the Carbon Leader. Similarly, in confirmation that sedimentation and carbon development were contemporaneous, the carbon seams in many instances enclose pebbles and sand grains within a seam several centimeters thick (e.g., Adam, 1991, p. 82, and Fig. 5, p. 86). An example of multiple layers of carbon from the Free State Saaiploas Mine (see Fig. 13) also illustrates this particular feature. In this particular instance, some of the clasts are floating in the carbon rather than being part of a close-packed framework structure. Floating clasts would be impossible had the carbon been emplaced as liquid bitumen along a suitably permeable horizon.

One of the most remarkable features of some carbon seams is the presence of well developed columnar microstructures. These too developed contemporaneously with sedimentation as revealed, for example, in Fig. 14. The occurrence of detrital mineral particles snugly entrapped between adjacent carbon columns can only be accounted for by a synsedimentary origin, and is suggestive that post-depositional compaction of the carbon seams was minimal.

4.5. Columnar carbon is stromatolite-like

The columnar carbon recorded by Hallbauer (1975a,b) in some carbon seams, while by no means commonplace is perhaps not exceptional given the Precambrian fossil (microbial) record (Schopf, 2004). Details of the columnar carbon may be revealed only fol-

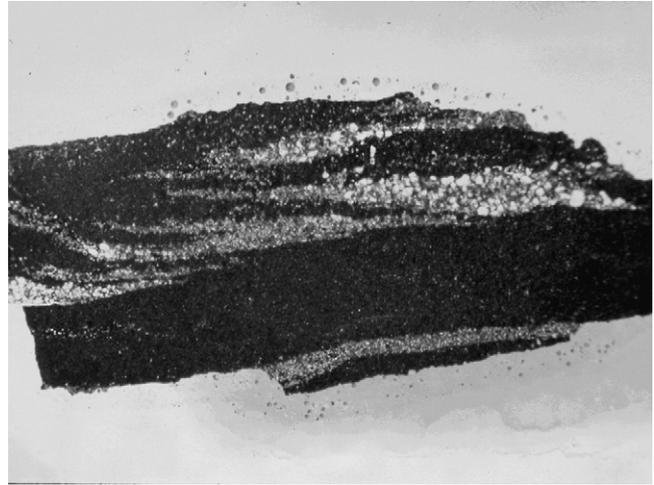


Fig. 13. Several consecutive carbon-draped foresets occur in erosion channel fill, Basal Reef, Saaiploas Mine, Orange Free State Goldfield. Cross-bedding shows asymptotic toesets. Toward the base, the thickest layer of carbon is ~0.5 cm thick. Many of the sandy grains in the thickest layers are matrix-supported, a feature in common with some other relatively thick Witwatersrand carbon seams. (see text for details). Specimen housed in private collection of DKH, Germany. Photograph by DKH.

lowing a lengthy chemical cleaning procedure in order to remove impurities (Hallbauer, 1975b; Neuerburg, 1975). After cleaning, the carbon is revealed as discrete stromatolite-like columnar structures (Fig. 14). At high magnification, a microbial-like highly ordered fibrous texture becomes evident (Fig. 15). The size and ordering of individual fibres falls well within the range of that characteristic of cyanobacteria (Dyer et al., 1988). There is nothing that has been made experimentally (cf. Yushkin, 1996; Grotzinger and Rothman, 1996) from either liquid or solid bitumen which even approaches matching the bacterioform-like detail evident in the examples of Witwatersrand carbon documented by Hallbauer (1986).

Another feature documented by Hallbauer (1975a) further strengthens the case for the stromatolite-like nature and origin of the columnar carbon (see Fig. 16). The likeness is complete even to bedding-parallel lamination preserved together with individual fil-

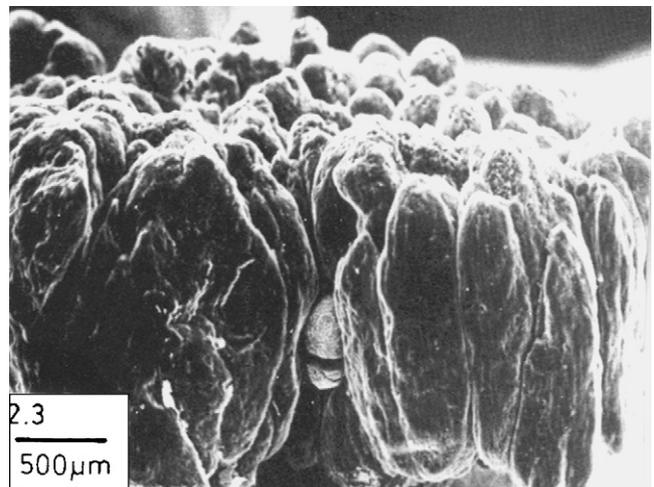


Fig. 14. Scanning electron micrograph showing columnar carbon from the Carbon Leader, Blyvooruitzicht Mine. Discrete characteristic growth-like clusters are rooted at separate bases and between them commonly enclosing detrital heavy mineral grains. Here a rounded oblong pyrite grain is shown trapped between several carbon columns; interstitial silicate grains have been dissolved during preliminary hydrofluoric acid cleaning. (after Hallbauer, 1982, Fig. 2.3, p. 960).



Fig. 15. Scanning electron micrograph showing a view of a small portion of a single carbon column reveals the rarely preserved high degree of structural order present in 4 μm diameter carbon filaments extending upward from their common (stratigraphic) base (out of view to left of the photo) Sample from the B Reef, Loraine Mine, Free State Goldfield (after Hallbauer, 1986, Fig. 5F, p. 741).

