Title:

Metal Distribution in Pyrobitumen of the Carbon Leader Reef, Witwatersrand Supergroup, South Africa: Evidence for Liquid Hydrocarbon Ore Fluids.

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Abstract:

High-grade gold and uranium mineralization in the Witwatersrand basin is intimately associated with pyrobitumen, implying that hydrocarbons may have played a role in the genesis of these ores. The nature of the pyrobitumen in the Carbon Leader Reef was therefore investigated to determine if hydrocarbons were essential to the ore-forming process. The relative proportions of trace elements in pyrobitumen seams and nodules are, in large part, similar to those of organic-rich shales located within the sedimentary succession. This indicates a strong genetic relationship between the pyrobitumen and the shales. A network of veins and veinlets filled with pyrobitumen, and the occurrence of oil inclusions in detrital and authigenic quartz grains, provide compelling evidence that the pyrobitumen was derived from a mobile (liquid hydrocarbon) precursor that circulated in the Carbon Leader Reef. Uranium, Au, Sb, Pb, Ag, Te, Th, Bi, Se and W are enriched relative to their concentrations in the shales. This is particularly the case for U and Au. The pervasive and relatively homogeneous distribution of the uranium is consistent with the presence of ubiquitous, submicroscopic uraninite in the pyrobitumen documented in an earlier study. In contrast, the distribution of the gold is heterogeneous, indicating the presence of irregularly distributed gold micrograins. These grains are concentrated mainly in the interstices between pyrobitumen nodules. Secondary minerals, such as brannerite, monazite-(Ce) and galena, are also concentrated in these interstices.

On the basis of this study, we propose that intrabasinal shale units of the Witwatersrand Supergroup were the source for the pyrobitumen in the Carbon Leader Reef. These shales produced and released liquid hydrocarbons during the burial of the sedimentary succession. Phyllosilicates enriched in trace metals were transferred from the shales into the newly produced liquid hydrocarbons and were transported stratigraphically upward by the latter into the Carbon Leader Reef. During migration, the liquid hydrocarbons dissolved detrital uraninite present in the basin, adding to the uranium budget. The liquid hydrocarbons were converted into pyrobitumen in response to further burial, and precipitated uraninite nanocrystals. Post-depositional, hydrothermal fluids interacted with the hydrocarbons and deposited gold by reduction on hydrocarbon surfaces. The interaction of these fluids with the hydrocarbons may have released U, Th, REE, Pb and Ti from the hydrocarbons and triggered the formation of secondary brannerite, monazite-(Ce) and galena. The results of this study provide convincing evidence that the

hydrocarbon liquids that formed the pyrobitumen seams in the Carbon Leader Reef played an essential role in the remobilization and redeposition of uranium and gold, respectively, in the Witwatersrand Supergroup.

1. Introduction

The Witwatersrand Basin in South Africa is the largest goldfield in the world, with an estimated past production of > 50,000 tonnes of gold (40 % of world production), and hosts a major uranium resource, with a past production of 1.35×10^6 tonnes U_3O_8 (Frimmel et al., 2005; Hartnady, 2009; Depiné et al., 2013). Despite its importance, there is still no agreement on the genesis of the ores. For over half a century, opinion has been divided over whether the ores are paleoplacers that have been modified by hydrothermal processes (Pretorius, 1991; Minter et al., 1993; Frimmel, 1997; Kirk et al., 2002; Frimmel et al., 2005), or are entirely hydrothermal in origin (Phillips and Myers, 1989; Barnicoat et al., 1997; Phillips et al., 1997; Law and Phillips, 2005). Proponents of the modified paleoplacer model are of the view that the gold and uranium were introduced as fluvially transported detrital grains into the Witwatersrand Basin from the Archaean hinterland, and were subjected to local hydrothermal remobilization (mm to cm scale) after burial. In contrast, the hydrothermal replacement model considers that the gold and uranium were introduced into the host conglomerates synchronously (Barnicoat et al., 1997) or separately (Phillips and Law, 2000) along thrust faults by hydrothermal fluids from the deeper parts of the Witwatersrand basin.

Recently, two quite different models for the genesis of the Witwatersrand deposits have been proposed, prompted in large part by a view that the current models do not satisfactorily account for the large mass of gold in the Witwatersrand deposits. Frimmel and Hennigh (2015) proposed that the source of the gold was a “huge reservoir of meteoric and shallow sea water” and that the gold in this reservoir was trapped by oxidative precipitation on the surfaces of the first oxygen-producing microbes (cyanobacteria) that appeared on the planet at about 3.0 Ga. According to this model, the gold in the resulting microbial mats (represented by carbon seams with which a significant proportion of the gold is associated; Nagy, 1993) was reworked into the placer deposits that now host the gold. In contrast, Heinrich (2015) proposed that eruptions of Archaean volcanoes released sulfurous gases and produced acid rain, which was able to dissolve gold in the hinterland, and transport it in river water to the basin. The subsequent precipitation of native gold is interpreted by him to have been chemically triggered by the reduction of gold on microbial mats as proposed by Frimmel and Hennigh (2015).

34 The above notwithstanding, the origin of the hydrocarbons in the Witwatersrand
35 deposits and their subsequent evolution are still matters of considerable debate. Bulk
36 and molecular isotopic data suggest that they are of biological origin, and were
37 derived from an intrabasinal source (Spangenberg and Frimmel, 2001). Some
38 researchers, including those referred to in the preceding paragraph, have interpreted
39 them to represent indigenous kerogen from algae or microbial mats. However, others
40 have interpreted them to be (pyro-) bitumen, derived from migrating liquid
41 hydrocarbons. In the case of the former interpretation, the algal / microbial mats
42 developed in situ and degraded shortly after sedimentation (Hallbauer and van
43 Warmelo, 1974; Hallbauer, 1975; Hallbauer, 1986). This model is supported by
44 features on the surfaces of “carbon seams” interpreted to represent desiccation
45 cracks and stromatolite-like structures (Mossman et al., 2008; Frimmel, 2014).
46 Supporters of the second model point to the preservation of liquid hydrocarbons as
47 inclusions in overgrowths on and healed fractures in detrital quartz grains, and
48 reflectance measurements, which classify the solidified hydrocarbons as a
49 pyrobitumen mesophase (Gray et al., 1998; Parnell, 1999; England et al., 2001;
50 England et al., 2002; Drennan and Robb, 2006; Fuchs et al., 2015).

51 Further support for the second interpretation of carbon seam formation was
52 provided recently by Fuchs et al. (2015) who presented evidence from the Carbon
53 Leader, one of the main gold reefs, that uranium occurs as nanoparticles or
54 aggregates of nanoparticles of uraninite (5-7 nm in diameter) in the carbon seams,
55 together with nanoparticles of titanium as anatase. On the basis of this evidence,
56 reports of hydrocarbon fluid inclusions (England et al., 2002) and uranium
57 concentrations in crude oils as high as 434 ppb uranium (Shah et al., 1970), they
58 proposed that the uranium was mobilized by formerly liquid hydrocarbons. According
59 to this model, circulating hydrocarbon liquids dissolved pre-existing detrital uranium-
60 and titanium-bearing minerals, transported them, probably as organometallic
61 complexes, and concentrated them as nanocrystalline uraninite and anatase in the
62 bituminous residues of the liquids.

