Reports

Meteorites: Optical Activity in Organic Matter

Abstract. *A low-amplitude, positive, Cotton effect, centered at about 340 millimicrons, has been observed in organic extracts of samples from ordinary (noncarbonaceous) chondrites. Ancillary evidence renders it likely that this optical activity derived from contamination by biologic materials on Earth.*

The origin of organic matter in meteorites has intrigued chemists for over a century (*1*), but only the recent advent of modern microanalytical techniques and highly sensitive instruments has enabled detailed investigations of carbonaceous material in meteorites. Of special interest are organic compounds that may have been implicated in biogenetic pathways (*2*), and optical activity is a particularly relevant physical property for study in this connection. All the biopolymers—that is, the nucleic acids, polysaccharides, and proteins—are dissymmetric (chiral) and optically active. Since optically active products cannot be synthesized under nondissymmetric (achiral) conditions, observation of optical activity is *ipso facto* powerful evidence of biotic sources.

Reports concerning the optical activity of organic substances from the Orgueil meteorite (a Wiik type-I carbonaceous chondrite) are conflicting. Nagy *et al.* (*3*) recently reported optical activity in saponified organic extracts; their sample, however, was colored and contained "some sulfur." Later their work was challenged by Hayatsu (*4*), who found no optical activity in purified samples; he suggested that the reported rotations might reflect the presence of "colloidal particles [that is, sulfur], reduced instrument sensitivity due to low transmittance of the solutions, or a combination of both." These observations have raised controversy (*5*). We now report investigation of optically active organic materials extracted from ordinary chondrites.

A fragment of the Homestead polymict, brecciated, gray, bronzite chondrite (*6*) was employed in the first part of our investigation. The outer crust (0.6 cm) was chiseled off and discarded. The 2502-g interior of the fragment was crushed and passed through a disc grinder fitted with new steel plates. Coarse metal was removed from the pulverized sample with a hand magnet, and the sample was sieved and recycled through the grinder until all particles passed 150 mesh. The powder was immersed for 1 week in 600 ml of 1:1 (by volume) benzene-methanol. After filtration, the solvents (*7*) and elemental sulfur (*8*) were removed from the filtrate, and the residual extract (135 mg), containing the organic matter, was fractionated by chromatography on silica gel (*7*). Successive elutions yielded these amounts of material: with *n*-heptane, 36.7 mg; with carbon tetrachloride, 10.5 mg; with benzene, 4.8 mg; and with methanol, 77.0 mg. The compositions of similar fractions of the organic extracts of terrestrial samples and of carbonaceous chondrites have been discussed (*7, 9*).

The alkane fraction (*n*-heptane eluate) was examined spectropolarimetrically (*10*); a plain positive curve was obtained in isooctane: $[\alpha]^{27}_{300}$ + 1.1° ± 1.1°; $[\alpha]^{27}_{210}$ + 4.6° ± 1.1° (*l*, 0.1 dm; *c*, 0.70 g/100 ml).

A 52.6-mg sample of the nonhydrocarbon fraction (methanol eluate) was separated by chromatography on alumina by a procedure previously employed in the separation of aromatic hydrocarbons (*7*). A yellow band was eluted with 4 to 8 percent methanol in benzene. The material recovered from this fraction consisted of 19.7 mg of a light-yellow liquid whose infrared spectrum featured a broad, complex, carbonyl band at 1720 cm^{-1} and a hydroxyl band at 3450 cm^{-1}.

The ultraviolet-absorption spectrum and optical rotatory dispersion curve of this fraction are displayed in Fig. 1, and ancillary information is collated in Table 1. The curve corresponds to a positive Cotton effect centered at about 340 mμ. Two fractions immediately following this main band {*A*: 3.4 mg; $[\alpha]^{27}_{355}$ + 17.0° ± 2.9°; *B*: 1.6 mg; $[\alpha]^{27}_{350}$ + 19° ± 6° (maximum rotations)} showed the same first extremum with a decrease in amplitude; an additional 3.1 mg of organic material, obtained by prolonged Soxhlet extraction, with methanol-benzene, of the alumina used for the chromatography, showed the following rotation characteristics in methanol: $[\alpha]^{27}_{D}$ + 6.1° ± 3° $[\alpha]^{27}_{350}$ + 25.2° ± 3° (peak); $[\alpha]^{27}_{340}$ + 15.0° ± 3° (last reliable value) (*11*).