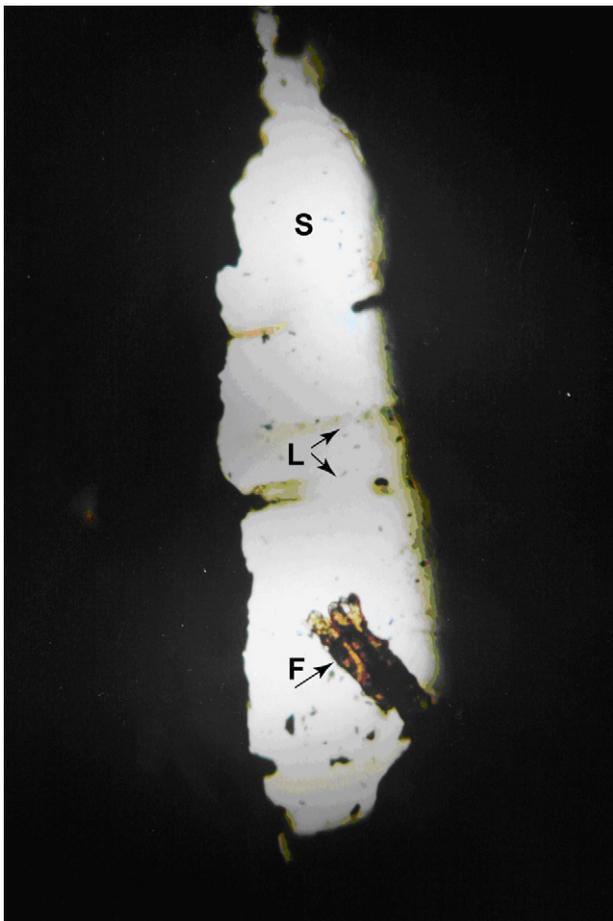


Fig. 16. Photomicrograph in transmitted light of thin section perpendicular to the bedding in a carbon seam showing very fine-grained interstitial siliceous matrix (S) and a faint bedding-parallel lamination (L) preserved between carbon columns. Note the several discrete microbial-like carbon filaments (F) within the matrix, extended outwards and upwards (lower right) from the base of the carbon column. Sample from Carbon Leader Reef, Blyvooruitzicht Gold Mine, Carletonville Goldfield (from Hallbauer, 1975a, p. M9, Fig. 8).



Fig. 17. The tops of some pebbles show old growth of lichen in the Namib Desert, Naukluft Park, southeast of Swakopmund, Namibia. Knife is 15 cm long. Photograph by WELM.

aments of carbon within the fine-grained siliceous matrix between the columns.

4.6. Carbon coating on pebbles, and carbon associated with rippled quartz arenites

Witwatersrand carbon occurs as fine grains, as thin films most readily visible in plan views of the basal bedding plane, and as seams up to 5 cm thick. Its occurrence as thin one-sided coatings of pebble-sized clasts in the Steyn Reef (see Minter, 1978, Fig. 20C, p. 824) has close modern analogies. For example, algal growths upon clasts lodged in shallow stream beds are observed in various climatic environments. Upon rocks exposed at the surface in some ephemeral Arctic streams, the senior author has observed and collected tough, 2–3-mm-thick lichen growths complete with fibrous structures perpendicular to rock base. Other present-day analogies to possible precursors of Witwatersrand carbon are found in desert environments, as illustrated by the growth of lichens and the preservation of algal/lichen remnants in the Namib Desert of Namibia. Fig. 17 illustrates carbon accumulation preferentially upon one side of lag pebbles in the Namib, a case which closely resembles the vastly more ancient example (Minter, 1978) from the Steyn Reef.

The Namib Desert also illustrates wind-transported organic materials and how, in a desert setting, they may end up concentrated on the lee side of depressions (Fig. 18). Possibly analogous, a Witwatersrand example (see Buck, 1983, Fig. 7B, p. 555) illustrates carbon associated with asymmetric ripples in quartz arenite of the Saaiplaas Quartzite Member, a channel-like sandbody within an extensive alluvial fan system in the Welkom Goldfield. Other views of this remarkable example (Figs. 19 and 20) show the underside of the ripple-marked arenite and the distribution of carbon as 2–3-mm-thick laminae within it. Here, the densest accumulation of carbon occurs at the crests of the leading edges of successive ripples (i.e., becoming more densely distributed in the direction of flow), with carbon specks becoming less concentrated on the stoss (upstream) side. These linear features are more likely to have been generated at low current velocities and possibly with wave influence, hence the low relief. This indicates that these features represent an interlude of quiescence within the channel in which shallow, gently flowing water prevailed, enabling settling of carbonaceous material.



Fig. 18. Wind-transported organic material forms linear accumulations (dark grey) on the pebble-armoured desert pavement in the Namib Desert, Naukluft Park. Small patches of scrub occur in the distance. Photograph by WELM.

This is a purely sedimentological feature, generated not by liquid bitumen or hydrothermal processes, but by the growth and deposition of biogenic carbon contemporaneously with placer development.

4.7. Carbon is more common in distal than in proximal settings and does not always carry gold

In the Witwatersrand, just as in the Huronian Supergroup, Canada (Mossman and Harron, 1983), carbon is not confined to coarse-grained proximal lithologies as might have been expected of liquid bitumen. Instead, it is far more common in small-pebble sand bodies of distal sedimentary settings. Thus, only thin patchy carbon seams and dispersed fine-grained carbon occur in shallow proximal braided-stream channels. Basal degradation surfaces are optimal sites for Witwatersrand carbon seams, likewise heavy mineral concentrations, including gold. A strong positive correlation of gold with carbon is common in this situation, except beneath coarse conglomerate where carbon distribution is patchy. Elsewhere, for example, on foresets and upper bedding planes (including carbon



Fig. 19. Sample of Saaiplaas Reef at the Free State Saaiplaas No. 2 Shaft shows asymmetric ripple-marked quartz arenite on the hanging wall at top of the reef. This oblique view shows carbon ripples located at the upper contact of the sandstone facies. Flow was from right to left. Note the abrupt margins of the dense carbon bands built up at the leading (lee) edges (A–E) of successive ripples and the decreasing concentration of carbon granules on the stoss (upstream) side of the ripples (For details, see Fig. 22). Sample is uraniferous but no gold or sulfide mineralization present except for two grains of pyrite. Photograph by DJM.

