Reports

Carbonaceous Rocks of the Soudan Iron Formation (Early Precambrian)

Abstract. *Carbon-rich rocks more than 2.7 billion years old, from the Soudan Iron Formation of northeastern Minnesota, contain pyrite balls in which are found microstructures of possible biologic origin. The* C^{13}/C^{12} *and* S^{34}/S^{32} *ratios and minor element composition of this rock are consistent with such an interpretation. Hydrocarbons of presumed vital origin are also present, although it is not certain that they are endemic to the rock.*

The oldest carbon-rich rocks so far known in North America are associated with the Soudan Iron Formation of northeastern Minnesota, in the Lake Superior region. Metamorphic minerals in associated rocks give a potassium-argon age of 2.5 billion (2.5×10^9) years (*1*), and the Saganaga granite, which intrudes the Soudan sequence, has given concordant uranium-lead (zircon) and potassium-argon (amphibole) ages of 2.7 billion years (*2*). The Soudan, therefore, has an age of deposition approaching (or possibly even exceeding) 3 billion years, and its carbonaceous rocks are among the oldest on earth. They are, so far as known, likely to be exceeded in age only by those of the Figtree System in South Africa, which are believed to be in excess of 3.2 billion years (*3*).

Some thin layers and lenses of the Soudan rocks are so rich in carbon that they approach the appearance of an impure graphitic coal, including pyrite balls 1 to 3.5 cm in diameter such as are common in coals of lesser age. Such an abundance of carbon in rocks so old provokes consideration of vital origin, and it becomes, therefore, of interest to learn what we can about these rocks and their possible bearing on the early history of life.

The present discussion relates primarily to the carbon-rich rocks found below ground in the Soudan Mine, northeastern Minnesota. More comprehensive discussion of the characteristics, geologic relations, and age of the Soudan Iron Formation is given by Goldich and others (*1*) and in references there cited.

Samples were first obtained for study from known surface outcrops north of Tower, and then, to minimize chances of recent contamination and to obtain material richer in carbon, from 545 m below ground at Soudan (*4*). Inspection of this material showed carbon, silicates, and pyrite as major constituents, with some free sulfur as a minor component. Splits from the Soudan Mine were, therefore, subsequently sent to the following collaborators for study: (i) Frank Grimaldi, Branch of Analytical Laboratories, U.S. Geological Survey, for chemical analyses (20 July 1964); (ii) H. G. Thode, of McMaster University, for study of the sulfur isotopes (20 July 1964); (iii) T. C. Hoering, of the Carnegie Institution of Washington, for carbon isotope analyses (20 July 1964); (iv) Melvin Calvin, of the University of California (11 Dec. 1963), W. G. Meinschein, of Esso Research and Engineering (14 May 1964), and John Oró, of the University of Houston (9 Dec. 1964), for studies of the organic matter.

Sedimentary and mineralogic features. The Soudan Iron Formation occurs as large sedimentary lenses interstratified with basalt flows and tuff layers. These sedimentary lenses range in composition along and across the strike from hematite-magnetite–rich ones to others that are mainly chert, contain hardly any iron minerals, and would not have been called iron formation if they could not have been followed laterally into the iron-rich layers. The carbonaceous and pyritic layers apparently may occur in any part of the sedimentary lenses at Tower and Soudan.

Such material has been found in surface outcrop at only two places, however, probably because it is easily eroded. Before x-ray diffraction came into use it had been assumed that practically all the black material was graphite and extremely fine pyrite. Modern x-ray equipment shows that the larger part of any sample consists of black-looking 7-Å–layer silicates like kaolinite (non-magnesian), as well as pyrite, and that the graphite cannot be a well-ordered one. Acid treatment similar to that described by French (*5*) yielded a very strong x-ray pattern of graphite, though suggesting considerable disorder of layers. Pyrite is the only other mineral not destroyed by this treatment.

