the "high silica" glasses from Belgium and China are also similar (Table 1) (*25*). They differ, however, in that Al-, Fe-, and Ca-rich glasses similar to those from Belgium have not as yet been described from Qidong. The Qidong spherules are associated with a minor positive Ir anomaly (300 parts per trillion) and a negative shift in $\delta^{13}C$ (*26*) interpreted as an indicator of a decrease in biomass productivity due to local mass extinctions at that time (*25*). Similar negative shifts in $\delta^{13}C$ have been recorded in several F/F sections worldwide (*14*).

The glassy spherules from Senzeilles are most likely the product of an extraterrestrial impact event that occurred during basal Famennian time. The presence of another spherule layer in the *crepida* zone in China (*26*) may indicate that perhaps two impact events occurred during early Famennian time, which may have been responsible for the worldwide biomass reductions and extinctions. Alternatively, the conodont correlations between China and Belgium might be subject to reinterpretation and the possibility exists that the two spherule-producing events may be coeval. This question can only be resolved by obtaining precise radiometric ages on both spherule populations.

Impact craters of Late Devonian age to be considered as possible sources of the Belgian spherules include the Siljan Ring in central Sweden, the largest impact structure in Europe (52 km in diameter), which has been ^{40}Ar-^{39}Ar dated at 368 ± 1.0 Ma (million years ago), corresponding with the biostratigraphic age of the Senzeilles microtektites (*27*). The crystalline rocks of the Baltic Shield contained in the Siljan Ring are consistent with the compositions of the glass spherules, although the crater has been highly eroded. Another candidate impact site is Charlevoix Crater (46 km in diameter) at the southern edge of the Canadian Shield in Quebec, Canada. This crater also has an age near the F/F boundary (*27*). Plate reconstruction of the location of Charlevoix for the Late Devonian would place it in close proximity to the Senzeilles section. The discovery of preserved glassy microtektites in the Senzeilles section strengthens the case for extraterrestrial impacts as the cause of worldwide benthic mass extinctions during the Late Devonian.

