Microtektites and Mass Extinctions: Evidence for a Late Devonian Asteroid Impact

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Glass spherules, similar to microtektites, have been found near the Frasnian-Famennian boundary (F/F) (Upper Devonian) at Senzeilles, Belgium, contemporaneous with one of the largest marine mass extinctions of the Phanerozoic. These spherules exhibit a wide range of compositions and display teardrop, dumbbell, and compound morphologies analogous to microtektites. In addition, they lack crystallites, have few or no vesicles, and have a low content of volatile material. These characteristics are supportive of an impact origin. The Siljan Ring (Sweden) and Charlevoix structure (Quebec, Canada) are candidate craters of this age. The presence of microtektites near the F/F boundary supports the hypothesis that an impact caused the Upper Devonian worldwide benthic mass extinctions.

The F/F boundary represents one of the largest marine mass extinction in the Phanerozoic. As many as 21% of all families and 50% of all genera disappeared (*1*). It is estimated that at least 70% of species were lost (*2*). The species affected most were reefal, perireefal, and shallow-water benthic organisms, especially corals, stromatoporoids, tentaculids, and brachipods. The cause of the event or series of events has been uncertain (*2*). Estimation of the duration of the mass extinction event has varied from several million years (*3*), to 1 million to 2 million years (*2*), to less than 0.1 million years (*4, 5*).

Several terrestrial mechanisms such as widespread glaciation over Gondwana (*6, 7*), paleoceanographic changes (*8–10*), or large marine transgressions or regressions (*11, 12*) have been proposed to explain the extinctions but there are serious discrepancies for these models (*2*). The idea of a Late Devonian extraterrestrial impact, first proposed by McLaren (*4*), was based on his interpretation of the abruptness of the worldwide disappearance of shallow-water benthic fauna at the base of the Famennian (*4, 5*). However, investigations of many F/F sections have failed to produce evidence of a large impact such as Ir anomalies, shocked minerals, or microtektite-like glass comparable to that found at the Cretaceous/Tertiary (K/T) boundary (*13, 14*).

We report the discovery of preserved microtektite-like glassy spherules associated with the F/F boundary at Senzeilles in the Dinant Basin, Belgium. The exposed section at Senzeilles (Fig. 1) consists of 4.8 m of blackish upper Frasnian Matagne Shale beneath 3.5 m of blackish and grayish F/F transition shale. These are overlain by over 35 m of Famennian-age greenish Senzeilles Shale containing sparse lenses of carbonate rocks. These sedimentary rocks were deposited in a quiet water environment well below wave base. Low oxygen concentrations in the Matagne Shale are indicated by the abundance of organic matter, pyrite, and an anaerobic fauna (*9*).

The glassy spherules were found concentrated within a 5- to 10-cm layer (Fig. 1) ~4.5 m above the base of the Senzeilles Shale (*15, 16*). The spherule layer does not constitute a lithologically differentiated unit in the Senzeilles section because, apart from the presence of spherules, there is no apparent change in sediment type. We have recovered over 400 spherules and glassy grains from this layer to date; calculations indicate a mean glass concentration of approximately 0.03 mg of glass per gram of sediment. The spherule horizon lies in the Lower *triangularis* conodont zone (*16*); the worldwide F/F extinction event has been placed close to or at the base of this zone (*4, 5*) (Fig. 1). The preservation of fully articulated ostracods indicates that sedimentation rates in this part of the section were relatively high. However, we are uncertain of the time between the suggested F/F boundary (Fig. 1) and the spherule bed (*17*).

The glassy spherules from Senzeilles range from 50 μm to more than 1 mm in diameter; most average 300 μm in diameter (Fig. 2A). They are generally yellowish and transparent to almost transparent and locally have frosted or etched surfaces. A few are dark and have a metallic shine. Most spherules are very well rounded, but some have an elongated, teardrop, or dumbbell shape (Fig. 2B). A few consist of two spheres apparently fused together (Fig. 2, C and D). Many spherules exhibit one or two small attached droplets (Fig. 2, B and E). Broken fragments typically display conchoidal fractures. The glass in the spherules is remarkably well preserved; it is not surrounded by a smectite or calcite rim and shows no evidence of internal devitrification or alteration (Fig. 2F).

