

New data on Hydrocarbons in Auriferous Conglomerates of the Witwatersrand Ore Region, Republic of South Africa

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Abstract—Genesis of deposits in the world's largest Witwatersrand auriferous region (South Africa) remains a debatable issue over several decades. Based on geological and mineralogical–geochemical investigations, we previously proposed a sedimentary–exhalative hypothesis for its origin. In the present communication, we have attempted to develop and scrutinize this concept based on the study of organic matter in ore and nonore conglomerates, quartz in conglomerate pebbles, and fluid inclusions in quartz from pebbles and cement of ore and nonore conglomerates.

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Genesis of ores of the world's largest Witwatersrand auriferous region (South Africa) remains a debatable issue over several decades. As is known, auriferous conglomerates account for 58% of the world's total gold reserves. Based on comprehensive geological and mineralogical–geochemical investigations, we proposed a new hypothesis of the predominant role of sedimentary–exhalative process in the formation and localization of gold deposits and occurrences (Kremenetsky et al., 1997). According to this concept, ore components are derived from hydrothermal solutions. The ores are precipitated in the course of both the discharge of hydrothermal solutions along conduits and the ordinary sedimentation on seafloor. In the present communication, we have attempted to develop and scrutinize this concept based on the study of organic matter in rocks, quartz in conglomerate pebbles, and fluid inclusions in quartz from pebbles and cement of ore and nonore conglomerates in the Witwatersrand Basin.

GEOLOGICAL SETTING OF THE ORE REGION

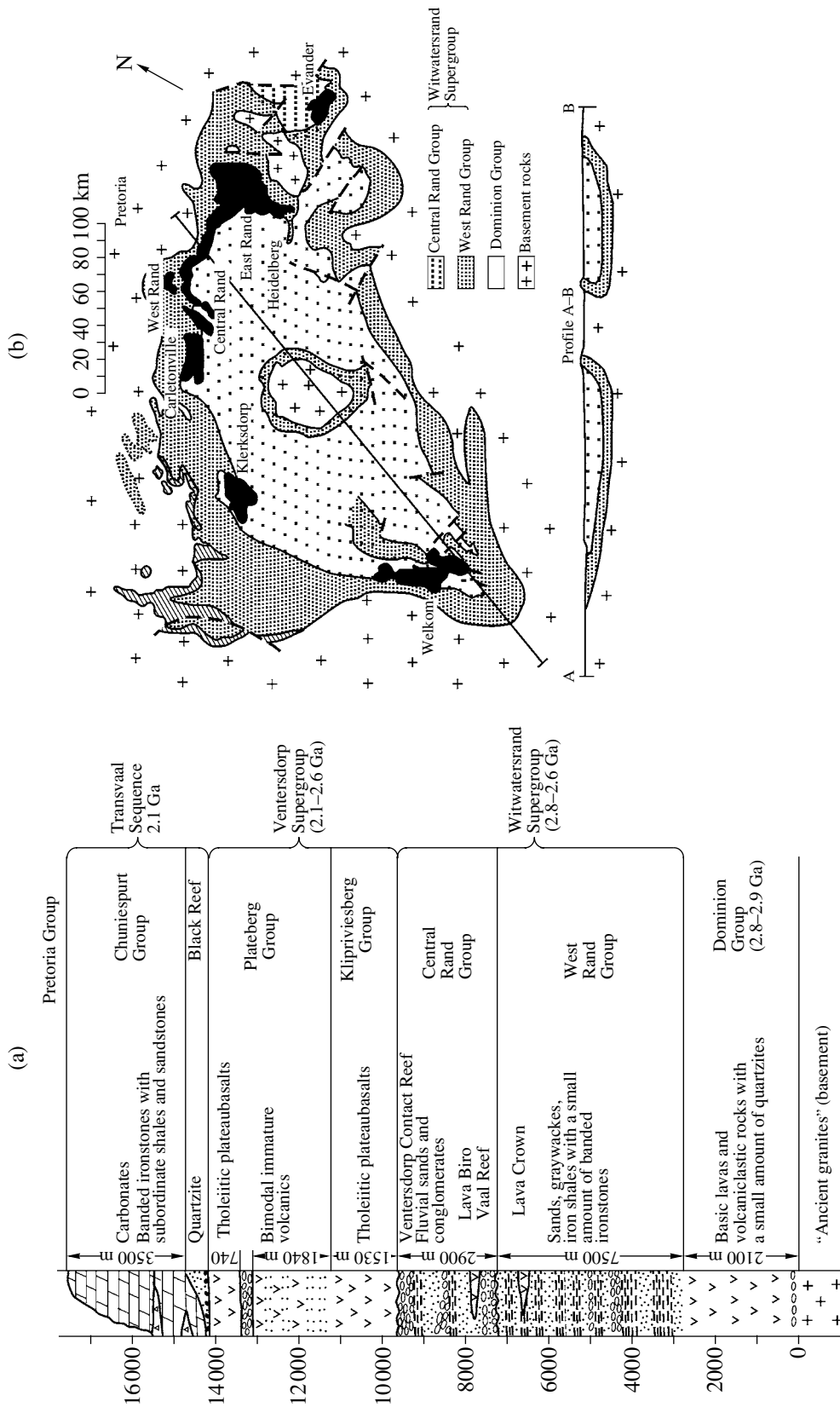
The Witwatersrand Basin is a typical Early Proterozoic structure formed over a long period (2.1–2.9 Ga) in the central and southern areas of the Kaapvaal Craton (figure). The NE-oriented riftogenic basin is 300 km long and 100 km wide (Robb and Meyer, 1990). Its stratigraphic section (figure) is as follows (from bottom to top): basal conglomerates and quartzites; basic volcanics of the Dominion Group (2.8–2.9 Ga); West Rand sediments (alternation of quartzites, conglomerates, iron shales, mudstones, and minor jaspilites; and quartzites with units of auriferous conglomerates and rare basic lavas of the Central Rand Group). Rocks of the West and Central Rand groups are united into the Witwatersrand Supergroup with an age of 2.6–2.8 Ga

(Barton et al., 1989). Metaterigenous sequences of the Witwatersrand Supergroup are overlain by tholeiitic plateaubasalts and bimodal volcanics of the Ventersdorp Supergroup (2.6–2.1 Ga). The uppermost unit is composed of carbonate–terigenous rocks of the Transvaal Group (2.1 Ga) with the Black Reef auriferous conglomerates at the base. Rocks of the Witwatersrand Basin are generally metamorphosed under conditions of the greenschist facies. The exception is provided by rocks adjacent to the Vredefort Uplift in the central part of the basin, where the rocks underwent contact metamorphism of the amphibole–hornfels facies owing to the impact of the Vredefort Granite (Phillips and Law, 1994; Gibson and Reimold, 1999).

Conglomerates account for no more than 0.2% of the terrigenous sequence in the more than 14-km-thick section (except the Transvaal Group). The conglomerates make up 16 independent units conventionally identified as reefs (figure). The reefs are exposed on the northern, northwestern, and northeastern walls of the basin and near the Vredefort Dome in the central part of the basin. In the first case, the reefs are composed of economic-grade quartz conglomerates. In the second case, they consist of polymictic conglomerates that lack the ore or contain a scarce gold mineralization. The Witwatersrand Basin periphery incorporates the Evander, East Rand, Central Rand, West Rand, Carletonville, Klerksdorp, and Welkom ore fields.

