Biogenic Carbon in Rocks of the Sudbury Impact Structure

D. Heymann(1), B. O. Dressler(2), K. K. Adry Bissada(3), Ewa Szymczyk(3)
(1)Department of Geology and Geophysics, Rice University, Houston, TX 77251-1892, USA
(2)185 Romfield Circuit Thornhill, Ontario L3T 3H7, Canada
(3)Geotechnology Research Institute, Houston Advanced Research Center, The Woodlands, Texas 77381, USA.

Abstract
The origin of carbon in the Black Member of the Onaping Formation of the Whitewater Group of the 1.8 Ga old Sudbury Impact Structure, Ontario, Canada was not understood. New isotopic del^{13}C measurements on twenty-three carbon samples together with nine previous del^{13}C measurements on samples from Whitewater Group rocks by other investigators strongly suggest that the origin is biogenic. Hence, the rocks of the Black Member of the Onaping Formation cannot have formed as instant fallback clastic sediments or instant tsunami-transported clastic sediments immediately after the impact.

Paper
At the center of the Sudbury Structure, a 1.8 x 10^9 y old terrestrial impact crater in the Canadian Shield (1,2), one finds rocks of the more than 3 km thick Whitewater Group. Significant amounts of carbonaceous matter (3) occur in the lowermost 1600 m thick sequence of breccias of the Onaping Formation (4), which are overlain by some 600 m of mudstones of the Onwatin Formation (5), which are overlain in turn by the about 850 m of wacke-turbidites of the Chelmsford Formation (6). All three are formations of the Whitewater Group. The four members of the Onaping Formation are, from bottom to top, the Basal, Green, Gray, and Black Members. Among these only the Black Member (BMOF) contains appreciable amounts of carbon throughout (4).

The origin of the carbon in the Onwatin and Chelmsford rocks is biogenic (7). However, theories vary on the origin of the estimated 10^{17} g of carbon in the BMOF (8). The carbon cannot have been derived from the local target rocks because these contain far too little carbonaceous matter for this much mass. Emplacement by fumarolic activity after the impact was proposed (9), but the distribution of the carbon throughout the formation speaks against this (4). Becker et al. (10) proposed that the carbon came from the impactor. Bunch et al. (11) proposed that the carbon formed by the reduction of CO_2 derived from target carbonates during the impact event. A biogenic origin was independently advocated by Beales and Lozej (12), by Avermann (13,14), and by Hansen (15).

The resolution of these issues is important because a biogenic origin of the BMOF carbon is incompatible with theories that the member is the metamorphosed product of an "instant fallback clastic sediment", or an "instant tsunami-transported clastic sediment" (16). Biogenic activity is not viable throughout the environment of an "instant sediment" at least 1 km thick other than perhaps at its very top after more quiet conditions have returned. A biogenic origin is more compatible with the theory that the BMOF breccia material was transported from the slopes and surroundings of the central crater depression much more slowly into a lake in the depression where the material settled (17). Since the BMOF rocks do not contain any fossil remains, the only experiment available for possibly settling the issues is a comparison of del^{13}C values (for a definition see Table 1) of carbon in the Chelmsford Formation, the Onwatin Formation, and the BMOF. If these are essentially the same, then the origin of carbon in the BMOF, like that in the Chelmsford and Onwatin Formations, is most likely biogenic. To this end we have determined carbon contents and del^{13}C values of three carbon samples from the Chelmsford Formation, six samples from the Onwatin Formation, and fourteen samples from the BMOF (18). The locations of collection are

shown in Fig. 1. To examine the theory of 'CO_2 reduction', del^{13}C values of two carbonate samples from the Espanola Formation were also determined (19).

Our results for the Whitewater Group samples are presented in Table 1. In Figure 2 we show all of the currently available del^{13}C values which include earlier results obtained by other investigators (7,14, 15,20). The three del^{13}C values between -22 and -26 permille come from a core in the upper 5-10 meters of the BMOF (20). The remaining values cluster in the range -27 to -36 permille, an appreciable spread, but one which is not uncommon among large Precambrian organic carbon deposits (7). Samples from the Chelmsford and Onwatin as well as the BMOF occur together in this cluster. We consider the weight of the thirty-two del^{13}C values of this cluster (20) sufficiently strong to conclude that the origin of the carbon in the BMOF is overwhelmingly biogenic.

