Abstract—Cosmic spherules are unique igneous objects that form by melting due to gas drag heating during atmospheric entry heating. Vesicles are an important component of many cosmic spherules since they suggest their precursors had finite volatile contents. Vesicle abundances in spherules decrease through the series porphyritic, glassy, barred, to cryptocrystalline spherules. Anomalous hollow spherules, with large off-center vesicles occur in both porphyritic and glassy spheres. Numerical simulation of the dynamic behavior of vesicles during atmospheric flight is presented that indicates vesicles rapidly migrate due to deceleration and separate from nonporphyritic particles. Modest rotation rates of tens of radians s\(^{-1}\) are, however, sufficient to impede loss of vesicles and may explain the presence of small solitary vesicles in barred, cryptocrystalline and glassy spherules. Rapid rotation at spin rates of several thousand radians s\(^{-1}\) are required to concentrate vesicles at the rotational axis and leads to rapid growth by coalescence and either separation or retention depending on the orientation of the rotational axis. Complex rapid rotations that concentrate vesicles in the core of particles are proposed as a mechanism for the formation of hollow spherules. High vesicle contents in porphyritic spherules suggest volatile-rich precursors; however, calculation of volatile retention indicates these have lost >99.9% of volatiles to degassing prior to melting. The formation of hollow spherules, by rapid spin, necessarily implies preatmospheric rotations of several thousand radians s\(^{-1}\). These particles are suggested to represent immature dust, recently released from parent bodies, in which rotations have not been slowed by magnetic damping.

INTRODUCTION

Micrometeorites (MMs) are interplanetary dust particles <2 mm that have survived atmospheric entry to be recovered from the Earth’s surface (Genge et al. 2008). Large numbers of MMs have been collected from Antarctic ice and traps (Maurette et al. 1991; Taylor et al. 2000; Duprat et al. 2007; Rochette et al. 2008) and deep sea sediments (Brownlee 1985; Prasad et al. 2013).

Micrometeorites are not, however, pristine samples of extraterrestrial materials since they experience heating during their atmospheric entry. The heating of particles is dependent on their dynamic behavior since high velocities and high entry angles result in increased heating (Love and Brownlee 1991). Many particles experience partial melting to produce highly vesicular scoriaceous MMs, while a significant proportion (50% in the 50–100 µm size range) almost entirely melt to produce cosmic spherules (Genge et al. 2008). These particles are interesting since higher velocity dust surviving accretion to the Earth is most likely to be preserved as cosmic spherules. Evaluating the origins of cosmic spherules, however, is difficult since their extensive melting has removed most of the pre-existing minerals. Studies of the compositions of cosmic spherules have, however, suggested the majority are derived from primitive materials similar to carbonaceous and ordinary chondrites, with a rare contribution from differentiated, basaltic, parent bodies (Kurat et al. 1994; Genge et al. 1997; Taylor et al. 2007; Cordier et al. 2011a, 2011b; Suavet et al. 2011b). Micrometeorites that survive atmospheric entry without significant heating may also represent the direct precursor materials of many cosmic spherules since a proportion of particles in any population incident on
the Earth undergoes minimal heating at low entry angles. The majority of unmelted MMs are either fine-grained MMs, dominated by phyllosilicates and having affinities to CI, CM2, and CR2 chondrites, or coarse-grained MMs, which are igneous objects dominated by olivine, pyroxene, and glass and mostly thought to represent chondrule fragments (Kurat et al. 1994; Genge et al. 1997, 2005, 2008; Genge 2008).

Cosmic spherules can be subdivided on the basis of texture and mineralogy into porphyritic olivine spherules, dominated by equant phenocrysts of olivine; barred olivine spherules, dominated by parallel growth olivine; cryptocrystalline spherules, dominated by olivine dendrites; and glassy spherules that lack crystals (Fig. 1; Taylor and Brownlee 1991; Genge et al. 2008). These textural varieties are thought to largely relate to increasing peak temperature in the order porphyritic olivine, barred olivine, cryptocrystalline to glassy spherules (Taylor and Brownlee 1991); however, differences in texture due to precursor materials are also likely to occur.

Vesicles have been described previously in cosmic spherules and are most common within porphyritic olivine spherules heated to the lowest, subliquidus, temperatures (Taylor et al. 2000; Genge et al. 2008), and are less frequent within supraliquidus barred olivine, cryptocrystalline, and glassy spherules. The presence of vesicles is significant since it may suggest that their host spherules had volatile-rich precursors. Dynamic forces experienced during entry heating, however, will cause migration and separation of vesicles and their abundance, therefore, will not reflect their original volatile contents but the details of their atmospheric entry. The significance of vesicles in cosmic spherules for the volatile contents of precursors and their behavior during atmospheric flight are examined in this paper through observations on vesicle distributions and numerical simulations on the dynamics of vesicles during atmospheric entry heating.

