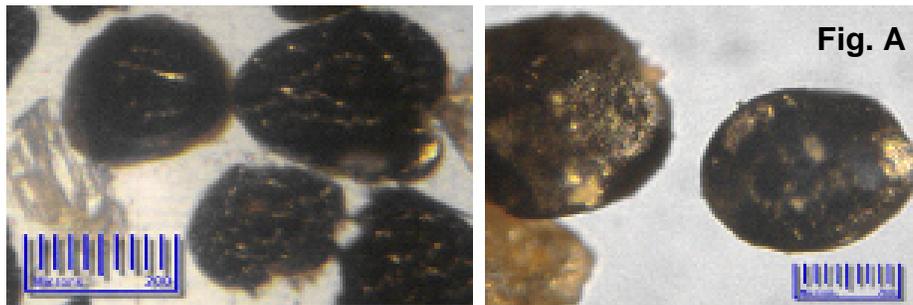


Extraction of Magnetic Grains from Sediment. (Protocol Version 2011-08-18)

We typically separated magnetic grains manually, but automated processing can be accomplished with, for example, a Franz magnetic separator. We avoided sonication with a ceramic magnet because that process typically collects only strongly magnetic grains and excludes the smallest MSp. We used only **grade-42 or grade-52 neodymium magnets**. All other magnets are too weak to extract enough magnetic grains. Typically, we used the size 2"×1"×0.5", which was convenient for both field and laboratory work. One source for these is K&J Magnetics, (<http://www.kjmagnetics.com/>), item # BY0X08-N52. **CAUTION: These powerful magnets can be dangerous. Keep them well away from metal objects, which they strongly attract. Also, their magnetic fields can damage credit cards, motel card keys, and electronic devices.**



- Outlying sediment samples either older or younger than the Younger Dryas Boundary layer (YDB) often were sampled at thicknesses of 5 cm to 20 cm. For the YDB, we collected bulk sediment samples at typical thicknesses of about **0.5 cm to 2 cm** and at weights of **at least 500-1000 grams**. **CAUTION: smaller weights and thicker YDB sections may be insufficient for detecting ANY markers.**
- Bulk samples were thoroughly mixed to homogenize the sediment and were then dried at room temperature. Last, they were weighed. All processing was done with non-metallic tools to avoid introducing foreign metals, and care was taken not to crush the carbon fraction.
- The magnet was placed into a durable 4-mil plastic bag to prevent grains from sticking to the magnet (Fig. B). Thicker supermarket freezer bags are also adequate for this purpose. Next, we added Adequate water to each sediment sample to create a slurry (Fig. C).



- We usually processed **~500 1000 grams for each stratum** in multiple batches. However, if a sample has abundant magnetic grains (for example, more than 1 gram/kg), you can use smaller aliquots of about 150-500 grams.
- The magnet, with bag tightly stretched around edges, was immersed in mixture (Fig. D). **NOTE: The magnet should be moved slowly and gently, or water action will dislodge the smaller grains.**
- The magnetic fraction (at arrow, Fig. E) was withdrawn along with the bag and magnet.



- The bag, magnet, and grains were then immersed in a second container of clean water. The grains were released from the magnet into the water by withdrawing the magnet from the bag (Fig. F).
- The above were repeated (~15-20x) until minimal additional grains could be extracted (~15-30 min).
- Excess sediment often is extracted along with the magnetic fraction, and so to remove it, the bag and magnet were used to retrieve the magnetic fraction from the second container (arrow, Fig. G). If the water is very dirty, it may be necessary to repeat the process with a third container containing clear water in order to further rinse the extracted magnetic grains. **This process is essential in order to clean the magnetic fraction well enough to visually detect the MSp.**



- After removing the magnet, the wet grains stuck to the bag and could be transferred to a lab dish by touching the bag to a small amount of water on the dish surface (Fig. H). After removing as many as

