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Formation, morphology and interpretation of darkened faecal spherulites

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ABSTRACT

Faecal spherulites are a common indicator of dung in archaeological deposits and most of the basic processes of their formation and taphonomy have been explained. However, a darkened form is also regularly found, ranging from slightly transparent through to completely opaque. These have been less well studied, so we set out here to understand what actually causes the darkening and to determine the range of conditions required to produce the changes.

Darkened spherulites were successfully created by heating dung to between 500 °C and 700 °C with the gaseous products constrained. The maximum production in our experiments was at 600 °C. The darkened spherulites often expanded during the alteration process and some of the expanded ones become distorted. SEM examination was only possible through destructive preparation processes, but examples were found showing expansion beyond the normal size range. These had a distinctive internal structure characterised by very fine crystallinity and larger scale fracturing, perhaps resulting from organic matter loss and/or $CaCO_3$ alteration. Prolonged oxidative heating failed to remove the darkening, leading to the possibility that it is partly a structural phenomenon, with opacification arising from compound relief.

Based on these findings, darkened spherulites can now be confidently interpreted as; resulting from dung being heated in conditions of limited gaseous exchange to between 500 and 700 °C, then not heated again beyond ca. 700 °C. These sorts of conditions could occur, around the edge of, or beneath, any fire where fresh dung is being burned or where the existing stratigraphy has a dung component.

1. Introduction

Faecal spherulites are very small (typically 5–20 μm), approximately spherical, radially crystallised bodies of calcium carbonate produced in the digestion of various mammals, but particularly the ruminant herbivores (Brochier, 1983; Brochier et al., 1992; Canti, 1997). They are now a widely-used indicator of herbivore presence in archaeology, mostly in caves and rock shelters of the Mediterranean region (e.g. Brochier, 2002; Karkanas, 2006; Angelucci et al., 2009; Polo-Díaz, 2010), but also open air sites where burial has been rapid or the surrounding sediments are suitably alkaline (Brochier, 1984; Matthews et al., 1996; Shahack-Gross et al., 2014). Spherulite production and preservation is, however, clearly a global phenomenon and they have been reported from other parts of Eurasia (Matthews and Postgate, 1994; Matthews et al., 1996; Castel et al., 2008; Badalyan et al., 2010), from Africa (Cremaschi and Trombino, 1999; Shahack-Gross et al., 2003) and from South America (Korstanje, 2002; Coil et al., 2003). They are increasingly being used within ethnoarchaeological studies (see review in Friesem, 2016) to provide numerical data, which can be combined with phytolith or archaeobotanical evidence in order to make deductions concerning husbandry, seasonality, dung usage and domestic activities (Cabanes et al., 2007; Portillo and Albert, 2011; Elliott et al., 2015; Gur-Arieh et al., 2013, 2014; Portillo et al., 2014; Portillo et al., 2017).

Most of the basic processes of spherulite formation and taphonomy are well-understood (Brochier et al., 1992; Canti, 1998, 1999; Shahack-Gross, 2011; Canti and Brochier, 2017). One aspect that is less clear, however, is their occurrence in a darkened or opaque form. Darkened spherulites were first described in layers of burnt manure from sub-recent deposits in a series of caves in Sicily

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(Brochier et al., 1992). In related experimental work, the darkening was replicated by burning sheep dung in an oxidising atmosphere at 500 °C (Brochier, 1996, 2002). According to the author, the darkening resulted from carbonisation of the internal organic component of the spherulites. There are various other references to darkened or opaque spherulites from archaeological contexts. Brochier (1993) reported them from the Neolithic tell of Çayönü (Turkey); they were observed by Iaconis and Boschian (2007) in one of the caves of Sant'Angelo (late Neolithic) and in Grotta dei Piccioni (early/middle Neolithic and Bronze age deposits) in central Italy. In both these cases the darkening of spherulites was interpreted as the result of dung burning. They were also mentioned in discussions of ash deposits at the tell of Al-Rawda (West-Central Syria) in Castel et al. (2008), and Polo Díaz et al. (2014) illustrated examples from early prehistoric burnt dung deposits of Cova Gran de Santa Linya (Spain).

1.1. *What do darkened spherulites look like?*

Ordinary spherulites are fundamentally transparent in plane polarised light (PPL), but the view frequently includes structural planes and organic matter which produce some internal relief and colouring. Under crossed polarised light (XPL), the tiny radial crystals are all in extinction when lying in the north, south, east and west directions, producing a dark cross which remains in position as the microscope stage is rotated. Elsewhere, the crystals not lying in these cardinal positions show interference colours arising from the strong birefringence of calcium carbonate. Thus, even a spherulite as small as 5 μm will show first order white between the limbs of the extinction cross.

Darkened spherulites in PPL (Figs. 1a and 2a) are somewhere in a range between brown and slightly transparent through to black and completely opaque. In most cases, the brown or black colouration takes up almost the whole sphere, with just a small clear fringe left at the perimeter. Occasionally, however, the dark sector occupies only the middle portion of the spherulite and tends then to be obscured by the extinction cross in XPL.

Darkened spherulites are frequently larger than ordinary spherulites, regularly being up to 25 μm in size and occasionally more. However, this is not always the case, and many darkened spherulites' diameters fall within the same size range as ordinary ones. These observations mean that some or all of them must expand during the darkening process. Although they are often nearly opaque in XPL (Figs. 1b and 2b), if the microscope light source is raised to high levels of brightness, the interference colours and extinction cross can still be seen, albeit obscured by the brown tone (Brochier, 2002). At the very edge, where the browning is not present, the perimeter fringe shows the normal interference pattern of spherulites. If a λ plate is inserted (Fig. 2c), this thin band displays the blue and yellow of the pseudo-uniaxial negative figure described in Canti (1998). Clearly then, although some (or all) of the darkened spherulites undergo expansion, the overall radial structure is not changed by the darkening process.

In addition, a small percentage of the darkened spherulites become distinctly non-circular and instead display distorted, often lobed shapes (Fig. 3). Many ordinary spherulites are already bilobate due to their crystal layout. In the crystallographic and biomineralogical literature, a successively infilling dumbbell shape (also known amongst crystallographers as "wheatsheaf" when elongated) is widely viewed as the true growth pattern of spherulitic crystallisation (Morse and Donnay, 1936; Keller and Waring, 1955; Keller, 1958; Keith and Padden, 1963; Hartshorne and Stuart, 1970; Hutter and Bechhoefer, 2000; Chen et al., 2006; Beck and Andreassen, 2010; see also Fig. 2 in Canti, 1998). Whilst this dumbbell is growing, a spherulite at the right orientation will often show the characteristic shape (e.g. Fig. 12f). Once the full

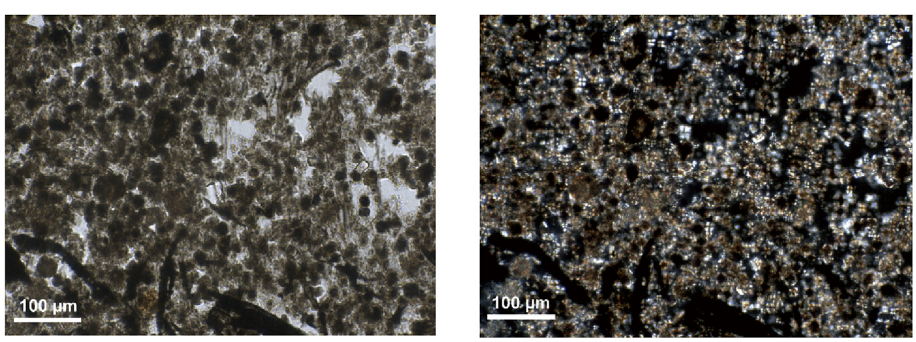

Fig. 1. (a) PPL view of part of a pellet of sheep dung heated at 600 °C for 1 h, giving a general view with about 30% darkened spherulites. (b) The same view in XPL.