**SAMPLES AND METHODS**

**Cosmic Spherules**

The spherules reported here were collected by melting and filtering of Antarctic blue ice at Cap Prudhomme, Antarctica, by M. Maurette and coworkers (Maurette et al. 1991). Micrometeorites were separated from dry batches of filtered, ice-derived particles and confirmed as extraterrestrial following
protocols described in Genge et al. (2008). One hundred and ninety-six cosmic spherules were examined by scanning electron microscopy on polished samples and their vesicle abundances determined in the plane of section. Due to the small number of vesicles in any particular spherule size distribution functions could not be determined, thus no correction can be applied for the plane of section. Observations made on cosmic spherules are, therefore, largely qualitative and numerical estimates are provided merely as a guide to general differences in vesicle abundances and sizes but are associated with large errors. Where possible secondary electron images of the outer surface of particles were examined to evaluate whether vesicles were present out of the plane of section.

The compositions of spherules were determined by energy dispersive spectroscopy (EDS) using a Zeiss EVO analytical scanning electron microscope at a beam current of 3 nA and an accelerating voltage of 20 kV in the Imaging and Analysis Centre of the Natural History Museum. Bulk analyses were obtained over rastered areas ~20 x 20 μm in size except for glassy V-type (vitreous) spherules, which were analyzed using a 4 μm spot. Compositions of ~50% of spherules were obtained by wave dispersive spectroscopy using a Cameca SX100 by averaging 5–10 wide beam (10 μm) analyses. Compositions were obtained against mineral standards and standard matrix corrections were applied. Analytical uncertainties are ~0.2 wt% for EDS and 0.05 wt% for WDS.

### Numerical Methods

To quantify the effects of deceleration on vesicle migration in MMAs a numerical model of atmospheric entry heating was constructed following the method of Love and Brownlee (1991). This model includes the effects of evaporation on particle size and the dynamic behavior of particles during atmospheric entry. It utilizes the US Standard Atmosphere 1976 model for atmospheric density and takes into account size changes in evaporation of particles using the Langmuir equation. For details of the entry heating model refer to Love and Brownlee (1991).

The motion of vesicles of different sizes during atmospheric entry were followed by numerical integration of their equation of motion (Equation 1), where \( a \) is the deceleration derived from the entry heating model, \( \eta \) is the viscosity, \( R \) is the radius of the vesicle, and \( \rho_m \) is melt density. Stokes law was used to calculate vesicle velocity and the calculation thus assumes the vesicle travels at terminal velocity. This is likely to be a good approximation due to the low velocities predicted and allows the density of the gas phase to be ignored.

\[
\frac{\partial x}{\partial t} = \frac{2\rho_m a R^2}{9\eta}
\]  

(1)

Both viscosity and melt density are a function of temperature, and thus time, during deceleration, and must be calculated separately. A melt density model was constructed using an S-type spherule composition derived from Cordier et al. (2011b) for an ordinary chondrite-like S-type spherule (Table 1). This composition is used since cosmic spherules are small samples that do not have the same bulk composition of macroscopic samples. Approximately 50% of large cosmic spherules (>200 μm) have been shown to have ordinary chondrite-like precursors (Cordier et al. 2011a), while the remainder are probably derived mainly from precursors similar to carbonaceous chondrites (Genge et al. 1997). Among smaller particles, carbonaceous chondrite precursors dominated (Taylor et al. 2011b). Only small differences in viscosity and density are likely between melts of carbonaceous and ordinary chondrites and the chosen composition is suggested to be broadly appropriate for all cosmic spherules. In porphyritic spherules, precursor materials experience partial melting, and thus density changes, during heating, the equilibrium melting behavior of this composition was modeled using the MELTS code (Ghiorso and Sack 1995; Asimow and Ghiorso 1998) to determine phase abundances and compositions. Although equilibrium is unlikely to be attained during rapid heating, single-phase melting temperatures diverge little from equilibrium behavior even at very high heating rates (Ubbelohde 1978). The main difference between the equilibrium predictions and behavior at high heating rates will be in phase compositions that can be dependent on diffusive exchange. Melt and particle density were calculated from phase compositions and abundances using the DENSICAL code (Niu and Batiza 1991) and mass balance considerations. The phase abundances, particle density and melt density with temperature are shown in Fig. 1.

