MICROTEKTITE-LIKE GLASS SPHERULES IN LATE DEVONIAN (367 MA) SHALES .

P. Claeys[1] and J-G Casier[2]. [1]Dept. Geology, Univ. Calif. Davis Ca. 95616; [2]Royal Inst. Nat. Sci. Brussels-Belgium.

Glass spherules are found closely associated with the Frasnian-Famennain (FF) boundary in two sections, Senzeille and Hony, located in the Dinant basin in the South of Belgium. These spherules are interpreted based on their chemistry and low water content as impact produced microtektite-like glass. Craters of Late Devonian ages include the Siljan Ring (Sweden), Charlevoix (Quebec) and Taihu Lake (China). The occurrence of microtektite-like glass closely associated with the FF mass extinction is intriguing. The relationships between the impact and the extinction event deserve further study.

In the Hony section, the spherule layer occurs at the very the base of Lower *triangularis* , the first conodont zone of the Famennian approximately 5 to 10 cm above the FF boundary. At Senzeille where the biostratigraphy is unclear, the spherule layer is present approximately 4.5 m above the base of the Senzeille shales [1]. In both location after crushing and acid dissolution of the shale, the spherule layer has produced between 0.03 and 0.1 mg of glass / g of sediment. Similar glass spherules have been reported from the Famennian Qidong section in China [2]. These Chinese glass spheres are found in the Lower *crepida* conodont zone and are according to conodont time scale +/- 1.5 m. y. younger than the Belgian ones.

The glassy spherules from Hony and Senzeille range in diameter from less than 50 microns to over 1 mm (250 microns in average). They are clear transparent (50%), yellowish (25%), reddish (5%) or have a dark metallic shine (20%). They are well rounded, less commonly they display elongated, dumbbell or tear drop shapes. Many are compound spherule or have small attached microspherules. The spherules are isotropic in polarized light and display conchoidal fractures. Their refractive indices varies from 1.48 to 1.56. Polished section examined under the SEM are smooth and glassy. A few spherules exhibit one or two large vesicles. No crystallites are present in the glass.

The spherules are often coated by a fine rim of calcite and clay minerals. This coating and their original low water content may explain their preservation for 367 m. y. In addition preservation may have been enhanced by rapid burial, abundance of fine grained silica, high organic content and the low porosity/permeability of the sediment in both location.

The glass spherules are interpreted as impact produced microtektites-like glass based on the following evidences: 1) Their morphology, shape and surface appearance, 2) The glass "exotic" chemistry and range of composition (Table), 3) The glass high K_2O/Na_2O ratio and high $[Al_2O_3/(Na_2O+K_2O)]$, 4) The lack of high temperature microliths in the glass matrix and 5) The low water content of the glass (0.009 Wt. % determined by FTIR spectroscopy).

The glass chemistry appears quite similar at both location (Table). The range of composition is broader than commonly reported for microtektites [3]. This range might be explained by an inhomogenious target rock. The Al-rich and Fe-rich glass composition suggest the presence of pelitic sediments mixed with carbonates to produce the high Ca glass. The high silica (> 88 %) glass from Hony occurs as darker zone under SEM-BSE in the glass matrix. Similar high-Si zones have been described in microtektite glass from the Famennian Qidong section in China and interpreted as partially melted quartz grains [2]. Quartz inclusions have also been reported in Muong-Nong type tektites and impact glasses [4; 5].

Several impact craters of Late Devonian ages may be considered as possible sources for the Belgian glass spheres. The two best candidates so far, are the Siljan Ring in Sweden, the largest impact structure in Europe (52 Km in diameter) and the Charlevoix structure in Quebec (46 Km in diameter). The Siljan Ring has been dated by ^{40}Ar-^{39}Ar method at 368 +/- 1 m.y. and Charlevoix crater at 350 +/- 20 m. y. (K-Ar method) [6]. The age of the FF boundary is estimated to be 367 Ma. [7]. The Siljan Ring target rock composition appears rather consistent with the Senzeille and Hony glass chemistry. The Siljan Ring is composed of Precambrian granites and Upper Silurian sandstones, shales and limestones [6]. Charlevoix crater rocks are a mixture of Precambrian

granite, gneiss, migmatites, charnockite, gabbro and anorthosite [6]. The Taihu lake (>70 Km in diameter) in China has only recently been identified as an impact crater. It is according to Wang [3] the possible source for the Chinese microtektites.

The discovery of preserved microtektites-like particles in two Late Devonian sections demonstrates that an impact occurred at or near the FF boundary. This boundary is also marked by one of the largest mass extinction in the fossil record [8]. At this point we believe there is not yet enough evidence to definitively correlate the FF mass extinction with the impact taking place in what appears to be the very base of the Famennian. The discovery of the microtektite layer at Hony just a few cm above the extinction event is intriguing and the possible link between extinction and impact certainly deserves further study. Now that the FF boundary has been strictly defined [9], we believe that this question can be resolved in the near future. It will require the same type of global research program that so successfully demonstrated the connection between impact and extinction at the Cretaceous-Tertiary boundary.

	HONY GLASS				SENZEILLE GLASS [1]			
SiO_2	60.00	49.38	62.32	88.60	63.46	50.41	40.0	44.78
Al_2O_3	24.58	32.89	21.16	4.02	22.78	30.90	18.97	20.21
FeO	3.96	8.33	1.49	0.95	1.58	7.25	31.75	5.40
MgO	1.05	1.49	0.93	0.45	2.12	2.37	2.12	2.10
CaO	0.46	1.96	9.77	0.05	3.26	4.11	1.46	23.11
K_2O	7.28	3.00	2.64	2.97	4.71	2.96	2.11	2.16
Na_2O	0.70	0.97	0.57	0.12	1.01	0.80	0.79	0.55
TiO_2	1.38	1.27	0.70	2.28	0.60	1.04	0.65	0.60
MnO	<DL	0.09	0.10	<DL	0.16	0.10	1.11	0.15
Cr_2O_3	<DL	<DL	<DL	<DL	<DL	<DL	0.09	0.09
NiO	<DL	<DL	<DL	<DL	<DL	<DL	0.10	0.05
S	<DL	<DL	0.17	<DL	<DL	<DL	0.30	<DL
TOTAL	99.41	99.38	99.85	99.44	99.68	99.94	99.45	99.20

Table of microprobe analyses of the Hony and Senzeille glasses. All Fe as FeO. An average of at least 10 analyses are presented for each distinctive group.

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