Why should a carbonaceous material having an age of at least 2.7 billion years not have gone to well-ordered graphite under metamorphism? As stated below, the temperature range to which Soudan rocks were subjected at Ely, Minnesota, is thought to have been between 350° and 400°C. If we accept this figure for Soudan (9 km WSW of Ely) it might be well to consider another possible explanation for the present condition of the x-rayed carbonaceous material. All of it, including pyrite and silicates, is of extreme fineness. If graphite were to coat all the grains with somewhat distorted layers a few unit-cells thick (of the order of 100 Å) it is conceivable that such material might resemble amorphous carbon. On the other hand, it is possible that this material may not have been exposed to temperatures as high as inferred.

Chemical composition. Samples of the carbonaceous rock, of related pyritic and siliceous phases, and of the enclosing iron ore, all from the Soudan mine, were kindly analyzed for us by L. Shapiro and F. Simon of the U.S. Geological Survey, utilizing wet-chemical, x-ray fluorescence, and spectrophotometric methods as appropriate for most accurate results. Data obtained by Shapiro and Simon are presented in Table 1 (*6*).

Of interest is the higher content of the characteristically biophilic elements titanium, lead, uranium, sulfur, potassium, and sodium in the rocks of high carbon content (samples 1 and 2 of Table 1) as compared with associated rocks. This would be consistent with, although not proof of, a vital origin for the carbon. The presence of lead and uranium also offers hope of eventually obtaining a direct age-determination on the carbonaceous rock itself.

The possibility of a vital origin for the organic components likewise provided impetus for their analytical study, and for investigation of the carbon and sulfur isotopes. Meinschein, Oró, and Calvin, in that order, have independently confirmed (*7*) the presence, among other hydrocarbons, of the distinctively biogenic isoprenoid alkanes pristane and phytane.