We took special care to exclude spurious rotations caused by stray light or low transmittance. Since the solutions were perfectly clear and showed no Tyndall effect, artifacts due to light scattering on colloidal particles were considered absent. The spectropolarimeter recorded no artificial rotations for

Table 1. Optical rotatory dispersion and absorption characteristics of a fraction from the Homestead meteorite. The rotation data were obtained on a Cary model-60 spectropolarimeter at 27° in isooctane; *c*, 0.394 g/100 ml. The slit-width was programmed for constant spectral slit width (10Å) through the whole range of wavelengths; precision is at least ± 0.001°, as judged from repeated scans using samples, solvent blanks, and standard solutions; the error reported in column 4 was based on this value. The absorption data were obtained on a Cary model-14 spectrophotometer under the same conditions, using cells of 1.00- and 0.10-cm path length. Abbreviations: pk, peak; tr, trough; sh, shoulder; *l*, optical path length; the last λ value listed corresponds to the lower limit of wavelength for which rotation data were meaningful.

λ (mμ)	*l* (cm)	$\alpha \times 10^3$ (deg)	$[\alpha]$ (deg ml g^{-1} dm^{-1})	Absorbence
377 pk	1.00	+14.0	+35.6 ± 2.5	0.488
369 tr	1.00	+10.4	+26.4 ± 2.5	.632
360 pk	1.00	+16.0	+40.6 ± 2.5	.935
351 tr	1.00	+ 1.9	+ 4.8 ± 2.5	1.430
345 pk	1.00	+ 6.6	+16.7 ± 2.5	1.810
340	1.00	0.0	0.0 ± 2.5	2.300
337 tr	0.50	− 6.0	−29.4 ± 5.1	1.295
331 pk	.50	− 4.2	−21.3 ± 5.1	1.62
316 sh	.20	− 4.0	−54.5 ± 13	1.01
309 tr	.20	− 7.0	−88.7 ± 13	1.30
280	.10	− 1.4	−36 ± 25	1.27

solutions with an optical density of up to $D = 4$; however, increasing electronic noise for $D > 2.5$ led us not to exceed this density. Artificial "Cotton effects" could be induced only in optically active solutions having a D greater than about 6. Performance of the instrument was checked between runs by use of standard solutions (mostly of optically active aromatic compounds, with high absorption and low rotation values); moreover, rotations were considered reliable only if dilution showed no deviations from Biot's law.

The credibility of the rotations observed by us is unassailable, but gas-liquid chromatographic, ultraviolet, infrared, and mass-spectrometric evidence does not define precisely the nature of the substance(s) giving rise to the Cotton effect. Judged by the low amplitude [α] 130° ml g^{-1} dm^{-1}) of this effect, the concentration of optically active material in the chondritic fraction is small. Although it is premature to speculate *in extenso* on the structure of the chromophore, the possibility cannot be excluded that a $n \rightarrow \pi^*$ transition of an α,β-unsaturated ketone contributes to this Cotton effect (*12*).

Since ordinary chondrites contain minerals that were formed at temperatures that would degrade organic compounds, the organic matter must have been incorporated at some later stage of their preterrestrial or terrestrial history. Because we suspected that the optically active Homestead fractions contained biologic compounds of terrestrial origin, we came to question the presence of any extraterrestrial organic matter in ordinary chondrites. However, our analyses of the organic extracts of fragments of the Bath, Waconda, and Holbrook chondrites, and of another fragment of the Homestead meteorite (*6*), seemingly did not support this suspicion: extracts of these chondritic samples were essentially uniform in composition, and the alkane fractions from the chondrites were almost identical with alkanes isolated from the Murray meteorite (a Wiik type-II carbonaceous chondrite; *13*).