REFERENCES AND NOTES

1. J. J. Sepkoski, Jr., *Milwaukee Publ. Mus. Contrib. Biol. Geol.* 51, 1 (1982); in *Patterns and Processes in the History of Life*, D. M. Raup and D. Jablonsky, Eds. (Springer-Verlag, Berlin, 1986), pp. 277–295.
2. G. R. McGhee, in *Mass Extinction: Processes and Evidences*, S. K. Donavan, Ed. (Belhaven, London, 1989), chap. 3, pp. 133–151.
3. D. M. Raup and J. J. Sepkowski, Jr., *Science* **215**, 1501 (1982).
4. D. J. McLaren, *J. Paleontol.* **44**, 801 (1970); *Geology* 13, 170 (1985).
5. The biomass decrease would correspond to a single bedding plane. This horizon would represent less time than the time span of one conodont zone (0.3 million years). C. A. Sandberg, W. Ziegler, R. Dreesen, J. L. Butler, *Cour. Forsch.inst. Senckenb.* **102**, 263 (1988); D. J. McLaren and W. D. Goodfellow, *Annu. Rev. Earth Planet. Sci.* **18**, 123 (1990).
6. M. V. Caputo, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **51**, 291 (1985).
7. ______ and J. C. Crowell, *Geol. Soc. Am. Bull.* **96**, 1020 (1985).
8. P. Cooper, *Geology* **14**, 835 (1986).
9. J. G. Casier, *Bull. Inst. R. Sci. Nat. Belg. Sci. Terre* **59**, 79 (1989).
10. W. Buggisch, *Geol. Rundsch.* **80–81**, 49 (1991).
11. W. Schlager, *Geol. Soc. Am. Bull.* **92**, 197 (1981).
12. M. R. House, *Nature* **313**, 17 (1985).
13. G. R. McGhee *et al.*, *ibid.* **308**, 629 (1984); G. R. McGhee *et al.*, in *Global Bio-Events*, O. Walliser, Ed. (Springer-Verlag, New York, 1986), pp. 629–631.
14. W. D. Goodfellow *et al.*, in *Proceedings of the Second International Symposium on the Devonian System*, Calgary, Alberta, Canada, December 1988, N. J. McMillan, A. F. Embry, D. J. Glass, Eds. (Canadian Society of Petroleum Geologists, Calgary, 1988), vol. 3, pp. 9–22.
15. Rare spherules (less than 10 of more than 400 glass grains collected) were found scattered at several levels in the Senzeilles Shale above the spherule horizon. We believe these are the product of reworking because these spherules lack delicate features and exhibit more abraded surfaces than the ones found concentrated in the spherule bed indicated in Fig. 1.
16. The International Subcommission on Devonian Stratigraphy defines the base of the Lower *triangularis* conodont zone as the F/F boundary. The base of the Senzeilles shales belongs to this zone according to P. Bultynck *et al.* [*Cour. Forsch.inst. Senckenb.* **102**, 7 (1988)].
17. It is suggested that the F/F boundary correlates with the contact between the Matagne and transition shale [J.-G. Casier, *Bull. Inst. R. Sci. Nat. Belg. Sci. Terre* **62**, 109 (1992)].
18. B. P. Glass, *Tectonophysics* **171**, 393 (1990).
19. H. Sigurdsson *et al.*, *Nature* **349**, 482 (1991).
20. Analyses of the water content in tektites indicate values ranging from <0.02 to 0.004% H_2O by weight. Obsidian glasses contain an order of magnitude more water. C. Koeberl and A. Beran, *Proc. Lunar Planet. Sci. Conf.* **18**, 403 (1988).
21. C. Koeberl, *Tectonophysics* **171**, 405 (1990).
22. J. Smit *et al.*, *Geology* **20**, 99 (1992).
23. G. A. Izett, *J. Geophys. Res.* **96**, 879 (1991); C. Koeberl and H. Sigurdsson, *Geochim. Cosmochim. Acta* **56**, 2113 (1992).
24. C. Koeberl, *Annu. Rev. Earth Planet. Sci.* **14**, 323 (1986); ______ and R. Storzer, in *Proceedings of the Second International Conference on Natural Glass*, Prague, Czechoslovakia, 21 to 25 September 1988, J. Konta, Ed. (Charles University, Prague, 1988), pp. 207–213.
25. K. Wang, *Science* **256**, 1547 (1992).
26. The δ values are per mil deviations from the Pee Dee belemnite (PDB) isotopic standard: $\delta = [(R/R_{std}) - 1] \times 1000$, where R is either $^{13}C/^{12}C$ or $^{18}O/^{16}O$ in the sample and R_{std} is the corresponding ratio in the standard [H. Craig, *Geochim. Cosmochim. Acta* **12**, 133 (1957)].
27. R. A. F. Grieve *et al.*, *Lunar Planet. Inst. Tech. Rep. 88-03* (Lunar Planetary Institute, Houston, 1988).

28. This work was supported in part by a grant from the Institut Royal des Sciences Naturelles de Belgique (IRScNB) to J.-G.C., National Science Foundation grant EAR 8816876 to A. Hoffmeister for FTIR analyses, and a University of California, Davis, grant to S.V.M.

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Oxygen Isotope Constraints on the Origin of Impact Glasses from the Cretaceous-Tertiary Boundary

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Laser-extraction oxygen isotope and major element analyses of individual glass spherules from Haitian Cretaceous-Tertiary boundary sediments demonstrate that the glasses fall on a mixing line between an isotopically heavy ($\delta^{18}O$ = 14 per mil) high-calcium composition and an isotopically light ($\delta^{18}O$ = 6 per mil) high-silicon composition. This trend can be explained by melting of heterogeneous source rocks during the impact of an asteroid (or comet) ~65 million years ago. The data indicate that the glasses are a mixture of carbonate and silicate rocks and exclude derivation of the glasses either by volcanic processes or as mixtures of sulfate-rich evaporate and silicate rocks.

Characterization of the composition of the rocks in the target area for the putative Cretaceous-Tertiary (K-T) boundary asteroid (or comet) impact is central to the evaluation of proposed crater localities (*1–4*) and to the potential climatic change induced by the outgassing of volatile-rich target materials (*1, 4*). In this report, we use oxygen isotope systematics of the impact-produced glass spherules (or tektites) in K-T boundary sediments from Haiti to constrain the composition of the target rocks. Glass spherules were separated for analysis (*5*) from the lower 10 cm of one of several smectite-rich spherule beds that have been interpreted to be of turbidite or gravity flow origin (*6–10*) and that occur within a fairly homogeneous sequence of calcareous rocks near the K-T boundary of the Beloc Formation in Haiti. These rocks contain both black and yellow glass spherules. Earlier studies of the Haitian K-T glasses have come to conflicting conclusions with regard to their origin. Some