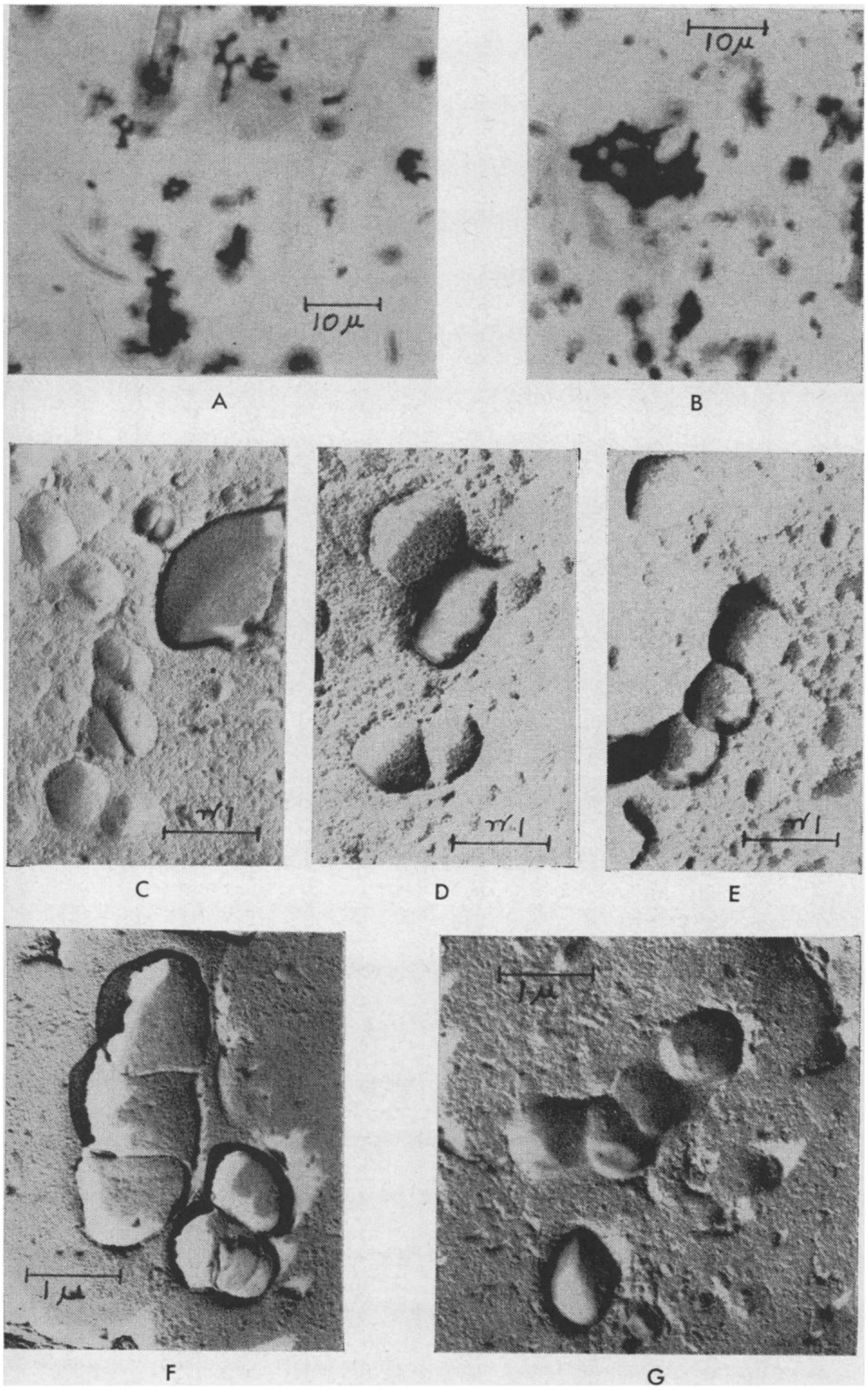

Fig. 1. Carbonaceous residues and pyritic microstructures from carbon-rich rocks of the Soudan Iron Formation. *A* and *B*, Kerogen-like residues, × 1100, from digestion of carbonaceous rock in hydrofluoric acid, followed by treatment in Schulze's solution to remove pyrite. *C*–*G*, Electron micrographs, × 13,600, of carbon-gadolinium replicas of microstructures from polished and oxidized surface of pyrite nodule.

Hoering, whose unpublished data are here reported with his permission, determined C^{13}/C^{12} ratios on a number of methanol eluates and solid "kerogen" from the carbon-rich Soudan material, using N.B.S. No. 20 as the reference standard. For comparison, he also made similar analyses of comparable material from younger Precambrian, Paleozoic, Tertiary, and Recent sediments from a variety of depositional environments. The great majority of these samples give comparable δC^{13} figures for both solid and extractable fractions, implying contemporaneity of the two. For the Soudan, however, a δC^{13} of −34.54 per mill was obtained on the solid fraction and a range of −25.06 to −25.99 per mill on four samples of methanol eluates. H. G. Thode and J. Monster (*8*) report −35.6 per mill as the average of four determinations of δC^{13} made of the solid carbon by them (Peedee belemnite standard). The inconsistency between the δC^{13} of the solid and extractable fractions of the Soudan organics implies fractionation during some time subsequent to deposition, or by different source organisms. It seems likely that either the extractable fraction has migrated into the rock and does not represent a primary component, or else C^{12} has been differentially removed from or C^{13} differentially added to this fraction during metamorphism to produce heavier carbon ratios in the extractables than are observed in the solid fraction. In view of this uncertainty, the various hydrocarbons observed in the extractable fraction cannot be taken as conclusive evidence of the vital origin of, or the nature of, vital processes (if any) involved in the production of the Soudan carbon. Nevertheless, the observed lightness of the carbon in both extractable and solid fractions is consistent with, if not presumptive evidence for, a vital origin (photosynthetic depletion of C^{13}), and migration of C^{12} from the volatile fraction would be a logical consequence of the thermal history of the rock, as discussed below.

Study of the S^{34}/S^{32} ratios by Thode and Monster (*8*) will be reported separately. Suffice it to say here

Table 1. Analyses of rocks from the Soudan Mine.

