GLASSY VESICULATED MICROCHONDRULE-LIKE SPHERULES IN THE MATRIX OF UNEQUILIBRATED ORDINARY CHONDRITES. E. Dobrică and A. J. Brearley, Department of Earth and Planetary Sciences, MSC03-2040, 1University of New Mexico, Albuquerque, NM 87131-0001, USA. (edobrica@unm.edu and brearley@unm.edu).

Introduction: The fine-grained matrices of the most unequilibrated ordinary chondrites (UOCs) contain primitive materials which can help constrain the physico-chemical conditions of dust formation in the solar nebula. During our ongoing studies of the matrices of the two UOCs MET 00526 (L3.05) and Semarkona (LL3.00) [1-3], we have identified a number of glassy spherical objects similar in size to the microchondrules which have been previously reported in UOCs [4-8]. However, based on detailed Transmission Electron Microscopy (TEM) observations, these glassy objects are characterized by distinctive textures and chemical compositions. Here, we discuss the implications of our observations for the formation of these glassy objects and their relationship to microchondrules.

Methods: Four polished thin sections of MET 00526 and Semarkona were initially studied on a FEGSEM operating at 30 kV using backscattered electron (BSE) imaging. After SEM characterization, TEM sections were cut through the center of three spherical objects (C24, C29, C31) identified in the matrix of MET 00526, using the focused ion beam (FIB) technique with a FEI Quanta 3D FEGSEM/FIB instrument. Bright- and dark-field TEM images and quantitative EDS X-ray analyses were carried out at 200 kV on a JEOL 2010F FEG TEM/Scanning TEM (STEM).

Results: Thirty-five spherical objects were identified in the fine-grained matrix of MET 00526 (N = 22) and Semarkona (N = 13) (Fig. 1). Some of the objects are subspherical in shape or have concave depressions on their surfaces similar to those in some glassy or cryptocrystalline chondrules [9]. Their sizes vary between 1-18 µm with an average of 6 µm for the objects identified in MET 00526 and between 2 to 30 µm (mean size ~10 µm) in Semarkona. They occur distributed randomly throughout the matrix in each in thin sections studied and, generally, they are observed as isolated spherules. However, several of them were found in clusters consisting of no more than three spherules. Several spherules present evidence of aqueous alteration such as a FeO-rich fibrous material on their rims. SEM observations suggest that most of the objects studied contain a significant number of vesicles distributed throughout the entire spherule or just within a zone around the edge of the spherule. The size of the largest vesicle in each spherule varies between 0.3-3 µm. Generally, the vesicles are spherical in the SEM images with a few exceptions.

Bright- and dark-field TEM images of the FIB sections (Fig. 2) show that the spherules have sharp boundaries with the matrix. The dominant constituent of all the spherical objects studied so far by TEM is glass with atomic Mg+Fe/Si ratios that vary between 0.4-0.6. The glass is FeO-rich and contains important amounts of other elements such as Na_2O and Al_2O_3 (Table 1). No evidence of chemical zoning was observed in the spherules analyzed.

TEM and STEM observations show that the vesicles have irregular morphologies (Fig. 2c-e). The size of the vesicles (a few nm to 900 nm) is not related to the size of the object. For example, an object 9.2 µm in diameter contains vesicles up to 800 nm in size, whereas a smaller object (3.8 µm) contains larger vesicles up to 300 x 900 nm in size (Fig. 2b). All the three analyzed spherules contain several elongated vesicles which have the same irregular morphologies as the more rounded ones. The size of the vesicles observed in the analyzed spherules appears to decrease progressively from the interior to the exterior.

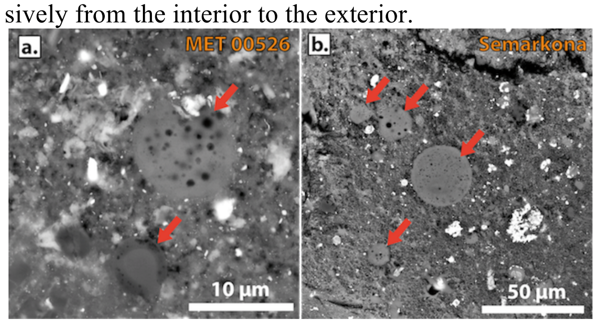

Figure 1. BSE images of the spherical objects (red arrows) identified in the fine-grained matrix of MET 00526 (a) and Semarkona (b). These objects are characterized by the presence of vesicles on the spherule rims (a – bottom arrow) or through the entire spherule (a – top arrow).

TEM studies show the presence of other minor minerals in the fine-grained matrix adjacent to the spherules such as merrilite, chromite, troilite ($Fe_{45-47}Ni_{0-1}S_{53-54}$), low-Ca pyroxene ($En_{48-98}$), ferroan olivine ($Fo_{20}$ to Fo_{39}) and Fe,Ni metal ($Fe_{94-100}Ni_{0-6}$). One microspherule is in contact with refractory minerals, consisting of two spinels and one hibonite grain. All these minerals were identified using quantitative EDS analysis and electron diffraction.

Discussion: We have identified several glassy vesiculated spherules in the fine-grained matrix of two UOCs. Their shape and size are reminiscent of microchondules. However, despite the similarity in size between the two types of objects, microchondrules are characterized by different textures and chemical compositions. Microchondrules are typically low-FeO

($Fs_{1-22}Wo_{0.9-52}$, $Fa_{0.5}$) objects or rarely contain high-FeO olivine (Fa_{58}) microphenocrysts [5]. All microchondrules described to date contain euhedral or anhedral minerals embedded in mesostasis glass and contain no vesicles. The chemical composition of microchondrule mesostasis is different (high Al_2O_3 and MgO and low FeO and CaO) [5] from the composition of the glassy vesiculated spherules analyzed in the fine-grained matrix of MET 00256.

