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# Oxygen isotope measurements of individual unmelted Antarctic micrometeorites

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**Abstract**

We present oxygen isotope measurements of 28 unmelted Antarctic micrometeorites measuring 150–250 μm (long axis) collected in the South Pole water well. The micrometeorites were all unmelted and classified as either fine-grained, scoriaceous, coarse-grained or composite (a mix of two other classes). Spot analyses were made of each micrometeorite type using an ion microprobe. The oxygen isotope values were measured relative to standard mean ocean water (SMOW) and range from $\delta^{18}O = 3‰$ to 60‰ and $\delta^{17}O = -1‰$ to 32‰, falling along the terrestrial fractionation line (TFL) within $2\sigma$ errors. Several analytical spots (comprising multiple phases) were made on each particle. Variability in the oxygen isotope ratios was observed among micrometeorite types, between micrometeorites of the same type and between analytical spots on a single micrometeorite indicating that micrometeorites are isotopically heterogeneous. In general, the lowest isotope values are associated with the coarse-grained micrometeorites whereas most of the fine-grained and scoriaceous micrometeorites have an average $\delta^{18}O \geqslant 22‰$, suggesting that the matrix in micrometeorites is isotopically heavier than the anhydrous silicate phases. The oxygen isotope values for the coarse-grained micrometeorites, composed mainly of anhydrous phases, do not lie along the carbonaceous chondrite anhydrous mineral (CCAM) line, as observed for olivines, pyroxenes and some kinds of chondrules in carbonaceous chondrites, suggesting that coarse-grained MMs are not related to chondrules, as previously thought. Our measurements span the same range as values found for melted micrometeorites in other studies. Although four of the micrometeorites have oxygen isotope values lying along the TFL, close to the region where the bulk CI carbonaceous chondrites are found, 21 particles have very enriched $^{17}O$ and $^{18}O$ values that have not been reported in previous analyses of chondrite matrix material, suggesting that they could be a new type of Solar System object. The parent bodies of the micrometeorites with higher $^{18}O$ values may be thermal metamorphosed carbonaceous asteroids that have not been found as meteorites either because they are friable asteroids that produce small particles rather than rocks upon collision with other bodies, or because the rocks they produce are too friable to survive atmospheric entry.


## 1. Introduction

A major challenge in understanding the formation and evolution of the Solar System is determining the distribution of oxygen isotopes among different solar system objects and interpreting the processes that resulted in their isotopic distributions. Studies of oxygen isotopic compositions of meteorites, including lunar and martian meteorites, have constrained the processes that formed the early Solar System (for a review, see Clayton (1993, 2003)). The isotopic compositions of small particles (micrometeorites and interplanetary dust particles) should also provide insights into these processes. Micrometeorites (MMs) are extraterrestrial particles with diameters between 25 and 2000 μm found on the Earth's surface. Most micrometeorites are

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collected from Antarctic and Greenland ice. They consist of matrix (mainly formed by tiny mineral grains and carbonaceous material), iron oxides, iron sulfides and anhydrous silicate phases (Kurat et al., 1994; Nakamura et al., 2001). Micrometeorites are considered to be chondritic materials because their bulk composition is close to carbonaceous chondrite abundances (except for S and Ni that are depleted due to weathering processes that occurred during their stay in the ice). Micrometeorites range from unmelted particles, which have been heated but not melted during atmospheric entry (peak temperature in the range 1100–1200 °C) (Greshake et al., 1998) and therefore retain most of their original mineralogy, to melted cosmic spherules. Few studies exist of oxygen isotopic compositions of micrometeorites. Past studies have analyzed oxygen isotopes in cosmic spherules from the deep sea (Clayton et al., 1986; Engrand et al., 1998) or Antarctic ice (Yada et al., 2003; Engrand et al., 2005; Taylor et al., 2005; Yada et al., 2005). Only individual phases of unmelted micrometeorites, such as silicates (Engrand et al., 1999a; Yada et al., 2002; Gounelle et al., 2005) and refractory grains (Greshake et al., 1996) have been analyzed for oxygen isotopes. In this work, we present multi-spot oxygen isotopic analyses of 28 unmelted Antarctic MMs, in order to compare their ratios to the values measured in melted micrometeorites and carbonaceous chondrites, and to constrain their origins.

## 2. Experimental procedures

### 2.1. Selection of micrometeorites

The samples were collected in the South Pole water well (Taylor et al., 1998). For this study, we analyzed particles that measure 150–250 μm (long axis). We selected the MMs as follows: first, all the black particles with irregular shapes were handpicked from the sample under a stereomicroscope. Then, these particles were mounted in *crystalbond* following the procedure described in Brownlee et al. (2002) and polished (Fig. 1). For identification of micrometeorites, the particles were surveyed using a scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) analyzer. A Jeol 35C microscope equipped with a Voyager 4 X-ray analysis system with a ThermoNoran light element X-ray detector was used and operated at an accelerating voltage of 20 kV. The EDX data were obtained by acquiring a 90-s integration time spectrum of each particle. The EDX spectra were used to identify and distinguish chondritic particles from contaminants. The principle for identification of chondritic-like particles is the comparison of the Kα lines of major elements (Si, Mg, Fe and O) and minor elements (Al, Ca, S, P and Ni) with the Kα lines of the same elements found in typical chondrites. This criterion has proved to be very effective for the selection of extraterrestrial particles (Brownlee et al., 1997; Genge et al., 1997; Nakamura et al., 1999; Osawa and Nagao, 2002; Yada et al., 2004). In addition, these protocols are the ones adopted for IDP identification by the CDPET (NASA cosmic dust catalog). An example of a typical spectrum of a particle identified as being a micrometeorite is found in Fig. 2. Following this criterion, we found that about 50% of the particles examined were chondritic. Most of the other particles, identified as contaminants, were iron oxide grains and aluminum oxide grains. All of the particles with chondritic composition were considered extraterrestrial and identified as micrometeorites. The 28 micrometeorites chosen for this study are listed in Table 1. To make it easier to recognize and discuss a micrometeorite, we have given each particle a name in place of its alpha-numeric designation.

### 2.2. Classification

All 28 micrometeorites were photographed with the SEM (Fig. 1) and then classified based on their texture as fine-grained, scoriaceous, coarse-grained or composite (Table 1). These textures were first observed and described by Brownlee et al. (1980) and later extended by Engrand and Maurette (1998) and are as follows: the scoriaceous particles are recognized because they contain vesicles between the mineral grains. The origin of the vesicles is still unknown, although it is thought that they form by evaporation of volatile phases during atmospheric entry. The fine-grained particles are composed of tiny (few μm) mineral grains (anhydrous silicates, iron oxides, sulfides, etc), whereas the coarse-grained particles have mineral grains (mostly anhydrous silicates) of about 5–10 μm in size. In this work, we have designated particles that are a mix of two other classes as composite. In Fig. 1, we show representative micrometeorites of each class that we studied.

