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# 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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1 **Title:**

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

5  
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27  
28 **Date: May 2020**

30 **Key Points:**

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

37

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40

41 **Abstract:**

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

65 entry heating of both CC and OC-like materials. I-type cosmic spherules have a narrow range  
66 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  
67 obtained entirely from the Earth's atmosphere, albeit with significant mass fractionation  
68 owing to evaporation during entry heating. The observed range of  $\delta^{18}\text{O}$  with size is suggested  
69 here to reflect entry angle with high values representing enhanced heating at high angle.  
70 Finally, G-type **cosmic spherules** have unexpected isotopic compositions suggesting little  
71 mass-fractionation from a CC-like source and are suggested to have sulphide-silicate  
72 precursors with relatively low melting temperatures. The results of this study provide **vital**  
73 **assessment** of the **wider** population of extraterrestrial dust arriving **to the** Earth.

74

#### 75 **Plain Language Summary**

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

89

## 90 1. INTRODUCTION

91

92 Micrometeorites are the most abundant extraterrestrial materials reaching the Earth's  
93 surface on an annual basis (Love and Brownlee, 1993). Cosmic spherules are  
94 **extraterrestrial** particles that undergo significant melting during atmospheric entry and  
95 represent **micrometeorites** that have experienced high temperature during **passage through**  
96 **the atmosphere**. Although a large fraction of this material never makes it to Earth's surface  
97 **and is evaporates (e.g. Love and Brownlee, 1991), surviving particles still** represent the  
98 most significant contributors of **extraterrestrial** material to the Earth's surface (Taylor et al.,  
99 1998; Yada et al., 2004; Plane, 2012; Prasad et al., 2013). Micrometeorites provide  
100 information on the nature of their **Extraterrestrial** parent bodies, the processes operating  
101 during atmospheric entry and the composition of the Earth's atmosphere. Extraterrestrial  
102 material that enters the upper atmosphere at >100 km altitude experiences gas drag heating  
103 thereby changing their original chemical and isotopic properties (Kurat et al. 1994;  
104 Beckerling and Bischoff 1995; Brownlee et al. 1997; Greshake et al. 1998; Engrand et al.,  
105 2005; Genge et al., 2008; Cordier et al., 2011; Rudraswami et al., 2012, 2015, 2016). The  
106 oxygen isotope compositions of particles that survive atmospheric entry are thus related to  
107 those of both their precursors and the upper atmosphere. **Currently, the oxygen isotope**  
108 **composition of the upper atmosphere (i.e. > 60 km) has not been determined yet and any**  
109 **isotopic information above this altitude need to be deciphered from micrometeorites as**  
110 **most of these particles have undergone heating leading to isotopic exchange between**  
111 **~80 and 120 km (Thiemens et al., 1995; Pack et al., 2017).**

112

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

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

123

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

135

## 136 2. SAMPLE COLLECTION

137

138 The **cosmic spherules** are collected from the central Indian Ocean from the depth of  
139 ~5200 m using a grab sampler having size 50×50 cm (length × breadth). This grab can

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

157

### 158 **3. INSTRUMENTAL TECHNIQUES**

159

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



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

173

174 A Cameca 1270 E7 ion microprobe at CRPG-CNRS (Nancy, France) was used for  
175 oxygen isotope analyses on selected phases or areas. **The selected phases were analyzed by**  
176  **$\text{Cs}^+$  beam having primary current of  $\sim 1$  nA and beam spot of  $\sim 5$   $\mu\text{m}$ . Faraday cups were**  
177 **used to measure secondary ions  $^{16}\text{O}^-$  and  $^{18}\text{O}^-$  with mass resolving power of  $\sim 2500$ , while**  
178  **$^{17}\text{O}^-$  was measured using mono-electron multiplier with mass resolving power  $\sim 7000$  to**  
179 **resolve the  $^{16}\text{OH}^-$  contribution. The isotopic errors ( $2\sigma$ ), considering the measurement**  
180 **errors as well as standard external reproducibility, are estimated to be  $\sim 0.7$ ,  $0.6$  and**  
181  **$0.8\%$  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**  
182 **phases were examined under SEM to discard those data that falls on visible cracks, pits**  
183 **or regions that were not part of this study.** The instrumental mass fractionation in olivine  
184 grains was corrected using San Carlos olivine, and for I-type and some G-type spherules that  
185 were dominated by magnetite we have used terrestrial magnetite standard. **Further**, detailed  
186 technical description of the SEM, electron microprobe and ion microprobe is given elsewhere  
187 (Rudraswami et al., 2019).

