



# The Oxygen Isotope Compositions of Large Numbers of Small Cosmic Spherules: Implications for Their Sources and the Isotopic Composition of the Upper Atmosphere

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**Title:**

**The oxygen isotope compositions of large numbers of small cosmic spherules:  
Implications for their sources and the isotopic composition of the upper atmosphere**

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**Key Points:**

- The ranges of different types of cosmic spherules suggest increasing mass fractionation consistent with estimates of peak temperature from textures.
- Porphyritic and barred spherules have derivation of a significant proportion mainly from ordinary and carbonaceous chondrites, respectively.
- G-types have experienced little mass fractionation with oxygen isotope composition similar to carbonaceous chondrite precursors.

## Abstract:

Cosmic spherules are micrometeorites that melt at high altitude as they enter Earth's atmosphere and their oxygen isotope compositions are partially or completely inherited from the upper atmosphere, depending on the heating experienced and the nature of their precursor materials. In this study, the **three oxygen isotope** compositions of 137 **cosmic spherules are** determined using 277 in-situ analyses by ion probe. Particles of each different type of cosmic spherule (scoriaceous, porphyritic, cryptocrystalline, barred, glass, calcium aluminium and titanium (CAT), G-type and I-type) in the diameter range ~52–480  $\mu\text{m}$  were analysed. The results confirm that the **three** oxygen isotope compositions of melted **micrometeorites** reflect a combination of their precursor composition, exchange with the atmosphere and mass fractionation owing to evaporation during entry heating. The data **appear to** reveal an increase in average  $\delta^{18}\text{O}$  values of silicate dominated (S-type) spherules in the series scoriaceous<porphyritic<barred<glass<CAT spherules (~20, 22, 25, 26 and 50‰) that is consistent with the evolution of oxygen isotopes by mass fractionation owing to increased average entry heating. The trend of  $\delta^{17,18}\text{O}$  is broadly parallel to the terrestrial fractionation line and thus suggests mass fractionation dominates changes in isotopic composition, with atmospheric exchange a less significant effect. The  $\Delta^{17}\text{O}$  values of spherules, therefore, are mostly preserved and suggest that ~80% of particles are related to the carbonaceous chondrites (CC) and are probably samples of C-type asteroids. The genetic relationships between different S-types can also be determined with scoriaceous, barred and cryptocrystalline spherules mostly having low  $\Delta^{17}\text{O}$  values ( **$\leq 0\text{‰}$** ) suggesting they are mainly derived from CC-like sources, whilst porphyritic mostly have positive  $\Delta^{17}\text{O}$  ( **$> 0\text{‰}$** ) suggesting they are largely from ordinary chondrite (OC)-like sources related to S(IV)-type asteroids. Glassy and CAT-spherules have  $\Delta^{17}\text{O}$  values suggesting they formed by intense

entry heating of both CC and OC-like materials. I-type cosmic spherules have a narrow range of  $\delta^{17}\text{O}$  (~20–25‰) and  $\delta^{18}\text{O}$  (~38–48‰) values, with  $\Delta^{17}\text{O}$  (~0‰) indicating their oxygen is obtained entirely from the Earth's atmosphere, albeit with significant mass fractionation owing to evaporation during entry heating. The observed range of  $\delta^{18}\text{O}$  with size is suggested here to reflect entry angle with high values representing enhanced heating at high angle. Finally, G-type **cosmic spherules** have unexpected isotopic compositions suggesting little mass-fractionation from a CC-like source and are suggested to have sulphide-silicate precursors with relatively low melting temperatures. The results of this study provide **vital assessment** of the **wider** population of extraterrestrial dust arriving **to the** Earth.

#### Plain Language Summary

**Extraterrestrial dust particles are often intensely heated during atmospheric entry, inducing significant changes of their mineralogy and chemical and isotopic compositions. Such heating processes make difficult to identify the nature of their precursors, and thus the sources of extraterrestrial dust falling on Earth. In this study, we report the oxygen isotope compositions of a large collection of cosmic spherules to assess their sources in the solar system. Previous studies have shown that oxygen isotopes are altered by heating and mixing with the atmosphere, but have yet analysed relatively small numbers of particles. Our results suggest that 80% of particles are related to carbonaceous chondrites, and are thus samples of C-type asteroids, with most of the remainder being related to ordinary chondrites that sample S-type asteroids. We also show, for the first time, that G-type cosmic spherules have a C-type asteroid source. We conclude that oxygen isotopes provide a valuable probe of the sources of extraterrestrial dust despite the changes that occur during atmospheric heating.**

## 1. INTRODUCTION

Micrometeorites are the most abundant extraterrestrial materials reaching the Earth's surface on an annual basis (Love and Brownlee, 1993). Cosmic spherules are **extraterrestrial** particles that undergo significant melting during atmospheric entry and represent **micrometeorites** that have experienced high temperature during **passage through the atmosphere**. Although a large fraction of this material never makes it to Earth's surface **and is evaporates (e.g. Love and Brownlee, 1991), surviving particles still** represent the most significant contributors of **extraterrestrial** material to the Earth's surface (Taylor et al., 1998; Yada et al., 2004; Plane, 2012; Prasad et al., 2013). Micrometeorites provide information on the nature of their **Extraterrestrial** parent bodies, the processes operating during atmospheric entry and the composition of the Earth's atmosphere. Extraterrestrial material that enters the upper atmosphere at >100 km altitude experiences gas drag heating thereby changing their original chemical and isotopic properties (Kurat et al. 1994; Beckerling and Bischoff 1995; Brownlee et al. 1997; Greshake et al. 1998; Engrand et al., 2005; Genge et al., 2008; Cordier et al., 2011; Rudraswami et al., 2012, 2015, 2016). The oxygen isotope compositions of particles that survive atmospheric entry are thus related to those of both their precursors and the upper atmosphere. **Currently, the oxygen isotope composition of the upper atmosphere (i.e. > 60 km) has not been determined yet and any isotopic information above this altitude need to be deciphered from micrometeorites as most of these particles have undergone heating leading to isotopic exchange between ~80 and 120 km (Thiemens et al., 1995; Pack et al., 2017).**

The present study undertakes oxygen isotope analyses of different types of **micrometeorites** in large numbers from partially heated scoriaceous **micrometeorites** to the

most heated **cosmic spherules** is an attempt to constrain the contribution of heating, exchange with atmosphere, and precursor to their isotopic composition. The ideal **cosmic spherules** for deciphering the composition of the upper atmosphere are I (iron) type spherules since all of their oxygen is acquired from the atmosphere (Pack et al., 2017). The analyses of Pack et al., (2017) suggest that it was possible to identify the  $\delta^{17,18}\text{O}$  in the upper atmosphere and concluded it is similar to the troposphere. The current study employs a larger set of I-type **cosmic spherules** to better evaluate their oxygen isotope composition and alteration during atmospheric entry.

**Unmelted micrometeorites and interplanetary dust particles have experienced minimal chemical and isotopic alteration during atmospheric entry, due to high zenith angle and low entry velocity. Hence, they are invaluable witnesses for estimating the pre-atmospheric oxygen isotopic composition of the altered S-type cosmic spherules and scoriaceous micrometeorites.** The mineralogy and bulk chemical compositions of **cosmic spherules** are changed significantly, but previous studies suggest **that** the  $\Delta^{17}\text{O}$  abundance is largely preserved in some significantly altered **cosmic spherules** (Engrand et al., 2005; Yada et al., 2005; Suavet et al., 2010; **Cordier and Folco, 2014**; Rudraswami et al., 2015, 2016; **Goderis et al., 2019**). Here we report the **in-situ** analyses of 277 spots for oxygen isotopes from selected **137 cosmic spherules** of different types (S, I and G-type) using an ion microprobe to outline the variation during atmospheric entry.

## 2. SAMPLE COLLECTION

The **cosmic spherules** are collected from the central Indian Ocean from the depth of ~5200 m using a grab sampler having size 50×50 cm (length × breadth). This grab can

penetrate to a depth of ~15 cm and pick up ~ 45 kg of wet sediments. The details of the sampling methodology have been reported in previous research publications, namely, Rudraswami et al., 2011, 2012; Prasad et al., 2013. Antarctica samples were collected from South Pole Water Well (SPWW), **Amundsen–Scott South Pole Station**, below ~100 m from the snow surface. The well dimension are ~24 m in diameter with water depth of ~15 m with a capacity of ~ 5000 m<sup>3</sup> (Taylor et al., 1998, 2000). In addition, further Antarctica samples were collected near Indian **research station Maitri** by melting blue ice and sieving using ~50 µm mesh. Nearly ~50 tons of blue ice was melted to extract the trapped cosmic dust particles that are expected to exhibit minimal terrestrial alteration (Rudraswami et al. 2018). **The selection of 137 particles were made after investigating ~3000, ~1500, ~2000 cosmic spherules from deep-sea, SPWW, Maitri collection, respectively.** The collected samples were mounted on epoxy **resin** for polishing to be able to use for further electron microscopy and isotopic studies using ion microprobe. Silicate (S) type particles analysed are as follows: scoriaceous (13), porphyritic (11), barred (18), cryptocrystalline (22), glass (37). A further I-type (15), G-type (19) and CAT (Calcium-Aluminium-Titanium, 3) spherules were also measured (Table 1 and Appendix A). Twenty-three spherules with metal bead are reported in Table 2 and Appendix A.

