CARBON-RICH AND NI-Fe-RICH SPHERULES AT THE END OF THE PERMIAN: APPLICATION TO MATERIALS OF SPACE EXPLORATIONS. Y. Miura, Dept. Earth Sci., Fac. Sci., Yamaguchi University, Yoshida 1677-1, Yamaguchi, Yamaguchi, 753-8512, Japan. yasmiura@yamaguchi-u.ac.jp

Introduction: In order to see the detailed materials of spherules at the end of the Permian (ca. 250Ma) reported by author et al.[1,2,3,4], the present paper is described textures and compositions of the spherules at the end of the Permian (used as PTB), especially carbon and iron-nickel contents. The samples are used from Meishan sections (the PTB) in Southern China, and compared samples of Akiyoshi limestone (the Permian in Japan) and Takamatsu-Kagawa buried crater (at the Cretaceous Ryoke granite in Japan). The main purpose of the paper is to support impact origin of the PTB event, and apply to materials of space explorations [1-5].

Composition of spherules of the PTB samples:
The composition of the spherules of the Meishan PTB samples are summarized as follows:
1) Almost all spherules (95 % form 20 spherules) are Fe-rich, except silica spherule.
2) Fe-rich spherules contain Si-Al at impact event from rocks.
3) Silica-rich spherule can be found also in the PTB samples.
4) S is contained in FeS grains of spherules.
5) Ni-rich spherules contain Fe and C-Al-Si-K-Ca-Co-Cu.
6) Carbon-rich spherules are found in 10% of all spherules.

The compositions of the spherules indicates that magnetic spherules of Meishan PTB samples are considered to be impact origin on crust rocks. This is mainly because there are no mantle-derived rock with much Mg. All elements found at the present spherules can be explained by impact event on limestone and silica-rich rock on the crust.

Carbon spherules of the Meishan PTB sample:
It is summarized as follows:
1) Carbon spherules are varied from 1µm to 20µm in size, though nanostructure of 10nm size is observed.
2) Carbon contents of spherules from the Meishan PTB are ranged from 56wt.% C to 90wt.%C with in-situ ASEM (JEOL) which are coexisted with Fe contents of 2 to 36wt% (as shown in Fig.1).
3) C-Fe diagram of 7 carbon-rich spherules shows that carbon phases are mixed with Fe. It is first detailed report for carbon 90wt.% from spherule and the PTB samples.
4) Small contents of Si, Al and Ca are related with C content (as shown in Fig.1).
5) Carbon-rich samples are found in magnetic fragments and direct in red-layered at the PTB sample.
6) Carbon contents of one spherule are almost homogeneous, but change on individual spherule. Much Fe contents of spherules are not found in network-type nano-carbon from backscattering image (BEI) of the high-resolution ASEM data. This suggests that mixed elements of Fe,Si,Al and Ca are remained during impact relation with major carbon at sea-deposit of limestone and Si-rich rock.
7) There are few Mg content of the Meishan PTB spherule, as well as localized S content on each grain in the spherule. This indicates that these spherules are formed on surface rocks (without mantle or volcanic rocks).

Carbon spherules of the drilled Akiyoshi limestone breccias samples:
It is summarized as follows:
1) Drilled Akiyoshi breccias of limestones from Yamaguchi, Japan are used as related limestone with Meishan PTB samples originally from Southern Equator transported by continental-drift after impact event. Carbon spherules and grains are varied from 0.5µm to 30µm in size, though nanostructure of 10nm size is observed.

Fig. 1. Electron micrographs (BEI) of carbon spherules (89%, 69% and 56%) with line profile of C, Fe and Si elements. Carbons are mixed with Fe and Ca as in two diagrams. The samples are the Meishan PTB sample from China. Red-layered PTB sample from the Meishan was collected and analyzed by author.

Carbon grains of the drilled Akiyoshi limestone breccias samples: It is summarized as follows:
1) Drilled Akiyoshi breccias of limestones from Yamaguchi, Japan are used as related limestone with Meishan PTB samples originally from Southern Equator transported by continental-drift after impact event. Carbon spherules and grains are varied from 0.5µm to 30µm in size, though nanostructure of 10nm size is observed.
2) Carbon contents of spherules from the Akiyoshi breccias are ranged from 41 wt.% C to 93 wt.% C with in-situ ASEM (JEOL) which are coexisted with Ca contents of 2 to 54 wt% (as shown in Fig.2).

3) C-Fe diagram of 11 carbon-rich spherules shows that carbon phases are mixed with Ca. It is first detailed report for carbon ca.90 wt.% from the Akiyoshi samples.

4) Small contents of Fe, Si, Al, Na, K and S are related with C content (as shown in Fig.2).

5) Carbon-rich samples are found in spherules and vein fragments of the drilled samples to 243 m in depth (which are offered from the Akiyoshi Science Museum, Japan).

6) There is few Mg content of the Permian Akishoshi limestone breccias, which indicates that these spherules are formed on surface rocks (without mantle or volcanic rocks).

7) Origin of carbons in the Akiyoshi breccias can be derived from limestone during impact reaction due to strong correlation with C and Ca as shown in Fig.2.

**Bulk contents of Fe, Ni, Co elements:** The bulk samples of Meishan PTB and Akiyoshi limestone breccias at two analyses are Fe=1.89, 2.98 (wt%), Ni=15, 8 (ppm), and Co=3, 2 (ppm) in the Meishan samples, and Fe=0.21, 0.05 (wt%), Ni=3, 3 (ppm), and Co=1, 1 (ppm) in the Akiyoshi samples by the ICP-AES analyses.

**Application to materials on space exploration:** It is summarized as follows: 1) Ca-rich (more than ca.50 wt%) can be found from C-bearing limestone target rocks (probably from the Earth and Mars). 2) Ni-Fe rich spherules can be found impact with iron meteorite rich projectile on the space.

**Summary:** The present results are summarized as follows: 1) The Meishan PTB spherules contain C-rich (up to ca.90 wt%) and Ni-Fe rich spherules (31 wt% Ni and 29 wt% Fe). 2) Akiyoshi drilled limestone breccias contain C-rich grains with Ca from limestone target rocks.


![Carbon micrographs of Akiyoshi limestone breccia](image1)

![Ni-Fe micrographs of Meishan PTB](image2)