63 In this paper, we report results of LA-ICP-MS, micro-PIXE / EBS and
64 compositional and microtextural analyses designed to investigate the distribution of
65 trace metals, including gold and uranium in pyrobitumen seams in the Carbon Leader
66 Reef. The results of this study show that liquid hydrocarbons, most likely derived
67 from underlying shale units, and their pyrobitumen residues, were directly involved in

the redistribution and concentration of gold, uranium and other trace metals, as agents of metal transport and deposition.

2. The Carbon Leader Reef

The Carbon Leader Reef is a gold-uranium-pyrite-bearing sedimentary unit with an average thickness of 1.2 m that is situated in the lower part of the Central Rand Group of the Witwatersrand Supergroup (Fig. 1). It is one of the main gold-producing reefs in the Witwatersrand with an estimated resource of 117.74 t gold and 1452 t U_3O_8 ; the average grade at the TauTona mine, Carletonville goldfield, the source of the samples used in this study, is 22.53 g/t gold and 0.28 kg/t U_3O_8 (AngloGoldAshanti, 2014). The Carbon Leader Reef consists of two sedimentary facies: (i) a lower tabular quartz-pebble conglomerate, up to 2 m thick, that grades upward into sandstone and (ii) an upper conglomerate, up to 20 cm thick, that overlies the latter and also grades into sandstone (Grové and Harris, 2010; AngloGoldAshanti, 2014). A thin hydrocarbon seam, up to 1.2 cm thick, occurs at the base of the lower quartz-pebble conglomerate parallel to the sedimentary bedding. This seam branches into smaller veins and veinlets that locally cross-cut the sedimentary layering. Locally, the hydrocarbons also occur as isolated nodules (“fly-speck carbon”). In the past, solid hydrocarbons in the Witwatersrand were often referred to as “Th-U-C-O-lite” or “carbon”. Later studies, however, showed that the hydrocarbons are morphologically and chemically complex structures, which are more accurately referred to as pyrobitumen (Gray et al., 1998; Frimmel et al., 2005; Drennan and Robb, 2006). Henceforth, we will use the term pyrobitumen to refer to these solids.

The Mesoarchean Witwatersrand Supergroup, of which the Carbon Leader Reef is part, is an ~7.5 km thick sedimentary succession of weakly metamorphosed sandstones, siltstones, shales and conglomerates that were deposited in a shallow marine to fluvio-deltaic environment (Fig. 1). The sediments experienced three episodes of post-depositional regional metamorphism due to: (i) the Ventersdorp volcanism (ca. 2.7 Ga); (ii) the emplacement of the Bushveld Igneous Complex (ca. 2.06 Ga); and (iii) the Vredefort meteorite impact event (ca. 2.02 Ga) (Coward et al., 1995; Robb and Meyer, 1995). These provided sufficient heat to promote the circulation of hydrothermal fluids. The regional metamorphic grade reached lower greenschist facies with the formation pyrophyllite, muscovite and chlorite, and peak

temperature-pressure conditions of ~300 - 350 °C and ≤ 3 kbar (Frimmel, 1994; Phillips and Law, 1994).

3. Methodology

The pyrobitumen in the lower gold-, uranium- and pyrite-bearing conglomerate of the Carbon Leader Reef is the focus of this study. The samples were taken from the TauTona mine (former Western Deep Levels 3 shaft) located in the Carletonville goldfield ~ 70 km to the southwest of Johannesburg, South Africa. Selected samples were embedded in epoxy resin and prepared as standard uncovered polished, thick sections. Additional doubly polished thick sections were prepared for the investigation of oil inclusions in quartz. Organic solvents, such as acetone, were not used during the preparation process.

3.1 Optical/scanning-electron microscopy and electron microprobe analyses

A combination of optical light microscopy and scanning electron microscopy was used to study the pyrobitumen and associated minerals, as well as for the selection of mineral-free areas within the pyrobitumen for LA-ICP-MS and micro-PIXE analyses. Hitachi SU8000 and Hitachi SU4700 field-emission scanning electron microscopes (FE-SEM) were employed for detailed examination of the samples. These are located at the Facility of Electron Microscopy Research (FEMR) at McGill University.

A Zeiss Axioskop epi-fluorescence microscope located in the Advanced BioImaging Facility (ABIF) at McGill University was used for the detection and study of liquid hydrocarbon inclusions. The microscope is equipped with an Hg-lamp, RGB camera, 10x and 100x Plan-Neofluar oil immersion objectives and exchangeable fluorescence cubes (e.g., DAPI, FTIC, Rhodamine), which cover the spectrum from UV to visible light.

A JEOL 8900 electron microprobe equipped with one EDS and five WDS detectors, located in the Department of Earth and Planetary Sciences, McGill University, was used to make element maps and backscattered electron images. The instrument was calibrated with appropriate mineral standards. The operating conditions were a 20 kV acceleration voltage, a 10 nA beam current and $< 1 \mu\text{m}$ beam size.

3.2 LA-ICP-MS

An Agilent 7700x quadrupole ICP-MS at the Geological Survey of Canada equipped with a Photon-Machines Analyte 193 excimer laser ablation system and a Helex two-volume ablation cell was used for trace element ablation analyses of pyrobitumen. Helium was used as the carrier gas. The analyses were performed at a laser repetition rate of 10 Hz, a laser pulse energy of $\sim 4 \text{ J}\cdot\text{cm}^{-2}$ and spot diameters from 34 to 63 μm , depending on the nature of the sample. Continuous line-scan analyses were conducted with a pre-ablation step, 5 $\mu\text{m/s}$ scanning speed and a beam size of 25 μm . Owing to the lack of suitable bituminous reference materials, the customized, synthetic oil standard “S-21” (by Conostan; <http://www.conostan.com/multi-element.aspx>) was used as the primary standard. The direct ablation of liquid calibration material has been successfully demonstrated as a reliable technique for analyses of solid organic material, including metalliferous bitumen (Günther et al., 1997; Mossman et al., 2010). The S-21 oil standard was spiked with 100 ppm of each of Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ti, V and Zn. The oil standard was introduced into capillary tubes, which were mounted vertically and broken to expose the oil in the upper end of the tube. Solid standards USGS GSE-1G (basalt glass; Guillong et al. (2005)) and Po726 (synthetic pyrrhotite doped with PGE and Au; Sylvester et al. (2005)) were used to extend the list of elements to include As, Au, Bi, Co, Hf, Nb, Pd, Pt, REE, Ru, Sb, Sc, Sr, Ta, Te, Th, Ti, U, W, Y and Zr. Samples were analyzed in cycles of approximately 15 analyses bracketed by analysis of each standard. NIST SRM 1632D (trace elements in coal (bituminous), https://www-s.nist.gov/srmors/view_detail.cfm?srm=1632d) was analyzed in each cycle as an unknown for quality control purposes.

