The nature and tropospheric formation of iberulites: Pinkish mineral microspherulites

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Received 22 June 2007; accepted in revised form 1 May 2008; available online 29 May 2008

Abstract

The circum-Mediterranean area has one of the highest dust accretion rates in the world. We have found pinkish mineral microspherulites (here referred to as iberulites), a new type of aerosol particle formed under special atmospheric conditions in periods corresponding to the highest levels of solid additions (summer). Because these particles are labile, they have gone unnoticed until now.

Image analysis shows that these particles are spherical in shape, most commonly 60–90 µm in diameter, and show a typical depression (vortex). Iberulites are considered complex mineral assemblages with different hygroscopic characteristics and also contain biological remains (plants, silica shells, plankton and probably viruses). Their bulk mineralogy includes silicates, carbonates, sulfates, halides, oxides and phosphate-vanadates. This mineralogical composition indicates that likely source areas are the Sahara and Sahel for primary minerals (inherited), while other minerals are the result of atmospheric neoformation (gypsum and alunite-jarosite).

We thus define an iberulite as a coassociation with axial geometry, constituted by well-defined mineral grains together with non-crystalline compounds, structured on a coarse-grained core and a smectite rind, with only one vortex and pinkish color, formed in the troposphere by complex aerosol–water–gas interactions.

We suggest the aqueous interphase hypothesis as the mechanism for tropospheric formation of iberulites, mainly in summer: interactions between water droplets and aerosols create complex hydrodynamic conditions, causing possible collisions (wake and front capture) that produce the “precursor water droplets” of iberulites. Atmospheric processing is required from this stage to iberulite maturation.

To date, we do not know to what extent these iberulites are present in time and space or whether they can serve as markers for environmental or paleoclimatic analyses or even lead to uncertainty in radiative transfer models.

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1. INTRODUCTION

Sources and transport pathways of mineral dust play an important role in global climate, biogeochemical cycling and health. Globally, airborne particle mass mostly consists of minerals of terrestrial, marine, atmospheric and cosmic origin (Parkin et al., 1977; Keller et al., 1992; Andreae and Crutzen, 1997; Buseck et al., 2000; Arimoto, 2001). Dust from windblown soils (mainly great deserts) is an important component of the earth-atmosphere system (Simonsen, 1995; Goudie and Middleton, 2001; Ramathan et al., 2001). Many studies have evaluated such additions. Model estimates of the amount of desert dust generated by the Sahara range from 270 to 670 Tg year−1, and Saharan dust transport to Europe ranges from 80 to 120 Tg year−1, reaching distant regions, like South America (Swap et al., 1996), the North Atlantic-Caribbean area (Prospero, 1999), Northern Europe (Franzen et al., 1994) and perhaps as far as the Himalaya (Carrico et al., 2003).
Guerzoni and Chester (1996), Romero et al. (2003) and Jernick (2005) reported the presence of marine nanoplancton, pollen, diatoms and bacteria in aerosols from these areas. Great importance is attached to the role of mineral aerosols as a reactive surface in the global troposphere (Wurzler et al., 2000; Usher et al., 2003), where heterogeneous nucleation phenomena can occur with the creation of new phases (neof ormations), mainly of sulfates and nitrates. The Iberian peninsula is affected by the North Atlantic Oscillation (NAO), and interannual variations in dust transport over the Atlantic Ocean and the Mediterranean Sea are well correlated with large-scale climatic variability (Guerzoni and Chester, 1996; Romero et al., 2003) and to interpret their evolution. This may contribute to the understanding of the behavior in natural systems (Berstch and Seaman, 1999), particularly the atmosphere, of complex mineral assemblages that are hard to detect due to their fragility. To date, no information has been available regarding these particles, since standard techniques are not sensitive enough to avoid destroying such labile components, and in addition, they can only be obtained by sampling under special climatic conditions conducive to their atmospheric formation. To this end, we monitored atmospheric dust deposition for the period 1999–2005 near the city of Granada (Spain).

2. SAMPLING AND METHODOLOGY

2.1. Geographic background

The sampling site is located in the Granada Depression (37°10′N–3°31′W, 640 m ASL), surrounded by dolomitic limestone and siliceous relief. The soils in the depression are Calcareous Fluvisols (IARA-CSIC, 1989), with irrigated crops within a radius of a few tens of kilometers around the monitoring station and olive groves and forestry further away. The area is not heavily industrialized.

The mean annual temperature is 15.1 °C, ranging from 6.7 to 24.8 °C (January and July, respectively), and mean precipitation is 357 mm over the last 30 years, which corresponds to a semi-arid Mediterranean climate (data from Granada airport, Spanish Meteorological Institute, INM). From 1980 to 2005, annual precipitation for S and SE Spain has been below the century average and the mean temperature has undergone a significant rise of 0.7 °C (Staudt, 2004).

Conventional aerodynamic data show a high annual percentage (approximately 63%) of calm, with predominantly gusty winds under 5 km/h up to 10 AM, followed by an increase up to 20 km/h around midday, dropping around 4 PM to approximately 0 km/h. These values in themselves minimize the incidence of local supplies to our samplers, but they were reduced still further by placing the traps on top of a building surrounded by irrigated land.

2.2. Sample collection

Weekly samples of atmospheric dust and iberulites were taken from 1999 to 2005, mainly in the summer months, using the method described by Díaz-Hernández and Miranda Hernández (1997). This is a very flexible technique that uses passive collectors; either dry or wet collectors present similar efficiency (Goossens and Offer, 1994). We used dry dust collectors, consisting of 3 cm deep, circular porcelain trays 14.3 cm in radius. Because material only rises into the air by suspension (Tsoar and Pye, 1987; Mainguet, 1992), it was important to prevent particles from the surrounding soil from entering the samplers by roll or creep. The collectors were therefore placed on top of a building (about 10 m above the ground) surrounded by a 1-m-high perimeter wall and open so as not to restrict wind movement (Frank and Kocurek, 1994; Offer and Goossens, 1994). This rooftop is covered with coarse gravel (20–35 mm diameter), which prevents incorporation of dust particles deposited on it (Goossens, 1994). In addition,
the plates were placed on a mast 2 m above the rooftop. The trays, washed with distilled water and dried, were checked daily mainly during the summer, obtaining varying rates of iberulite deposition. A record was kept of collection times.

The deposited dust was carefully collected using a brush, stored in glass vials and weighed to a precision of 0.1 mg. Since the porcelain surface is very smooth, the dust was not embedded and breakage of the iberulites was avoided by carefully brushing them down the deposition trays. In summer months, the atmospheric conditions of the area prevent formation of dew, so dust and iberulite adherence to the tray and brush was minimal.

Authors including Buat-Ménard et al. (1989), Pye (1992) and Drees et al. (1993) often used long and irregular sampling periods. In these conditions, rates are normally expressed on the basis of a sample weight over a certain time for a sampling surface. In this study, sampling was scheduled on a weekly basis from 2000 to 2005, and rates of dust input were converted to an equivalent g m\(^{-2}\) day\(^{-1}\) basis for comparison, although the amount of sample collected was very small and could be a limiting factor for later analysis.

2.3. Sample selection criteria during the study period

Samples of events with iberulites were selected in order to better characterize the phenomenon and obtain a general overview. The selection criteria were having a sufficient amount of sample, and collection during dryfall, thus avoiding red rain to prevent dissolution and neoformation. Table 1 shows the selected events and their main weather features. Although iberulite events were recorded in 2003, the quantity of samples collected was insufficient for correct analysis, so they were not included.

In the same years that these events were recorded, TSP levels (Total Suspended Particles) were also obtained from the ambient air quality monitoring network of the European Monitoring Evaluation Program (EMEP network). These data offer a general framework for our dust collections. The monitoring station used was ES07 (Viznar), located 10 km from our sampling station and supervised by the Spanish Environment Ministry. TSP levels were obtained by weighing the aerosols collected using a high-volume sampler (MCV, Model CAV-A/HF).