The present communication is based on factual material collected from the Black, Ventersdorp, Contact, Vaal, and Dominion ore-bearing reefs, as well as from the Klerksdorp, Carletonville, and Central Rand ore fields.

Lithological–mineralogical investigations revealed that the major portion (~80%) of conglomerate pebbles



(a) Geological setting of the Witwatersrand Basin and (b) composite stratigraphic section of its sedimentary sequence.

is composed of milky white, light gray, dark gray, and nearly black quartz grains. The remaining portion consists of quartzites, cherts, shales, and others. The cement is composed of fine-grained quartz, muscovite (sericite), chlorite, epidote, carbonates, ore minerals (mainly, pyrite), and organic matter (hydrocarbons) of different morphologies. The organic matter is observed as coating along fissures and millimeter-scale or microscopic dissemination in quartz pebbles. The hydrocarbons also fill up interstices between quartz pebbles. According to (Hallbauer, 1975, 1986; Minter, 1993; and others), the Witwatersrand section contains carbonaceous interlayers formed from remains of filiform blue-green algae, primitive lichens, and fungi. These interlayers are commonly abundant along the periphery of fans and in shallow lagoons.

According to (Pretorius, 1976), prokaryotic microorganisms (bacteria) were the highest forms of life during sedimentation in the Witwatersrand Basin. The carbonaceous material played an essential role in ore formation, because this material was the source of a significant amount of uranium minerals, gold, pyrite, platinoids, and others (Table 1). Therefore, study of the composition and genesis of hydrocarbons can provide insights into the formation of economic deposits of gold and rare metals.

At the same time, genesis of the carbonaceous material is differently interpreted by researchers. Some researchers believe that the carbonaceous material is a biogenic product related to the decomposition of various organisms (Hallbauer, 1975, 1986). According to (Galimov and Kodina, 1984; Khvorova and Serova, 1991; Kremenetsky *et al.*, 1997; and others), the organic matter is a hydrothermal product accumulated on the seafloor in the course of ordinary sedimentation; the injection of hydrocarbon fluid took place at the postore stage; and the source of hydrocarbons was abundant, as suggested by their abundance in the entire Witwatersrand Basin (Parnell and Carey, 1997).

According to (Galimov and Kodina, 1984), the activity of black smokers in the Guaymas Basin (Gulf of California) is a present-day example of such hydrothermal processes.

We analyzed the composition and distribution of carbonaceous material in bulk samples, pebbles, cement and fluid inclusions in ore and nonore conglomerates from some deposits of the Klerksdorp, Carletonville, and Central Rand ore fields within the Ventersdorp, Vaal, and Dominion reefs. We also attempted to identify the source of carbonaceous material, specify its formation temperature, and elucidate mechanisms of the transport of ore components and the differentiation of ore-forming fluid in the Witwatersrand Basin.

METHODS

The bulk samples, pebbles, and cement were investigated by gas chromatography using an Agat-3700 gas

chromatograph (N.N. Guseva, analyst) and a Millichrom-1 highly effective chromatograph (V.T. Pilipenko, analyst) at the VIMS. They were also analyzed by thermochromatography at the VNIILGG (E.P. Belkina and L.V. Sheveleva, analysts). The C_{org} content in quartz pebbles was measured by the laser microprobe at the IMGRE (Yu.G. Kosovets, analyst). Contents of high alkanes (C_{18} – C_{26}) in quartz pebbles from the Ventersdorp Contact and Klof reefs were determined by the chloroform extraction method.

Compositions of quartz-hosted fluid inclusions in pebbles and cement of ore conglomerates in the Ventersdorp Contact and Klof reefs were analyzed by the gas chromatography at the TsNIGRI (Yu.V. Vasyuta, analyst). Contents of F, Cl, NO_2 , HPO_4 , Br, NO_3 , and SO_4^{2-} were determined in aqueous extract of fluid inclusions and recalculated to the sample weight in mg/g.

Petrography of samples was investigated with a polarizing microscope.

RESULTS

Analysis of carbonaceous material revealed its diverse composition. Table 2 presents compositions of alkanes (methane, ethane, propane, butane, pentane, hexane, and octane), alkenes (ethylene, propylene, butylene, and pentylene), isomers, nonhydrocarbon compounds (helium, hydrogen, oxygen, nitrogen, carbon monoxide and dioxide, and water). Table 3 shows compositions of arenes (naphthalene, phenanthrene, anthracene, fluorene, trephelene, chrysene, perylene, benzpyrene, and benzperylene).

In bulk samples of ore conglomerates (Table 4), the total content of alkanes and alkenes varies from 2434.8 cm^3/kg (Ventersdorp Contact Reef) to 6043.4 cm^3/kg (Vaal Reef). The alkanes/alkenes ratio varies from 1.19 (Dominion Reef) to 6.2 (Ventersdorp Contact Reef). The content of the methane varies from 67% (Dominion Reef) to 92% (Ventersdorp Contact Reef). The ethane is increased at some places (Vaal Reef). Some reefs (e.g., Dominion Reef) are also characterized by high contents of alkenes (ethylene and propylene). The isomer/normal compound (alkane) ratio ranges from 0.06 (Ventersdorp Contact Reef) to 0.6 (Dominion Reef). The content of arenes in ore conglomerates varies from 77 ng/g (Ventersdorp Contact Reef) to 180.8 ng/g (Dominion Reef). The species composition of arenes is also diverse (Table 4).

In bulk samples of nonore conglomerates (Table 4), the total content of alkanes and alkenes is usually lower relative to the ore conglomerates: 1237.2 cm^3/kg in the Black Reef and 5082.6 cm^3/kg in the Dominion Reef. The alkanes/alkenes ratio varies from 0.92 to 4.16, respectively. Like the ore conglomerates, the nonore conglomerates are enriched in methane (75% in the Black, Ventersdorp Contact, and Dominion reefs and 91% in the Vaal Reef). Additionally, some reefs (e.g.,

Table 1. Contents of Au and U (g/t) in carbonaceous interlayers in various deposits of the Witwatersrand Basin (Hallbauer, 1986)

Deposit, reef	Au	U	Au/U
Carbon Leader	1600	18800	0.09
Carbon Leader (Western Deep Levels deposit)	8000	35700	0.22
Carbon Leader (Western Deep Levels deposit)	3600	57500	0.06
Basal Reef (St. Helena deposit)	1500	21300	0.07
Basal Reef (St. Helena deposit)	29300	60200	0.48
Vaal Reef (Vaal Reef deposit)	29900	34200	0.87

Ventersdorp Contact and Dominion) are enriched in propylene (Table 2). The content of propylenes accounts for 50% of the total content of alkenes in the Dominion Reef conglomerate.

The isomer/normal compound ratio varies from 0.12 to 0.3. The content of arenes in nonore conglomerates ranges from 0 (Dominion Reef) to 77.3 ng/g (Black Reef).