### 3. INSTRUMENTAL TECHNIQUES

Prior to oxygen isotope analyses by ion microprobe, documentation of the texture, chemical composition and type of spherules was performed on polished sections. The scanning electron microscope (SEM, JEOL JSM-IT300LV at National Institute of Oceanography, Goa) was used to recognise the texture and type of spherules, while an electron probe micro analyzer (EPMA, Cameca SX5 at National Institute of Oceanography,



Goa) was used to acquire the major and minor elemental composition. Most **cosmic spherules** are in the size range of less than a few hundred  $\mu\text{m}$  thus the instrument can perform a detailed study of specific areas in particles. **Chemical analyses were performed using electron microprobe on selected cosmic spherules phases with accelerating voltage ~15 kV, ~ beam current ~12 nA, ~1–2  $\mu\text{m}$  beam diameter for spot analyses, and ~5  $\mu\text{m}$  beam diameter for bulk analyses (Rudraswami et al., 2019). Multiple measurements obtained using different standards are < 1% error for major elements and for minor elements are within a few percent.**

A Cameca 1270 E7 ion microprobe at CRPG-CNRS (Nancy, France) was used for oxygen isotope analyses on selected phases or areas. **The selected phases were analyzed by  $\text{Cs}^+$  beam having primary current of ~1 nA and beam spot of ~5  $\mu\text{m}$ . Faraday cups were used to measure secondary ions  $^{16}\text{O}^-$  and  $^{18}\text{O}^-$  with mass resolving power of ~2500, while  $^{17}\text{O}^-$  was measured using mono-electron multiplier with mass resolving power ~7000 to resolve the  $^{16}\text{OH}^-$  contribution. The isotopic errors ( $2\sigma$ ), considering the measurement errors as well as standard external reproducibility, are estimated to be ~0.7, 0.6 and 0.8‰ for  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $\Delta^{17}\text{O}$  ( $= \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ), respectively. All the analyzed phases were examined under SEM to discard those data that falls on visible cracks, pits or regions that were not part of this study.** The instrumental mass fractionation in olivine grains was corrected using San Carlos olivine, and for I-type and some G-type spherules that were dominated by magnetite we have used terrestrial magnetite standard. **Further**, detailed technical description of the SEM, electron microprobe and ion microprobe is given elsewhere (Rudraswami et al., 2019).

#### 4. RESULTS

We have classified 137 cosmic spherules and partially melted scoriaceous micrometeorites based on classification scheme by Genge et al. (2008) in order to understand the nature of oxygen isotope composition. The oxygen isotope study of cosmic spherules includes: scoriaceous: 13 particles, porphyritic: 11, barred: 18, cryptocrystalline: 22, glass: 37 and CAT: 3, along with I-type: 15 and G-type: 18 (Table 1 and 2). The back-scattered electron images of nine S-type spherules are shown in Fig. 1, while the bulk chemical compositions of all the spherules are summarized in Appendix A. Some of the spherules analysed have FeNi metal bead – these include one porphyritic, three barred, two cryptocrystalline, fourteen glass and one G-type (Fig. 2). Four spherules that have metal beads separated from the main silicate body have a narrow range of oxygen isotope compositions, except MS-I3-P55 (Table 2). The chemical compositions of FeNi beads present in various types of spherules (Fig. 2) are given in Appendix A. The bulk chemical compositions, however, does not show any correlation with oxygen isotope data. Finally, CAT spherules are formed by extreme heating and evaporation during atmospheric entry (Taylor et al., 2000, 2005) and thus provide an endmember of atmospheric entry behaviour.

The oxygen isotope compositions of the analysed cosmic spherules are shown by spherule type in Figure 3 and 4. The over-all compositional range is  $\delta^{17}\text{O}$  –6 to +36‰ and  $\delta^{18}\text{O}$  –3 to +72‰ and forms a field scattered mostly around the terrestrial fractionation line (TFL) with some adjacent to carbonaceous chondrite anhydrous mineral (CCAM) line. The S-type spherules show average  $\delta^{18}\text{O}$  values that increase in the series porphyritic < barred < cryptocrystalline < glass with values of ~20, 22, 25 and 26‰, respectively. The  $\delta^{18}\text{O}$  range is similar for all groups; however, porphyritic spherules exhibit the smallest range and lowest

values at  $\sim 0.7\text{‰}$ . The highest  $\delta^{18}\text{O}$  values are exhibited by the CAT spherules with an average of  $\sim 50\text{‰}$ , maximum of  $\sim 72\text{‰}$  and a minimum of  $\sim 30\text{‰}$ . Scoriaceous **micrometeorites** have the lowest average, maximum and minimum values at  $\sim 11$ , 20 and  $-3\text{‰}$ , respectively.

The  $\Delta^{17}\text{O}$  compositions of S-type particles show significant variations (Figure 5). Porphyritic spherules have a higher average and smaller range at  $-3$  and  $2\text{‰}$  compared with barred ( $-6$  and  $2\text{‰}$ ) and cryptocrystalline spherules ( $-5$  and  $2\text{‰}$ ), the majority of barred and cryptocrystalline spherules plot below the TFL in the three isotope plot, whilst the porphyritic spherules scattered closely around this line, with 7 out of 11 plotting above. For barred and cryptocrystalline spherules the highest  $\Delta^{17}\text{O}$  values are those particles with the highest  $\delta^{18}\text{O}$  and plot above the TFL. Glass spherules have a broadly similar average to barred, porphyritic and cryptocrystalline combined, and a slightly smaller range at  $-4$  and  $3\text{‰}$ . Scoriaceous **micrometeorites** have an average  $\Delta^{17}\text{O}$  most similar to barred and cryptocrystalline spherules, but a smaller range at  $-5$  to  $0.2\text{‰}$ . The smallest range of  $\Delta^{17}\text{O}$  amongst silicate dominated particles is exhibited by the CAT spherules and these all plot close to the TFL.

I-type **cosmic spherules** have oxygen isotope compositions distinct from the S-types and scoriaceous **micrometeorites** having a small range of high  $\delta^{18}\text{O}$  values of  $\sim 39$  to  $48\text{‰}$ . The  $\Delta^{17}\text{O}$  ratios of I-types are very low and they all fall within  $\sim 1\text{‰}$  of the TFL. None of the I-type spheres measured for oxygen isotopic composition contained metal beads that could be seen in the polished section. However, spherule AAS-62-61-P87 has a void space indicating that bead has been plucked off from the spherules probably during polishing leaving behind void space (Fig. 2). This particle has a thinner magnetite rim ( $\sim 3\mu\text{m}$ ) than others. The trend of the magnetite thickness **versus  $\delta^{18}\text{O}$  from the present study, along with that observed by**

**Engrand et al. (2005), suggests** an increase in  $\delta^{18}\text{O}$  with thickness (width) of the rim; however, there is no such strong correlation observed with diameter of the I-type spherules (Fig. 6).

In contrast to I-type spherules, G-types have lower  $\delta^{18}\text{O}$  values with a range from ~7 to 35‰, with maximum values smaller than any spherule of I-type. The average  $\Delta^{17}\text{O}$  of G-types ranges between -6 and 1‰ and thus plots mainly below the TFL in a three isotope plot (Fig. 5). The  $\Delta^{17}\text{O}$  values of G-types increase towards the TFL with increasing  $\delta^{18}\text{O}$ . There is only one G-type spherule SP005-P207 that has FeNi bead in it (Fig. 2).

The porphyritic spherule SP005-P1078 has two beads with a significant abundance of sulfur (~17 wt%). Sulfur at ~5 wt% was also seen in cryptocrystalline spherules SP005-P1176. Few glass spherules have metal beads with sulfur (Appendix A): SP005-P157 (~33 wt%), SP005-P1071 (~15 wt%), SP005-P34 (~6 wt%), SP005-P294 (4 wt%) and SP005-P296 (~1wt%). We have also compiled the data of all metal bead spherules (one porphyritic, three barred, two cryptocrystalline, fourteen glass and one G-type) **to explore** the trend of Ni (wt%) with  $\delta^{18}\text{O}$  values with different texture (Fig. 7). **Two data sets were examined from different cosmic spherules**, one from cryptocrystalline SP005-P1176 and one from glass MS-I35-P39, most of them have nickel composition <30 wt% and there is no visible trend of Ni vs.  $\delta^{18}\text{O}$ . Similarly, **we investigated whether  $\delta^{18}\text{O}$  varies with size of cosmic spherules (Fig. 8) with the expectation that heating, and thus mass fractionation, may increase with particle size. No correlation, however, was observed with the size of particles. Finally the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data was compared with those of meteorites as shown in Figure 9 since previous studies have suggested that the oxygen isotope compositions of spherules can be related to those of their precursors by consideration of the nature of exchange**

processes occurring during entry heating Suavet et al. (2010).