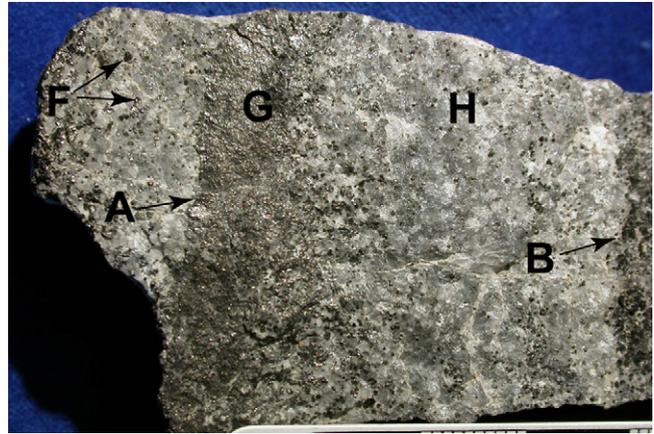


Fig. 20. Close up of left hand side of sample shown in Fig. 19 highlights the granular character of the carbon. Note: individual granules of carbon (F); leading (lee) edges (A, B) of carbon ripples; greatest relative concentration of carbon granules (G) on lee (downstream) portion of ripple; decreased concentration of granules on stoss (upstream) side (H) of ripple. Specimen housed in the Department of Geological Sciences, University of Cape Town. Photograph by DJM.

seams), carbon is seldom associated with comparably high gold values (Minter, 1975b, 1978, 1991), although uranium values are more likely to occur throughout the placer unit (see below). Buck and Minter (1985) have documented a strong sedimentary control on the concentrations of placer minerals. Muller (1991, p. 62) likewise concluded that gold concentration is a function of depositional setting.

The fact that carbon may be barren of gold was recognized long ago by Sharpe (1949). A case in point is Buck's (1983, Fig. 7B, p. 555) illustration of non-auriferous carbon. The absence of heavy mineral concentrate in this instance is probably because the surface is not an unconformity.

As noted by various workers (Gray et al., 1998; Robb and Meyer, 1995; Smits, 1992; Landais et al., 1990), neither does the occurrence of carbon concentrations within a reef guarantee the presence of uranium. Accordingly, strict revisionist interpretation of the carbon as liquid bitumen that has been polymerized due to proximity to uraninite is invalidated. In any case, from a strictly hydrodynamic standpoint, liquid bitumen would tend to rise to the top of an arenaceous and/or conglomeratic reef, and this is not where Witwatersrand carbon is generally most abundant.

According to Minter (1978), the carbon tends to be barren of gold mineralization where it is not associated with a heavy mineral concentration surface (Minter, 1978, p. 825–826). Results of research on the Vaal Reef at Vaal Reefs and Western Reefs gold mines in the Klerksdorp Goldfield (Minter, 1973) showed that over 70% of the total gold, but only about 20% of the uranium, occur adjacent to the basal contact of the placer (Minter, 1978, pp. 818 and 820). Unlike gold, the uranium tends to be distributed throughout the placer. It occurs in leucoxene within the placer units, though not in the leucoxene of hanging wall and footwall sediments (Minter, 2006). Thus, while gold and uranium concentration patterns might be said to be “sympathetic” (Minter, 1978, p. 818), they are not necessarily coincident with abundance of carbon. A good statistical correlation holds true only on a local scale. Resulting distribution patterns on a regional scale are complicated by various controlling variables such as facies changes, variation in the amount of carbon, location on the paleoslope, redistribution of the metals (particularly uranium), and the heterogeneous geometry of fluvial sediments. Overall, Minter (1973) showed that gold and uranium grades are of the same order regardless of the



Fig. 21. Oblique view of the top of an auriferous carbon seam (following cleaning by hydrofluoric acid), shows microparticles of gold (maximum diameter $\sim 100 \mu\text{m}$) embedded between ashed columns of former carbon. Sample from Basal Reef, Saaiplaas Gold Mine, Free State Goldfield (after Hallbauer, 1975b, Fig. 10, p. 118).

thickness of the basal carbon seam. He makes the point that this evidence supports neither Liebenberg's (1955) hypothesis of origin of carbon seams by irradiation of hydrocarbons (by uraninite), nor precipitation of uranium from solution by carbon (Minter, 1973, p. 82).

4.8. Filamentous gold and minute rounded particles of gold occur within carbon seams

Several remarkable morphological features of the constituent gold become evident on careful study of the carbon seams. Two morphological types of gold are documented by Hallbauer (1975b). The least common consists of minute, relatively rounded grains, nestled between columns of carbon (Fig. 21). It could well be that some of these will turn out to be toroidal grains, but this prediction remains to be tested. The main gold in carbon seams occurs in a filamentous form (Fig. 22) encountered nowhere else in the Witwatersrand Basin; it closely resembles the bacterioform gold as documented by Reith et al. (2006) in auriferous soils in south-eastern Australia. Like the numerous delicate toroidal gold grains documented by Minter (1999), these filamentous forms have also evidently survived diagenesis and low-grade metamorphic conditions. Whether the Witwatersrand filamentous gold qualifies as microbial gold is of course a moot point given that morphology is not an infallible criterion for determination of origin (Mossman et al., 1999). The best gold concentrates in the Witwatersrand occur on basal scour surfaces as bed load. Specifically, it is from carbon seams which occur upon these surfaces that Hallbauer (1986) identified the secondary filamentous gold forms (Fig. 22). In contrast, carbon seams located higher up in placer units and thus not spatially asso-

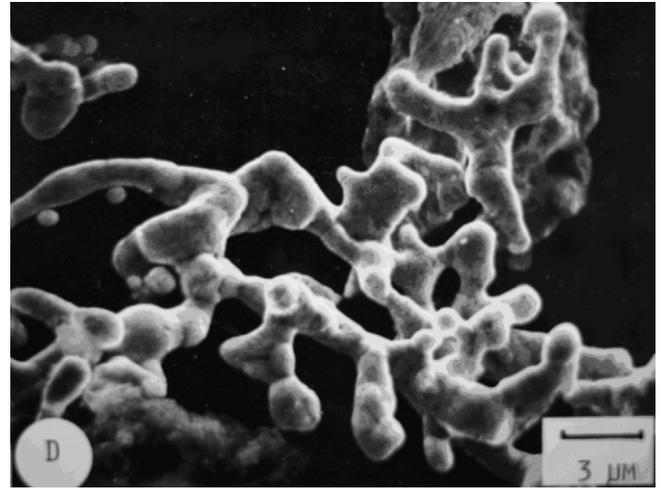


Fig. 22. Filamentous gold from the Carbon Leader extracted after ashing in a low temperature plasma furnace (at 60°C). Size and morphology of the gold filaments closely resemble geologically recent microbial gold documented by Reith et al. (2006). Sample from Carbon Leader Reef, Blyvooruitzicht Gold Mine, Carletonville Goldfield. Bar gives scale. Scanning electron photomicrograph by DKH.

ciated with long duration bed load, are poorly mineralized (see also Minter, 1978, 1991).