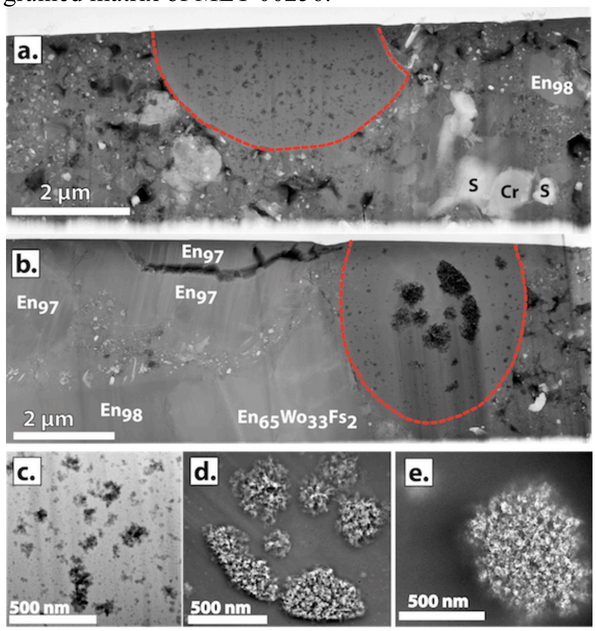

Figure 2. Dark- (a-c) and bright-field (d-e) TEM images of two FIB sections of MET 00526 (a – C24; b – C31). a-b) The red dashed lines show the sharp boundaries between the glassy vesiculated spherules and the matrix. c-e) The morphology of vesicles. Minor phases identified in the FIB sections: S = low-Ni sulfides, Cr = chromite, En = low-Ca pyroxene and EnWoFs = high-Ca pyroxene.

The glassy texture and spherical morphology of these objects indicates that they were once molten droplets. The presence of vesicles also strongly supports this conclusion and suggests that degassing occurred during the melting episode. The observed zonation in the size of the vesicles provides evidence that volatile loss occurred preferentially on the exterior of the spherules, resulting in smaller vesicles. However, more limited loss on the interior of the object allowed larger vesicles to form. The high Na contents of the glass indicates that the precursors of these objects were volatile-rich, so the vesicles may have formed by loss of Na or other volatile elements during melting. The fact that such small objects only underwent partial degassing and were quenched to a glass indicates exceptionally fast heating and cooling rates.

To understand if these melt droplets were formed by collisions between partially molten chondrules, we compared their chemical compositions with chondrule mesostasis glass. The major and minor element compositions of glass-rich chondrules are generally similar [10] to the bulk compositions of the glassy spherules in MET 00526, except for the higher amounts of FeO in the spherules (19.4-21.5 wt% FeO *cf.* <0.7-9 wt% FeO in glass-rich chondrules) and lower amounts of Al_2O_3 (6.4-7.6 wt% Al_2O_3 *cf.* 13-30 wt% Al_2O_3 in glass-rich chondrules). Moreover, the bulk compositions of FeO-rich type II chondrules in MET 00526 [11] are also quite different from the glassy vesiculated spherules (high Na_2O, Al_2O_3 and SiO_2 and low MgO). Mesostasis in type II chondrules in MET 00526 is also compositionally distinct from the spherules (Table 1) [1].

	N	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO
C29	5	6.5	9.8	7.6	54.5	0.7	1.3	19.5
C24	15	4.6	7.3	7.4	58.6	0.5	1.6	19.9
C31	4	4.1	8.2	6.4	58.0	0.5	1.3	21.5
Mes*	20	7.9	1.8	14.2	66.3	1.1	2.0	6.7

Table 1. Concentration of major and minor elements (in wt% oxide) determined by EDS measurements in three glassy vesiculated spherules (C24, C29 and C31) from MET 00526 (*N* = number of analyses) and the average compositions of mesostases (Mes*) in randomly selected type II chondrules of MET 00526 [1]. The spherules are compositionally distinct from known chondrule compositions.

Conclusion: We identified a number of glassy vesiculated spherules in the matrix of UOCs, MET 00526 and Semarkona. Their distinct texture and chemical compositions suggest that they have been formed by melting of volatile-rich precursor materials during heating events in the solar nebula and hence appear to represent a distinct type of microchondrule. The presence of abundant submicron vesicles in these microchondrule-like spherules indicates that these events were so rapid that only partial loss of volatiles occurred. This suggests that both heating and cooling of the microchondrule-like spherules must have been extremely rapid.

References: [1] Grossman J.N. and Brearley A.J. (2005) *Meteorit. Planet. Sci.* **40**, 87. [2] Berlin J., *et al.* (2011) *Meteorit. Planet. Sci.* **46**(4), 513-533. [3] Righter K. (2007) *Antarctic Meteorite Newsletter* **30**, 1-4. [4] Krot A.N., *et al.* (1996) in *Chondrules and the Protoplanetary Disk*, Cambridge p. 181-186. [5] Krot A.N., *et al.* (1997) *Geochim. Cosmochim. Acta* **61**, 463-473. [6] Michel-Levy M.C. (1988) *Meteorit. Planet. Sci.* **23**, 45-48. [7] Rubin A.E., *et al.* (1982) *Geochim. Cosmochim. Acta* **46**, 1763-1776. [8] Rubin A.E. (1989) *Meteorit. Planet. Sci.* **24**, 191-192. [9] Krot A.N., *et al.* (2002) *Meteorit. Planet. Sci.* **37**, 1451-1490. [10] Nehru C.E., *et al.*, (2008) *Lunar Planet. Sci.*, 1697. [11] Berlin J. (2009) *Ph.D. thesis,* University of New Mexico, Albuquerque, New Mexico.

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