The del^{13}C-values of the two Espanola carbonate samples are -0.43 and -0.47 permille which is normal for Precambrian carbonates. Since carbon which forms from CO_2 in equilibrium with that gas is not likely to change its del^{13}C value by more than about -10 permille (21) it must be shown that a change by about -30 permille is possible by non-equilibrium reduction in the hot impact plume (11).

We actually favor the following scenario. When pre-impact atmospheric conditions returned at Sudbury there was a cavity of at least some 100 km diameter in which the Basal, Green and Gray Members of the Onaping Formation were in place (see refs. 13,14). Neither contained much, if any carbon. The bulk of the BMOF breccia clasts were still widely scattered, perhaps on terraces, mountain slopes, and other features around the central cavity, but with little, if any carbonaceous matter present. When the masses of rock and rock flour of the region had cooled sufficiently, a lake could begin to form in the cavity and breccia clasts could begin to be transported into it by local streams. Almost simultaneously, abundant biogenic activity, most likely of cyanobacteria and methanogens, began in the relatively warm waters. When the lithology of the lake-deposits changed from the breccias of the BMOF to the mudstones of the Onwatin Formation, and still later to the turbidites of the Chelmsford Formation, large masses of biogenic organic carbon continued to be generated.

The biogenic matter must be older than the greenschist facies metamorphism recorded in the rocks of the Onaping, Onwatin, and Chelmsford Formations which seems to have occurred mostly during middle-and late-stages of the Penokean Orogeny some 1.75 Ga ago and which has erased any record of life-forms involved, except for possibly a few relics of blue-green algae in a rock from the Onwatin Formation (14). Raman spectra obtained by us of carbon in rocks of the Onaping, Onwatin, and Chelmsford Formations are identical and fully consistent with common greenschist facies metamorphism on the scale developed by Pasteris and Wopenka (22).

The rocks of the BMOF of the Sudbury Structure are possibly among the world's largest burial grounds of metamorphosed Precambrian biota (23).

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3. Carbonaceous matter of the Whitewater Group rocks consists mostly of the element carbon plus some hydrogen.
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18. Carbon content: Powdered samples of about 0.2 g were analyzed with a standard LECO carbon and sulfur analyzer at the Houston Advanced Research Center (HARC).

del^{13}C at Rice University: Powdered rock samples of about 0.2 mg were first treated with toluene to remove soluble organic carbon, then with HCl to remove carbonates. Carbon dioxide for the mass-spectrometric analysis was generated by O_2 flash-combustion in a Carlo-Erba NA-1500 microanalyzer. CO_2 for the semi-automated VG 602E mass spectrometer was separated from other gases by gas-chromatography.

del^{13}C at HARC, 10 to 20 mg of carbonaceous matter, or 40-50 mg of de-carbonated rock sample was added to 2 g of copper oxide. The mix was heated in vacuum to 550 °C. Purified CO_2 was eventually admitted into the Finnigan Mat Delta S isotope ratio mass spectrometer.
19. Fifity mg of carbonate was treated with 1ml of anhydrous phosphoric acid at about 5 Torr pressure. After 1-2 days of digestion at 50 °C the CO_2 was purified and admitted into the Finnigan Mat Delta S isotope ratio mass spectrometer.
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23. In addition to samples collected by R. O. Dressler, samples for this study were made available by Bevan French, Richard Grieve, and Glen Johns. The Ontario Geologic Survey (Andy Fyon) paid for shipping the large rock samples from Canada to Houston. R. B. Dunbar and D. Mucciarone did the carbon isotopic measurements at Rice University. Thanks y'all!

Table 1. Carbon contents and carbon isotopic compositions of carbonaceous matter in rocks from the Chelmsford Formation, the Onwatin Formation, and the Black Member of the Onaping Formation.