5. Discussion

Proof of microbial mat cover upon Precambrian siliciclastic strata comes from the identification of microfilamentous textures similar to modern cyanobacteria as documented in siliciclastic storm deposits in the Witwatersrand Supergroup (Noffke et al., 2006), in 2.9 Ga shelf quartz arenites of the Mozaan Group (Pongola Supergroup) (Noffke et al., 2001, 2003a), and in 3.4 Ga silicified shallow marine arenites of the Buck Reef Chert in the Barberton greenstone belt (Tice and Lowe, 2004, 2006). As described under observation 7, carbon accumulations in distal reaches of the Steyn placer at Free State Saaiplaas gold mine in the Welkom Goldfield may have served as biofilms, which helped stabilize the sediments. The virtual restriction of Witwatersrand carbon seams, whether auriferous or not, to thin, discrete, laterally extensive stratigraphic horizons (and nowhere else) is characteristic of microbial mat cover.

Compared to better documented equivalent structures in carbonate sedimentary rocks, microbial structures in siliciclastic sedimentary rocks are more subtle, having minimal relief, being apparent only upon bedding plane surfaces and having a lower preservation potential. Nevertheless microbially-mediated ripple marks and various soft-sediment deformation structures reminiscent of modern-day features are well known from the Precambrian geological record (Sakar et al., 2004). Among the most impressive microbial structures now documented are microbial bedding plane surface marks (Banerjee and Kumar, 2005; Hagadorn and Bottjer, 1997), and numerous examples of microbial layering (Gerdes et al., 2000; Bekker et al., 2004; Scheiber et al., 2007).

An example of layering thought to have been derived from current reworking of microbial mats is highlighted by the concentration of fine-sand to rounded granules of carbonaceous grains in 3.416 Ga wave-rippled arenites from the Buck Reef Chert in the Barberton greenstone belt, South Africa (Tice and Lowe, 2004). In some cases in this unit, layering is defined by concentration of carbonaceous grains as in the description by Tice and Lowe (2004). In the Witwatersrand sedimentary column, the occurrence of resedimented "granulated" (so-called "fly speck") carbon in lag gravels and on the bottom of scour surfaces, is commonly encountered.

An example has been documented from the Vaal Reef paleoplacer in the Klerksdorp Goldfield showing carbon seams together with disrupted granules of carbon "... along the surface of the angular unconformity, at the base, and on top of the lag accumulation" (Minter, 1978, Fig. 15B, p. 814).

Another example of a microbial structure illustrated by Tice and Lowe (2004, Fig. 4) from the Buck Reef chert shows carbonaceous material draped over a coarse detrital quartz grain. This mode of occurrence is identical, although microscopic by comparison to the phenomenon as documented by Button (1979) in the recent gravels of the Sabi River (Zimbabwe), and for that matter to the asymmetrical coating of carbonaceous substances on the tops of Witwatersrand pebbles (Minter, 1975b).

A hierarchical list of criteria for recognizing Archean microfossils has been drawn up by several authorities (e.g., Buick, 1990; Schopf, 2004). In all but exceptional circumstances, the consensus seems to be that authentic Archean microfossils ought to "... occur in thin sections of low-grade rocks of sedimentary origin, consist of kerogen, exceed the minimum size for independently viable cells, co-exist with others of similar morphology, have a hollow structure and display cellular elaboration." (Buick, *ibid.*, p. 441). The putative microfossil assemblage documented by Hallbauer (1975a,b) from Witwatersrand carbon seams satisfies all these criteria.

Concerning mycelium-like filamentous aggregates of silicified fibres identified (as symbiotic with associated alga) by Hallbauer and van Warmelo (1974) from ashed residues of columnar carbon, E.S. Barghorn remarked (in Schidlowski, 1975, p. N 19) that "... the indigenous character of these aggregates cannot be doubted, but their interpretation as fungi is incorrect." However, fungi are eukaryotes, and the oldest traces of side-chain alkylated steranes, putative key biomarkers of eukaryotes, have been reported from hydrocarbons extracted from 2.7 Ga shales from the Pilbara craton (Brocks et al., 1999, 2003). Diverse steranes indicating eukaryote input have also been found in fluid inclusions from the 2.45 Ga uraniferous conglomerates of Elliot Lake (Dutkiewicz et al., 2006) and the 2.1 Ga Franceville Series at Oklo (Dutkiewicz et al., 2007).

The biogenic origin of the carbon, readily acknowledged by revisionists and "modified placerists" alike (Hoefs and Schidlowski, 1967; Barnicoat et al., 1997; Spangenberg and Frimmel, 2001; Frimmel et al., 2005), is supported by the results of a detailed carbon isotopic study. Spangenberg and Frimmel, (*ibid.*, p. 346–348) attributed a range in $\delta^{13}\text{C}$ from -23.6‰ to -39.2‰ (mean of $-26.0 \pm 1.7\text{‰}$) of the Witwatersrand carbon seams to inhomogeneity in the primary composition of the (insoluble) organic matter; extractable organic matter in the carbon seams is depleted in ^{12}C by up to 2.4‰ compared with the associated insoluble organic fraction and the two are thus considered diagenetically linked. We concur with Spangenberg and Frimmel's (2001, p. 352) conclusion with respect to bitumen that "... the potential source of the hydrocarbons could be biogenic organic matter buried in the Witwatersrand reef sediments." However, we would add that multiple bitumen migration and/or a mixture of kerogen and bitumen account for the carbon isotopic data.

As in many Phanerozoic sedimentary sequences, vitrinite or vitrinite-like organic matter never occurs alone but is invariably accompanied by one or more other macerals. The same is true for Witwatersrand carbon seams, although the kerogen/bitumen ratio in these will likely range widely if only by virtue of differential small-scale migration of derivative hydrocarbons, and inevitable "sampling problems". Spangenberg and Frimmel's (2001) conclusion that the carbon seams are indeed indigenous to the Witwatersrand is thoroughly reinforced by observations 1–8, as set out above.