188

189 **4. RESULTS**

190

191       **We have classified 137 cosmic spherules and partially melted scoriaceous**  
192 **micrometeorites based on classification scheme by Genge et al. (2008) in order to**  
193 **understand the nature of oxygen isotope composition. The oxygen isotope study of**  
194 **cosmic spherules includes: scoriaceous: 13 particles, porphyritic: 11, barred: 18,**  
195 **cryptocrystalline: 22, glass: 37 and CAT: 3, along with I-type: 15 and G-type: 18 (Table**  
196 **1 and 2). The back-scattered electron images of nine S-type spherules are shown in Fig.**  
197 **1, while the bulk chemical compositions of all the spherules are summarized in**  
198 **Appendix A.** Some of the spherules analysed have FeNi metal bead – these include one  
199 porphyritic, three barred, two cryptocrystalline, fourteen glass and one G-type (Fig. 2). Four  
200 spherules that have metal beads separated from the main silicate body have a narrow range of  
201 oxygen isotope compositions, except MS-I3-P55 (Table 2). The chemical compositions of  
202 FeNi beads present in **various** types of spherules (Fig. 2) are given in Appendix A. The bulk  
203 chemical **compositions**, however, **does** not show any correlation with oxygen isotope data.  
204 Finally, CAT spherules are formed by extreme heating and evaporation during atmospheric  
205 entry (Taylor et al., 2000, 2005) and thus provide an endmember of atmospheric entry  
206 behaviour.

207

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

215 values at  $\sim 0.7\text{‰}$ . The highest  $\delta^{18}\text{O}$  values are exhibited by the CAT spherules with an  
216 average of  $\sim 50\text{‰}$ , maximum of  $\sim 72\text{‰}$  and a minimum of  $\sim 30\text{‰}$ . Scoriaceous  
217 **micrometeorites** have the lowest average, maximum and minimum values at  $\sim 11$ , 20 and  $-$   
218  $3\text{‰}$ , respectively.

219

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

231

232 I-type **cosmic spherules** have oxygen isotope compositions distinct from the S-types  
233 and scoriaceous **micrometeorites** having a small range of high  $\delta^{18}\text{O}$  values of  $\sim 39$  to  $48\text{‰}$ .  
234 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-  
235 type spheres measured for oxygen isotopic composition contained metal beads that could be seen in  
236 the polished section. However, spherule AAS-62-61-P87 has a void space indicating that bead  
237 has been plucked off from the spherules probably during polishing leaving behind void space  
238 (Fig. 2). This particle has a thinner magnetite rim ( $\sim 3\mu\text{m}$ ) than others. The trend of the  
239 magnetite thickness **versus  $\delta^{18}\text{O}$  from the present study, along with that observed by**

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

243

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

249

250 The porphyritic spherule SP005-P1078 has two beads with a significant abundance of  
251 sulfur (~17 wt%). Sulfur at ~5 wt% was also seen in cryptocrystalline spherules SP005-  
252 P1176. Few glass spherules have metal beads with sulfur (Appendix A): SP005-P157 (~33  
253 wt%), SP005-P1071 (~15 wt%), SP005-P34 (~6 w%), SP005-P294 (4 wt%) and SP005-P296  
254 (~1wt%). We have also compiled the data of all metal bead spherules (one porphyritic, three  
255 barred, two cryptocrystalline, fourteen glass and one G-type) **to explore** the trend of Ni  
256 (wt%) with  $\delta^{18}\text{O}$  values with different texture (Fig. 7). **Two data sets were examined from**  
257 **different cosmic spherules**, one from cryptocrystalline SP005-P1176 and one from glass  
258 MS-I35-P39, most of them have nickel composition <30 wt% and there is no visible trend of  
259 Ni vs.  $\delta^{18}\text{O}$ . Similarly, **we investigated whether  $\delta^{18}\text{O}$  varies with size of cosmic spherules**  
260 **(Fig. 8) with the expectation that heating, and thus mass fractionation, may increase**  
261 **with particle size. No correlation, however, was observed with the size of particles.**  
262 **Finally the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  data was compared with those of meteorites as shown in Figure 9**  
263 **since previous studies have suggested that the oxygen isotope compositions of spherules**  
264 **can be related to those of their precursors by consideration of the nature of exchange**

