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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

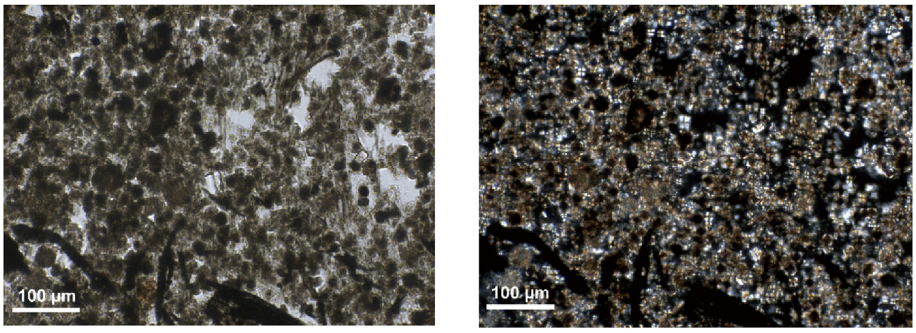

Fig. 1. (a) PPL view of part of a pellet of sheep dung heated at 600 °C for 1 h, giving a general view with about 30% darkened spherulites. (b) The same view in XPL.

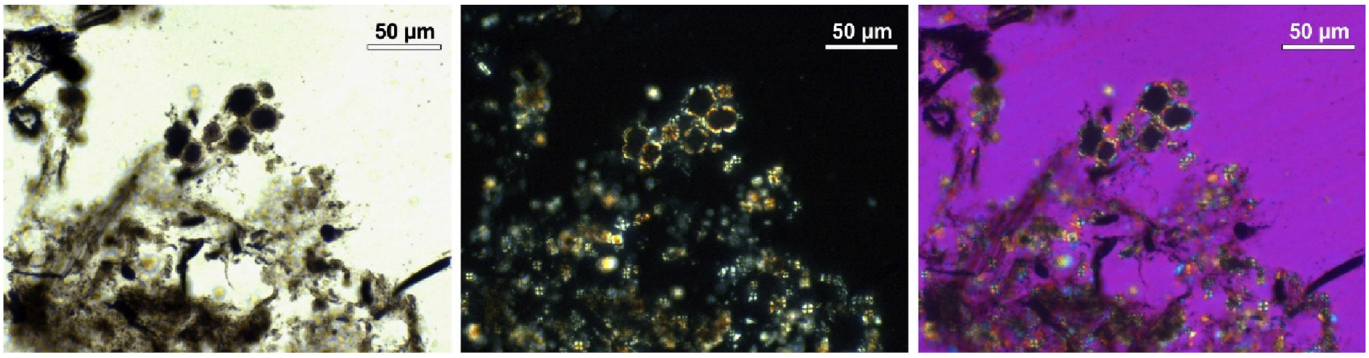

Fig. 2. Close-up of a cluster of a) PPL and b) XPL darkened spherulites. c) same as b) with λ plate inserted to show the remnant of the pseudo-uniaxial negative colours on the perimeter (see Canti, 1998). (For interpretation of the references to colour in this figure legend, the reader is referred to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