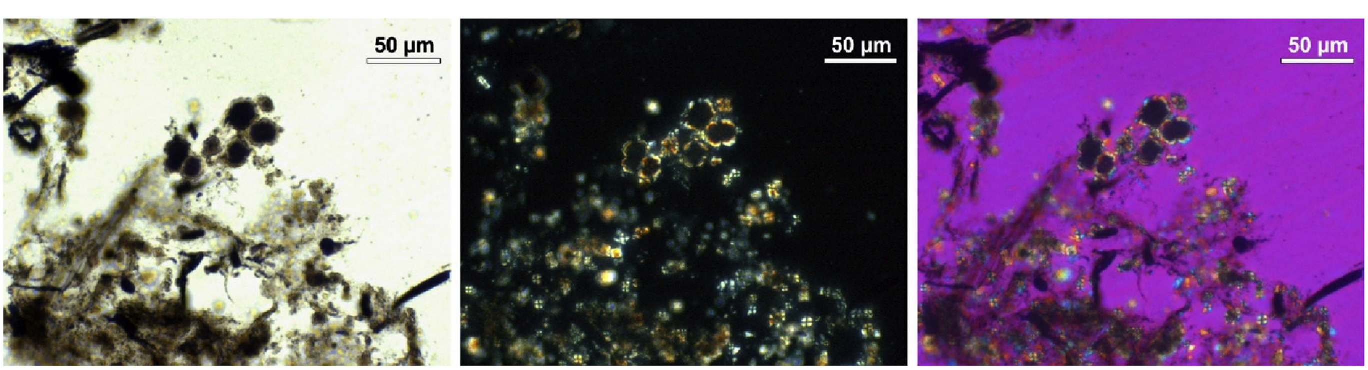

Fig. 2. Close-up of a cluster of a) PPL and b) XPL darkened spherulites. c) same as b) with λ plate inserted to show the remnant of the pseudo-uniaxial negative colours on the perimeter (see Canti, 1998). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

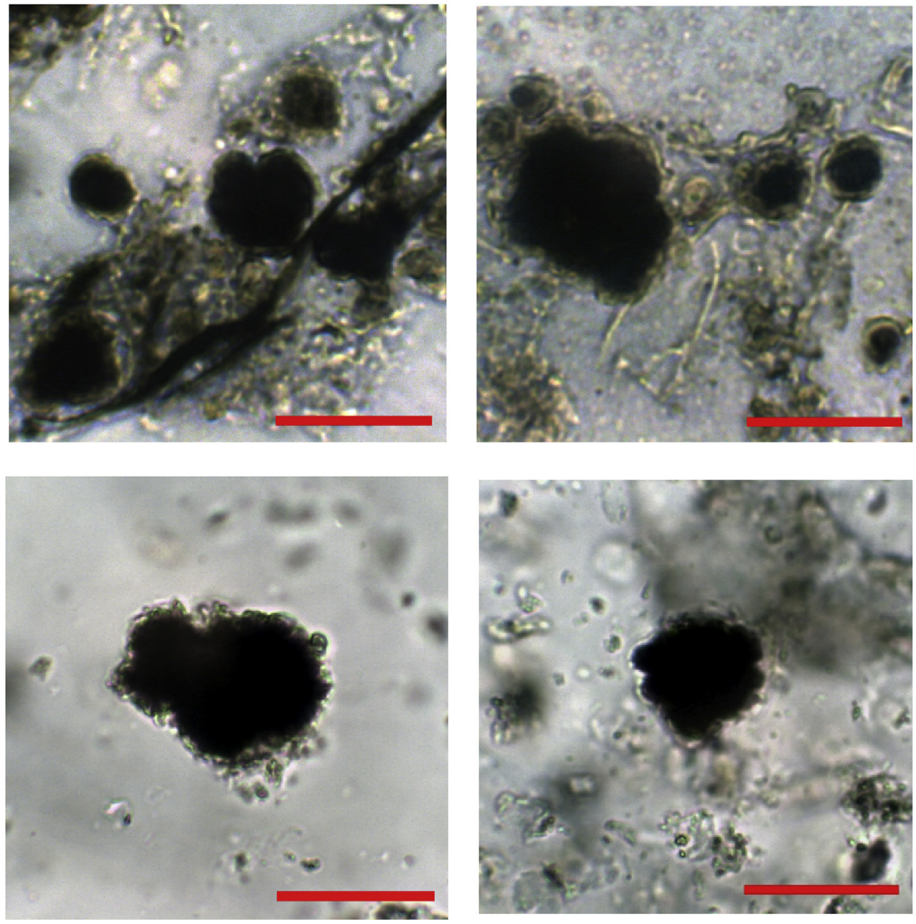

Fig. 3. Examples of the distorted shapes regularly found amongst darkened spherulites. Scale bars = 50 μm.

sphere has been produced, however, the developmental origin may no longer be visible.

This morphological characteristic of normal spherulites makes it difficult to quantify the distortion rate, because some dumbbell-shaped spherulites already show a lobed morphology depending on the angle they are resting at in the microscope slide. However, an estimate is that around 2–5% of darkened spherulites show the distortions, and they appear to be the ones that have enlarged the most.

1.2. Research rationale

The key issue for microscopists recording darkened spherulites in liquid mounts or thin sections is to know what they mean for site interpretation. We therefore set out to understand what actually causes the spherulites' darkening including their expansion and distortion, and to determine the range of conditions required to produce the changes. Based on this information, it should be possible to determine how subsequent natural or anthropogenic processes are likely to affect the preservation of darkened spherulites.

2. Producing darkened spherulites – methods and results

Samples of fresh dung were collected from both sheep and goat at the Archeopercorso Bostel di Rotzo, Vicenza, Italy. They were dried and examined for spherulite content, then high yielding ones were used either individually or amalgamated in all the experiments described below. The experimentation was iterative and went through three distinct stages, of which the first two need only summarising.

2.1. Whole faecal pellets

Initially, whole spherulite-rich faecal pellets from both goat and sheep were burnt in small pots (Carbolite furnace RWF 12/13), then thin sectioned according to standard methods for soil micromorphology (Murphy, 1986). A range of temperatures and burn durations was tested to see if there was a simple relationship. As expected, lower temperatures (ca. 200–400 °C) mostly had no effect and higher temperatures (700 °C and above) routinely destroyed the spherulites, producing isotropic morphologies (CaO is isotropic) in the pellet remains, which required a period of recarbonation in air to develop birefringence again. In these cases, the original spherulites were no longer visible, being replaced by a wide variety of $CaCO_3$ neoformations. In the key temperature range of 400 °C–700 °C, high variability was found. Sometimes darkened spherulites were abundantly produced (see Fig. 1), but other times either incomplete combustion or complete destruction occurred in similar repeat experiments, or even at different places within one pellet in the same experiment. Attempts were made to overcome the variability by averaging large areas through image analysis, but the results were inconsistent.

The conclusion of these experiments was that a single faecal pellet will always reach a variety of temperatures unrelated to the measured temperature of the furnace, because of small variations

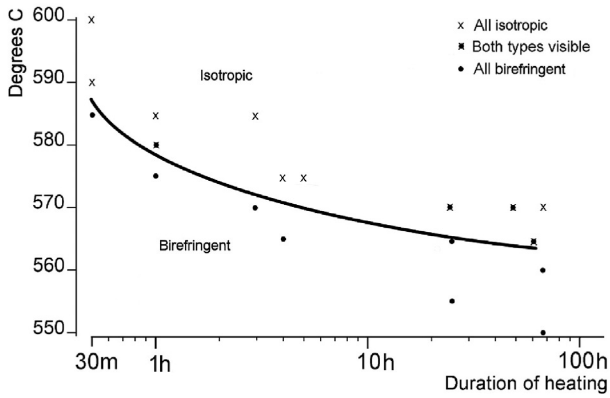

Fig. 4. Fence diagram for the development of isotropy amongst spherulites in <125 μm dung powder thinly scattered onto a microscope slide and heated for different times and temperatures. The isotropy results from conversion to CaO.

in the organic matter content and porosity, as well as local air currents inside the furnace, all of which lead to unpredictable or patchy ignition.

2.2. Ground faecal pellets spread out

In order to overcome the variable combustion problem, dry-ground <125 μm spherulite-rich faecal material was scattered thinly onto a microscope slide and heated slowly so that oxidation was uniform and ignition minimised, thus avoiding patchy overheating. The slide was then examined by using a drop of refractive liquid (rather than cutting a thin section) either immediately, or after a period of recarbonation in a moist atmosphere. This method appeared to produce consistent, uniform heating, but failed to produce darkened spherulites in anything other than very small numbers. Additionally, it regularly caused conversion of the spherulites to CaO within a repeatable range of temperatures and times (Figs. 4 and 5).

The conclusion of these experiments was that the darkening of the spherulites might be something occurring in a phase of reduction (similar to the charring of plant matter) and that this highly oxidising method was simply burning off the organic framework of the spherulites too quickly. In order to routinely produce darkened spherulites, the experiments had, therefore, to both avoid overheating (due to ignition) and maintain reducing conditions.