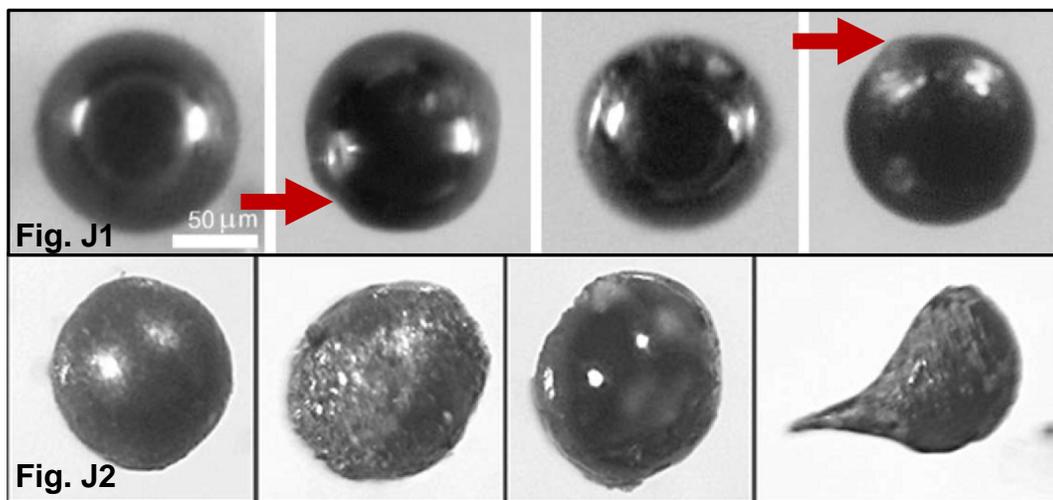
possible, pour the remaining water slowly over the magnet to extract the remaining grains.

- After drying, the magnetic fraction was weighed and catalogued. The dried fraction appears as below (Fig. I).
- The magnetic fraction was analyzed by PGAA, INAA, SEM/EDX, or ICP-MS for at least major oxides along with up to ~50 elements, including iridium, thorium, uranium, chromium, and nickel.



Extraction of Magnetic Spherules (M_{Sp}).

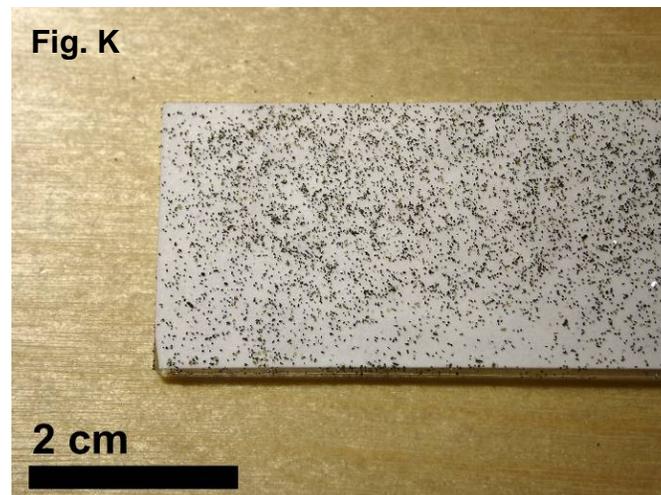
- The magnetic fraction was extracted as described above. M_{Sp} range from 2 to 150-um in size, and are most often highly rounded (>90%), although not always perfectly spherical, as shown at arrows in Fig. J1 (from Firestone, 2007) and Fig. L. A small number are not spherulitic at all, as shown in Fig. J2 and Fig. L) and will not be highly polished and reflective. Typically, they will be recognizably different from the terrestrial magnetite. Some judgment is required in selecting candidates until SEM analysis can provide definitive identification of rapid-quench textures, as shown in Fig. L below.