### Table 1. Showing composition used for simulation particles after (Cordier et al. 2011a).

| Comp   | Weight % |
|--------|----------|
| SiO₂   | 39.53    |
| TiO₂   | 0.13     |
| Cr₂O₃  | 0.50     |
| Al₂O₃  | 2.73     |
| FeO    | 26.38    |
| MnO    | 0.32     |
| MgO    | 27.98    |
| CaO    | 2.04     |
| Na₂O   | 0.40     |
| Total  | 100.0    |
Melt viscosity was calculated from liquid compositions derived from the thermodynamic modeling using the formulation of Giordano et al. (2008) for silicate magmas. The viscosity of crystal-melt mixtures at subsolidus temperatures was evaluated using the Einstein-Roscoe relation (Equation 2; Einstein 1906; Roscoe 1952) from the volume fraction of crystals $\phi$ and using a threshold parameter $\omega = 0.6$. Crystal content causes significant increases in the effective viscosity. The viscosity-temperature profile for the model particle composition is shown in Fig. 1.

$$\eta_{\text{eff}} = \eta \left(1 - \frac{\phi}{\omega}\right)^{-2.5}$$  

(Vesicle migration to the trailing face of particles was calculated as distance travelled over the suprasolidus proportion of flight for particles with the deceleration calculated at each time step used to evaluate the velocity of vesicles of different sizes.)

Centrifugal forces on vesicles during rotation will also influence their dynamics. The motion of a vesicle in a rotating particle will principally occur due to the outwards increase in pressure in the liquid due to centrifugal forces resulting in migration of the vesicle toward the center of the particle. Genge and Grady (1998) gives the acceleration of a droplet/vesicle of radius $R$ in terms of radial distance from the rotational axis $r$, due to centrifugal force as:

$$\frac{\partial r}{\partial t} = \frac{2\rho_\text{m} \omega^2 R^2 r}{9\eta}$$  

(Again gas density can be assumed to be negligible in comparison to melt density. Since the inwards acceleration is dependent on the distance from the rotational axis $r$, an initial position at half the particle radius is assumed in these calculations. The change in melt viscosity with peak temperature attained by MMs is thus the only important factor. The angular velocity is assumed to be constant.)

The equations of motion and heating of particles, and the equations of motion for vesicles were evaluated using the Runge-Kutta 4th order method for numerical integration. A time step was chosen such that temperature changes by less than 5% in a single timestep. Typical timesteps varied between 0.1 to 0.005 secs and simulations were achieved in 500 to 5000 timesteps. Repeat simulations with different timesteps indicate variation of peak temperature by less than 2%. Peak temperature calculated from the simulations is consistent with those of Love and Brownlee (1991) to within 2% with differences largely due to the change in particle density on melting. No volume increase was assumed to occur on melting due to vesiculation since the aim of the simulations was to investigate the behavior of individual vesicles rather than the effect of vesicle exsolution on peak temperatures.

The main uncertainties in the model involve minor differences in compositions and thus physical properties such as viscosity both between different cosmic spherules and as a result of nonequilibrium behavior during melting. Variation in spherule compositions certainly occurs; however, most are broadly chondritic and physical properties are unlikely to change more than a few percent. Nonequilibrium behavior definitely occurs with the survival of Mg-rich crystals to higher temperatures than predicted by phase relations. There are usually only a small volume (<5 vol%) of these relict crystals (e.g. Genge et al. 1997; Taylor et al. 2000, 2011b), consequently they are unlikely to effect the viscosity or density by more than a few percent. Perhaps the largest divergence from reality, however, is that no consideration of vesicle growth mechanism is included in the model; consequently, no quantitative statements on vesicle volume can be given. The objective of the model is, however, to investigate the dynamic behavior vesicles under deceleration and spin in order to make inferences on their evolution rather than to attempt to predict quantitative abundances that are likely to be subject to large uncertainties.

**RESULTS**

**Vesicles in Cosmic Spherules**

Vesicle abundances within cosmic spherules vary significantly from ~70% by volume to zero (Fig. 2 and Table 2; Taylor et al. 2011a). Vesicles are most abundant within porphyritic olivine spherules and within unusual spherules with off-center large vesicles, termed herein hollow spherules. In porphyritic spherules vesicles occur in 76% of the 71 particles examined and within individual particles often exhibit a wide range of sizes from only a few microns to up to 70% of the radius of the particle. The largest vesicles within porphyritic spherules form hollow spherules described in more detail below. No significant correlation was observed between vesicle and mineral abundance in porphyritic spherules with vesicles in magnetite-rich (>5% volume magnetite), magnetite-poor (<5%), and relict-bearing (generally forsteritic olivine) particles within uncertainty of the average for porphyritic spherules. Differences in vesicle occurrence, however, are observed with texture in porphyritic spherules. All particles with small olivine crystals (<2% of particle radius), termed micro-Po spherules, contained vesicles (Fig. 2a), while 65% (out of 18) of spherules dominated
by coarse equant olivine, and 16% of those with skeletal olivines contained vesicles (Fig. 2b). Particles with skeletal olivine are also often glass-rich (>40% glass with iron-oxide dendrites).