2.3. Enclosed in small tubes

The simplest way to achieve a partially reduced atmosphere is to put the burning material in a container so that the CO_2 produced by combustion (which is heavier than air) sits on top of the charring material instead of being removed by air currents within the furnace. The container size and the level to which it is filled could clearly affect the degree of reduction, so a number of types were tested, all based on various small glass tubes available in the laboratory. They were 4, 10 and 15 mm diameter and all about 10 mm high. Dried, ground, <125 μm spherulite-rich faecal material was added in various quantities ranging from a tiny ~3 mm diameter cone of powder sitting on the base of a pot through to half-filling the pots. These different pot size/fill types were tested as replicates of the temperature/time experiments described below. They produced relatively small variation, and tubes of 4 mm (diameter) x 25 mm long were chosen and then used for all the subsequent temperature experiments described in this paper. To improve repeatability, a similar quantity of dung powder (ca. 10 mm^3) was always used, and a metal rod almost exactly the same diameter as the pot was inserted after the dung powder (Fig. 6). This helped prevent any stray draughts entering from above.

The tubes were warmed up for 20 min to get to temperature, fired for the specified period, then cooled naturally (typically 45–80 min) to get them back below 300 °C (thus preventing any further oxidation). On removal from the furnace, they were given 5 min resting to get down to handling temperature. All through the time of heating and cooling, the tubes were kept upright to promote retention of CO_2 in the pot.

3. Examining darkened spherulites – methods and results

3.1. Distinguishing darkened spherulites by light microscopy

The ashed dung powder from the burns carried out in small tubes was dispersed in Cargille Meltmount and coverslipped to make permanent slides. Spherulites were examined in PPL and XPL on an Olympus BH2 microscope with or without λ plate. For each

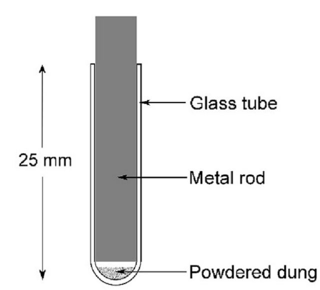

Fig. 6. Diagram of glass tube with rod inserted for burning the dung powder to help retain CO_2 layer over the dung.

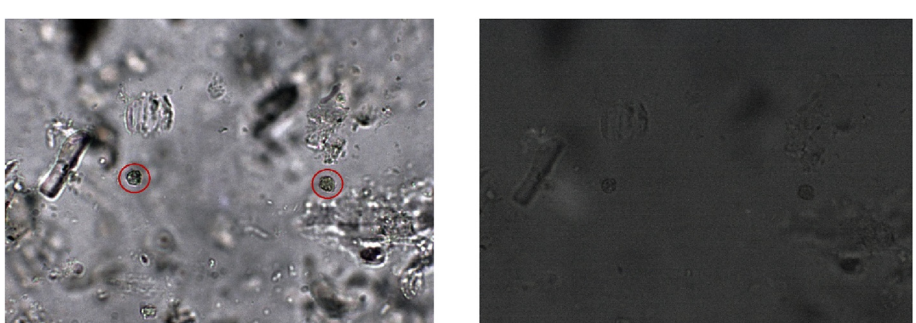

Fig. 5. Isotropic spherulites from dung powder spread thinly and heated at 600 °C for 1 h (a) PPL and (b) partial-XPL (analyser rotated a few degrees off 90° to show outlines better).

time/temperature combination, 1000 spherulites were counted on the slide at 200× magnification (with occasional examination at 400×) and designated to either darkened or normal. As described above, darkening usually takes up almost the whole sphere, with just a small clear fringe left at the perimeter. These examples clearly fall into the 'darkened' category. Occasionally, however, the dark sector occupies only the middle portion of the spherulite, or the dark areas are complex and incomplete. In these situations, we counted as darkened only those spherulites whose total dark area was large enough to cover half or more of the spherulite's overall

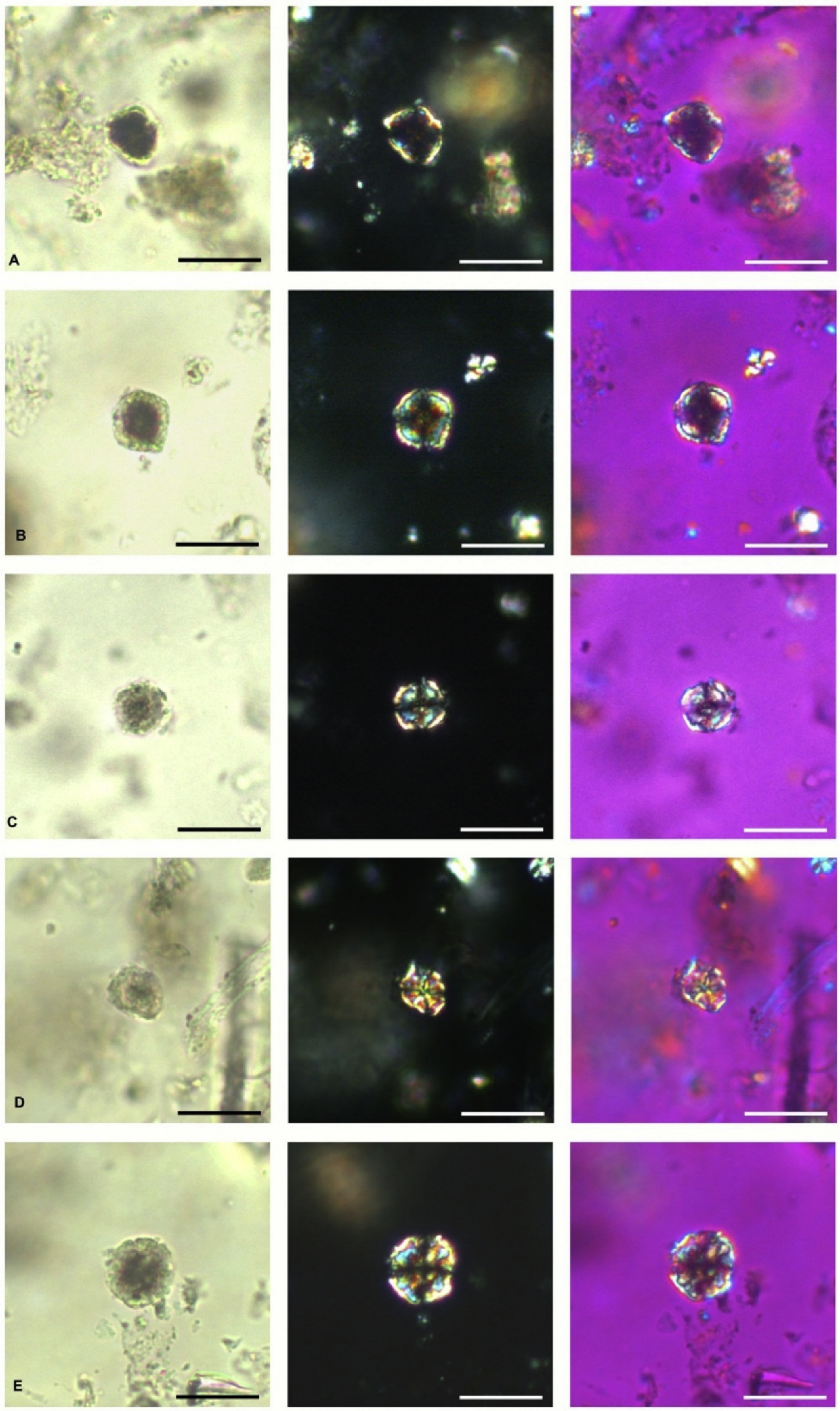

Fig. 7. Examples chosen to show the decision boundary for partially darkened spherulites. (a) darkened (b) borderline darkened. (c) borderline not darkened. (d & e) not darkened, with (e) showing an incomplete central dark area. See text for description of the identification criteria (scalebars are all 20 μm).

Table 1
Quantities of darkened spherulites produced in different burns in the small tubes.

Temperature regime	% darkened
400 °C for 0.5 h	0.7
400 °C for 1 h	0.4
400 °C for 2 h	0.0
400 °C for 3 h	0.2
500 °C for 0.5 h	0.2
500 °C for 1 h	0.7
500 °C for 2 h	2.4
500 °C for 3 h	3.9
500 °C for 4 h	4.1
500 °C for 5 h	5.4
500 °C for 6 h	3.8
500 °C for 7 h	4.8
500 °C for 8 h	7.0
600 °C for 0.5 h	6.4
600 °C for 1 h	10.2
600 °C for 2 h	12.9
600 °C for 3 h	14.7
600 °C for 4 h	18.9
600 °C for 5 h	15.4
600 °C for 6 h	26.2
600 °C for 7 h	24.7
600 °C for 8 h	25.6
700 °C for 0.5 h	16.7
700 °C for 1 h	18.4
700 °C for 2 h	16.9
700 °C for 3 h	All isotropic – none darkened

diameter. This notional dividing line coincides roughly with the ability to see some darkening under XPL as well as PPL. If a central dark area is smaller than half the overall diameter it tends to be obscured by the extinction cross; if larger, the impression produced is that the central junction of the extinction cross has an area of swelling extending into each of the quadrants. Examples of spherulites meeting or not meeting the criteria for being darkened are shown in Fig. 7.