### 2.3. Sample preparation for ion microprobe analysis

In preparation for the oxygen isotopic measurements the micrometeorites were removed from the *crystalbond* using acetone. Each micrometeorite was then crushed between two tungsten carbide plates to make it as flat and homogeneous as possible. The flattened particles were then pressed into gold foil. This procedure often broke the micrometeorite into smaller pieces. Pieces of San Carlos olivine, which we used as standards, were also flattened and pressed into the same gold foil. This ensured that samples and standards underwent exactly the same preparation and that they were at the same height during analysis (see details in next Section 2.4). The entire mount, containing micrometeorites and standards, was coated with gold prior to isotopic analysis.

### 2.4. Ion microprobe analysis

Oxygen isotope analyses of the micrometeorites were carried out with the Cameca IMS 6f ion microprobe at Arizona State University using techniques described in Jones et al. (2004b). Because we observed high $\delta^{18}O$ values in some of the MMs we wanted to confirm our results.

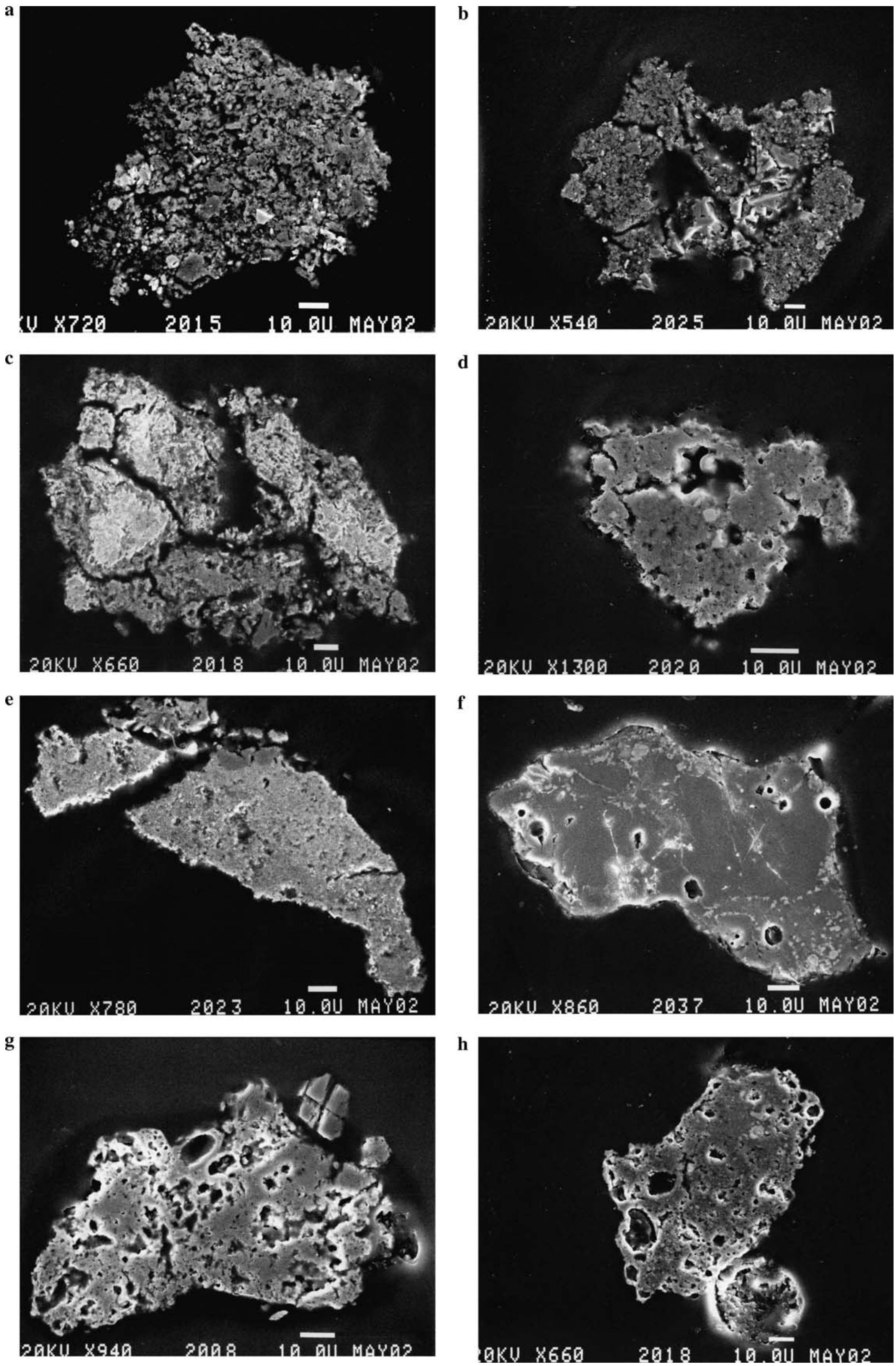


Fig. 1. Micrographs of representative micrometeorites showing the different classes studied. First row, fine-grained particles Nezta and Popo; second row fine-grained particles Maya and Paricutin; third row fine-grained particle Nahui and coarse-grained particle Mate; last row composite particles Yayee and Peyotl.

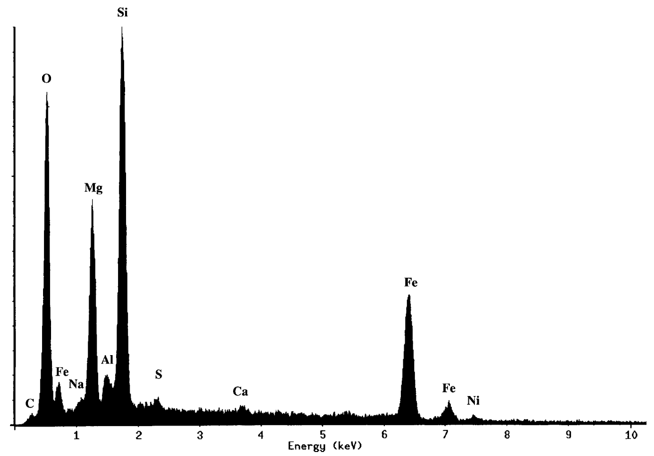


Fig. 2. An example of a typical energy-dispersive X-ray spectrum of a chondritic micrometeorite. The major peaks (Fe, Si and Mg) and the minor peaks (Al, Ca and S) are found in the same proportions as in chondrites.