Because the Bath, Waconda, Holbrook, Homestead, and Murray meteorites had fallen in different regions and the fragments used by us had different storage and handling histories, it seems unlikely that they could have been equivalently contaminated; their compositional uniformity may thus be taken as *prima facie* evidence of indigenous origin.

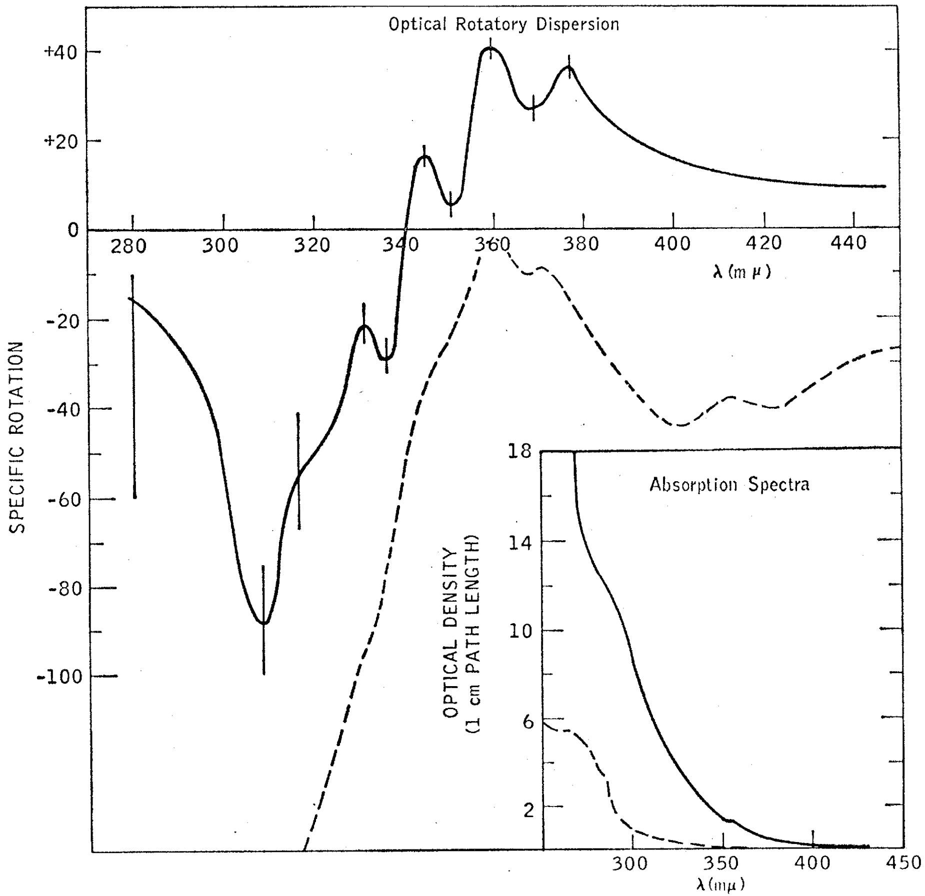

Fig. 1. Optical rotatory dispersion and ultraviolet-absorption data (isooctane) for the nonhydrocarbon organic fraction isolated from a Homestead-meteorite fragment (solid line) and hand extracts (dashed line). Uncertainty is indicated by vertical bars.

In trying to determine whether or not the optically active constituents of chondritic extracts were laboratory contaminants, we composited the analytical blanks for all our meteoritic analyses with analytical blanks for similar analyses of terrestrial rocks, and analyzed an 114-g fragment of the Holbrook hypersthene chondrite (*6*). The composite of analytical blanks contained 7.1 mg of organic material, which showed no optical activity in isooctane solution (c, 0.14 g/100 ml) in the regions between 450 to 300 mμ (l, 0.1 dm) and 300 to 235 mμ (l, 0.01 dm). The intact 114-g Holbrook fragment was extracted 16 successive times in an ultrasonic extractor (*14*) before it was disintegrated with 48-percent hydrofluoric acid; the sludge was extracted with benzene. Gas chromatograms of alkane fractions isolated from successive extracts of the intact fragment and its sludge did not differ significantly. The organic nonhydrocarbons in the extract of the sludge were optically active; their optical rotatory dispersion curve showed a positive Cotton effect centered at about 340 mμ.

