INTERNAL STRUCTURE OF TWO TYPE-I DEEP-SEA SPHERULES BY X-RAY COMPUTED MICROTOMOGRAPHY.

Huan Feng[1], K. W. Jones[1], Bruce Stewart[1], G.F. Herzog[2], C. Schnabel[2], and D.E. Brownlee[3]. [1]Dept. Applied Science, Brookhaven National Laboratory, Upton, New York 11973; [2]Dept. Chemistry, Rutgers University, Piscataway, NJ 08854-8087; [3]Dept. Astronomy, Univ. Washington, Seattle, WA 98915.

Summary **-** X-ray tomographs of two submillimeter type-I deep-sea spherules reveal the presence of oxide rims, intergrown oxides in the interior, branched holes emanating from the surface, and micrometer-size nuggets rich in platinum-group elements.

Introduction **-** The submillimeter micrometeorites known as the type-I spherules form in a complex series of steps that includes varying degrees of reaction with atmospheric oxygen [1]. Cores rich in metallic iron and nickel remain in some spherules while in others virtually all iron has reacted to form wüstite ($Fe_{1-x}O$), hematite (Fe_2O_3), or magnetite (Fe_3O_4) [2,3]. The most oxidized type-I spherules seem often to contain µm-size nuggets rich in platinum-group elements (PGE) [3-5]. Perhaps because the nuggets are hard to find [5], we have little information about their frequency of occurrence. Computed x-ray tomography (CMT) holds the promise of revealing quickly and non-destructively the internal structures of extraterrestrial objects [6,7]. We demonstrate here some of the capabilities of the method when applied to type-I spherules.

Experimental Methods **-** We glued each spherule to the end of a glass rod. The spherules were then irradiated at the National Synchrotron Light Source with a filtered white beam of x-rays from a bending magnet. The x-ray beam, 3 mm wide and 0.5 mm high, had a Gaussian intensity profile in the vertical direction that varied by <10% over the central 300 µm. Data were corrected for the variation of beam intensity by applying a white-field normalization during the data reconstruction. X-rays transmitted by the spherules were detected by using a YAG:Ce scintillator viewed through a magnifying lens by a position-sensitive CCD camera (active area: 3088 pixels wide; 2056 pixels high). For these measurements, 1 voxel or volume element corresponds to 3.6^3 μm^3 when binning and optical magnification are taken into account. The data for the tomographic volumes were obtained by making 1000 exposures as the sample was moved in 0.18° steps between 0° and 180°. Each complete cycle of sample rotation, data storage, and data readout took ~ 10 s; CCD camera exposure time was 0.07 s/cycle. Data acquisition for the volume of 658 × 658 × 100 voxels shown in Fig. 2 was completed in < 2 h. The complete volume was constructed from the individual frames by using fast-filtered, back-transform reconstruction software developed at Brookhaven National Laboratory. To check the results of the tomography, we potted spherule KK1-98-6 in epoxy and examined successively polished sections prepared at depths of 8, 13, 16, 22, 27, 28, and 31 µm. The nugget was found in the last section. For compositional analysis of the nugget we used a SEM in quantitative energy-dispersive mode with polished metal standards and ZAF corrections.

Results **-** Figure 1 shows a typical slice through spherule KK1-98-2. The color scale is set so that the color changes from red to blue as the relative attenuation of x-rays increases. Following [8], we identify the exterior rim as magnetite, the intergrown darker blue phase as wüstite, and the red areas as voids or holes. These assignments are consistent with the relative absorbances estimated for magnetite and wüstite from their elemental composition and density. We note, however, that tomography does not let us distinguish hematite from magnetite.

Figure 2 shows part of a three-dimensional reconstruction of KK1-98-6. The red shell again corresponds to very low x-ray attenuation observed near the outer surface of the meteorite. The shell has been cut away at the top, bottom, sides, and front to facilitate viewing the interior. In this figure the yellow surfaces correspond to the same low x-ray attenuation as do the red, but in the interior of the micrometeorite. The relative attenuation on the light blue surfaces is more than twice the value on the yellow and red surfaces. Variations of shading simulate the reflection of light from a source behind the viewer's left shoulder. We identified the compact blue region close to the surface of the spherule (upper right) as a PGE nugget based on the high, measured relative x-ray attenuation coefficients. Direct microscopic observation, electron microprobe analysis, and SEM imaging (Figure 3) provided confirmation. We found the nugget at a depth of ~31 µm in agreement with the CMT observations. Electron microprobe analysis gave (wt %): Fe 8.60; Ni 2.73; Ru 22.0; Os 29.0; Ir 20.3; Pt 17.3; Pd < 0.2; Rh < 0.2. Examination of the CMT results for KK1-98-2 revealed a small, flat, high-attenuation region close to the surface that also appears to be a PGE nugget.

