Reports

Carbon Isotope Composition of Carbonaceous Matter from the Precambrian of the Witwatersrand System

Abstract. *Polymerized hydrocarbons occurring in the gold-uranium conglomerates of the Witwatersrand System (South Africa) show* δC^{13} *values between* -22.4 *and* -32.8 *per mille, their isotopic composition thus falling into the range of sedimentary organic carbon. Accordingly, organic derivation of the material seems very probable. This conclusion is consistent with a model of the existence of organic evolution and biologic activity in times certainly older than* 2.15×10^9 *years.*

The occurrence of carbonaceous matter or "thucholite" (*1*) in gold conglomerates from the Witwatersrand was well known by early workers (*2*), and there have been recent extensive microscopic and microchemical investigations of these hydrocarbon-uraninite complexes (*3–5*). The results of this work leave little doubt that the material was derived from hydrocarbons, originally present in the gaseous or liquid phase, or both, that had migrated through the strata and were consequently polymerized by the α- and γ-radiation emanating from the primary uranium compounds of the rock. Since the process of polymerization entailed transition into the solid state, the "carbon" material was likely to be trapped in the immediate surroundings of the sources of radiation; thus the association between uraninite and hydrocarbons is very intimate. Figure 1A shows some granules of uraninite (explained by most investigators as detrital grains) surrounded by compact or spongy aureoles of carbonaceous matter, the latter also entering, and replacing the individual grains, along cracks and fissures. As the replacement proceeds, the primary uraninite phase more and more diminishes, but normally small relics of the mineral tend to survive the resorption processes (Fig. 1B).

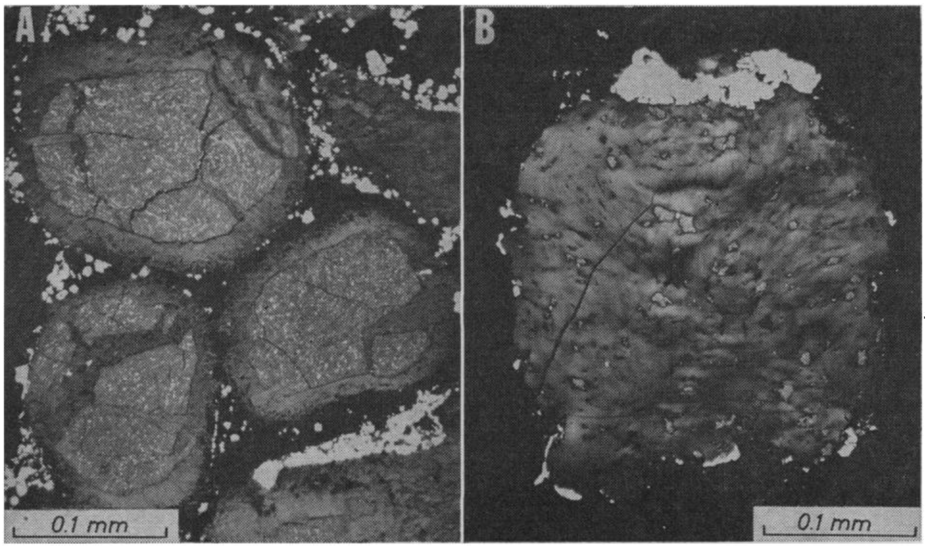

Fig. 1. (A) Detrital grains of uraninite, with dust-like inclusions of galena (white), surrounded by aureoles of carbonaceous matter (different shades of gray due to pronounced reflection pleochroism). The grains are gradually being replaced by the hydrocarbons along cracks and fissures (from "B" Reef, Loraine Gold Mines, Orange Free State; oil immersion). (B) Warty granule of carbonaceous matter in which uraninite has been resorbed except for small relict bodies. The uraninite relics show the usual dusting with minute specks of galena. Note outgrowths of secondary sulfides (white) around the granule (from Basal Reef, President Brand Mines, Orange Free State; oil immersion).

Since the bulk of the uraninite is concentrated at the footwall of a reef as part of the heavy suite, the carbonaceous material also is preferably accumulated in the footwall layers. Various reefs, including the famous "Carbon Leader" of the West Rand or the Basal and "B" reefs of the Orange Free State goldfield, are characterized by a basal thucholite seam sometimes more than 1 cm thick.

Several authors (*5, 6*) have regarded organic detritus as the ultimate source of the carbonaceous material. As sedimentation of the Witwatersrand System is believed to have been completed about 2.15×10^9 years ago (*7*), this postulate is necessarily based on the premise of a flourishing primitive life in early Precambrian times. Recent investigations (*8*) render this theory not unlikely; furthermore, organized elements showing excellent cell structures have been lately discovered in Witwatersrand rocks (*9*). As a contribution toward elucidation of the genesis of these carbonaceous materials, we thought it useful to study the distribution of the stable carbon isotopes in seven samples from different reefs and localities.

For this purpose, 20 mg of each sample was mixed with an excess quantity of V_2O_5 in a quartz combustion tube; the whole system was then subjected to 10^{-2} torr before the mixture was combusted at 1000°C for about 10 minutes, the resulting CO_2 being transferred to a mass spectrometer.