2.4. Sample analysis procedures

A quarter of each sample was taken and the dust separated from the iberulites. Each fraction was weighed using a microbalance (Mettler Toledo, AX26). Amounts of mineral dust and iberulites were significantly higher than the weighing error (\(d = 0.002\) mg/0.01 mg).

2.4.1. Optical observations and image analysis

Sample trays were screened using a stereo-microscope with oblique illumination at different magnifications. This routine procedure enabled us to establish the sampling periods containing iberulites and to separate the iberulites from the surrounding material (dust) by carefully hand-picking with a very thin pin, avoiding sample contamination and breakage. Color was determined by Munsell charts (1995) and natural light using an iberulite concentrate.

Morphometric features of our iberulites were determined by digital image analysis. Color photographs of iberulite concentrate were taken using a stereo-microscope, opposing mixed light and a black background to remove shadows and assist in particle selection. These images were analyzed to determine particle length, surface area, perimeter and circularity. The largest and smallest lengths of each particle were measured, representing the primary and secondary axes of the best fit ellipse; the area of each iberulite was obtained in square pixels; perimeter was measured as the length of the outside boundary of each selection; finally, circularity was defined as \(4\pi \times \text{(area/perimeter\(^2\))}\), where a value of 1.0 indicates a perfect circle.

2.4.2. Particle size distribution

The grain-size distribution of iberulite constituents and dust was obtained with a CIS-1 Galai\(^\text{a}\) Laser Sizer, because they are easily dispersible. Distribution was determined three times, at 15-min intervals, in an ethanol suspension to prevent dissolution of soluble salts (mainly chlorides). Acquisition times varied depending on the suspension

| Event code: 01-08-08 indicates year, month and central day of sampling period. Sampling period means beginning and end of said period in terms of clock time. |

<table>
<thead>
<tr>
<th>Event (date)</th>
<th>Sampling period</th>
<th>General climatological observations</th>
<th>Red rain</th>
<th>Rates (g m^{-2} day^{-1})</th>
<th>% Iber.</th>
<th>Major axis ((\mu m))</th>
<th>Minor axis ((\mu m))</th>
<th>Roundness index</th>
</tr>
</thead>
<tbody>
<tr>
<td>010808</td>
<td>5th (6:00 PM)–11th (6:00 PM)</td>
<td>Last day very hot, haze, threat thunderstorm</td>
<td>No</td>
<td>0.050</td>
<td>34</td>
<td>80</td>
<td>70</td>
<td>0.95</td>
</tr>
<tr>
<td>020618</td>
<td>13th (4:20 PM)–24th (8:15 AM)</td>
<td>Haze, cumulo-nimbus, threat thunderstorm</td>
<td>No</td>
<td>0.082</td>
<td>23</td>
<td>80</td>
<td>80</td>
<td>0.95</td>
</tr>
<tr>
<td>040720</td>
<td>16th (8:00 PM)–23th (8:00 AM)</td>
<td>Period intensely hot and hazy</td>
<td>No</td>
<td>0.020</td>
<td>23</td>
<td>80</td>
<td>80</td>
<td>0.95</td>
</tr>
<tr>
<td>040822</td>
<td>20th (3:15 PM)–24th (2:15 AM)</td>
<td>Heat, haze and threat of thunderstorms</td>
<td>Later</td>
<td>0.001</td>
<td>16</td>
<td>70</td>
<td>60</td>
<td>0.95</td>
</tr>
<tr>
<td>050401</td>
<td>1st (6:00 PM)–2nd (6:30 AM)</td>
<td>Abnormal rise in temperature, cloudy</td>
<td>Later</td>
<td>0.113</td>
<td>47</td>
<td>70</td>
<td>60</td>
<td>0.95</td>
</tr>
</tbody>
</table>
concentration. The suspension was previously exposed to ultrasonic dispersion in a water bath for 3 min. The size range of the instrument was 0.2–150 μm (0.3% resolution of full scale). The data were expressed in 0.5 μm ranges once the measurement limit was determined.

2.4.3. Electron microscopy techniques

Scanning Electron Microscopy (SEM) was used with selected iberulite samples to obtain morphological and chemical information. The samples and equipment were set up according to the specific aim of analysis.

A high-resolution Field-Emission Scanning Electron Microscope (FESEM, Leo 1530) equipped with a Link INCA 200 (Oxford Instruments) microanalysis system was used for the morphological study and to identify mineral phases. For SEM/EDX mapping (Zeiss DSM950), the samples were soaked in Epon resin and cut with a diamond knife ultramicrotome (Reichert Ultracut S) to expose their interior. The same samples were used to obtain SE (Secondary Electrons) and BSE (Back Scattered Electrons) in a LEO 1430VP microscope.

Iberulites were dehydrated in pure ethanol for 15 min and then placed in an ethanol/Epon resin mixture and shaken for an hour. They were then polymerized and cut into thin sections (70–90 nm) with an ultramicrotome. This process frequently detached some large-size grains; these samples were examined using a high-resolution Philips CM-20. Point-to-point resolution was 0.27 nm and beam sizes were 200 nm (TEM, Transmission Electron Microscopy) and 10 nm (STEM, Scanning Transmission Electron Microscopy).

Quantitative microanalyses were carried out in an EDAX system equipped with a Si (Li) detector, using a 5-nm beam diameter and a 10 x 20 nm scanning area. Electron diffraction patterns were obtained from selected areas (SAED) and High-Resolution Transmission Electron Microscopy (HRTEM) lattice-fringe images were obtained as suggested by Buseck et al. (1988).

2.4.4. X-ray diffraction (XRD)

The mineralogy of dust and iberulites was determined with an Enraf-Nonius Powder Diffraction System 120 (Natural History Museum, London) and a Brucker AXS D8 Advance (University of Granada), in both cases using diffracted-beam Cu-Kα. The measurement conditions were 3°–70° 2θ, range step scan 0.02° and 8 seg/step as very little sample was available. Analysis time was about 8 h for both systems. The diagram, phase identification and profile analyses were carried out using DIFRACPlus SEARCH, Bruker® and XPowder software (Martin, 2004).

2.4.5. Electrophoretic mobility (Ue) measurements

These measurements were made using an automated electrophoresis instrument (Malvern Zetasizer, 2000, Malvern, England) at 25 ± 0.5 °C. The ζ-potential was calculated using the Smoluchowski formula (Arroyo and Delgado, 2002).

Electrophoretic mobility was carried out on dust and iberulites (from each event) and pure selected mineral patterns (albite, calcite, dolomite, gypsum, hematite, kaolinite, muscovite, orthoquartz, and smectite as major components of the iberulites and dust). Determinations were made in triplicate using suspensions in bidistilled water containing 0.1–0.2 g/L solids, previously exposed to ultrasonic dispersion in a water bath for 1 min. This concentration was necessarily lower for iberulites and dust.

3. RESULTS

3.1. Deposition levels and periods of appearance of iberulites

We first detected iberulites while investigating the contribution to the soils of a medium-sized forest fire on 16–18 August 1999 (Sierra de la Almijara, Granada, Spain), located some 50 km from the sampling station (Díaz-Hernández, 2000). Monitoring was carried out regularly during the months following the fire (including winter) until iberulites were again collected on 26 June 2000, with no forest-fires intervening. Dust samples were collected over the period 2000–2005 in order to exactly define the appearance patterns of iberulites, centering only on studying and monitoring iberulite events. Table 1 summarizes the dust rates and iberulite percentages in the selected event samples, although these amounts were probably somewhat higher due to the difficulty of carrying out complete separation. The amounts of iberulites obtained on 17 and 19 August (1999) was around 0.038 g m⁻² (i.e., 0.019 g m⁻² day⁻¹). The deposition of iberulites on these two days (iberulites were not observed on successive days) was equivalent to 10–12% of the total dust obtained on these dates. These deposition rates (including rates for 1999) suggest a close relation (R² = 0.66) between the amounts of dust and the iberulites collected on these days (higher dust rates imply higher iberulite rates).

