Reports

Endogenous Carbon in Carbonaceous Meteorites

Abstract. *Seven carbonaceous chondrites have been analyzed for soluble organic compounds, carbonate, and residual carbon. Carbon-13/carbon-12 isotopic measurements on these fractions gave the following values relative to a marine carbonate standard: carbonate, +40 to +70 per mil; residual carbon, −15 to −17 per mil; soluble organic material, −17 to −27 per mil, with one value of −5.5 per mil. These values are interpreted to indicate that carbonate, residual carbon, and part of the extractable organic material are endogenous to these meteorites.*

Over a century ago, European scientists first isolated carbon compounds from the carbonaceous chondrites Kaba and Orgueil (*1*). Little attention was given to this accomplishment until the publication of Mueller's paper in 1953 (*2*). During the last decade a great effort has been exerted to separate and identify the organic molecules in meteorites (*3*). Both soluble and insoluble organic carbon have been identified, the former consisting partly of saturated hydrocarbons (*4*), and the latter, probably of highly condensed aromatic structures (*5*). Quantitative data were not well documented, and the origins of the organic carbon were not satisfactorily established (*6*).

It is generally accepted that the carbonaceous material remaining after extraction with organic solvents and demineralization with hydrochloric and hydrofluoric acids is representative, in chemical composition, of the meteoritic carbon prior to the entry of the meteorite into the earth's atmosphere. Which of the extractable organic components, if any, are endogenous is still undecided because of the ubiquitous distribution of the same compounds on this planet.

Boato (*7*) measured $^{13}C/^{12}C$ ratios in intact meteorites, and the results appeared to overlap those typical of terrestrial carbon (*8*). Clayton (*9*) showed that carbonate minerals from the Orgueil meteorite are highly enriched in ^{13}C relative to terrestrial carbonate. More recent studies (*10, 11*) have given $\delta^{13}C$ (*12*) values of −19 to −28 per mil for extractable organic components and −18 to −29 per mil for the carbonate-free fractions remaining after treatment with acid. Since these values are essentially the same as those for reduced carbon compounds on earth (*13*), it has not been possible to use carbon isotope ratios as a criterion for differentiating between organic compounds of extraterrestrial origin and those of terrestrial origin. We believe that the results presented below provide the first evidence for the endogenous character of extractable organic compounds in carbonaceous chondrites.

Seven carbonaceous chondrites (two of type I, four of type II, and one of type III) were analyzed (*14*). An attempt was made to separate several groups of carbon compounds in order (i) to obtain a mass balance for carbon, (ii) to identify critical compounds that may be indicative of terrestrial contamination, and (iii) to measure the $^{13}C/^{12}C$ ratios of the separated compounds.

A small portion of each meteorite was analyzed to obtain the $\delta^{13}C$ value of the intact sample. This analysis was carried out by combusting the meteorite in an atmosphere of oxygen at 1050°C, capturing and purifying the resultant carbon dioxide, and subsequently measuring the $^{13}C/^{12}C$ ratio in a dual-collecting mass spectrometer (*8*). A separate sample was extracted with a benzene-methanol (80 : 20, by volume) solvent mixture under reflux. The extract was treated with freshly prepared copper turnings to remove sulfur and then with 2 percent (by weight) potassium hydroxide solution to extract the fatty acids as the water-soluble potassium salts. The acid-free extract was concentrated by evaporation and a portion was reserved for combustion and isotopic measurements. The remainder of the acid-free extract was chromatographed on a column packed with 60- to 100-mesh Florisil (Matheson, Coleman & Bell), and the fraction eluted with hexane was collected and analyzed. The procedures used in the subsequent estimation and identification of normal alkanes, pristane, phytane, and saturated and unsaturated fatty acids have been described by Smith *et al.* (*15*). The insoluble residue from the solvent extraction was dried and then allowed to react with 85 percent phosphoric acid solution in evacuated flasks for several days at temperatures not exceeding 50°C. The liberated carbon dioxide was captured and purified by distillation over silver nitrate and passage through Dry Ice traps; the volume of carbon dioxide was measured manometrically. To determine whether organic matter was solubilized during this treatment, the acid was recovered by washing, concentrated by evaporation, and oxidized with chromic acid in evacuated flasks. The carbon dioxide evolved was collected, and the volume was measured as before. After removal of a portion for combustion, the residual meteorite was exhaustively extracted with concentrated hydrochloric acid on a boiling water bath, evaporated to dryness twice with 50 percent hydrofluoric acid under the same condition, and then was treated with hydrochloric acid and evaporated again. This procedure dissolved most of the minerals, leaving an organic carbon-rich residue. This residue, that remaining from the phosphoric acid treatment of the meteorite, and the organic fraction soluble in the benzene-methanol mixture were combusted (*8*); the volume of carbon dioxide formed was measured, and $^{13}C/^{12}C$ ratios were determined by mass spectroscopy.