- We used ASTM sieves to screen the each full magnetic fraction into three typical fractions: greater than 150 um (ASTM #100 screen), between 150 um and 53 um (ASTM #270 screen), and less than 53 um. If the magnetic fraction was very fine, we used an ASTM #400 screen to further separate the grains to

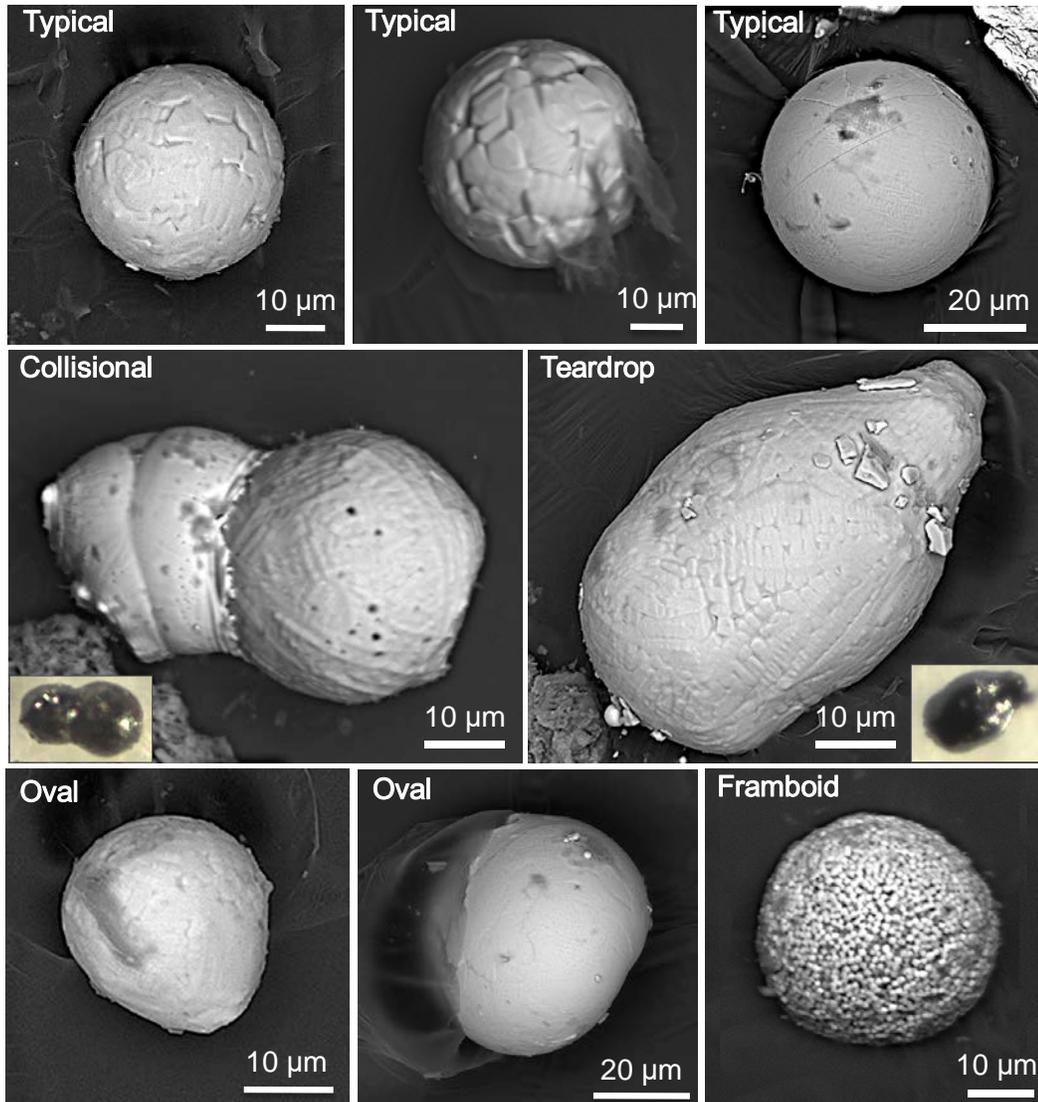
less than 38-um. The smallest samples of <53 um or <38-um typically contained the most abundant MSp, but sizes varied by site, so that some judgment is necessary to select the optimum screens. **CAUTION: Size separation is essential, since the magnetic grains undergo sorting by size inside a vial, causing most of the small MSp to settle to the bottom. It is vital to analyze the sized fractions separately, since without separate testing, only the top layers get tested, potentially leading to a significant undercount. For a large multi-gram magnetic fraction, it may be necessary to use a microsplitter, in order to assure even splitting of grains.**