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

266

## 267 **5. DISCUSSION**

268

### 269 **5.1. Oxygen isotope of I-type cosmic spherules**

270

271 I-type **cosmic spherules** are thought to form by the atmospheric entry of FeNi metal  
272 interplanetary dust particles rather than by separation from silicate particles. **Their origin as**  
273 **metal grains is supported by their sizes, which are larger than immiscible metal beads**  
274 **present in S-type cosmic spherules. Furthermore, the flux of micrometeorites is**  
275 **significantly larger than that of meteorites, implying that I-types are not separated from**  
276 **these larger meteoroids** (e.g. Genge et al., 2017). The presence of the spallogenic isotope  
277  $^{10}\text{Be}$  within I-type spherules confirms they were exposed in space as metal grains, since this  
278 highly lithophile element would have been removed if they separated from silicates (Yiou et  
279 al., 1985). The textures and mineralogies of I-type **cosmic spherules** are also consistent with  
280 their formation by progressive oxidation with the formation of an oxide mantle at the expense  
281 of the FeNi metal bead (Brownlee et al., 1984; Engrand et al., 2005; Genge et al., 2017b). **I-**  
282 **type cosmic spherules, therefore, could be used as a proxy for the isotopic composition**  
283 **of the thermosphere/mesosphere and stratosphere. Since this requires an independent**  
284 **assessment of the degree of evaporation, and thus analyses of  $\delta^{56}\text{Fe}$**  (Engrand et al. 2005;  
285 Pack et al., 2017) **it was not possible in the current study.**

286

287 **Although most are formed by melting of metal grains, there** are probably some I-  
288 type particles formed by metal separation from S-types, as suggested by Brownlee et al.  
289 (1984), since metal-beads are observed to migrate to the margins of these spherules during

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

298

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

312

313 Engrand et al. (2005) indicated that  $\delta^{18}\text{O}$  correlates with size for particles larger than  
314  $>400 \mu\text{m}$ . I-type particles from the present study are less than  $300 \mu\text{m}$  and have a smaller

315 range and average of  $\delta^{18}\text{O}$  than the larger spherules studied by [Engrand et al., \(2005\)](#), but  
316 have a similar minimum  $\delta^{18}\text{O}$ . **An increasing trend of  $\delta^{18}\text{O}$  with size was observed except**  
317 **for** few outlier datasets such as AAS-38-167-1-P115 and AAS-38-167-1-P116 (circled in [Fig.](#)  
318 [6](#)). The oxygen isotope data values did not correlate with the total abundance of magnetite in  
319 I-type spherules, **which is likely to be a proxy for total oxidation**, nevertheless,  $\delta^{18}\text{O}$   
320 strongly correlated with the thickness of the magnetite rim ([Fig. 6 and Table 2](#)). The  
321 thickness of the rim is large in spherules dominated by magnetite unlike those that are  
322 wustite-dominated. This undoubtedly relates to increased mass fractionation as a result of  
323 larger degrees of evaporation from larger particles – largely a consequence of their higher  
324 peak temperatures ([Genge, 2016](#)). The increase in the range and maximum value of  $\delta^{18}\text{O}$  with  
325 particle size is consistent with the variation of their peak temperatures with entry parameters  
326 as modelled numerically by [Genge \(2016\)](#). At near vertical entry angle peak temperature  
327 increases **rapidly** with particle size, resulting in significant increases in mass fractionation,  
328 whilst at low entry angles peak temperature increases less with size, causing smaller changes  
329 in mass fractionation with size. **The range of the data thus agree with theoretical**  
330 **constraints on the entry heating of these particles.**

331

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

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

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

360

## 361 **5.2. Oxygen isotope of S-type cosmic spherules**

362

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



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

379

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

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

399

400 **Previous studies on coarse-grained porphyritic spherules have indicated that**  
401 **they are derived from fragments of chondrules, principally from ordinary chondrites,**  
402 **whilst fine-grained porphyritic spherules can be correlated with fine-grained matrices**  
403 **having affinities to CM and CR chondrites (Van Ginneken et al., 2017). In addition, the**  
404 **presence of relict grains, major and minor elements, and oxygen isotope studies support**  
405 **these conclusions (e.g. Cordier et al., 2011, Rudraswami et al., 2015; Van Ginnken et al.,**  
406 **2017). Our data is consistent with suggestion** that barred and porphyritic spherules are  
407 mostly genetically different particles, which are predominantly derived from coarse-grained,  
408 chondrule-derived materials, whilst barred spherules are principally derived from fine-  
409 grained materials such as chondrite matrix.