6. Conclusions

Oil generation and migration were active geological processes in Early Earth history. In some Witwatersrand ores, carbon seams of generally acknowledged biogenic origin contain kerogen and solid bitumen in varying proportions; fluid inclusion oil(s) are commonly also present in these same rocks. As in the Phanerozoic, these forms of reduced carbon have also been well documented from various Precambrian metasedimentary rocks in recent years. In the Witwatersrand, kerogen represents the remnants of once-living organisms indigenous to the enclosing sedimentary rocks. Fluid inclusion oil(s) and bitumen(s) were derived from the organic matter by thermal maturation through the oil window from within-basin carbonaceous shales and carbon seams.

The reality and versatility of microbial activity in the Witwatersrand siliciclastic succession is a matter of record. Numerous observations bearing on the spatial distribution of the carbon seams confirm the existence of indigenous carbon within these Archean placer deposits. Among the most crucial lines of evidence are examples of synsedimentary faulting of carbon seams and paleochannels which truncated auriferous carbon seams early in the sedimentological history of the Witwatersrand. These and numerous other features of the spatial distribution of the carbon seams provide a classic example where field evidence trumps laboratory data in the reconstruction of geological processes.

Acknowledgements

We gratefully acknowledge P.K. Mukhopadhyay's diligent petrographic analyses of selected Witwatersrand carbonaceous samples. L. Aspler contributed numerous insightful observations on the geology of Witwatersrand-like deposits. Journal reviewers H. Frimmel and C. Anhaeusser are thanked for providing very helpful constructive criticism. The work was supported by a Natural Sciences and Engineering Research Council of Canada discovery grant to D.J.M. and by an Australian Research Council discovery grant including a QEII fellowship to A.D.

References

- Adam, T., 1991. Carbon distribution in the Proterozoic Carbon Leader placer, Western Deepes Levels Ltd. –East Mine, Witwatersrand, South Africa. In: Carbon in Witwatersrand Reefs Symposium. Geological Society of South Africa, June 6–7, 1991, pp. 79–89.
- Banerjee, S., Kumar, S., 2005. Microbially originated wrinkle structures on sandstone and their stratigraphic context: Paleoproterozoic Koldaha Shale, central India. *Sedim. Geol.* 176, 211–224.
- Barnicoat, A.C., Henderson, J.H.C., Knipe, R.J., Yardley, B.W.D., Napier, R.W., Fox, N.P.C., Kenyon, A.K., Muntingh, D.J., Strydom, D., Winkler, K.S., Lawrence, S.R., Cornford, C., 1997. Hydrothermal gold mineralization in the Witwatersrand basin. *Nature* 386, 820–824.
- Bekker, A., Holland, H.D., Wang, P.-L., Rumble III, D., Stein, H.J., Hannah, J.L., Coetzee, L.L., Beukes, N.J., 2004. Dating the rise of atmospheric oxygen. *Nature* 427, 117–120.
- Boice, A.E., Tipple, B.J., Pratt, L.M., 2007. Isotopic evidence for microbial sulfate reduction and methanotrophy during the late Archean, Witwatersrand Basin, South Africa. *Life in the Universe: Seventh Conference on Chemical Evolution and the Origin of Life. Chapter 4 (Book of Abstracts)*. Abus Salam International Centre for Theoretical Physics. (15–19 September, 2003) Trieste, Italy.
- Brocks, J.J., Logan, G.A., Buick, R., Summons, R.E., 1999. Archean molecular fossils and the early rise of eukaryotes. *Science* 285, 1033–1036.
- Brocks, J.J., Buick, R., Summons, R.E., Logan, G.A., 2003. A reconstruction of Archean biological diversity based on molecular fossils from the 2.78 to 2.45 billion year-old Mount Bruce Supergroup, Hammersley Basin, Western Australia. *Geochim. Cosmochim. Acta* 67, 4321–4335.
- Bros, R., 1993. Géochimie isotopique (Sm-Nd, Rb-Sr, K-Ar, U) des Argiles du Bassin Proterozoique de Franceville et des Reacteurs d'Oklo (Gabon). Thèse, L'Université Louis Pasteur de Strasbourg, 154 pp.
- Buck, S.G., 1983. The Saaiplaas quartzite member: a braided system of gold-and uranium-bearing channel placers within the Proterozoic Witwatersrand Supergroup of South Africa. *Spec. Publ. Int. Assoc. Sedimentol.* 6, 549–562.