Eleven porphyritic spherules with metal droplets, or their ferrihydrite weathering residues, were observed in the current study of which five contained vesicles (Fig. 2c). In these particles, vesicles vary widely in abundance up to 30 vol% and are distributed throughout the spherules. In two particles a broad increase in size of vesicle was observed from the metal droplet toward the opposite side of the particle (Fig. 2c). Previous studies have shown that vesicles in barred and cryptocrystalline spherules with metal droplets that vesicles, when present, are often located close to the surface on the opposite side of the particle to the metal droplet (Genge and Grady 1998; Suavet et al. 2011a). Such spherules often have long axes that pass through both the metal droplet and vesicle.

Vesicles are significantly less abundant among barred olivine spherules (12% out of 32 particles) and among cryptocrystalline spherules (6% out of 47 particles). In general vesicles within these particles are <5% of particle radii, although in three particles vesicles ~20% of particle radii were observed. In particles with
elongate aspect ratios vesicles are generally present close to the surface at one end of the particle (Figs. 2d and 2e).

In glassy spherules, vesicles occur in 32% (out of 28 particles) of the studied particles and occur as either small voids (<5% of particle radii) close to the surface (Fig. 1f), or as hollow spherules with large vesicles. Hollow spherules comprise five of the observed nine vesicle-bearing glassy spherules.

Hollow spherules include both porphyritic (Figs. 2h, 2i) and glassy V-type spherules (Fig. 2g) and typically comprise a large central off-center vesicle comprising >50% by volume of the particle. Often in section these particles have a crescent moon outline due to fragmentation of the meniscus during polished grain mount preparation. Some vesicle-rich particles resemble hollow spherules but have several central vesicles of which the central void is the largest (Fig. 2i).

### Compositions of Cosmic Spherules

All studied cosmic spherules have broadly chondritic compositions (Fig. 3) but exhibit volatility dependent depletions in K, Na, and S, as well as depletions in Fe, Ni, and Cr. Major elements of the spherules (Fig. 4) plot within a field on an Si-Mg-Fe ternary diagram from compositions similar to Mg-rich olivine toward Fe; similar to previously reported cosmic spherules (Kurat et al. 1994; Genge et al. 1997; Cordier et al. 2011b). Fourteen vesicle-rich (>20 vol%) spherules were analyzed including four hollow spherules (CP94-050-004, CP94-050-019, CP94-050-027, and CP94-050-023). Bulk compositions of vesicle-rich spherules plot within the range of vesicle-poor spherules with hollow spherules having both Fe-rich and Mg-poor compositions. The two V-type hollow spherules are both Mg-rich (CP94-050-004 and CP94-050-019), while both porphyritic olivine spherules have Fe-rich compositions. Minor element compositions of vesicle-rich spherules also fall in the range of vesicle-poor spherules.

| Vesicles | Hollow | Total |
|----------|--------|-------|
| Po       | 54     | 71    |
| micro    | 22     | 2     |
| coarse   | 15     | 2     |
| skeletal | 3      | 1     |
| relict   | 4      |       |
| Bo       | 4      | 32    |
| C        | 3      | 47    |
| V        | 9      | 5     |
| I-type   | 3      | 13    |
| G-type   | 1      | 5     |

Table 2. Showing the abundance of cosmic spherules with vesicles by type. The number of vesicle-bearing spherules that are hollow are also shown. Textural subtypes of Po (porphyritic olivine) spherules including micro-, coarse, skeletal, and relict are also given. Abbrev: Bo—barred olivine, C—cryptocrystalline, V—glassy.
The Dynamic Behavior of Vesicles during Atmospheric Deceleration and Rotation

In agreement with expectation, the simulations of vesicle migration due solely to deceleration of particles during atmospheric entry indicate rapid separation of vesicles compared to duration of molten flight except in partially melted particles in which crystal contents result in high effective viscosities (Fig. 5). Vesicle migration distance relative to particle size is a complex function of peak temperature, duration of heating, and deceleration. Comparison of peak temperatures and migration distances in Figs. 5 and 6 show that at low peak temperatures, in particles that are only partially melted, migration distances are primarily controlled by melt viscosity, and thus temperature. In higher temperature supraliquidus particles’ vesicle migration is influenced more by deceleration and to a lesser extent the duration of the heating pulse. The dependence on melt viscosity results in increasing migration with entry velocity, entry angle, and particle size. Small particles with high entry angles, however, experience higher decelerations that drive vesicle separation resulting in a region of large migration distances observed in the 16 km s\(^{-1}\) simulations where peak temperatures are higher and low viscosities allow rapid migration (Fig. 5). Ultimately, vesicle separation is most rapid for high velocity particles entering the atmosphere at high angle. Vesicles are also more likely to separate from large particles at any specific entry parameters, at least at low entry velocity.