3.2. Percentage darkened at different temperatures and times

Table 1 shows the results of timed burns in the small blocked tubes (see the experimental diagram in Fig. 6). This has produced a very clear pattern of increasing darkened spherulite production with greater time and temperature up to a maximum at 600 °C for 6 h (Fig. 8). Additional time or higher temperatures thereafter, do not produce greater numbers of darkened spherulites.

3.3. Size distribution

Size distributions of 565 unheated spherulites were measured, as well as 1489 spherulites from the sample heated at 600 °C for 6 h. ImageJ software (https://imagej.net/) was used to measure the diameter of each spherulite visible in a series of photomicrographs taken at 200× magnification.

Although this is only a single data set, general conclusions can be drawn without claiming statistical rigour. The size distribution curves in Fig. 9 clearly show that, on average, under a heating regime of 600 °C for 6 h with gases constrained, spherulites expand and the distribution of their sizes becomes broader. Unheated spherulites were mostly (83%) clustered in the 3–8 μm range, with an average diameter of 5.2 μm (st. dev. 1.7), whereas heated but undarkened spherulites lay instead mostly (78%) in the range between 6 μm and 12 μm with an average diameter of 9.3 μm (st. dev. 2.8). As they expand, some spherulites undergo additional changes rendering them darker and these changes are associated with even

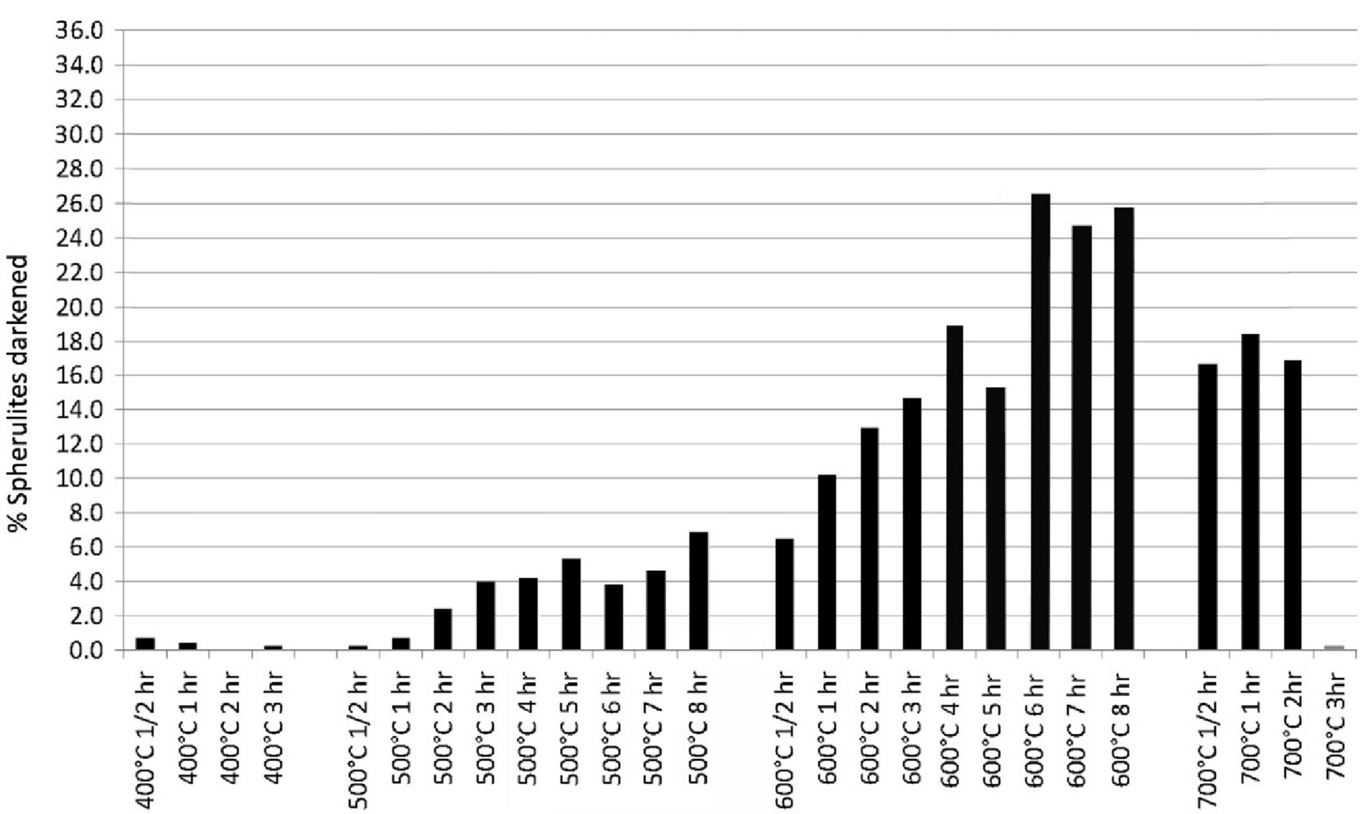

Fig. 8. Diagram of % spherulites darkened in different burns in the small tubes (data as Table 1).

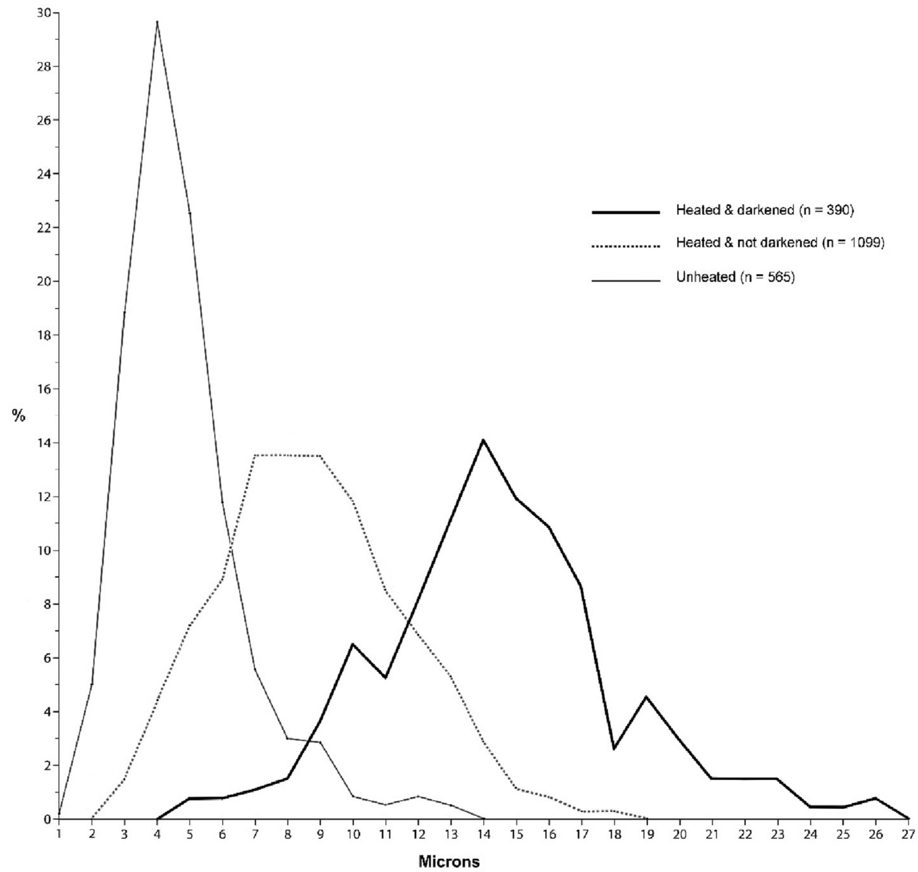

Fig. 9. Size distributions of darkened and normal spherulites, from measurements of 1489 spherulites heated at 600 °C for 6 h and 565 unheated spherulites from the same dung powder.

greater expansion. Darkened spherulites were mostly (75%) clustered in the range between 12 μm and 19 μm, with an average diameter of 14.8 μm (st. dev. 3.5). Moreover, darkened spherulites reached sizes (21–27 μm) that the heated but undarkened ones never attained in these samples.