We present (Table 1) the results of the mass-spectrometric analyses as per-mille difference in the $C^{13}:C^{12}$ ratio between the sample and a standard [N.B.S. isotope reference sample No. 20 (Solenhofen limestone)]. Expressed in a formula, the relation is:

$$\delta C^{13} = \frac{[C^{13}/C^{12}(\mathrm{sa})] - [C^{13}/C^{12}(\mathrm{st})]}{C^{13}/C^{12}(\mathrm{st})} \times 1000$$

where sa is sample and st is standard. All values have been corrected for O^{17} (present in the CO_2 molecule in minor amounts) by applying Craig's correction factors (*10*).

Table 1 shows a variation in δC^{13}

between −22.4 and −32.8 per mille, the average being −28.1 per mille. The two samples from Virginia excepted, the values have a relatively narrow range lying between −27.1 and −32.8 per mille. Accordingly, the carbonaceous material represents a very "light" carbon variety. It is still difficult to account for the relatively "heavy" Virginia samples; naturally, these values must have some geochemical significance (*11*).

In order to evaluate these data properly, we must first review some principles governing the distribution of the stable carbon isotopes within the geochemical cycle. The most important process responsible for fractionation of the carbon isotopes, as represented by the $C^{13}:C^{12}$ ratio of atmospheric CO_2, is the fixation of CO_2 by plant photosynthesis. Whereas atmospheric CO_2 normally shows δC^{13} values between −7 and −8 per mille, organic carbon is considerably lighter, the diminution of the heavy carbon isotope accounting for a shift of the δC^{13} values into the range of about −25 per mille in the case of terrestrial plants. Organic sediments such as coals tend to retain these values, while other sedimentary organic carbon (especially of the hydrocarbon type) is often characterized by further decrease of the C^{13} isotope. This decrease applies preferably to oils, tars, and generally all bituminous substances, the latter usually showing δC^{13} values between −25 and −32 per mille (*12, 13*). The enrichment of C^{12} over C^{13} may thus be even more pronounced in sediments than in the organisms themselves that were the primary source of these carbon concentrations. Since earlier investigations have shown that an age effect can hardly be responsible for an increase of the C^{12} isotope, it has been postulated that the organic constituents of sedimentary rocks were partially subjected to processes effecting isotopic fractionation additional to that caused by photosynthesis (*12*).

Comparison of the data yielded by the Witwatersrand "carbon" with earlier results (*12, 14*) shows that the figures match well those reported for sedimentary organic carbon, mainly of the bituminous type. In particular, the coincidence of the δC^{13} values for the thucholite with the figures found for crude oils (*13*) is very striking, seeming to suggest that the carbonaceous material is genetically related to oil rather than to coal—a conclusion corroborating earlier genetic concepts based on geologic and microscopic evidence only. An explanation of the "carbon" as a chemical derivative of pre-Witwatersrand carbonate rocks can safely be precluded, since the difference in δC^{13} values between carbonates and organic carbon is too high (*12, 15*); besides, it is difficult to imagine a process effecting conversion of carbonates to hydrocarbons in rocks whose thermal history is only mild. Moreover, there is absolutely no geologic evidence hinting at such a possibility, since the Witwatersrand System, as well as the underlying basement rocks, contains no carbonate intercalations.

Table 1. δ-Carbon-13 values of seven "carbon" samples from the Upper Witwatersrand System of the Orange Free State goldfield. Negativity in values implies that the samples are "lighter" (that is, poorer in C^{13}) than the standard.

Source of sample		δC^{13}
Reef	Mining company	(‰)
Basal	Virginia	−22.4
Basal	Virginia	−22.9
"B"	Loraine	−27.1
Basal	Free State Geduld	−30.3
"B"	Loraine	−30.5
Basal	President Brand	−30.9
Basal	Western Holdings	−32.8

Because the magnitude of the isotopic fractionation in the Witwaterand thucholite is of the same order as in sedimentary carbon of known or highly probable biologic association, one must seriously consider the possibility of biogenic derivation of the source material of these carbon concentrations. As other investigators (*4, 5*) have emphasized, there is little doubt that this material is indigenous to the Witwatersrand sediments; the subsequent migration prior to final polymerization of the resultant mobile hydrocarbons has certainly covered a limited range. This fact implies that the waters of the Witwatersrand basin must have harbored a rich bacterial and algal life whose decomposition products contributed to formation of the "carbon" assemblages. According to this genetic scheme, the hydrocarbons constitute a kind of "chemofossil," providing indirect (geochemical) proof of biologic activity in early Precambrian times. One should note that the same conclusions were drawn by Hoering (*15*) with regard to minor carbon concentrations in various Precambrian sediments that had yielded δC^{13} values between −18.8 and −31.7 per mille.

Such reasoning is, of course, based on the premise that no other mechanism was then operating that could have given rise to an isotopic fractionation of a similar scale. The premise includes the assumption that the isotopic composition of the CO_2 present in the primeval atmosphere was not basically different from that of later times, and that the fractionation factors in the processes of migration and polymerization kept within a range comparable with common observational standards (*16*). While fully realizing some uncertainties arising from these points, we feel that an integration of all geologic and geochemical data now available strongly supports the concept of biogenic derivation of these "carbon" concentrations, and a model of the existence of photosynthesis in time certainly older than 2.15 × 10^9 years.

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11. Note that R. Berger (in *Abstr. Western Nat. Meeting Amer. Geophys. Union 6th Los Angeles*, Sept. 1966) reported δC^{13} values of about −45 per mille (Peedee belemnite standard) for the Pied des Monts (Quebec) thucholite originally described by H. S. Spence [*Amer. Mineralogist* **25**, 711 (1940)].
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