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Role of clay minerals in the formation of atmospheric aggregates of Saharan dust



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HIGHLIGHTS

 \bullet Iberulites are >100 μm aggregates of Saharan dust described in SE Spain.

- Iberulites contain quartz, feldspar, carbonate, clay, sulphates and Fe oxyhydroxides.
- Clay appears to be enriched in the iberulites with respect to the aerosol.
- Clay morphology and hygroscopicity are important in shaping the iberulites.
- Variable gypsum in iberulites linked to anthropogenic SO₂ emissions.

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ABSTRACT

Saharan dust can travel long distances in different directions across the Atlantic and Europe, sometimes in episodes of high dust concentration. In recent years it has been discovered that Saharan dust aerosols can aggregate into large, approximately spherical particles of up to 100 μ m generated within raindrops that then evaporate, so that the aggregate deposition takes place most times in dry conditions. These aerosol aggregates are an interesting phenomenon resulting from the interaction of mineral aerosols and atmospheric conditions. They have been termed "iberulites" due to their discovery and description from aerosol deposits in the Iberian Peninsula. Here, these aggregates are further investigated, in particular the role of the clay minerals in the aggregation process of aerosol particles. Iberulites, and common aerosol particles for reference, were studied from the following periods or single dust events and locations: June 1998 in Tenerife, Canary Islands; June 2001 to August 2002, Granada, Spain; 13–20 August 2012, Granada; and 1 -6 June 2014, Granada. Their mineralogy, chemistry and texture were analysed using X-ray diffraction, electron microprobe analysis, SEM and TEM. The mineral composition and structure of the iberulites consists of quartz, carbonate and feldspar grains surrounded by a matrix of clay minerals (illite, smectite and kaolinite) that also surrounds the entire aggregate. Minor phases, also distributed homogenously within the iberulites, are sulfates and Fe oxides. Clays are apparently more abundant in the iberulites than in the total aerosol deposit, suggesting that iberulite formation concentrates clays. Details of the structure and composition of iberulites differ from descriptions of previous samples, which indicates dependence on dust sources and atmospheric conditions, possibly including anthropic activity. Iberulites are formed by coalescence of aerosol mineral particles captured by precursor water droplets. The concentration of clays in the iberulites is suggested to be the result of higher efficiency for clay capture than for the capture of larger mineral grains. The high hygroscopicity of clay minerals probably causes retention of water in the evaporation stage and some secondary minerals (mainly gypsum) are associated with clays.

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1. Introduction

Mineral aerosols originating from soils and surface sediments are complex mixtures of particles lofted into the atmosphere by





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eolian processes affecting mainly arid and semi-arid lands. The Sahara produces an enormous quantity of aeolian dust that influences climate and soil composition in vast and distant areas. Saharan dust is transported at great distances along relatively well-known trajectories connecting North Africa with Europe and the Americas (Swap et al., 1992; Franzen et al., 1994; Shinn et al., 2000). The North Atlantic Oscillation controls the evolution of Saharan air masses loaded with dust or plumes and therefore the dust transport over the Atlantic Ocean and the Western Mediterranean Sea (Moulin et al., 1997; Rodwell et al., 1999; Bout-Roumazeilles et al., 2007). Large dust outbreaks during the summer reach the South of the Iberian Peninsula, where the duration of individual Saharan plume events is estimated to vary between 2 and 3 days (Rodríguez et al., 2001).

The particles from the dust of the Saharan plumes are mainly composed of silicates, a characteristic that they share with those from dust storms in the Gobi and Arizona deserts (Goudie and Middleton, 2001). The average chemical composition of the dust from these sources is similar to that from all world dust storms and to the mean composition of the Earth's surface rocks (Goudie and Middleton, 2001; Lawrence and Neff, 2009). Mineral aerosols consist of particles with typical size of less than 20 µm, which can undergo long-range transport (Seinfeld and Pandis, 2006). Particularly, atmospheric aerosols with particle size <2 µm may reside one week in the atmosphere (Tegen and Lacis, 1996; Miller et al., 2006; Kok, 2011). These long residence times in the atmosphere cause interaction with atmospheric components (water, gases, other aerosols). Given their small particle size, clays are abundant components in atmospheric dust, especially in longed-lived aerosols (Engelbrecht and Derbyshire, 2010). All clays have large surface areas of predominantly hydrophilic character. Besides, smectite and vermiculite have swelling layers that admit large proportions of water between them. As a result, the clay component of dust interacts strongly with atmospheric water, which is retained by the clay in variable amounts.

In some studies, dust has been found to consist of large aggregates (Díaz-Hernández and Párraga, 2008; Jeong et al., 2014). The aggregates investigated by Díaz-Hernández and Párraga (2008) were from the Sahara, often reaching sizes > 100 μ m, and were interpreted to form by a complex process of aerosol inclusion into water droplets, from which they inherited their external morphology. They were termed "iberulites" because they are a very rare phenomenon first described by Díaz-Hernández and Párraga (2008) and found in the Iberian Peninsula. They are a new type of aerosol particle forming in the atmosphere, during Saharan dust plume events under very specific atmospheric conditions. The aggregates found by Jeong et al. (2014) were from Asia, different in shape, no larger than 60 μ m, and interpreted as generated in the source area.

In this paper we study iberulites and common aerosols from the Sahara, with special emphasis on clay minerals and their role in the formation of iberulites and in the physico-chemical processes taking place within them. The clay mineralogy of Saharan dust has been addressed in numerous occasions and shown to depend on sources, trajectory and sampling location (Goudie and Middleton, 2001; Bout-Roumazeilles et al., 2007, and references therein). Recently, chemical and mineralogical investigation of clay minerals from iberulites (Díaz-Hernández and Párraga, 2008) and common aerosols from similar dust sources (Díaz-Hernández et al., 2011) show the presence of smectite, illite, kaolinite and chlorite. Our mineralogical, textural and compositional data indicate that, due to their particle size, hygroscopicity and physical flexibility, clay minerals are essential for the formation of these large mineral aggregates within water droplets in the atmosphere. They appear to be concentrated in the iberulites with respect to the other mineral phases in the aerosol. Clays influence the fabric and porosity of the aggregates. In addition, they influence the drying process of the aggregate and thus salt precipitation within it.