## 5. DISCUSSION

### 5.1. Oxygen isotope of I-type cosmic spherules

I-type cosmic spherules are thought to form by the atmospheric entry of FeNi metal interplanetary dust particles rather than by separation from silicate particles. Their origin as metal grains is supported by their sizes, which are larger than immiscible metal beads present in S-type cosmic spherules. Furthermore, the flux of micrometeorites is significantly larger than that of meteorites, implying that I-types are not separated from these larger meteoroids (e.g. Genge et al., 2017). The presence of the spallogenic isotope  $^{10}\text{Be}$  within I-type spherules confirms they were exposed in space as metal grains, since this highly lithophile element would have been removed if they separated from silicates (Yiou et al., 1985). The textures and mineralogies of I-type cosmic spherules are also consistent with their formation by progressive oxidation with the formation of an oxide mantle at the expense of the FeNi metal bead (Brownlee et al., 1984; Engrand et al., 2005; Genge et al., 2017b). I-type cosmic spherules, therefore, could be used as a proxy for the isotopic composition of the thermosphere/mesosphere and stratosphere. Since this requires an independent assessment of the degree of evaporation, and thus analyses of  $\delta^{56}\text{Fe}$  (Engrand et al. 2005; Pack et al., 2017) it was not possible in the current study.

Although most are formed by melting of metal grains, there are probably some I-type particles formed by metal separation from S-types, as suggested by Brownlee et al. (1984), since metal-beads are observed to migrate to the margins of these spherules during

deceleration (Genge and Grady, 1998). These are likely to be in the minority, and likely to be of smaller size ( $<50\text{ }\mu\text{m}$  in diameter). In such cases, there is bound to be some iron isotope fractionation during immiscibility **that could potentially influence the use of  $\delta^{56}\text{Fe}$  as a proxy for evaporation. Fractionation is, however, likely** minor **during immiscibility** in comparison to evaporation simply because the mass difference is small and diffusion rates in silicate melts are more controlled by electronic structure and speciation rather than atomic mass. In the present study, we consider all I-type particles **to have had** FeNi metal **precursors**.

The oxygen isotope of 15 I-types has  $\delta^{18}\text{O}$  ranging between 38.5–48.4‰, while for  $\delta^{17}\text{O}$  of 20.0–25.2‰ with  $\Delta^{17}\text{O}$  value within analytical uncertainty of the terrestrial fractionation value. The spread in  $\delta^{18}\text{O}$  is  $\sim 10\text{‰}$ , while that in  $\delta^{17}\text{O}$  are  $\sim 5\text{‰}$ . These isotopic values cover a larger range and are heavier than those used by Pack et al., (2017) as a proxy for mesospheric composition ( $\delta^{17}\text{O}= 19.3\text{--}21.6\text{‰}$ ,  $\delta^{18}\text{O}= 37.8\text{--}42.5\text{‰}$ ); albeit on only four **cosmic spherules** between  $\sim 400$  and  $550\text{ }\mu\text{m}$  in size. In contrast Engrand et al (2005) obtained a wider range of values of ( $\delta^{17}\text{O}= 19.1$  to  $29.4\text{‰}$ ,  $\delta^{18}\text{O}= 38.4$  to  $57.4\text{‰}$ ) for a set of twelve I-type spherules ranging in size from  $\sim 408$  to  $575\text{ }\mu\text{m}$ . They showed an increase in  $\delta^{18}\text{O}$  with the diameter of the spherule which is also true for the thickness of the magnetite rim (**Fig. 6**). The thickness of rim correlation seen in many I-type spherules also holds true for the current study where rim thickness is much smaller ( $<11\text{ }\mu\text{m}$ ). **As the oxidised rim thickness increases so does the  $\delta^{18}\text{O}$  value, however,** this correlation also holds **over the entire diameter** range of the spherules.

Engrand et al. (2005) indicated that  $\delta^{18}\text{O}$  correlates with size for particles larger than  $>400\text{ }\mu\text{m}$ . I-type particles from the present study are less than  $300\text{ }\mu\text{m}$  and have a smaller

range and average of  $\delta^{18}\text{O}$  than the larger spherules studied by [Engrand et al., \(2005\)](#), but have a similar minimum  $\delta^{18}\text{O}$ . **An increasing trend of  $\delta^{18}\text{O}$  with size was observed except for** few outlier datasets such as AAS-38-167-1-P115 and AAS-38-167-1-P116 (circled in [Fig. 6](#)). The oxygen isotope data values did not correlate with the total abundance of magnetite in I-type spherules, **which is likely to be a proxy for total oxidation**, nevertheless,  $\delta^{18}\text{O}$  strongly correlated with the thickness of the magnetite rim ([Fig. 6 and Table 2](#)). The thickness of the rim is large in spherules dominated by magnetite unlike those that are wustite-dominated. This undoubtedly relates to increased mass fractionation as a result of larger degrees of evaporation from larger particles – largely a consequence of their higher peak temperatures ([Genge, 2016](#)). The increase in the range and maximum value of  $\delta^{18}\text{O}$  with particle size is consistent with the variation of their peak temperatures with entry parameters as modelled numerically by [Genge \(2016\)](#). At near vertical entry angle peak temperature increases **rapidly** with particle size, resulting in significant increases in mass fractionation, whilst at low entry angles peak temperature increases less with size, causing smaller changes in mass fractionation with size. **The range of the data thus agree with theoretical constraints on the entry heating of these particles.**

I-types with metal beads and smaller magnetite rims have been shown to have lower  $\delta^{18}\text{O}$  due to lower degrees of heating than those with no bead and thick magnetite rim ([Engrand et al., 2005](#)); however, we cannot verify this as no metal bead-bearing I-types were analysed in the current study. Furthermore, without  $\delta^{56}\text{Fe}$  measurements we cannot independently determine the degree of evaporation, and thus the magnitude of mass fractionation in oxygen cannot be determined, except by Rayleigh fractionation with an assumed atmospheric composition. The range of mass fractionation in I-type spherules is nevertheless consistent with previous studies. These spherules have experienced a similar

range of evaporation, albeit greater than the spherules observed by Pack et al (2017) and less than some of those analysed by Engrand et al. (2005).

At altitudes >100 km in the thermosphere, increases in  $\delta^{17,18}\text{O}$  of spherules could be caused by dissociation and recombination rates of oxygen molecule resulting in enrichment of heavier isotopes by mass independent fractionation (Colegrove et al. 1965; Thiemens et al., 1995). The I-type spherules in this study have oxygen isotope compositions within uncertainty of the TFL; hence the average atmospheric oxygen have acquired  $\Delta^{17}\text{O} = 0.3 \text{ ‰}$  within the uncertainty of  $\sim 0.6 \text{ ‰}$  (2 standard deviation). We can, therefore, safely say that if the thermosphere has a  $\Delta^{17}\text{O}$  value greater than  $1 \text{ ‰}$  of the troposphere, then only a small proportion of this oxygen is incorporated into I-type spherules and may be further diluted by oxygen acquired at peak deceleration at lower altitudes in the mesosphere. Higher precision oxygen isotope compositions such as reported by Pack et al. (2017) might be capable of resolving  $\Delta^{17}\text{O}$  differences arising from capture of thermospheric gas with oxygen isotope compositions that diverge from the TFL. However, these high precision data reported no thermospheric oxygen with higher  $\Delta^{17}\text{O}$  involved in the oxidation of the I-type cosmic spherules. We would predict that those spherules with the lowest entry angles are most likely to exhibit such divergences since at any particular size these undergo more of their deceleration at higher altitude. These spherules are likely to exhibit the lowest  $\delta^{18}\text{O}$  values for their size since low angle particles have lower peak temperatures and thus experience less evaporation and mass fractionation.