Vesicle separation time is strongly dependent on vesicle size. Vesicles 10 \(\mu\)m in radius separate a factor of \(\sim 4\) faster than 5 \(\mu\)m radii vesicles and are thus removed more rapidly from spherules. Large vesicles are, thus, likely to be lost even from subsolidus porphyritic spherules if the abundance of crystals is \(< 40\ \text{vol}\%\). Vesicle growth will, therefore, rapidly deplete spherules of vesicles by migration to the trailing face in oriented particles.

Figure 7 shows the migration distances of vesicles within particles rotating at different constant angular velocities. The simulations indicate that migration to the rotational axis over the duration of molten flight requires rotation rates of several thousand radians s\(^{-1}\). Migration distances are also larger at higher entry velocities and entry angles due to peak temperature, and thus melt viscosity, but are influenced by the duration of melting and particle size, which decreases due to evaporation. Vesicle size is also important with large vesicles migrating more rapidly to the rotational axis.

**DISCUSSION**

**Vesicle Separation Mechanisms**

The numerical simulations indicate that vesicles separate rapidly from spherules during deceleration...
except in particles heated to subliquidus temperatures, which are likely to form porphyritic spherules on cooling; explaining the much higher abundance of vesicles in such particles (Table 2). The dependence of migration on vesicle size, however, suggests that vesicles >5 \( \mu m \) radius will separate even from porphyritic spherules during flight. For scoriaceous micrometeorites, formed by <50% partial melting (Genge et al. 1997), no migration occurs owing to their high viscosities.

Migration distances of vesicles in suprasolidus particles, thought to form barred olivine, cryptocrystalline, and glassy spherules on cooling, are significantly larger than particle sizes over the duration of molten flight and should result in the complete removal of vesicles. Migration distances, and thus the potential for vesicle escape, are most dependent on peak temperature.

Observations of vesicle abundance within spherules are broadly consistent with the numerical simulation of the separation of vesicles due to deceleration since they show decreasing vesicle occurrence from porphyritic to barred to cryptocrystalline spheres, in agreement with the inferred increasing peak temperatures at which these particles are thought to form. The textures of these spherules have been interpreted to relate to increasing destruction of crystal nuclei during heating due to increasing peak temperature and increased supercooling during crystallization (Taylor and Brownlee 1991). Glassy spherules, however, which would be expected to have the highest peak temperatures on the basis of their low crystallization nuclei, exhibit a higher vesicle occurrence than either barred or cryptocrystalline spherules, a feature previously noted by Taylor et al. (2011a), although the majority of these particles are anomalous hollow spherules. Contrary to the predictions of the numerical simulations, supraliquidus spherules contain finite abundances of small vesicles that should have separated due to deceleration.

Retention of Vesicles Due to Low Spin Rates

Simulations of the migration of vesicles due to spin indicates that high rotation rates of several thousand radian s\(^{-1}\) will concentrate vesicles toward the rotational axis. In most porphyritic spherules no obvious concentration of vesicles occurs toward the median in most particles to suggest that rapid spin is responsible for vesicle retention. However, even modest spin rates of a few tens to hundreds of radians s\(^{-1}\) is capable of slowing migration by deceleration, depending on the orientation of the rotational axis, due to the change in migration direction. Particles with rotational axes exactly perpendicular to the direction of flight, for example, will impede separation of most vesicles since they will oscillate around their mean positions (Fig. 8).
Rotational axes oblique to the direction of flight will also impede vesicle migration due to the change in migration direction; however, a component of the deceleration will still cause net vesicle migration and separation along the rotational axis, albeit on longer timescales.

The orientation of spin axes of cosmic dust particles during atmospheric flight is highly uncertain. Some particles with metal beads and vesicles located at either end of an elongate particle have been shown by studies of remnant magnetism to have been oriented during atmospheric flight with metal bead migration occurring to the leading face and vesicles to the trailing face (Suavet et al. 2011a). These particles are either not rotating, or more likely, have rotational axes oriented in the direction of flight. Only a small number (~10%) of such particles with evidence for flight orientation exist. If the orientation of rotational axes is random then a proportion of particles can be assumed to spin on axes oblique to the direction of motion. Such particles could
explain the retention of small vesicles within supraliquidus spherules and, potentially, large vesicles in porphyritic spherules.