410

411 [Van Ginneken et al \(2017\)](#) found one cryptocrystalline spherule  $\Delta^{17}\text{O} < -2\text{‰}$  (Group  
412 2 of [Van Ginneken et al., \(2017\)](#)), whilst 6 particles had  $\Delta^{17}\text{O} > -0.5\text{‰}$  (Group 3 and 4). **The**

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

422

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

434

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

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

446

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

454

455 Previous bulk oxygen isotope measurements of high Ca and Al spherules made by  
456 Cordier et al. (2011) have shown significantly lower  $\delta^{18}\text{O}$  values **than observed here**, having  
457 **a** range of ~15 to 19‰, **with only one having a value of** ~28‰. It is possible **the** spherules  
458 **analysed by Cordier et al., (2011) are fragments of** Ca-Al-rich precursors, rather than **the**  
459 **refractory products of** extreme evaporation. **One** CAT spherule (MY240184) analysed by  
460 Yada et al. (2005) **yielded a** high  $\delta^{18}\text{O}$  value of ~93‰. This value is much higher than our  
461 highest  $\delta^{18}\text{O}$  value of ~71‰, and our lowest value is also higher than given by Cordier et al.  
462 (2011). The extremely high value of  $\delta^{18}\text{O}$  indicates excessive heating and evaporation for an

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

468

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

485

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

488 60–300  $\mu\text{m}$ ) have sources dominated ( $\sim 80\%$ ) by carbonaceous chondrites, with the remainder  
489 derived from sources similar to ordinary chondrites. Experimental oxygen isotope analyses of  
490 different type of S-type **cosmic spherules** has demonstrated an increase in  $\delta^{17,18}\text{O}$  due to  
491 alteration during atmospheric entry (Fig. 3). The alteration in barred, cryptocrystalline, glass  
492 **spherules** are similar as they fall on TF line. Some of the porphyritic **spherules seem to be**  
493 **preserved  $\delta^{17,18}\text{O}$  and** does seem to alter significantly like glass, barred, cryptocrystalline  
494 spherules. This is also observed in previous studies that have shown some data on CCAM  
495 line (Rudraswami et al., 2015, 2016). Among the S-type **cosmic spherules**, the scoriaceous  
496 spherules **appear to have been the least affected by atmospheric entry since their** oxygen  
497 isotope fall **mainly** on CCAM line (Fig. 4). The bulk of the data from scoriaceous and  
498 porphyritic have  $\Delta^{17}\text{O} < 0\%$  similar to those seen in carbonaceous chondrites (Fig. 5),  
499 **although with significant numbers of porphyritic spherules having higher values.**  
500 **Similarly** barred, cryptocrystalline, and G-type **mostly have lower  $\Delta^{17}\text{O}$  than the TFL and**  
501 **are likewise related to carbonaceous chondrite. By comparison glassy spherules have a**  
502 **range of compositions.** The data suggest that  $\Delta^{17}\text{O}$  does not alter much irrespective of  
503 altitude, but variation in  $\delta^{17,18}\text{O}$  is visible. Although the  $\Delta^{17}\text{O}$  tends to increase with increase in  
504  $\delta^{17,18}\text{O}$  values (Rudraswami et al., 2016), most of the partially altered scoriaceous particles  
505 show  $\Delta^{17}\text{O} < 0\%$ , **suggesting** a carbonaceous chondrite origin as seen in Figs. 4 and 5, **rather**  
506 **than as a consequence of heating.** The origin of these particles from precursors consisting  
507 of hydrated fine-grained matrix is supported by their textures and mineralogy (Genge et al.,  
508 2008; Taylor et al., 2012; Badyukov et al., 2018; Suttle et al., 2019) and the presence of  
509 relict cores of matrix (Genge, 2006) and fragmented olivine within some particles (Genge et  
510 al., 2017a).