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workers have concluded that an impact mixing origin is most consistent with the variations in major and trace elements, and isotopic compositions (*1, 2, 7, 8*), whereas other workers have concluded that the glasses are volcanic in origin on the basis of major element compositions, the oxidation state of iron, and the apparent absence of lechatelierite (*9–11*). Following a report (*1*) of two conventional oxygen isotope analyses for composite samples of high-SiO_2 (black) and high-CaO (yellow) glasses, we carried out a detailed study of the oxygen isotope and major element variability between individual glass spherules utilizing the recently developed laser-extraction oxygen isotope technique (*12, 13*) and electron microprobe analyses.

Major element analyses (*14*) of 52 glass spherules show that SiO_2 ranges from 46 to 69% by weight as CaO ranges from 28 to 4% (Table 1 and Fig. 1), in general agreement with earlier results (*1, 2, 7–10*). There is a compositional gap between the black glasses and yellow glasses, and the average compositions of each group are close to two compositions of glass from another K-T section at Mimbral, Mexico (*15*) (Fig. 1). Oxygen isotope ratios from individual pieces of the Haitian K-T glasses (*16*) range from $\delta^{18}O$ of 6.0 to 10.5 per mil in the black glasses and from 13.3 to 14.5 per mil in the yellow glasses (Table 1); the estimated uncertainty is ±0.2 per mil (*17*). The average values for the black (7.7 per mil) and yellow (13.6 per mil) glasses are consistent with two conventional oxygen isotope analyses (7.7 and 13.3 per mil, respectively) (*1*) (Fig. 2). The analyses of individual glass spherules show a linear relation between $\delta^{18}O$ and SiO_2 and CaO content (Fig. 2). The variation among only the black glasses (>59 SiO_2 by weight) is along the trend that includes both the black and yellow glasses (Fig. 2); thus, the same process is most likely responsible for both trends.

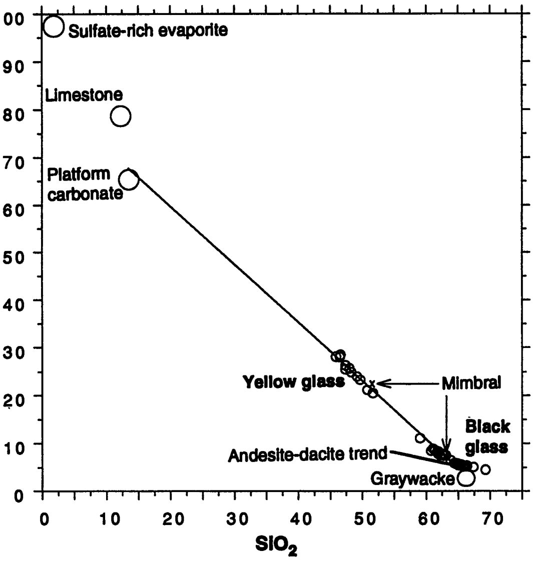

Fig. 1. Plot of SiO_2 versus CaO (weight percent) for K-T glasses (small circles) and averages for several devolatilized rock types (*27, 32*). Analyses of glass from the K-T section at Mimbral, Mexico (*15*), are labeled "Mimbral." Note that the variation between the glasses with ≤64% SiO_2 can be explained as a mixture between dacite (or graywacke) and platform carbonate (or limestone), but is inconsistent with a mixture between dacite (or graywacke) and sulfate-rich evaporite.

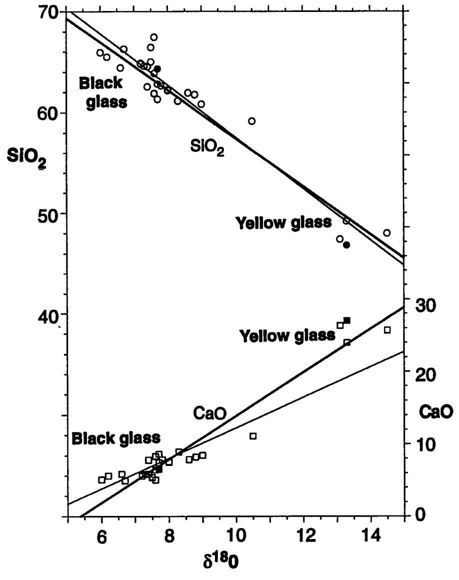

Fig. 2. Plot of $\delta^{18}O$ versus SiO_2 and CaO for K-T glasses. Open circles (SiO_2) and squares (CaO) are the 28 samples reported in Table 1. Solid symbols are the two conventional $\delta^{18}O$ analyses and average SiO_2 and CaO measurements from Sigurdsson *et al.* (*1*). Dark lines are linear regressions of analyses of both black and yellow glass. Light lines are linear regressions of black glasses only, to demonstrate that the variation within the glasses defines a similar trend whether or not the yellow glasses are included.