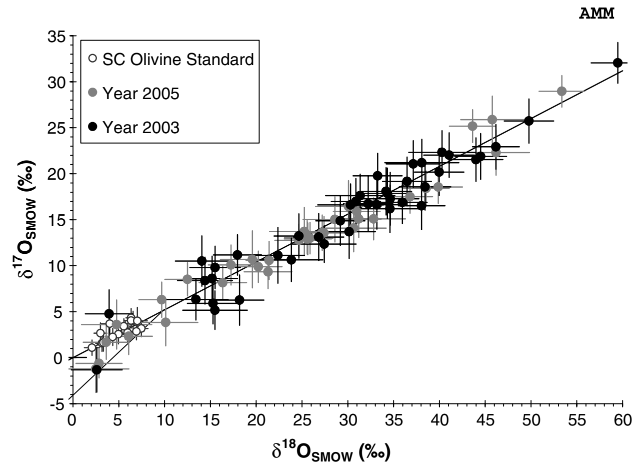


Fig. 3. Oxygen three-isotope plot of unmelted micrometeorites (values are relative to SMOW). All spots obtained during the two runs are plotted. The data fall along the terrestrial fractionation line (TFL) within $2\sigma$ errors.

Table 1
Classification of all the micrometeorites studied

| Sample | Name | Size (μm) | Group |
|---|---|---|---|
| SPWW-J4E | Aconcagua | 50 | Fine-grained |
| SPWW-J4B2 | Amate | 65 | Scoriaceous |
| SPWW-I18 | Anahi | 90 | Fine-grained |
| SPWW-J5H | Arrayan | 95 | Coarse-grained |
| SPWW-J7E | Chapultepec | 90 | Coarse-grained |
| SPWW-I17 | Chinchulin | 110 | Scoriaceous |
| SPWW-J6H | Issaqua | 100 | Fine-grained |
| SPWW-J2G | Itati | 90 | Composite |
| SPWW-J5B | Ixta | 90 | Coarse-grained |
| SPWW-J7D | Mate | 100 | Coarse-grained |
| SPWW-J3A | Maya | 80 | Fine-grained |
| SPWW-J7F | Mezcal | 90 | Coarse-grained |
| SPWW-I12 | Milonga | 70 | Fine-grained |
| SPWW-J7G | Mitla | 100 | Coarse-grained |
| SPWW-I6 | Nahuel | 90 | Composite |
| SPWW-J1G | Nahui | 80 | Fine-grained |
| SPWW-J4A | Netza | 100 | Fine-grained |
| SPWW-I13 | Ollin | 100 | Fine-grained |
| SPWW-J6A | Papirus | 90 | Fine-grained |
| SPWW-J4F | Paricutin | 55 | Fine-grained |
| SPWW-J4D | Peyotl | 60 | Composite |
| SPWW-J5G | Popo | 95 | Fine-grained |
| SPWW-I11 | Tango | 100 | Scoriaceous |
| SPWW-J6E | Totem | 90 | Scoriaceous |
| SPWW-J6F | Snoqualmie | 100 | Scoriaceous |
| SPWW-J7C | Squamish | 100 | Scoriaceous |
| SPWW-J8F | Xipolite | 85 | Fine-grained |
| SPWW-J2B | Yayee | 100 | Composite |

Therefore, we performed a second analysis on the same micrometeorite samples in February 2005. The only instrumental change between the two analytical sessions was the use of a new sample Z-stage on the ion microprobe, which adjusts the height of the sample thereby minimizing instrumental mass fractionation that could result from variation in sample height. Although individual measurements may vary between the two runs, the range of values obtained in both runs is similar (Fig. 3).

Samples were bombarded with a 0.3–0.5 nA $Cs^+$ beam of 19 keV. The $Cs^+$ beam was tuned in aperture illumination mode, producing craters of ~20 μm in diameter and ~1–2 μm in depth on randomly chosen sample surfaces. Secondary ions were collected by peak-jumping into either a Faraday cup $^{16}O^-$ or electron multiplier ($^{17}O^-$ and $^{18}O^-$) at a mass resolving power of ~6200, which is sufficient to completely resolve the $^{16}OH^-$ interference on $^{17}O^-$. Our standard, San Carlos olivine, was measured repeatedly during the analyses to monitor instrumental mass fractionation. The sample values were corrected for instrumental mass fractionation, which averaged about −7‰ and −10‰ for $\delta^{18}O$ during the two analytical sessions, respectively. Uncertainties on individual analyses, taking into account the variation on repeated analyses of the standard, are ~3‰ ($2\sigma$). Even though San Carlos olivine was used to calibrate instrumental mass fractionation for all the sample measurements, the magnitudes of matrix effects under such analytical conditions are small (less than a few ‰) (Leshin et al., 1997; Hua et al., 2005). The matrix effects among Crestmore (Fo ~100%), San Carlos (Fo ~89%) and Eagle Station (Fo ~80%) olivines are less than 2‰ (Y. Guan, personal communication). In addition, similar analytical protocols have been used to measure oxygen isotopic compositions of other meteorite samples (Leshin et al., 2001; Jones et al., 2004a,b) and micrometeorites (Engrand et al., 1999a; Engrand et al., 2005; Yada et al., 2005) and no large instrumental mass fractionation or matrix effects have been observed. Therefore, no corrections for matrix effects were made on the micrometeorite oxygen isotope data.

Analyses with the SEM of the crushed particles showed that they were formed of a mixture of phases composed of fine and coarse grains smaller than 10 μm in size. Because the ion microprobe beam size is around 20 μm in diameter, analysis of mixed phases was unavoidable. For this reason, between two to seven spots per particle were analyzed. The distance between the analyzed spots ranged from ~50 to

~150 μm. When there were multiple pieces of the same particle spot analyses were made on different pieces.

## 3. Results

### 3.1. Oxygen isotope ratios and variability

Oxygen isotope values were measured relative to standard mean ocean water (SMOW), and are listed in Tables 2–5. Fig. 3 shows the data for all particles obtained during both runs.

The $\delta^{18}O$ values of all the individual spot measurements vary from about −1‰ to 60‰. The averaged $\delta^{18}O$ values for each micrometeorite range from 3‰ (Ixta) to 60‰ (Peyotl). The largest range of oxygen isotopic compositions within a single micrometeorite was observed in Popo (Table 2). Seven measurements on five different pieces of this particle (each measuring, after crushing, about 100 μm in long axis) gave a range for $\delta^{18}O$ from about −1‰ to 35‰. In addition, within the same class, micrometeorites can have very different values of $\delta^{18}O$, for example the coarse-grained micrometeorites Ixta (2.6‰) and Mate (up to 25.6‰). All the oxygen isotopic data of the