The surfaces of the spherules exhibit different degrees of dissolution. Some preserve their original smooth glassy surface and show only very fine-scale etching and precipitation of clay needles. Others display more intense etching and more irregular and pitted surfaces (Fig. 2A). The spherules are isotropic in polarized light and exhibit a wide range of refractive indices (1.485 for high Si to 1.568 for high Fe, low Si glasses) (Table 1). Although some spherules contain a few large vesicles and crenelated etched rims, most appear smooth and glassy when examined by scanning electron microscopy (SEM) and lack crystallites and vesicles (Fig. 2F). The Senzeilles spherules morphologically resemble microtektites and differ from volcanic glass, which usually contains phenocrysts or microliths of high-temperature minerals (*18, 19*).

The exceptional preservation of the

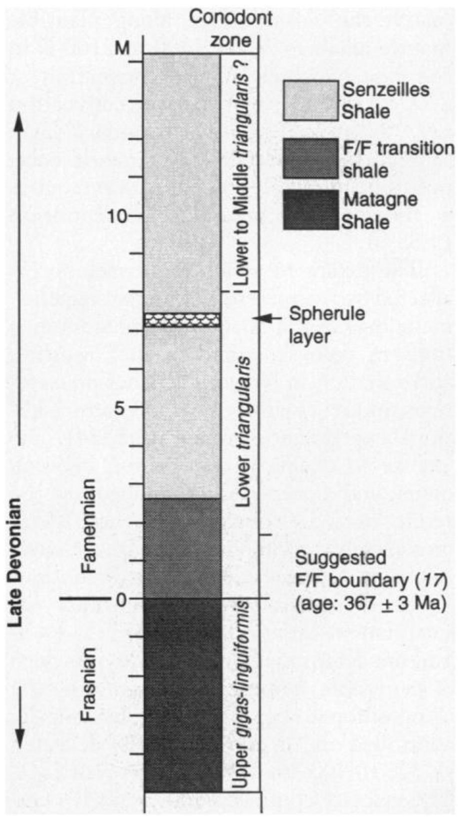

Fig. 1. Stratigraphic column of Senzeilles section showing the location of the spherule layer, lithology, conodont zonations (*16*), and the proposed F/F boundary (*17*). The global mass extinction event is located somewhere between the top of the *linguiformis* and the base of the Lower *triangularis* zone, where the Senzeilles microtektites are found (*5*).

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Senzeilles glass spherules may be due to their low water content, which appears similar to that reported for tektite glasses (*20*). Fourier transform infrared spectroscopy (FTIR) performed on the Senzeilles glass yielded ~0.009% H_2O by weight. In addition, glass preservation must have been enhanced by rapid burial, the abundance of fine-grained silica in the sediment, and the high organic content of the Senzeilles sediment. The associated low porosity and permeability also limited fluid flow through these rocks.

The Senzeilles glass spherules exhibit a broad range of compositions. We recognize five compositional end-members (Table 1). The most abundant types are K-, Al-, and Fe-rich; Si- and Ca-rich glass spherules are less common. This range in variability is greater than that of most Cenozoic tektites and microtektites (*18, 21*). However, K/T boundary tektites from Mimbral, Mexico (*22*), and Beloc, Haiti (*19, 23*), also display a significant range in composition, although none precisely match the compositional range of the Senzeilles glass spheres.

These Late Devonian glass spheres exhibit compositional characteristics attributed to tektites: (i) a broad range of compositions, (ii) a high K_2O/Na_2O ratio, (iii) high $[Al_2O_3/(K_2O + Na_2O)]$ ratio, and (iv) a low water and volatile content (*18, 21*). The Si-rich glass spheres, however, display anomalous compositions, different from those of any tektite, microtektite, or volcanic glass reported in the literature. Their in situ occurrence, however, rules out contamination.

Impact glasses and tektite-like glasses associated with the Zhamanshin crater in Khazakhstan (1.09 million years old) show a range of compositions comparable to the Senzeilles glassy spherules (*24*). The variability of chemistry of the Zhamanshin crater glasses has been attributed to the presence of a variety of target rocks (*24*). The inhomogeneous composition of the Senzeilles glass might also be related to a mixture of target rocks. Several small (80 μm), dark, high-index glass shards also displaying conchoidal fractures and quenched flow structures were found associated with the spherules. They are generally rich in Si but have minor amounts of Al, K, and Ca. They also lack any crystallites. A few of these glass fragments are enriched in S.