The results (Table 1) indicate that the major portion of the identified carbon remains in the acid-insoluble carbonaceous residues. In the case of the type III carbonaceous chondrite, this amounts to 63 percent (by weight) of the original carbon, whereas in chondrites of types I and II less than 50 percent of the total identified carbon is generally found in this fraction. An extraction with the benzene-methanol mixture of these insoluble organic residues from the Mighei and Orgueil meteorites indicated that only traces of hydrocarbons, insignificant in the car-

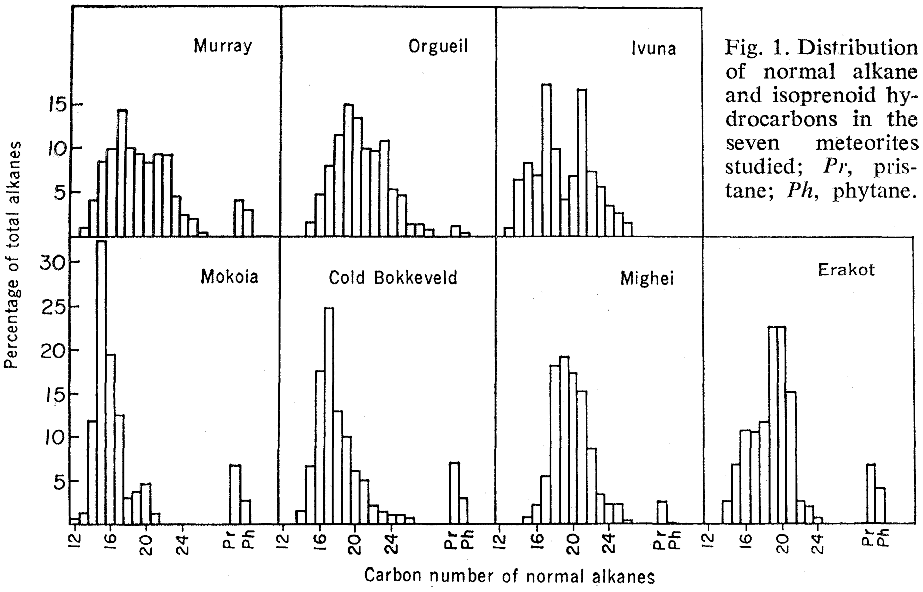

Fig. 1. Distribution of normal alkane and isoprenoid hydrocarbons in the seven meteorites studied; *Pr*, pristane; *Ph*, phytane.

bon balance, could be extracted from such residues. An x-ray diffraction pattern showed no evidence for graphite in the Orgueil residue.

The abundances of carbonate and soluble organic fractions were about the same (Table 1), together generally comprising less than 10 percent of the total meteorite carbon. The fraction soluble in phosphoric acid amounted to only about 2 percent of the total carbon. It thus appears that losses of unidentified volatile compounds have occurred during the analytical procedure which prevent one from determining a complete carbon balance at this point.

The yields and distributions of fatty acids extracted in potassium hydroxide are given in Table 2. In every case, the normal C_{16} and normal C_{18} acids were the two components present in largest amounts and were accompanied by significant quantities of the corresponding unsaturated acids. This distribution probably results from bacterial contamination (*16*). Saturated fatty acids in the range C_{14} to C_{28}, with a predominance of an even number of carbon atoms, have been isolated from the Orgueil meteorites (*17*).

