Carbon Isotope Abundance in Meteoritic Carbonates

Abstract. *The C^{13}/C^{12} ratio in the carbonate minerals of Orgueil, a carbonaceous chondrite, is 6 percent greater than the ratio in any known terrestrial carbon. The effect may be produced by a chemical isotope fractionation involving processes not common on earth, or it may be the result of incomplete homogenization of substances with different histories of nucleosynthesis.*

For several light elements (C, N, O, Si, S, H) there are variations in the abundance of their stable isotopes in naturally occurring terrestrial samples. Variations are typically on the order of a few percent in isotope ratio, and they are due to small chemical fractionation effects. The isotopic compositions of these elements in meteorites have usually been found to fall within the range of terrestrial materials of similar chemical composition. For example, Thode *et al.* (*1*) have shown that the S^{34}/S^{32} ratio in troilite (FeS) from iron and stone meteorites is very uniform and is equal to the ratio in sulfides in many large basic igneous rock bodies of the earth. It has been shown (*2*) that the O^{18}/O^{16} ratio in stone meteorites is indistinguishable from that in terrestrial basic igneous rocks. The C^{13}/C^{12} ratio in ordinary chondrites falls within the range of carbon isotope abundances in terrestrial igneous rocks (*3*), while the ratio in the reduced and organic carbon in carbonaceous chondrites spreads over the range between terrestrial igneous carbon and terrestrial sedimentary carbonates. Boato (*3*) also investigated the D/H ratio in carbonaceous chondrites (in which hydrogen is present primarily in hydrated minerals) and found a range of about 50 percent, with about half the meteorites having a higher D/H ratio than any known terrestrial hydrogen.

The carbonaceous chondrite Orgueil (*4*) has been the subject of many recent studies, concerned particularly with the morphology of certain small structures and with the nature of its organic compounds (*5*). The principal minerals in Orgueil are a magnetic spinel and a hydrous silicate related to chlorite or serpentine (*6*). The meteorite contains about 3 percent combustible carbon in poorly characterized compounds. Two carbonate minerals have been reported in Orgueil (*6*): dolomite, $CaMg(CO_3)_2$, and breunnerite, $(Fe,Mg)CO_3$, totaling about 0.3 percent by weight.

In the present report, the O^{18}/O^{16} and C^{13}/C^{12} ratios of the carbonate in Orgueil have been determined (*7*). The results of four determinations of C^{13}/C^{12} and O^{18}/O^{16} ratios are given in Table 1. Isotopic analyses were done on a 6-inch, 60°-sector, double-collecting mass spectrometer of the type described by McKinney *et al.* and Nier (*8*). Isotopic analyses are reported as parts per thousand enrichment of the heavy isotope relative to the Chicago carbonate standard PDB-1 (*9*).

$$\delta = \left(\frac{R}{R_{\text{std}}} - 1\right) 1000,$$

where R = O^{18}/O^{16} or C^{13}/C^{12}. The accuracy of isotopic analyses was lower than is customary for stable isotope work because the gas samples were very small, and because the carbon isotope ratios differed so much from the isotope standard. It is estimated that the reproducibility of these analyses is about ± 1 per mill, so that the variations observed are probably due to inhomogeneity of the samples. Carbon dioxide was produced by the method of McCrea (*10*), by the reaction of 100-percent phosphoric acid at 25°C with the carbonate minerals without separation of the minerals from the meteorite (*11*). The reaction of phosphoric acid with magnesium and iron carbonates is slow, requiring several weeks for completion, so that the carbon dioxide may be sampled at different stages of the reaction. The carbon dioxide sample was purified by distillation from a trap at the melting point of ethanol (−112° C) to a trap at liquid nitrogen temperature. This procedure does not remove all contaminants, but leaves small amounts of sulfur dioxide derived from some meteoritic mineral, and organic substances which come mostly from residues of laboratory solvents, but some of which appear to be indigenous to the meteorite. Two of the samples (A and B) were heated in an oven at 100°C for 24 hours, which reduced the organic background to negligible amounts. Samples C and D, aliquots of the same meteorite fraction, were not heated and gave carbon dioxide samples which were contaminated with acetone and methyl bromide. The latter yields a fragment in the mass spectrometer $CHBr^{++}$ which contributes to the ion beam of $m/e = 46$, which is used to determine O^{18} content ($C^{12}O^{16}O^{18}$). In samples C and D this contamination accounted for about 2 percent of the mass 46 ion beam, and these analyses for O^{18} were discarded.

Table 1. Isotopic analyses of Orgueil carbonate.

Reaction time (days)	CO_2		δC^{13} (per mill)	δO^{18} (per mill)
	(μmole)	(% by wt.)		
	*Sample A (0.160 g)**			
1–22	8.5	0.23	+64.3	−1.0
	Sample B (1.817 g)†			
1–30	23	0.064	+59.1	−3.3
	Sample C_1 (1.981 g)‡			
0.1–1	18	0.18	+58.6	
	Sample C_2‡			
1–7	40		+64.4	
	Sample D (0.702 g)‡			
0–20	23	0.19	+59.8	

* (U.S. Natl. Museum). Extracted with organic solvents; density separation with bromoform; $3.3 > \rho > 2.8$; nonmagnetic fraction; heated to 110°C 24 hours before reacting. † (Paris). Extracted with organic solvents; heated 110°C 24 hours before reacting. ‡ (U.S. Natl. Museum). Extracted with organic solvents; density separation with bromoform; $2.88 > \rho > 2.5$.