In another control experiment, the two analysts who isolated the optically active fractions from the meteorites analyzed n-heptane washings of their hands in the same manner as the chondritic extracts. Compositionally, the alkanes and organic nonhydrocarbons from the hand extracts were unlike their chondritic counterparts, but 22.8 mg and 12.8 mg, respectively, of a light-yellow liquid was eluted by 4 to 8 percent methanol in benzene when the nonhydrocarbon fractions of the hand extracts were chromatographed on alumina columns. The optical rotatory dispersion curves of the two samples in isooctane were essentially the same; the curve corresponding to the 12.8-mg fraction accompanies its absorption spectrum in Fig. 2. The conditions of measurement were: (in the wavelength range 450 to 290 mμ) c, 0.256 g/100 ml; l, 0.1 dm; (in the range 320 to 218 mμ) c, 0.163 g/100 ml; l, 0.02 dm (both sets of data for measurements of rotation); (absorption measurements) c, 0.256 g/100 ml; l, 1.0 and 0.10 cm.

The shape of the optical rotatory dispersion curve of the nonhydrocarbons from the hand extracts in the

Table 2. Surface extraction of a Holbrook fragment.

Extraction		Extract (mg)		
Cycle (No.)	Duration (days)	Crude	Purified*	
			A	*B*
1	1	29.9	3.4	18.5
2	4	30.7	2.2	23.3
3	3	5.6	0.4	3.3
4	5	11.1	.3	2.8
5	6	9.3	.3	1.8
6	9	2.6	.3	2.1
7	6	2.4	.1	0.9
8	10	1.3	.2	.3
9	2	3.2	.2	2.1†
10	2	0.4	.5	0.7
11	3	1.3	.2	1.2
12	2	1.0	.3	0.3
13	2	0.7	.0	.0

*After chromatography of the crude extract on silica gel; fraction *A* (*n*-heptane eluent) contains alkanes; fraction *B* (methanol eluent), organic nonhydrocarbons. Difference in weight between crude and purified extracts mainly indicates the mineral content of the former. † First extraction after transfer of the intact fragment to the ball mill–extractor unit; the increased amount of inorganic extractable material reflects the crushing of parts of the surface of the chondrite on the walls of the ball mill during transfer.

region between 290 and 390 mμ strongly suggests a positive Cotton effect superimposed on a negative background. The hand extracts were evidently complex mixtures; thus we cannot exclude the possibility that they contained some components with low-amplitude positive Cotton effects near 340 mμ and others with high-amplitude negative Cotton effects centered at shorter wavelengths. If this were so, the resultant summation curve (Fig. 2) may owe its positive component to a substance or substances that are structurally and stereochemically related to, or even identical with, the substance(s) giving rise to the positive Cotton effect in the nonhydrocarbon fraction of the Homestead extracts. This possibility is underscored by the direct comparison of the two curves in Fig. 1, which reveals striking similarities in the positions and shapes of the positive Cotton effects found in the fractions from the Homestead chondrite and hand extracts.

If, as we have indicated, terrestrial contaminants may account for the optical activity in chondrites, one may predict that similar Cotton effects may be commonly found in surface extracts of meteorites and terrestrial rocks that have been displayed and handled without conscientious attempts to prevent contamination. By the same token, reliable information regarding properties and distributions of indigenous organic matter in chondrites and terrestrial rocks may be obtainable only by study of samples that have been either carefully collected and stored to avoid contamination or scrupulously cleansed of superficial contaminants.

Because repeated extractions of the intact 114-g Holbrook fragment (by ultrasonic extractor) did not remove all optically active substance, we exhaustively extracted an intact 2519-g fragment (Fig. 3; *15*) of this meteorite. This fragment had a complete fusion crust that was easily damaged because of the brittleness of the stone (Fig. 3, upper left corner); it had an old central crack. The system of holes in this fragment reflects the removal of a core for mass-spectrometric studies at M.I.T. of the distribution of organic matter.