In quartz from ore conglomerate pebbles from the Ventersdorp Contact Reef, the total content of alkanes and alkenes is similar to that in the parental ore conglomerates. The total content of alkanes and alkenes is 2760 cm³/kg. The alkanes/alkenes ratio varies from 2.3 (cement) to 4 (transparent quartz from ore conglomerate of the Ventersdorp Contact Reef). The isomer/normal compound ratio ranges from 0.08 to 0.2 in quartz pebbles and is equal to 0.16 in the cement. The content of arenes is 24.2 ng/g in the light gray quartz from the ore conglomerate pebble and 60.6 ng/g in the cement (Table 4). The analyzed quartz includes the following PHCs: naphthalene, phenanthrene, fluorethene, chrysene, perylene, and benzpyrene. The naphthalenes and fluorethenes account for 50.8 and 20.2%, respectively, of the total PHC. The ore conglomerate cement additionally contains anthracene and benzperylene. As compared to quartz, the cement is characterized by a different distribution of hydrocarbons. Naphthalenes and benzperylenes in the cement account for 46.2 and 44.8%, respectively, of the total PHC (Table 5). Increase in the content of complex hydrocarbons (including benzperylenes) indicates the cooling of hydrothermal solutions (Simoneit, 1986).

The PHC composition in quartz from the Witwatersrand ore conglomerate differs from that in its counterpart from deposits of the hydrothermal quartz vein formation (Table 5).

Table 6 shows that the maximal content of high alkanes C₁₈–C₂₆ (octadecane, pentadecane, eicosane, heneicosane, docosane, tricosane, tetracosane, pentacosane, and hexacosane) is mainly related to eicosane (C₂₀), heneicosane (C₂₁), and tricosane (C₂₃). For the sake comparison, Table 6 also presents data of A.G. Bushev on quartz grains from quartz vein deposits characterized by a wide spectrum of organic substances. Relative to quartz from the Witwatersrand con-

glomerate, its counterpart from quartz vein deposits is notably depleted in hydrocarbons.

Analysis of organic matter from the ore and nonore conglomerates revealed its specific features that provide insights into the genesis of deposits and ore occurrences in the Witwatersrand Basin.

Comparison of the component composition of bitumens in ore conglomerates from various units of reefs and their nonore analogues in the study region shows the presence of complex organic matter in both types of conglomerate. The organic matter is represented by paraffin-cycloparaffins, polyaromatic hydrocarbons, and resinous components (Table 7). Relative to nonore conglomerates, ore components contain two times more bitumens, four times more paraffin-cycloparaffins, four times more PHCs, and two times more resinous components. The component composition of bitumens in ore conglomerates is as follows: PHCs 46.5%, paraffin-cycloparaffins 24.9%, and resinous components 28.6%. The highest content of bitumens is recorded in the Vaal Reef ore conglomerate. The bitumen distribution in nonore conglomerates is different: resinous components 62.9%, paraffin-cycloparaffins 14.3%, and PHCs 22.7%.

Ore conglomerates of Witwatersrand are enriched in methane and ethane. The presence of heptanes, octanes, and hexanes, which are atypical of vein quartz deposits, indicates that conditions were favorable for polymerization of simple hydrocarbons into more complex varieties.

The total content of alkanes and alkenes is maximal (up to 6043.4 cm³/kg) in the Vaal Reef ore conglomerate. In nonore conglomerates (Table 4), the total content increases from the Black and Vaal reefs to the Ventersdorp Contact and Dominion reefs (up to 5082.6 cm³/kg).

The alkanes/alkenes ratio is maximal in ore conglomerates and minimal in nonore conglomerates of the Ventersdorp Contact Reef.

Hydrocarbons of the benzene series (C₅–C₈) are virtually similar in ore and nonore conglomerates, except for samples from the Dominion Reef, where the content of hexane is higher relative to other hydrocarbons (55.6 cm³/kg in the ore conglomerate and 192 cm³/kg in the nonore conglomerate).

We can identify two types of quartz-hosted fluid inclusions. Type I is composed of one-phase liquid inclu-

Table 2. Contents of saturated and unsaturated hydrocarbons and nonhydrocarbon components (He, H₂, O₂, N₂, and CO₂) in conglomerates and quartz of pebbles in various reefs (cm³/kg)

Reef	Sample no.	Sample characteristics	methane	ethane	ethylene	propane	propylene	isobutane	normal butane	butylene	isobutylene	neobutylene
Black Reef	BR-4	Ore conglomerate	2300	510.7	230.4	166.9	325.1	12.5	50.4	372.0	1920	64.0
	L-9	Nonore conglomerate	720	139.8	154.0	37.9	20.6	2.2	19.3	45.1	78.85	7.7
Ventersdorp Contact Reef	W-17	Ore conglomerate	1921.0	112.9	116.6	40.45	130.3	2.85	7.94	55.6	29.6	10.7
	W-17/p	White transparent quartz from ore conglomerate pebble	2900	382	281	114	280	9	62	199	64	22
	W-17/c	Ore conglomerate cement	1438	234	203	60	245	12	26	251	118	52
	W-63/p	Light gray quartz from ore conglomerate pebble	1420	200	150	53	130	8	15	140	80	37
	42f/g	Nonore conglomerate	1740.8	319.2	529.9	108.6	983.0	8.3	28.8	704.0	420.0	99.2
Klof Reef	W-2	Quartzite (base of ore conglomerate)	3360	320	2200	80	380	35	36	240	200	64
	W-13	Light gray quartz from nonore conglomerate	1622	294	181	89	245	11	35	368	128	96
Vaal Reef	VR-4	Ore conglomerate	3932.2	1055	652.8	266.9	206.6	20.8	86.4	416.0	340.0	69.6
	20/1	Nonore conglomerate	3276.0	188.2	255.7	80.9	312.1	17.9	18.8	149.2	138.0	39.9
Dominion Reef	DR-5	Ore conglomerate	1209.2	341.4	673.8	124.4	394.5	3.5	50.6	329.5	53.5	64.9
	DR-3/3	Nonore conglomerate	2109.4	285.6	353.3	117.9	1126.4	10.4	55.2	488.0	872.0	30.4

Note: (Methane) CH₄, (ethane) C₂H₆, (ethylene) C₂H₄, (propane) C₃H₈, (propylene) C₃H₆, (isobutane) *i*-C₄H₁₀, (butylene) *i*-C₄H₈, (isobutylene) *i*-C₄H₈, (neobutylene) *i*-I C₄H₈, (isopentane) *i*-C₅H₁₂, (neopentane) *n*-C₅H₁₂, (pentylene) C₅H₁₀, (hexane isomer I): *i*-C₆H₁₄, (hexane isomer II) *i*-C₆H₁₄, (normal hexane) *n*-C₆H₁₄, (isoheptane) *i*-C₇H₁₆, (normal heptane) *n*-C₇H₁₆, (isooctane) *i*-C₈H₁₈, (normal octane) *n*-C₈H₁₈, (hydrogen) H₂, (oxygen) O₂, (nitrogen) N₂, (carbon dioxide) CO₂, (carbon monoxide) CO, (helium) He, (water) H₂O; (n.a.) not analyzed.