**Influence of Vesicle Growth Mechanisms**

The numerical simulations of vesicle migration presented here assume a fixed vesicle size throughout the molten portion of flight; however, vesicle nucleation and growth is likely to be important in their migration and separation. The nucleation of vesicles in heated cosmic dust depends on the origin of the volatiles. Taylor et al. (2011a) have suggested that devolatilization of sulfides is the principal mechanism by which vesicles form and would imply continual production of vesicles from sulfides during molten flight until the latter are depleted. In this study, however, vesicle abundances within particles with metal-sulfide beads is less than the average value for porphyritic spherules. No significant difference is observed between the compositions of vesicle-rich and hollow spherules, compared to the overall range of cosmic spherule compositions (Figs. 3 and 4), that would suggest these have appreciably different precursors. Iron enrichment of the silicate portions of cosmic spherules by decomposition and oxidation of iron sulfides as suggested by Taylor et al. (2011a) is also not observed, although this does not necessarily preclude the formation of vesicles from sulfides. The spatial association of sulfides with vesicles observed by Taylor et al. (2011a) indeed is compelling evidence that at least a proportion of vesicles are derived by this mechanism.

Fine-grained MMs represent one possible precursor material to cosmic spherules and contain phyllosilicates and carbonaceous materials that are a potential source of volatiles for vesicles formed on heating. Devolatilization of phyllosilicates and carbonaceous materials, however, largely occurs at subsolidus temperatures (<700 °C). The dynamics of gas release from porous fine-grained particles during heating may nevertheless allow trapping of volatile-bearing gases during partial melting. Igneous rims that form an outer melted layer on volatile-rich particles, due to temperature gradients by endothermic decomposition

![Fig. 9. Showing backscattered electron images of micrometeorites heated to lower peak temperatures than cosmic spherules. Showing (a) an unmelted fine-grained MM with a vesicular igneous rim (black arrow), (b) a scoriaceous MM with abundant vesicles, (c) a coarse-grained MM dominated by olivine and pyroxene phenocrysts and a glassy vesicular mesostasis, and (d) a coarse-grained MM with an attached selvage of fine-grained matrix around its exterior.](image-url)
reactions (Genge 2006), may also act to enhance gas retention by sealing particles during the melting process (Fig. 9a). Evidence for direct trapping of volatile species released by phyllosilicates and carbonaceous materials is observed in the vesicle-rich nature of scoriaceous MMs (Fig. 9b) that contain up to 70 vol% vesicles. Furthermore, several fine-grained (micro-)porphyritic olivine hollow spherules are observed in the current study (Fig. 2h). Microporphyritic spherules have been suggested by Van Ginneken et al. (2015) to form by melting of fine-grained, carbonaceous chondrite-like matrix and support the generation of volatiles by decomposition of phyllosilicates and organics. In the case of gas trapping by melt the existence of vesicles from the onset of cosmic spherule formation, as assumed in the current simulations, is perhaps a reasonable assumption.

Growth of vesicles by exsolution of volatiles from the melt is a further possible mechanism for vesicle formation in spherules; however, given the short duration of the heating pulse (1-10 secs) and the diffusion dependent growth of vesicles (Sparks 1978), such a mechanism is likely to be relatively unimportant. Similarly growth of vesicles by Ostwald ripening is unlikely to be kinetically impeded by diffusion rates.

Growth of vesicles in cosmic spherules, however, is likely to occur due to vesicle interaction by coalescence. Differences in the migration velocities of vesicles due to initial size will ensure that larger vesicles capture smaller vesicles in their path resulting in increases in vesicle size. The resulting large vesicles will more rapidly be removed from particles by deceleration. Spin may also play an important role in vesicle growth by coalescence since the concentration of vesicles toward the rotational axis is likely to result in interactions and growth. If larger vesicles become concentrated toward the rotational axis they will be rapidly removed by deceleration if the rotational axis has a small angle to the direction of flight (Fig. 10).

**Formation of Hollow Spherules**

Hollow spherules with large off-center vesicles are anomalous since the retention of such large vesicles is contrary to their rapid migration during deceleration, in particular due to the occurrence of glassy hollow spherules which should have experienced high peak temperatures and had low melt viscosities. The occurrence of hollow spherules as porphyritic and glassy V-type particles, without barred olivine or cryptocrystalline examples, is also problematic since these form at lower peak temperatures than V-type particles and are more likely to retain vesicles.