A specially constructed Soxhlet-type borosilicate-glass extractor, using a 12-liter, three-neck, round-bottomed, reflux flask was employed so that the intact 2519-g Holbrook fragment could be extracted. Before this fragment was placed in the extractor, successive 10-liter portions of 9 : 1 benzene-methanol (by volume) were refluxed in the extractor until 24-hour extraction blanks weighing less than 0.2 mg were obtained. The Holbrook fragment was then maintained in the extractor at 0.34 atm (gauge) by a stream of nitrogen filtered through silica gel. Successive extracts were obtained by adding 12-liter portions of purified benzene-methanol (9 : 1 by volume) (*7*) to the 12-liter flask, withdrawing 2-liter blanks of the added solvents, and refluxing the remaining solvent over the fragment. All solvent blanks contained less than 1 μg of residual organic compounds, determined by gas chromatography.

After eight extraction cycles (lasting 44 days in all) in this Soxhlet-type unit, the chondrite was transferred to a specially designed stainless-steel ball mill which could be connected to an extracting unit (*16*). Again, all parts of the new unit had been precleaned down to an absolute blank in organic matter, and cleaned (Soxhlet-extracted) aluminum foil was used to manipulate transfer of the 2519-g Holbrook fragment. Extractions in the new unit were also carried out under 0.34 atm (gauge) of filtered nitrogen. These additional extractions of the chondrite for 11 days (five cycles) proved that accessible regions of the fragment had been exhaustively cleaned.

After removal of the solvents the crude extracts were chromatographed on silica gel (*5*). The *n*-heptane eluates (alkanes) and methanol eluates (organic nonhydrocarbons) were the principal chromatographic fractions (Table 2); only traces of aromatic hydrocarbons and of other organic materials were present in the carbon tetrachloride and benzene eluates, and no elemental sulfur was found in extracts.

The nonhydrocarbon fractions from extraction cycles 1 through 8 were combined and filtered through glass wool to yield a total of 40.6 mg of material; in 15 ml of benzene, this was

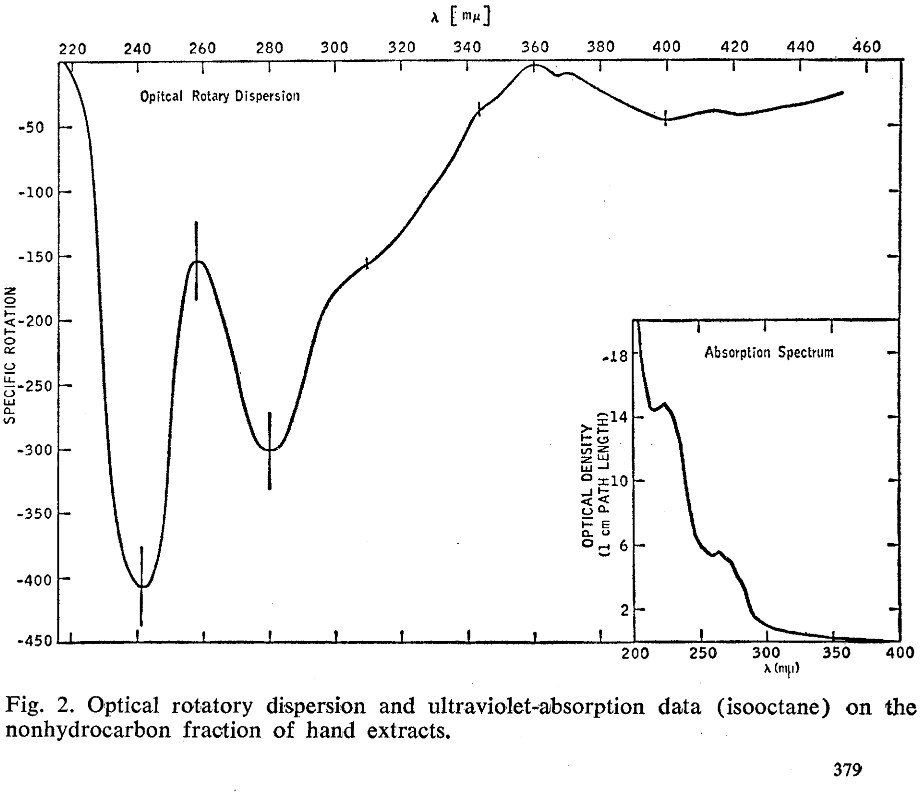

Fig. 2. Optical rotatory dispersion and ultraviolet-absorption data (isooctane) on the nonhydrocarbon fraction of hand extracts.