isopentane	neopentane	pentylene	hexane isomer	normal hexane	isoheptane	normal heptane	isooctane	normal octane	hydrogen	oxygen	nitrogen	carbon dioxide	carbon monoxide	helium	water
10.4	17.6	I-6.4 II-23.0 III-42.2 IV-15.4	I-0 II-1.3 III-7.0	13.4	112.9	11.5	288.6	8.3	22.5	n.a.	0	12.9	n.a.	1.2	n.a.
1.2	6.5	I-4.1 II-10.1 III-32.0 IV-5.6	I-0 II-0.6 III-1.2	25.6	59.2	6.5	113.4	2.4	6.6	n.a.	5.6	21.8	n.a.	n.a.	n.a.
1.5	3.3	I-2.7 II-4.4 III-15.2 IV-2.2	I-0 II-0.3 III-0.6	2.6	56.4	5.9	63.3	3.0	5.2	n.a.	5.3	11.4	n.a.	n.a.	n.a.
42	32	I-14 II-18 III-118 IV-11	I-4.3 II-5.6	53	34.1	197	Total i 346	18.6	6.91	0.14	5.6	19.7	6.9	1.26	n.a.
2.4	6	I-16 II-31 III-24 IV-16	I-12 II-5.6	18	38	120	Total i 216	20	8.98	0.64	19.7	19.7	6.9	1.05	1.842
6	13	86	I-2.0 II-3.0	8.0	19.0	120	27	44	9.68	n.a.	1.43	34.44	≈12	0.70	1.291
7.2	40.0	I-17.9 II-25.6 III-125.4 IV-15.4	I-0 II-1.6 III-2.6	48.6	56.3	10.2	111.4	3.2	6.4	n.a.	6.7	77.5	n.a.	n.a.	n.a.
20	37	28	I-30 II-23	33	100	46	94	80	11.61	n.a.	0	22.96	≈13.8	0.70	0.875
18	23	I-16 II-45 III-65 IV-29.5	I-3.1 II-8	23	Σi 42	87	Total i 234	20	6.03	1.28	12.56	39.4	11.5	1.05	n.a.
32.0	12.8	I-30.8 II-87.0 III-192.0 IV-46.1	I-0 II-2.6 III-12.8	23.0	248.9	10.2	169.0	2.2	10.0	0.6	3.2	5.4	n.a.	0.11	n.a.
6.3	8.8	I-9.5 II-21.6 III-63.0 IV-10.4	I-0 II-6.22 III-3.0	4.7	162.9	5.3	260.85	1.8	4.8	0.15	3.1	71.4	n.a.	n.a.	n.a.
2.8	21.6	I-4.1 II-14.5 III-33.45 IV-7.4	I-0 II-0.9 III-1.5	55.6	153.1	2.0	1945.5	8.3	5.8	n.a.	11.7	97.0	n.a.	n.a.	n.a.
16.0	18.4	I-25.6 II-51.2 III-172.8 IV-33.3	I-0 II-0 III-2.6	192.0	135.6	16.6	270.0	6.5	16.5	0.65	23.8	108.0	n.a.	n.a.	n.a.

Table 3. Composition of polyaromatic hydrocarbons (PHC) in ore conglomerates and their nonore analogues

Reef	Sample no.	Sample characteristics	Naphthalene		Phenanthrene		Anthracene		Fluorethene		Pyrene	
			mg/g	% of total PHC	mg/g	% of total PHC	mg/g	% of total PHC	mg/g	% of total PHC	mg/g	% of total PHC
Black Reef	BR-4	Ore conglomerate	26.7	23.5	5.8	51.0	–	–	19.4	17.0	–	–
	L-9	Nonore conglomerate	21.4	51.0	2.7	6.4	–	–	10.9	26.0	–	–
Ventersdorp Contact Reef	W-17	Ore conglomerate	18.9	24.4	6.2	8.0	–	–	–	–	–	–
	W-63p	Light gray quartz from ore conglomerate pebble	12.3	50.8	2.8	11.6	–	–	4.9	20.2	–	–
	W-17c	Ore conglomerate cement	28.3	46.2	0.5	0.8	0.2	0.3	0.8	1.3	1.4	2.3
Vaal Reef	42f/g	Nonore conglomerate	42.4	55.0	13.3	17.3	–	–	5.1	6.6	–	–
	VR-4	Ore conglomerate	7.3	9.0	26.0	32.2	–	–	1.9	2.4	–	–
	VR-5	Ore conglomerate	130.1	13.1	735.8	74.3	–	–	17.9	1.8	–	–
Dominion Reef	20/1	Nonore conglomerate	22.0	54.0	3.9	9.5	–	–	6.0	14.7	–	–
	DR-5	Ore conglomerate	71.1	39.3	19.8	10.9	–	–	12.0	6.6	–	–
	DR-3/3	Nonore conglomerate	–	–	–	–	–	–	–	–	–	–
Reef	Sample no.	Sample characteristics	Chrysene		Perylene		Benzopyrene		Benzperylene			
			mg/g	% of total PHC	mg/g	% of total PHC	mg/g	% of total PHC	mg/g	% of total PHC		
Black Reef	BR-4	Ore conglomerate	3.6	3.2	–	–	5.1	4.5	52.9	46.6		
	L-9	Nonore conglomerate	3.4	8.1	–	–	3.6	8.6	–	–		
Ventersdorp Contact Reef	W-17	Ore conglomerate	0.8	1.0	–	–	–	–	51.4	45.3		
	W-63p	Light gray quartz from ore conglomerate pebble	1.3	5.4	1.3	5.4	1.6	6.6	–	–		
	W-17c	Ore conglomerate cement	0.6	1.0	0.9	1.5	1.1	1.8	27.4	44.8		
Vaal Reef	42f/g	Nonore conglomerate	0.9	1.2	–	–	–	–	15.4	20.0		
	VR-4	Ore conglomerate	0.8	0.9	–	–	1.1	1.4	43.7	54.1		
	VR-5	Ore conglomerate	4.6	0.5	–	–	11.4	1.2	90.2	9.1		
Dominion Reef	20/1	Nonore conglomerate	3.4	8.3	–	–	5.6	13.7	–	–		
	DR-5	Ore conglomerate	4.1	2.3	–	–	3.0	1.7	70.8	39.1		
	DR-3/3	Nonore conglomerate	–	–	–	–	–	–	–	–		

Note: (–) Not detected.

sions up to 0.03 mm in size (less commonly, ~0.05 mm). They are confined to cracks and arranged as chains or clusters. Type II is composed of two-phase fluid inclusions from ~0.015 to 0.03 mm in size (maximal size 0.45 mm). The gaseous phase is usually 10% (rarely, 15%). The inclusions are oriented along cracks. The gaseous phase is as much as 90% in some large (~0.05 mm) two-phase inclusions. Solid inclusions of mineral phases recorded in some inclusions are characterized by elongate habit (0.03 wide and 0.14 mm long).

In quartz-hosted fluid inclusions in pebbles and cement, the highest content of hydrocarbons is typical of methane (the HC content is higher in pebbles than in the cement). In pebbles from the Ventersdorp Contact Reef, contents of methane, ethane, and propane are

higher in the light gray quartz relative to the dark gray variety. In contrast, contents of methane, ethane, and propane are markedly higher in the dark gray quartz from the Kloof Reef. This dark gray quartz also contains isobutane. The relationship is reverse for alkenes (Table 8). High contents of ethene, propene, and butene are typical of both dark and light gray quartz grains from the Kloof Reef pebbles. The fluid inclusions also contain CO₂, H₂O, Cl, and SO₄²⁻ (Table 8).

V.S. Kurazhkovskaya (Moscow State University) investigated IR spectra of the pebble-hosted quartz from various reefs of Witwatersrand and found that the ore conglomerate includes two types of water. Water in fluid inclusions is not bound with the crystal structure, while the molecular water in clusters is subordinate.