Fig. 1 shows the distribution of dustfall rates during 1992, with maxima occurring with winds from the south (38%), contributing 50% of the total for that year. The dustfall rate for this region was thus calculated as 23.06 g m⁻² year⁻¹ (Díaz-Hernández and Miranda Hernández, 1997), with no iberulites screened in any of the samples. This annual distribution pattern shows a repetitive tendency (summer and spring maxima coincide) and is similar to that obtained in the TSP collected between 1999 and 2005 at the nearby ES07 monitoring station (Fig. 2). The value obtained falls within the range of rates described by Simonson (1995) in a global context and by Loïe-Pilot et al. (1986), Pye (1992) and Büchner (1994) in the Mediterranean area, none of whom mentioned the presence of iberulites.

Given the difficulty of separating iberulites from dust, we evaluated the importance of the phenomenon by taking the number of days they were detected in one month as an estimate: frequency is high if detected on 15 or more days (**), medium between 5 and 15 days (*) and less than 5 days (°) the phenomenon is considered occasional (low). Fig. 2 shows that iberulites are mainly found during the summer (driest months); outside the summer months (November–February) iberulites were only rarely collected (sporadically in February or March, around springtime), probably because of the low TSP contents in the atmosphere (lower supply together with scavenging by rainfall).
and also due to disintegration caused by dew and frost. This general framework indicates that the appearance of iberulites is a discontinuous phenomenon, occurring mainly in a dryfall context corresponding to the highest levels of solid additions (Fig. 2).

In addition, iberulites sometimes coincide with red dust rains (muddy rains) in the summer period, as long as rainfall is not heavy, since this would tend to disintegrate them and only isolated mineral particles would be collected. Some iberulites were preserved in these circumstances (Fig. 3A), but their possible chemical and physical alteration prevented their use in later analyses. Saharan red rains are related to specific synoptic situations of atmospheric circulation during periods of intense insolation. These weather patterns can be observed on the synoptic charts at 850–700 hPa during the monitoring period (synoptic surface charts and High-Resolution Local Area Model (HIRLAM) (Source: INM, data not shown)).
As a demonstration, Fig. 3 shows the images of a typical warm red rain episode taken between 3 PM on 16 August and 7 PM on 17 August 2005. The larger micrograph represents the general appearance of the sampler, where the impacts of relatively large muddy raindrops can be seen. Some iberulites deposited in this event are also indicated. The adjoining details (micrographs B–H) show a sequence ordered according to the water content of the raindrop. The higher the water content, the larger the impact trace becomes, as well as flatter and more irregular, with higher dilution of the solid charge. On the other hand, if the water content is low, impact size is smaller, with more cohesion between its constituent particles, producing globular forms with jagged edges and hollow interiors.

3.2. Morphology

In order to avoid repetition, all the compositional patterns mentioned in this section were obtained by EDX.

3.2.1. Global morphology and image analysis

The iberulites are mostly spherical in shape and vary in size when observed with a binocular microscope (Fig. 4).

Micrograph 5 gives a panoramic view of the iberulites from the event of 1 April 2005. Details of the iberulites from the five events analyzed here can be seen in micrographs 1, 2, 3, 4 and 5-2. They are often associated with filaments of plant matter (3A, 5.1A, 5.2A and 5-2B), in which case their shape is adapted to the axis of the filament, and are sometimes associated with crystals (5-1A and 5-2A). They are basically pink (10YR6/4 color), with frequent reddish and blackish speckles. Gray and red colors (4A) have occasionally been observed. The surfaces of most of the iberulites show a typical conical depression, which we call the vortex (1A, 1B and 2A), and which can at times be so deep as to be translucent (1B and 2A). The vortex is roughly conical with the base at the surface and the vertex inside the microspherulite.

Morphological patterns of iberulites (Fig. 5) were obtained by image analysis of the iberulite concentrate from each event. The global sample determined from the event data obtained ($n = 5121$ iberulites) shows sphericity: roundness index = 0.95, major axis = 75 μm, minor axis = 65 μm. Ninety-six percent presented a roundness index ≥ 0.85, 54% of the population had a 60- to 90-μm major axis and 61% a 60- to 90-μm minor axis (Table 1). These distribution patterns are similar across the events, although events 020618
and 040720 showed more dispersion in their modes, although always around the same values. The values furthest from the modes were found in elongated iberulites, associated with plant filaments (4, 3A, 5-1A and 5-2B). The similarity between the radii of the two axes suggests that the iberulites are closer to spherical forms than oblate spheroids.

The equivalent volume was calculated by determining the projected area of each spherule, which allowed us to estimate a bulk density of 0.65 g cm$^{-3}$ after determining the total weight of the iberulites in a high-precision balance. Mean porosity was estimated at around 50%, based on analysis of SEM images of nine sectioned iberulites from events in 2001, 2004 and 2005, soaked in Epon resin. We believe these values are consistent, considering the variety of constituents in iberulites and the influence of the vortex on volume calculations.

3.2.2. External and internal morphological features

The structural elements that characterize an iberulite are the vortex, the core and the rind.

SEM images (Fig. 6) of iberulites show only one vortex (micrograph A), which does not appear to be either an impact or “ejection” crater. The vortex is a typical morphological feature that distinguishes them from other spheroids, especially from cosmic spherules (Fig. 7). The microspherulite surface can be relatively rough and porous, formed by assemblage linking of neighboring mineral particles, frequently with angular edges. Around the vortex, the surface is smoother, indicating a predominance of very small (<0.5 μm) laminar habitation minerals. The spherical morphology of these iberulites may be distorted by adaptation to plant filaments, giving them an elliptical shape, with the axis corresponding to the filament, which can be of highly variable length (Fig. 6B).

Because iberulites are fragile, it is relatively easy to study their interiors. Fig. 6C and D shows a core formed by angular mineral particles of very variable sizes coexisting with other more rounded particles and apparently without a cementing matrix. The coarser components are concentrated in the core of the spherulite, finer particles occupy the intermediate zone and the thin, rind-like outer coating
consists of laminar habit minerals (clays and to a lesser extent gypsum).

3.2.3. Biological constituents

Apart from plant filaments, iberulites are frequently associated with remains of skeletal structures typically made of silica (diatoms). The diatoms are distributed anywhere inside the iberulites, but are often found near the surface (Fig. 8A), beneath the rind. We also observed broken frustules with rounded edges in sectioned iberulites (Fig. 8B), apparently indicating prior erosion.

Although knowledge about fragmented biological particles in the atmosphere is very limited (Jaenicke, 2005), we have frequently found biological remains, generally linked to the outer parts of iberulites, that are probably marine planktonic forms like coccolithophores (Fig. 8C). These are biogenic skeletons, formed by calcite in this case, that present a characteristic pedunculate morphology in a very good state of conservation (Fig. 8C). In one case (Fig. 8C1), rounded calcite forms of dubious definition were observed, in whose folds we found a specimen that could either be an unusual icosahedral capsid from a virus or an early growth stage of Emiliana Huxleyi.

3.2.4. Crystal growth phenomena

We detected numerous crystals with a well-defined habit with a formation related to the processes affecting the iberulites (Fig. 9), indicating that recrystallization and mineral neoformation phenomena occurred.

The halite produced well-developed crystals, probably due to its availability and facility to participate in processes of dissolution and precipitation. Micrographs A and A1 show a prismatic halite crystal on a calcium sulfate-covered filament. Micrograph B shows a halite cube attached to an iberulite; the halite cube has abundant granular deposits on three adjoining faces and no dissolution figures can be seen. The cube is anchored to the iberulite by a thin external rind, which, in this case, presents a delicate equilibrium. Micrographs C and C1 show accumulations of calcium sulfate as “toothlike” gypsum crystal growths produced from inside the vortex.