fractionated on a 50-g alumina column (*17*) prewet with 10 ml of benzene. Thus was obtained as the main fraction 20.5 mg of a colorless material, eluted with 100 ml of 20 percent methanol in benzene. The optical rotatory dispersion of this fraction in methanol solvent had the following characteristics: $[\alpha]^{27}_{400} + 2.3° \pm 0.5°$ (ℓ, 1 dm; c, 0.205); $[\alpha]^{27}_{355} + 12.7° \pm 5°$ (peak); $[\alpha]^{27}_{335}\ 0° \pm 5°$; $[\alpha]^{27}_{310} - 29.2° \pm 5°$ (trough) (ℓ, 0.1 dm; c, 0.205); $[\alpha]^{27}_{290} - 12° \pm 10°$ (last observable value) (ℓ, 0.1 dm; c, 0.102).

The close correspondence of this Cotton effect with that observed in the Homestead extract seems to indicate more than mere coincidence. Since the overall optical activity in the Holbrook extract (as measured by the amplitude of the Cotton effect: $[\alpha]$ 42° ml g^{-1} dm^{-1}) is lower than that in the corresponding Homestead extract, the seeming absence of fine structure in the Cotton effect may merely reflect lower accuracy of the measurement.

After completion of the 13th extraction cycle, the ball mill was sealed and temporarily disconnected from the extraction unit. The chondrite was crushed by ball-milling for 16 hours, and subsequently extracted over a period of 2 days in the manner described. After work-up, 8.2 mg of extract was yielded, of which 8.0 mg represented elemental sulfur; thus only 0.2 mg at most contained organic material. Overnight repetition of the crushing, extraction for 3 days, and work-up produced 6.2 mg more extract, which was fractionated into 4.4 mg of elemental sulfur and 1.0 mg containing organic nonhydrocarbons. It is of interest that only negligible amounts of organic matter could be isolated from the interior of the meteoritic fragment: essentially all the organic material was recovered by extraction of the *uncrushed* fragment.

The optical properties of organic materials in terrestrial rocks were then determined, one of which was a clay-with-dendrite teaching specimen (*18*) that had been handled by students for about 65 years. The six other rocks analyzed had been carefully collected and stored for use in organic geochemical research; they ranged in age from Eocene (4×10^7 years) to Precambrian (2.7×10^9 years). Organic nonhydrocarbon fractions, chromatographically equivalent to the optically active chondritic fractions, were obtained from the benzene-methanol extracts of all samples; only the fraction from the teaching specimen was optically active: a positive Cotton effect centered at about 330 mμ was practically indistinguishable from the Cotton effect found in the Holbrook extract.

Our observation was of the first complete Cotton effect observed in organic samples isolated from meteorites. However, although our evidence does not permit rigorous exclusion of the possibility that some or even all optical activity in the Homestead extracts resides in indigenous organic matter, and although, in the absence of sufficient reliable data on the porosity and permeability of chondrites, we cannot assert that all organic matter obtained by surface washings of the Holbrook meteorite had in fact been stored in the outer layers of the stone, the cited ancillary evidence renders it likely that the observed optical activity originated in contamination by biologic materials on Earth.