Table 2
Oxygen isotope measurements (‰ relative to SMOW) of high-$^{16}O$ (particles Milonga to Popo) and low-$^{16}O$ (particles Maya to Papirus) fine-grained MMs

| Sample | Analytical spots | $\delta^{18}O \pm 2\sigma$ | $\delta^{17}O \pm 2\sigma$ |
|---|---|---|---|
| Milonga | a | 25.3 ± 3.8 | 13.7 ± 2.6 |
| | b | 30.9 ± 2.7 | 17 ± 2.5 |
| | c | 33.2 ± 2.8 | 16.6 ± 2.6 |
| Ollin | a | 21.3 ± 2.6 | 9.3 ± 1.8 |
| | b | 30.1 ± 2.9 | 13.7 ± 2.9 |
| Nahui | a | 24.7 ± 2.6 | 12.8 ± 1.8 |
| | b | 34.3 ± 2.5 | 17.9 ± 2.7 |
| Anahi | a | 17.3 ± 2.5 | 10.1 ± 2.2 |
| | b | 29.2 ± 2.7 | 14.9 ± 2.7 |
| Netza | a | 19.6 ± 3.5 | 10.7 ± 3.1 |
| | b | 24.7 ± 2.7 | 13.2 ± 2.4 |
| Aconcagua | a | 15.3 ± 2.8 | 5.9 ± 2.2 |
| | b | 25.6 ± 2.6 | 12.9 ± 1.7 |
| Xipolite | a | 28.6 ± 3.5 | 15 ± 2.5 |
| | b | 36.5 ± 2.7 | 19.2 ± 2.6 |
| Issaqua | a | 16.4 ± 2.6 | 8.2 ± 1.8 |
| | b | 32.2 ± 2.7 | 16.7 ± 3 |
| Popo | a | −1.2 ± 2.6 | 0 ± 2.5 |
| | b | 2.5 ± 3.6 | −1.2 ± 2.6 |
| | c | 6.1 ± 2.6 | 2.3 ± 2 |
| | d | 10.1 ± 3.5 | 3.8 ± 2.6 |
| | e | 22.4 ± 2.9 | 11.1 ± 3 |
| | f | 25.9 ± 2.5 | 13 ± 1.7 |
| | g | 34.6 ± 3.1 | 17.3 ± 2.9 |
| Maya | a | 31.2 ± 2.4 | 15.1 ± 2 |
| | b | 38.4 ± 2.8 | 18.6 ± 2.5 |
| Paricutin | a | 37.1 ± 3 | 21.1 ± 2.5 |
| | b | 41.1 ± 2.8 | 22 ± 2.4 |
| | c | 43.6 ± 2.5 | 25.2 ± 1.8 |
| Papirus | a | 27.2 ± 2.6 | 13.6 ± 1.9 |
| | b | 38.1 ± 2.6 | 16.5 ± 2.6 |

The errors are $2\sigma$.

Table 3
Oxygen isotope measurements (‰ relative to SMOW) of coarse-grained MMs

| Sample | Analytical spots | $\delta^{18}O \pm 2\sigma$ | $\delta^{17}O \pm 2\sigma$ |
|---|---|---|---|
| Ixta | a | 2.6 ± 2.8 | −1.3 ± 2.4 |
| | b | 2.8 ± 2.5 | −0.6 ± 1.6 |
| Arrayan | a | 9.7 ± 2.5 | 6.3 ± 1.9 |
| | b | 15.5 ± 2.8 | 9.8 ± 2.3 |
| Mate | a | 18 ± 2.6 | 11.2 ± 2.2 |
| | b | 25.6 ± 2.5 | 13.1 ± 1.8 |
| Chapultepec | a | 14.4 ± 3 | 8.4 ± 2.6 |
| | b | 21.4 ± 2.5 | 10.6 ± 2.1 |
| Mezcal | a | 3.6 ± 2.5 | 1.7 ± 1.9 |
| | b | 3.9 ± 2.6 | 4.8 ± 2.6 |
| Mitla | a | 4.8 ± 3.8 | 3.6 ± 2.7 |
| | b | 15.2 ± 2.8 | 8.6 ± 2.4 |

The errors are $2\sigma$.

Table 4
Oxygen isotope measurements (‰ relative to SMOW) of scoriaceous MMs

| Sample | Analytical spots | $\delta^{18}O \pm 2\sigma$ | $\delta^{17}O \pm 2\sigma$ |
|---|---|---|---|
| Squamish | a | 18.2 ± 2.7 | 6.3 ± 2.7 |
| | b | 39.9 ± 2.6 | 18.6 ± 1.8 |
| Snoqualmie | a | 34.6 ± 3.6 | 16.2 ± 2.6 |
| | b | 36.8 ± 2.5 | 17.5 ± 1.8 |
| | c | 38.5 ± 2.5 | 18.4 ± 1.9 |
| | d | 44.5 ± 2.8 | 21.9 ± 2.5 |
| Chinchulin | a | 31 ± 2.6 | 15.9 ± 1.8 |
| | b | 46.2 ± 2.6 | 22.9 ± 2.4 |
| Tango | a | 34.2 ± 2.8 | 18.1 ± 2.6 |
| | b | 46.2 ± 3.7 | 22.3 ± 2.5 |
| Amate | a | 20.2 ± 2.6 | 9.9 ± 1.7 |
| | b | 44 ± 2.9 | 21.5 ± 2.4 |
| Totem | a | 49.8 ± 2.7 | 25.7 ± 2.4 |
| | b | 53.4 ± 2.5 | 29 ± 1.7 |

The errors are $2\sigma$.

Table 5
Oxygen isotope measurements (‰ relative to SMOW) of composite MMs

| Sample | Analytical spots | $\delta^{18}O \pm 2\sigma$ | $\delta^{17}O \pm 2\sigma$ |
|---|---|---|---|
| Itati | a | 12.5 ± 2.5 | 8.5 ± 1.8 |
| | b | 14.1 ± 2.9 | 10.5 ± 2.7 |
| Nahuel | a | 26.8 ± 2.7 | 13.1 ± 2.6 |
| | b | 30.6 ± 3.6 | 14.1 ± 2.6 |
| | c | 33.3 ± 2.7 | 19.8 ± 2.5 |
| Peyotl | a | 59.5 ± 2.9 | 32.1 ± 2.2 |
| Yayee | a | 27.4 ± 2.5 | 13.6 ± 1.8 |
| | b | 40 ± 2.7 | 20.2 ± 2.6 |

The errors are $2\sigma$.

Table 6
Average of oxygen isotope values (relative to SMOW) for all the micrometeorites studied

| Sample | Average $\delta^{18}O$ (‰) | Average $\delta^{17}O$ (‰) | Group |
|---|---|---|---|
| Aconcagua | 20.5 | 9.4 | fg |
| Amate | 32.1 | 15.7 | sc |
| Anahi | 23.3 | 12.5 | fg |
| Arrayan | 12.6 | 8.1 | cg |
| Chapultepec | 17.9 | 9.5 | cg |
| Chinchulin | 38.6 | 19.4 | sc |
| Issaqua | 24.3 | 12.5 | fg |
| Itati | 13.3 | 9.5 | comp |
| Ixta | 2.7 | −1.0 | cg |
| Mate | 21.8 | 12.2 | cg |
| Maya | 34.8 | 16.9 | fg |
| Mezcal | 3.8 | 3.3 | cg |
| Milonga | 29.8 | 15.8 | fg |
| Mitla | 10 | 6.1 | cg |
| Nahuel | 30.2 | 15.7 | comp |
| Nahui | 29.5 | 15.4 | fg |
| Netza | 22.2 | 12.0 | fg |
| Ollin | 25.7 | 11.5 | fg |
| Papirus | 32.6 | 15.1 | fg |
| Paricutin | 40.6 | 22.8 | fg |
| Peyotl | 59.5 | 32.1 | comp |
| Popo | 14.3 | 6.6 | fg |
| Tango | 40.2 | 20.2 | sc |
| Totem | 51.6 | 27.4 | sc |
| Snoqualmie | 38.6 | 18.5 | sc |
| Squamish | 29.1 | 12.5 | sc |
| Xipolite | 32.6 | 17.1 | fg |
| Yayee | 33.7 | 16.9 | comp |

fg: fine-grained; cg: coarse-grained; sc: scoriaceous; comp: composite.