The following arguments indicate that the ion beam of $m/e = 45$ is composed entirely of isotopic species of carbon dioxide: (i) there is no correlation between the mass 45 ion beam and the concentration of non-CO_2 substances; (ii) the 45/44 ratio is the same for different reaction times; (iii) the ratio of doubly charged ions with $m/e = 22.5$ and 22.0 is the same as the ratio of singly charged ions. It has not been proved that the enrichment of the carbon dioxide of mass 45 is due to $C^{13}O^{16}O^{16}$ rather than a very large increase in $C^{12}O^{16}O^{17}$, but the latter seems a very remote possibility.

The oxygen isotope ratio is indistinguishable from that found for terrestrial carbonates precipitated in the oceans. The carbon isotope ratio, however, lies well outside the range observed for all types of carbon on earth, that is, from +5 per mill to about −60 per mill.

The question arises as to whether this unusual isotopic composition is the result of chemical isotopic fractionation or of pre-meteoritic nuclear processes. The isotopic difference between the oxidized and reduced forms of carbon in Orgueil is about 70 per mill, that is, the carbonate carbon is 7 percent richer in C^{13} than the reduced carbon. In terrestrial environments, when oxidized and reduced forms of carbon are formed together, as, for example, in birds' eggs, or marine shell-fish, the isotopic fractionation is found to be rather uniform at about 25 per mill (C^{13} enriched in the carbonate phase). Single-stage equilibrium fractionations for carbon compounds as large as 70 per mill at room temperature have been calculated by Urey (*12*). (In general, the direction of equilibrium fractionation effects is to concentrate C^{13} in phases of higher oxidation state relative to those of lower oxidation state.) Apparently mechanisms for the establishment of such equilibria at low temperatures are not found in nature on earth. Kinetic carbon isotope effects of the order of 40 or 50 per mill have been reported (*13*), but in the case of decarboxylation of organic acids, the direction of the effect is to concentrate C^{13} in the reduced carbon relative to the carbon dioxide. Multistage processes produce extreme isotope effects in terrestrial systems, such as the evaporation-precipitation cycles of water (*14*) in which a small single-stage fractionation of about 7 per mill for O^{18} can be repeated several times to give products which differ from the starting materials by as much as 40 per mill. Such multistage processes are unknown in the terrestrial carbon cycle; production of the isotopic anomaly in Orgueil would require processes in the meteorite parent body without terrestrial counterpart. Although the observed carbon isotope distribution in Orgueil is unlike any known terrestrial case, the possibility of its production by chemical means cannot be ruled out at the present time.

In the absence of biological activity, it may be very difficult to find chemical pathways connecting carbonate minerals and complex organic compounds at the low temperatures of meteorites. The isotopic differences observed may not be due to chemical isotope effects, but may represent an original inhomogeneous distribution of isotopes among chemical species resulting from a sampling of materials with different histories of nucleosynthesis. Among the most likely nuclides to show such effects should be C^{13}, N^{15}, and O^{17}, which were probably formed within the solar system by spallation reactions resulting from bombardment of small solid planetesimals by charged particles from the sun (*15*).

The other meteorite known to contain carbonates is Ivuna, which is also a carbonaceous chondrite. The only material available in these laboratories was a 1.3-mg hand-picked carbonate fraction, which produced 3.8 μmole of CO_2. This gas was compared with Orgueil sample A in the mass spectrometer, and was found to be indistinguishable from the Orgueil sample in isotopic abundances within a rather large error of about 1 percent in isotopic ratios (*16*).

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References and Notes

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Passive Cutaneous Anaphylaxis with Antibody Fragments

Abstract. *Pepsin-digested rabbit antibody (5S) provoked reverse passive cutaneous anaphylaxis in the guinea pig, but was somewhat less effective, mole for mole, than the native antibody. Fixation of guinea pig complement by the pepsin-digested antibody could not be demonstrated either in vitro or in vivo. Splitting of the 5S fragment into two monovalent fragments (3.5S) markedly reduced the capacity to provoke reverse passive cutaneous anaphylaxis.*

Digestion with pepsin suppresses the reactivity of *7S* rabbit antibodies with complement (C′) (*1*, *2*). The digestion yields *5S* antibody fragments which precipitate and have two combining sites, like the undigested antibody molecules, but lack fragment III (*3*). Since it has been postulated that C′ plays an essential role in some forms of immediate hypersensitivity (*4*), *5S* antibody fragments may prove useful in defining this role. Moreover, the *5S* fragments can be split, by reduction of a single disulfide bond, into two 3.5*S* fragments, which are univalent and unable to precipitate (*5*). Previous reports indicated that the nonprecipitating "univalent") antibodies, which may be found in human and animal sera after immunization, can elicit passive anaphylaxis (*6*). Whether these undigested, nonprecipitating antibodies are indeed univalent is, however, uncertain (*7*). The univalence of the 3.5*S* fragments is more firmly established from quantitative hapten-binding studies (*3*). Comparison of the 5*S* and 3.5*S* antibody fragments may therefore help to assess the importance of antibody valence or molecular weight or both in immediate hypersensitivity.

Human gamma globulin (HuGG) was chosen as the antigen because it is one of the few (*8*) which is effective in the reverse as well as in the direct technique of passive cutaneous anaphylaxis (PCA) in the guinea pig, a well-established model of immediate hypersensitivity (*9*). To minimize the anticomplementary action of HuGG, fractional precipitation of unheated Cohn's Fraction II was performed with ammonium sulphate as described by Christian (*10*) and the supernatant of the 0.96*M* precipitation was used. With this preparation, C′ fixation of the antigen controls in the experiments to be described never exceeded five 50-percent hemolytic units ($C'H_{50}$) out of 100.

Antisera against HuGG were obtained by immunization of rabbits with HuGG and adjuvants. The gamma