Since we cannot follow individuals through the heating process, we only have this size distribution data to assess the nature of the expansion. The curves in Fig. 9 would seem to result from all the spherulites having expanded on heating, making the tiniest ones move into the heated but undarkened size range and those that were largest before heating move into the larger size ranges. Whether or not this is the right interpretation of the curves, it is clear that many heated spherulites showed large size increases when they were darkened. Microscopic observation confirms this; they were regularly found to be double the size of heated undarkened spherulites and sometimes more.

3.4. Mineralogy

X ray diffraction was carried out on the raw dung powder and on the sample heated at 600 °C for 7 h. The results (Fig. 10) show clearly that the dung is rich in calcite and quartz both before and after burning. No other calcium carbonate polymorphs were found.

3.5. SEM morphology

In order to understand the expansion phenomenon associated with darkening, it is necessary to see ordinary and darkened spherulites under the SEM, either as whole objects or cut through to make cross-sections. This is difficult to achieve, due to a coating of organic material (or oxidised derivatives from it) which is invariably present on the outside.

Various preparation methods were tested with the aim of uncovering the spherulites' mineral component including heat treatment and hydrogen peroxide, but the surface coating remained stubbornly present obscuring the morphology (Fig. 11).

An alternative approach was tried in which <125 μm spherulite-rich dung was given prolonged heating to various temperatures between 400 and 650 °C in order to reduce the organic matter as much as possible; then the whole mass repeatedly chopped (on the slide) with a fresh scalpel blade. The slide was attached to an SEM stub, surrounded with silver dag in order to earth it, and the top side gold-coated. This successfully produced a few cross sections (Fig. 12 a – e), but they were very scarce on the slide, relying as they did on occasional chance interactions of the blade and a spherulite at the right angle to produce a possible shear (Fig. 12e), or to rip apart the two halves of the dumbbell (Fig. 12b, c and d).

Another method involved scattering the same type of burnt dung powder onto a sticky tape, pressing a second piece of tape onto it (sandwiching the powder in between), and then ripping them apart (black SEM discs were tried and also proprietary decorators' edging tape which has a weaker glue). No systematic variation with temperature or tape-type was found, but this approach generally produced significantly larger numbers of spherulites with the structure displayed (Fig. 13 a - f).

Uncovering and morphological exposure of spherulite structure was only achievable by these destructive preparation approaches followed by examination of the debris.

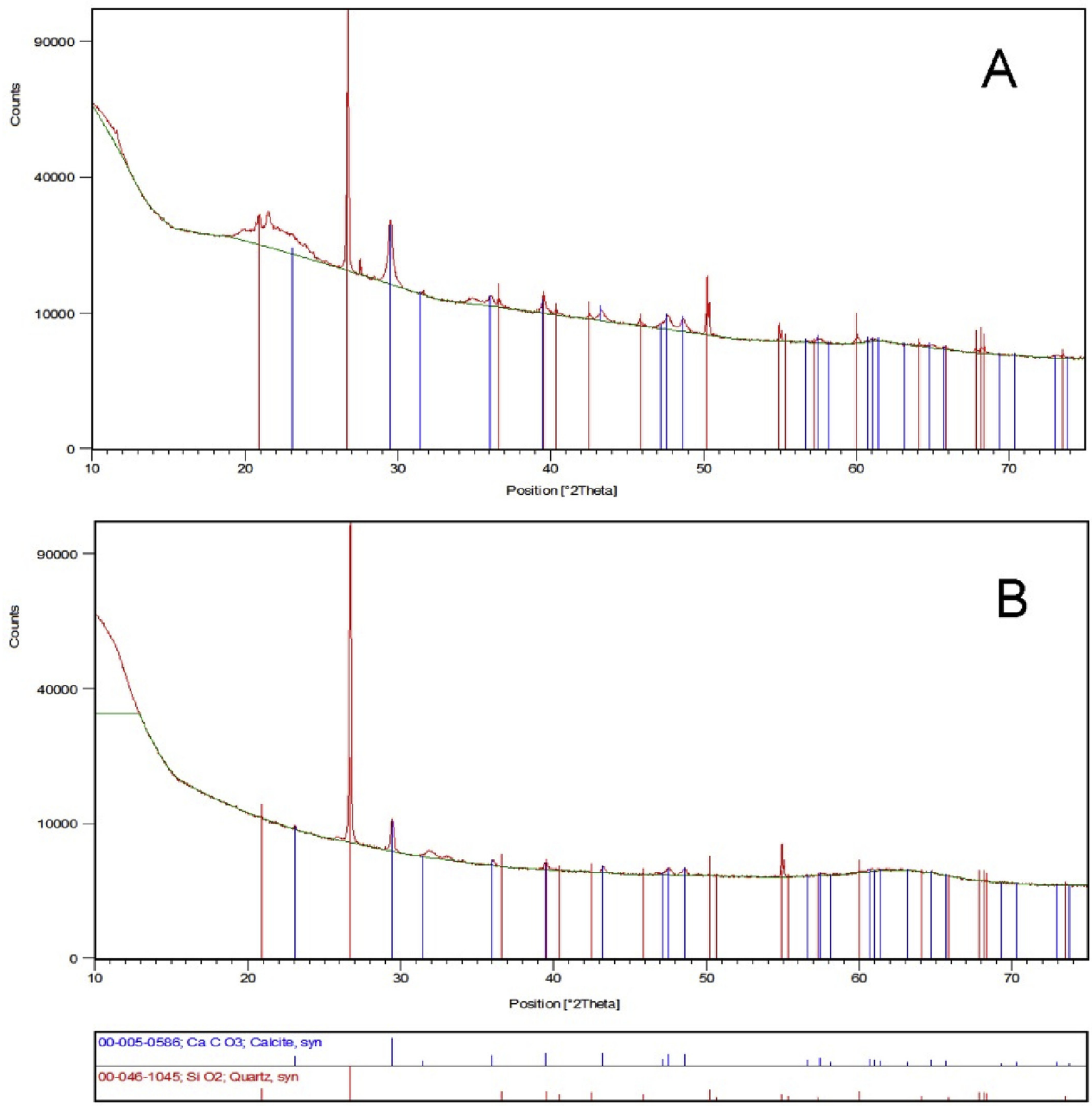

Fig. 10. X ray diffraction results from the dung powder (A) unheated and (B) heated to 700 °C for 6 h. Calcite and quartz are the main constituents in both cases, with additional peaks probably from incidental materials ingested by the animals - aluminium phosphate (21.5 in A) and carbonate hydroxylapatite (31.9 in B). A likely candidate for the small peak at 27.6 in A has not been found.

The techniques failed when tried on unheated spherulites, presumably as a result of protection by the coating, so we still have no SEM image of the unheated internal structure.

In order to identify a darkened spherulite, we had to rely on the size and morphology of the product, rather than being able to take a proven dark spherulite through from polarised light to the electron beam. Eventually, using one of our highest-yielding experimental residues (600 °C for 8 h) pulled apart with tapes, a few examples were found with the enlarged and expanded structures which we believe to be darkened spherulites (Fig. 14).

4. Discussion

There is a distinct expansion morphology displayed in examples (a) to (e) on Fig. 14. The densely packed radial structure visible in the normal-size spherulites on Figs. 12 and 13 is replaced by a layout in which seemingly individual radial crystals (or aligned groups of crystals) can be seen as independent bodies with tiny