Sample Name*	Catalog Number†	Carbon content (wt percent)	Del 13C permille‡
CHELMSFORD FORMATION			
West of Chelmsford on highway 144 (Location 6).			
CHE1	CHEM1	0.52	-31.85
CHE2	CHEM2	0.61	-31.35
CHE3	CHEM3	0.44	-31.95
ONWATIN FORMATION			
High Falls (Location 1)			
ONW1	BO.O.1	2.38	-31.31
ONW2	ON1	4.07	-28.21
Vermillion Lake Road (Location 5)			
ONW3	ON2	3.16	-31.64
ONW4	ON3	2.07	-29.71
ONW5	ON4	4.86	-31.26
ONW6	ON5	4.36	-29.3
BLACK MEMBER ONAPING FORMATION			
High Falls (Location 1)			
ONAB1	not known	0.6	-34.52
ONAB2	BO.OF.1	0.3	-35.22
ONAB3	CSF.66.49	0.89	-27.12
ONAB4	CSF.66.43	0.89	-33.08
ONAB5	CSF.66.37	0.73	-29.55
ONAB6	BO.OF.3	1.12	-31.6
ONAB7	BO.OF.2	0.62	-31.89
North Capreol (Location 2)			
ONAB8	BO.CA.3	0.78	-31.45
South Capreol (Location 2)			
ONAB9	BO.CA.4	1.15	-30.16
East Capreol (Location 2)			
ONAB10	CSF.94.7A	2.44	-33.68
ONAB11	CSF.94.5	1.06	-32.77
South Chelmsford (Location 3)			
ONAB12	BO.CM.1	1.89	-29.5
ONAB13	BO.CM.2	1.14	-29.01
Nickel Offset Road (Location 4)			
ONAB14	BO.NO.1	1.64	-30.29

* ONAB = Black Member of Onaping Formation; ONW = Onwatin Formation; CHE = Chelmsford Formation.

† BO samples are from the collection of the Ontario Geologic Survey. CSF.xx.yy are samples collected by B. M. French; 19xx denotes year of collection, yy the sample number.

‡ $\mathrm{del}^{13}\mathrm{C} = 1000\ [\ \{^{13}\mathrm{C}/^{12}\mathrm{C}\}_{\mathrm{sample}}/\{^{13}\mathrm{C}/^{12}\mathrm{C}\}_{\mathrm{standard}} - 1]$. The international PDB standard was used. Errors are 0.6% of listed values.