Discussion **-** Spherules KK1-98-2 and -6 have similar features. Neither one retains a metal core. Both have rims, probably of magnetite, interiors consisting of magnetite intergrown with wüstite, holes that appear to propagate from the surface to the interior, and a nugget rich in PGE. The tomography shows for the first time the three-dimensional structure of the holes and of the PGE nuggets. The holes could have formed in several ways. They could be: voids created by contraction [7]; ghosts of bubbles [7,10]; cavities left when metal cores escaped; or regions where oxides that were swept backward around the surface of the decelerating droplet failed to coalesce completely (J.S. Delaney, pers. comm.). That holes in type-I spherules connect to the surface is also demonstrated in the many SEM images of [3]. We conclude that contraction alone, which would not seem to require any such connection, is not a complete explanation.

The tomography indicates structure within the PGE nuggets. Attenuation coefficients vary by ~50%, with the highest values occurring in the middle and top right portions (Fig. 2). Relative attenuation coefficients, and by implication composition, change most rapidly just below what was probably the leading surface of the spherule where oxidation presumably took place.

Conclusions **-** With synchrotron CMT one can distinguish and map non-destructively holes, two oxide phases, and PGE nuggets in the interiors of type-I spherules. Metal cores should be easy to identify as well. Holes are seen to be branched, antler-like structures that connect to the surface. Micrometer-scale spatial variations in the x-ray attenuation properties of PGE nuggets indicate compositional gradients. Genge et al. [9] argue for widespread reduction of oxidized Fe to metal in siliceous micrometeorites during passage through the Earth's atmosphere. X-ray tomography would make it possible to test this assertion non-destructively.

References - [1] Brownlee D.E. et al. (1997) *Meteoritics Planet. Sci. 32*, 157-175. [2] Kosakevich A. and Disnar J.R. (1997) *Geochim. Cosmochim. Acta 61*, 1073-1082. [3] Czajkowski J. (1987) Ph.D. Dissertation, University of California, San Diego. [4] Brownlee D.E. et al. (1984) *Nature 309*, 693-694. [5] Bonté Ph. et al. (1987) *Proc. 17th Lunar Planet. Sci. Conf., Part 2, J. Geophys. Res. 92*, E641-E648. [6] Arnold J.R. et al. (1983) *Science 219*, 383-384. [7] Tsuchiyama A. et al. (1997) *Lunar Planet. Sci., XXVIII*, 1453-1454. [8] Engrand C. et al. (1998) *Lunar Planet. Sci., XXIX*, CD-ROM, 1473.pdf. [9] Genge M.J. and Grady M.M. (1998) *MAPS 33*, 425-434. [10] Wang J. et al. (1994) *Lunar Planet. Sci. XXV*, 1459-1460

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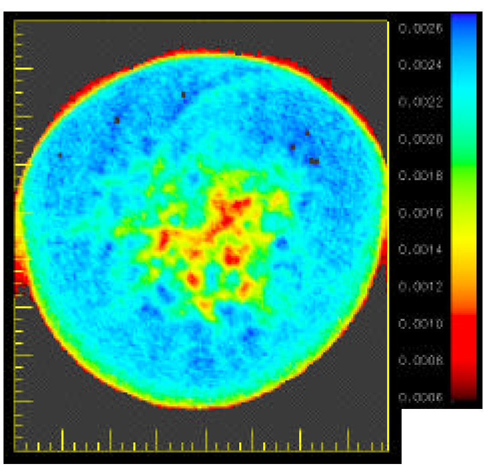

Figure 1. CMT 2-D image of central slice through KK1-98-2 (diameter ~ 400 µm). The light blue rim is likely magnetite; the central red region is part of a hole. Color scale to right shows relative x-ray attenuation coefficients.

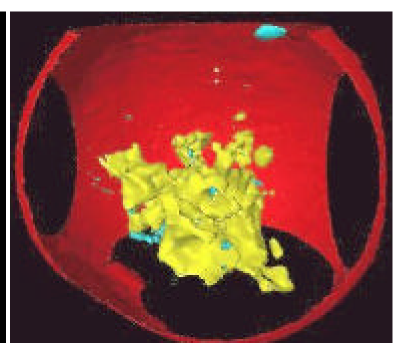

Figure 2. CMT 3-D image of the interior of KK1-98-6 with parts of (red) surface cut away. The yellow portion is a hole; the compact, high-attenuation feature in the upper right is a PGE nugget. The range of attenuations represented from red to blue is roughly twice that shown in Figure 1.

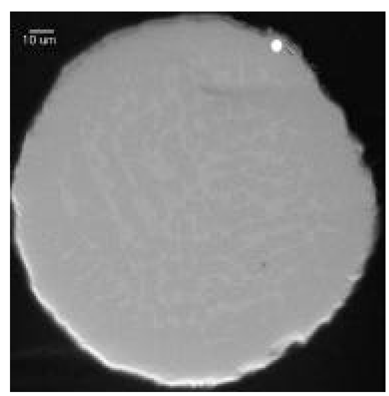

Figure 3. SEM image of polished section at a depth of 31 µm in KK1-98-6 confirming the presence of a PGE nugget, the bright feature in the upper right.