Simulations of the migration of vesicles due to rapid spin indicate that vesicles can be concentrated to the rotational axis by spin rates of several thousand radian s⁻¹ which, as discussed above, can impede vesicle separation if the orientation of the rotational axis is oblique to the direction of flight. Concentration of vesicles in the core of particles may be the result of vesicle coalescence since the median line of the particle, perpendicular to the rotational axis, provides the most opportunity for growth of vesicles by interactions (Figs. 8a, 8b). Complex rotation, in which a rotational axis oblique to the direction of flight precesses rapidly around an axis parallel to the direction of flight, however, may be required to concentrate and maintain such large vesicles close to the center of the particle.

The occurrence of glassy hollow spherules is consistent with concentration of vesicles at the rotational axis since simulations indicate this process is most effective for high peak temperature particles with low melt viscosity. The relative efficiency of spin, in concentrating vesicles to the rotational axis, compared with deceleration, in separating vesicles to the trailing face of particles may also explain why hollow spherules include porphyritic and glassy spheres, but not barred and cryptocrystalline. In porphyritic spherules, removal of vesicles by deceleration is less efficient due to low viscosity and during migration by spin vesicle interactions may result in coalescence and growth of a large vesicle, while in lower viscosity barred and cryptocrystalline spherules separation by deceleration is
sufficiently efficient to remove vesicles concentrated at the rotational axis.

An alternative explanation for the formation of hollow spherules is difficult to postulate; however, the growth of vesicles from a volatile-bearing grain, such as a sulfide melt droplet, at a late stage during molten flight is a possibility. Observations that metal and sulfide rapidly separate to the leading face of particles, however, suggests such a scenario is unrealistic.

**IMPLICATIONS**

**Vesicles as Indicators of Precursor Volatile Content**

The presence of vesicles in cosmic spherules could be interpreted as an indicator that the precursor materials contained volatile-rich materials such as phyllosilicates and/or carbonaceous materials and were, therefore, broadly similar to fine-grained MMNs. Similarly the absence of vesicles could be interpreted to indicate volatile-poor precursors similar to coarse-grained MMNs.

The rapid separation of vesicles from all but porphyritic spherules, shown by the simulations, suggest that an absence of vesicles in barred, cryptocrystalline or glassy spherules does not imply a volatile-poor precursor, but could arise by vesicle separation. The absence of vesicles in porphyritic spherules, however, may be more significant. Observations that fine-grained (micro) porphyritic spherules all contain vesicles imply these do have volatile-bearing precursors. In contrast, porphyritic spherules with skeletal olivines and glassy matrices might form by melting of volatile-poor coarse-grained precursors, or alternatively could have formed by near complete melting at almost liquidus temperatures resulting in loss of vesicles. The morphology of the olivines in skeletal spherules is consistent with large supercooling suggesting a paucity of crystallization nuclei; however, this could arise due to high temperature or perhaps by melting of a coarse-grained precursor. The presence of sparse vesicles in 16% of spherules with skeletal olivines additionally probably cannot be taken as evidence for a volatile-bearing origin since vesicles are observed within the glassy mesostases of coarse-grained MMNs (Fig. 9c) and these particles can have selvages of fine-grained, volatile-bearing matrix attached to their exteriors (Fig. 9d), and can also contain sulfides which could produce vesicles. Despite these complexities, it is clear that vesicle-poor textural groups of porphyritic spherule have implications either for their peak temperature, or the nature of their precursors. Study of the composition of such spherules, in particular the Ni-contents of their olivines, as shown by Cordier et al. (2011a), together with vesicle contents should allow these two possibilities to be discriminated.

If vesicle-rich, fine-grained porphyritic spherules are assumed to have formed from volatile-bearing precursors similar to fine-grained MMNs, then the proportion of volatiles retained in vesicles compared to that lost to degassing can be estimated. The mass of gas within vesicles can be approximated from their internal pressure and an equation of state for the gas at the temperature at which vesicle size becomes constant. The overpressure within a vesicle can be calculated from the surface tension of the silicate magma (0.35 N m⁻¹ after Walker and Mullins 1981), and the size of the vesicle from the Young–Laplace equation (Equation 4) for a spherical vesicle or droplet, where γ is the surface tension and R the radius of the vesicle. The pressure within the melt in the cosmic spherule also can be calculated from this equation. The mass of gas within vesicles of different sizes compared with total particle mass for pure H₂O, CO₂, and SO₂ vapor is shown in Fig. 11. The ideal gas law was used to calculate the mass of gas contained in vesicles at a trapping temperature of 1000 °C. Given the uncertainties involved in this calculation use of more sophisticated equations of state for the gases is not necessary. The masses calculated, even for large vesicles comprising most of the particles are less than 0.1 wt% of the particles, and are, therefore, more than three orders of magnitude smaller than typical volatile contents within CM2 chondrites. Clearly although vesicles retain volatiles from the precursor particle either the majority of volatiles are lost by degassing at subsolidus temperatures, indicating that gas trapping is a highly inefficient process, or particles were initially volatile-poor.
Role of Vesicles in Fractionation of Nonvolatile Elements