Our data effectively rule out a volcanic origin for the Haitian K-T glass spherules. Neither fractional crystallization nor vapor fractionation of a magma can produce shifts in whole rock $\delta^{18}O$ values of >1 per mil even over the widest range of SiO_2 variability (30%) (*18–20*). Thus, neither of these processes could be responsible for the 4.6 per mil decrease in $\delta^{18}O$ of the black glasses that accompanies a 7% increase in SiO_2 content. Large-scale magmatic assimilation of carbonate could produce the observed chemical trends, but we do not consider it a viable process because (i) it would require assimilation of ~20% carbonate by weight without any accompanying mineral crystallization (even at the nanometer scale) (*21*), and (ii) appropriate magmatic compositions (59% SiO_2, 11% CaO, and a $\delta^{18}O$ value of 10.5 per mil) have never been observed. The yellow glasses would require even larger shifts in $\delta^{18}O$ of 8.5 per mil over an 18% range in SiO_2. Such shifts would require either ~45% assimilation of carbonate without accompanying crystallization or an unprecedented magmatic endmember with 47% SiO_2, 28% CaO, and a $\delta^{18}O$ value of 14.5 per mil.

The major and trace element (*1, 2, 7–10*), and radiogenic isotope (*1, 2, 22*) compositions of the black glasses are consistent with a sedimentary rock with an average composition similar to an andesite or dacite (for example, graywacke). We take the cluster of data with 64% SiO_2 as the nominal composition of the high-SiO_2 endmember, but the compositional variation among the black glasses [(*2, 7*) Fig. 1] probably indicates that the siliceous endmember had a variable SiO_2 content ranging from ~64 to 69%. Devolatilized carbonate (*23*) or sulfate-rich evaporite (*24*) rocks have been proposed as the source of CaO for the yellow glasses (*1, 2, 7*). Extrapolation of experimental fractionation data (*25*) to the high temperatures of impact melting indicate that no oxygen isotope fractionation would occur during devolatilization, which is consistent with measurements of $\delta^{18}O$ values of CO_2 shock-devolatilized from $CaCO_3$ (*26*). To produce the average observed yellow glass composition (46.8% SiO_2, 27.0% CaO, and a $\delta^{18}O$ value of 13.3 per mil) (*1*) a mixture of 34.4% by weight of average devolatilized platform carbonate (13.3% SiO_2, 66.0% CaO, and a $\delta^{18}O$ value of 29 per mil) (*27, 28*) with 65.6% black glass is required. This calculation takes into account the molar percentage of oxygen in each end member and yields a yellow glass composition (46.8% SiO_2, 27.0% CaO, and a $\delta^{18}O$ value of 13.4 per mil) that coincides with the average of the yellow glasses analyzed. If we perform the same calculation but instead use an average composition for a devolatilized sulfate-rich evaporite (~1% SiO_2, ~99% CaO, and a $\delta^{18}O$ value of 14 per mil) (*29, 30*) as the starting material, the resulting yellow glass with the proper CaO content (27.0%) would have a much lower than observed δ^{18}O value of 8.4 per mil and slightly higher SiO_2 content of 50.3%. The composition of an idealized devolatilized carbonate end member that accounts for the variation in all major oxides is calculated to be: SiO_2 (13.3%), TiO_2 (0.9%), Al_2O_3 (7.3%), FeO (3.7%), MnO (0.1%), MgO (7.4%), CaO (66.3%), Na_2O (0.1%), and K_2O (−1.3%). This composition is within the observed range of platform carbonate rocks (*31*) for all elements except Na_2O and K_2O, which are among the most volatile elements during vapor fractionation of silicate melts (*32*) and may have been partially devolatilized during impact. A δ^{34}S measurement of 13 ± 4 per mil for the yellow glass (*1*) suggests that some oxidized sulfur (most likely in the form of gypsum or anhydrite) was present in the carbonate rocks. Melting experiments (*1*) indicate that sulfur was probably present in the target materials in excess of the maximum sulfur content of 0.3% by weight observed in the yellow glass (*1, 2, 33*). However, our data show that the contribution of sulfate-rich evaporite to the yellow glass was minor (<10% by weight), which is at odds with the assumption of (*4*) that all of the Ca in the yellow glass was derived from evaporite rather than carbonate rocks. We suggest that a major atmospheric effect of the K-T impact was degassing of CO_2 from carbonate rocks, which could cause an enhanced greenhouse effect leading to global warming for ~10^4 to 10^5 years (*4, 34*). Impact-derived dust and sulfate aerosol may have caused an antigreenhouse effect leading to net global cooling during the first several years after impact (*4*).