The clay minerals mentioned above have the following characteristics that are used for their mineralogical and chemical identification. Smectite has two tetrahedral sheets and one octahedral sheet in each layer (TOT layer). A small negative layer charge is compensated by hydrated cations in the interlayer space. Smectite is unequivocally recognized by the expansion of the distance between layers to ~17 Å when treated with ethylene glycol. Illite has also TOT layers with high negative charge and interlayer K compensating for it. Interstratified illite-smectite is a group of minerals in which layers of one and the other mineral stack together within crystals. Kaolinite has TO layers with no charge and no interlayer cations. Chlorite has TOT layers intercalated with hydroxyl layers (total layer unit TOTH). Contrary to smectite, illite, kaolinite and chlorite do not change their interlayer space with ethylene glycol treatment.

2. Material and methods

The four studied samples were selected from a collection of atmospheric dust obtained by dry passive collectors from 1998 to 2014 (Table 1). It must be emphasized that all correspond to atmospheric dry deposition. Sample TF6-98 consists of common aerosol particles with no large aggregates, collected during June of 1998 at the south western slope of the Teide mountain, in the Tenerife island, Canary archipelago, off the northwest coast of north Africa. The other samples contain a range of iberulite proportions (Table 1). All of them were collected in the Granada basin, an intramountain depression in the Betic Cordilleras, southern Spain. Sample GR6-14 corresponds to an iberulite-rich deposition (Fig. 1). Sample GR8-12 consists only of iberulites (2.5 mg total weight) separated from the total aerosol. In all cases, medium-sized trays $(0.064 \text{ m}^2 \text{ of surface area and 5 cm deep})$ were used to obtain quantities suitable for analysis. They were placed in rural areas, on the roof of buildings ~8 m above the ground, and on structures ~2 m above the roof (total height ~10 m). In Granada, the dust collectors were further protected from local dust contribution by surrounding irrigated land and by a dense tree barrier (Díaz-Hernández and Miranda, 1997).

Samples were carefully examined under a stereomicroscope and classified according to presence and abundance of aggregates. In the case of sample GR8-12 the iberulite aggregates were handpicked under the stereomicroscope. The isolated iberulites were studied using SEM and EPMA. High-resolution secondary electron (SE) images and microanalysis of carbon-coated samples of iberulites from sample GR8-12 were obtained with a field-emission SEM Auriga (Carl Zeiss) equipped with a LinK INCA 200 (Oxford Instruments) analytical system. During sample preparation, carbon coating was carefully performed to avoid or minimize the generation of artifacts at nanometer scale. The interior of the iberulites was also investigated by embedding them in resin, their preparation as polished sections and carbon coating. Back-scattered electron (BSE) images and energy-dispersion X-ray (EDX) spot analyses (200 nm of diameter) were performed on the polished sections with the same instrument.

X-ray chemical-element maps were obtained for iberulites in polished sections from samples GR6-14 and GR8-12, with an EPMA apparatus CAMECA SX100 operated at 15 kV of acceleration voltage and 5 nA of probe current. Spot size was 1 μ m. X-ray images were obtained by moving the polished section while maintaining the beam in a fixed position. The step-to-step displacement and acquisition time were 1 μ m and 500 ms respectively. Element maps were processed with the software DWImager (Torres-Roldán

cation and tim	le of collection of the studied sam	ples, as well as proportion of ideru	liftes in the aerosol.		
Sample	Location	Coordinates	Altitute (m ASL)	Time of collection	Iberulite proportion
TF6-98	Teide mountain, Tenerife	28°5.983'N 16°40.837'W	628	June 1998 ^a	No iberulites
GR01-02	Granada basin, Spain	37°10'N 3°31'W	640	June 2001–August 2002	Low
GR8-12	Granada basin, Spain	37°10'N 3°31'W	640	13–20 August 2012 ^a	Only iberulites ^b
GR6-14	Granada basin. Spain	37°10′N 3°31′W	640	1–6 June 2014 ^a	~30% wt.

Table 1

GR6-14

Location and	time of (collection of	the studied	samples a	s well as	proportion o	f iberulites in	the se	rosol
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Single dust event.

Separated from the overall aerosol. The original aerosol had an iberulite proportion of ~20% wt.



Granada basin. Spain

Fig. 1. Pinkish, round aggregates of aerosol particles (iberulites) from sample GR6-14 as seen under the stereoscopic microscope. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and García-Casco, unpublished) to obtain images where minerals are identified. Colour mineral-phase maps overlie a grey-scale base-layer that represents the texture of the analysed surface. This gray-scale layer is calculated with the formula shade of $grey = \Sigma$ (*counts_i* · *A_i*), (where *A* is atomic number and *i* is Si, Ti, Al, Fe, Mg, Ca, Na, and K).

Further analyses were performed using aerosols with no iberulites (sample TF6-98), aerosols containing diverse amounts of iberulites (GR01-02 and GR6-14) and the sample containing exclusively iberulites (GR8-12). They were milled with an agate mortar and pestle for one minute for powder X-ray diffraction (XRD) analysis. Only samples TF6-98, GR01-02 and GR6-14 were sufficiently large to carry out powder analysis. Their powders were deposited on a zero-background holder and the XRD diagrams recorded at the University of Granada using a PANalytical X'Pert Pro diffractometer (Cu-Ka radiation, 45 kV, 40 mA) equipped with an X'Celerator solid-state linear detector. This detector covers an angle of 2.1° and integrates the diffracted intensity over this angle dynamically as it scans. The diffraction patterns were obtained by a continuous scan between 3 and $50^{\circ}2\theta$, with a $0.01^{\circ}2\theta$ resolution, and 15 min total scan time (equivalent to 20 s counting time per $0.01^{\circ}2\theta$). Sample GR8-12 (2.5 mg) was prepared as an oriented mount, which enhances the intensity of basal diffraction peaks of clays. The powder was suspended in water, deposited on a zerobackground sample holder and analysed first as air-dried and later as a glycolated oriented mount (60 °C overnight in an ethyleneglycol atmosphere). In this sample the resulting oriented mount was an extremely thin film. The mount was analysed in the Natural History Museum (London) with a PANalytical X'Pert Pro diffractometer with the following experimental conditions: continuous scan between 3 and 50°2 θ , resolution of 0.0167°2 θ , and scanned for 25 h (equivalent to 67 min per $0.0167^{\circ}2\theta$).