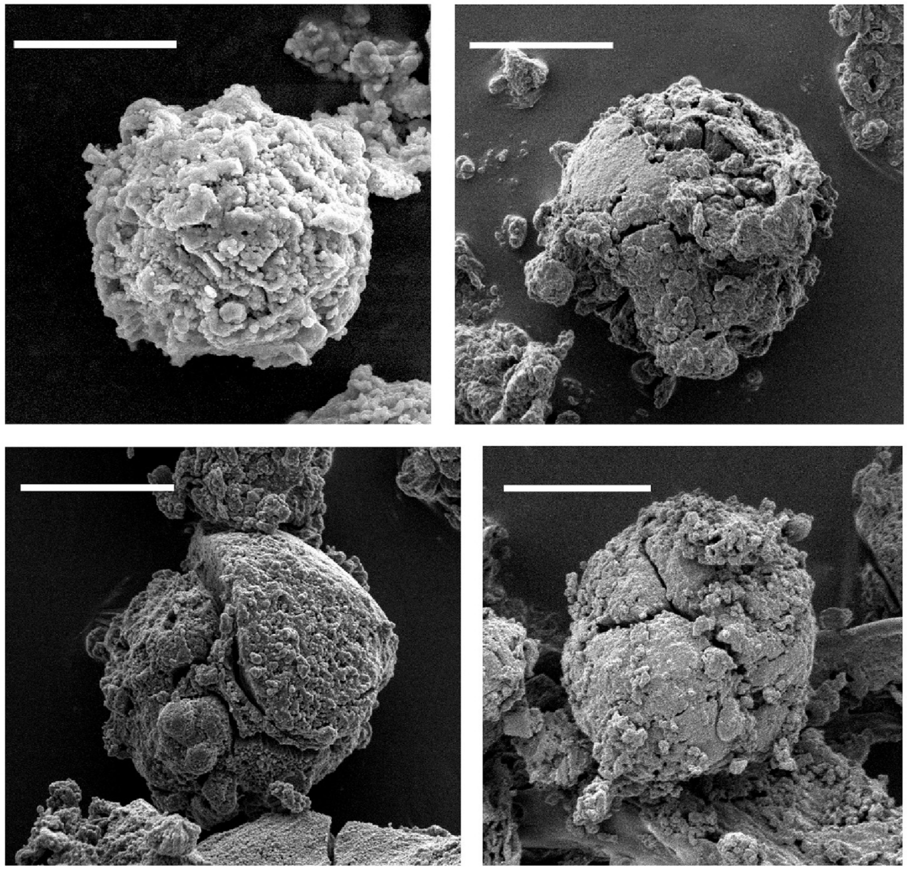

Fig. 11. Typical spherulites as they appear under SEM if no mechanical or chemical preparation is carried out to disrupt the coating. All heated at 650 for 1 h. Scale bars are 5 μm.

spaces between them. At the same time, the overall sphere has been fractured by the expansion process (see especially 14(a), but also to a lesser extent (b), (c) and (d)) and whole segments of it are dislocated from their original position while still retaining approximately the original radial layout. This dislocation may explain the lobes and other distortions visible in a small percentage of darkened spherulites (see Fig. 3 and associated discussion).

4.1. What is causing the expansion?

Calcite heated to the types of temperatures quoted in this paper has a moderate coefficient of thermal expansion along the c axis of around $25 \times 10^{-6}/^{\circ}C$ (Chessin et al., 1965; Rao et al., 1968). This would lead to about 1.0–1.5% length increase for each crystal, which would certainly have an impact on the dense spherulitic structure and would likely be irreversible on cooling if crystals were forced to move relative to each other. However, it could only account for a small proportion of the effect seen in our experiments.

The expansion from 'unheated' to 'heated & not darkened' on Fig. 9 appears to leave the spherulites unchanged in all respects except size. It could thus be interpreted as the first stage in a gradual progression towards the even greater expansion inherent in the darkening phase. However, assuming no destruction occurs after darkening, this progression would imply the production of more and more darkened spherulites as heating continues, and we did not find this to be the case. More likely, therefore, is that some spherulites expand but never darken, whilst others proceed on to darkening; both groups stopping at their respective end points, regardless of further heating. It may be that the smaller spherulites are the ones that expand a little but stay undarkened and the larger ones expand more dramatically, undergoing both distortion and darkening. However, this cannot be deduced from the curves alone and proving it would require additional experimentation.

The greater expansion, associated with darkening (see very large spherulites on Fig. 14) entails the apparent development of individual crystal units. This could result from the burning out of an organic matrix. In addition, heating could result in pitting and fracturing due to water-loss in a similar way to the changes found in biogenic carbonates by Gaffey et al. (1991). Such processes might also lead to some displacement if the combustion gases were trapped, causing the intercrystalline spaces to expand.

Crystal re-arrangement could also be occurring as a result of early stages in the calcination process. We can see from Fig. 4 that spherulites burnt at 600 °C would be turning into CaO if the gases were freely exchanging with the atmosphere. They must, therefore, be close to this point in the tube-burnt examples and would be starting to undergo the complex changes that govern its dynamics. The dissociation temperature of $CaCO_3$ is strongly related to the concentration of CO_2 (Boynton, 1980, Fig 6.2) and a number of authors have recorded the expansion and decrepitation of either calcite crystals or limestone under various conditions in laboratory studies or real-life lime manufacture (Boynton, 1980, 163–164; see also Stanmore and Gilot, 2005).

The larger scale fracturing of the overall sphere can be seen as resulting from major stresses set up by the processes discussed above and leading to a variety of crack morphologies. However, the destructive sample preparation methodology unfortunately limits the deductions possible from these photographs.

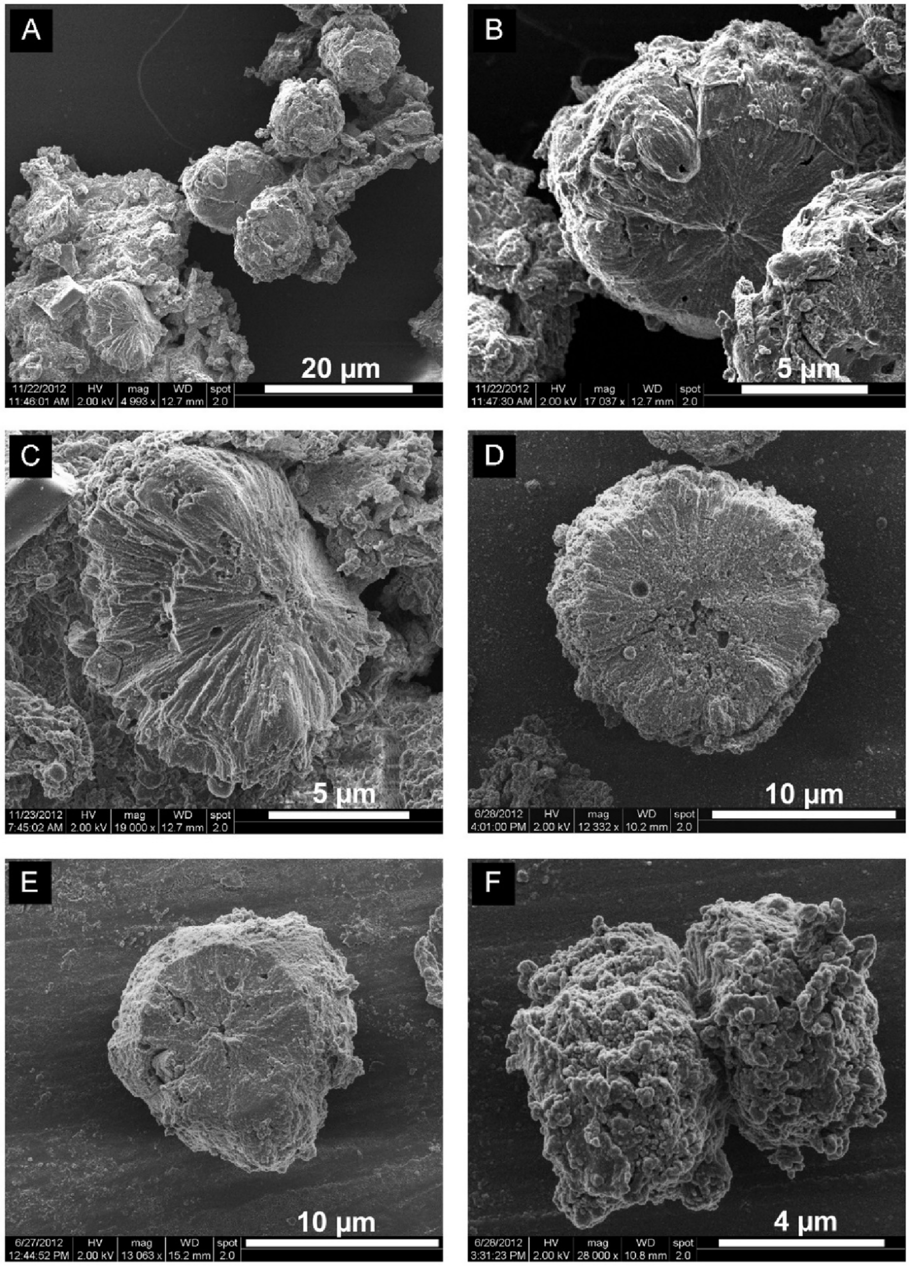

Fig. 12. Examples of spherulite structure revealed by the scalpel chopping method (see text). a) Group of whole and fragmented spherulites. b) and c) Enlargements of structures from a). d) and e) Broken or cut spherulites showing radial structure. f) Whole dumbbell. a) to d) were heated at 550 °C for 3 days; e) and f) were 400 °C for 3 days.