The distribution of the normal alkanes and the isoprenoids, pristane and phytane, in the solvent extracts from the meteorites is shown in Fig. 1. Both the yields and the distribution of the alkanes are in very reasonable agreement with published data (*18*). The normal alkanes from the two type I meteorites and from the Murray meteorite show a tendency toward a bimodal distribution; all other specimens exhibited a smooth distribution of normal alkanes with a pronounced maximum between C_{15} and C_{19}. There was a slight predominance of compounds with an odd number of carbon atoms relative to normal alkanes with an even number of carbon atoms only in the extract from the Orgueil sample in the range of compounds above C_{21}. Pristane and phytane were present in all the samples examined; pristane was always more abundant (*19*). The identified normal alkanes and isoprenoids (Fig. 1) represent 2 to 12 percent of the total residue extracted from the benzene-methanol mixture.

Table 1. Distribution of carbon in meteorite fractions; ppm, parts per million.

Meteorite	Carbonaceous chondrite type	Total (% by wt.)	Soluble organic* (% by wt.)	Carbonate (% by wt.)	Residue after H_3PO_4 treatment (% by wt.)	Residue after HCl + HF treatment (% by wt.)	Alkanes† (ppm)	Fatty acids‡ (ppm)
Ivuna	I	4.03	0.07	0.20	2.54	1.57	93	49
Orgueil	I	3.75	.11	.13		2.15	24	48
Mighei	II	2.85	.09	.21		0.72	71	91
Cold Bokkeveld	II	2.35	.11	.07	1.71	1.27	50	11
Erakot	II	2.30	.13	.05	1.54	0.89	61	23
Murray	II	2.24	.11	.13	1.72	1.06	46	3
Mokoia	III	0.74	.06	.00	0.61	0.47	66	11

* Includes alkanes and excludes organic acids. † Alkane content × 0.857 (C/CH_2). ‡ Mean values calculated on the basis of the carbon content of the normal C_{17} acid.

Data for $^{13}C/^{12}C$ ratios are given in Table 3. Measurements on the intact meteorites give $\delta^{13}C$ values in the range −5.6 to −18.3 per mil. These values have a bimodal distribution of −5 to −12 per mil for type I and type II carbonaceous chondrites and −17 to −20 per mil for type III carbonaceous chondrites (*7, 20*). The particular distribution reflects the presence or absence of carbonate. The oxidized carbon is highly enriched in ^{13}C relative to terrestrial carbonate, as Clayton observed for the Orgueil meteorite (*9*). Our data show, however, that this oxidized fraction may be divided into two subgroups: (i) type I carbonaceous chondrites with $\delta^{13}C = +60$ to $+70$ per mil, and (ii) type II carbonaceous chondrites with $\delta^{13}C = +40$ to $+50$ per mil. The insoluble organic residues have $\delta^{13}C$ values falling in a narrow range of −14.8 to −17.1 per mil. The soluble organic material showed a wider range, varying from −5 to −27 per mil.

Before one can use data on meteoritic carbon compounds for interpretive purposes, it must first be established that these compounds are endogenous to the meteorite. Until now, the evidence for this has been inconclusive (*3, 18*). We believe that the data presented here suggest that the most abundant forms of carbon recognized in the carbonaceous chondrites are of extraterrestrial origin.

Our study also shows that some forms of carbon are most probably terrestrial contaminants. For example, the presence of the unstable unsaturated fatty acids in quantities amounting to almost 30 percent of the total recognizable alkanoic acids and the predominance of C_{16} and C_{18} acids indicate that these acids are recent biological contaminants introduced either from microorganisms present within the meteorites (*16*) or from handling.

Data for hydrocarbons are more difficult to assess, because (i) they are only a minor component of most living systems, (ii) they are present in a great variety of structures, and (iii) they can be formed both by biological and abio-

Table 2. Yields and distribution of methylated alkanoic acids. Values for individual acids are expressed as percentages of the total.

Meteorite	Number of carbon atoms in chain acids										
	12	13	14	15	16*	16	17	18*	18	20	20†
Ivuna			8	10	16	32	3	13	11		
Orgueil	2		9	5	12	37	1	21	11		
Murray	8	2	9	4	9	32	4	16	10		
Erakot	9		12	4	10	25	2	12	11	2	2
Cold Bokkeveld					8	50		16	26		
Mighei	14		4	2	4	20	2	4	20		29
Mokoia	2		9	6	20	21	4	11	7		9

* Unsaturated. † Unidentified.

logical processes. There is no doubt that some meteorites show definite contamination in the form of extractable normal alkanes (*18*), which accounts for a major portion of the carbon in the extract. In general, the abundance distribution of the alkanes is so similar to that present in geologically old sedimentary terrestrial rocks that uncertainty as to the origin of the normal alkanes has led to controversy regarding their formation by biological processes in other planetary bodies of the solar system (*4*). Unless a deliberate effort has been made to introduce hydrocarbon contamination, it may be assumed as a first-order approximation that, if terrestrial alkanes are of recent biological origin, they should be less abundant than fatty acids. Since these alkanes amount to $\leqslant$ 12 percent of the total soluble organic component, it may be reasoned that 80 to 90 percent of this latter component is endogenous to the carbonaceous chondrites.