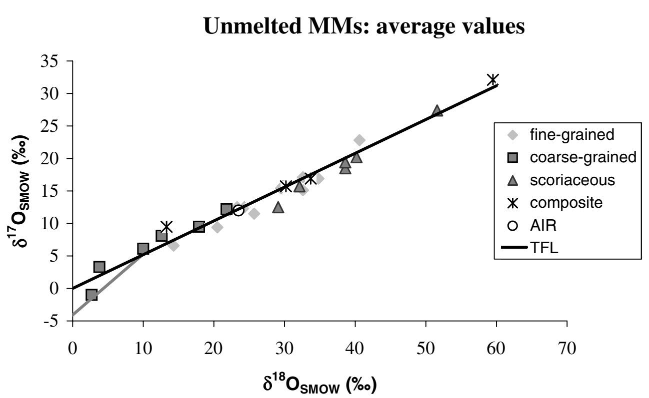


Fig. 4. Oxygen three-isotope plot of the averaged values (relative to SMOW) obtained during the runs of both years and over several spots. The points have been plotted according to the type of particle. The value for the oxygen on the stratospheric air ($\delta^{18}O = 23.5$‰ Kroopnick and Craig, 1972; Thiemens et al., 1995) is shown for reference.

micrometeorites fall, within $2\sigma$ errors, along the terrestrial fractionation line (TFL) of slope 0.52.

### *3.2. Correlation between micrometeorite type and isotope values*

Table 6 and Fig. 4 show the average of all oxygen isotope measurements for each micrometeorite. In general, the lowest $\delta^{18}O$ values are associated with the coarse-grained micrometeorites ($\delta^{18}O \leqslant 22$‰, Table 3) whereas most of the fine-grained (Table 2) and scoriaceous (Table 4) micrometeorites have $\delta^{18}O \geqslant 22$‰. This association suggests that the tiny grains that make up the matrix in fine-grained MMs are isotopically heavier than the larger anhydrous silicate phases making up the coarse-grained MMs. An isotopically heavy matrix is further supported by previous studies of olivine and pyroxene phenocrysts in unmelted MMs that showed low $\delta^{18}O$ values ranging from −11.0‰ to 8.5‰ (Engrand et al., 1999a; Gounelle et al., 2005).

All the scoriaceous particles have $\delta^{18}O \geqslant 29$‰. However, there are also some fine-grained particles (Maya, Milonga, Nahui, Paricutin, Xipolite and Papirus) that have $\delta^{18}O \geqslant 29$‰ (Table 2 and Fig. 4). The overlap of oxygen values between some members of these two classes suggests that the phases that vaporize to form the vesicles in scoriaceous particles have the same isotopic composition as the rest of the micrometeorite.

Four particles (Itati, Peyotl, Yayee and Nahuel) were classified as composite (Table 5). The particle Nahuel has an average $\delta^{18}O = 30.2$‰. Although this particle is a mixture of coarse and fine-grained regions, it does not plot between the fine-grained and the coarse-grained particles but rather in the region between the fine-grained and the scoriaceous particles (see Fig. 4). Similarly, the particles Itati (average $\delta^{18}O = 13.3$‰) and Peyotl ($\delta^{18}O = 59.5$‰) have regions with vesicles and areas that are fine-grained (see Fig. 1). However, they do not plot between the fine-grained and the scoriaceous values: Itati plots in the low end of the fine-grained values, and Peyotl plots beyond the scoriaceous values at their high end. Only the composite particle Yayee (see Fig. 1), which has an average $\delta^{18}O = 33.7$‰, plots between the fine-grained and the scoriaceous values. These observations show that a mixture of phases does not necessarily mean a $\delta^{18}O$ value proportional to the phases involved in the mixture.

## 4. Discussion

### *4.1. Origin of the observed isotopic distribution*

The large range of $\delta^{18}O$ values observed includes some of the highest reported to date for bulk extraterrestrial materials (see Fig. 6). Because of the unexpectedly high $\delta^{18}O$ values found we examined processes that could have affected our data: (a) instrumental mass fractionation, (b) isotopic exchange with Antarctic water, (c) isotopic exchange with the oxygen in the air, (d) fractionation due to evaporation of oxygen-bearing phases during atmospheric entry heating, (e) solar wind implantation and (f) evaporation of O-bearing organic molecules enriched in the $^{16}O$ isotope.

We considered instrumental mass fractionation and think this is not an issue (see Section 2.4). The same analytical protocols have been used routinely to measure oxygen isotopic compositions of other meteorite samples (e.g., Leshin et al. (2001); Jones et al. (2004a,b)) and high $\delta^{18}O$

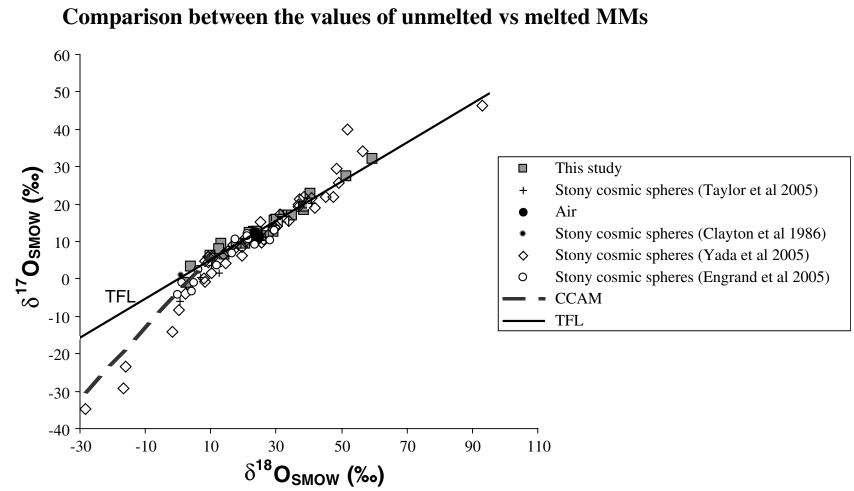


Fig. 5. Oxygen three-isotope plot of the values (relative to SMOW) obtained during this study, compared to the data from other studies on melted micrometeorites Clayton et al., 1986; Engrand et al., 1998; Yada et al., 2003, 2005; Taylor et al., 2005.