4.2. What is causing the darkening?

Following J.E. Brochier's (1996) suggestion, and the success of our tube burning methodology, we assumed that the darkening of the spherulites was due to charring of organic matter in the matrix of the spherulite. It follows that, if enlarged darkened spherulites were re-heated for long enough in fully oxidising conditions, it should be possible to burn away all the darkened organic matter and leave an enlarged clear spherulite. This would need to be carried out at a temperature high enough to induce complete oxidation of the organic matter, but low enough not to cause the transformation to CaO and breakdown of the spherulite structure. A range of temperatures and heating times are recommended in the literature for the measurement of organic matter by loss-on-ignition (e.g. 375 °C for 16 h (Ball, 1964); 430 °C for 24 h (Davies, 1974); 500 for 16 h (Rowell, 1994)). Since loss-on-ignition consists essentially of the removal of organic matter, it was relatively simple to use the fence diagram in Fig. 4 to choose a suitable temperature. Erring on the side of caution, we chose to oxidise at 500 °C. Our aim was to completely destroy the organic matter, and at 500 °C there was no risk of transformation to CaO, even with very long burns.

A small quantity of the material previously tube-heated at 600 °C for 7 h (24.7% darkened; see Table 1) was spread thinly on a slide and heated to 500 °C for various durations. After cooling, the powder was gently wetted with a refractive liquid to see if enlarged but clear spherulites were present. None could be found, and even with further exhaustive heating carried out up to 15 days duration there were still large numbers of darkened spherulites present (Fig. 15).

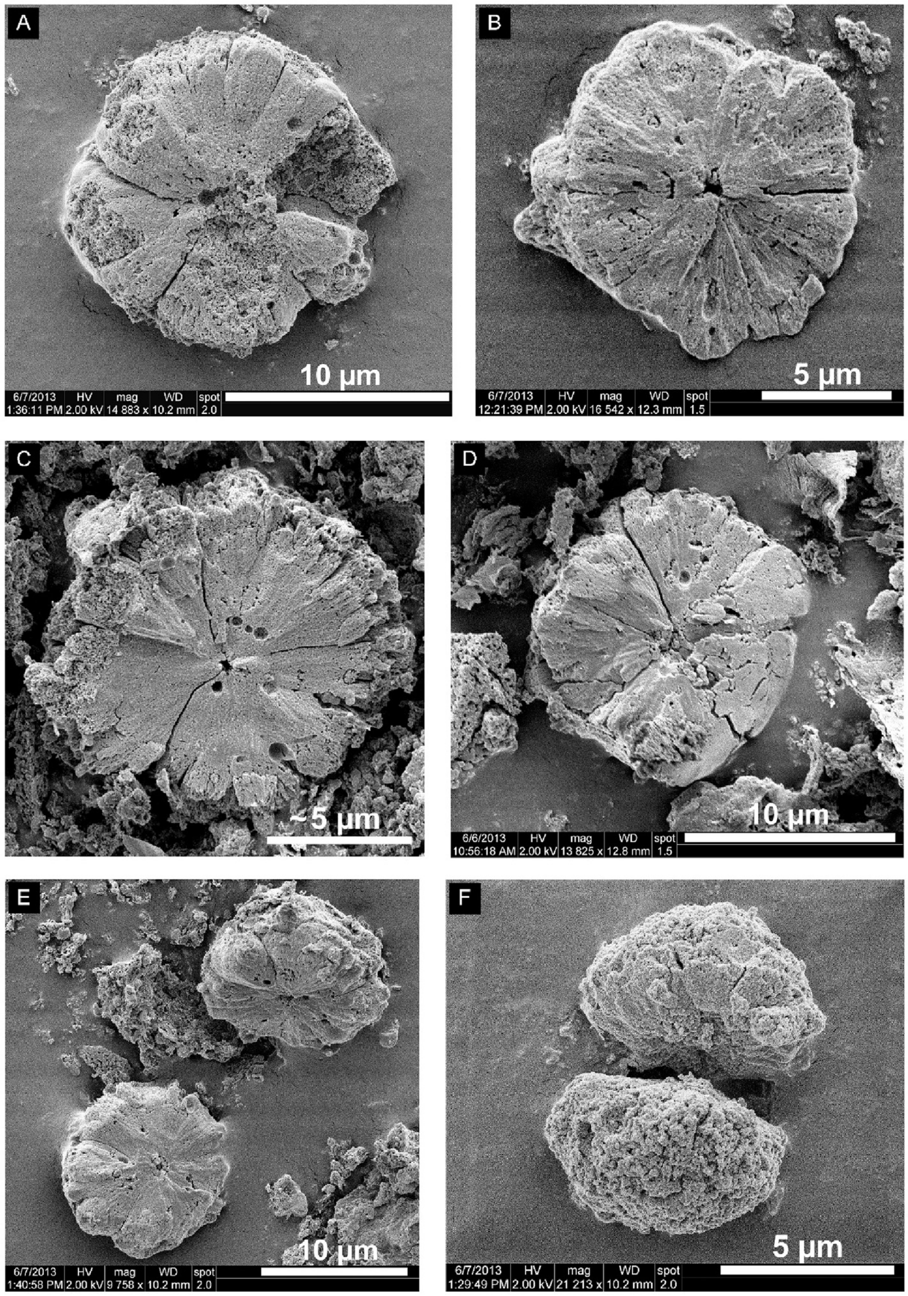

Fig. 13. SEM views of spherulites from dung powder heated at 650 °C for 3 h, and pulled apart by tapes. It seems likely that a) to d) are upturned halves of pulled dumbbells as shown more clearly in e) and f).

Although this result shows *some* reduction in the numbers of darkened spherulites after long periods of heating, it prompted us to question whether organic matter might not be the only cause of darkening. It is hard to believe that such organic material could be so deeply embedded between calcite crystals that it failed to oxidise even after 15 days of heating.

An alternative might be that spherulite darkening partly results from compound relief (Canti, 2003) produced by the microscale crystal separation which can clearly be seen on the enlarged examples in Fig. 14. The expansion process has led to the creation of numerous tiny crystal edges, each of which would have a bold outline (relief) in transmitted light. Stacked up to a thickness of 10–20 µm, the overall effect would be to strongly opacify the spherulite, whilst retaining the fundamental crystal layout which can still be seen under XPL if the light source intensity is maximised. Fig. 16 attempts to simulate this effect by taking the front face of the spherulite fragment in Fig. 14c and drawing outlines round the crystal edges to represent the pattern of relief. Successive smaller and smaller versions of this pattern are then overlaid to represent similar faces as they would occur back through the thickness of the spherulite. Opacity develops in just a few iterations, depending on the thickness and darkness of the relief, and the degree of offset inherent in each overlay positioning.

5. Summary and conclusion

Our experimentation has produced a number of clear results.