## 5.2. Oxygen isotope of S-type cosmic spherules

The oxygen isotope compositions of S-type cosmic spherules and scoriaceous micrometeorites differ from those of I-type spherules since oxygen is present as a significant



component of their pre-atmospheric precursors. Silicate **micrometeorites**, therefore, inherit the isotopic composition of their precursor which is then modified during atmospheric entry by exchange with atmospheric oxygen and mass-fractionation owing to partial evaporation on heating. These two processes cause oxygen isotope compositions to evolve in different ways on an oxygen three isotope plot. Mass-fractionation owing to preferential loss of light oxygen during partial evaporation causes changes in composition according to relative mass of the isotope. On a three isotope plot, therefore, oxygen isotope compositions **under a mass-dependent regime** evolve parallel to the TFL along a slope 0.52 line towards  $\delta^{18}\text{O}$ -rich values (Figs. 3 and 4). In contrast exchange with air causes isotope compositions to converge towards the oxygen isotope composition of the atmosphere resulting in  $\Delta^{17}\text{O}$  values **approaching** zero whilst the  $\delta^{18}\text{O}$  value trends towards that of the air. These two processes have been previously discussed by Sauvet et al. (2010), Cordier et al (2011) and Van Ginneken et al. (2017) and are superimposed on the isotopic variability of the original precursors. (Fig. 9).

Two broad genetic groups of S-type cosmic spherule can be recognised by their  $\Delta^{17}\text{O}$  values within the analysed particles. Porphyritic spherules have higher average  $\Delta^{17}\text{O}$  values scattered at small values ( $\Delta^{17}\text{O} = \sim \pm 2\text{‰}$ ) above and **similarly for** below the TFL, whilst barred and cryptocrystalline spherules have lower average  $\Delta^{17}\text{O}$  values that fall mainly below the TFL. Porphyritic spherules have  $\Delta^{17}\text{O}$  similar to Ordinary, Enstatite, R and CI chondrites, whilst barred and cryptocrystalline spherules have lower values consistent with CM, CR, CV and CO chondrites (Fig. 9). Although broadly consistent with these meteorite groups, the isotope compositions of porphyritic, barred and cryptocrystalline spherules significantly overlap. The small number of barred and cryptocrystalline spherules (~10%) with the highest

$\Delta^{17}\text{O}$  values, however, are consistent with evolution from CI and ordinary chondrite-like materials, whilst those porphyritic spherules with  $\Delta^{17}\text{O} < -0.5\text{‰}$  is consistent with CM, CR and perhaps **CV, CK** sources, particularly if their  $\Delta^{17}\text{O}$  has evolved towards zero as a result of exchange with air. Eighteen percent of spherules from porphyritic, barred, cryptocrystalline, glass, scoriaceous **micrometeorites** have  $\Delta^{17}\text{O} > -0.5\text{‰}$  and  $\delta^{18}\text{O}$  less than CI chondrite and can only be derived from precursors with oxygen isotopes similar to Ordinary or Enstatite chondrites as previously suggested by [Cordier et al. \(2011\)](#). Glassy spherules analysed in this study have a broader range of  $\Delta^{17}\text{O}$  than barred, cryptocrystalline and porphyritic spherules, which nearly matches the range of all three groups suggesting these particles can be derived from any of the chondrite groups.

**Previous studies on coarse-grained porphyritic spherules have indicated that they are derived from fragments of chondrules, principally from ordinary chondrites, whilst fine-grained porphyritic spherules can be correlated with fine-grained matrices having affinities to CM and CR chondrites (Van Ginneken et al., 2017). In addition, the presence of relict grains, major and minor elements, and oxygen isotope studies support these conclusions (e.g. Cordier et al., 2011, Rudraswami et al., 2015; Van Ginneken et al., 2017). Our data is consistent with suggestion** that barred and porphyritic spherules are mostly genetically different particles, which are predominantly derived from coarse-grained, chondrule-derived materials, whilst barred spherules are principally derived from fine-grained materials such as chondrite matrix.

[Van Ginneken et al \(2017\)](#) found one cryptocrystalline spherule  $\Delta^{17}\text{O} < -2\text{‰}$  (Group 2 of [Van Ginneken et al., \(2017\)](#)), whilst 6 particles had  $\Delta^{17}\text{O} > -0.5\text{‰}$  (Group 3 and 4). **The**

current study reveals that the oxygen isotopes of cryptocrystalline spherules cover a wide range rather than previous observed with the majority (~70%) having  $\Delta^{17}\text{O} < -0.5\text{‰}$ . These are thus similar to barred olivine spherules and derived from CR, CM, CO or CV chondrites (Fig. 5 and 9). This implies that cryptocrystalline spherules are formed by increased heating of precursors similar to those of barred olivine spherules, a suggestion consistent with the higher average  $\delta^{18}\text{O}$  of cryptocrystalline particles observed in the current study. Likewise, the broad range of  $\Delta^{17}\text{O}$  in glassy spherules and their higher average  $\delta^{18}\text{O}$  is consistent with their formation by increased heating of precursors similar to both porphyritic olivine and cryptocrystalline spherules.

The increase in  $\delta^{18}\text{O}$  in S-type cosmic spherules, relative to their precursors, resulting from entry heating of S-type cannot be directly related to the degree of heating and evaporation without knowledge of the degree of atmospheric mixing and the composition of the precursor., Alexander et al. (2002), however, have shown that cosmic spherules that suffered the highest peak temperatures also exhibit the largest increase in  $\delta^{18}\text{O}$  values, implying that evaporation dominates  $\delta^{18}\text{O}$  evolution. Exchange with air makes it more challenging to assess  $\delta^{18}\text{O}$  in terms of heating since it will also cause increases in  $\delta^{18}\text{O}$  for particles with values less than that of air ( $\delta^{18}\text{O} = 23.5\text{‰}$ ; Thiemens et al., 1995). Exchange with air means the  $\delta^{18}\text{O}$  cannot be directly related to heating alone. Whether  $\delta^{18}\text{O}$  increase is largely the result of exchange of atmospheric oxygen in silicate melt or mass fractionation by evaporation depends on which of these two processes dominate.

The average  $\delta^{18}\text{O}$  observed in the current study increases in the series porphyritic < barred < cryptocrystalline < glassy < CAT spherules. The textures of this series of spherules has been interpreted as representing increasing peak temperature, with texture controlled by

crystallisation under increasing super-cooling due to progressive destruction of crystallisation nuclei with increasing temperature (Taylor et al., 1991; Genge et al. 2008). The increase in average  $\delta^{18}\text{O}$  through this series is, therefore, evidence that mass fractionation owing to heating dominates over exchange with the atmosphere. The approximately equal maximum and minimum values of  $\Delta^{17}\text{O}$  with  $\delta^{18}\text{O}$ , shown by the band of data points in a three isotope plot around TFL (Fig. 5), also testifies to the dominance of mass fractionation. If exchange with air was dominant, in contrast,  $\Delta^{17}\text{O}$  would become less with increasing  $\delta^{18}\text{O}$  values up until those of air.

**The** extreme heating of the calcium aluminium titanium-rich (CAT) spherules enriched in refractory elements such as Ca, Al, and Ti makes **their** oxygen isotope composition very interesting (Taylor et al., 2000; Genge et al., 2008). The oxygen isotope composition of  $\delta^{17,18}\text{O}$  is much **heavier in these particles** than any other spherules indicating not only atmospheric exchange but also coupled evaporation during entry. CAT spherules with the highest average  $\delta^{18}\text{O}$  values of the analysed particles are consistent with the extreme partial evaporation implied by their refractory compositions (Taylor et al., 2000).

Previous bulk oxygen isotope measurements of high Ca and Al spherules made by Cordier et al. (2011) have shown significantly lower  $\delta^{18}\text{O}$  values **than observed here**, having a range of ~15 to 19‰, **with only one having a value of** ~28‰. It is possible **the** spherules **analysed by Cordier et al., (2011) are fragments of** Ca-Al-rich precursors, rather than **the refractory products of** extreme evaporation. **One** CAT spherule (MY240184) analysed by Yada et al. (2005) **yielded a** high  $\delta^{18}\text{O}$  value of ~93‰. This value is much higher than our highest  $\delta^{18}\text{O}$  value of ~71‰, and our lowest value is also higher than given by Cordier et al. (2011). The extremely high value of  $\delta^{18}\text{O}$  indicates excessive heating and evaporation for an

extended period during atmospheric entry, which results in **evaporative** loss of **moderately volatile elements**, such as Fe, followed by Si and Mg, **and a corresponding** enrichment of the remaining Ca, Al and Ti (Wang et al., 2001, Yada et al., 2005). That one of the CAT spherules (SP007-P236) has the highest  $\delta^{18}\text{O}$  value ( $\sim 71\%$ ) of any of the S-type spherules **in our study** supports the above assertion.