Vesicle migration may play a role in fractionation of nonvolatile elements due to physical interaction with other phases. Genge and Grady (1998) suggested that vesicles can transport metal-sulfide melts by meniscus attachment resulting in removal of sulfide during vesicle separation. Cordier et al. (2011b) have also suggested that solid grains, such as chromite, may be removed from spherules by the same mechanism. The fractionation of nonvolatile elements through the separation of vesicles from spherules provides a unique mechanism for compositional changes during entry heating that will depend on the volatile content of the precursor particle.

The Origin of Cosmic Dust Spin

Spin of cosmic dust particles during entry heating is an important factor in the dynamics of vesicles during atmospheric heating. Spin can impede separation of vesicles through change in their migration direction if the rotational axis is at a high angle to the direction of flight. High spin rates can concentrate vesicles toward the rotation axis, and thus median of spherules. If rotational axes are at a low angle to the direction of flight, concentration to the rotational axis, and growth by coalescence, leads to rapid separation of vesicles due to deceleration. Conversely, rapid spin around rotational axes at oblique angles to the direction of flight may lead to the formation of hollow spherules, in particular if complex rotation occurs with precession of the rotational axis. The origin of spin of cosmic dust particles is, therefore, an important factor in the nature of vesicle distributions.

Particle spin-up necessarily implies a net torque which consequently must occur prior to the formation of a symmetric spherule by melting. Spin-up of asymmetric particles due to collisions of air molecules is a highly likely scenario in the early stages of atmospheric entry prior to melting. Experimental results on asymmetric particles settling in fluids suggest that spin-up leads to rotational axes that become stabilized oriented in the direction of motion (Weinberger 1972). Such flight parallel spin axes are probably responsible for the formation of flight-oriented particles.

Spin axes oriented obliquely to the direction of flight are highly unlikely to arise due to atmospheric spin-up and are thus probably a preatmospheric feature of cosmic dust. Two main mechanisms exist for the spin-up of dust particles in interplanetary space (1) off-center collisions between dust particles, which are mostly likely to occur shortly after dust production when dust densities are high (Grun et al. 1985), and (2) torques associated with asymmetric particles under solar radiative and corpuscular irradiation (Paddack and Rhee 1976; Lazarian and Hoang 2008). Dust rotation in interplanetary space, however, is damped by interactions with the interplanetary field and induced fields within particles, or surface charges (Horanyi 1996). Dust particles with significant preatmospheric spin during atmospheric entry are likely to generate complex rotations due to atmospheric spin-up if their preatmospheric rotational axes happen to be at a large angle to the direction of flight. Conversely, spherules that are flight oriented are likely to have had negligible preatmospheric spin or spin axes that happened to be at a very small angle to flight direction.

The model presented here for the formation of hollow spherules by rapid complex spin is, therefore, consistent with the expected behavior of dust precursors that had preatmospheric spin rates of several thousand radian s\(^{-1}\). In contrast, the observation that some particles are flight oriented implies negligible preatmospheric spin. Although speculative, the constraints of magnetic damping of dust particle rotation in interplanetary space would imply that dust particles recently released from their parent bodies are more likely to retain rapid spin rates generated during or shortly after dust production. Hollow spherules, therefore, may provide a means of identifying at least a proportion of recently produced interplanetary dust.

CONCLUSIONS

Simulations of vesicle dynamics during entry heating indicate rapid separation of vesicles due to deceleration in particles heated to supraliquidus temperatures. The finite abundances of vesicles within supraliquidus barred olivine, cryptocrystalline, and glassy spherules are attributed to particle spin which can impede vesicle loss given appropriately oriented spin axes. Observations of vesicle contents indicate that even in low temperature porphyritic spherules the majority of the precursor volatile content has been lost by degassing at subsolidus temperatures. Anomalous hollow spherules, observed among porphyritic and glassy spherules, are suggested to form by rapid spin at rotation rates of several thousand radians s\(^{-1}\). Such fast rotations are suggested to be preatmospheric in origin and a feature of recently produced interplanetary dust.
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