This assumption can now be tested by evaluating the $\delta^{13}C$ values shown in Table 3. The insoluble organic residue has a median $\delta^{13}C$ value of about −16 per mil. All values for the solvent-extractable carbon compounds are isotopically lighter, with the exception of those from the Murray meteorite.

Carbon-hydrogen compounds on earth generally have $\delta^{13}C$ values of −15 to −60 per mil (*13*). Molecules containing carboxyl groups are isotopically enriched in ^{13}C relative to the "lipid" components, and appear at the heavier end of the range (*21*). Carbon from petroleum, and kerogen from Precambrian sedimentary rocks, have $\delta^{13}C$ values between −25 and −35 per mil (*22*). By comparison then, all the meteoritic, nonextractable carbon has measured $\delta^{13}C$ values outside the terrestrial range for equivalent complex reduced molecules and therefore appears to be endogenous to the meteorite. The similarity between the $^{13}C/^{12}C$ data for this component and for the compounds soluble in the benzene-methanol mixture, in the case of the Orgueil, Mighei, and Cold Bokkeveld meteorites, suggests there is a generic relationship between these fractions. These isotopic data also suggest that the extractable components from the Erakot, Ivuna, and Mokoia meteorites may be comprised of about 20 percent, 50 percent, and 75 percent, respectively, of a terrestrial contaminant with a $\delta^{13}C$ value of −30 per mil. The effect of contamination is generally greatest in the meteorites containing the lowest carbon content. Noncarbonaceous meteorites with carbon contents of $\leqslant$ 0.1 percent have $\delta^{13}C$ values (−25 to −30 per mil) in the range of common terrestrial contaminants (*20*). The contamination in the Ivuna meteorite may be partly related to the small size (230 mg) of the sample analyzed.

Three distinct $^{13}C/^{12}C$ groupings appear to be present in the carbon compounds of meteorites: (i) values of $\delta^{13}C$ greater than +40 per mil, representative of the carbonate fraction, (ii) $\delta^{13}C$ rang between −4 and −8 per mil mil, representing complex polynuclear insoluble carbon compounds and possibly extractable material, and (iii) graphite and iron carbide (cohenite) with a $\delta^{13}C$ range between − 4 and − 8 per mil (*11, 20, 23*). These compounds may have formed independently of each other in a synthetic reaction mixture in which they reached equilibrium or they may be the result of a series of sequential processes.

Fractionation factors between 1.06 and 1.09 (as measured between the carbonate and reduced organic phases of the meteorite) have been observed in nature for coexisting carbon dioxide gas and methane formed at low temperatures (10° to 30°C) during microbiological fermentation (*24*). They can also be accounted for theoretically by equilibration of carbon dioxide and methane at temperatures below 50°C (*25*). Therefore, an equilibration between gases containing oxidized and reduced forms of carbon may have occurred at an early stage in planetary formation. Terrestrial calcium carbonate is not known to equilibrate with coexisting complex reduced organic molecules (hydrocarbons or kerogen) after deposition in sediments. Since carbonates are seen only as minor components of the total carbon in meteorites, the isotopic value of the primordial carbon must have been closer to that of the presently identifiable reduced carbon compounds. The narrow range (2.3 per mil) of $\delta^{13}C$ values of the residual insoluble carbon suggests that this component may have formed rapidly and possibly under highly energetic conditions (high temperature or plasma irradiation) from reduced carbon (for example, methane) where there was minimum opportunity for equilibration among different molecular phases. The $\delta^{13}C$ values for graphite and iron carbide in meteorites either could represent carbon from a different source or could be the result of high-temperature equilibration processes that have resulted in the loss of isotopically lighter

Table 3. Isotopic abundances of carbon-13 (as $\delta^{13}C$) for meteorite fractions relative to the Pee Dee belemnite standard. Values given are the averages of at least two measurements differing by < 1 per mil.