Constituent	Concentration			
	Samples from carbonaceous lens			4. Sample of typical Iron-Formation rock
	1. Carbon-rich rock	2. Pyritic rock	3. Siliceous rock	
	Percentage			
SiO_2	24.6	18.6	82.8	45.4
Al_2O_3	18.6	13.9	2.5	0.11
Fe_2O_3				52.1
FeO	0.32	0.44	0.28	1.4
MgO	.00	.00	.00	0.00
CaO	.14	.08	.00	.14
Na_2O	.17	.16	.03	.03
K_2O	2.6	2.9	.38	.04
H_2O-	1.4	1.5	.23	.00
H_2O+	4.4	2.9	.97	.35
TiO_2	1.0	1.1	.12	.00
P_2O_5	0.035	0.047	.010	.024
MnO	.00	.00	.00	.00
CO_2	<.05	<.05	<.05	<.05
SO_3	1.08	1.77	.42	<.02
S	0.09	0.11	.10	.01
FeS_2	22.4	36.1	9.6	.24
Organic*	24.2	20.2	2.4	.0
Total	101.0	99.81	99.75	99.84
Loss on ignition	38.5	38.6	6.3	0.00
	Parts per million			
V_2O_5	73	68	20	68
Pb	150	210	50	<5
U	3.2	6.5	0.87	0.18

* As carbonaceous residue resulting from attack with HCl followed by HF, corrected for pyrite content.

that the sulfur isotope ratios found would be consistent with either a nonvital or a vital origin.

Thermal history. The possible range of metamorphic temperatures indicated for the Soudan Iron Formation in the Zenith Mine at Ely, Minnesota, have been investigated by J. F. Machamer, utilizing the composition of carbonate minerals and the stability range of $2M_1$ muscovite (*9*). Machamer arrives at the conclusion that "The minimum possible temperature was thus from 200 to 350°C., and the maximum was probably higher than 400°C.; the general temperature range during most of the period of ore deposition was probably from 350 to 400°C." At such temperatures we might expect some loss of light isotopes from the volatile fraction.

The results of x-ray diffraction studies of the carbon from the Soudan Mine by Gruner, as discussed above, can be interpreted as consistent with the temperatures suggested. They may, however, imply lower temperatures, possibly toward the lower part of the range suggested by Machamer.

Methods of microscopical study. Microstructural detail of carbonaceous rocks from the Soudan Iron Formation has been studied by Cloud in order to ascertain whether any structures indicative of a vital origin might be preserved. This involved study of both thin sections and HF residues of all rock variations at magnifications up to 960 under the Leitz Ortholux microscope, and, with the help of Hannelore Hagen, of HF residues of the carbonaceous rock and polished surfaces of the pyrite at magnifications up to 13,600 under the Philips North American model 100B electron microscope operated at 80 kv.

Study of the pyrite under the electron microscope was carried out by means of a method developed and brought to our attention by Ehlers, Schopf, Stiles, and Birle (*10*). A flat cut through a pyrite ball from carbonaceous rock of the Soudan Mine was given a high polish and then allowed to oxidize under cover in a humid atmosphere for 3 days. A solution of nitrocellulose in amyl acetate was applied to its surface, allowed to dry, and stripped free. This was shadowed with palladium at an angle of 45 degrees and carbon at 90 degrees and then dissolved in amyl acetate. The palladium-carbon replicas were then examined under the electron microscope.

Microstructures observed. Observations with the light microscope revealed nothing of paleontological interest in the thin sections and only dubious materials in the HF residues. Some of the kerogen-like material remaining after degradation in HF and washing in Schulze's solution (*11*) showed a curiously branched and meshwork structure (Fig. 1, *A* and *B*) that could be interpreted to imply derivation from degraded tissue of some sort, but which might also be an artifact of crystallization. The illustration here of this material is not meant to imply an interpretation that it represents identifiable biologic remains, but merely to exemplify the best results of usual methods of study.

The electron microscope likewise revealed nothing clearly conclusive. The HF residues showed only clumped nondescript masses of carbonaceous material. The pyrite also showed mainly nondescript blobs. A few of the microstructures observed in the pyrite, however, are of a size and a degree of organization that would be consistent with their interpretation as bacteria or microscopical blue-green algae. These are small blister-like objects 0.8 to 1.5 μ across, some of which occur in pairs or in series of 3 to 5 or 6. The ones in series may be barely in contact or show an overlapping or perhaps a spiral structure. Although minute blisters in the nitrocellulose peels offer a source of confusion in such studies, such blisters are quite circular and unlike the objects described and illustrated in Fig. 1, *C–G*. We believe that the latter are in fact embedded in the Precambrian pyrite and a part of it. Reservation about the biologic origin of these objects rests primarily on their irregularity of shape and rarity in the rock. Although they are rather more persuasive than many putative Precambrian fossils, we are not sure that these objects are not some pattern of abiogenic colloidal material fortuitously incorporated in the pyrite. As all the information available about their morphology is adequately portrayed in Fig. 1, *C–G*, further discussion would be superfluous at this time.