W. G. MEINSCHEIN
Department of Geology, Indiana University, Bloomington
CLIFFORD FRONDEL
Department of Geological Sciences, Harvard University, Cambridge, Massachusetts
PETER LAUR
KURT MISLOW
Department of Chemistry, Princeton University, Princeton, New Jersey

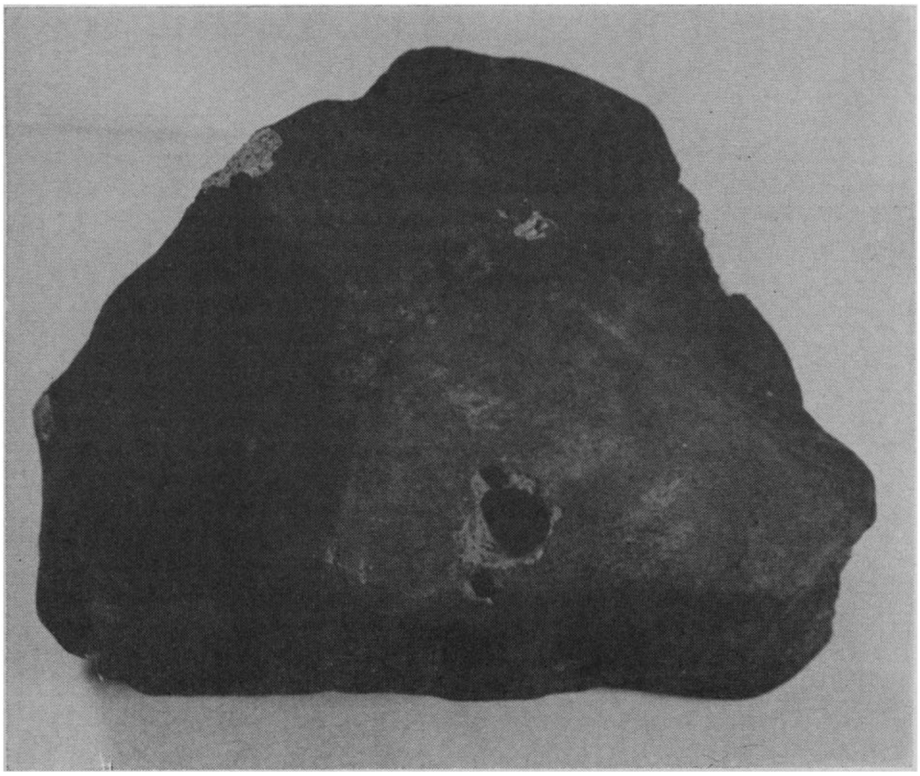

Fig. 3. Fragment of the Holbrook chondrite used by us.

References and Notes

1. J. J. Berzelius, *Ann. Phys. Chem.* **33**, 113 (1834).
2. H. C. Urey, *Science* **151**, 157 (1966).
3. B. Nagy *et al.*, *Nature* **202**, 228 (1964).
4. R. Hayatsu, *Science* **149**, 443 (1965).
5. B. Nagy, *ibid.* **150**, 1846 (1965); R. Hayatsu, *ibid.* **153**, 859 (1966).
6. G. T. Prior, *Catalogue of Meteorites* (British Museum, London, 1953), ed. 2 by M. H. Hey, from the Harvard Univ. collection; histories of the fragments used by us are available from C. Frondel.
7. W. G. Meinschein, *Bull. Amer. Assoc. Petrol. Geologists* **43**, 925 (1959); ———, B. Nagy, D. J. Hennessy, *Ann. N.Y. Acad. Sci.* **108**, 553 (1963).
8. M. Blumer, *Anal. Chem.* **29**, 1039 (1957).
9. M. H. Briggs and G. Mamikunian, *Space Sci. Rev.* **1**, 647 (1963); W. G. Meinschein, *Nature* **197**, 833 (1963).
10. With a Cary model-60 instrument.
11. The difference between the weight of the material placed on the column and the total weight of the eluates indicates mainly the mineral contents of the crude extract.
12. P. Crabbé, *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry* (Holden-Day, San Francisco, 1965), chap. 9.
13. Murray sample (from the Smithsonian collection) supplied by E. P. Henderson to W. F. Libby and distributed by the latter.
14. W. G. Meinschein, *Science* **150**, 601 (1965).
15. From the Harvard Mineralogical Museum.
16. The need to retain the meteoritic fragment in a sealed system during extraction of the intact fragment, during pulverization of the fragment, and during subsequent extraction of the powder was recognized by W. H. Johnston.
17. Harshaw Scientific; activated powder catalyst grade AL-0101 P.
18. From Harvard Mineralogical Museum.

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