3.3. Constituent particle size

The size distribution of constituent particles of the dust and iberulites are shown in Fig. 10, in which we consider each event separately, as well as the average event. All dis-
Fig. 6. SEM images showing morphological aspects of iberulites. (A) External textural differences in a single iberulite; smoothest textures are around the vortex and the rest of the surface shows adhering mineral grains. (B) Iberulite pierced by long plant filament; in this case the iberulite is ellipsoidal in shape and its body can be found either at the center or at the ends of the filament. These filaments are of plant nature and highly variable length and can deform the spherical shape. In this case, the peduncle of the iberulite presents high gypsum content. (C and D) Internal views of two iberulite halves, formed by mineral particles with angular edges, showing small spaces between them. The external surface is covered by a thin rind of laminar habit minerals. These mineral particles range gradually from large (core) to small (rind).
The average dust and iberulite events had similar compositions of fine particles (32% and 30%, respectively) and coarse particles (68% and 70%, respectively) with a very similar distribution pattern (Fig. 10). The particles making up the iberulites and dust would thus be included in the clay (<2 µm) and fine silt (2–20 µm) fractions.

The abundance of coarse particles (close to the fine size limit) indicates that these particles are mainly generated by mechanical processes from soils in and around the Sahara, whereas the fine particles have different sources (Seinfeld and Pandis, 2006), and could originate in part from friction and collision of coarse particles both on the ground and in the atmosphere. The fine fraction (mainly < 100 nm, Pruppacher and Klett, 1997) would assist the formation of cloud droplets as cloud condensation nuclei (CCN).

### 3.4. Electrophoretic mobility

Electrophoretic mobility was measured to estimate the degree of aggregation of iberulites. The ζ-potential measured for iberulite particles and dust was similar for each event and approximately similar taken together. The extreme values for these potentials corresponded to the iberulites of the 2004 (~39 mV) and 2005 (~24 mV) events, possibly due to mineralogical differences. The ζ-potential measured for iberulite particles and dust is the average of those of their main constituent minerals, which were all negative, ranging from −43 mV (muscovite) to −23 mV (kaolinite).

### 3.5. Mineralogical composition

#### 3.5.1. Iberulite bulk mineralogy (XRD)

The bulk mineralogical composition of the dust in all events (Fig. 11) consists largely of dolomite and quartz (>30%), accompanied by calcite, gypsum, halite and illite in lower proportions (12–2%); minor phases included beidellite, hematite, kaolinite, montmorillonite and albite (~2%). The bulk mineralogical composition of iberulites in all events consists largely of quartz (>30%), accompanied by calcite (7–38%); gypsum, dolomite and halite (3–10%); and illite, beidellite and hematite (2–4%); in lower proportions, minor phases included kaolinite, montmorillonite and feldspars. The extremely small amount of iberulite samples prevented the identification of other phases, especially in iberulite sample 040822.

All the events had a rather similar mineralogical composition in both dust and iberulites. However, the iberulites contained higher amounts of phyllosilicates than the dust: the iberulites in any event contained between two and four times as much beidellite (and hematites) as the dust, and the kaolinite contents of the iberulites are consistently twice those of the dust.

The high proportion of dolomite in the dust of all events is noteworthy (over 36%), whereas the most found in iberulites was 7%, probably due to local Iberian inputs. This dolomite contribution to the dust would explain the relative decrease of the other minerals, in which case they would present very similar quantitative compositions. Moreover, the iberulites collected in the 2002 event showed a high

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Fig. 7. Comparative SEM images of two iberulites (A and B) and two similar cosmic spherules (C and D). We have selected two cases of cosmic spherules that present the most similar appearance to iberulites. We underline that the iberulite vortex has a different shape, number and texture than the pit(s) on the cosmic spherules, and the shallow features in each micrometeorite are identical, while in each iberulite they vary. Finally the composition of iberulites and cosmic spherules are quite different. Cosmic spherules micrographs courtesy of Dr. D. W. Parkin (www.bath.ac.uk/ceos/index.html).
(38%) calcite content, probably from the source area. It should be noted that the percentages of beidellite (and hematite) could be slightly higher through loss of crystallinity (amorphization detected by TEM).

3.5.2. Iberulite electron microscopy analysis

EDX analysis of the surface (rind) indicates that the major constituents are O, Si, and Al; Ca, Mg and S contents are also noteworthy. The minor constituents are Fe, K, Cl, Na, Ti and Sr in decreasing order of abundance, and more rarely V and Ba. The spectra suggest a great abundance of clay minerals (phyllosilicates), accompanied by sulfates (Ca, Na, K, Mg and Al) and halides (Na, Ca, K and Mg) (Fig. 9). In some cases, phosphate-vanadate, barite and celestine were detected as well.

EDX analysis of the core (Fig. 6) showed the major constituents to be O, Si, Ca and Al (in decreasing order of abundance); Mg, Na, K and Fe were present in intermediate amounts, and S, Cl, and P in very minor amounts, but not in all the iberulites. On the basis of the clear morphological features of many mineral grains, we identified the larger ones as calcite, dolomite, quartz, feldspars, micas, and iron oxides, and occasionally clay minerals, rutile, ilmenite and apatite, among others.

In order to gain a more comprehensive view of the element distribution, we performed EDX mapping (Al, Ca,
Cl, Fe, K, Mg, N, Na, S and Si). Fig. 12 shows that gypsum mainly occurs in the rind of the iberulites in all the events examined, generally associated with phyllosilicates and occasionally with carbonates. This is corroborated by the halo shown in S mapping and by the yellow halo resulting from the superposition of the S (green) and Ca (red) spectra. The maps of N, Cl and Na gave poor resolution images. The maps of Si, Fe, Mg and K do not show preferential distribution in the body of the iberulite.

TEM-EDX analyses were carried out on all events. The individual minerals indicated that major constituents were O, Si, and Al, followed by Ca, Mg, Na, K, Fe, Ti, Cl and S; minor constituents were P, Sr, Ba, Ce, La, Y, V, Ni, Mn, Br, Pb, Mo, and Cr, with the first three (P, Sr and Ba) being detected on more than one occasion.

This analysis gave similar mineralogical characteristics to those found by SEM, which agrees with the zonation observed in the sections of iberulites (core, intermediate zone and rind). However, based on the results of TEM-EDX spectra and SAED, we identified some mineral grains more precisely, in particular from the rind and adjacent zones (more external areas of the intermediate zone), thus establishing the typology of phyllosilicates presented in Table 2. The most frequent spectra were those of beidellite and montmorillonite, while those of paragonite, pyrophyllite and chlorite were very rare. From all the structural formulæ calculated, we selected those we considered most representative of the species concerned. These were classified following the criteria of Weaver and Pollard (1973), Borchart (1989) and Meunier (2005).

Other minor minerals are of interest as they indicate both the origins of the aerosols and the atmospheric alteration processes of either individual dust grains or iberulite genesis. We thus have some minerals considered primary, which are resistant to alteration and probably originated in highly weathered soils (rutile, ilmenite, grossular, hematite, aluminium oxide-hydroxide and amorphous iron oxides), or which may be related to volcanic rocks (calcium amphibole, monticellite). Another group of minerals could be related to phosphate deposits in the Western Sahara (Bu-Craa).

HRTEM micrographs of iberulite rinds from each event show an important quantity of small individualized crystals of several minerals smaller than 0.5 μm. Fig. 13 shows iberulite rinds of an event. In these images, smectite particles can be observed whose crystallites are arranged in a more or less disorderly stacking (tactoids or quasicrystals), forming the relatively thick walls of a polygonal network. Micrograph A shows honeycomb smectite (triangular net-
work), where incipient alteration of smectite to amorphous silica and gypsum can be inferred and chlorides can also be seen, while micrograph B1 shows smectite or amphibole alteration to alunite.