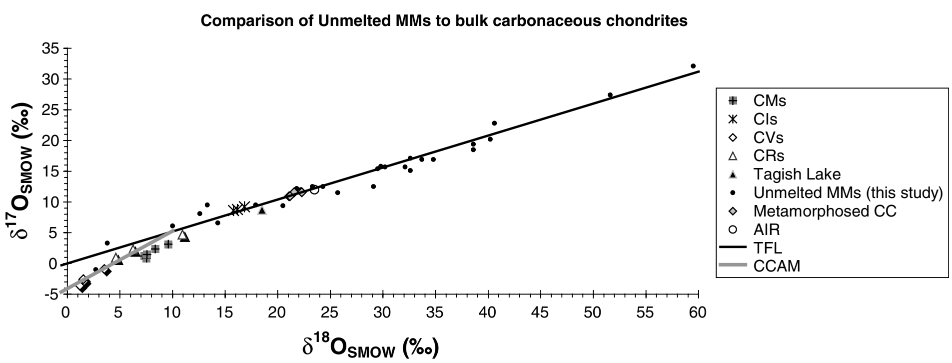


Fig. 6. Oxygen three-isotope plot of the values (relative to SMOW) obtained during this study, compared to the data from other studies on bulk carbonaceous chondrites Leshin et al., 1997; Clayton and Mayeda, 1999; Clayton and Mayeda, 2001; Leshin et al., 2001 and metamorphosed carbonaceous chondrites Mayeda and Clayton, 1990; Clayton and Mayeda, 1999.

values were not observed. Furthermore, Yada et al. (2002, 2003, 2005) measured stony cosmic spherules using a different ion microprobe and found $\delta^{18}O$ values in the same range as observed in this study. It therefore seems unlikely that the data obtained during this study resulted from instrumental mass fractionation.

Isotopic exchange with Antarctic ice or melt water would drive the $\delta^{18}O$ to lighter isotopic values because the average $\delta^{18}O$ of Antarctic water is about $-50‰$ (Clark and Fritz, 1997; Stuiver and Grootes, 2000; Smith et al., 2002). Our data show that the micrometeorites are enriched in $^{18}O$ indicating no significant effect from the water on the oxygen ratios measured.

The oxygen isotope values of the MMs do not cluster near the value for air ($\delta^{18}O = 23.5‰$ (Kroopnick and Craig, 1972; Thiemens et al., 1995)), but rather spread along the TF line (see Fig. 4), both above and below the atmospheric value. This suggests that the oxygen isotope values of MMs are not the result of simple mixing or replacement with atmospheric oxygen. Also, the lack of an $^{18}O$ rich oxygen source in the high atmosphere (Thiemens et al., 1995; Thiemens, 1999), where MMs experience peak heating, argues against atmospheric oxygen exchange with the micrometeorites. Fusion crusts of meteorites provide evidence for the isotopic effects of oxidation and exchange during atmospheric entry. Data for several meteorite fusion crusts show $\delta^{18}O$ values as high as 16‰ (Clayton et al., 1986), further supporting that the high isotopic values observed in MMs are attributed to their parent body (see Section 4.4.3) and not to their atmospheric entry.

Fractionation due to evaporation can be discussed relative to what is observed on stony cosmic spherules, assuming that melted and unmelted micrometeorites come from the same precursor population. Isotopic fractionation of Fe, Mg and Si due to entry heating (evaporation) has been observed only in a small subset of stony cosmic spherules (Alexander et al., 2002; Taylor et al., 2005). The textures of the micrometeorites analyzed here indicate that they were not melted (Fig. 1). In addition, our particles are chondritic and loss of oxygen due to vaporization would be accompanied by evaporation of iron, magnesium and silicon (Davis et al., 1990; Davis et al., 1991), rendering them non-chondritic in composition. Moreover, if loss of the lighter isotope were taking place during atmospheric heating, then cosmic spherules should have higher $\delta^{18}O$ than the unmelted micrometeorites. However, from Figs. 5, 7 and 8 and Table 7 we

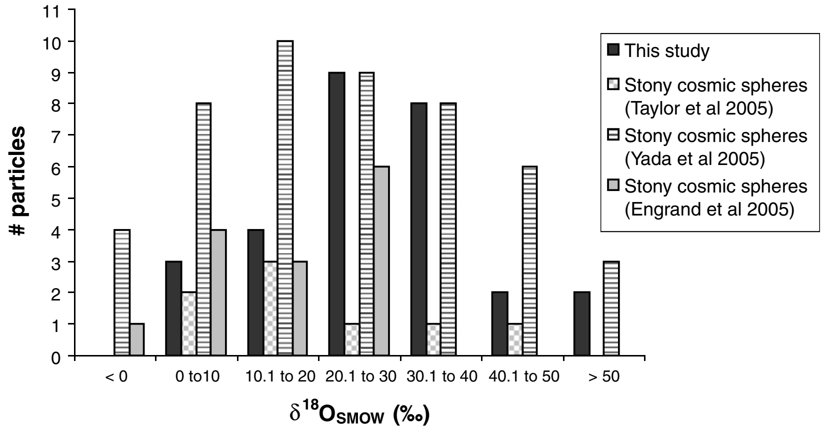


Fig. 7. Comparison of the number of particles and the range of $\delta^{18}$O (relative to SMOW) between unmelted MMs (this study) and stony cosmic spheres. Data from Engrand et al., 1998; Taylor et al., 2005; Yada et al., 2005.

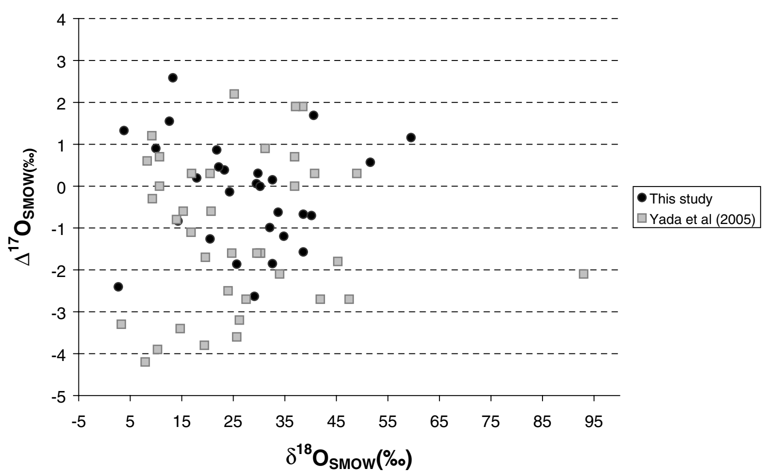


Fig. 8. Plot of $\delta^{18}$O vs $\Delta^{17}$O of unmelted MMs (this study) and melted spheres that fall along the TFL (from Yada et al., 2005). The values are relative to SMOW.