- MSp are rare, often making it necessary to inspect the entire magnetic fraction from **500-1000 grams** of sediment. Sometimes, there were only 6 MSp per 1000 grams of sediment, and yet, this amount was above background. **CAUTION: If only 0-2 MSp are detected, it is necessary to analyze additional aliquots in order to obtain an accurate count. It may be necessary to analyze the entire magnetic fraction from 1 kg of sediment.**
- To find MSp, we dusted the magnetic grains lightly across a microscope slide at about **10-20 mg per slide** (Fig. K), being careful to **avoid leaving dense clusters of grains**, which made it difficult to distinguish the MSp. A white background makes it easier to locate the MSp. As an alternate to the slide, a lab dish with low sides can be used, so the material does not roll off.



- We scanned using a **reflected-light (top-lit) zoom microscope** with a mechanical stage **at a magnification of not less than 200× up to 300×**. At lower resolution, the MSp may be easily overlooked. Generally, an adequate search for MSp from each individual bulk sample took a total of about 1 to 3 hours, varying by size of the magnetic fraction and number of MSp in the fraction.
- The MSp were tallied and photographed at a magnification of ~300× to 500×. Abundances were extrapolated to determine number of MSp per kg of bulk sediment.
- MSp were sometimes removed manually using a sharpened, moistened, wooden probe, or a single-bristle brush. They were placed either inside a conical-bottom vial filled with alcohol or onto a microprobe/SEM adhesive tab.
- Selected MSp were sectioned and/or analyzed by SEM-EDS. Typical MSp display dendritic quench-melt texturing (Fig. L). Framboids (Fig. L) are noticeably different from YDB quench-melted spherules.

IMPORTANT: Performing SEM imaging and EDS analysis is crucial to distinguishing true impact-melted magnetic spherules from cosmic spherules, framboids, and round detrital grains.



SPHERULE SUMMARY. Identifying the MSp can be very difficult because they are micron-sized. To increase the chance of success, here is a summary of the most important points:

- 1) Homogenize the dried bulk sediment before removing an aliquot of sediment.
- 2) Use a grade-42 or grade-52 neodymium magnet to extract the magnetic fraction.
- 3) Be prepared to extract the magnetic fraction from up to 500-1000 grams of sediment.
- 4) Sieve the extracted magnetic grains by size. Begin work with the >53-um or >38-um fraction.
- 5) Spread the magnetic sample evenly across a white-backed microscope slide.
- 6) Use a reflected light (top-lit) zoom microscope with a mechanical stage to search for MSp at a magnification of not less than 200×.
- 7) Stop when you have found more than ~ 5-10 MSp, or until you have analyzed the entire magnetic fraction.
- 8) Use SEM/EDX to search for evidence of dendritic quench-melt crystallization.

PROTOCOL: Extraction of Carbon Spherules (CSp), Glass-like Carbon, and Charcoal.

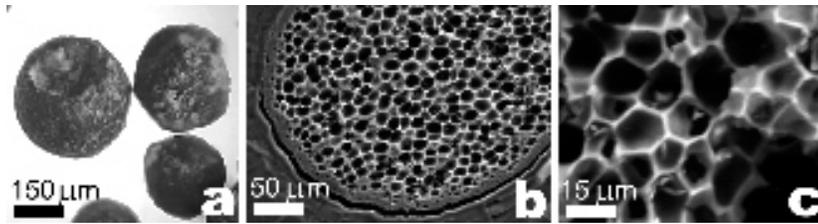


Fig. M. Carbon spherules.