4. DISCUSSION

Iberulites were first encountered in August 1999 (Díaz-Hernández, 2000) and continue to be collected at the time of writing. This indicates that their appearance is not accidental, but responds to discontinuous natural phenomena. The lack of previous references to iberulites may be due to (1) the most commonly used sampling methods; (2) the fact that they are exclusive to the study region and/or (3) because previously non-existent environmental conditions are conducive to their formation. Loyé-Pilot et al. (1986) and Guerzoni and Chester (1996) presented papers focusing on African dust transport and impact centering on the Mediterranean basin, but did not mention iberulites, or anything similar. None of the LITE, MINOS, MIN-ATROC, SAMUM and SHADE field experiments have reported any descriptions of particles similar to iberulites.

Satellite imagery (MODIS for example) can only monitor the evolution of Saharan air masses loaded with dust (plumes) over large sampling periods (Fig. 14) because the satellites only retrieve total optical thickness from the measured radiances.

On the other hand, it is well known (e.g., Alarcón et al., 1995; Díaz-Hernández and Miranda Hernández, 1997; Moulin et al., 1998; Escudero et al., 2005) that in the western Mediterranean basin, the highest levels of airborne dust additions to soils generally occur when powerful, advective, high-dust Saharan air masses penetrate into the troposphere and are transported over the Iberian Peninsula (many times across the eastern Atlantic Ocean, Fig. 14) mainly from May to September, induced by anticyclonic activity over the eastern or southeastern Iberian Peninsula, and more sporadically in January, February and October (Figs. 1 and 2). During this transport, atmospheric processing of this material could occur, because these periods coin-

Fig. 10. Particle size distribution of iberulite constituents and dust. Average event was obtained by averaging the data of the other events. Fine particles are $D_p < 2.5 \mu m$, and coarse particles $D_p > 2.5 \mu m$, based on the volume distribution (Seinfeld and Pandis, 2006).
cide with the collection times of iberulites. In the January–June period, this dust transport is mainly caused by cyclonic activity over western or southern Portugal (Rodríguez et al., 2001; Alpert et al., 2004; INM).

In addition, a considerable increase of red rain episodes has been recorded in the western Mediterranean basin since the 1980’s (Quereda et al., 1996; Avila and Penuelas, 1999; Avila et al., 2007). We too have recorded this phenomenon between 2000 and 2006, with the following variability: 2000 (3 episodes), 2001 (7), 2002 (7), 2003 (1), 2004 (10), 2005 (11) and 2006 (7). Fig. 3 shows microscope images of drop impacts from one of these rain episodes, with 2005 in particular being the driest year in Spain since 1887 (INM).

We have also observed that all the red rain episodes were closely associated with hazes, although not all the hazes were accompanied by red rain, and the iberulites were collected during this warm weather. These hazes were not local or even regional, but coincided with Saharan heat waves affecting at least all of the southern Iberian Peninsula. The water for these red rains generally comes from thermal lows or summertime extratropical convective precipitations (one of the major moisture sources) due to evaporation from the land surface (Barry and Chorley, 1998; Fig. 14A and B). However, in spring or autumn, the water can occasionally come from cooler, moister Atlantic fronts (Avila et al., 1998; Fig. 14C).
The iberulites collected in all the events were produced in both wet deposition (red rain) and dryfall contexts. The images in Fig. 3 show a possible connection between the specimens collected during a red rain episode (dust, muddy raindrops and iberulites). The micrograph sequence shown (B–H) indicates a decrease in water content of the muddy raindrops, which would be minimal in the case of the iberulites (which, together with the dust, would be the smallest objects in micrograph A). The muddy raindrops in photos E–H could have become iberulites if their water had evaporated before reaching the ground. All of this could indicate physical interaction between soil particles and water droplets.

4.1. Hypothesis

Our interpretation of the morphological, structural and compositional properties of iberulites will lead to an understanding of their formation mechanisms.

4.1.1. Morphology of the Iberulites

Iberulite morphology shows that sphericity is a common feature, similar to that found in other types of particles produced in different media. Regarding the atmosphere, particle aggregation phenomena are common, occurring as irregular, internally mixed minerals of terrestrial and marine origin with no patterns of structural organization.
Table 2
Phyllosilicates in iberulite rind detected by TEM-EDX microanalysis

<table>
<thead>
<tr>
<th>Species</th>
<th>Elemental composition</th>
<th>Structural formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phyllosilicates from smectite rind</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beidellite</td>
<td>Si, Al, Mg, Fe, Na, Ca, K</td>
<td>[Si$<em>{3.79}$Al$</em>{0.21}$]O$<em>{10}$ (Al$</em>{1.83}$Mg$<em>{0.03}$Fe$</em>{0.17}$)(OH)$<em>2$Ca$</em>{0.10}$Na$_{0.12}$</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Si, Al, Mg, Fe, K, Ca</td>
<td>[Si$<em>{3.98}$Al$</em>{0.02}$]O$<em>{10}$ (Al$</em>{1.23}$Mg$<em>{0.33}$Fe$</em>{0.31}$)(OH)$<em>2$Ca$</em>{0.03}$K$_{0.19}$</td>
</tr>
<tr>
<td>Di-trioctahedral smectites</td>
<td>Si, Al, Mg, Fe, Ca, K</td>
<td>[Si$<em>{3.66}$Al$</em>{0.34}$]O$<em>{10}$ (Al$</em>{0.50}$Mg$<em>{0.93}$Fe$</em>{0.07}$)(OH)$<em>2$Ca$</em>{0.09}$K$_{0.07}$</td>
</tr>
<tr>
<td>Magnesian smectites</td>
<td>Si, Al, Mg, Fe, Ca, K</td>
<td>[Si$<em>{3.30}$Al$</em>{0.20}$]O$<em>{10}$ (Al$</em>{0.65}$Mg$<em>{1.31}$Fe$</em>{0.32}$)(OH)$<em>2$Ca$</em>{0.03}$K$_{0.02}$</td>
</tr>
<tr>
<td>Magnesic-ferric smectites</td>
<td>Si, Al, Mg, Fe, K</td>
<td>[Si$<em>{3.70}$Al$</em>{0.14}$]O$<em>{10}$ (Al$</em>{0.62}$Mg$<em>{1.16}$Fe$</em>{0.24}$)(OH)$<em>2$K$</em>{0.09}$</td>
</tr>
<tr>
<td>Illite</td>
<td>Si, Al, Mg, Fe, K</td>
<td>[Si$<em>{3.66}$Al$</em>{0.34}$]O$<em>{10}$ (Al$</em>{1.61}$Mg$<em>{0.07}$Fe$</em>{0.21}$)(OH)$<em>2$Na$</em>{0.39}$K$_{0.32}$</td>
</tr>
<tr>
<td>Paragonite</td>
<td>Si, Al, Mg, Fe, Na, K</td>
<td>[Si$<em>{1.97}$Al$</em>{0.01}$]O$<em>{10}$ (Al$</em>{1.96}$Mg$<em>{0.03}$Fe$</em>{0.02}$)(OH)$_2$</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>Si, Al, Mg, Fe</td>
<td></td>
</tr>
<tr>
<td>Kaolinite$^b$</td>
<td>Si, Al, Mg, Fe</td>
<td></td>
</tr>
<tr>
<td>Chlorite + Smectite$^b$</td>
<td>Si, Al, Mg, Fe</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Major minerals are not shown as they were previously recognized by XRD and SEM-EDX.

$^b$ Formulae not determined because of Al volatilization in the first case, and because the second is a mixture.

---

Fig. 13. Arrangement of smectite particles and other minerals in the rind, observed using HRTEM images of iberulite sections. The A microfabric shows moderate alteration with atmospheric neoformation products: the inner part of the rind is more altered (gypsum and amorphous silica) than the outer (only halite), while the B1 microfabric is strongly altered: an incipient alunite crystallite emerges by starting to crystallize in an amorphous smectite (gel). Qz, quartz; Si, amorphous silica; Sm, smectites; Ab, albite; Fe, iron oxides; Ha, halite; Gy, gypsum; Alu, alunite; Ill, illite; Ru, rutile; Amp, amphibole.