For samples TF6-98, GR01-02 and GR6-14, the fraction $< \sim 2 \ \mu m$ was extracted from the whole powders by suspending them in distilled water, decanting the suspension for 8 h and pipetting the upper 10 cm of the suspension. The clay was concentrated from the supernatant by centrifugation, oven-dried and ground. Suspensions of the ground clay were deposited onto circular glass slides to generate oriented mounts. They were analysed as air-dry samples only, at the University of Granada, using the conditions indicated above for the powder samples. All XRD data were processed using the XPOWDER program (Martín-Ramos et al., 2012) for visualization of the XRD patterns and mineral identification.

The <2 µm size fraction from sample TF6-98 (that did not contain iberulites) and a few iberulites from sample GR8-12 were studied by TEM. The powders or a few iberulite aggregates were embedded in an epoxy resin and sectioned with a diamond ultramicrotome (<100 nm thick slides) that were deposited on a copper grid and coated with carbon. TEM and STEM (HAADF: high-angle annular dark field) images, selected area electron diffraction (SAED) patterns, single spot microanalyses and X-ray chemicalelement maps were obtained with a FEI TITAN G2 TEM apparatus operated at 300 kV and equipped with four energy dispersive X-ray (EDX) detectors (SuperX system). Fully quantitative analyses (analytical electron microscopy, AEM) of clays were also obtained with this instrument in STEM mode using a beam of 5 nm in diameter and a scanning area of 20×100 nm. These EDX analyses were corrected by the thin-film method of Lorimer and Cliff (1976). The k-factors were determined using muscovite, albite, biotite, spessartine, olivine, and titanite standards.

3. Results

3.1. XRD mineralogical analysis

The bulk mineralogy of the powders from samples TF6-98, GR01-02 and GR6-14 is shown in Fig. 2A. In the samples from Granada (GR01-02 and GR6-14), the most prominent phases are quartz, dolomite and calcite. Feldspars are prominent in sample TF6-98. Halite is only observed in the sample from Tenerife. Gypsum occurs in low amounts in all samples. Illite is present in the three samples, in the order GR01-02 > GR6-14 > TF6-98. Kaolinite is clearly observable in the three samples. A smectite-like phase is present in GR01-02 as a small, narrow peak, and possibly also as a wide peak in the same area. Sample GR6-14 may also present a wide smectite peak.

The XRD patterns of the oriented mounts of the fraction $<2 \ \mu m$ (Fig. 2B) are similar but the proportion of clay minerals is enhanced. Smectite becomes more obvious in sample GR01-02 (small, sharp peak at 14.5 Å), but cannot be positively identified in the other two samples (the hump in the background at low angle, caused by X-ray cut-off, interferes with a positive detection). Gypsum and quartz are also present in this fine fraction of the three samples. Feldspar, halite and polyhalite are present in TF6-98, and dolomite in GR01-02.

Sample GR8-12, consisting exclusively of iberulites and with no particle size separation, was prepared as an oriented mount. The XRD patterns in air-dry state and after glycolation (to identify smectite) are shown in Fig. 3. There is a prominent peak at ~13 Å



Fig. 2. Mineralogical composition of aerosol samples from the XRD patterns: A) Powder patterns of the whole samples (common aerosol plus iberulites). B) Oriented aggregates of the <2 μ m size fraction. The intensity increase at 3–6°2 θ (in B) is partially caused by X-ray cut-off at very low angle. The hump at 15–40°2 θ (in B) is caused by the glass slide supporting the oriented mount. The figures on the dash lines are *d*-spacing values in Å. (Mineral abbreviations: Cal = calcite; Dol = dolomite; Fsp = feldspars; Gp = gypsum; Hl = halite; Ilt = illite; Kln = kaolinite; PHI = polyhalite; Qz = quartz; Sme = smectite).

that corresponds to a smectite-like phase. Contrary to what should be expected, there is no displacement of this peak after glycolation to ~17 Å. However, there are other changes that indicate that this peak does correspond to a smectite-like phase: 1) the peak sharpens and becomes more intense; 2) a wide band between 7.5 and $9^{\circ}2\theta$ in the air-dry sample disappears in the glycolated sample (arrow in Fig. 3). These changes indicate that the wide band is a smectite-like phase and that glycolation shifts the *d*-spacing of these layers to 13.33 Å. The lack of expansion to



Fig. 3. XRD patterns of air-dried and glycolated (EG) oriented mounts for clay mineral identification in sample GR8-12, containing only iberulites. The figures on the dot lines are *d*-spacing values in Å. The arrow indicates a wide peak in the air-dry specimen that disappears in the EG specimen (see text).

~17 Å is most likely due to the fact that the corresponding mineral phase is vermiculite or smectite with a high layer charge, which causes only partial expansion with ethylene glycol to ~13 Å (MacEwan and Wilson, 1984). The 001 peaks of illite and kaolinite are also observed, together with the two most prominent quartz peaks.