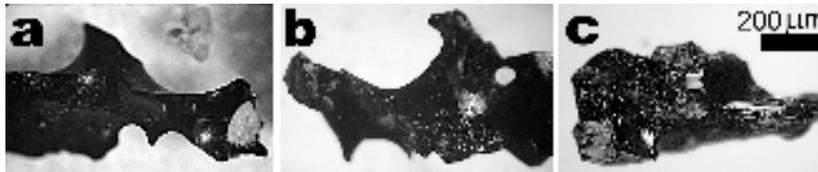


Fig. N. Glass-like carbon.

- Since CSp and glass-like carbon (Figs. M-N) generally are less dense than water, floatation was used for separation. Ample water was added, and the slurry was agitated to free the floating fraction (arrows, Fig O).
- Use an ASTM #200 screen to remove the floating fraction. Since some CSp will pass through a screen, the remainder were skimmed off manually and placed onto a lab dish to dry (Fig. P).
- This was repeated until the entire floating fraction was removed.
- Then, to recover the less buoyant fraction of carbon that did not float, the remaining slurry was agitated and rinsed repeatedly. This stratified the sediment and brought the remaining non-floating carbon fraction to the surface of the sediment sample, but still beneath the water. Any visible carbon, which included charcoal and glass-like carbon, was poured off and separated manually.
- The sample was then dried at room temperature, so as not to destroy the carbon.
- The CSp were separated in two steps. First, they were collected gravimetrically by agitating the dried sample on a smooth, inclined surface, down which they roll easily. Second, the residue was spread on a slide and viewed with an optical microscope (Fig. Q). In order to see 10-micron CSp, it is necessary to use a reflected-light (top-lit) zoom microscope at a **magnification of 180x to 300x**. **At lower resolution, the CSp can be easily overlooked.**

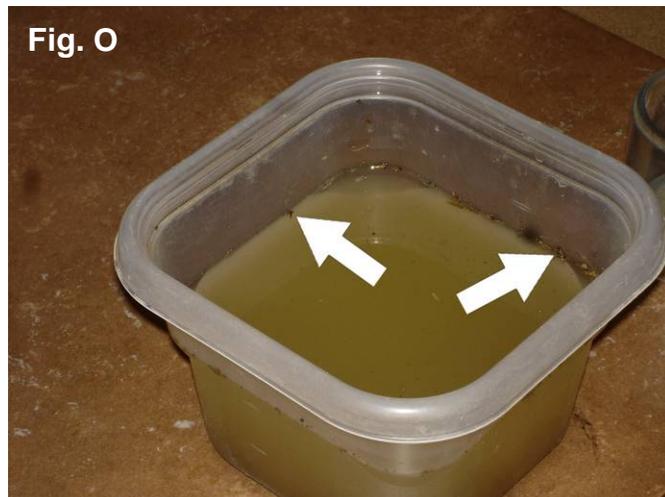


Fig. O



Fig. P

- Glass-like carbon and charcoal, contained in the same sample, were identified visually and extracted manually, using a thin, sharpened, moistened, wooden probe.
- All three types of carbon were weighed separately, and abundances were calculated in #/kg for CSp or g/kg for charcoal and glass-like carbon.
- CSp and glass-like carbon were tested using various analytical methods, including SEM-EDS, PGAA, INAA, and ICP-MS.
- About 1-10% of the CSp contain NDs, along with only a few pieces of glass-like carbon. **Thus, it is essential to crush 15-20 CSp together in order to detect NDs with STEM and/or TEM, as described in a separate protocol.** They were confirmed using high-resolution electron microscopy (HRTEM), selected area electron diffraction (SAD), fast-Fourier transform (FFT), electron energy loss spectroscopy (EELS), and energy-filtered TEM (EFTEM).

If you have questions on the above, you are welcome to email Allen West (allen7633@aol.com).

For soot and diamond extraction, email Wendy Wolbach (wwolbach@condor.depaul.edu).