(e.g., Andreae et al., 1986; Buseck et al., 2000). All of these forms are different from iberulites. One distinctive feature of iberulites separating them from all of these spheroids and aggregates is the vortex, whose origin is not due to the random nature of other phenomena (erosion, impact, ejection, etc.), but is related to iberulite genesis and is common to all of them.

Beard and Chuang (1987), Beard et al. (1989) and Pruppacher and Klett (1997) studied morphologies with similar vortices to those of iberulites in the context of airflow around circulating water droplets: this suggests that water droplets could act as precursors for iberulites, together with the associated mechanisms. These authors examined the drop shapes and established that the drops clearly maintained their sphe-
ricity up to a radius of $a = 500 \mu m$, when a breakup mechanism started, beginning with drop base flattening and an increasingly large concave depression until the equivalent radius reached 4.5 mm. This can be observed in the raindrop impacts shown in Fig. 3. Micrograph A presents a large variety of impacts, with varying sizes and subcircular shapes; all are less than 1 mm in diameter. Sequences E–H shows the traces of raindrops decreasing in size, with the smallest having equidimensional axes.

As iberulite sphericity is high, their formation mechanisms could be linked to the processes undergone by water droplets not passing the aforementioned 500 $\mu m$ radius threshold. On the basis of the studies of Le Clair et al. (1970, 1972), Pruppacher and Beard (1970) and Lin and Lee (1973), we understand that the precursor water drops of the iberulites should have a size range of $150 \mu m < a < 500 \mu m$ (Reynolds number regimes $20 < N_{Re} < 300$), corresponding to the conditions in which the standing eddy at the downstream end of the water drop (rear) forms as a result of the wake produced by the drop in free fall. In this setting, a water sphere falling in air has vigorous internal circulation with a stagnation ring slightly upstream of the equator; a simultaneous reverse circulation towards the rear of the sphere develops for $100 < N_{Re} < 300$ (i.e., $300 < a < 500 \mu m$). In these conditions, a vortex could form in the tail of a falling precursor water drop, and in both its formation and its fall it could trap dust and other drops. The extent of development of this vortex would be conditioned by the strength and size of the wake, which increases according to the Reynolds number. The iberulite in Fig. 6A shows an example of this vortex.

Although the average diameter of the specimens collected is 60–90 $\mu m$, the larger sizes were probably deposited before reaching the sampling station.

4.1.2. Structure and particle-size distribution in iberulites

SEM images show that most of the iberulites from all events have the same structural pattern of three different parts, following the model shown in Fig. 15: the core (tens of microns), a medium layer, and a thin (a few microns) outer rind, considering particle size, the thickness of each layer and its composition.

Beard and Grover (1974) and Grover and Pruppacher (1985) suggested that for $N_{Re}P \approx 30 (a \approx 200 \mu m)$ droplets, small particles (<1 $\mu m$) captured by the standing eddy on the downstream side of the drop are favored by gravity pulling them toward the rear of the drop (wake capture), whereas relatively large particles (>1 $\mu m$) may be captured on the upstream lower side of a falling drop (front capture). Both capture effects would strongly increase with increasing collector radius of precursor water drops and so trap other dust particles and drops (Pinsky et al., 2001). This is consistent with our observations, as the highest concentration of fine particles is found on the upper hemisphere of the iberulites, acting as a crust or rind around the vortex. On the other hand, coarse particles concentrate more on the lower hemisphere, mainly trapped by the lower side of the iberulite (Fig. 6A,C and D).

It therefore appears that the iberulites collected represent the last stage in precursor water drop evolution. Once the water drop–dust grain (colloidal suspension) system is set up, the hydrodynamic phenomena affecting the precursor
water drops during fall produce important regimes of internal circulation inside them (Le Clair et al., 1972; Pruppacher and Klett, 1997), reaching maximum internal velocity near the drop surface. These regimes move the constituent particles according to their inertia: the most mobile are the smallest, tending to become located in the rind, while the largest and heaviest remain in the core and intermediate zone. The components of the core and intermediate zone have no cementing matrix, but, because of their colloidal nature, have moderate $\zeta$-potential surface charges, so that when new particles are captured by a water drop, electrical repulsion exists between them due to this interfacial charge, although this may not prevent weak flocculation in the drop (Hunter, 2000). This explains the high porosity and the ease with which the iberulite disintegrates when manipulated or wetted. Nonetheless, the rind does have a cementing matrix consisting of minerals of laminar habit (phyllosilicates) connecting small mineral grains; amorphous and crystalline iron oxides are also linking agents of the rind constituents.

We can thus define an iberulite as a coassociation with axial geometry, made up of well-defined mineral grains together with non-crystalline compounds, structured on a coarse-grained core and a pinkish smectite rind with only one vortex.

4.1.3. Mineralogical transformation processes on the smectite layer (rind) of the iberulites

EDX spectra and images taken of each of the iberulite parts show a greater abundance of mineral species in the rind than in the core. This could be attributed to a profusion of heterogeneous and multiphase reactions in the smectite rind, which has a special distribution due to the thinness and flexibility of the crystallites. Their aggregates form “honeycombed” structures in which water can be found in various states (Meunier, 2005). These clay suspensions become true gels trapping large amounts of water in the pores of the alveolar structure (Figs. 6A and D1, and 13A).

The successive processes described below would occur in a final stage of the evolution of precursor water drops to iberulites, when they are already structured and formed, with an aqueous phase restricted to the more hygroscopic smectite coating, as opposed to an almost dry core.

The non-silicate minerals found in the rind are mainly sulfates (gypsum and to a lesser extent alunite-jarosite and other mixed sulfates), sodium and calcium chloride, amorphous silica and amorphous iron oxihydroxide. The SEM images show the chlorides to be generally well crystallized (idiomorphs) (Fig. 9A1 and B), whereas the sulfates (except for those shown in Fig. 9C) are present as pulverulent masses, flakes or, in most cases, impregnations (Fig. 13). The occurrence of chlorides and sulfates in the core is minimal. This leads us to think that the presence of these minerals could be the result of two distinct, consecutive processes in the atmosphere: first H$_2$SO$_4$ attack, and second the incorporation of sea salt into the outermost layer of the iberulite rind.

In our case, the H$_2$SO$_4$ could have three origins: (a) condensation of gaseous sulfuric acid on iberulite surface; (b) absorption of atmospheric SO$_2$ into liquid water droplets in clouds, which would be deposited directly on the iberulite surface; and (c) SO$_2$ could be both absorbed onto some particle surfaces (such as quartz grains, feldspars and calcites; Fig. 13), and spread to alveolar smectite compartments, whose water would have an alkaline pH (data not shown). This would provide a suitable chemical environment for the aqueous-phase conversion to H$_2$SO$_4$ (Seinfeld and Pandis, 2006). In addition, due to the ease with which smectites swell, the SO$_2$ could enter more easily into the interlaminar space since the surface area of the smectites increases (Borchardt, 1989). Adsorption of SO$_2$ to active sites with hydroxyl groups (octahedral sheets) would occur in the hydrated interlaminar space and on the edges of the clays, causing irreversible oxidation to sulfuric acid. Ozone and metal components (Fe and Ti) would act as catalyzers and the high pH would make the oxidation reaction proceed at a
substantial rate (Usher et al., 2003). This would lead to the rapid transformation of some primary minerals into products of atmospheric neoformation (secondary minerals): the gypsum crystals would be mainly the product of \( \text{H}_2\text{SO}_4 \) attack on the interlayer cations of the smectites (Table 2). Once these cations are consumed, acid attack could continue to destroy the octahedral and tetrahedral sheets of the smectites and other phyllosilicates (illite and kaolinite, among others), creating mixed sulfates (Andreae et al., 1986). The alunite-jarosite found in the smectite rind would be of similar origin. The alunite could also come from acid attack on orthose or amphibole grains (Fig. 13B1), while the jarosite could be produced by acid attack on Fe- and K-rich phyllosilicates. If acid attack progresses further, the phyllosilicate grains would be completely destroyed, producing the amorphous silica and Fe observed in the TEM-SAED. The lazurite could come from the source area or could also have been formed in the atmosphere by sulfuric acid attack on a grain dust silicate (Fig. 12, central micrograph in the bottom row).