3.2. SEM study of iberulite aerosols

Observation of the surface of iberulites with secondary electrons (Fig. 4A), showed spherical to near spherical objects several tens of μ m wide, with a rough surface on which μ m-sized particles were present. EDX microanalysis of the surface shows S and Ca (likely indicating the occurrence of gypsum) together with the usual chemical elements corresponding to clays (Fig. 4B). In a more detailed observation, the surface of the iberulites appeared coated by clay platelets arranged with their basal surfaces tangential to the surface of the iberulite (Fig. 4C). Higher magnification images of the coating clays showed a very rough surface texture, and the occurrence of aggregates of nanoparticles are the calcium sulfate detected by EDX.

BSE images from polished sections of the iberulites (Fig. 5) shows that in their interior there are grains of quartz several μ m in diameter (no spectra shown), feldspar grains (spectrum 4; the morphology and chemistry of this grain is interpreted as feldspar, with the EDX analysis including also surrounding or coating kaolinite and a sulfate phase), very fine-grained aggregates of clay platelets more abundant towards the surface of the iberulites



Fig. 4. SEM secondary electron images and EDX microanalysis of iberulites from sample GR8-12. A) Low magnification image of an iberulite showing an irregular surface formed by the assemblage of mineral particles. B) EDX spectrum representative of the average composition of the iberulite surface in A, interpreted as clay and gypsum. C) Closer view of the surface of an iberulite, which appears covered by platy clay particles. D) Close-up image of the surface showing the presence of aggregates of round mineral particles of nanometre size, interpreted to be gypsum, on the clay particles.

(Fig. 5B and D, spectrum 1), Fe oxides (not shown) and coarser mica flakes. Mica particles have variable composition, from phengite (spectrum 2) to muscovite (spectrum 3). Clay packets usually have sizes <1 μ m in length and 100 nm in thickness (Fig. 5B and D). EDX microanalyses indicate that clays are illite or smectite (spectrum 1) and kaolinite (spectrum 5; this analysis collected X-rays from several mineral grains, but the prominence of the Si and Al peaks, and the relative Si/Al intensities indicate kaolinite). Medium to low intensity S and Ca peaks appear frequently in the spectra (spectra 1, 4 and 5), probably corresponding to gypsum. Other detected mineral phases include monazite (spectrum 5) and Ti oxides (not shown).

3.3. Mineral distribution and chemistry of iberulite aerosols by EPMA

A detailed compositional and mineralogical study of the iberulite aggregates was performed by EPMA for GR8-12 and GR6-14 samples. Mineral identification was based on chemistry and supported by morphology. The ideal structural formulas of the phyllosilicates found in the iberulites are provided here to clarify the basis of the identifications. The octahedral cations are in parenthesis. Smectite interlayer cations are in square brackets. Muscovite Si₃Al₁(Al₂) K₁O₁₀(OH)₂; phengite Si₃Al₁(AlMgFe)₂K₁O₁₀(OH)₂; illite Si_{3.3}Al_{0.7}(AlMgFe)₂K_{0.8}O₁₀(OH)₂; smectite Si_{3.8}Al_{0.2}(AlMgFe)₂[CaMgNa]_{0.2}O₁₀(OH)₂; kaolinite Si₂Al₂O₅(OH)₄; Fig. 6 shows texture images (where the gray shade is a function of the average atomic number, Z, with lighter shades corresponding to higher Z) and Fe, Ti and S X-ray maps of four iberulites. Iron is widely distributed in the mineral aggregate whereas Ti is highly concentrated in small particles. The most intense signal of Fe and Ti K α X-rays of Fig. 6B and C corresponds to particles of Fe- and Ti-oxides and mica (elongated particles). The less intense Fe signal in Fig. 6B is attributed to Fe in smectite and illite. Sulphur is distributed across the aggregates, most likely in gypsum. A few particles, with very intense S K α signal, apparently consist exclusively of S (*e.g.*, arrow in Fig. 6D).

Mineral phase maps show that the coarser components of the iberulites are quartz, feldspars, carbonates and minor amounts of some other aluminosilicate (Fig. 7A and B). Illite and smectite particles (it is not possible to distinguish them chemically in the images) are distributed within the entire aggregates (vellow in Fig. 7C). Small kaolinite particles and coarser mica particles with laminar habit of several tens of µm in length are less abundant and also distributed across the grains. Interestingly, kaolinite appears as alteration rims in some coarse aluminosilicate grains with composition Al₂SiO₅ (arrow in middle grain, Fig. 7A). Also, some muscovite plates appear completely altered to illite + smectite (arrow in Fig. 7C), and a feldspar grain (arrow in top grain, Fig. 7A) partially altered to sericite (K- and Al-rich illite; appears as muscovite in Fig. 7C). The area of each of the detected mineral phases in these four iberulites is an approximation to their relative abundance in the aggregates. Averaging the four iberulites studied, illite + smectite are the most abundant phases with 48% of the area, followed by calcite (19%), quartz (18%), mica (6%), kaolinite (4%), feldspars (3%), dolomite (1%) and an Al₂SiO₅ mineral phase (1%). The average total clay content is 52%. The illite + smectite area in the four iberulites is fairly constant, 47-49%. The kaolinite content



Fig. 5. SEM back-scattered electron images and EDX microanalyses obtained from iberulites in polished sections from sample GR8-12. A) Low magnification image of an iberulite containing mineral particles of several µm with angular shapes (mainly quartz), as well as masses of finer particles (clays) that appear located next to the surface (composition in spectrum 1). The large void in the centre is most likely caused during sample preparation. B) Detail of the region in the box in A, mainly composed by finegrained minerals of laminar habit (clays). C) Iberulite with a well-preserved core, showing the arrangement of mineral particles with very different size and morphology. Large mica flakes are observed (*e.g.* spectra 2 and 3). D) High magnification image of box in C, showing the arrangement of clay particles in a clay-rich region. Spectrum 4 most probably corresponds to a feldspar grain, although contamination with kaolinite and a sulfate phase is likely. Spectrum 5 includes sulfate(s), an LREE phosphate and clay (probably kaolinite).

varies from 2% in the three iberulites from the 2014 event (three upper aggregates in Fig. 7) and 10% in the iberulite from the event in 2012.