511

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

522

523 **Some the particles that have metal beads need to be looked for source related**  
524 **variation, such as, whether they are abundant in CC-derived (below TFL), OC-derived**  
525 **(above TFL), or both. Also, it will be remarkable to see if the metal beads more or less**  
526 **abundant in  $\delta^{18}\text{O}$ -rich particles that have experienced more intense heating and**  
527 **probably higher decelerations.** The presence of metal beads is related to low  $\delta^{18}\text{O}$  in I-type  
528 spherule compared to those with magnetite rich I-type particles demonstrating the mass-  
529 dependent fractionation by evaporation for particles during atmospheric entry ([Engrand et al.,](#)  
530 [2005](#)). Metal beads are present in all types of spherules in small number, except scoriaceous  
531 **micrometeorites**, and rarely in porphyritic spherules ([Rudraswami et al., 2014](#)). The oxygen  
532 isotope data on barred spherules with **at least one** metal bead has shown low  $\delta^{18}\text{O}$  values of  
533  $\sim 12\text{--}16\text{‰}$ , except MS-I3-P21 that has  $\sim 23\text{‰}$  probably due to larger size resulting in  
534 enrichment of heavier oxygen isotope during entry. This variation in oxygen isotope  
535 **composition** in barred spherules is similar to the I-type spherule correlation as suggested by  
536 [Engrand et al. \(2005\)](#). The Ni content in MS-I3-P21 is less ( $\sim 19\text{ wt\%}$ ) compared to other

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

540

541 Glass spherules have undergone more heating than barred spherules and often have  
542 metal beads. The  $\delta^{18}\text{O}$  values in metal-bearing glass spherules have shown scatter with the  
543 increase in Ni content in metal bead (Fig. 7). The Fe is more **volatile** than Ni and having  
544 large presence of Ni in metal bead, and those spherules showing low  $\delta^{18}\text{O}$  is surprising and  
545 has to do primarily with precursor properties and entry parameters. However, if the oxygen  
546 isotope composition of precursor were similar, then Fe would have got evaporated  
547 proportionately showing relation to  $\delta^{18}\text{O}$ . MS-I35-P39 is the only glass spherule where it has  
548 shown high Ni content of ~64 wt%; one of the reasons is a different type of precursors that is  
549 contributed and also the entry parameter as indicated earlier. (Fig. 7). We **have measured a**  
550 **single** G-type spherule with bead that has very low nickel content (~10 wt%) and  $\delta^{18}\text{O}$  value  
551 of ~28‰ which fit in range of bead bearing glass spherules. The metal bead in porphyritic  
552 spherule is strange, and SP005-P1078 has two metal bead where its average composition has  
553 shown presence of sulfur (~17 wt%) along with Fe and Ni (Appendix A) indicating that these  
554 metals are not due to entry phenomena but were existing in its precursor, **and most likely**  
555 **have got altered due to oxidation during entry** (Fig. 2a). The  $\delta^{18}\text{O}$  composition of ~32‰ is  
556 much larger and comparable to other spherules that have shown some sulfur composition in  
557 glass spherules (SP005-P157, SP005-P1071, SP005-P34, SP005-P294, and SP005-P296).  
558 The lone cryptocrystalline spherule also has low  $\delta^{18}\text{O}$  values compared to high Ni content of  
559 ~64 wt%. Four particles, namely two from glass, one from CAT and one from I-type, has  
560 shown metal bead escaped from the spherules (Fig. 2). The  $\delta^{18}\text{O}$  of the **spherules that have**  
561 **escaped segregated** metal bead is ~35–40‰, except MS-I3-P55 with low values. However,