Table 4. Distribution of hydrocarbons and nonhydrocarbon compounds in ore conglomerates, their nonore analogues, cement, and quartz from ore conglomerate pebbles

Components	Black Reef		Ventersdorp Contact Reef		Vaal Reef	
	BR-4 ore	L-9 nonore	W-17 ore	42 f/g nonore	VR-4 ore	20/1 nonore
Alkanes, cm ³ /kg	3078.8	958	2097.09	2299.4	4342.5	3584.5
Alkenes, cm ³ /kg	1078.5	279.2	337.7	2500.4	1700.9	861.4
Total (alkanes + alkenes) content, cm ³ /kg	4157.3	1237.2	2434.8	4799.8	6043.4	4445.9
Alkanes/alkenes	2.9	3.4	6.2	0.92	2.55	4.16
Isocompounds/normal compounds	0.57	0.21	0.06	0.12	0.13	0.13
Arene content, ng/g	113.5	77.3	77.3	77.1	80.8	40.9
N ₂ , cm ³ /kg	n.d.	5.6	5.3	6.7	3.2	3.1
O ₂ , cm ³ /kg	n.a.	n.a.	n.a.	n.a.	0.6	0.15
CO, cm ³ /kg	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
H ₂ , cm ³ /kg	22.5	6.6	5.2	6.4	10	4.8
CO ₂ , cm ³ /kg	12.9	21.8	11.4	77.5	5.4	71.4
He, cm ³ /kg	1.2	n.d.	n.d.	n.d.	0.11	n.d.
H ₂ O, cm ³ /kg	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Components	Dominion Reef		Ventersdorp Contact Reef			Klof Reef	
	DR-5 ore	DR-3/3 nonore	Transparent quartz from ore conglomerate pebble, W-17/p	Light gray quartz from ore conglomerate pebble, W-63/p	Ore conglomerate cement, W-17/c	Light gray quartz from nonore conglomerate, W-13	Quartzite (base of ore conglomerate), W-2
Alkanes, cm ³ /kg	1813.1	2801.6	3758.6	1873	1922	2193	3992
Alkenes, cm ³ /kg	1519.15	2281	942	543	838	1065.5	2912
Total (alkanes + alkenes) content, cm ³ /kg	3332.25	5082.6	4700.6	2416	2760	3258.5	6904
Alkanes/alkenes	1.19	1.23	3.99	3.45	2.29	2.06	1.37
Isocompounds/normal compounds	0.6	0.3	0.11	0.06	0.14	0.13	0.08
Arene content, ng/g	180.8	n.d.	n.a.	24.2	60.6	n.a.	n.a.
N ₂ , cm ³ /kg	11.7	23.8	5.6	1.43	5.6	12.56	n.a.
O ₂ , cm ³ /kg	n.a.	0.65	0.14	n.a.	0.64	1.28	n.a.
CO, cm ³ /kg	n.a.	n.a.	6.9	12	6.9	11.5	13.8
H ₂ , cm ³ /kg	5.8	16.5	6.91	9.68	8.98	6.03	11.61
CO ₂ , cm ³ /kg	97	108	19.7	34.4	19.7	39.4	22.96
He, cm ³ /kg	n.a.	n.a.	1.26	0.7	1.05	1.05	0.7
H ₂ O, cm ³ /kg	n.a.	n.a.	n.a.	1.29	1.84	n.a.	0.875

Note: (n.a.) Not analyzed; (n.d.) not detected.

The quartz-hosted fluid inclusions have also been investigated by other geologists. According to (Shepard, 1977), fluid inclusions in quartz pebbles are arranged along subparallel planes; some inclusions parallel to bedding emphasize the orientation of cracks; and the relation between planes of inclusions and microfissures (cracks) indicates the involvement of flu-

ids in fracturing. According to (Frimmel and Gartz, 1997), fluid infiltration in Witwatersrand took place in two stages; the fluids are composed of water with a small amount of CO₂; and they are characterized by moderate salinity, probably, related to CaCl₂.

Roedder (1972) identified five types of fluid inclusions with different relationships between phases and

Table 5. Contents of arenes in quartz from conglomerate pebbles of Witwatersrand and quartz vein deposits

Component	Formula	Ventersdorp Contact Reef				Quartz vein deposits*					
		W-63		W-17c		Khakandzha deposit, Kamchatka		Darasun deposit, Transbaikal region		Taseev deposit, Transbaikal region	
		mg/g	% of total PHC	mg/g	% of total PHC	mg/g	% of total PHC	mg/g	% of total PHC	mg/g	% of total PHC
Naphthalene	C ₁₀ H ₈	12.3	50.8	28.3	46.2	n.a.	–	105.7	36.3	191.4	63.6
Phenanthrene	C ₁₄ H ₁₀	2.8	11.6	0.5	0.8	9.1	7.6	n.a.	–	n.a.	–
Anthracene	C ₁₄ H ₁₀	n.a.	–	0.2	0.3	17.6	14.7	40.5	13.9	95.4	31.7
Pyrene	C ₁₆ H ₁₀	n.a.	–	1.4	2.3	n.a.	–	n.a.	–	n.a.	–
Fluorethene	C ₁₆ H ₁₀	4.9	20.2	0.8	1.3	44.8	37.3	11.2	3.8	11.5	3.8
Triphelynene	C ₁₈ H ₁₂	n.a.	–	n.a.	n.a.	n.a.	–	n.a.	–	n.a.	–
Chrysene	C ₁₈ H ₁₂	1.3	5.4	0.6	0.98	13.1	10.9	3.2	1.1	2.5	0.8
Perylene	C ₂₀ H ₁₂	1.3	5.4	0.9	1.5	17.8	14.8	4.3	1.5	n.a.	–
Benzopyrene	C ₂₀ H ₁₂	1.6	6.6	1.1	1.8	17.6	14.7	n.a.	–	n.a.	–
Benzperylene	C ₂₂ H ₁₂	n.a.	–	27.4	44.8	n.a.	–	126.3	43.4	n.a.	–
Total		24.2		61.2		120		291.2		300.8	

Note: (W-63) Nonuniformly colored (white transparent to smoky) quartz; (W-17c) fine-grained quartz cement with inclusions of pyrite, sericite, and other minerals; (n.a.) not analyzed; (–) not detected. *Data of A.G. Bushev (Fedorovskii All-Russia Research Institute of Mineral Resources, VIMS).

Table 6. Relationship of high alkanes in bitumens contained in quartz from conglomerates of Witwatersrand and some auriferous quartz vein deposits

Component	Formula	Witwatersrand				Quartz vein deposits**	
		W-2 Klof Reef	W-17	W-63	W-17c	Kamchatka	Transbaikal region
						Khakandzha	Darasun
Tetradecane	C ₁₄	–	–	–	–	–	–
Pentadecane	C ₁₅	–	–	–	–	–	–
Hexadecane	C ₁₆	–	–	–	–	1.2	–
Heptadecane	C ₁₇	–	–	–	–	1.9	4.8
Octadecane	C ₁₈	16.9	8	8.7	–	2.5	6.8
Penadecane	C ₁₉	13.8	13	11.1	3	8.4	10.5
Eicododecane	C ₂₀	7.7	21	25.4	12.1	9.9	11.1
Heneicosane	C ₂₁	18.5	18.8	18.3	21.2	14	11.6
Docosane	C ₂₂	6.2	4.3	6.3	18.2	14.9	10.1
Tricosane	C ₂₃	18.5	14.5	9.5	27.3	12.7	8.4
Tetracosane	C ₂₄	–	8.7	13.5	18.2	10.6	9.3
Pentacosane	C ₂₅	12.3	11.7	7.2	–	8.7	6.3
Hexacosane	C ₂₆	6.1	–	–	–	–	–

Note: (W-2) Quartzite; (W-17) white transparent quartz; (W-63) nonuniformly colored quartz; (W-17c) cement; *C₂₇–C₃₈ are absent in samples from Witwatersrand; (–) not detected; **data of A.G. Bushev (VIMS).