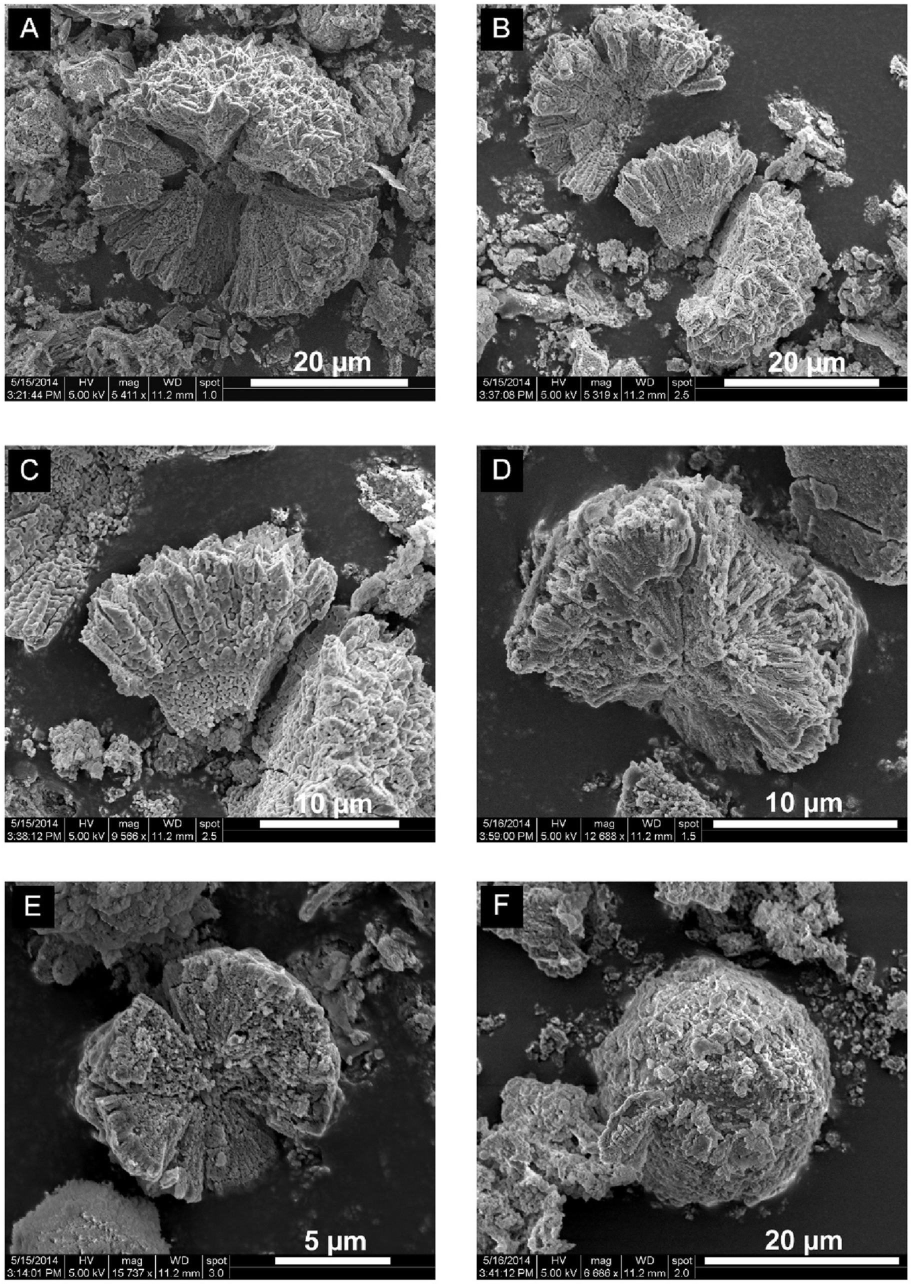

Fig. 14. SEM views of spherulites from dung powder heated at 600 °C for 8 h, and pulled apart by tapes. a) to d) Based on morphology and size, these are believed to be expanded darkened spherulites. e) Shows expanded structure on a medium sized spherulite. f) Probable covered expanded spherulite.

1) Darkened spherulites are produced by heating of fresh dung. If whole pellets or other dung aggregates are burnt, patchy concentrations or complete destruction can occur in the same experiment due to unpredictable burn characteristics.
2) Darkening occurs where the combustion gases are constrained and temperatures are within a range between 500 and 700 °C, with a maximum production at around 600 °C. Darkened spherulites may well commonly exist for a short time, but they will only be preserved if the fire is extinguished before they get too hot.
3) Only very small numbers of spherulites are darkened if the combustion gases are free to exchange with the air.
4) Repeatable production in the laboratory can be achieved by heating in a blocked tube, i.e. constraining the gaseous products. This suggests that reduction may be part of what is causing the darkening and that the same effect is simply localised in some parts of the whole pellet burns (see point 1). The maximum number darkened in the blocked tube was around 26% from burning at 600 °C for 6 h. Longer heating periods did not increase the darkened spherulite percentage.
5) Most spherulites undergo expansion on heating at 600 °C. Some expand a smaller amount without changing their optical characteristics, whilst others expand more, also darkening and frequently becoming distorted, with the development of distinct lobes.
6) Individual darkened spherulites cannot be identified in transmitted light then examined under SEM due to the continued presence external coatings. However, after destructive

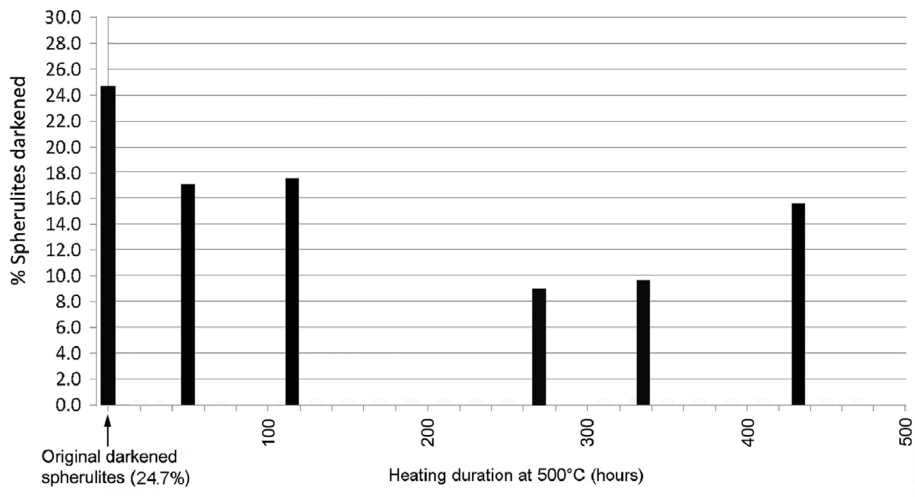

Fig. 15. Darkened spherulite percentages recorded after spreading out and re-heating at 500 °C for extended time periods (48, 115, 266, 337 and 434 h). A blind test carried out on the counting methodology showed it to be accurate to ± 1.5%.

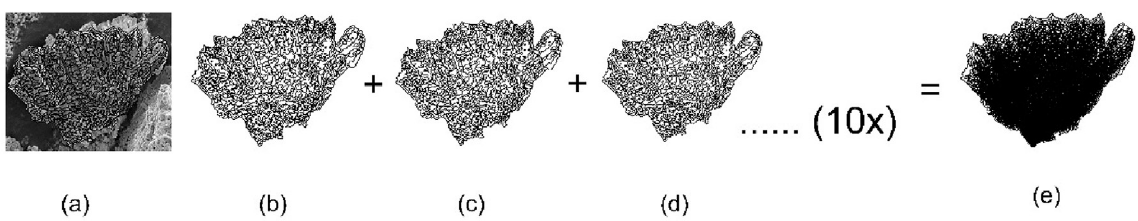

Fig. 16. Diagram to illustrate how compound relief would opacify the fragment of expanded spherulite shown in Fig. 14c. (a) outlines drawn on the crystal edges. (b), (c) and (d) crystal outlines successively reduced in size, representing similar crystal planes back through the thickness of the spherulite. If 10 iterations are overlaid, the result is nearly opaque (e).

preparation methods, the expanded remains of burnt spherulites can be seen. Their size and morphology suggest a process involving organic matter burn out and/or crystal re-arrangement which leaves the fundamental radial structure intact. Dislocation of sphere segments appears to account for the distortion features seen on some of the large darkened spherulites.

7) The darkening itself is unlikely to be entirely due to organic matter, as very long oxidative heating does not remove it. We suggest that it is also the result of the compound relief produced by multiple crystal edges inside the expanded spherulite. Darkened spherulites are not going to be rendered transparent over time by oxidation, and therefore enlarged clear ones will not be found.
8) Darkened spherulites are likely to be very delicate due to the expansion process. They will be easily destroyed by mechanical processes and dark segments should then be visible.

Although many of the details are still to be understood, finding darkened spherulites in archaeological stratigraphy can now be confidently interpreted as resulting from dung being heated in conditions of limited gaseous exchange in, around or beneath a fire which is then not heated again beyond ca. 700 °C. Such situations would probably occur around any fire where fresh dung is being burned or where the existing stratigraphy has a dung component. Since they are still calcite, preservation will be (as with normal spherulites) pH and moisture dependent, the main occurrence being in caves and rockshelters. Darkened spherulites could also occur in household contexts, where the additional information about burning conditions could assist in the deductions concerning cooking and other domestic activities involving dung usage.

In all our experimental work, we generally found no more than about 30% of the spherulites became darkened. However, archaeological samples with greater percentages have been found. More than 50% of the spherulites appear to be darkened in part of the Chalcolithic sequence at San Cristóbal rock shelter, Northern Spain (Polo-Díaz et al., 2016, Fig. 6b and c) and up to 70% in the central phosphatised feature in Plate 2f of Polo-Díaz (2010), from nearby Los Husos II.

The reason for this discrepancy is not known, but an interesting possibility for further research would be to determine whether the degree of reduction plays a part in the darkening process. We only promoted reduction by partially blocking the gaseous exchange, and a more complete experiment could, for example, burn the spherulites in pure CO_2 to see if it increased the numbers expanded or the numbers darkened or both.

Also, the age of the fresh dung could be significant. Moisture content changes will occur in storage, which could affect the organic component of the spherulites and play a part in determining how many will undergo the darkening process when heated.

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