Table 7
Comparison of oxygen isotope values for unmelted MMs and stony cosmic spherules

| Sample | Collected in | $\delta^{18}$O (‰) | Line | Reference |
|---|---|---|---|---|
| Bulk unmelted MMs | Antarctic ice | 3 to 59.5 | TFL | This study |
| Individual silicates in unmelted MMs | Antarctic ice | −9.9 to 8 | CCAM | Engrand et al. (1999a), Yada et al. (2002) |
| Refractory phases in unmelted MMs | Antarctic ice | −40 to −14 | CCAM | Greshake et al. (1996) |
| Stony cosmic spheres | Antarctic ice | 7.9 to 93 | TFL | Yada et al. (2003, 2005) |
| Stony cosmic spheres | Antarctic ice | −28.2 to 3.3 | $^{16}$O-rich | Yada et al. (2003, 2005) |
| Stony cosmic spheres | Antarctic ice | 48.5 to 56.5 | $^{16}$O-poor | Yada et al. (2003, 2005) |
| Stony cosmic spheres | Antarctic ice | 0.5 to 40.7 | Individual spots | Taylor et al. (2005) |
| Stony cosmic spheres | Antarctic ice | 1.5 to 29 | Slope 0.6 | Engrand et al. (1998) |
| Stony cosmic spheres | Deep sea | 18 to 25.6 | Slope 0.6 | Clayton et al. (1986) |

can see that those stony spherules falling along (or very close) the TFL have oxygen ratios in the range of the unmelted particles of our study. Based on a consideration of the isotopic fractionations of elements other than oxygen (Cr, Fe and Ni), Engrand et al. (2005) concluded from a study of 14 stony cosmic spheres that fractionation of oxygen isotopes by evaporation is small.

Another mechanism of oxygen fractionation due to evaporation is thermal metamorphism of phyllosilicates. Dehydration experiments performed by Mayeda and Clayton (1998) on the phyllosilicate serpentine and on Murchison, a carbonaceous chondrite, showed that progressive dehydration removed isotopically light water resulting in $\delta^{18}$O enrichment in the residual rock of 4.0‰. This observation suggests that if fractionation of the oxygen isotopes in MMs occurred by evaporation of water in phyllosilicates during atmospheric entry, the fractionation would produce an increase in $\delta^{18}$O of at most 4.0‰, which would not explain the heavy values observed in many of our micrometeorites.

Micrometeorites might have high $\delta^{18}O$ as a result of their journey in space and exposure to solar wind. However, solar wind implantation is produced only in the outermost tens of nanometers of the particle, and the ion microprobe sampled up to 1–2 μm in depth. Given that oxygen is a major element, it seems unlikely that the solar implantation alone could explain the high $\delta^{18}O$ values measured in the MMs.

The evaporation during atmospheric entry of volatile organic phases rich in $^{16}O$ would enrich the micrometeorite in $^{18}O$. However, micrometeorites contain only ~2% carbon (Matrajt et al., 2003) and the organic phases are probably extremely rare. Therefore, it is highly unlikely that most of the $^{16}O$ would have been contained purely in a minor phase that vanished during evaporation.

We conclude that the oxygen isotope values presented here represent the isotopic compositions of the micrometeorites before they entered the Earth's atmosphere.

### 4.2. Isotope heterogeneity in MMs

The range of the values measured within individual MMs is greater than the analytical uncertainties, showing that MMs are isotopically heterogeneous. It could be argued that the observed variation in oxygen isotope values is the result of differences in mineralogy among analytical spots. It is unlikely that the isotope heterogeneity observed in these MMs is only due to differences in mineralogy among analytical spots because the 20 μm ion microprobe beam size sampled a mixture of several phases rather than an individual phase. It is more likely that the heterogeneity observed in our samples is intrinsic to them and is related to the isotopically heterogeneous nature of the parent body of MMs, given that even some melted micrometeorites show isotopic heterogeneity at the micron scale. For example, Engrand et al., 2005 found a porphyritic cosmic spherule with a significant variability in $\delta^{18}O$ ranging from 1.5‰ to 24.7‰, and within this cosmic sphere they found two olivines with almost identical composition ($Fo_{98.7}$ and $Fo_{98.8}$) but with $\delta^{18}O$ values that differed by more than 10‰. Another example was found by Yada et al. (2005) during the analysis of a chemical homogenous glass cosmic sphere, in which a variability in $\delta^{18}O$ ranging from 29.1‰ to 54.6‰ (more than 24‰ difference) was found. Therefore, the wide range observed in the oxygen isotope values of MMs may be explained by an isotopically heterogeneous precursor: either the samples come from several different objects of the asteroid belt, or the samples come from a single, isotopically heterogeneous, parent body.

### 4.3. Comparison with melted micrometeorites and interplanetary dust particles (IDPs)

#### 4.3.1. Comparing unmelted MMs with cosmic spherules

In Fig 5, we compare our data to oxygen isotope values measured on cosmic spherules by others (Clayton et al., 1986; Engrand et al., 1998; Taylor et al., 2005; Yada et al., 2005). Our measurements are similar to the values found for melted micrometeorites that fall along the TFL: both melted and unmelted micrometeorites studied as whole particles fall along the TFL with $\delta^{18}O$ values in the range 5.8‰ to 93‰. The overlapping isotope values suggest that those melted micrometeorites falling along the TFL and the unmelted micrometeorites have similar precursors. Our data also support the hypothesis that oxygen isotope ratios in micrometeorites do not significantly change during atmospheric entry heating. If isotopic fractionation due to heating were taking place, then melted micrometeorites should have the highest $\delta^{18}O$ values, unless their precursors had lower oxygen isotope ratios. But the latter is unlikely given the extremely wide range of $\delta^{18}O$ values found on cosmic spherules (Yada et al., 2005).

#### 4.3.2. Comparing unmelted MMs with IDPs

Oxygen isotopes have been measured on IDPs (McKeegan, 1987; Greshake et al., 1996; Messenger, 1998; Engrand et al., 1999b; Floss and Stadermann, 2003; Messenger et al., 2003; Aléon et al., 2006). However, only three of them (McKeegan, 1987; Engrand et al., 1999b; Aléon et al., 2006) analyzed the entire particle rather than individual mineral grains within the IDP. Since we analyzed whole particles, we compare our data to these three works.

McKeegan, 1987 analysed 5 IDPs and found a $\delta^{18}O$ range from −41.2‰ to −5.1‰, and a $\delta^{17}O$ range from −37.1‰ to −5.8‰. None of these particles fall along the TFL within $1\sigma$, but rather along a line with slope = 0.95. Based on such results the author concluded that it is unlikely that these IDPs were derived from carbonaceous chondrites and thus that they probably represent a new type of collected extraterrestrial material.