All CAT spherules have small  $\Delta^{17}\text{O}$  values close to the TFL largely similar to porphyritic spherules, suggesting their precursors might be derived from a similar source (Fig. 5). That all the CAT spherules are derived from the same source is surprising since extreme partial evaporation **might** be expected to largely source independent, if most likely for those sources with higher average entry velocities, and thus eccentricities. **Nevertheless, Cordier and Folco (2014) analyzed several CAT spherules with most of them have oxygen isotopic composition below TFL line, although as suggested above these may have been derived from refractory precursors and thus different to typical CAT spherules.** The lack of isotopic diversity in CAT spherules **observed in this study** could, however, be due to the low number of particles and poor sampling statistics **compared to other types of cosmic spherules** (Fig. 9). **At present, it seems that there are few CAT spherules above and some below TFL, indicating two different populations that do not overlap each other. Based on the above/below TFL dichotomy it is likely that CAT spherules can originate from both CC and OC bodies, and can be formed either by extreme evaporation of chondritic precursors, or by melting of refractory precursors, presumably including fragments of CAIs.**

The present study of scoriaceous, porphyritic, barred, cryptocrystalline, glass, and CAT spherules indicate that S-type spherules in this size range (most have diameters of

60–300  $\mu\text{m}$ ) have sources dominated ( $\sim 80\%$ ) by carbonaceous chondrites, with the remainder derived from sources similar to ordinary chondrites. Experimental oxygen isotope analyses of different type of S-type **cosmic spherules** has demonstrated an increase in  $\delta^{17,18}\text{O}$  due to alteration during atmospheric entry (Fig. 3). The alteration in barred, cryptocrystalline, glass **spherules** are similar as they fall on TF line. Some of the porphyritic **spherules seem to be preserved  $\delta^{17,18}\text{O}$  and** does seem to alter significantly like glass, barred, cryptocrystalline spherules. This is also observed in previous studies that have shown some data on CCAM line (Rudraswami et al., 2015, 2016). Among the S-type **cosmic spherules**, the scoriaceous spherules **appear to have been the least affected by atmospheric entry since their** oxygen isotope fall **mainly** on CCAM line (Fig. 4). The bulk of the data from scoriaceous and porphyritic have  $\Delta^{17}\text{O} < 0\text{‰}$  similar to those seen in carbonaceous chondrites (Fig. 5), **although with significant numbers of porphyritic spherules having higher values. Similarly** barred, cryptocrystalline, and G-type **mostly have lower  $\Delta^{17}\text{O}$  than the TFL and are likewise related to carbonaceous chondrite. By comparison glassy spherules have a range of compositions.** The data suggest that  $\Delta^{17}\text{O}$  does not alter much irrespective of altitude, but variation in  $\delta^{17,18}\text{O}$  is visible. Although the  $\Delta^{17}\text{O}$  tends to increase with increase in  $\delta^{17,18}\text{O}$  values (Rudraswami et al., 2016), most of the partially altered scoriaceous particles show  $\Delta^{17}\text{O} < 0\text{‰}$ , **suggesting** a carbonaceous chondrite origin as seen in Figs. 4 and 5, **rather than as a consequence of heating.** The origin of these particles from precursors consisting of hydrated fine-grained matrix is supported by their textures and mineralogy (Genge et al., 2008; Taylor et al., 2012; Badyukov et al., 2018; Suttle et al., 2019) and the presence of relict cores of matrix (Genge, 2006) and fragmented olivine within some particles (Genge et al., 2017a).

Finally, no significant difference was noted between the isotopic compositions of S-type spherules with and without metal-beads. The lack of discrete compositions for spherules with FeNi metal beads suggests that these can be present within spherules derived from any chondritic source, in contrast to the suggestion of [Cordier et al., \(2011b\)](#) based on the Ni-contents of olivines that argued metal separation is most common for those particles derived from carbonaceous chondrite-like sources. The relatively small number of these particles analysed, however, may not sufficiently reveal whether metal beads are more common from one source or another. The separation of metal owing to deceleration during flight, or the lack of exposure of metal beads on the plane of section, are likely to make this comparison less than rigorous.

**Some the particles that have metal beads need to be looked for source related variation, such as, whether they are abundant in CC-derived (below TFL), OC-derived (above TFL), or both. Also, it will be remarkable to see if the metal beads more or less abundant in  $\delta^{18}\text{O}$ -rich particles that have experienced more intense heating and probably higher decelerations.** The presence of metal beads is related to low  $\delta^{18}\text{O}$  in I-type spherule compared to those with magnetite rich I-type particles demonstrating the mass-dependent fractionation by evaporation for particles during atmospheric entry ([Engrand et al., 2005](#)). Metal beads are present in all types of spherules in small number, except scoriaceous micrometeorites, and rarely in porphyritic spherules ([Rudraswami et al., 2014](#)). The oxygen isotope data on barred spherules with at least one metal bead has shown low  $\delta^{18}\text{O}$  values of ~12–16‰, except MS-I3-P21 that has ~23‰ probably due to larger size resulting in enrichment of heavier oxygen isotope during entry. This variation in oxygen isotope composition in barred spherules is similar to the I-type spherule correlation as suggested by [Engrand et al. \(2005\)](#). The Ni content in MS-I3-P21 is less (~19 wt%) compared to other

three barred spherules (23–30 wt%) indicating no relation as far as barred spherules are considered, however, we cannot draw a statistically significant conclusion with few particles (Fig. 7).

Glass spherules have undergone more heating than barred spherules and often have metal beads. The  $\delta^{18}\text{O}$  values in metal-bearing glass spherules have shown scatter with the increase in Ni content in metal bead (Fig. 7). The Fe is more **volatile** than Ni and having large presence of Ni in metal bead, and those spherules showing low  $\delta^{18}\text{O}$  is surprising and has to do primarily with precursor properties and entry parameters. However, if the oxygen isotope composition of precursor were similar, then Fe would have got evaporated proportionately showing relation to  $\delta^{18}\text{O}$ . MS-I35-P39 is the only glass spherule where it has shown high Ni content of ~64 wt%; one of the reasons is a different type of precursors that is contributed and also the entry parameter as indicated earlier. (Fig. 7). We **have measured a single** G-type spherule with bead that has very low nickel content (~10 wt%) and  $\delta^{18}\text{O}$  value of ~28‰ which fit in range of bead bearing glass spherules. The metal bead in porphyritic spherule is strange, and SP005-P1078 has two metal bead where its average composition has shown presence of sulfur (~17 wt%) along with Fe and Ni (Appendix A) indicating that these metals are not due to entry phenomena but were existing in its precursor, **and most likely have got altered due to oxidation during entry** (Fig. 2a). The  $\delta^{18}\text{O}$  composition of ~32‰ is much larger and comparable to other spherules that have shown some sulfur composition in glass spherules (SP005-P157, SP005-P1071, SP005-P34, SP005-P294, and SP005-P296). The lone cryptocrystalline spherule also has low  $\delta^{18}\text{O}$  values compared to high Ni content of ~64 wt%. Four particles, namely two from glass, one from CAT and one from I-type, has shown metal bead escaped from the spherules (Fig. 2). The  $\delta^{18}\text{O}$  of the **spherules that have escaped segregated** metal bead is ~35–40‰, except MS-I3-P55 with low values. However,



there are exception and the general trend favours increase in  $\delta^{18}\text{O}$  values with the high Ni content (Fig. 7). **This is due to heating and melting of the particles that lead to evaporation thereby increasing the  $\delta^{18}\text{O}$ , and oxidation resulting in increase of Ni in the residual metal.**

No systematic variation of  $\delta^{18}\text{O}$  of scoriaceous **micrometeorites** with size is observed, but for porphyritic spherules there is slight increase in the maximum and minimum  $\delta^{18}\text{O}$  with increasing size of particles, albeit with significant scatter (Fig. 8). There is no clear pattern when it comes to G-type particles. Nevertheless, the particle size has a greater role in elemental loss, **owing to increased heating**, and also changes the isotopic pattern as it enters the Earth's atmosphere (Rudraswami et al., 2015, 2016). It is likely that the lack of well-defined correlations between size and oxygen isotope composition for S-type particles, in contrast to I-types, relates to isotopic variability in the precursors that will partly obscure any systematic variations with entry parameters. **Additionally, carbonaceous chondrite precursors are more abundant for smaller size cosmic spherules, with ordinary chondrites contributing more at larger sizes (e.g. Cordier and Folco, 2014). Changes in the sources of cosmic spherules with size complicate evaluating changes in isotopic composition owing to heating since both contribute to final distributions of isotopic composition.**

### **5.3. Oxygen isotope of G-type Cosmic Spherules**

G-type particles have unique textures largely dominated by magnetite dendrites within a silicate glass mesostasis that are intermediate between S- and I-type **cosmic spherules** (Taylor et al., 1991; Genge et al., 2008). The oxygen isotope composition of G-types are

similar to barred, cryptocrystalline and glass **cosmic spherules**, and very different from I-types having low  $\delta^{18}\text{O}$  values and a wider range of  $\Delta^{17}\text{O}$ . The intermediate chemical nature of G-types would imply that their precursors have abundant FeNi metal with sub-ordinate silicate. The low  $\delta^{18}\text{O}$  values of most G-types, however, it is not consistent with the significant accretion of atmospheric oxygen and large mass-fractionation as observed for I-types. Furthermore, the  $\delta^{18}\text{O}$  range of G-types is smaller than porphyritic, barred, and cryptocrystalline spherules suggesting less significant mass-fractionation.