A calibration protocol for the pyrobitumen analyses was developed for this multistandard approach, involving the use of S-21 as the primary standard and C as an internal standard to correct for ablation yield. A carbon concentration of 86 % was adopted for the S-21 oil standard and a previously determined carbon concentration was used for the pyrobitumen. To extend the list of elements analyzed beyond those in S-21, the concentration of Fe was determined for each analysis using S-21 and this standard was then used as the internal standard for calibration using GSE-1G (employing GeoRem Preferred concentration values (October, 2007), <http://georem.mpch-mainz.gwdg.de>, except an in-house determined value for Te) and Po726.

The GLITTERTM software package (Griffin et al., 2008) was used for the offline selective integration of time-resolved signal intensities and the calculation of element concentrations, as well the detection limits and 1 σ uncertainties. During signal processing, careful attention was paid to avoiding integration of rapid transient signals from possible mineral micro-inclusions.

3.3 Micro-PIXE and micro-EBS

The micro-PIXE and –EBS analyses were performed using the nuclear microprobe at the Materials Research Department of iThemba LABS, Somerset West, South Africa. The facility uses a 6 MV single-ended Van de Graaff accelerator and Oxford magnetic quadrupole triplet for beam focusing (Prozesky et al., 1995). A proton beam of 3.0 MeV energy and ~2 nA current was focused to a 5 x 5 μm^2 spot, and raster-scanned over selected areas of samples, using square or rectangular scan patterns of variable size (up to 2.5 mm x 2.5 mm scan areas) and a variable number of pixels (up to 128 x 128), up to the total charge of 13 – 16 μC per scan. The PIXE spectra were registered with a Si(Li) detector (30 mm^2 active area, working distance 24 mm), positioned at a take-off angle of 135°. The effective energy resolution of the PIXE system (for the Mn K α line) was 150-160 eV, measured for individual spectra. The X-ray energy range was set between 1 and 42 keV. Proton elastic backscattering (EBS) spectra were collected with an annular Si surface barrier detector (100 μm thick) positioned at an average angle of 176 °.

Each selected area was measured twice, using two different X-ray absorbers interposed between the sample and PIXE detector. Application of the thicker absorber (100 μm Al) restricted the practical X-ray energy range to above 4 keV. Additional measurements of low-energy X-rays (1-4 keV) were made using a 125 μm thick Be absorber. The proton current in this case was ~200 pA in order to reduce the number of pileups in the PIXE spectra.

Quantitative results were obtained using a standardless method employing GeoPIXE II software (Ryan et al., 1990; Ryan, 2000). The calibration of the analytical system was tested by measurements of reference materials: pure elements, pure minerals and USGS (United States Geological Survey) fused glass standards BIR-1 and BCR-2. Elemental mapping was performed using the Dynamic Analysis method (Ryan and Jamieson, 1993; Ryan et al., 1995; Ryan, 2000), which generates elemental images using series of X-ray lines (in this case K, L or M lines). The maps

are (i) overlap-resolved, (ii) with subtracted background, and (iii) quantitative, i.e., reported in ppm or wt.% units. Maps were constructed assuming an average bitumen-matrix composition obtained from EPMA analyses. Qualitative EBS maps for C and O were constructed using energy “gates” with background subtraction.

4. Results

4.1 Solid and liquid organic matter

Two morphologically different types of pyrobitumen seams were identified: (i) massive and (ii) nodular seams. There are also isolated nodules, as noted earlier. Massive seams are continuous on a scale of centimeters and display a homogeneous internal structure; small fractures are commonly present (Fig. 2A, B). They contain trace proportions of small ($< 8 \mu\text{m}$) uraninite grains (aggregates of nanocrystals; Fuchs et al., 2015) and filamentous gold. The latter is restricted to fractures, where it is accompanied by sericite and authigenic quartz, or is concentrated at the edges of the seams. The nodular seams are composed of tightly packed spindle-shaped nodules developed perpendicular to the plane of the seam (Fig. 2C, D). These seams contain much higher concentrations of uraninite and native gold. Angular to subangular uraninite grains (nanocrystalline aggregates) 5 to 50 μm in diameter occur pervasively within the nodules, whereas the native gold occurs in the interstices between the nodules and at their margins (Fig. 2D, E, F). The pyrobitumen seams and their interstices are devoid of demonstrably detrital minerals (e.g., quartz and pyrite pebbles), but occur in beds containing these minerals. The isolated pyrobitumen nodules (Fig. 2E) occur among the detrital minerals, and small groups of nodules form loosely packed aggregates. Small grains of uraninite (nanocrystalline aggregates) occur erratically within the nodules, whereas native gold lines them (Fig. 2E, F). Native gold is accompanied by authigenic minerals, such as sericite (mainly muscovite and pyrophyllite), florencite-(Ce), crandallite, monazite-(Ce), brannerite, xenotime-(Y), galena, pyrite, and quartz (Fig. 2D). Some of these texturally late minerals, notably brannerite, monazite-(Ce), florencite-(Ce) and galena, occur in direct contact with pyrobitumen (Fig. 2G) and contain elements (U, Ti, Th, Ce and Pb, Fig. 2H, I, J, K, L) that are also enriched in the pyrobitumen (see section 4.2). As noted earlier, regional metamorphism affected the Carbon Leader Reef and circulating post-depositional hydrothermal fluids

interacted with the hydrocarbons within the reef. It is thus possible that these minerals derived the above elements from pyrobitumen during interaction of the latter with hydrothermal fluids.

The two morphological types of pyrobitumen seams (massive and nodular) and the isolated nodules are linked by discordant pyrobitumen-filled veinlets that cut the conglomerates (Fig. 3A, B, C). The pyrobitumen-filled veinlets snake along grain boundaries and occupy fractures in detrital quartz grains as well as along fractures through authigenic quartz and sericite (Fig. 3A, B). Very small, aggregates nanocrystalline aggregates of uraninite (up to 5 μm in diameter) are present in all pyrobitumen veins; there are also rare examples of micron-scale uraninite euhedra (Fig. 3C).