The compositional ranges of the several identified minerals is shown in Fig. 7D–F. The mica composition varies from muscovite (region 1 in Fig. 7D) to phengite (region 2 in Fig. 7D), in agreement with SEM-EDX results (Fig. 5, spectra 2 and 3). A Ti-rich phengite also occurs in the iberulites (Fig. 5F, spectrum 2, and elongated particle in Fig. 6C). The illite plus smectite composition ranges widely. Presumably, illite occupies the region between fields 1 and 2 (Fig. 7E), and smectite has the greater compositional variation reaching the Fe + Mg-rich region 3. The compositional range of kaolinite may reflect the presence of kaoliniterich interstratified kaolinite-smectite or kaolinite derived from smectite pedogenically, which preserve some Fe and Mg from smectite (Fig. 7F).

3.4. TEM and AEM study of clays from aerosols

Given that the clay mineralogy of all samples is similar (smectite, illite and kaolinite), two samples were selected for the TEM study, the <2 μ m size fraction of aerosols with no iberulites (sample TF6-98), and iberulites (sample GR8-12). Low-magnification STEM images and X-ray maps from sample TF6-98 (Fig. 8) show a mixture of nanometre-sized mineral particles as illite (bright elongated particle in Fig. 8F), plagioclase (spectrum 3), Fe oxy-hydroxides (small bright particles in Fig. 8E), montmorillonite (spectrum 1), nontronite (spectrum 2) and either beidellite or albite partially altered to kaolinite (spectrum 4). Most of the material contains Si, Al, Mg and Fe, corresponding to montmorillonite (Fig. 8B–D). Iron enrichment is observed in small and irregular parts of the map (Fig. 8E), corresponding to Fe oxy-hydroxides. There is also Fe accumulation in a clay-like particle corresponding to nontronite



Fig. 6. Chemical maps of iberulite sections from EPMA. The three large iberulites are from sample GR6-14 and the small one from GR8-12. A) Grey-scale base-layer or Z image containing the basic textural information. B) to D) Element X-ray maps of Fe, Ti and S. Lighter shades represent more intense X-ray signals (see count scales). The arrow in D indicates a grain apparently containing only S.

flakes (Fig. 8E). Potassium enrichment is associated with illite plates (Fig. 8F). Very low amounts of gypsum are detected on one of the smectite particles (spectrum 1). There is no positive detection of

kaolinite particles in the TEM study carried out on aerosols without iberulites (TF6-98). The reason for this is not clear, since XRD analysis displays a noticeable kaolinite peak (Fig. 2). Perhaps Fe and



Fig. 7. Chemistry and distribution of mineral grains within the iberulites shown in Fig. 6, from EPMA data. A–C) Mineral phase maps obtained from grain composition. Illite and smectite cannot be resolved and they appear together. Arrows in A point to a K-feldspar and one aluminosilicate (Als) particle with their surface altered to clay minerals (see text for details). There are also grains of albite (Ab) composition. Arrow in C points to a large plate of muscovite completely altered to illite + smectite. D–F) Chemical variations of muscovite, illite + smectite and kaolinite within the K–Al–Fe + Mg field. Colours in D–F indicate the number of pixels with the corresponding composition (following the scale on the left). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. TEM image and chemical maps of the <2 µm size fraction of sample TF6-98. A) STEM image (type HAADF) with the spots analysed by AEM (spectra in G). B)—F) Si, Al, Mg, Fe and K X-ray maps. The spectra and the chemical distribution of elements indicate the presence of montmorillonite (spectrum 1), nontronite (spectrum 2), illite (bright particle in F), plagioclase (spectrum 3), beidellite or albite partially altered to kaolinite (spectrum 4) and iron oxy-hydroxides (bright areas in E).

Mg substitution or mixed-layering with smectite mask the expected kaolinitic composition.

In the TEM study special attention was given to illite and smectite because they were the most frequently observed phases with this technique. In sample TF6-98, illite occurs as packets 20-100 nm thick (Fig. 9A) that sometimes are partially altered to smectite flakes (Fig. 9B). Smectite appears in curved packets of variable size from 3 to 50 nm thick, with imperfect layer terminations and variable fringe contrast (Fig. 9B–D). Smectite packets sometimes include particles of iron oxy-hydroxides with a marked dark contrast (Fig. 9C). In some few cases, smectite occurred as unoriented aggregates of very small packets including nanometresized salt particles containing S and Cl (dark-contrast particles in Fig. 9D and inset). Compositionally, smectites show a broad range from beidellite to Fe + Mg-rich montmorillonite, equivalent to the regions 2 and 3 in Fig. 7E, respectively. TEM-AEM analyses of individual particles showed that Fe is higher than Mg in the cases of high Fe + Mg content, so that some analysed particles could be

defined as nontronite. The TEM study of iberulites from sample GR8-12 provided results similar to those described above, with the only difference that it was possible to detect kaolinite. The low magnification TEM image in Fig. 10A corresponds to a clay rich area of an iberulite of sample GR8-12. There are kaolinite and illite particles up to 100 nm thick and 400 nm long. The lattice image of one of the kaolinite packets shows the typical 0.7 nm *d*-spacing corresponding to kaolinite layers (Fig. 10B). In some areas the lattice fringes of kaolinite disappear due to electron damage. The K X-ray map (Fig. 10E) indicates the location of illite crystals on the right of the region in Fig. 10A. The Si-rich grains of Fig. 10C correspond to very small quartz grains with less than 200 nm in diameter (see that these two grains have no Al, K or Fe). There are Fe oxyhydroxides within the clay as indicated by the bright areas in the Fe X-ray map (Fig. 10F).