Meteorite	Total (per mil)	Carbonate (per mil)	Soluble organic* (per mil)	Insoluble organic (per mil)
Ivuna	− 7.5	+65.8	−24.1	−17.1
Orgueil	−11.6	+70.2	−18.0	−16.9
Murray	− 5.6	+42.3	− 5.3	−14.8
Cold Bokkeveld	− 7.2	+50.7	−17.8	−16.4
Erakot	− 7.6	+44.4	−19.1	−15.1
Mighei	−10.3	+41.6	−17.8	−16.8
Mokoia	−18.3	None	−27.2	−15.8

* Excludes organic acids.

methane (*26*). The isotopically heavy extractable organic matter in the Murray meteorite (δ^{13}C, −5.3 per mil) may have resulted from some such high-temperature equilibration.

We believe that the $^{13}C/^{12}C$ data presented here are the first indication of a nonrandom isotopic distribution of carbon in meteorites. This property can now be included among others in descriptions of the generic relationships of the carbonaceous chondrites. The data strongly suggest that both oxidized and reduced forms of carbon are indigenous to the meteorites. The data also show which fractions are the least contaminated by terrestrial carbon.

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$$\delta^{13}C\ \text{mil} = 1000 \times \frac{^{13}C/^{12}C\ \text{sample} - {}^{13}C/^{12}C\ \text{std. (PDB)}}{^{13}C/^{12}C\ \text{std. (PDB)}}$$

where PDB is the Pee Dee belemnite standard.

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Nonphotographic Alpha Autoradiography and Neutron-Induced Autoradiography

Abstract. *With a new combination of two techniques, (i) alpha-particle or fission fragment registration in thin polymer foils by etching and (ii) automatic counting and magnification of the etched perforations by local evaporation of a thin metal layer with an electric spark, the sensitivity of conventional photographic methods for determining quantity and spatial distribution of alpha emitters, fissile materials, and of elements undergoing (n, α) reactions can be drastically improved, without need for darkroom processing and microscopic evaluation.*

The conventional method for determining the quantity and spatial distribution of fissile materials in biological samples is α autoradiography by photographic nuclear track emulsion. This method, which may require exposure times of as much as several years (*1, 2*), not only delays research but also introduces new problems due to changes in the emulsion, such as fading or fogging, or to the limited half-life of some nuclides. A new imaging technique, neutron-induced autoradiography (NIAR), permits the results to be obtained within a few hours of sample preparation. The basic procedure may be illustrated by the following experiment designed to determine the quantity and distribution of ^{239}Pu in the tubular bone of a beagle dog.

A thin bone sample mounted on a glass slide was covered with a polycarbonate plastic film (*3*) 6 or 10 μm thick and was exposed to thermal neutrons in the thermal column of the Bulk Shielding Reactor at Oak Ridge National Laboratory. The film was then clamped between two nonetchable plastic retainer rings to simplify further handling. Submersion of the mounted film at 60°C in 28 percent KOH for 1 hour etched pinholes with a diameter of several micrometers at the location of each fission fragment impact. After the etched film was rinsed and dried, it was placed on a circular brass electrode similar to one recently described (*4*) but larger in diameter. The film was covered with a piece of aluminized Mylar with the aluminized side facing the etched film and making contact with an outer, grounded electrode. A positive charge of 500 volts was applied; the sparks that occurred through the perforations in the etched film were coupled to a portable scaler through a quenching circuit. Each spark caused the evaporation of aluminum from the aluminized Mylar in an area that was several orders of magnitude larger than the original hole in the detector film (*5*). Therefore, no multiple sparking occurred through individual holes and a plainly visible "replica" of the holes remained in the aluminum layer.

The local density of evaporated Al spots is proportional to the local concentration of fissile material, and the integral number of sparks in a given sample can be related to the total content of a fissile material in a layer roughly corresponding in thickness to the range of fission fragments in the sample. If the sample is very thin and the detection efficiency for fission fragments is 100 percent, a 2π geometry results in 1 spark (count) per fission, since there are two fission fragments per fission. The sensitivity of the tested bone sample was estimated to be approximately 0.9 spark per fission.

The neutron fluence must be adjusted to the concentration of the fissile material because too small a density of spots results in poor resolution of the image and poor counting statistics, whereas a density exceeding 3000 spots