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

566

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

581

### 582 **5.3. Oxygen isotope of G-type Cosmic Spherules**

583

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

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

594

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

609

#### 610 **5.4. Implications**

611

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

632

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

637 by evaporation is mostly dependent on peak temperature and the duration of the heating  
638 pulse. Peak temperature increases with entry velocity or with entry angle with high velocity,  
639 high entry angle particles experiencing larger peak temperatures and evaporation. The  
640 duration of the heating pulse, conversely increases with decreasing entry angle. In two  
641 particles experiencing the same peak temperature, for example, the particle with the lower  
642 entry angle (which would necessarily have a higher entry velocity to attain the same peak  
643 temperature) would experience a larger degree of partial evaporation owing to the longer time  
644 spent at high temperature. The time spent above the solidus has been shown to increase from  
645 1-2 s at steep entry angles to >12 s at shallow entry angles (e.g. [Genge, 2016, 2017](#)). Other  
646 properties of particles might, however, influence mass fractionation of oxygen. Volatile- or  
647 moderately volatile-rich precursors may undergo more significant partial evaporation than  
648 those particles with refractory starting compositions, increasing the mass fractionation of  
649 oxygen. The degree of mass-fractionation may, therefore, in part be source dependent, albeit  
650 with significant variation related to the different components present, such as fine-grained,  
651 volatile-rich matrix, chondrules and calcium-aluminium-inclusions.

652

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

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

666

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

676

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

686

687 **6. CONCLUSIONS**

688

689 **The oxygen isotope compositions of cosmic spherules are a complex signatures of**  
690 **parent body along with atmospheric entry processes arising due to both mass**  
691 **fractionation and isotopic exchange with terrestrial oxygen.** We performed 277 in situ  
692 oxygen isotope analyses using ion microprobe in 137 micrometeorites collected from deep-  
693 sea and Antarctica along with many spherules that have metal bead to understand the isotopic  
694 pattern. There is an increase in average  $\delta^{18}\text{O}$  from scoriaceous< porphyritic< barred<  
695 cryptocrystalline< glass< CAT which is clearly related to mass-fractionation and evaporation,  
696 and thus peak temperature the particle has acquired during atmospheric entry. It also suggests  
697 that mass-fractionation due to heating dominates over exchange with air for S-types.  
698 Porphyritic spherules have small  $\Delta^{17}\text{O}$  scattered around the TFL, barred and cryptocrystalline  
699 spherules fall mainly below the TFL confirming that porphyritic are primarily derived from  
700 chondrule fragments, many from OCs, whilst barred and cryptocrystalline are from  
701 carbonaceous chondrite matrix. Cryptocrystalline spherules have mostly negative  $\Delta^{17}\text{O}$   
702 similar to barred olivine spherules suggesting they form by further melting at higher peak  
703 temperature of these particles. It suggests these too are mainly derived from fine-grained  
704 carbonaceous chondrite matrix. Glass spherules have  $\Delta^{17}\text{O}$  with a range similar (but not quite  
705 as large) as porphyritic, barred and cryptocrystalline spherules together. This suggests these  
706 form by extensive melting of these types. CAT spherules have small  $\Delta^{17}\text{O}$  scattered around  
707 TFL and making close associates of porphyritic spherules. G-types **that are** expected to have  
708 significant exchange of atmospheric oxygen and mass-fractionation at high temperatures;  
709 however, their small range of  $\delta^{18}\text{O}$  suggests the opposite. The G-type with unique dendrites  
710 of magnetite and silicate appears to be dominated by carbonaceous chondritic precursors.  
711 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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723 is NIO's contribution No. xxxx.

724

725 **APPENDIX A. SUPPLEMENTARY DATA**

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

727



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870  
871

872 **Figure Captions**

873

874 **Figure 1.**

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

880

881 **Figure 2.**

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

890

891 **Figure 3.**

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

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

898

899 **Figure 4.**

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

905

906 **Figure 5.**

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

911

912 **Figure 6.**

913 (a) The plot of  $\delta^{18}\text{O}$  vs. magnetite rim thickness of I-type spherules appears to increase with  
914  $\delta^{18}\text{O}$  values. (b) The plot of  $\delta^{18}\text{O}$  versus the diameter of I-type spherules with sizes less than  
915 300  $\mu\text{m}$  from this study. Results of I-type spherules data for both magnetite thickness and  
916 diameter from [Engrand et al. \(2005\)](#) have been included in the plot for comparison. The plots  
917 indicate that with increase in  $\delta^{18}\text{O}$  values the magnetite rim and diameter of spherule **range**  
918 also increases. The circle marked in b is the data seems **anomalous and is** slightly far from  
919 the trend.



920

921 **Figure 7.**

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

929

930 **Figure 8.**

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

935

936 **Figure 9.**

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

944