The chemical AEM analyses of samples TF6-98 and GR8-12 were transformed into structural formulas and their values plotted in the Al-(Fe + Mg)-K field (Fig. 11). This plot compares well with that



Fig. 9. TEM lattice-fringe images of clay minerals and associated phases from aerosol sample TF6-98. A) Illite packet and its SAED pattern (inset) indicating an average *d*-spacing of 1.05 nm⁻¹ in the reciprocal lattice, *i.e.*, of 0.95 nm in the original lattice. B) Curved clay platelets of illite (left) and smectite (right), interpreted as an illite packet that has been opened and altered. C) Iron oxy-hydroxides (dark contrast) within smectite particles. D) Randomly oriented smectite nanoparticles with dark-contrast nanocrystals. The S and Cl detected by EDX (inset) indicate that the nanocrystals could be gypsum, halite or polyhalite, all of them detected by XRD.

from Fig. 7E. According to the structural formulas, most analysed particles are smectitic, because their layer charge does not reach 0.6 per half formula unit. Only two crystals displayed a layer charge >0.6, at 0.61 and 0.73 per half formula unit, both of them from sample GR8-12. No analysis reached a K content of 0.8 atoms per half formula unit, a typical value for illite. However, these chemical values could correspond to mixtures of illite and smectite. Kaolinite crystals, only detected in sample GR8-12, showed the presence of some Fe and Mg (data point marked with an arrow in Fig. 11).

4. Discussion

4.1. Mineral composition of iberulite aggregates

The mineralogy of the studied aerosol samples, both iberulites and common aerosols, matches well previous studies of Saharan dust (Table 2). Quartz, plagioclase, K-feldspar and carbonates are always present, and clays are represented by illite, kaolinite and smectite, with the frequent addition of chlorite. Other phases identified are salts such as gypsum and halite.

In this contribution, the focus is on the iberulites, and mineralogical results from concurrent aerosols are used to contextualize the composition of iberulite aggregates. It is widely recognized that the composition of the Saharan dust has a decreasing influence of the specific source area with increasing distance of transportation (Chamley, 1989), which means that there is a process of dust mixing from several sources as it travels. The atmospheric processing by gravitational settling causes the relative mineral proportions to change as the travelled distance increases, with the finer-sized minerals becoming more abundant. This is reflected in Table 2, which shows a clear increase in the relative proportion of clay minerals in Saharan dust with increasing distance of travel. Within clay minerals, Table 2 shows a great variation of composition depending on plume events and no apparent correlation to travelled distance. Such differences are probably linked to dust sources and preferential aggregation and deposition during transport.

The mineralogical description of dust aerosols and, in particular, iberulites, is not exhausted with the major phases that can be detected and quantified using XRD. In particular, Díaz-Hernández and Párraga (2008) describe hematite and amorphous Fe oxy-hydroxides in iberulites using TEM. We also found Fe oxy-hydroxide phases of very small size (20–50 nm) clearly discernible only using TEM (Figs. 8E, 9C and 10F) and possibly with EPMA (small grains in white in the two bottom aggregates in Fig. 6B). Although these phases are below detection limit for macroscopic techniques, they may be of importance in aerosols in general and in iberulites in particular. Most likely, they cause the pinkish colour of iberulites (Fig. 1) and the reddish colour frequently observed in Saharan dust. In such a case, Fe oxy-hydroxides would control light absorption and play an important role in the thermal behaviour of



Fig. 10. TEM images and chemical data of an iberulite from sample GR8-12. A) Low magnification image of illite and kaolinite crystals. The EDX spectrum corresponds to illite. B) Lattice fringe image and EDX spectrum of the two kaolinite packets within the box in A. The incomplete fringe contrast in the central area is due to electron damage to the crystal structure. C) to F) Si, Al, K and Fe X-ray maps of the area shown in A.



Fig. 11. Composition of smectite and illite particles and one kaolinite particle (arrow) from samples TF6-98 (common aerosols) and GR8-12 (iberulites; crosses super-imposed on the dots), plotted in the ternary diagram Al–K–(Fe + Mg), from TEM-EDX data. Two reference compositions are provided (open dots) on the basis of half formula unit (or $O_{10}[OH]_2$), corresponding to an end-member illite with no Fe or Mg, and to a typical montmorillonite.

these dust aerosols in the atmosphere (Sokolik and Toon, 1999; Balkanski et al., 2007).

No quantification of the mineral phases was carried out in our study because the sample containing only iberulites (from GR8-12) was so small that no XRD powder analysis could be performed. Its corresponding XRD study was on an oriented mount that enhances clay 00l peak intensities and precludes quantification. An approach to mineral phase quantification was carried out on the mineral maps developed on EPMA data (Fig. 7) by measuring the surface area corresponding to each type of mineral phase identified in the analyses. In order to test whether this result from four iberulite aggregates is representative there is the need to carry out similar analyses in many others, which are not available at the moment. In addition, the cross section of the grains within the aggregate observed in preparations for EPMA analysis is not identical to their volume. However, it can be assumed that the volume and cross section of mineral particles are approximately proportional because particles with large aspect ratios (e.g., dimension perpendicular to the image/cross section) will be uncommon. Finally, the density of all minerals involved is not the same although very similar as the values are within 2.5–2.84 g cm⁻³, so that ignoring density differences is a good approximation. Possibly, then, the main uncertainty in the mineral proportion assessment is the representativity of the small statistical sample studied, where three aggregates are from an event in 2014 and one from 2012 (bottom one in Fig. 7).