Earlier, we pointed out that several previous studies have documented the occurrence in a number of Witwatersrand reefs of hydrocarbon fluid inclusions in overgrowths on, and healed fractures within, detrital quartz using fluorescence microscopy (e.g., Dutkiewicz et al., 1998; England et al., 2002). We applied the same technique to the quartz of the Carbon Leader Reef, and discovered hydrocarbon-bearing inclusions in the authigenic quartz cement and in healed microfractures within detrital quartz grains, wherever the two generations of quartz are proximal to pyrobitumen. The hydrocarbon-bearing inclusions are very small ($\leq 3 \mu\text{m}$ in diameter) and are subordinate to aqueous inclusions. They typically contain three phases (aqueous liquid, hydrocarbon liquid and vapor, Fig. 4A). The hydrocarbon liquid is readily distinguished by its strong fluorescence under long-wave UV, blue and green light, and is evident by intense blue, green and red colors (Fig. 4B, C, D). Solid or viscous hydrocarbon inclusions were also observed, mainly within the authigenic quartz. They are irregularly shaped, up to $\sim 8 \mu\text{m}$ in diameter, and consist of large aggregates of small brown, resin-like droplets (Fig. 4E) that fluoresce under long-wave UV and blue light, producing blue and green emission colors (Fig. 4F, G).

4.2 Trace element chemistry of pyrobitumen

Pyrobitumen of the Carbon Leader Reef samples was analyzed for its trace element concentrations using laser-ablation ICP-MS (Fig. 5, STab. 1). Individual samples of the massive seams (Bit #1, Bit #2 and Bit #5), massive seams with weakly pronounced nodular morphology (Bit #3) and nodular seams (Bit #4) were analyzed.

All analyzed samples (massive and nodular seams) have similar trace element compositions.

Uranium is by far the most abundant trace element in the pyrobitumen, with a mean concentration of 27,930 ppm (median: 19,390 ppm; Fig. 5). Other metals with mean concentrations in excess of 100 ppm are Pb (9410 ppm), Th (2,002 ppm), Fe (783 ppm), Ti (618 ppm), Y (600 ppm) and Ca (324 ppm). Anomalous Pb isotope ratios of 57.63 for $^{206}\text{Pb}/^{208}\text{Pb}$ and 7.93 for $^{206}\text{Pb}/^{207}\text{Pb}$ indicate that most of the lead in the pyrobitumen was produced by radiogenic decay of ^{238}U , ^{232}Th and ^{235}U in uraninite. The mean concentration of Au is 1306 ppm and Ag 159 ppm; however, their median concentrations are much lower, 15.6 ppm and 9.6 ppm, respectively, indicating that the analyses were compromised by micro-sized grains. The following elements have mean concentrations in the range of 10 to 100 ppm: Mn (64 ppm), Zr (63 ppm), Sb (51 ppm), Ni (43 ppm), As (39 ppm), Cr (28 ppm), Sr (19.1 ppm), Cu (16.6 ppm) and Sc (15.7 ppm). All other elements analyzed, except the rare-earth elements (REE), are present in concentrations below 10 ppm, as shown in Figure 5 and supplemental Table 1. Palladium and Pt have very low concentrations, 124 ppb and 4 ppb, respectively.

As has been mentioned already and is discussed further below, opinion is divided over whether the carbon seams represent former algal / microbial mats or liquid hydrocarbons that were released from black shales deeper in the basin. If the latter represents the source of the pyrobitumen, it would be reasonable to expect some similarity in the distribution of the trace elements in the pyrobitumen to that in the black shales of the Witwatersrand basin. We have therefore compared the distribution of the trace elements in the pyrobitumen to that of carbonaceous shales located in the West Rand and Central Rand Group (Witwatersrand Supergroup). As is evident from the spider-diagrams in Figure 6, the pyrobitumen and the shales exhibit quite similar element distribution patterns. The concentration profile for Ca, Sc, Ti, V, Cr, Fe, Co, Ni, Sr, Zr, Nb and Hf in the pyrobitumen parallels that in the shales, although the absolute concentrations in the pyrobitumen are lower, for some elements over two orders of magnitude lower (Fig. 6A). The list of elements for which the profiles are parallel can be extended to Mn, Zn, As, Se, Mo and Cd, which were not considered in the Witwatersrand shale studies, if the comparison is to international shale standards (NASC, black shale average #1, black shale average #2, Fig 6B). In contrast, Y, Ta, Au, Pb, Th and U are enriched in the pyrobitumen by

between one and four orders of magnitude over their concentrations in the Witwatersrand black shales. This list is expanded to include Ag, Sb, Te, W, Tl and Bi, if the comparison is to the international shale standards (Fig. 6B). The relationships evident in Figure 6 are also illustrated in Figure 7 to permit better visualization of the extent of depletion and enrichment of different trace elements in the pyrobitumen relative to the average Witwatersrand black shale (Fig. 7A) and the composite shale standards (Fig. 7B).

In order to understand the enrichment of elements in the pyrobitumen other than the ore elements gold and uranium, histograms were made of the correlation coefficients (Pearson's correlation coefficient at the 95 % confidence level) for these elements with gold and uranium (Fig. 8A, B). To gain further insight into the causes of this enrichment, concentrations of trace elements showing significant correlation with gold and uranium ($r > 0.5$) were plotted in bivariate diagrams against the concentrations of Au and U (Fig. 8C - F). As expected, Ag ($r = 0.99$) and Te ($r = 0.95$) concentrations show very strong linear correlations with that of Au (Ag alloys with Au and, although gold tellurides have not been reported for the Witwatersrand Reefs, they are very common elsewhere) and Bi ($r = 0.56$) a moderate correlation (gold also occurs commonly as Bi-bearing sulfosalts in other deposits, although these phases have not so far been reported from the Witwatersrand Basin) (Fig. 8C, D). Likewise, as expected, concentrations of Th ($r = 0.96$) and Pb ($r = 0.96$) correlate strongly with concentrations of U (Th, like U is an actinide, and the radiogenic isotopes of both elements decay to Pb) (Fig. 8E). Concentrations of W ($r = 0.96$), Sb ($r = 0.96$), Bi ($r = 0.9$) and Se ($r = 0.88$) also correlate strongly with that of U. Single outliers highlighted by the field delineated with a dashed line in Figures 8E and 8F are characterized by overall high trace element concentrations, and suggest the presence of the small uraninite inclusions within the pyrobitumen. The good correlation of U with Th, Pb, W and Bi is also consistent with the results of analyses of large rounded to subrounded uraninite grains, which report appreciable concentrations of Th, Pb, W and Bi (e.g., Depiné et al., 2013). The strong linear correlation of Sb and Se with U is unexpected and thus far not explained. The only other trace element that is significantly enriched in the pyrobitumen relative to black shales is Y. Although it does not show a significant correlation with Au or U, Y accompanies native gold as xenotime-(Y) in the interstices between pyrobitumen nodules and, as discussed below, may also be present in the structure of the pyrobitumen or occur within it as nanoparticles.