Table 7. Composition of bitumens in ore and nonore conglomerates

Reef	Sample no.	Sample characteristics	Content of bitumens	Component composition of bitumens (mg)			Au	U
			mg	Paraffin-cycloparaffins	PHC	Resinous components	g/t	
Black Reef	BR-4	Ore conglomerate	5.9	2.2	1.0	2.7	1.7	–
	L-9	Nonore conglomerate	6.6	1.1	0.4	5.1	0.02	11
Ventersdorp Contact Reef	W-17	Ore conglomerate	3.5	0.5	0.5	2.5	83.4	67
	W-63p	Light gray quartz from ore conglomerate pebble	2.9	0.3	0.3	2.3	62.5	38
	W-17p	Ore conglomerate cement	4.1	1.0	0.4	2.7	83.4	67
	42c/3	Nonore conglomerate	5.4	0.8	0.4	4.2	0.07	0.5
Klof Reef	W-2	Quartzite (base of ore conglomerate)	3.6	0.2	1.4	2.0	40.9	70
Vaal Reef	VR-4	Ore conglomerate	11.0	3.6	4.6	2.8	3.1	135
	VR-5	Ore conglomerate	19.2	3.0	11.4	4.8	–	–
	20/1	Nonore conglomerate	4.4	0.5	0.8	3.1	0.1	5.7
Dominion Reef	DR-5	Ore conglomerate	6.9	1.6	2.8	2.5	0.1	170
	DR-3/3	Nonore conglomerate	6.0	0.8	3.5	1.7	0.025	7.4

Note: (–) Not detected.

CO₂. In some quartz grains, he detected fluid inclusions with hydrocarbons, cassiterite crystallites, and notable concentrations of Sn and Cs.

Other researchers have also recorded hydrocarbons in the quartz-hosted fluid inclusions from both pebbles and cement. The cryometric analysis (Naumov *et al.*, 1976; Prokof'ev *et al.*, 1990) detected methane in the cement-hosted quartz. According to (Prokof'ev *et al.*, 1990), this quartz contains two types of two-phase fluid inclusions: water-rich inclusions (gas bubble 10–15%) and gas-rich inclusions (aqueous solution 10–15%); the size of inclusions commonly does not exceed 5–10 μm (up to 15 μm in some cases); the inclusions homogenize at 195–230°C; they contain both pure gases (CO₂ and H₂S) and their mixtures; the gases were delivered to the ore-forming hydrothermal system from different sources; and they were mixed in the course of the discharge of hydrothermal solutions within the deposit.

According to (Krendelev *et al.*, 1973), acid gases (H₂S, SO, and others) are present in quartz-hosted fluid inclusions from pebbles in auriferous conglomerates of Witwatersrand; quartz pebbles from ore conglomerates include H₂S, SO₂, NH₄, and other compounds (up to 68.6%), O₂ (6–19%), and CO₂ (12–18%); and sulfidization of the Witwatersrand conglomerate is related to impact of solutions with a temperature of approximately 220–400°C.

Ore and nonore conglomerates, as well as quartz of pebbles and cement, contain hydrogen, oxygen, nitrogen, carbon, and helium (Table 2).

Hydrogen is present in both ore and nonore conglomerates, as well as in quartz of pebbles and cement of ore conglomerates. The hydrogen content in ore conglomerates varies from 22.5 cm³/kg in the Black Reef to 5.2 cm³/kg in the Ventersdorp Contact Reef, 10.0 cm³/kg in the Vaal Reef, and 5.8 cm³/kg in the Dominion Reef. The H₂ content is higher in nonore conglomerates of the Ventersdorp Contact and Dominion reefs. Its content is maximal (16.5 cm³/kg) in nonore conglomerates of the Black Reef.

Hydrogen, a constant component of magmatic gases, makes up compounds with carbon, oxygen, sulfur, and other elements. Hydrogen is abundantly emitted as methane.

A minor amount of oxygen is present in quartz pebble and cement of ore conglomerates (Table 2). In the Vaal Reef, the oxygen content varies from 0.6 cm³/kg in the ore conglomerate to 0.15 cm³/kg in the nonore variety. The oxygen content is as high as 1.28 cm³/kg in the pebble-hosted quartz from nonore conglomerates of the Klof Reef, 0.14 cm³/kg in its counterpart from ore conglomerates of the Ventersdorp Contact Reef, and 0.64 cm³/kg in the cement of these ore conglomerates. The hydrogen content is notably higher than the oxygen content, testifying to a reductive environment of ore formation. The H₂/O₂ ratio in the pebble-hosted quartz is 4.7 in nonore conglomerates, 49 in ore conglomerates, and 14 in the cement. In the Vaal Reef, this ratio varies from 32 to 16.7 in nonore and ore conglomerates, respectively.

Table 8. Composition of fluid inclusions in quartz and cement from ore conglomerates (mg/g $\times 10^{-3}$)

Component	Ventersdorp Contact Reef				Klof Reef			
	dark gray quartz W-17p-1	cement W-17/c	light gray quartz W-63/p	sulfides W-63/s	quartzite W-1	dark gray quartz W-2/p	light gray quartz W-2b/p	cement W-17/c
Alkanes								
Methane CH ₄	1.570	0.680	1.700	0.180	0.314	2.300	1.500	0.800
Ethane C ₂ H ₆	0.125	0.132	0.181	0.023	0.027	0.260	0.146	0.140
Propane C ₃ H ₁₀	0.011	0.014	0.010	n.d.	0.024	0.045	0.014	0.018
Isobutane C ₄ H ₁₀	n.d.	n.d.	n.d.	n.d.	n.d.	0.009	n.d.	n.d.
Normal butane C ₄ H ₁₀	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Alkenes								
Ethene C ₂ H ₄	0.136	0.044	0.041	0.018	0.169	0.176	0.220	0.116
Propene C ₃ H ₆	0.045	0.040	0.017	n.d.	0.097	0.090	0.053	0.072
Butene C ₄ H ₈	0.027	0.030	n.d.	0.036	0.104	0.068	0.018	0.074
Content of nonhydrocarbon components*								
CO ₂ , mg/g	25.000	20.000	17.000	17.000	24.000	38.000	24.000	30.000
H ₂ O, mg/g	2.210	1.840	1.290	1.960	0.875	3.817	3.082	3.547

Note: Analyses were carried out at the Central Institute of Geological Exploration for Base and Precious Metals, TsNIGRI (Yu.V. Vasyuta, analyst); *F, Cl, NO₂, HPO₄, Br, NO₃, and SO₄²⁻ were not detected in samples W-17p/1, W-17/c, W-63/s, W-1, and W-2c; only Cl and SO₄²⁻ were analyzed in samples W-63/p, W-2/p, and W-2b/p.