If these microstructures are indeed primitive bacteria or blue-green algae, they would support a vital origin for the Soudan carbon and be consistent with the interpretation of the reported pristane and phytane as endemic to the rock in which found. This would take the geological record of autotrophic and possibly photosynthetic life back to more than 2.7 billion years, an age in keeping with that suggested by the stromatolites of the Bulawayan limestones in South Africa (*3, 12*) and more than 0.7 billion years greater than that of the Gunflint Iron Formation (*13*).

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References and Notes

1. S. S. Goldich and others, *Minn. Geol. Surv. Bull.* **41**, 5, 42–43, 51–52 (1961).
2. D. Anderson, Ph.D. thesis, University of Minnesota, March 1965; G. N. Hanson, Minnesota Geological Survey, unpublished. We are indebted to these gentlemen for permission to quote their data.
3. L. O. Nicolaysen, in *Petrographic Studies: A Volume in Honor of A. F. Buddington*, A. E. J. Engel *et al.*, Eds. (Geological Society of America, New York, 1962), pp. 569–598; see pp. 574–575.
4. All samples here reported on were obtained from a carbonaceous lens in the lower part of the Soudan Iron Formation, 21st level of the Soudan Mine, Soudan, Minn. The exact location is 545 m below ground, directly beneath the center of NW¼, NW¼, SW¼, sec. 27, T62N, R15W. Locality X of 9 December 1963. For guidance and assistance underground in the Soudan Mine, Cloud is indebted to George Nemanich of Soudan, Minn. He is also grateful to U. W. Hella, director, Division of State Parks, Minnesota Department of Conservation, for permission to go underground and for authorizing the cooperation of Nemanich in entering a closed-off area of the mine.
5. B. M. French, *Science*, **146**, 917 (1964). Our treatment consisted of boiling for an hour in concentrated HF, followed by boiling for another hour in a 50-percent solution of HCl.
6. For the analytical data, and for permission to quote, we are indebted not only to the analysts but also to F. S. Grimaldi and Irving May who arranged for performance of these analyses in the laboratories of the U.S. Geological Survey.
7. W. G. Meinschein, J. Oró, M. Calvin, telephoned reports to Cloud. The occurrence of pristane and phytane has subsequently been reported in a paper from Calvin's laboratory [T. Belsky, R. B. Johns, E. D. McCarthy, A. L. Burlingame, W. Richter, M. Calvin, *Nature* **206**, 446 (1965)].
8. H. G. Thode and J. Monster, letters of 8 and 11 February 1965 to Cloud.
9. J. F. Machamer, "Geology and origin of the iron ore deposits of the Zenith Mine, Ely, Minnesota," *Minn. Geol. Surv. Spec. Publ.*, in press.
10. E. G. Ehlers, J. M. Schopf, D. V. Stiles, J. D. Birle, "Fossil iron bacteria preserved in pyrite," in preparation. Information and authorization to use and publish by courtesy of J. M. Schopf.
11. 15 g $KClO_3$ + 150 ml H_2O + 300 ml concentrated HNO_3.
12. A. M. Macgregor, *Geol. Soc. So. Africa Trans.* **43**, 9 (1941); **54**, xxvii (1952).
13. E. S. Barghoorn and S. A. Tyler, *Science* **147**, 563 (1965); P. E. Cloud, Jr., *Science*, **148**, 27 (1965).
14. Research leading to this publication was done under NSF grant GP-1807. The mineralogy and microscopic organization of the material has been investigated at the University of Minnesota by us. It was originally hoped that the results of all related studies might be coordinated in a single publication or group of simultaneously published papers to which this paper would be introductory. That not being feasible, we present our observations, together with some previously unpublished data from others, in order that this information may be available for subsequent reference as appropriate.