The isotopic compositions of G-types are not what would be expected for dense, metal-dominated particles. Some of the observed G-types have compositions close to the CCAM line and thus their precursors are likely to be similar to that observed for porphyritic spherules. Compositions close to the likely precursors suggests minimal mass fractionation and thus partial evaporation of silicates. One possible explanation for the formation of these particles might be if they were mixtures of iron-sulphide and silicates, rather than metal. The low melting temperatures of sulphides may allow spherule formation at a temperature low enough to prevent significant partial evaporation of silicates, precluding significant mass fractionation. Sulphides would react with atmospheric oxygen removing sulphur as  $\text{SO}_2$  and leaving iron-rich silicate. A similar explanation was proposed earlier for the lack of iron-sulphides in I-type **cosmic spherules**, with vesicles present in metal beads, and extrusion of metal into the surrounding oxide mantle as evidence for oxidative loss of sulphides ([Genge et al., 2017](#)). The lack of abundant vesicles in G-types, however, isn't entirely compatible with this interpretation and thus their origins remain enigmatic.

#### **5.4. Implications**

This study has shown that the analysis of the oxygen isotope compositions of large numbers of spherules is required to enable the interpretation of their sources and the processes affecting them during atmospheric entry. In particular comparisons of the isotope systematics correlated with textural type allows the genetic relationships between different types of particles to be determined. High precision studies of smaller numbers of large particles such as [Cordier et al. \(2011\)](#) and [Van Ginneken et al \(2017\)](#) successfully showed that both mass-fractionation by partial evaporation and exchange with air significantly modify the precursor compositions of **cosmic spherules** and introduce an inherent uncertainty in the parent body affinity. [Cordier et al. \(2011\)](#) established that those spherules with  $\Delta^{17}\text{O}$  values  $>-0.5\text{‰}$  and  $\delta^{18}\text{O}$  values less than CI chondrites are related to the Ordinary, Enstatite or R chondrites. Van [Ginneken et al. \(2017\)](#) showed that barred and porphyritic spherules have sufficiently different  $\Delta^{17}\text{O}$  values to necessitate various broad sources. Whilst high precision oxygen isotope studies, provide insights into the relationships between small numbers of large particles, ion microprobe analyses allow comparison of larger populations of particles, including smaller particles down to diameters of  $\sim 60\text{ }\mu\text{m}$  providing complementary information. In this study, the large number of particles analysed enables the majority of cryptocrystalline particles to be related to the barred olivine spherules through increased heating, whilst glass spherules can be shown to be derived by extensive superheating and nuclei destruction from similar precursors to porphyritic, barred and cryptocrystalline spherules.

The complexity of oxygen isotope evolution during entry heating is a consequence of the simultaneous operation of both mass fractionation and exchange with air. These two processes, however, are likely to be related by the entry parameters of **micrometeorites** (i.e. entry angle and entry velocity) as suggested by [Sauvet et al \(2010; 2011\)](#). Mass fractionation

by evaporation is mostly dependent on peak temperature and the duration of the heating pulse. Peak temperature increases with entry velocity or with entry angle with high velocity, high entry angle particles experiencing larger peak temperatures and evaporation. The duration of the heating pulse, conversely increases with decreasing entry angle. In two particles experiencing the same peak temperature, for example, the particle with the lower entry angle (which would necessarily have a higher entry velocity to attain the same peak temperature) would experience a larger degree of partial evaporation owing to the longer time spent at high temperature. The time spent above the solidus has been shown to increase from 1-2 s at steep entry angles to >12 s at shallow entry angles (e.g. [Genge, 2016, 2017](#)). Other properties of particles might, however, influence mass fractionation of oxygen. Volatile- or moderately volatile-rich precursors may undergo more significant partial evaporation than those particles with refractory starting compositions, increasing the mass fractionation of oxygen. The degree of mass-fractionation may, therefore, in part be source dependent, albeit with significant variation related to the different components present, such as fine-grained, volatile-rich matrix, chondrules and calcium-aluminium-inclusions.

The exchange of air with **cosmic spherules** during atmospheric entry may also depend on entry parameters to some extent. At high entry velocity, direct implantation of oxygen into the surface layers of particles is possible since incident energies exceed those of covalent bonding for silicates. At lower velocities the exchange with air is likely to be dominated by chemical reactions, with iron-dominated metal rapidly oxidising by reaction with atmospheric oxygen increasing the degree of exchange. The original oxidation state of the precursor may also be a factor with oxidised materials such as oxide-bearing type II chondrule fragments reacting less with atmospheric oxygen than reduced type I chondrules. Furthermore, reactions that incorporate some of the incident atmospheric oxygen into a gas

phase may reduce exchange with air by loss of the gas. The reaction of sulphides to produce SO<sub>2</sub>, for example, is likely to minimize the atmospheric oxygen retained by **cosmic spherules** and might in part explain the low  $\delta^{18}\text{O}$  observed within G-type spherules in this study.

The oxygen isotope compositions of I-type **cosmic spherules** have been determined by several studies (e.g. [Engrand et al., 2005](#); [Pack et al., 2017](#)) and have been suggested to be a proxy for mesospheric atmospheric compositions. In these studies, however, the  $\Delta^{17}\text{O}$  of particles is usually sufficiently close to TFL to be consistent with an atmospheric composition lacking significant non-mass fractionation effects. An independent means of identifying the degree of evaporation, such as  $\delta^{56}\text{Fe}$ , is required to use the oxygen isotope compositions as a proxy for those of the atmosphere. Differences in the degree of evaporation suggested by  $\delta^{56}\text{Fe}$  and  $\delta^{60-64}\text{Ni}$ , however, question the validity of this method (e.g. [Engrand et al., 2005](#)).

Given the expectation that non-mass fractionation effects should become important in the thermosphere, it is expected that spherules that undergo deceleration at the highest altitudes are most likely to show anomalous oxygen that does not fall on the TFL. Particles with the lowest entry angles are most likely to exhibit this behaviour and maybe only a very small proportion of I-types – emphasising the importance of studies of large numbers of particles. Since deceleration altitude is related to particle size, as well as entry velocity, small I-types are most likely to sample thermospheric atmosphere. These particles, which will prove invaluable in probing isotopic composition of the current and past atmosphere of our planet, are currently challenging to analyse at sufficient precision to provide rigorous results.

## 6. CONCLUSIONS

The oxygen isotope compositions of cosmic spherules are a complex signatures of parent body along with atmospheric entry processes arising due to both mass fractionation and isotopic exchange with terrestrial oxygen. We performed 277 in situ oxygen isotope analyses using ion microprobe in 137 micrometeorites collected from deep-sea and Antarctica along with many spherules that have metal bead to understand the isotopic pattern. There is an increase in average  $\delta^{18}\text{O}$  from scoriaceous< porphyritic< barred< cryptocrystalline< glass< CAT which is clearly related to mass-fractionation and evaporation, and thus peak temperature the particle has acquired during atmospheric entry. It also suggests that mass-fractionation due to heating dominates over exchange with air for S-types. Porphyritic spherules have small  $\Delta^{17}\text{O}$  scattered around the TFL, barred and cryptocrystalline spherules fall mainly below the TFL confirming that porphyritic are primarily derived from chondrule fragments, many from OCs, whilst barred and cryptocrystalline are from carbonaceous chondrite matrix. Cryptocrystalline spherules have mostly negative  $\Delta^{17}\text{O}$  similar to barred olivine spherules suggesting they form by further melting at higher peak temperature of these particles. It suggests these too are mainly derived from fine-grained carbonaceous chondrite matrix. Glass spherules have  $\Delta^{17}\text{O}$  with a range similar (but not quite as large) as porphyritic, barred and cryptocrystalline spherules together. This suggests these form by extensive melting of these types. CAT spherules have small  $\Delta^{17}\text{O}$  scattered around TFL and making close associates of porphyritic spherules. G-types **that are** expected to have significant exchange of atmospheric oxygen and mass-fractionation at high temperatures; however, their small range of  $\delta^{18}\text{O}$  suggests the opposite. The G-type with unique dendrites of magnetite and silicate appears to be dominated by carbonaceous chondritic precursors. These show the genetic relationships with precursor materials very well and allow some

712 quantitative estimates of precursor affinities. The progressive heating of different S-type  
713 spherules with bead and non-bead do have some correlation with oxygen isotope enrichment  
714 of  $\delta^{18}\text{O}$ .

715

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## APPENDIX A. SUPPLEMENTARY DATA

Supplementary data related to this article is provided in the electronic annex.