The differences in total clay content found between the four individual iberulites is small (standard deviation of 5.4%) and provide an argument in support of a representative statistical sample. It can be observed that the clay mineral content of the Saharan dust collected in Granada during the entire year 1992 is ~33%, very close to the values of dust collected in the Sahara (28–29%) and approximately half of that in dust collected in Granada, our assessment of ~52% clay in iberulites is significantly higher than the ~33% content in total dust. This large difference suggests that clays are concentrated in iberulites with respect to the total mineral aerosol sample. This implies that the formation of

Table 2

Place of collection	Event	Sme	Ilt	Kln	Plg	Chl	Qz	Fsp	Cal	Dol	Hl	Gp	Am ^a	Total	Clay	References
NE Spain	1987	10	39.5	7.5	8.5		15	6	7.5	6				100	65.5	Avila et al. (1997)
NE Spain	1988	12	40.5	9	8.5		15	5	5.5	5				100.5	70	Avila et al. (1997)
NE Spain	1991	17.5	26.5	4.5	7		17.5	3.5	19.5	6				102	55.5	Avila et al. (1997)
NE Spain	1992	33.5	27.5	13	6.5		13	4.5	1.7	1.2				100.9	80.5	Avila et al. (1997)
Cape Verde	1974	8	32	18	4.9	9	16.5	2	4.4			6		100.8	67	Glaccum and Prospero (1980)
SE Spain	1992 (all year)	10.2	10.8	8.1		3.7	27.6	0.8	12.5	13.7	4.5	4.5	4	100.4	32.8	Diaz-Hernandez et al. (2011)
Africa 20-27°N 5°E	4–23 May 1974	6	8	8	4	2	32	17	20			3		100	28	Paquet et al. (1984)
Africa 27-35°N 5°E	4–23 May 1974	7.25	7.83	4.93	4.35	5.8	20	10	40					100.2	29	Paquet et al. (1984)

Mineralogy (wt%) of Saharan dust collected in-situ and at different distances from the Sahara. Unless indicated otherwise, the samples were collected on specific plume events.

^a Am: non-crystalline substances.

iberulites in the atmosphere (Díaz-Hernández and Párraga, 2008) selects clay minerals preferentially within the dust plume. We suggest that this may be due to their higher hygroscopicity or small particle size, both of which facilitate capture by water droplets.

It is also clear that gypsum is depleted in the iberulites studied here as compared to the total aerosol content. XRD patterns of the latter (Fig. 2) show obvious gypsum peaks, whereas XRD traces of the iberulites do not display them (Fig. 3). Gypsum or other calcium sulfate phases are present in the iberulites as detected by SEM-EDX (Fig. 4) and EPMA S-element analysis (Fig. 6D), although the relative proportion of such phases is obviously very small and consistent with being below the detection limit of XRD. However, Díaz-Hernández and Párraga (2008) did detect gypsum in iberulites from other events using XRD. A most common origin of gypsum in mineral aerosols is interaction of atmospheric SO₂ with (mainly) calcite (Glaccum and Prospero, 1980; Gieré and Querol, 2010). However, gypsum derived from the source is a possibility (Table 2, data from aerosols collected in Africa by Paquet et al., 1984). In our case, gypsum may have its origin in the aerosol before iberulite formation, in the iberulite while it forms, and in the dust source. The variable gypsum content in iberulites from different events may be due to different atmospheric conditions (in the most broad sense) affecting the formation of sulfate minerals in the iberulite or in the transported aerosol before iberulite formation starts. The presence of gypsum and other sulfate phases and its relation to the abundant clays observed in the iberulites is further discussed below.

4.2. Role of clay in the formation of the iberulites

Figs. 4, 5 and 7 illustrate the structure of the iberulite aggregates. The SEM micrographs of their surfaces show that they are covered by a layer of clay minerals (Fig. 4) with overlapping flakes parallel to the surface. Even if large non-clay mineral grains are located next to the surface, the iberulites are typically covered by a thin clay layer (Figs. 5C and 7). Clay coatings surrounding some K-feldspars and other aluminosilicate grains (arrows in Fig. 7A) as well as sericite pseudomorphs after muscovite (arrow in Fig. 7C) formed during chemical weathering in the source soils, and they are not related to the particle arrangement of the iberulites. On the clay cover there are multiple sulfate particles (probably gypsum), typically <100 nm across (Fig. 4D). Inside the aggregates, there seems to be a rather random distribution of mineral particles, with clays providing a matrix of variable thickness surrounding other mineral grains in an irregular fashion. Such structure is evident in Figs. 7 and 5C. The empty space in the centre of Fig. 5A was produced during sample preparation. Gypsum is also distributed within the iberulites, seemingly in connection with the clay matrix (Fig. 6D). There are a few S-rich particles of relatively large size (Fig. 6D), notably that marked with an arrow, near to the iberulite surfaces. These particles appear to contain only S, which can be interpreted as that they consist of ammonium sulfate for two reasons. First, this salt has been reported in dust aerosols. Recent analysis of Asian dust with X-ray absorption near-edge structure has demonstrated the presence of ammonium sulfate as a major sulphur species (Ma et al. (2013) and references therein). Also, ammonium sulfate has been identified in Saudi Arabia aerosols (Posfai et al., 2013). The second reason is that our EPMA apparatus is not equipped to detect N. Thus, the textural features shown in this paper for the distribution of clays and sulfates in the iberulites, both homogeneously distributed within the iberulites, are different from those originally described by Díaz-Hernández and Párraga (2008), who located both the clay minerals and the sulfates mainly in the outer part of the aggregates.