Nitrogen is widespread in the magmatic, metamorphic, and hydrothermal processes. This element is the major volatile component in some natural fluids. The atmosphere was devoid of oxygen and composed of N₂, CH₄, and CO₂ 2.5 Ga ago (Cloud, 1972, 1973; Walker, 1987). Nitrogen is similar in both ore and nonore conglomerates (Table 2). The highest nitrogen content is recorded in nonore conglomerates of the Klof and Dominion reefs (12.56 and 23.8 cm³/kg, respectively).

Carbon makes up compounds with hydrogen, oxygen, sulfur, nitrogen, phosphorus, fluorine, chlorine, and other metals and nonmetals. Carbon monoxide and dioxide are most widespread in nature. They are the major components of volcanic gases. In addition, carbon occurs in organometallic compounds. Hydrocarbons are stable in reducing environments of the Earth's crust and they can break down under conditions of drastic pressure drop near the surface. The CO₂ content varies from 5.4 cm³/kg (Vaal Reef) to 97.0 cm³/kg (Dominion Reef). The CO₂ content is appreciably higher in all nonore reefs relative to the ore reefs. The ratio of CO₂ contents in ore and nonore conglomerates varies from 0.08 to 0.9. The CO content varies from 6.9 to 12 cm³/kg in quartz. In the cement, the CO content is similar to that in the pebble-hosted quartz.

Helium is abundant in quartz and cement of ore and nonore conglomerates (Table 2). According to (Ivanov, 1996), this is related to the delivery of helium together with hydrothermal solutions in tectonically active oce-

anic zones. Contents of ³He and ⁴He in the seafloor water near oceanic ridges are 20–25 times higher than in the atmosphere. Their contents have positive correlation with temperature and Mn content. High He contents are also typical of stagnant waters that interacted with enclosing rocks for a prolonged period. In contrast, the He content is low in zones of active water exchange with the exception of some uranium deposits. In the studied samples, the He concentration is very high (up to 1.4 $\times 10^{-3}$ mg/l against the background of 10⁻⁶ mg/l) in fracture zones that crosscut the most permeable gravels and pebbles. In conglomerates and sandstones, the He concentration decreases to 2.7 $\times 10^{-5}$ and 1.7 $\times 10^{-4}$ mg/l. High He concentrations can be related to high U concentrations in the ores. The He concentration is as high as 1.2 cm³/kg in ore conglomerates of the Black and Vaal reefs (Table 2).

Data on aqueous extracts show that quartz pebbles in ore conglomerates of the Ventersdorp Contact and Klof reefs contain Cl (0.044–0.098 mg/t) and SO₄²⁻ (0.013–0.018 mg/t). However, we did not detect F, NO₂, HPO₄²⁻, Br⁻, and NO₃⁻.

DISCUSSION

Let us compare compositional characteristics of organic matter in ore and nonore reefs, as well as quartz pebbles therein, with literature data and concepts con-

cerning the composition and temperature of ore-forming hydrothermal solutions.

According to (Pikovskiy *et al.*, 1996), the formation of PHCs in the Earth's crust is closely associated with hydrothermal activity. The presence of homologues of naphthalene, phenanthrene, chrysene, pyrene, pyrene, as well as individual unsubstituted structures (benzpyrene and benzperylene), is a typical hydrothermal association. Similar results were obtained by Simoneit (1986). He believes that PHCs are ubiquitous in products of high-temperature pyrolysis usually dominated by pyrene, benzpyrene, pyrene, and benzperylene. As was demonstrated above, ore and nonore conglomerates of Witwatersrand include an analogous PHC association. For example, the content of acenes (naphthalene and anthracene) is higher (7.4–30.2% of the total sum) than that of arenes, such as phenanthrene, chrysene, and triphenylene (0.8–3.3%). The sole exception is provided by an ore conglomerate sample from the Vaal Reef with high contents of acenes (51.2%) and arenes (91.7%). Simoneit (1986) investigated hydrocarbon gases and revealed the relationship between methane, ethane, and propane. According to this researcher, the $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$ ratio is <50 for gases of thermal origin and >1000 for biogenic hydrocarbon gases. In several works devoted to the genesis of carbonaceous material (Florovskaya and Pikovskiy, 1971; Florovskaya and Melkov, 1975; Florovskaya *et al.*, 1980), the high content of hydrocarbons and their diversity are considered a typical feature of hydrothermal process. Only simple compounds, such as CH_4 , CH_2 , CH_3 , CN , CN_2 , CO , H_2 , NH_3 , H_2O , CO_2 , and so on, could exist under conditions of magmatic melt. Decrease in temperature and pressure promoted the formation of various hydrocarbons, the synthesis of which was responsible for the release of H_2O and CO_2 .

According to (Slobodskoi, 1978, 1981), hydrocarbon compounds were involved in the gaseous transfer of metals as organometallic compounds in the course of volcanic and hydrothermal processes. These compounds can exist in abyssal conditions. They occur as volatiles in reduced medium and break down in oxidized medium on (or near) the Earth's surface and in seas and oceans.

Thus, our data and materials of previous researchers suggest that the hydrothermal sedimentary genesis of deposits in the Witwatersrand ore region (Kremenetsky *et al.*, 1997) was related to the input of deep metalliferous fluids and the development of a temporary reducing environment against the background of the general oxidizing regime in the sedimentary basin. The reducing regime was favorable for the precipitation of the major mass of gold and a part of uranium (bound with inorganic hydrocarbons) transported by endogenous fluids in the basin. According to (Parnell and Carey, 1997), a significant amount of gold is associated with hydrocarbon interlayers. However, a later work (Parnell, 1999) suggests that gold may not be related to carbon. High-

grade gold concentrations can appear after the deposition of carbon and remain in close association with carbon flows. The reduced carbon compounds react with metals (in particular, gold and uranium) to form metals (Au and U), sulfides (pyrite, pyrrhotite, and others), and complex hydrocarbons that are encountered in the cement of conglomerates. Slobodskoi (1978, 1981) believes that organometallic compounds can exist in deep conditions due to the following factors: (a) potential capacity of virtually all elements to establish chemical bonds with carbon; (b) constant presence of carbon in endogenous systems and its participation in deep processes; and (c) high reducing potential that is typical of the abyssal environment and the consequent presence of carbon compounds (CH_2 , CH_4 , C_2H_6 , and others) that can be actively involved in the formation of organometallic compounds.

The organometallic compounds are unstable at high temperatures and decomposed in the course of exhumation and the consequent decrease in pressure and the increase in oxygen potential. CO , CH_4 , C_2H_6 , and so on are widespread in the deep reducing environment, while H_2O and CO_2 dominate near the surface. Decomposition of organometallic compounds provokes the splitting of free radicals and the release of metals. Moreover, decomposition of compounds containing both metal and sulfur can produce metallic sulfides.