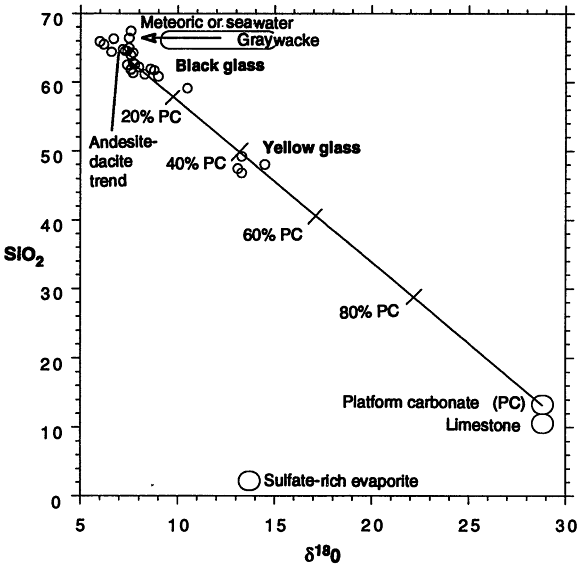

Fig. 3. Plot of δ^{18}O versus SiO_2 for K-T glasses and averages for several devolatilized rock types. Average rock values for SiO_2 are from (*27, 32*) and for δ^{18}O are from (*18, 28, 30*). The line with tick marks represents a calculation of mixtures between average black glass (SiO_2 = 64%) and various weight percentages (including volatiles) of average platform carbonate. Note that the variation between the glasses can be explained as a mixture between dacite (or graywacke mixed with meteoric or seawater) and platform carbonate (or limestone), but is inconsistent with a mixture between dacite (or graywacke) and sulfate-rich evaporite.

Table 1. Major element and oxygen isotope data for K-T boundary glasses and australasian Muong Nong–type tektites. All oxides are in weight percent; wt, weight