The incorporation of sea salt into the outermost layer of the rind would probably occur at the same time as that of biogenic planktonic exoskeletons. Since these have no signs of corrosion, they must have been incorporated after the acid attack described above (Fig. 8C, C1 and C2). As observed in Fig. 9A and B, the sea salts are adhered to the iberulite surfaces and thus are not the result of atmospheric neoformation reactions on other components, nor are they the result of internal mixing of NaCl and original dust particles (they do not appear in the core).

4.1.4. Space–time sequence of iberulite formation in the troposphere

Satellites provide an excellent picture of dust transport on the global scale (Prospero et al., 2002). The most prominent features in Fig. 14 are the large plumes stretching from the Sahara and Sahel towards the west coast of Africa and then shifting towards the Azores, Gulf of Cadiz and southern Iberian Peninsula. The MODIS images chosen correspond to summer 2004 and spring 2005 and are the most representative of the events associated with iberulite formation. The MODIS image in Fig. 16 clearly illustrates the framework of the process, even though only a few iberulite specimens were collected at the monitoring station during this event (5–8 March 2004) (Fig. 2). Other trajectories exist (Fig. 14), but this one is frequently observed.

Mineralogical composition enables us to establish the relationship with the likely source areas (Fig. 16, label 1), which are the same as those established by other authors in North Africa, mainly consisting of arid soils and standing out as the strongest and most persistently active dust sources (Glaccum and Prospero, 1980; Goudie and Middleton, 2001; Prospero et al., 2002 and references therein).

The major minerals of the arid soil surface on a global scale (Claquin et al., 1999) are quartz, feldspars, illite, smectite, carbonates, gypsum, and iron oxides both for the clay and silt fractions, as well as our iberulites. The presence of mineral assemblages like quartz, dolomite and calcite is a good indication of Saharan origin (Avila et al., 1997), while a composition of mainly smectites and illite suggests an origin in the Aridisols of central Algeria and eastern Morocco,
including the southern slopes of the Saharan Atlas Mountains (Paquet et al., 1984; Prospero, 1999). Kaolinite is more abundant in dust from the lower latitudes of West and Central Africa. Bearing in mind these references, the mineral components of the iberulites studied in this paper may have the same origins. The higher dolomite content in the dust compared to the iberulites suggests possible local contamination of this mineral, suggesting that the iberulites formed before reaching the sampling station.

The coatings of iron oxides and iron oxide domains in the internal mixtures of iberulites must proceed from the soils (Ferralsols) of the source area as free oxides (hematite) or as oxides adhering to the clay minerals, calcite, and quartz (Lafon et al., 2004). North African dust contains appreciable quantities of iron (Jackells et al., 2005): the pinkish color can be attributed to these iron coatings.

Pokras (1991) and Romero et al. (2003) reported remains of silica diatom shells in dust samples. Their presence in the interior of iberulites establishes different source areas, like the Central and Western Sahara and Sahel, especially the northern region in the Bodelé Depression (Washington et al., 2006). Dry lake beds around Lake Chad contain fine particulate matter (particulate organic matter, minerals and diatoms) that is easily picked up, eroded and transported by wind.

Dust is carried from the Sahara within a mixed layer called the Saharan Air Layer (SAL), which typically rises to 500 mb (6 km, Kishcha et al., 2003; Alpert et al., 2004). Its base is near the surface over the Central to West Sahara, but it rises rapidly in a westward direction (Fig. 16, label 2) to be transported far offshore.

During transit in the atmosphere (several days, often a week or more, Prospero (1999) and MODIS), the dust can be transported thousands of kilometers by winds. Studies of dust mobilization in soils from arid regions show that particles <10 μm in diameter can be released in large numbers, but the 5-μm mode is attributed to long-distance transport (Gillies et al., 1996). This is our case (Fig. 10).

Once over the Atlantic Ocean, these large, dense masses of dust fly towards the Canary and Azores archipelagoes (Fig. 16, label 3). Because of the high concentration of dust (our average event has 32% fine and 68% coarse), many small cloud droplets nucleate that coalesce inefficiently into raindrops (Rosenfeld, 2000; Rosenfeld et al., 2001), i.e., the more cloud droplets there are, the smaller they will be and also much less likely to collide with each other and create precipitation (Toon, 2003). However, this would not prevent some cloud droplets of about 2–30 μm radius from coalescing (the minimum size required for the onset of precipitation is about 20 μm; Pruppacher and Klett, 1997). These authors determined that 12–24 min are necessary to form raindrops with radii of about 100 μm, starting from a droplet spectrum centered at about 10 μm. The water droplets formed in these circumstances would be precursors of iberulites, as explained in Sections 4.1.1 and 4.1.2. This implies that the cloud droplets contain very fine dust grains partly originating in nucleation (CCN), but that this load can increase by impaction scavenging. During fall, they would reach terminal speed with a more or less acute horizontal component (Fig. 16, label 3). According to Andreae et al. (1986), droplets in marine cumuli have lifetimes ranging from 17 min to 3 h, which allows for the incorporation of new mineral particles. It is likely that in this stage, local (marine) muddy rain can occur, similar to that described in Fig. 3.

Simultaneously, there could be interaction between conducting water drops, charged aerosols and the atmospheric electric field in a fair weather situation (<150 V m⁻¹; Harrison (2004)). Complex hydrodynamic and electrostatic interactions occur affecting the collision efficiency of 150 ≤ a ≤ 600 μm water drops in air and aerosol particles of up to 3 μm radius (Grover and Beard, 1975). Thus, rear collision through the vortex between electrically charged drops and particles is more likely. Gay et al. (1974) found that 300 μm water drops falling in an electrified field between 25 and 40 V m⁻¹ at 20 °C and 1013 mb experienced upward motion (experiencing a combined gravitational and electrical force of mg ± QE, where m = mass, Q = drop charge and E = vertical electrical field). This increases the atmospheric residence time. Also during fall, the water in the drop evaporates, which is a sine qua non condition for iberulite formation; the loss of mass would cause a gradual loss of speed. Evaporation can occur either because the precursor water drop leaves a cloudy region or because it falls to lower, warmer levels of the troposphere. When it is practically dry (in a matter of minutes), only the weakly bound mineral components remain, many of them highly porous (Fig. 8B), with a thin layer of laminar minerals on the periphery, mainly on the hemisphere containing the vortex and with the structural configuration caused by the hydrodynamic phenomena explained above. Overall, their bulk density is very low (0.65 grams/cm³ and porosity about 50%), so they could act as flying spheres, possibly able to remain in the air for a long time and cover large distances (Fig. 16, label 4). During this transport, the smectite rind may retain some water or rehydrate because of its high degree of hygroscopicity. At this point, the iberulites would be completely formed, but would have not yet acquired the compositional maturity observed after collection due to the absence of mineral species later detected in the smectite layer. According to Glaccum and Prospero (1980), the dust does not contain any primary halite or gypsum. During the precursor water droplet stage, water action could cause the virtual dissolution of mineral cations. However, since the initial mineral phase (mainly silicates and carbonates) has low solubility, and environmental humidity should not, in theory, supply a high saline load at high altitudes as it is still above the marine boundary layer (MBL), it could be expected that these iberulites would not yet have the peripheral saline minerals observed. Otherwise, these salts would be evenly distributed throughout the microspherulite body and not in specific areas. However, we can see that the salts are preferentially located in the rind, particularly in the case of sulfates and chlorides, with the former beneath the latter (see 4.1.3 and Figs. 9 and 13).