- Buck, S.G., Minter, W.E.L., 1985. Placer formation by fluvial degradation of an alluvial fan sequence: the Proterozoic Carbon Leader placer, Witwatersrand Supergroup, South Africa. *J. Geol. Soc. Lond.* 142, 757–764.
- Buick, R., 1990. Microfossil recognition in Archean rocks: an appraisal of spheroids and filaments from a 3500 M.Y. old chert-barite unit at North pole, Western Australia. *Palios* 5, 441–459.
- Bustin, R.M., Cameron, A.R., Grieve, D.A., Kalkreuth, W.D., 1983. Coal Petrology, its principles, methods and application. *Geol. Assoc. Can. Short Course Notes* 3, 230.
- Button, A., 1979. Algal concentration in the Sabi River, Rhodesia: depositional model for Witwatersrand carbon. *Econ. Geol.* 74, 1876–1882.
- Cheatle, A., 1991 June. Carbon in the “C” Reef at South Vaal. In: *Carbon in Witwatersrand Reefs Symposium*. *Geol. Soc. S. Afr.* 6–7, 51–55.
- Danchin, R., 1970. Aspects of the geochemistry of some South African fine-grained sediments. Unpublished Ph.D. thesis, University of Capetown, 215 pp.
- Dott Jr., R.H., 2003. The importance of eolian abrasion in supermature quartz sandstones and the paradox of weathering on vegetation-free landscapes. *J. Geol.* 111, 387–405.
- Drennan, G.R., Boiron, M.C., Cathelineau, M., Robb, L.J., 1999. Characteristics of post-depositional fluids in the Witwatersrand basin. *Mineral. Petrol.* 66, 83–109.
- Dutkiewicz, A., Rasmussen, B., Buick, R., 1998. Oil preserved in fluid inclusions in Archean sandstones. *Nature* 395, 885–888.
- Dutkiewicz, A., Volk, H., George, S.C., Ridley, J., Buick, R., 2006. Biomarkers from Huronian oil-bearing fluid inclusions: an uncontaminated record of life before the Great Oxidation Event. *Geology* 34 (6), 437–440.
- Dutkiewicz, A., George, S.C., Mossman, D.J., Ridley, J., Vzolok, H., 2007. Oil and its biomarkers associated with the Paleoproterozoic Oklo natural fission reactors Gabon. *Chem. Geol.* 244, 130–154.
- Dyer, B.D., Krumbein, W.E., Mossman, D.J., 1988. Nature and origin of stratiform kerogen seams in lower Proterozoic Witwatersrand-type paleoplacers—the case for biogenicity. *Geomicrobiology. J.* 6, 33–47.
- Engelbrecht, C.J., Baumbach, G.W.S., Maticen, J.L., Fletcher, P., 1986. The West Wits Line. In: *Anhaeusser, C.R., Maske, S. (Eds.), Mineral Deposits of Southern Africa*, 1. *Geol. Soc. South Africa*, pp. 599–648.
- England, G.L., Rasmussen, B., Krapez, B., Groves, D.J., 2001. The origin of uraninite, bitumen nodules and carbon seams in Witwatersrand gold-uranium-pyrite ore deposits, based on a Permo-Triassic analogue. *Econ. Geol.* 96, 1907–1920.
- England, G.L., Rasmussen, B., Krapez, B., Groves, D.J., 2002. Archean oil migration in the Witwatersrand Basin of South Africa. *J. Geol. Soc.* 159 (2), 189–202.
- Flynn, R., 1991. The erosion channel complex, West Driefontein Gold Mine. In: *Carbon in Witwatersrand Reefs Symposium*, *Geol. Soc. South Africa*. June 6–7, 1991, pp. 67–76.
- Frimmel, H.E., 2005. Archean atmosphere evolution: evidence from the Witwatersrand gold fields, South Africa. *Earth-Sci. Rev.* 70, 1–46.
- Frimmel, H.E., Hallbauer, D.K., Gartz, V.H., 1999. Gold mobilizing fluids in the Witwatersrand basin: composition and possible sources. *Mineral. Petrol.* 66, 55–81.
- Frimmel, H.E., Groves, D.J., Kirk, J., Ruiz, J., Chesley, J., Minter, W.E.L., 2005. The formation and preservation of the Witwatersrand Goldfields, the world’s largest gold province. In: *Hedenquist, J.W., Thompson, J.F.H., Gordfarb, R.I., and Richards, J.P. (Eds.), Econ. Geol. 100th Anniversary Volume*, Littleton, Soc. Econ. Geologists, pp. 769–797.
- Gartz, V.H., Frimmel, H.E., 1999. Complex metasomatism of an Archean placer in the Witwatersrand basin, South Africa: the Ventersdorp Contact Reef—a hydrothermal aquifer? *Econ. Geol.* 94, 689–706.
- Gerdes, G., Noffke, N., Klenke, Th., Krumbein, W.E., 2000. Microbial signatures in peritidal sediments—a catalogue. *Sedimentology* 47, 279–308.
- Gray, G.J., Lawrence, S.R., Kenyon, K., Cornford, C., 1998. Nature and origin of “carbon” in the Archean Witwatersrand basin. *S. Afr. J. Geol. Soc. Lond.* 155, 39–59.
- Grotzinger, J.P., Rothman, D.H., 1996. An abiotic model for stromatolite morphogenesis. *Nature* 383, 423–425.
- Hagadorn, J.W., Bottjer, D.J., 1997. Wrinkle structures: microbially mediated sedimentary structures common in subtidal siliciclastic settings at the Proterozoic-Phanerozoic transition. *Geology* 25, 1047–1050.
- Hallbauer, D.K., 1975a. Geochemistry and morphology of mineral components from the fossil gold and uranium placers of the Witwatersrand. *U.S. Geol. Surv. Prof. Pap.* 1161, M1–M18.
- Hallbauer, D.K., 1975b. Plant origin of the Witwatersrand carbon. *Miner. Sci. Eng.* 7 (2), 111–113.
- Hallbauer, D.K., 1982. A review of some aspects of the geochemistry and mineralogy of the Witwatersrand gold deposits. In: *Glen, H.W. (Ed.), Proceedings, 12th CMMI Congress*, Johannesburg. *South Africa Inst. Mining and Metallurgy*, pp. 957–964.
- Hallbauer, D.K., 1986. The mineralogy and geochemistry of Witwatersrand pyrite, gold, uranium, and carbonaceous matter. In: *Anhaeusser, C.R., Maske, S. (Eds.), Mineral Deposits of Southern Africa*, 1. *Geol. Soc. South Africa*, pp. 731–752.
- Hallbauer, D.K., van Warmelo, J., 1974. Fossilized plants in thucholite from Precambrian rocks of the Witwatersrand, South Africa. *Precambrian Res.* 1, 199–212.
- Hoefs, J., Schidlowski, M., 1967. Carbon isotope composition of carbonaceous matter from the Precambrian of the Witwatersrand system. *Science* 155, 1096–1097.
- Jolley, S.J., Freeman, S.R., Barnicoat, A.C., Phillips, G.M., Knipe, R.J., Pather, A., Fox, N.P.C., Strydom, D., Birch, M.T.G., Henderson, I.H.C., Rowland, T.W., 2004. Structural controls on Witwatersrand gold mineralization. *J. Struct. Geol.* 26 (6–7), 1067–1086.
- Jordaan, M.J., Kingsley, C.S., Muntingh, D.J., 1991. Paleo-environmental controls on the distribution of carbonaceous matter in the Witwatersrand paleoplacers. In: *Carbon in Witwatersrand Reefs Symposium*. *Geol. Soc. South Africa*. June 6–7, 1991, pp. 45–49.