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Cosmogenic Radionuclides in the Bondoc Meteorite

Abstract. *Long-lived cosmogenic radionuclides were measured in the stone phase and in a mechanically separated metallic nodule from a fragment of the Bondoc mesosiderite. Activity levels of the various radionuclides in both phases, along with results of mass-spectrometric measurements of rare-gas isotopes in the stone phase, indicate that heavy shielding was the chief cause of the low specific activities observed.*

The discovery and some of the properties of the Bondoc meteorite, a mesosiderite of unusual structure, have been discussed by Nininger (*1*). Measurement of its Al^{26} content gave 5.0 ± 1.7 disintegrations per minute per kilogram (dpm kg^{-1}), about a factor of 10 lower than that in the average chondrite. The low Al^{26} activity can be explained by one or more of three causes—namely, short period of exposure to cosmic rays, great terrestrial age, or shielding.

In order to better resolve these possibilities we have measured a number of cosmogenic radionuclides both in a metallic nodule and in the remaining silicate phase of the Bondoc meteorite, which was purchased from the American Meteorite Laboratory. The results are given in Table 1.

The fact that both the metallic nodule and the remaining phase contain Mn^{53} activity ($T_{1/2} = 2 \times 10^6$ years) in reasonable amounts precludes a short cosmic-ray exposure period of 4 to 10 $\times 10^4$ years. Manganese-53 activity per unit mass of iron (the most probable target for production) is 0.13 ± 0.01 dpm g^{-1} in both samples; this fact strongly suggests that both nodule and stone phase were together in space at the same depth in the pre-atmospheric body for at least the last million years. The Be^{10} activity ($T_{1/2} = 2.7 \times 10^6$ yr) of 1.8 ± 0.3 dpm kg^{-1} is lower, by a factor of about 11, than that found in most chondrites. If this were due to a short cosmic-ray exposure (370,000 years), the expected Al^{26} activity ($T_{1/2} = 7.4 \times 10^5$ yr) would be 29 percent of its normal saturated value—that is, $54 \times 0.29 = 16$ dpm kg^{-1}—which is not in agreement with the measured values.

Table 2 lists concentrations of stable, rare-gas isotopes in the silicate phase of Bondoc; Cobb's data (*2*) were obtained on a portion of the specimen we studied. The sample studied by Hintenberger *et al.* (*3*) may have come from the same 10-kg fragment from which ours was taken. Exposure ages can be calculated from the data in Table 2 by use of nuclide production rates of 2.0 and 0.249×10^{-8} cm^3 (STP) g^{-1} per million years (*4*) for He^3 and Ne^{21}, respectively. The resulting ages range from 4 to 12×10^6 years. Even 4×10^6 years is too long to account for the low activities that have been observed. In view of the observed deficiencies in radionuclide contents, the actual exposure age is probably greater than 20 million years.

The appreciable levels of Ni^{59} ($T_{1/2} = 7.5 \times 10^4$ yr), Cl^{36} ($T_{1/2} = 3 \times 10^5$ yr), and Mn^{53} activities in the nodule preclude the possibility that great terrestrial age is the cause of the general reduction in specific activities. The observed Ni^{59} activity is equivalent to about 0.7 dpm g^{-1} nickel, to be compared with a maximum of 2.3 dpm g^{-1} nickel in irons (*5*). This lower Ni^{59} activity corresponds to a terrestrial age of up to about 130,000 years, which is sufficient to reduce the saturated Cl^{36} activity by about 25 percent and too low to have any effect on Mn^{53} activities. Yet the observed Cl^{36} activity is lower by a factor of 3 to 6 than average values in irons, and the Mn^{53} activity is lower by a factor of 2 to 3. Even allowing for the probability that production of Ni^{59} from nickel may be enhanced by a factor of 2 to 4 in a stony matrix (*6, 7*) only increases the possible terrestrial age to a maximum of 300,000 years, still too low to account for the Cl^{36} result, to say nothing of the Mn^{53} result.