The non-sea-salt sulfates (NSS: gypsum, alunite-jarosite, among others) were probably not incorporated into the iberulites like the conventional sea-salt sulfates, but would be neoformed minerals in the iberulite rind before deposition of the sea salt: they are mainly found as an outer fringe
on all iberulites in all events (Fig. 12, bottom row of micrographs) with identical distributions on the smectite rind. The process causing this sulfate fringe would occur on the outside of immature iberulites by gas-iberulite transfer reactions and heterogeneous oxidation of SO$_2$ (see Section 4.1.3). As the carbonate planktonic skeletons are well preserved, they would not yet have been incorporated into the iberulite surface at the time of the reaction. The minerals of the iberulite interior (especially the carbonates) would therefore not undergo acid attack, as the core is already dry (no corrosion or coating has been observed).

The presence of NSS in the iberulites of all the events studied requires transit through areas with high content of atmospheric sulfur species (Fig. 16, label 4). We must discard anthropogenic emissions due to the geographic context in which the immature iberulites are moving. Alternatively, there are two main sources of sulfur: the volcanic context of the Canary, Madeira and Azores archipelagoes, which supplies a background of diffuse and continuous emissions, and oceanic dimethyl sulfide (DMS). However, Wang et al. (1995), Thornton et al. (1997) and Raes et al. (2000) suggest that DMS contributes only 1–10% of the SO$_2$ in the upper troposphere in the Northern Hemisphere. Given that the trajectory of the immature iberulites carries them over the MBL at altitudes of around 5 km, they would come into contact with the SO$_2$ emissions from these archipelagoes, which in most cases concentrate in the upper part of or far above the MBL (Graf et al., 1997).

SO$_2$ accumulation is therefore probable in the vicinity of the Teide stratovolcano (3710 m ASL). During the ACE-2 campaign over the Canary Islands area, de Reus et al. (2000) observed a marked decrease in ozone concentration linked to high mineral dust concentrations. This means that dust surfaces provide a sink for the direct removal of ozone; ozone depletion would in turn boost SO$_2$ oxidation (Gobbi et al., 2000; Usher et al., 2003). In our case, the iberulite smectite rind would appear to be the most efficient sink, as the sulfate content of iberulites is higher than that of dust (Fig. 11).

Having flown over the Canary Islands, the plume would continue to descend gradually towards the MBL (850 mb, ~1.5–2 km, Formenti et al., 2003; Alpert et al., 2004). This would imply a 22% increase in collision efficiency of drops with sea salts for a change in ambient conditions (995 mb, 14 °C to 800 mb, 25 °C, De Almeida, 1977), reaching their final maturation (Fig. 16, label 5).

These chlorides could therefore originate in the sea-salt particles that either precipitated onto the iberulite surface or adhered to the smectite layer as idiomorphic crystals because of their hygroscopicity (Fig. 9A and B). Redissolution processes have also been observed in these salts (data not shown). Sea-salt supply would thus occur at the same time as the incorporation of the planktonic organisms found on the iberulite surfaces (Fig. 8C), adding weight. We do not detect any signs of acid attack on these biogenic skeletons because the SO$_2$ concentration in the MBL (from the DMS) must be much lower than in label 4.

This stage (iberulite maturation) could take place over the triangle formed by the Canary Islands, the Azores and the Iberian Peninsula. Specifically, we have observed (Figs. 14 and 16) that masses of dust frequently enter and remain stationary in the Gulf of Cadiz before entering the Iberian Peninsula.

Finally, in the atmosphere of the southern Iberian Peninsula, these dust plumes containing iberulites could both produce a dryfall or become associated with local red rains (wet deposition) when supplied with more humidity from summer cumulo-nimbus formation. The muddy raindrops of the red rains observed in Fig. 3 would form over the sampling station and could be considered aborted potential iberulites, lacking many of the attributes mentioned above. It is possible that gravitational settling may have sedimented larger iberulites before reaching the sampling station.

As already suggested, the mechanisms most likely to produce iberulite morphology are based on the theory of fluid mechanics (Pruppacher and Klett, 1997). However, other alternative hypotheses, single or combined (electrorotation, Kelvin–Helmholtz and Von Karman vortices), could be considered to cause these vortex morphologies, although we believe that they do not fully explain these features.

5. CONCLUDING REMARKS

An iberulite is a new type of spherical aerosol particle collected in the southern Iberian Peninsula. It is internally mixed and structured, mechanically generated, with a diameter ranging from about 30 to 190 μm, with a low density (0.65 g cm$^{-3}$) and about 50% mean porosity. Iberulites are different from classic atmospheric aerosols (<20 μm) (Seinfeld and Pandis, 2006). Because of their features, they probably have different physical and chemical characteristics than do other aerosol particles.

One of the important features of iberulites is that, together with the dust from which they are formed, they provide reaction sites for many heterogeneous reactions involving SO$_2$, HO$_2$, O$_3$, etc., bringing together other components and forming other minerals, as well as permitting aggregation.

On the basis of these facts, our interpretation is that iberulites are the result of atmospheric processing that could last several days. Their stages of formation, maturation and deposition can be summarized as follows:

1. Dust outbreak and elevation to the upper layers of the troposphere by the SAL.
2. Transport, size selection and flight over land and the Atlantic Ocean.
3. Formation of precursor water drops and gradual descent to lower tropospheric levels. This implies several processes that can be either simultaneous or consecutive (coalescence, formation of vortex, incipient downdraught).
4. Flight over areas with volcanic sulfur emissions (Canary Islands). Incorporation of SO$_2$ into the iberulite surface.
5. Descent to the MBL of the Iberian-Moroccan Atlantic and incorporation of sea-salt particles and plankton.
6. Final sequenced fall of mature iberulites onto the southern Iberian Peninsula.

The foregoing processes would give rise to the pinkish mineral microspherulites (iberulites), which can be consid-
ered complex (mixed) mineral assemblages formed in the atmosphere, are different from those found in other natural or anthropic ecological environments, and provide a particularly good opportunity to investigate relevant reactions in the atmosphere.

We consider that iberulites are tangible evidence of hydrodynamic theory applied to the interaction of water drops and dust particles, giving rise to shapes with a vortex that have until now been confined to and explained in laboratory studies.

6. FINAL CONSIDERATIONS

The key question is whether the newly recognized microspherules are abundant and/or distinctive enough to require changes in existing models for atmospheric dust deposition (at least in areas around the Mediterranean). For example, is there evidence that their formation has been increasing since 1992? Is there evidence that they accelerate the deposition of dust in unexpected ways, or do mass flux calculations indicate that they might? Alternatively, if iberulites do not influence the flux in a major way, do (or could) they play an important role in some other way, e.g. as a marker for environmental or paleoclimatic analyses (as long as they can be found fossilized in the stratigraphic record)?

Because the quantities of iberulites obtained in the sampling station range from 11% to 47%, could they have a non-negligible direct impact on the radiation budget at any point of their trajectory?

We do not know the frequency and magnitude of the processes involved in iberulite formation in the past and thus do not know if these additions of iberulites to the soils, particularly those of the Mediterranean, are another reason for their being different.

ACKNOWLEDGMENTS

This work benefited from discussions with Prof. B.M. Simonson (Department of Geology, Oberlin College, Ohio, USA), Dr. E. Reyes (Department of Isotopic Biogeochemistry, Consejo Superior de Investigaciones Científicas, Granada, Spain), Prof. A. Delgado (Department of Applied Physics of the Granada University, Spain), Prof. D. Martin (Department of Mineralogy and Crystallography of the Granada University, Spain) and Dr. J. Cuadros (Department of Mineralogy, the Natural History Museum, London). We thank the Technical Services of Granada University for the SEM and TEM images, especially Drs. M. Abad, I. Guerra and A. González, as well as A. Romero for extensive assistance with the illustrations. We are grateful to Prof. D. W. Parkin (Bath University, UK) for permission to reproduce micrometeorite images. We also wish to thank the Instituto Nacional de Meteorología for access to its database and the Spanish Ministry of the Environment for providing the records of station ES07. MODIS is a NASA project. Finally, the authors thank the associate editor and the anonymous reviewers for their constructive suggestions.

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