Sample	SiO_2	TiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	MnO	FeO*	wt (mg)	CO_2 (μmol)	δ^{18}O (per mil)
Black glass												
A1a	64.78	0.65	15.50	3.72	1.68	5.80	2.56	0.16	5.16	3.3	45.1	7.2
A2b	61.29	0.69	15.28	3.84	1.55	8.59	3.09	0.18	5.50	2.6	39.7	7.7
A3a	62.53	0.67	15.16	3.86	1.59	7.79	2.86	0.17	5.38	2.5	32.7	7.4
A3b	64.53	0.64	15.41	4.00	1.72	5.85	2.55	0.19	5.11	5.1	69.1	7.4
A4a	61.89	0.73	15.14	3.83	1.52	8.32	3.04	0.17	5.37	1.6	21.4	7.6
A4b-1	61.13	0.72	15.10	3.89	1.48	8.88	3.16	0.19	5.44	2.1	25.5	8.3
A4b-2	61.13	0.72	15.10	3.89	1.48	8.88	3.16	0.19	5.44	3.4	26.6	8.5
A4b-3	61.13	0.72	15.10	3.89	1.48	8.88	3.16	0.19	5.44	3.0	21.1	8.7
A5b	62.78	0.69	15.03	4.03	1.72	7.42	2.78	0.16	5.40	3.0	25.0	7.7
B1a	61.74	0.69	15.51	3.43	1.41	8.20	3.07	0.16	5.80	6.7	96.6	8.8
B2a	66.26	0.61	15.19	4.00	1.78	4.92	2.40	0.16	4.69	1.6	17.8	6.7
B2b	65.48	0.66	15.31	3.72	1.67	5.60	2.51	0.14	4.91	3.4	22.2	6.2
B3b	61.84	0.70	15.25	3.80	1.56	8.27	2.99	0.16	5.44	6.2	86.6	7.6
C1b	61.93	0.69	15.35	3.89	1.68	7.86	2.99	0.17	5.45	4.0	35.8	8.6
C2a	62.23	0.69	15.22	3.83	1.72	7.52	2.97	0.19	5.64	1.6	16.8	8.0
C2b	64.44	0.64	15.59	3.72	1.65	5.87	2.61	0.19	5.30	4.4	65.5	6.6
C4a	67.44	0.60	14.93	2.97	1.35	5.04	2.69	0.15	4.83	6.1	70.5	7.6
C6a	60.82	0.74	15.31	4.05	1.61	8.42	3.12	0.19	5.73	2.1	8.9	9.0
C6b	62.15	0.69	15.55	3.76	1.60	7.50	2.92	0.16	5.67	6.1	64.8	8.0
D2a	62.63	0.70	14.96	3.88	1.58	7.81	2.92	0.15	5.38	3.1	20.0	7.8
D2b	64.99	0.64	15.61	3.89	1.68	5.44	2.53	0.15	5.08	2.9	15.9	7.5
D3a	64.58	0.61	15.57	3.81	1.70	5.83	2.64	0.16	5.10	3.1	12.7	7.3
D4b	66.42	0.56	14.65	3.24	1.57	5.37	2.86	0.15	5.17	1.2	12.1	7.5
D6a	65.92	0.63	15.45	3.63	1.70	5.08	2.62	0.15	4.82	3.2	20.7	6.0
E1a	59.14	0.67	15.05	3.97	1.59	11.08	3.14	0.12	5.23	†	†	10.5
E2a	63.87	0.64	15.43	3.91	1.70	6.41	2.63	0.12	5.30	†	†	7.6
E4a	64.85	0.63	15.62	4.19	1.92	5.58	2.43	0.11	4.66	†	†	7.2
Yellow glass												
D4a	47.42	0.64	12.79	2.55	0.65	26.44	4.46	0.15	4.81	1.7	12.7	13.1
D5b	49.18	0.67	13.26	2.40	0.70	23.98	4.58	0.19	5.04	1.3	11.5	13.3
E3a	48.00	0.58	12.81	2.82	0.76	25.67	4.39	0.09	4.88	†	†	14.5
Muong Nong–type tektites												
8301-1	77.20	0.65	11.64	1.10	2.52	1.15	1.57	†	4.21	2.1	12.5	10.6
8301-2	77.20	0.65	11.64	1.10	2.52	1.15	1.57	†	4.21	2.4	14.5	10.6
8319-1	78.01	0.62	10.84	1.05	2.38	1.65	1.62	†	3.83	2.7	18.1	10.4
8319-2	78.01	0.62	10.84	1.05	2.38	1.65	1.62	†	3.83	3.7	24.0	10.5

*Total Fe is reported as FeO. †Not determined. Major oxides for Muong Nong–type tektites from (*39*).

In the case of moldavite tektites, where a direct link has been made between the moldavites and the Miocene surficial sands from the Ries crater, the tektites have δ^{18}O values 4.5 per mil lower than values for the target material (*35*). This difference has been explained by the impact-induced admixture of isotopically light meteoric water that was present in the pore spaces of the target sandstones (*35*). The australasian tektites (δ^{18}O values of 9 to 11 per mil) were derived from Jurassic sandstone and shale (*36*), which would be expected to have had original δ^{18}O values of ~14 per mil, yet the observed values are ~4 per mil lower [(*20*); Table 1] perhaps also because of water incorporation. Thus, it is possible that the siliceous endmember for the K-T tektites was either a graywacke (δ^{18}O values of 9 to 15 per mil) that was mixed with meteoric or seawater during tektite formation such that the δ^{18}O value of the black glass was lowered to a value of ~7.5 per mil (Fig. 3) or was a dacite in which the δ^{18}O value remained unchanged during impact.

We have demonstrated that δ^{18}O varies inversely with SiO_2 both within the black glasses and between the black and yellow glasses (Fig. 2). This trend can only be produced by mixing between carbonate and silicate rocks and is a likely result of the large impact that is hypothesized to have occurred at the K-T boundary (*37*). Studies of tektites from the moldavite (*35*) and australasian (*36*) strewn fields have led to the common conclusion that the tektite ejection process selectively samples only the top ~100 m of target material and, therefore, a thin veneer of carbonate over siliceous materials may be sufficient to produce the observed trends of chemical variation between the glasses. Proposed impact sites at both Manson, Iowa, and Chicxulub, Mexico, are in geologic terranes where appropriate mixtures of carbonate and silicate target materials are present (*1–4*).