## REFERENCES

- Alexander, C. M. O'D., S. Taylor, J. S. Delaney, P. Ma, and G. F. Herzog (2002), Mass-dependent fractionation of Mg, Si, and Fe isotopes in five stony cosmic spherules, *Geochim. Cosmochim. Acta*, 66, 173–183.
- Badyukov D. D., F. Brandstaetter, and D. Topa (2018), Fine-Grained Scoriaceous and Unmelted Micrometeorites: Sources and Relationships with Cosmic Spherules, *Geochemistry International* 56, 1071–1083.**
- Beckerling, W., and A. Bischoff (1995), Occurrence and composition of relict minerals in micrometeorites from Greenland and Antarctica—implications for their origins, *Planet. Space Sci.*, 43, 435–449.
- Brownlee, D. E., B. A. Bates, and M. M. Wheelock (1984), Extraterrestrial platinum group nuggets in deep-sea sediments, *Nature*, 309, 693–695.
- Brownlee, D. E., B. Bates, and L. Schram (1997), The elemental composition of stony cosmic spherules, *Meteorit. Planet. Sci.*, 32, 157–175.
- Clayton, R. N., N. Onuma, L. Grossman, and T. K. Mayeda (1977), Distribution of pre-solar component in Allende and other carbonaceous chondrites, *Earth Planet. Sci. Lett.* 34, 209–224.
- Clayton, R. N., T. K. Mayeda, E. J. Olsen, and J. N. Goswami (1991), Oxygen isotope studies of ordinary chondrites, *Geochim. Cosmochim. Acta*, 55, 2317–2337.
- Clayton, R. N., and T. K. Mayeda (1999), Oxygen isotope studies of carbonaceous chondrites, *Geochim. Cosmochim. Acta*, 63, 2089–2104.
- Colegrove, F. D., W. B. Hanson, and F. S. Johnson (1965), Eddy diffusion and oxygen transport in the lower therm, *J. Geophys. Res.*, 70, 4931–4941.

752 Cordier, C., L. Folco, C. Suavet, C. Sonzogni, and P. Rochette (2011), Major, trace element  
753 and oxygen isotope study of glass cosmic spherules of chondritic composition: The  
754 record of their source material and atmospheric entry heating, *Geochim. Cosmochim.*  
755 *Acta*, 75, 5203–5218.

756 Cordier, C., M. Van Ginneken, and L. Folco (2011a), Nickel abundance in stony cosmic  
757 spherules: constraining precursor material and formation mechanisms, *Meteorit.*  
758 *Planet. Sci.*, 46, 1110–1132.

759 **Cordier, C., and L. Folco (2014), Oxygen isotopes in cosmic spherules and the**  
760 **composition of the near Earth interplanetary dust complex, *Geochim.***  
761 ***Cosmochim. Acta*, 146, 18–26.**

762 Engrand, C., K. D. McKeegan, L. A. Leshin, G. F. Herzog, C. Schnabel, L. E. Nyquist, and  
763 D. E. Brownlee (2005), Isotopic compositions of oxygen, iron, chromium, and nickel  
764 in cosmic spherules: Toward a better comprehension of atmospheric entry heating  
765 effects, *Geochim. Cosmochim. Acta*, 69, 5365–5385.

766 Genge, M. J., and M. M. Grady (1998), Melted micrometeorites from Antarctic ice with  
767 evidence for the separation of immiscible Fe-Ni-S liquids during entry heating,  
768 *Meteorit. Planet. Sci.*, 33, 425–434.

769 Genge, M. J. (2006), Igneous rims on micrometeorites, *Geochim. Cosmochim. Acta*, 70,  
770 2603–2621.

771 Genge, M. J., C. Engrand, M. Gounelle, and S. Taylor (2008), The classification of  
772 micrometeorites, *Meteorit. Planet. Sci.*, 43, 497–515.

773 Genge, M. J. (2016), The Origins of I-type Spherules and the Atmospheric Entry of Iron  
774 Micrometeoroids, *Meteorit. Planet. Sci.*, 51, 1063–1081.

775 Genge, M. J. (2017), The entry heating and abundances of basaltic micrometeorites, *Meteorit.*  
776 *Planet. Sci.*, 52, 1000–1013.

777 Genge, M. J., M. D. Suttle, and M. Van Ginneken (2017a), Thermal shock fragmentation of  
778 Mg silicates within scoriaceous micrometeorites reveal hydrated asteroidal sources,  
779 *Geology*, 45, 891-894.

780 Genge, M. J., B. Davies, M. D. Suttle, M. Van Ginneken, and A. G. Tomkins (2017b), The  
781 mineralogy and petrology of I-type cosmic spherules: Implications for their sources,  
782 origins and identification in sedimentary rocks, *Geochim. Cosmochim. Acta*, 218,  
783 167-200.

784 **Goderis S., B. Soens, M. S. Huber, S. McKibbin, M. van Ginneken, V. Debaille, R. C.**  
785 **Greenwood, I. Franchi, V. Cnudde, S. V. Malderen, F. Vanhaecke, C. Koeberl,**  
786 **D. Topa, and P. Claeys (2019), Cosmic spherules from Widerøefjellet, Sør**  
787 **Rondane Mountains (East Antarctica) *Geochimica et Cosmochimica Acta*,**  
788 **270, 112-143.**

789 Greshake, A., W. Klock, P. Arndt, M. Maetz, G. J. Flynn, S. Bajt, and A. Bischoff (1998),  
790 Heating experiments simulating atmospheric entry heating of micrometeorites: Clues  
791 to their parent body sources, *Meteorit. Planet. Sci.*, 33, 267–290.

792 Kurat, G., C. Koeberl, T. Presper, F. Brandstatter, and M. Maurette (1994), Petrology and  
793 geochemistry of Antarctic micrometeorites. *Geochim. Cosmochim. Acta*, 58, 3879–  
794 3904.

795 Love, S. G., and D. E. Brownlee (1993), A direct measurement of the terrestrial mass  
796 accretion rate of cosmic dust, *Science*, 262, 550–553.

797 Pack, A., A. Howeling, D. C. Hezel, M. T. Stefanak, A. K. Beck, S. T. M. Peters, S.  
798 Sengupta, D. Herwartz, and L. Folco (2017), Tracing the oxygen isotope composition  
799 of the upper Earth's atmosphere using cosmic spherules, *Nature Communications*, 8,  
800 15702

801 Plane, J. M. C. (2012), Cosmic dust in the earth's atmosphere. *Chem. Soc. Rev.*, 41, 6507–  
802 6518.

803 Prasad, M. S., N. G. Rudraswami, and D. K. Panda (2013), Micrometeorite flux on earth  
804 during the last ~50,000 years, *J. Geophys. Res.*, 118, 2381–2399.

805 Rudraswami, N. G., K. Parashar, and M. S. Prasad (2011), Micrometer and nanometer-sized  
806 platinum group nuggets in micrometeorites from deep-sea sediments of the Indian  
807 Ocean, *Meteorit. Planet. Sci.*, 46, 470–491.

808 Rudraswami, N. G., M. S. Prasad, E. V. S. S. K. Babu, T. Vijaya Kumar, W. Feng, and J. M.  
809 C. Plane (2012), Fractionation and fragmentation of glass cosmic spherules during  
810 atmospheric entry, *Geochim. Cosmochim. Acta*, 99, 110–127.

811 Rudraswami, N. G., M. S. Prasad, E. V. S. S. K. Babu, and T. Vijaya Kumar (2014),  
812 Chemistry and petrology of Fe–Ni beads from different types of cosmic spherules:  
813 implication for precursors. *Geochim. Cosmochim. Acta*, 145, 139–158.

814 Rudraswami, N. G., M. S. Prasad, K. Nagashima, and R. H. Jones (2015), Oxygen isotopic  
815 composition of relict olivine grains in cosmic spherules: Links to chondrules from  
816 carbonaceous chondrites, *Geochim. Cosmochim. Acta*, 164, 57–70.