4.3 Distribution of uranium and gold in pyrobitumen

Earlier, we reported that uraninite is evenly dispersed through the pyrobitumen, whereas the occurrence of native gold in the pyrobitumen is largely restricted to fractures; it also occurs in interstices between pyrobitumen nodules and on the surfaces of pyrobitumen seams. This implies that uranium may have been transported by a hydrocarbon precursor to the pyrobitumen, as proposed by Fuchs et al. (2015) and, in contrast, that gold was trapped by the pyrobitumen. In order to address this issue further, time-resolved LA-ICP-MS line scans were made into parts of this phase, which were deemed to be free of inclusions, based on examination of scanning electron microscope images. Figure 9 shows a continuous line-scan from a quartz grain into a massive pyrobitumen seam. The black dashed vertical lines bracket the domains of the ablated quartz and pyrobitumen in the line scan, the boundaries of which are marked by sharp changes in the counts for Si and C. The increase of carbon counts at the contact with the pyrobitumen is accompanied by a strong increase in uranium counts to a plateau value over much of the scan through the pyrobitumen; near the end of the scan there is a peak in uranium counts. The occurrence of a plateau concentration indicates that uranium is either structurally bound (e.g., as organometallic complexes) in the pyrobitumen or is present as evenly distributed nanoparticles, whereas the peak points to the presence of a submicroscopic uraninite grain or large nanocrystal aggregate. Similar distribution patterns are observed for lead (^{206}Pb) and thorium (^{232}Th). The former reflects the fact that lead is a decay product of uranium and the latter that thorium is present in the uraninite. Although the concentration of Au is clearly higher in the pyrobitumen than in the quartz, the numerous peaks in the counts indicate that it is present mainly as small, submicroscopic native gold grains.

4.4 Rare-earth elements in pyrobitumen

The pyrobitumen was also analyzed for its rare-earth element (REE) composition using LA-ICP-MS. The heavy REE are more abundant than the light REE, with Y having the highest mean concentration (600 ppm), followed by Dy (171 ppm), Tb (117 ppm) and Er (76 ppm) (STab. 1). By comparison, the light REE, La and Ce, have concentrations of 4 ppm and 29 ppm, respectively. This is opposite to what might be expected from their Archaean upper crustal abundances (Dy, 3.4 ppm; Tb, 0.6 ppm; Er, 2.1 ppm; La, 20 ppm and Ce 42 ppm; Taylor and McLennan (1995)),

and suggests that factors other than element availability controlled their concentration in the pyrobitumen. To address this issue further, quantitative micro-PIXE and micro-EBS elemental maps were prepared to assess the distribution of rare-earth elements in the organic structure of the pyrobitumen. Two map sets for C (micro-EBS), Dy, Gd and Y (micro-PIXE) in the massive pyrobitumen seams are displayed in Figure 10. For the most part, dysprosium and Gd are evenly distributed within the pyrobitumen. The same applies to Y, except for some zones of higher concentration, indicating the presence of small xenotime-(Y) inclusions. The almost homogeneous distribution of the heavy REE, however, indicates that they are present in the structure of the pyrobitumen or are present as nanoparticles.

As discussed earlier, the distribution of many of the metals in the pyrobitumen seams to parallel that in the black shales from which we propose the pyrobitumen ultimately originated. However, as intimated above, this may not hold for the REE. In order to evaluate the issue further, the mean REE values for the five analyzed samples (Bit #1 to #5) were normalized to chondrite and compared to corresponding chondrite-normalized values for carbonaceous shales located in the West and Central Rand (Witwatersrand Supergroup; Fig. 11A). As is evident from the profiles in this figure, the REE distributions of the pyrobitumen and the shales are very different. The profiles show that the pyrobitumen is enriched in the light REE (La, Ce) relative to chondrite, that there is an increase in concentration to Sm, a plateau from Gd to Dy and a gentle decrease to the heavy REE (Yb, Lu). They also show a weak negative Eu anomaly. In contrast, the REE profiles of the Witwatersrand black shales are characterized by light REE (La, Ce) enrichment and a gradual decrease in concentration toward the heavy REE (Yb, Lu). As concentrations for a number of REE were not reported in the studies of the Witwatersrand shales, the chondrite-normalized pyrobitumen REE values were also compared to those of international shale composites and the Archaean upper crust (Fig. 11A). Not unexpectedly, the expanded profiles mimic those of the Witwatersrand Supergroup, i.e., the REE distribution in the pyrobitumen is markedly different from those of average international standards and the Archaean upper crust.

Given that uraninite can also contain significant REE, and xenotime-(Y) is a common detrital mineral in the quartz-pebble conglomerates of the Witwatersrand Supergroup, including those of the Carbon Leader, we compared the REE distribution of uraninite and xenotime to that of the pyrobitumen (Fig. 11B). The REE

data for the uraninite were taken from a study of morphologically different uraninite types in the Vaal and Carbon Leader Reefs (unpublished data, S. Fuchs). Based on their morphology, the uraninite grains in these reefs can be divided into two types: (i) detrital, rounded uraninite and (ii) irregular secondary grains comprising submicrometric aggregates of smaller grains (Fig. 12). The secondary grains are observed in both reefs, whereas clearly detrital uraninite grains occur only in the Vaal Reef. However, both types of uraninite display the same chondrite-normalized REE profiles. Most significantly, the uraninite profiles are remarkably similar to those of the pyrobitumen, although the absolute REE concentrations of the pyrobitumen are very much lower. Kositsin et al. (2003) reported REE data for detrital xenotime-(Y) grains from the Vaal, Denny's and B-Reefs. The shapes of their chondrite-normalized REE profiles are very similar to those of the pyrobitumen from Gd to Lu but, in contrast to the pyrobitumen, the profiles display strong negative Eu anomalies and greater relative depletions in the light REE. These observations suggest strongly that the pyrobitumen inherited its REE signature from uraninite, possibly with a contribution from xenotime-(Y), but not from the shales.

5. Discussion

5.1 Introduction

The origin and evolution of the pyrobitumen seams and nodules, as has already been mentioned, are subjects of considerable debate. Early investigators interpreted them to be the remnants of former algal mats that grew into columnar structures from carpet-like colonies on conglomerate beds (Hallbauer and van Warmelo, 1974; Hallbauer, 1975; Hallbauer, 1986). The discovery of inclusions of liquid hydrocarbons in quartz overgrowths on detrital quartz grains and in healed fractures in the latter, however, led to the proposal that the seams and nodules are residues (pyrobitumen) of liquid hydrocarbons (Gray et al., 1998; Parnell, 1999; England et al., 2001; England et al., 2002; Drennan and Robb, 2006). According to this hypothesis, the hydrocarbons were produced during burial, when intrabasinal organic-rich shales (starting with those of the West Rand) passed progressively through the oil window at a temperature of 100 °C - 150 °C and a geothermal gradient of 15 °C - 35 °C.km⁻¹ (England et al., 2002). As has also been noted, the microbial (algal) mat hypothesis has recently been revived with the discovery of morphological features interpreted to

represent desiccation cracks and drape ripples on hydrocarbon surfaces, and stromatolite-shaped nodules (Mossman et al., 2008; Frimmel, 2014; Frimmel and Hennigh, 2015). Below, we discuss the two hypotheses in the context of the ore metals bound to and in pyrobitumen of the Carbon Leader Reef, and make the case that the pyrobitumen was derived from liquid hydrocarbons released by black shales.