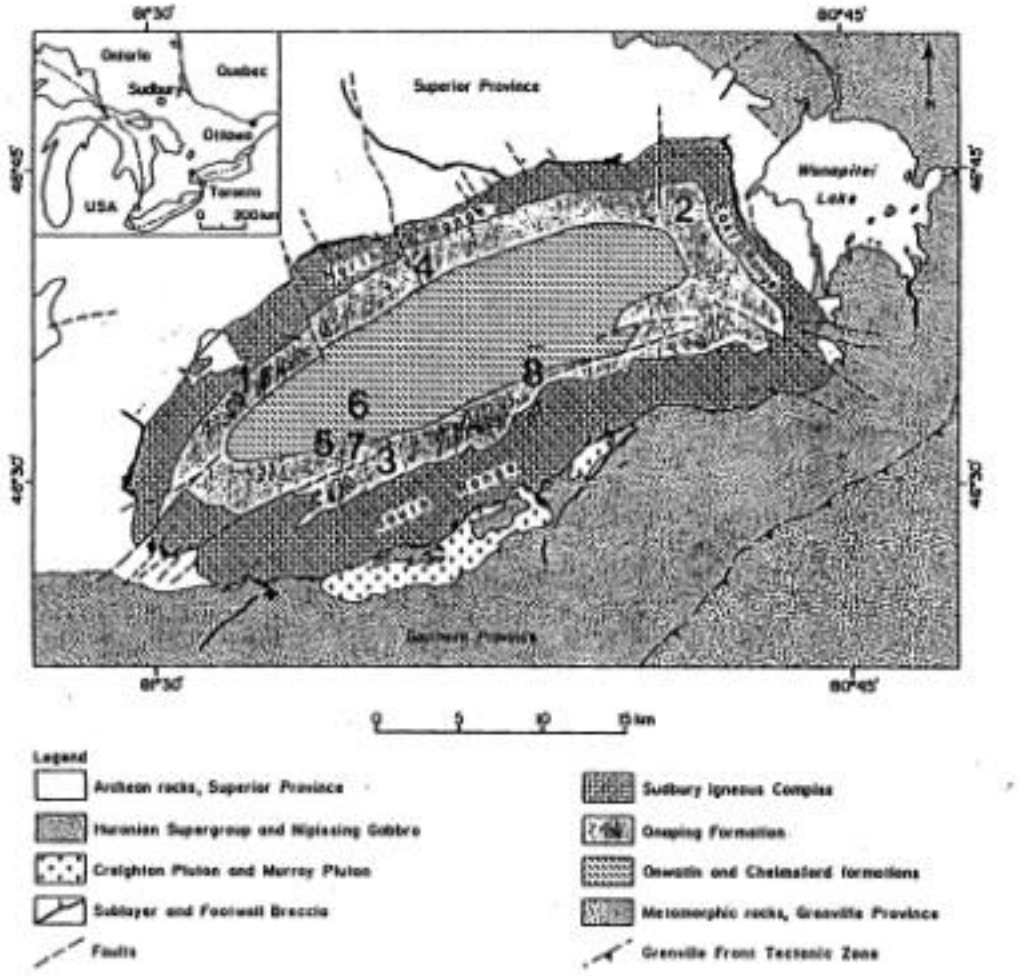

Fig. 1. The location of the structure (inset) and its general geologic features. The numerals correspond to locations as reported in Table 1. Samples from a given "location" could have been collected from sites up to about 5 km apart. 1 = Dowling Township; High Falls. 2 = Capreol Area. 3 = South Chelmsford. 4 = Nickel Offset Road. 5 = Vermillion Lake Road. 6 = West of Chelmsford on highway 144. 7 = Errington Mine (Anthraxolite samples not reported in this work). 8 = Core A drilled by Whitehead et al. (ref. 20).

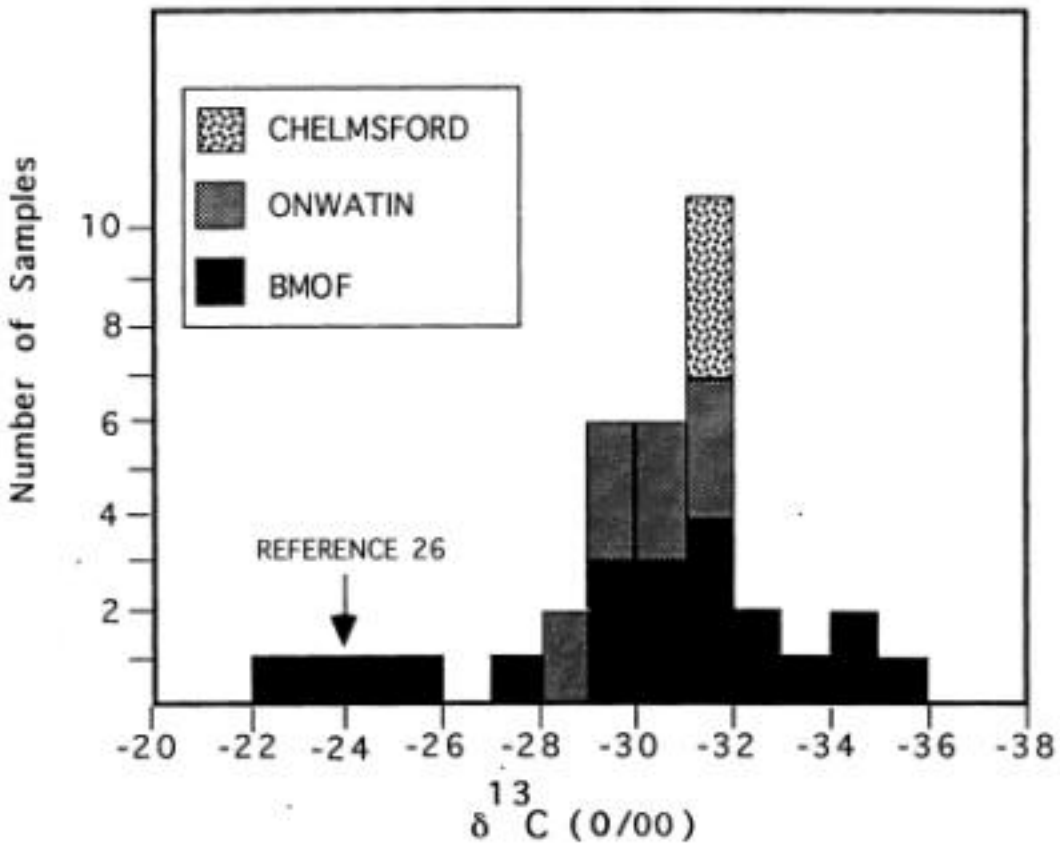

Fig. 2. Frequency diagram of all known del^{13}C values of carbonaceous matter in Whitewater group rocks. Data include results from References 7,14, 15, and 20.