817 Rudraswami, N. G., M. S. Prasad, S. Dey, J. M. C. Plane, W. Feng, J. D. Carrillo-Sánchez,  
818 and D. Fernandes (2016), Ablation and Chemical Alteration of Cosmic Dust Particles  
819 during Entry into the Earth's Atmosphere, *Astrophys. J. Supp. Series*, 227,  
820 doi:10.3847/0067-0049/227/2/15

821 Rudraswami, N. G., D. Fernandes, A. K. Naik, M. S. Prasad, J. D. Carrillo-Sánchez, J. M. C.  
822 Plane, W. Feng, and S. Taylor (2018), Selective Disparity of Ordinary Chondritic  
823 Precursors in Micrometeorite Flux, *Astrophys. J.*, 831, 853:38, doi.: 10.3847/1538-  
824 4357/aaa5f7

825 Rudraswami, N. G., Y. Marrocchi, M. S. Prasad, D. Fernandes, J. Villeneuve, and S. Taylor  
 826 (2019), Oxygen isotopic and chemical composition of chromites in micrometeorites:  
 827 Evidence of ordinary chondrite precursors, *Meteorit. Planet. Sci.*, 54, 1347–1361.  
 828 Suavet, C., A. Alexandre, I. A. Franchi, J. Gattacceca, C. Sonzogni, R. C. Greenwood, L.  
 829 Folco, and P. Rochette (2010), Identification of the parent bodies of micrometeorites  
 830 with high-precision oxygen isotope ratios, *Earth Planet. Sci. Lett.*, 293, 313–320.  
 831 Suavet, C., C. Cordier, P. Rochette, L. Folco, J. Gattacceca, C. Sonzogni, and D. Damphoffer  
 832 (2011), Ordinary chondrite-related giant (>800  $\mu\text{m}$ ) cosmic spherules from the  
 833 Transantarctic Mountains Antarctica, *Geochim. Cosmochim. Acta*, 75, 6200–6210.  
 834 **Suttle, M. D., L. Folco, M. J. Genge, S. S. Russell, J. Najorka, and M. van Ginneken**  
 835 **(2019) Intense aqueous alteration on C-type asteroids: Perspectives from giant**  
 836 **fine-grained micrometeorites, *Geochim. Cosmochim. Acta*, 245, 352–373.**  
 837 Taylor, S., and D. E. Brownlee (1991), Cosmic spherules in the geologic record, *Meteoritics*,  
 838 26, 203–211.  
 839 Taylor, S., J. H. Lever, and R. P. Harvey (1998), Accretion rate of cosmic spherules  
 840 measured at the South Pole, *Nature*, 392, 899–903.  
 841 Taylor, S., J. H. Lever, and R. P. Harvey (2000), Numbers, types, and compositions of an  
 842 unbiased collection of cosmic spherules, *Meteorit. Planet. Sci.*, 35, 651–666.  
 843 Taylor, S., C. M. Alexander, J. Delaney, P. Ma, G. F. Herzog, and C. Engrand (2005),  
 844 Isotopic fractionation of iron, potassium, and oxygen in stony cosmic spherules:  
 845 Implications for heating histories and sources, *Geochim. Cosmochim. Acta*, 69, 2647–  
 846 2662.  
 847 Taylor, S., G. Matrajt, and Y. Guan (2012), Fine-grained precursors dominate the  
 848 micrometeorite flux, *Meteorit. Planet. Sci.*, 47, 550–564.

- Thiemens, M. H., T. Jackson, E. C. Zipf, P. W. Erdman, and C. Van Egmond (1995), Carbon dioxide and oxygen isotope anomalies in the mesosphere and stratosphere, *Science*, 270, 969–972.
- Van Ginneken, M., J. Gattacceca, P. Rochette, C. Sonzogni, A. Alexandre, V. Vidal, and M. J. Genge (2017), The parent body controls on cosmic spherule texture: Evidence from the oxygen isotopic compositions of large micrometeorites, *Geochim. Cosmochim. Acta*, 212, 196-210.
- Wang, J., A. M. Davis, R. N. Clayton, T. K. Mayeda, and A. Hashimoto (2001), Chemical and isotopic fractionation during the evaporation of the FeO - MgO - SiO<sub>2</sub> - CaO - Al<sub>2</sub>O<sub>3</sub> - TiO<sub>2</sub> rare earth element melt system, *Geochim. Cosmochim. Acta*, 65, 479–494.
- Yada, T., T. Nakamura, N. Takaoka, T. Noguchi, K. Terada, H. Yano, T. Nakazawa, and H. Kojima (2004), The global accretion rate of extraterrestrial materials in the last glacial period estimated from the abundance of micrometeorites in Antarctic glacier ice, *Earth Planets Space*, 56, 67–79.
- Yada, T., T. Nakamura, T. Noguchi, N. Matsumoto, M. Kusakabe, H. Hiyagon, T. Ushikubo, N. Sugiura, H. Kojima, and N. Takaoka (2005), Oxygen isotopic and chemical compositions of cosmic spherules collected from the Antarctic ice sheet: Implications for their precursor, *Geochim. Cosmochim. Acta*, 69, 5789–5804.
- Yiou, F., G. M. Raisbeck, D. Bourles, C. Lorius, and N. I. Barkov (1985), <sup>10</sup>Be in ice at Vostok Antarctica during the last climatic cycle, *Nature*, 316, 616–617

## Figure Captions

### Figure 1.

The representative back-scattered electron image of different type of **cosmic spherules** selected for the oxygen isotope studies: a) scoriaceous, b) porphyritic, c) barred, d) cryptocrystalline, e) glass, f and g) CAT, along with h) I-type and i) G-type. **The back-scattered images scale bars indicates 50  $\mu\text{m}$ .** The detail bulk chemical compositions of the particles are given in [Appendix A](#).

### Figure 2.

The backscattered electron image of polished sections of the **cosmic spherules** with metal bead where oxygen isotope analyses were performed on silicate. (a) SP005-P1078 is one porphyritic spherules that have two metal **beads**. (b) MS-I3-P59, (c) MS-I3-P39, and (d) SP005-P10 are glass spherules with the metal bead. (e) SP007-P4, (f) SP005-P1176 and (i) SP005-P207 is barred, cryptocrystalline and G-type with metal bead. (g) SP007-P255 and (h) AAS-62-61-P87 are CAT and I-type spherules have metal bead **void formed either by the dissolution of the metal bead whilst on the seafloor or by plucking during the polishing process. The back-scattered images scale bars indicates 50  $\mu\text{m}$ .**

### Figure 3.

The oxygen isotope compositions of **cosmic spherules**: a) porphyritic, b) barred, c) cryptocrystalline, d) glass, e) I-type and f) G-type obtained using ion microprobe. The oxygen isotope data are given in Appendix A. The solid lines represents the terrestrial fractionation (TF) and the carbonaceous chondrite anhydrous mineral (CCAM) line with slope~0.52

and ~0.94, respectively (Clayton et al., 1977; Clayton and Mayeda, 1999). All error bars shown are smaller than the size of symbol.

**Figure 4.**

The oxygen isotope compositions of least altered and most altered cosmic spherules, scoriaceous and CAT spherules analyzed using ion microprobe. The oxygen isotope data are given in Appendix A. The solid lines represent TF and CCAM line with slope ~0.52 and ~0.94, respectively (Clayton et al., 1977; Clayton and Mayeda, 1999). All error bars are small than the size of the symbol.

**Figure 5.**

Plot of  $\Delta^{17}\text{O}$  for different types of spherules analysed in this study. Most of the data are below the TF line suggesting cosmic spherules are contributed by carbonaceous chondrites. Conversely, I-type spherules are near the TF line. The number at the corner of each plot is the average value of the  $\Delta^{17}\text{O}$  along with error. All error bars shown are  $2\sigma$ .

**Figure 6.**

(a) The plot of  $\delta^{18}\text{O}$  vs. magnetite rim thickness of I-type spherules appears to increase with  $\delta^{18}\text{O}$  values. (b) The plot of  $\delta^{18}\text{O}$  versus the diameter of I-type spherules with sizes less than 300  $\mu\text{m}$  from this study. Results of I-type spherules data for both magnetite thickness and diameter from Engrand et al. (2005) have been included in the plot for comparison. The plots indicate that with increase in  $\delta^{18}\text{O}$  values the magnetite rim and diameter of spherule range also increases. The circle marked in b is the data seems anomalous and is slightly far from the trend.



**Figure 7.**

The variation of Ni (wt%) in metal bead and  $\delta^{18}\text{O}$  from different types (porphyritic, barred, cryptocrystalline, glass, G-type) of spherules. Glass spherule has good statistics where we can suggest increase trend in Ni content with respect to  $\delta^{18}\text{O}$ . Other spherules do not have good statistical representation. Few particles excluded from this plot are MS-I3-P55 (glass), MS-I35-P22 (glass), SP007-P255 (CAT) and AAS-62-61-P87 (I-type). They have shown void space due to removal of metal bead **either by the dissolution of the metal bead during its residence time on seafloor, during sample polishing, or** during atmospheric entry.

**Figure 8.**

The behaviour of  $\delta^{18}\text{O}$  from different types (porphyritic, barred, cryptocrystalline, glass, G-type) of spherules with respect to the diameter of the spherules. There seems to overall increase in  $\delta^{18}\text{O}$  values with the increase in diameter but not uniform probably due to complexity involved in entry parameter and precursor original oxygen isotope composition.

**Figure 9.**

Compiled oxygen isotopic compositions  $\Delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  values of different types of **cosmic spherules** analyzed in this study using ion microprobe. The range of oxygen isotope composition of various chondritic parent bodies (such as CI, CM, CV, CO, CK, CR, H, L, LL, EC, and R) are illustrated (Clayton et al., 1991; Clayton and Mayeda, 1999). The shaded region is the value of the isotopic composition of the micrometeorite from the various precursor. The different group 1, 2, 3, 4 with a diverse isotopic range of  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  is earlier defined by Suavet et al. (2010).