5.2 The origin of the pyrobitumen

In order to test the hypothesis that the pyrobitumen originated from liquid hydrocarbons released by black shales, we compared the trace element concentrations of the pyrobitumen to those of black shales in the West and Central Rand Group. As reported earlier, the trace element distribution (Ca, Sc, Ti, V, Cr, Fe, Co, Ni, Sr, Zr, Nb and Hf) of the pyrobitumen is very similar to that of the shales, especially for those elements that are relatively depleted in the pyrobitumen (Figs. 6 and 7). This provides strong evidence for a genetic relationship between the pyrobitumen and the shales, and indicates that both formed under similar geochemical conditions.

Under the anoxic / euxinic conditions that prevailed in the Witwatersrand basin, the accumulation of trace elements in the fine-grained, organic-rich sediments would have been due mainly to chemical and microbe-mediated processes. More specifically, the trace elements would have been concentrated from seawater by the formation of organometallic complexes, adsorption of metallic ions or ionic species onto organic or mineral substrates and the precipitation of authigenic minerals such as sulfides and / or (oxy) hydroxides (e.g., Coveney, 2000; Ripley and Shaffer, 2000; Algeo and Maynard, 2004; Rimmer, 2004; Tribovillard et al., 2006). Any detrital contribution would have been relatively small.

Oil production from the shale units in the Witwatersrand basin is interpreted to have taken place as the shale units passed through the oil window at temperatures of 100 °C to 150 °C (England et al., 2002). When this occurred, trace metals bound in the shale kerogens and incorporated within or adsorbed onto the surfaces of clay minerals would have been transferred into the newly formed oil phase. Small clay particles would also have been adsorbed directly onto the oil phase and transported mechanically with it (Yan and Masliyah, 1994; Yan and Masliyah, 1996; Sullivan and Kilpatrick, 2002), thereby further contributing to the trace element signature of the liquid hydrocarbons and ultimately the pyrobitumen.

In principle, an indigenous, syngenetic kerogen-precursor (from algal/ microbial mats) buried in a conglomeratic reef, could also have produced liquid hydrocarbons that yielded a pyrobitumen residue. If this were the case, however, the trace element concentrations of the pyrobitumen residue would reflect a conglomerate source and not that of black shale. For example, there would have been a high input from detrital minerals (e.g., pyrite, zircon and rutile) to the trace element budget evident in high concentrations of Fe, Zr, and Ti. This was clearly not the case.

In view of the observations of the preceding paragraphs, we propose that shales of the West and Central Rand Groups, e.g., the shale units of the Roodepoort and Promise Formations, were the source of the liquid hydrocarbons that gave rise to pyrobitumen in the Carbon Leader Reef and also the source of many of the trace elements. We propose also, from the presence of an extensive system of pyrobitumen veins cutting oil-bearing detrital and authigenic quartz and connecting pyrobitumen seams to solidary / groups of nodules ("fly-speck carbon") (Fig. 3A, B, C), that migration of liquid hydrocarbons through the Carbon Leader Reef, and accumulation of metals in it, occurred after sediment burial and was long-lived.

5.3 The source of uranium and related trace elements in the pyrobitumen

Although the composition of the pyrobitumen mimics that of the shales of the West and Central Rand Groups for many trace elements, the pyrobitumen is unusually enriched in uranium (~ 1.9 wt% median concentration; Fig. 5, STab. 1) and HREE (Fig. 6, Fig 11), as well as in trace elements that correlate strongly with uranium (Th, W, Sb and Pb; Fig. 7, Fig. 8B). Significantly, some of these trace elements (Th, W, HREE and Pb) are also strongly enriched in detrital uraninite in the Witwatersrand basin (e.g., Depiné et al., 2013), suggesting that uraninite may be the source of their enrichment and that of uranium in the pyrobitumen. Some of the trace elements (U, Th and the HREE), however, could have come partly from detrital xenotime-(Y), which is enriched in U and Th and has a HREE profile very similar in shape to that of the pyrobitumen (compare with Kositsin et al., 2003).

We propose that the pyrobitumen acquired its uranium mainly through the dissolution of detrital uraninite by its liquid hydrocarbon precursor, an interpretation that is supported by textures providing evidence of partial dissolution and replacement of detrital uraninite by hydrocarbons (Fig. 12; see also Eakin and Gize (1992); Law and Phillips (2006)). This interpretation is also supported by the

discovery in the pyrobitumen of nanocrystals of uraninite that maintain a consistent diameter of 5 to 7 nm (Fuchs et al., 2015). The similar concentrations and distribution patterns of trace elements in all analyzed samples show that uraninite nanocrystals are ubiquitous in the pyrobitumen of the Carbon Leader Reef, and the redistribution of these metals and the in situ formation of uraninite occurred reef-wide. Additional textural evidence for the in situ formation of uraninite from hydrocarbons is provided by the presence of small, euhedral uraninite grains in texturally late pyrobitumen veins (Fig. 3B, C) linking pyrobitumen seams and nodules.

The manner in which the uranium was dissolved in the precursor liquid hydrocarbons is unknown, but as V and Ni (the most abundant metals in crude oils), occur in crude oils dominantly as porphyrin species (Filby and Vanberkel, 1987), it is reasonable to speculate that uranium dissolved in the liquid hydrocarbons as a porphyrin species. Significantly, vanadium in crude oils is incorporated in the porphyrin structure as the vanadyl (oxidized) ion, VO^{2+} , which may indicate that uranium dissolved as the uranyl (UO_2^{2+}) ion, particularly given that it is known to form strong porphyrin complexes (Sessler et al., 2001). If this were the case, then uranium could subsequently have precipitated as uraninite nanocrystals through a redox reaction involving destabilization of the uranyl porphyrin during pyrobitumen formation. It is also possible that the uranium was dissolved as a uranous (UO^{2+}) porphyrin (Girolami et al., 1994), in which case the uraninite precipitation reaction would not have involved a redox change. We therefore propose that uranium and the other trace metals enriched in the pyrobitumen, all of which form strong porphyrin complexes (Dunning et al., 1960; Doukkali et al., 2002; Wei et al., 2005; Ali and Abbas, 2006) were transported in the precursor hydrocarbon liquid as porphyrin species.