Díaz-Hernández and Párraga (2008) found a preferential distribution of sulfates in the outer part of the iberulites using S-Ca maps from SEM-EDX, in contrast with our uniform distribution obtained with EPMA S maps (Fig. 6D). They studied iberulites collected between 1999 and 2005, whereas those studied here were collected in 2012 and 2014. Gypsum is present in noniberulite aerosols deposited during the events of both studies, as observed by XRD analysis. In contrast, Díaz-Hernández and Párraga (2008) found gypsum in the XRD patterns of iberulites, whereas gypsum was not detected in our XRD analysis of iberulites (Fig. 3). Also, they found greater quantities of sulfate grains in their iberulites (using SEM) than we did (using EPMA). We interpret that sulfate-containing aerosol particles are captured by water droplets (iberulites precursors) and that these sulfates become distributed uniformly across the iberulites as water evaporates, as described in the present contribution. The concentration of sulfates on iberulite surfaces from the 1999-2005 period (Díaz-Hernández and Párraga, 2008) probably have a different origin, and we hypothesize that they were the result of processes occurring late during iberulite formation and thus taking place only at their surface. It is possible that industrial emissions containing SO₂ were active in SE Spain during the collection time span (1999–2005). Reaction of SO₂ with the water contained in the iberulite precursors at an advanced stage of formation would explain the concentration of sulfates on the surface. These industrial operations in the area may have since ceased or been modernized to decrease contamination output, thus explaining the current lack of sulfates on or near the surface of the iberulites. This possibility could not be confirmed but it is in good agreement with the known trends of decreased anthropogenic SO₂ output worldwide (Sharma et al., 2004; Kelly et al., 2005; Marmer et al., 2007; Quinn et al., 2009; Hirdman et al., 2010; Hand et al., 2012; Tørseth et al., 2012; Waldner et al., 2014). If the above interpretation is valid, it is implied that the larger part of the sulfates in the iberulites studied by Díaz-Hernández and Párraga (2008) was produced by interaction with SO₂ gases at the last stages of iberulite formation, and that the capture and/or retention of sulfate phases by iberulite precursors at an early stage is not efficient.

The different distribution of clay minerals in iberulites as

observed in the present contribution and that of Díaz-Hernández and Párraga (2008) appears to be related to the analytical tool used for observation. Cross-section SEM images from Díaz-Hernández and Párraga (2008) and in the present paper might suggest clay aggregation towards the surface of iberulites (Fig. 5). Also, the thin clay layer on the outer surface (Fig. 4) may bias the interpretation in this direction. However, the EPMA chemical mapping of the cross sections reveals high clay contents throughout the entire aggregates (Fig. 7).

Iberulites cannot be structures generated at the source areas for several reasons. First, such big particles (>50 µm) are not likely to travel long distances (Jeong et al., 2014). Typical size distributions of aerosol particles (other than those generated by volcanic eruptions) reach a maximum diameter of 50 µm (Gieré and Querol, 2010). Second, their spherical shape and the vortexes that can be observed in some of them (Díaz-Hernández and Párraga, 2008) match those of water drops modelled by hydrodynamic forces during fall. Thus, it must be concluded with Díaz-Hernández and Párraga (2008) that iberulites are generated by the interaction of dust aerosol and water droplets, with aerosol particles acting as condensation points and then by capture of more aerosol particles as the drops fall. This process does not require them to be formed exactly above the site where they are deposited, and allows for certain horizontal travel constrained by their large size and thus short residence time in the atmosphere.

The enrichment of clay minerals in iberulites as compared to the composition of the total aerosol sample suggested in our study could be explained by the greater efficiency of water drops in capturing clav particles over coarser particles. This is very likely in the light of the research by Beard and Grover (1974) and Grover and Pruppacher (1985), as described by Díaz-Hernández and Párraga (2008). During the fall of the water drops, there is a redistribution of the particulate material within them. In the initial stages, the water drops undergo strong internal circulation (Le Clair et al., 1972) that relocates the particles. The volume of a typical raindrop (1–5 mm diameter) is much larger than the volume occupied by the aerosol particles within it (iberulites have diameters of up to ~100 μ m; Fig. 1). In the later stages, the volume of the raindrop decreases as water evaporates and the particles are increasingly confined, producing a particle distribution shaped by water flow and the electrical forces between mineral particles and between water molecules and particles. When the volume of the raindrop reaches that of the added volume of the mineral particles inside, the aggregate is shaped by the drop surface, explaining the spherical shape and the vortexes described by Díaz-Hernández and Párraga (2008). In this process, the mineral grains are distributed in a somewhat random fashion, with lumps of small clay particles mixing with larger mineral grains. However, a layer of clay platelets is deposited at the very surface. It is not clear why this is so but we can conjecture two possibilities. One is that some clay particles remain just below the water-air interface during the fall, parallel to the surface of the raindrop. As the water evaporates, these platelets are finally attached flat on the surface of the iberulite. Another possibility is that the clay particles at the surface of an iberulite about to dry out are reoriented by surface tension and/or electrical forces and located flat on the surface. Given their large surface-to-volume ratio, the particles cover the aggregate almost entirely. Any dissolved species will precipitate in the late stages of drying, more likely where water takes longer to evaporate. Clay minerals are hygroscopic due to residual surface charge and large surface area. Thus, it is plausible that residual water accumulates on clay surfaces and within clay lumps, driving dissolved ions to these regions. This would explain the apparent association of gypsum with clay in the iberulites (Figs. 4, 5D and 6D).

5. Conclusions

In circum-Mediterranean areas, aerosol mineral particles from Saharan plumes can coalesce by interaction with atmospheric water into large spherical aggregates (up to ~100 μ m), termed iberulites.

Common and iberulite-rich aerosols from the Sahara contain mainly quartz, carbonates, feldspars and clays (illite, smectite and kaolinite). The texture of the iberulites studied consists of coarse mineral particles embedded in a matrix of clay minerals, which also surrounds the entire spheroidal aggregate. The clays appear to be enriched in the iberulites as compared to common aerosols and play a significant role in their formation. They are responsible for some particular textural features of the iberulites, such as the external clay coating and clay distribution between coarser mineral particles, which is likely to provide mechanical strength to these aggregates.

Some details of the structure and composition of the iberulites studied here are different from those of previously observed samples, suggesting modifications driven by the dust sources and atmospheric conditions, possibly including anthropic activity. Specifically, the comparison of samples from iberulite sets recovered years apart in the Granada area (SE Spain) shows a recent decrease of sulfate content, which we interpret to be caused by decreased SO₂ anthropic emission.

Minor Fe oxy-hydroxides phases, distributed homogenously within the iberulites and responsible for their pinkish colour, must be taken into account in relation to radiation absorption processes and the thermal behaviour of these dust aerosols in the atmosphere.

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