Glassy spherules morphologically resembling the Senzeilles spherules have been found in the Lower Famennian *crepida* zone, four conodont zones above the F/F boundary in Qidong (Hunan, China) (*25*). The Qidong spherules contain internal vesicles and lechatelierite inclusions. There is considerable overlap in the glass compositions between the spherule populations from China and Belgium, with Qidong "matrix glass" corresponding to our "K-rich" glass;

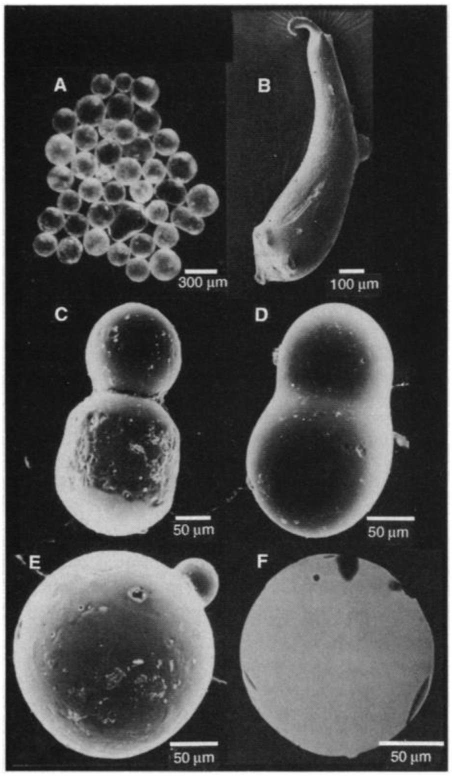

Fig. 2. Light microscope (A) and SEM micrographs (B through F) of glass spherules from the Senzeilles shales. (**A**) Reflected-light micrograph showing the morphology and surface textures of glass spherules. Note the compound and elongate, oval forms. (**B**) Complex elongate quenched-glass droplet with preserved delicate projections (IRScNB no. a2823). (**C**) Compound spherules of Ca-rich composition, with a smooth surface and furrow separating the two spheres. (**D**) K-rich double sphere. (**E**) Transparent microtektite-like sphere with attached small droplet. (**F**) SEM micrograph in the backscattered mode of a polished section of an opaque gray sphere showing the lack of microlites and vesicles.

Table 1. Microprobe analyses of the Senzeilles spherules showing the different types of glasses found. The number of analyses is given in parentheses. All Fe is given as FeO. <DL = below detection limit. Standard ZAF corrections, calibration on oxides; basaltic glass was used as the working standard.

Component	K-rich		Al-rich		Fe-rich		Ca-rich		Si-rich	
	Average (%) (27)	Range (%)	Average (%) (11)	Range (%)	Average (%) (6)	Range (%)	Average (%) (5)	Range (%)	Average (%) (35)	Range (%)
SiO_2	63.46	58.8–66.9	50.41	46.4–51.6	40.0	38.8–40.5	44.78	42.6–47.3	80.52	77.9–81.8
Al_2O_3	22.78	19.3–25.5	30.9	29.2–32.7	18.97	18.7–19.2	20.1	19.2–20.8	0.46	0.05–1.5
FeO	1.58	1.07–2.3	7.25	5.5–12.21	31.75	30.9–32.2	5.4	4.74–6.02	0.18	0.01–0.43
MgO	2.12	1.41–2.60	2.37	1.94–2.51	2.12	1.82–2.20	2.1	1.89–2.46	3.86	3.76–4.16
CaO	3.26	2.0–4.60	4.11	3.2–4.8	1.46	1.24–1.77	23.11	22.2–24.2	8.30	8.07–8.45
K_2O	4.71	4.38–5.58	2.96	2.3–3.31	2.11	1.88–2.16	2.16	1.96–2.87	0.16	0–0.65
Na_2O	1.01	0.82–1.02	0.8	0.57–0.94	0.79	0.67–0.87	0.55	0.45–0.60	7.28	6.43–7.66
TiO_2	0.6	0.48–0.74	1.04	0.78–1.27	0.65	0.59–0.69	0.6	0.53–0.61	<DL	
MnO	0.16	0.04–0.24	0.1	0.0–0.26	1.11	0.9–1.27	0.15	0.09–0.25	<DL	
Cr_2O_3	<DL		<DL		0.09	0.06–1.10	0.09	0.04–0.21	<DL	
NiO	<DL		<DL		0.1	0.06–0.22	0.05	0.03–1.15	<DL	
CuO	<DL		<DL		<DL	<DL	0.08	0.03–0.16	<DL	
S	<DL		<DL		0.3	0.19–0.32	<DL		<DL	
Total	99.68		99.94		99.45		99.28		100.76	

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.

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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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