5.4 Hydrothermal concentration of gold in and around pyrobitumen

Gold, Ag and Te are enriched in the pyrobitumen relative to the West and Central Rand Group shales (Fig. 5, 6, 7, STab. 1). In contrast to uranium, however, the time-resolved LA-ICP-MS line scans show sharp peaks of gold concentration (Fig. 9). This suggests strongly that the gold is present mainly as discrete submicroscopic and irregularly distributed grains of native gold. The positive correlation of Au with Te and Bi also suggests that gold is probably present as a yet unidentified gold telluride (e.g., calaverite AuTe_2) or gold alloy (e.g., Maldonite, Au_2Bi). Post-depositional

hydrothermal fluids are the most likely source for the gold in the pyrobitumen seams. Based on microthermometric analyses of fluid inclusions in quartz and phase equilibria, these fluids are interpreted to have been slightly reducing, moderately saline, moderately acidic, and to have reached maximum temperatures of 300 °C to 350 °C (Drennan et al., 1999; Frimmel et al., 1999). Interaction of the gold-bearing aqueous solutions with the still liquid or solidified hydrocarbons in the reef would have triggered gold precipitation through the reaction:

assuming as seems reasonable for the above conditions, that the gold was transported as Au(HS)[°] (Williams-Jones et al., 2009). This interaction would have oxidized the pyrobitumen to form CO₂, lowering the oxygen fugacity and driving reaction 1 to the right. Textural evidence for this hydrocarbon-triggered precipitation of gold from hydrothermal fluids in the Carbon Leader is provided by the occurrence of microscopic filamentous gold grains that coat pyrobitumen nodules and fill interstices between them and fractures (Fig. 2D, E, F).

In addition to native gold, migrating hydrothermal fluids also deposited significant quantities of other authigenic minerals (such as brannerite, monazite-(Ce), galena, crandallite, and florencite-(Ce)). They may also have altered the hydrocarbons, as proposed by Gray et al. (1998) to explain the spindle-shaped (nodular) nature of the pyrobitumen mesophase. Given that the metals comprising these minerals are particularly enriched in the pyrobitumen, e.g., U, Ti, Th, Pb and the REE (Fig. 2G - L), and some of the metals, notably Ti and Th, are notoriously insoluble in hydrothermal fluids, we propose that they were released by the pyrobitumen during its hydrothermal alteration and immediately redeposited in the adjacent space. According to this hypothesis, release of these metals occurred via simple exchange reactions such as,

and

where “OM” represents the organic matter, and H⁺ is exchanged with the metal. Note that, if the valence state of the uranium in the organic matter was 4+, the redox state would not have changed during the transfer of uranium into brannerite and the

hydrothermal solution would not have participated in the transfer (uranium is only soluble in hydrothermal fluids as U^{6+}). The above hypothesis is supported by experiments showing that metals can be effectively stripped from hydrocarbons, when they come in contact with water, particularly at low to intermediate pH (Manning and Gize, 1993; Giordano, 2000).

5.5 Timing of gold-uranium mobilization

The evidence presented in this paper for post-depositional mobilization of both gold and uranium is consistent with results of studies investigating the timing of the gold mineralization in the Witwatersrand basin (e.g., Kositsin et al., 2003; Schaefer et al., 2010; Mathur et al., 2013). Of particular interest for our study is the finding of (Schaefer et al., 2010) that organic matter intimately associated with gold mineralization in the Vaal reefs displays open system Re-Os isotope behaviour, which continued until $\sim 2.26 \pm 0.19$ Ga, i.e., approximately 450 Ma after the end of sedimentation. This supports our conclusion that liquid hydrocarbons circulated in the Witwatersrand basin and served to mobilize uranium and trigger hydrothermal gold mineralization long after the accumulation of the quartz pebble conglomerates that are the hosts to the metals and pyrobitumen seams.

6. Conclusions

In this paper, we have shown that hydrocarbons were essential in the formation of the high-grade gold and uranium ores of the Carbon Leader Reef. We have also shown that the pyrobitumen seams in this reef were derived from migrating hydrocarbon liquids that most likely originated from carbonaceous shales that are in vicinity of the Carbon Leader Reef, such as those of the Roodepoort and Promise Formation. These hydrocarbons mobilized trace metals from the carbonaceous shales, and also from detrital uraninite and xenotime-(Y), and concentrated them in the Carbon Leader Reef. The subsequent loss of light hydrocarbons led to the formation of residual pyrobitumen and further concentration of the trace metals. The distribution of uranium and its strong correlation with metals that are commonly present in uraninite suggest that the uranium is concentrated in uraninite nanocrystals, which are ubiquitous in the pyrobitumen, as shown by our earlier study. The interaction of the pyrobitumen and its hydrocarbon liquid precursor with hydrothermal gold-bearing fluids led to the deposition of native gold. The intense

interaction of the hydrocarbons with hot hydrothermal fluids, probably at low pH, caused leaching / stripping of metals from the pyrobitumen and the in situ formation of brannerite, galena and monazite-(Ce).

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9. Figure captions

Fig. 1 Simplified geological map and stratigraphic column of the Witwatersrand Basin and surrounding areas showing the location of the study site (modified from England et al., 2002; Frimmel et al., 2005). The stratigraphic position of the Carbon Leader Reef is indicated with a red arrow, and the positions of the shale units analyzed by Wronkiewicz and Condie (1987), and used for comparison in Fig. 6, 7 and 11, are indicated with black arrows.

Fig. 2 Reflected-light microscopic images (A, B, E, F), SEM backscattered electron images (C, D, G, M, N, O) and electron microprobe-based element-distribution maps (H, I, J, K, L) of pyrobitumen and associated minerals in the Carbon Leader Reef. (A) A massive pyrobitumen seam, which is irregularly shaped, homogeneous and mineral free, but bound by detrital minerals, such as pyrite (Py) and quartz (Qtz). (B) A massive pyrobitumen seam, similar to that in (A), showing a laser-ablation hole. (C) A highly mineralized pyrobitumen seam consisting of spindle-shaped nodules. Angular uraninite (Urn) grains are embedded within the pyrobitumen nodules. (D) Interstitial space between pyrobitumen nodules in the seam shown in (C). Gold (Au) usually lines the rims of the nodules, whereas uraninite (Urn) occurs within the nodules. Crandallite (Crd) and irregular brannerite (Br) grains are also present in the interstices. (E) A single pyrobitumen nodule lined by filamentous gold (Au) and surrounded by quartz crystals. Very small, angular uraninite (Ur) grains occur within the nodule. (F) Pyrobitumen nodules. Gold (Au) occurs at the interface between quartz (Qtz), sericite (Ser) and the nodules; small uraninite grains are distributed erratically within the nodules. (G) Electron microprobe backscattered electron image (BSE) and corresponding element-distribution maps for U (H), Ti (I), Th (J), Ce (K) and Pb (L) of interstices in a nodular pyrobitumen seam. Brannerite, galena and monazite-(Ce) line the nodules.

Fig. 3 SEM backscattered electron images of pyrobitumen veins. (A) Pyrobitumen veins in quartz surrounding uraninite-bearing (Urn) pyrobitumen nodules. (B)

Pyrobitumen veins cutting detrital quartz grains as well as authigenic sericite / quartz. (C) Enlargement of the area labeled with C displayed in (B), showing the presence of euhedral, in situ-formed uraninite in the pyrobitumen vein.