- Landais, P., Dubessy, J., Robb, L.J., Nouel, C., 1990. Preliminary chemical analyses and Raman spectroscopy on selected samples of Witwatersrand kerogen. *University of the Witwatersrand. Econ. Geol. Res. Unit Inf. Circ.*, 222.
- Liebenberg, W.R., 1955. The occurrence and origin of gold and radioactive minerals in the Witwatersrand System, the Dominion Reef, the Ventersdorp Contact Reef, and the Black Reef. *Trans. Geol. Soc. S. Afr.* 58, 101–227.
- Mastalerz, M., Glikson, M., Stankiewicz, B.A., Volkova, I.B., Bustin, R.M., 2001. Organic and mineral matter in a Precambrian shungite deposit from Karelia, Russia. In: *Glikson, M., Mastalerz, M. (Eds.), Organic Matter and Mineralization*. Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 102–119.
- Minter, W.E.L., 1973. The sedimentology of the Vaal Reef in the Klerksdorp area. *University of the Witwatersrand, Johannesburg*, Unpublished Ph.D. thesis, 170 pp.
- Minter, W.E.L., 1975a. The distribution and sedimentary arrangement of carbon in South African Proterozoic placer deposits. In: *Armstrong, F. (Ed.), Genesis of uranium and gold-bearing quartz-pebble conglomerates*. *U.S. Geological Survey Professional Paper*, 1161, pp. P1–P3.
- Minter, W.E.L., 1975b. Preliminary notes concerning the uranium-gold ratio and the gradient of heavy-mineral size distribution as factors of transport distance down the paleoslope of the Proterozoic Steyn Reef placer deposit, Orange Free State Goldfield, Witwatersrand, South Africa. In: *Armstrong, F. (Ed.), Genesis of Uranium and Gold-bearing Quartz-pebble Conglomerates*. *U.S. Geol. Surv. Prof. Pap.* 1161, pp. K1–K3.
- Minter, W.E.L., 1976. Detrital gold, uranium, and pyrite concentrations related to sedimentology in the Precambrian Vaal Reef placer, Witwatersrand, South Africa. *Econ. Geol.* 71, 157–176.
- Minter, W.E.L., 1978. A sedimentological synthesis of placer gold, uranium and pyrite concentrations in Proterozoic Witwatersrand sediments. In: *Miall, A.D. (Ed.), Fluvial Sedimentology, Memoir of the Can. Soc. Petroleum Geologists. Mem.* 5, Calgary, pp. 801–829.
- Minter, W.E.L. 1982. The Golden Proterozoic (Chapter 4, pp. 115–150). In: *Tankard, A.J., Jackson, M.P.A., Eriksson, K.A., Hobday, D.K., Hunter, D.R., Minter, W.E.L. (Eds.), Crustal Evolution of Southern Africa: 3.8 Billion Years of Earth History*. Springer-Verlag, New York, Heidelberg and Berlin. 523 p.
- Minter, W.E.L., 1991. A review of the spatial arrangement of carbon in ancient placer sediments and its relationship to associated heavy minerals. In: *Carbon in Witwatersrand Reefs Symposium*, *Geol. Soc. South Africa*. June 6–7, 1991, pp. 37–38.
- Minter, W.E.L., 1999. Irrefutable detrital origin of Witwatersrand gold and evidence of eolian signatures. *Econ. Geol.* 94 (5), 665–670.
- Minter, W.E.L., 2006. The sedimentary setting of Witwatersrand placer mineral deposits in an Archean atmosphere. Special volume on the evolution of the earth’s atmosphere: In: *Kessler, S.E., Ohmoto, H. (Eds.), Evolution of Early Earth’s Atmosphere, Hydrosphere and Biosphere—Constraints from Ore Deposits*. *Pardee Symposium, Geol. Soc. Am. Mem.* 198, pp. 105–119.
- Mossman, D.J., 1987. Stratiform gold occurrences of the Witwatersrand-type in the Huronian Supergroup, Ontario, Canada. *J. Geol. Soc. S. Afr.* 90 (2), 168–178.
- Mossman, D.J., Harron, G.A., 1983. Origin and distribution of gold in the Huronian Supergroup, Canada—the case for Witwatersrand-type paleoplacers. *Precambrian Res.* 20, 543–583.
- Mossman, D.J., Nagy, B., 1996. Solid bitumens: an assessment of their characteristics, genesis, and role in geological processes. *Terra Nova* 8 (2), 114–128.
- Mossman, D.J., Thompson-Rizer, C.L., 1993. Towards a working nomenclature and classification of organic matter in Precambrian and Phanerozoic sedimentary rocks. *Precambrian Res.* 61, 171–179.
- Mossman, D.J., Nagy, B., Rigali, M.J., Gauthier-Lafaye, F., Holliger, P., Leventhal, J.S., 1993. Petrography and paragenesis of organic matter associated with the natural fission reactors at Oklo, Republic of Gabon: a preliminary report. *Int. J. Coal Geol.* 22 (5), 179–194.
- Mossman, D.J., Reimer, T.O., Durstling, H., 1999. Microbial processes in gold migration and deposition: modern analogues to ancient deposits. *Geosci. Can.* 26 (3), 131–140.
- Mukhopadhyay, P.K., 1992. Maturation of organic matter as revealed by microscopic methods: applications and limitations of vitrinite reflectance, and continuous spectral and pulsed laser fluorescence spectroscopy. In: *Wolf, K.H., Chilingarian, G.V. (Eds.), Diagenesis III*. Elsevier, pp. 435–510.
- Muller, C.J., 1991. The occurrence of carbon in the Carbon Leader Ref. and some important considerations. In: *Carbon in Witwatersrand Reefs Symposium*, *Geol. Soc. South Africa*. June 6–7, 1991, pp. 61–64.
- Nagy, B., 1993. Kerogens and bitumens in Precambrian ore deposits: Witwatersrand, South Africa, Elliot Lake, Canada and the natural fission reactors, Oklo, Gabon. In: *Parnell, J. (Ed.), Bitumens in Ore Deposits*. *Soc. Geology Applied to Mineral Deposits*, Berlin, Springer, Special Publication No. 6, p. 287–333.
- Neuerburg, G.J., 1975. A procedure using hydrofluoric acid for quantitative mineral separation from silicate rocks. *J. Res. U.S. Geol. Surv.* 3, 377–378.
- Noffke, N., Gerdes, G., Klenke, Th., Krumbein, W.E., 2001. Microbially induced sedimentary structures—a new category within the classification of primary sedimentary structures. *J. Sedim. Res.* 71, 649–656.
- Noffke, N., Gerdes, G., Klenke, Th., 2003a. Benthic cyanobacteria and their influence on the sedimentary dynamics of peritidal depositional systems (siliciclastic, evaporitic salty and evaporitic carbonatic). *Earth Sci. Rev.* 62, 1–14.
- Noffke, N., Hazen, R., Nhleko, N., 2003b. Earth’s earliest microbial mats in a siliciclastic marine environment (2.9 Ga Mozaan Group, South Africa). *Geology* 31 (8), 673–676.