REFERENCES AND NOTES

1. H. Sigurdsson *et al.*, *Nature* **353**, 839 (1991).
2. G. A. Izett, *J. Geophys. Res.* **96**, 20879 (1991).
3. A. R. Hildebrand *et al.*, *Geology* **19**, 867 (1991).
4. H. Sigurdsson, S. D'Hondt, S. Carey, *Earth Planet. Sci. Lett.* **109**, 543 (1992).
5. Samples were disaggregated by dissolving the carbonate matrix in dilute HCl. Spherules and fragments of unaltered black and yellow glass were hand-picked under a microscope.
6. A. R. Hildebrand and W. V. Boynton, *Science* **248**, 843 (1990).
7. H. Sigurdsson *et al.*, *Nature* **349**, 482 (1991).
8. F. J-M. R. Maurrasse and G. Sen, *Science* **252**, 1690 (1991).
9. J. B. Lyons and C. B. Officer, *Earth Planet. Sci. Lett.* **109**, 205 (1992).
10. C. Jéhanno *et al.*, *ibid.*, p. 229.
11. C. B. Officer *et al.*, *GSA Today* **2**, 69 (1992).
12. Z. D. Sharp, *Geochim. Cosmochim. Acta* **54**, 1353 (1990).
13. C. P. Chamberlain and M. E. Conrad, *Science* **254**, 403 (1991).
14. Major element analyses were performed on 52 samples using a Cameca MBX electron microprobe. Analytical totals ranged from 94 to 98% (largely due to a poor polish necessitated by recovery of the samples) and were normalized to 100%.
15. J. Smit *et al.*, *Geology* **20**, 99 (1992).
16. Twenty-eight samples were recovered by dissolving away the acetone-soluble mounting medium and analyzed for oxygen isotopic composition. The apparatus is similar to that of Sharp (*12*), but differs in its laser beam delivery system. A 10-W continuous CO_2 laser beam was allowed to melt each sample in a BrF_5 atmosphere. After freezing the sample on a liquid nitrogen trap, the oxygen was passed through a mercury transfer pump to remove fluorine gas. The oxygen was then converted to CO_2 on a hot carbon rod. Samples ranged from 8.9 to 96.6 μmol of CO_2 and were analyzed for oxygen isotopic composition on a Finnigan Delta E mass spectrometer and are reported relative to standard mean ocean water (SMOW).
17. The uncertainty associated with the reported $\delta^{18}O$ values is estimated to be ±0.2 per mil based on three independent experiments: (i) a rather large (10 mg) K-T glass spherule (sample A4a) was broken into three pieces and each was analyzed separately (Table 1); (ii) pairs of analyses made on two Australasian Muong Nong–type tektites (samples 8301 and 8319) agreed within 0.1 per mil (Table 1); and (iii) 30 replicate laser analyses of a quartz standard (*38*) with a conventional $\delta^{18}O = 11.7$ per mil, yielded $\delta^{18}O = 11.7 \pm 0.16$ per mil (1σ).
18. H. P. Taylor and S. M. F. Sheppard, *Rev. Mineral.* **16**, 227 (Mineralogical Society of America, Washington, DC, 1986).
19. L. S. Walter and R. N. Clayton, *Science* **156**, 1357 (1967).
20. H. P. Taylor and S. Epstein, *J. Geophys. Res.* **74**, 6834 (1969).
21. N. Oskarsson *et al.*, *Lunar. Planet. Sci.* **XXII**, 1009 (1991).
22. W. R. Premo and G. A. Izett, *Meteoritics*, in press.
23. We use the term carbonate to represent a rock composed mainly of the mineral calcite ($CaCO_3$) but which also contains common impurities including dolomite and silicates.
24. We use the term sulfate-rich evaporite to represent a rock containing gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$).
25. T. Sharma and R. N. Clayton, *Geochim. Cosmochim. Acta* **29**, 1347 (1965).
26. M. B. Boslough *et al.*, *Earth Planet. Sci. Lett.* **61**, 166 (1982).
27. K. H. Wedepohl, in *Handbook of Geochemistry*, K. H. Wedepohl, Ed. (Springer-Verlag, Berlin, 1969), vol. 1, pp. 250–269.
28. J. R. O'Neil and R. N. Clayton, in *Isotopic and Cosmic Chemistry*, H. Craig, S. Miller, G. J. Wasserburg, Eds. (North-Holland, Amsterdam, 1964), pp. 157–168.
29. F. H. Stewart, *U.S. Geol. Surv. Prof. Pap. 440-Y*Y1 (1963).
30. G. E. Claypool *et al.*, *Chem. Geol.* **28**, 199 (1980).
31. A. P. Vinogradov and A. B. Ronov, *Geochemistry* (*U.S.S.R.*) (*Engl. Transl.*) **6**, 533 (1956).
32. L. S. Walter and M. K. Carren, *Geochim. Cosmochim. Acta* **28**, 937 (1964).
33. C. Koeberl and H. Sigurdsson, *ibid.* **56**, 2113 (1992).
34. J. D. O'Keefe and T. J. Ahrens, *Nature* **338**, 247 (1989).
35. W. von Engelhardt *et al.*, *Geochim. Cosmochim. Acta* **51**, 1425 (1987).
36. J. D. Blum *et al.*, *ibid.* **56**, 483 (1992).
37. L. W. Alvarez *et al.*, *Science* **208**, 1095 (1980).
38. M. E. Conrad and C. P. Chamberlain, *Geology*, in press.
39. B. P. Glass and C. Koeberl, *Meteoritics* **24**, 143 (1989).
40. We thank J. B. Lyons and C. B. Officer for providing the bulk Haitian sample, and C. Koeberl for providing the Muong Nong samples. This work was supported by grants from the National Science Foundation and a Burke Research Initiation Award from Dartmouth College.