Fig. 4 Transmitted-light microscope image of oil / bitumen inclusions with corresponding epi-fluorescence microscope images. (A) Three-phase oil-water-gas inclusion in a detrital quartz grain (secondary inclusion). The oil (hydrocarbon) phase is strongly fluorescent under long-wave UV (B), blue (C) and green light excitation (D). (E) Viscous or solid, brown resin-like inclusions in authigenic quartz trapped along a healed fracture. Under long-wave UV (F) and blue (G) light excitation, they are luminescent with strong blue and green colors.

Fig. 5 Boxplot-whisker plots of the concentrations of trace elements in the pyrobitumen seams. The boxes represent the first (25 %) to the third (75 %) quartile, and the horizontal line within the boxes the median values (second quartile) of the dataset. The whiskers indicate the minimum and maximum values. The element concentrations are given in ppm.

Fig. 6 Spider diagrams comparing the trace element concentrations in pyrobitumen to that of carbonaceous shales. For the pyrobitumen (bit), the red line illustrates the median trace element concentrations of the pyrobitumen, and the pink-shaded area around it, the first to the third quartile (25 % - 75 %) of the dataset. (A) Trace element concentrations in pyrobitumen compared to those of average concentrations of carbonaceous shale units within the sedimentary succession of the Witwatersrand basin. (B) Trace element concentrations in pyrobitumen compared to average concentrations of international black shale composites #1 and #2 (black shales) and the North American Shale Composite (NASC). In both spider diagrams (A and B), the distribution of many trace elements (e.g., Ca, Sc, Ti, Co) in the pyrobitumen is similar to that of the shales although the absolute concentrations are lower. However, several elements have distinctly higher concentrations in the pyrobitumen (e.g., Au, Pb, Th, U and Y). The data sources for the shales indicated by superscripts on the diagrams are: ¹Wronkiewicz and Condie (1987), ²Quinby-Hunt et al. (1989), ³Ketris and Yudovich (2009), ⁴Gromet et al. (1984), ⁵Condie (1993) and ⁶Morgan et al. (1978). The abbreviations used for the shale units in the Witwatersrand basin are: Orange Grove (OG) and Parktown-Brixton (Pt-Brx) shales of the Hospital Hill Subgroup, the Promise (Prm) shales of the Government Subgroup and the Roodepoort (Ro) shales of the Jeppestown Subgroup (all in West Rand Group), the

Booyens (Boy) shales of the Johannesburg Subgroup and K-8 (K8) shales of the Turffontain Subgroup (both in Central Rand Group).

Fig. 7 Histograms of trace element depletion and enrichment in pyrobitumen relative to (A) carbonaceous shales of the Witwatersrand Supergroup and (B) international black shale composites #1 and #2, and the North American Shale Composite (NASC). The data sources for the shales indicated by superscripts on the diagrams are: ¹Wronkiewicz and Condie (1987), ²Quinby-Hunt et al. (1989), ³Ketris and Yudovich (2009), ⁴Gromet et al. (1984), ⁵Condie (1993) and ⁶Morgan et al. (1978).

Fig. 8 Histograms and bivariate plots for trace elements enriched in pyrobitumen relative to shale. (A) Histogram of correlation coefficients for trace elements versus Au, (B) histogram of correlation coefficients for trace metals versus U. Bivariate plots of element pairs with correlation coefficients, $r \geq 0.5$; (C) Au-Ag, (D) Au-Te, Ag-Bi, (E) U-Pb, U-Th and (F) U-Sb, U-W, U-Bi and U-Se. Linear fit lines and correlation coefficients (r) were calculated at the 95 % confidence level for each element pair. The black dashed fields in E and F indicate outliers due to uraninite micro-inclusions.

Fig. 9 Time-resolved LA-ICP-MS signal intensities for a line scan across a quartz grain and mineral-free pyrobitumen. The black dashed lines indicate the position of the laser. Uranium, gold, thorium and lead concentrations are considerably higher in the pyrobitumen than the quartz. The plateau-shaped, line for uranium concentration indicates that uranium / uraninite is homogeneously distributed within the pyrobitumen, whereas the sharp peaks in the gold line indicate that it occurs mainly as native gold micro-inclusions.

Fig. 10 Micro-PIXE and micro-EBS element distribution maps of C, Gd, Dy and Y in a massive pyrobitumen seam. The two map sets (A – D and E – H) show that the rare-earth elements have elevated concentrations and are pervasively distributed within the pyrobitumen.

Fig. 11 (A) Chondrite-normalized REE profiles of pyrobitumen compared to those of carbonaceous shales within the sedimentary succession of the Witwatersrand basin, North American Shale Composite (NASC) and upper crust. (B) Chondrite-normalized REE profiles of pyrobitumen compared to those of detrital and secondary uraninite and xenotime-(Y). The shape of the REE profile of the pyrobitumen is remarkably similar to that of the uraninite and to a lesser extent the xenotime-(Y) profile, which has a large negative Eu anomaly and a greater depletion in the light REE, although

the absolute REE concentrations of the latter are much higher. The data sources for the shales and detrital xenotime are indicated by superscripts on the diagrams. They are: ¹Wronkiewicz and Condie (1987), ²Quinby-Hunt et al. (1989), ³, ⁴Gromet et al. (1984), ⁵Condie (1993) and ⁶Morgan et al. (1978), ⁷Taylor and McLennan (1995), ⁸Birdwell (2012) and ⁹Kositcin et al. (2003). The abbreviations used for the shale units in the Witwatersrand basin are: Orange Grove (OG) and Parktown-Brixton (Pt-Brx) shales of the Hospital Hill Subgroup, the Promise (Prm) shales of the Government Subgroup and the Roodepoort (Ro) shales of the Jeppeshtown Subgroup (all in the West Rand Group), the Booyens (Boy) shales of the Johannesburg Subgroup and K-8 (K8) shales of the Turffontain Subgroup (both in Central Rand Group).

Fig. 12 Uraninite grains with variable morphology. (A) Rounded detrital uraninite grain within a pyrobitumen vein in the Vaal Reef. (B) Secondary angular uraninite aggregate in a pyrobitumen seam of the Carbon Leader Reef. (C) Secondary uraninite aggregate in Carbon Leader Reef with a delicate, “sponge-like” texture.

10. Supplemental data

Caption for the supplemental table in the appendix:

STable 1 Trace element concentrations of pyrobitumen samples, including mean, median, minimum, maximum values, limits of detection (in ppm) and standard deviation (1σ).

Fuchs, S., Williams-Jones, A.E., Jackson, S.E., Przybylowicz, W.J., 2016a. Metal distribution in pyrobitumen of the Leader Reef, Witwatersrand Supergroup, South Africa: Evidence for liquid hydrocarbon ore fluids. *Chemical Geology*. DOI:10.1016/j.chemgeo.2016.02.001.

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depletion enrichment

depletion enrichment

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min. Concentration max.

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