- Noffke, N., Beukes, N., Gutzmer, J., Hazen, R., 2006. Spatial and temporal distribution of microbially induced sedimentary structures: a case study from siliciclastic storm deposits of the 2.9 Ga Witwatersrand Supergroup, South Africa. *Precambrian Res.* 146 (1–2), 35–44.
- Parnell, J., 1996. Phanerozoic analogues for carbonaceous matter in Witwatersrand ore deposits. *Econ. Geol.* 91, 55–62.
- Parnell, P., 1999. Petrographic evidence for emplacement of carbon into Witwatersrand conglomerates under high fluid pressure. *J. Sedim. Res.* 69 (1), 164–170.
- Parnell, J., 2001. Paragenesis of mineralization within fractured pebbles in Witwatersrand conglomerates. *Mineralium Deposita* 36, 689–699.
- Phillips, G.N., Law, J.D.M., 2000. Witwatersrand gold fields: geology, genesis and exploration. *Rev. Econ. Geol.* 13, 439–500.
- Plumstead, E.P., 1969. Three thousand years of plant life in Africa. Alex du Toit Memorial Lecture 11. *Trans. Geol. Soc. S. Afr.* 72, 11–18, Annexure to v. 72.
- Pretorius, D.A., 1976. Gold and uranium in quartz-pebble conglomerates. *Econ. Geol.* 75th Anniv. Vol. 117–138.
- Rasmussen, B., 2005. Evidence for pervasive petroleum generation and migration in 3.2 and 2.63 Ga shales. *Geology* 33 (6), 497–500.
- Reith, F., Rogers, S.L., McPhail, D.C., Webb, D., 2006. Biomineralization of gold: biofilms on bacterioform gold. *Science* 313, 233–236.
- Robb, L.J., Meyer, F.M., 1995. The Witwatersrand Basin, South Africa: Geological framework and mineralization processes. University of the Witwatersrand. *Econ. Geol. Res. Unit, Info. Circ.* 296, 37.
- Sakar, S., Banerjee, S., Eriksson, P.G., 2004. Microbial mat features in sandstones illustrated. In: Eriksson, P., Altermann, W., Nelson, D., Mueller, W., Catuneau, O. (Eds.), *The Precambrian Earth: Tempos and Events*, 12. *Developments in Precambrian Geology*, pp. 673–675.
- Scheiber, J., Bose, P., Eriksson, P.G., Banerjee, S., Sarkar, S., Altermann, W., Catuneau, O., 2007. Atlas of Microbial Mat Features Preserved within the Siliciclastic Rock Record, 2. *Atlases in Geoscience* 2, 1st ed. Elsevier, Amsterdam, 311.
- Schidlowski, M., 1975. Uraniferous constituents of the Witwatersrand conglomerates: ore microscopic observations and implications for Witwatersrand metallogeny. In: Armstrong, F. (Ed.), *Genesis of uranium and gold-bearing quartz-pebble conglomerates*. U.S. Geol. Surv. Prof. Pap. 1161, pp. N1–N29.
- Schopf, W., 2004. Earth's earliest biosphere: status of the hunt. In: Eriksson, P., Altermann, W., Nelson, D., Mueller, W., Catuneau, O. (Eds.), *The Precambrian Earth: Tempos and Events*, 12. *Developments in Precambrian Geology*, pp. 516–591.
- Sharpe, J.W.N., 1949. The economic auriferous bankets of the upper Witwatersrand beds and their relationship to sedimentation features. *Trans. Geol. Soc. S. Afr.* 52, 265–288.
- Smith, N.D., Minter, W.E.L., 1980. Sedimentological controls of gold and uranium in two Witwatersrand paleoplacers. *Econ. Geol.* 75, 1–14.
- Smits, G., 1984. Some aspects of the uranium minerals in the Witwatersrand sediments of the Early Proterozoic. *Precambrian Res.* 25, 37–59.
- Smits, G., 1992. Mineralogical evidence for geochemical environment at the earth's surface during deposition of Witwatersrand reefs. *Trans. Inst. Min. Metall., Sect. B: Appl. Earth Sci.* 101, B99–B107.
- Snyman, C.P., 1965. Possible biogenetic structures in Witwatersrand thucholite. *Trans. Geol. Soc. S. Afr.* 68, 225–235.
- Spangenberg, J., Frimmel, H., 2001. Basin-internal derivation of hydrocarbons in the Witwatersrand basin, South Africa: evidence from bulk and molecular ¹³C data. *Chem. Geol.* 173, 339–355.
- Spilsbury, E.G., 1908. Discussion on "The origin of the gold in the Rand banket" by J.W. Gregory. *Trans. Inst. Min. Metall.* 17, 1–3.
- Stach, E., Mackowsky, M-Th., Teichmuller, M., Taylor, G.H., Chandra, D., Teichmuller, R., 1982. *Stachs textbook on Coal Petrology*, 3rd ed. Gebrueder Borntraeger, p. 535.
- Stupp, H.D., 1984. Metallogene syngenetischer Gold-Uran-Vorkommen in Konglomeraten der präkambrischen Pongola-Supergruppe und Moodies Gruppe, einschliesslich eines Beitrages zur Geneser epigenetischen Goldlagerstätte von Klipwal, Kaapvaal Kraton, Sädafrika. Ph.D Thesis, Universität Köln, 196 p.
- Thompson-Rizer, C.L., 1987. Some optical characteristics of solid bitumen in visual kerogen preparations. *Org. Geochem.* 11 (5), 385–392.
- Tice, M.M., Lowe, D.R., 2004. Photosynthetic microbial mats in the 3416-Myr-old ocean. *Nature* 431, 549–552.
- Tice, M.M., Lowe, D.R., 2006. Hydrogen-based carbon fixation in the earliest known photosynthetic organisms. *Geology* 34 (1), 37–40.
- Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*. Springer-Verlag, p. 538.
- Yushkin, N.P., 1996. Natural polymer crystals of hydrocarbons as models of prebiological systems. *J. Cryst. Growth* 167, 237–247.
- Zumberge, J.E., Sigleo, A.C., Nagy, B., 1978. Molecular and elemental analyses of carbonaceous matter in the gold and uranium-bearing Vaal Reef carbon seams, Witwatersrand sequence. *Miner. Sci. Eng.* 10, 223–246.