In reefs of the Witwatersrand Basin, gold is mainly confined to Fe-rich rocks (pyritized conglomerates and sandstones) and carbonaceous rocks (conglomerates with patches and interlayers of coaly substance and the subordinate quartzites with hydrocarbon interlayers). Gold was probably transported to the middle and upper parts of the crust by abyssal (postmagmatic) hydrothermal solutions. Their reducing nature is suggested by the presence of organic and hydrogen compounds of metals. According to Shakhnovsky (2001), upper mantle gases are mainly composed of water vapor and carbon dioxide that serve as donors in the abyssal synthesis of hydrocarbons. Hydrocarbons can form in the course of H_2O and CO_2 breakdown in a reducing environment characterized by the presence of bivalent Fe ions that are active reducers.

Young (1917) noted the existence of gold-carbon (thucholite) in reefs of the Witwatersrand Basin. Results of the chemical analysis of pure carbon concentrate from the Carbon Leader Reef (Blivurnitzeit deposit) show that the concentrate includes as much as 3000 g/t of Au. Gold is ubiquitous in the reef. The Au content is particularly high in zones enriched in hydrocarbons. According to (Feather and Koen, 1975), hydrocarbons are genetically related to gold. Gold precipitates due to the interaction of carbon-free fluid and hydrocarbons in shales of the Witwatersrand Basin (Barnicoat *et al.*, 1997). Gold is present as $\text{Au}(\text{HS})_2^-$ in the hydrothermal solution. Processes of accumulation and decomposition of biogenic organic matter are

accompanied by the release of H₂S that promotes the precipitation of gold in a reducing environment.

Gold is associated with not only hydrocarbon, but also iron and sulfur.

Analysis of the relationship between hydrocarbons (resinous components, PHCs, and paraffins), gold, and uranium (Table 7) in the ore and nonore conglomerate samples showed that the highest concentration of resinous components is typical of ore conglomerates from the Vaal reef, while the Au content in them varies from 3.1 to 67 g/t. In contrast, the nonore conglomerates are barren, and the content of resinous components in them ranges from 1.7 to 5.1 g/t. The ore conglomerate/uranium ratio is slightly different. Correlation between the resinous components and uranium is negative in the nonore conglomerates (except for the Black Reef sample) and positive in the ore conglomerates.

Correlation between PHCs and Au is distinct in ore conglomerates of the Black Reef. The correlation is absent in the Klof and Ventersdorp Contact reefs. In nonore conglomerates, the PHC content varies from 0.4 to 3.5 g/t, while the Au content ranges between 0.025 and 0.1 g/t. In ore conglomerates of the Klof and Ventersdorp Contact reefs, the Au content increases from 0.1 (Dominion Reef) to 83.4 g/t (Ventersdorp Contact Reef), but the PHC content shows an insignificant variation (0.3–4.6 g/t) with the exception of the Vaal Reef sample enriched in PHC (11.4 g/t) and Au (66.6 g/t). Uranium has a positive correlation with PHC. Maximal contents of PHC and U are typical of the Vaal reef. Contents of paraffins, resinous components, and PHCs are also maximal in the Vaal Reef but, this reef is characterized by irregular distribution of Au (3.1–66.6 g/t) and distinct correlation between U and paraffins.

Data on contents of various hydrocarbons, gold, and uranium in the auriferous conglomerate samples indicate that organic compounds played different roles in the ore-forming process in the Witwatersrand Basin.

CONCLUSIONS

(1) Ores of the Witwatersrand deposit are saturated in methane and the subordinate ethane. They contain heptanes (0.125–0.158 cm³/kg), octanes (0.07–0.254 cm³/kg), and hexene (0.102–0.3 cm³/kg). Hence, the environment was favorable for the polymerization of simple hydrocarbons into more complex varieties. In bitumens, heneicosane (C₂₁) and eicosane (C₂₀) are the major high alkanes. The bitumens show two maximums that coincide with heneicosane (C₂₁) and tricosane (C₂₃) and probably reflect different stages of ore formation.

The CH₄/(C₂H₆ + C₃H₈) values calculated for hydrocarbon gases in ore and nonore conglomerates and in ore conglomerate of the Ventersdorp Contact Reef do not exceed 50; i.e., they support the conclusions in (Galimov and Simoneit, 1982) about the hydrothermal origin of gases. In ore conglomerates of the Black, Ventersdorp Contact, Vaal, and Dominion reefs,

this ratio varies from 2.6 to 12.5; in the nonore conglomerates, from 4.1 to 12.2. In varicolored quartz from ore conglomerate pebbles of the Ventersdorp Contact Reef, the ratio ranges between 4.2 and 5.8. This ratio is equal to 8.4 in quartzite and 4.9 in the cement of ore conglomerate.

In general, ores of the Witwatersrand Basin are very similar to low-temperature veins in terms of the content of organic matter. However, they are distinguished from vein deposits by the abundance of heptanes, octanes, and hexenes that are atypical of ordinary veins. They are also enriched in naphthalene and benzperylene that represent the simplest and most complex arenes, respectively. The presence of complex alkanes, alkenes, and arenes can be related to the high radioactivity of ores. As is known, α and γ radiations promote the polymerization of hydrocarbons. High contents of phenanthrene and benzperylene in ore conglomerates, probably, suggest their proximity to the hydrothermal source. At the same time, the naphthalene, which is also present in nonore conglomerates, could either be transported away from the hydrothermal source or be related to organic bacterial processes.

(2) Hydrocarbon compounds were involved in the gaseous transport in hydrothermal processes, most probably, as organometallic compounds (Slobodskoi, 1978, 1981). These compounds are volatile in the reducing environment. Therefore, they break down in the oxidizing (surface and subsurface) environment of marine basin and produce new phases. At present, such new phases are observed in the conglomerate cement as independent metals (Au, Pt), sulfides (pyrite, pyrrhotite, and others), and complex hydrocarbons. Terminal products of the oxidation of organometallic compounds are represented by carbon dioxide, methane, and other gases.

(3) Hydrocarbons and carbon dioxide were partly introduced in the course of the discharge of hydrothermal solutions into the sedimentary basin. This could trigger an intense cyanobacterial activity and transformation of a portion of hydrothermal hydrocarbons into the organic sedimentary form. According to (Lein *et al.*, 1990), present-day oceanic hydrothermal ores contain organic matter delivered from various sources of ore-forming solutions (C_{org} mobilized from sediments, carbon from magmatic melt, and carbon extracted from seawater). In addition, the organic matter can also occur as mechanical admixture derived from plankton.

Our concept of hydrocarbon accumulation does not contradict data proposed by other researchers. The present-day analogue of this model is represented by black smokers in the Guaymas Basin in the Bay of California (Galimov and Kodina, 1984) that is characterized by high bioproductivity, reducing regime in bottom sediments, and relatively high content of organic matter. The Guaymas Basin marked by intense development of microbiological processes that promote the formation of biogenic methane. Areas with high ther-

mal flux in this basin are characterized by the thermal transformation of organic matter, the release of chemogenic methane, and the formation of high-molecular gaseous hydrocarbons. Sediments of this basin include PHCs of the phenanthrene, pyrene, chrysene, benzopyrene, perylene, and other series. The high PHC content suggests that the Guaymas Basin incorporates the highest-temperature products of the short-term thermolysis. According to Geptner *et al.*, 1999, the PHCs are mostly represented by homologues of naphthalene (80%) and could be derived from volcanic eruptions and hydrothermal solutions in highly permeable zones of the Earth's crust. Moreover, the presence of PHCs indicates a reducing environment of the hydrothermal process.

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