In contrast, both Engrand et al. (1999b) and Aléon et al. (2006) found that the particles they studied were, from an oxygen isotope point of view, mostly related to carbonaceous chondrites. Engrand et al. (1999b) studied 4 IDPs and found a $\delta^{18}O$ range from −19.7‰ to −13.2‰, and a $\delta^{17}O$ range from −19.5‰ to 6.9‰. Only one of these particles fall along the TFL within $1\sigma$. The other three cluster between the TFL and the CCAM lines. Aléon et al., 2006 studied 5 IDPs and found a $\delta^{18}O$ range from ~ −28‰ to ~28‰, and a $\delta^{17}O$ range from ~ −12‰ to ~12‰. All the particles fall along the TFL within $2\sigma$.

The data found for both melted (Yada et al., 2005) and unmelted micrometeorites studied as whole particles (this study) show that, from an oxygen point of view, most MMs are not linked to carbonaceous chondrites. Some MMs might be linked to those IDPs that fall along the TFL and which $\delta^{18}O$ values are positive (⩾0‰). However, those MMs that have high $\delta^{18}O$ values are not represented in the collected extraterrestrial material available so far.

### 4.4. Possible parent bodies

#### 4.4.1. A new type of solar system object

The extremely $^{18}O$-enriched values observed in 21 MMs have not been reported in previous analyses of chondrite matrix material (see Table 6). Furthermore, the isotopic values found in these micrometeorites show a wide range. These observations suggest that $^{18}$O-enriched micrometeorites (unmelted + cosmic spheres) are a new type of Solar System material not present in our meteorite collections. A similar conclusion was reached from a detailed study of the mineralogy of unmelted micrometeorites by Noguchi et al. (2002) and from the mineralogy and oxygen isotope values of some cosmic spheres by Yada et al. (2005) and Engrand et al. (2005). The parent body of these MMs is probably enriched in heavy oxygen isotopes compared to other planetary materials. If the parent body were a friable object which produces mainly dust (micrometeorites) instead of rocks (meteorites) upon collision, it could explain the absence of $^{18}$O-enriched meteorites in the meteorite collections. Alternatively, the rocks produced by the parent body may be too friable to survive atmospheric entry without breaking apart.

### 4.4.2. *CI-like precursor*

Four of our MMs have oxygen isotope values lying along the TFL in the same region as the bulk CI carbonaceous chondrite values ($\delta^{18}O = 16.1‰$ (Leshin et al., 1997; Clayton and Mayeda, 1999)) (Fig. 6). This suggests that these particles could be sampling CI-like parent bodies. A CI-like parent body is further supported by the observation of 9 unmelted micrometeorites that have mineralogies almost identical to those of CI chondrites (Noguchi et al., 2002), and by the observation of a stony cosmic sphere composed of a single olivine whose $\delta^{18}$O is in the range of the $\delta^{18}$O values in olivine grains from CI chondrites (Taylor et al., 2005). In addition, Engrand et al. (2005) found four stony cosmic spheres whose $\delta^{18}$O values have affinity with those of CIs and suggested that these particles could have CI-precursors. However, our knowledge of the level of microscale isotopic heterogeneity of carbonaceous chondrite matrices is very limited and thus it is not yet possible to compare the data presented here with carbonaceous chondrite compositions.

### 4.4.3. *A metamorphosed carbonaceous chondrite-like precursor*

In Fig. 6, we compare our data to data from metamorphosed carbonaceous chondrites (Mayeda and Clayton, 1990; Clayton and Mayeda, 1999). The four metamorphosed meteorites shown in this figure have chemical and petrographic characteristics which would have classified them as CI or CM before metamorphism (Clayton and Mayeda, 1999). Petrographic observations of 23 unmelted MMs suggest that 95% of them have affinities with CM meteorites (Kurat et al., 1994), and recent mineralogy data shows that some unmelted MMs also have affinities with CI meteorites (Noguchi et al., 2002). Our oxygen isotope results, combined with data of Taylor et al. (2005) and Engrand et al. (2005) also points to a certain affinity of some particles with CI chondrites. This affinity with CIs suggests that the extremely heavy particles found during this study may have come from a metamorphosed CI-precursor. Clayton and Mayeda (1999) discussed the dehydration and thermal metamorphism processes on phyllosilicate-rich materials and their consequences for an oxygen isotope fractionation, showing that the direction of the fractionation is a preferential loss of isotopically light water, with concomitant heavy-isotope enrichment in the mineral residue. Such processes of parent body heating would be a mechanism for getting very heavy oxygen, like the one observed in many of our particles. Perhaps the parent body of these MMs was isotopically heterogeneous because only part of it was thermal metamorphosed, which would explain the broad range in isotope values found in our samples.

Thermal metamorphism is a process that could only happen on the parent body of these MMs and not during their atmospheric entry. Support for this comes from the oxygen isotope data measured in the fusion crust of several CI and CM chondrites (Clayton et al., 1986; Clayton et al., 1997). These data show that although the $\delta^{18}$O values tend to increase in the fusion crust compared to the interior of the meteorite, the increment is less than 3‰. The occurrence of thermal metamorphism probably requires longer times than the ones encountered during the flash heating of the atmospheric entry event.

### 4.4.4. *Pieces of chondrules*

Genge (2005) studied the mineralogy of 236 unmelted MMs and suggested that the coarse-grained MMs may be chondrules or pieces of chondrules. During our study, we examined 6 particles that are coarse-grained (see Table 1): Ixta, Arrayan, Mate, Chapultepec, Mezcal and Mitla. Their $\delta^{18}$O values vary from 2‰ to 25‰; their $\delta^{17}$O from −1.3‰ to 13‰ (see Table 3). Yet, the chondrules from carbonaceous chondrites have a narrower range of $\delta^{18}$O (from −3‰ to 7‰) and of $\delta^{17}$O (from −7‰ to 5‰) (Clayton, 1993). Also, the MMs plot along the TFL whereas the chondrules plot along the CCAM line. Therefore, from an oxygen isotope point of view the coarse-grained MMs we studied do not seem to derive from chondrules.

## 5. Conclusions

We measured the oxygen isotope ratios in 28 unmelted Antarctic micrometeorites. The average isotopic composition of the MMs show a wide range (from $\delta^{18}O = 3‰$ to 60‰ and $\delta^{17}O = -1.2‰$ to 32‰) and fall along the terrestrial fractionation line. Individual oxygen isotope measurements vary both among the micrometeorites and within a single micrometeorite showing that these micrometeorites are isotopically heterogeneous. In general, fine-grained and scoriaceous particles, mainly composed of matrix, have higher $\delta^{18}$O values than the coarse particles, mainly composed of anhydrous silicates, suggesting that the matrix of the micrometeorites is isotopically heavier than the anhydrous silicates.

Four MMs have oxygen isotope values close to those of bulk CIs, suggesting that their parent body could be a CI-like object. The extremely heavy oxygen isotope data suggest that oxygen heavy-rich micrometeorites are a new type of Solar System material not yet represented in our meteorite collections. We suggest that their parent body was a friable, thermal metamorphosed carbonaceous asteroid (or family of asteroids), that either produces only dust size particles upon collision with other bodies or produces rocks that are too friable to survive atmospheric entry.

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