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Scale and Structure in Natural Food Webs

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The degree to which widely accepted generalizations about food web structure apply to natural communities was determined through examination of 50 pelagic webs sampled consistently with even taxonomic resolution of all trophic levels. The fraction of species in various trophic categories showed no significant overall trends as the number of species varied from 10 to 74. In contrast, the number of links per species increased fourfold over the range of species number, suggesting that the link-species scaling law, defined on the basis of aggregated webs, does not reflect a real ecological trend.

For over two decades, ecologists have tried to establish generalizations about the structure of natural food webs. From trends in published webs, three scaling laws (*1–3*) have been proposed. The first, the species scaling law, proposes that the basal (autotrophs and detritus), intermediate (preying on others and themselves preyed upon), and top (having no predators) fractions of species do not vary with the total number of species (S) in the web. The second, the link scaling law, proposes that the fractions of top-intermediate, top-basal, intermediate-intermediate, and intermediate-basal links do not vary with S. The third, the link-species scaling law, proposes that the total number of links (L) is proportional to S and that linkage density ($d = L/S$) does not vary with S.

These laws have been supported by studies, each including up to 113 webs (*1–5*). They have also been criticized for lack of uniformity in data collection, linkage criteria, and species aggregation in the food webs used to develop and test the laws (*6, 7*). For example, some webs present "whales" as several distinct trophic groups, whereas others make whales a single group that feeds on plankton, macroinvertebrates, and seals. Aggregation tends to be uneven across trophic levels; basal species are often lumped into categories such as "plankton" while top species are aggregated only slightly or not at all (*8*). To address this problem, Briand and Cohen developed scaling laws for webs where biological taxa were first aggregated into "trophic species," those having identical predators and prey (*1*). Others have argued that this aggregation disguises trophically important interactions (*6, 9*), and it remains uncertain whether the scaling laws reflect trends in natural nonaggregated webs. Recently Martinez (*10*) suggested that they do not, and Briand, Cohen, and others have proposed that link-species scaling in particular might be scale-dependent (*2, 4, 11, 12*). However, investigations have used either descriptions of webs from various sources that differ in sampling methods and completeness (*13, 14*) or a single, highly resolved web successively aggregated by computer algorithms (*10*).

I have analyzed the scaling laws using a large group of nonaggregated natural webs sampled consistently and constructed from identical linkage criteria (*15, 16*). The 50 webs represent the pelagic communities of small lakes and ponds in New York State sampled as part of the Adirondack Biota Project (*17*). Taxa at all trophic levels (fish, invertebrate predators, zooplankton, and phytoplankton) are resolved to genus

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