



Aspects of the chemical and microscopic characteristics of plant ashes found in archaeological soils

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Abstract

Ash from plants occurs in archaeological soils all over the world. It is particularly significant in cave deposits but is also found on open air sites where dissolution has been discouraged by aridity, deep burial or calcareous surrounding sediments. This paper describes the main microscopic characteristics of ash, as well as providing details and illustrations of their origin from plant mineral and organomineral compounds. Chemical summaries are presented which reflect the major trends in phytomineralogy and highlight some additional groupings running through plant physiology. Emphasis is placed on the importance of understanding the complete range of transformations acting on ash as a result of heating and cooling, followed by weathering and dissolution. Finally, some future directions for ash research are suggested, both from within the central topic of plant ashes and extending to other types of ash.

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1. Introduction

Pedological methods have been applied in archaeology for many years. In the past, they were mainly used for the examination of buried soils underlying archaeological horizons, but have since become increasingly valuable for studying the archaeological stratigraphy itself. Techniques such as soil chemical analysis and thin section micromorphology are now regularly used on such diverse materials as occupation horizons, floors, stabling deposits and industrial wastes (Matthews et al., 1996; Gebhardt and Langohr, 1999;

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Simpson et al., 1999). Layers of plant ashes, including wood ash, are typical of the deposits now being analysed by these sorts of methods (Fig. 1). They are encountered on archaeological sites worldwide and can be of considerable significance in understanding cultural activity. Ash is frequently a major component of cave stratigraphies (e.g. Singer and Wymer, 1982; Brochier, 1983a; Boschian and Montagnari-Kokelj, 2000) as a result of their regular occupation and reduced leaching characteristics. At open-air sites, it is found in arid situations (Cremaschi and Trombino, 1999), in pit fills where the shape and bulk of the deposit discourages dissolution, and in layers (or more commonly lenses) where the surrounding sediments are neutral to alkaline (e.g. Canti, 1992).

(a)



(b)

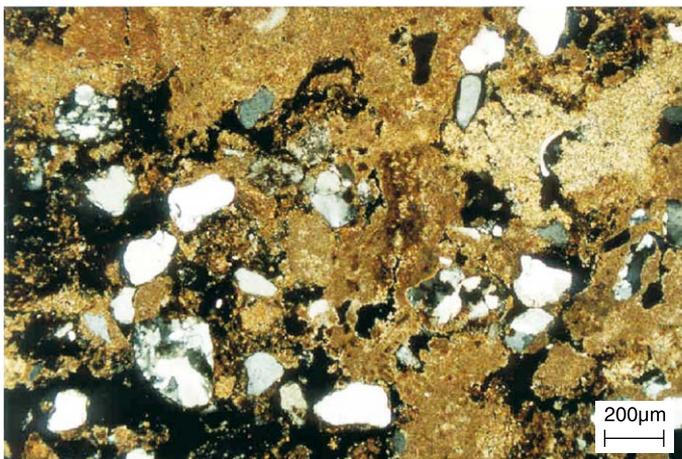


Fig. 1. (a) Field photograph of soil containing an ash layer at Flixborough, Humberside, UK. (b) Thin section from Flixborough, showing wind-blown sand grains and variably iron-stained ash deposit (all the fine matrix) in crossed polarised light (XPL).

Previous work has shown that plant ashes can have a fairly wide range of chemical compositions due to the use of different fuels (Sanderson and Hunter, 1981), different atmospheres (Humphreys and Hunt, 1979), or burning at different temperatures (Etiégni and Campbell, 1991). A review of ash formation was published by Courty et al. (1989), but subsequent work (e.g. Brochier et al., 1992, Brochier, 2002) has shown some of the basic ideas to be incorrect. Morphological examination has been carried out by Brochier (1983a,b) and Schiegl et al. (1996), but not all the characteristics have been fully clarified, particularly with regard to the origin of some components, the chemical make-up and how ash is likely to be preserved in the archaeological record.

2. Ash micromorphology

Fresh ash found in the field is usually a mix of fully or partially oxidised plant tissues and soil. Along with the plant residues, therefore, ash may contain quartz grains, burnt soil carbonates, charcoal and soil aggregates. However, the bulk of the ash is usually dominated by the plant residues, and it is the detail of these materials that will be discussed here. Fig. 2 shows the main microscopic features of mixed plant ashes. These are firstly the microcrystalline calcium carbonate aggregates (either polygonal or roughly circular and typically 10–30 µm in size, see Fig. 2a and b); secondly, elongated silica structures (Fig. 2c–f); thirdly, vesicular glassy slags (Fig. 2a and b, right-hand side); and fourthly very fine crystalline material (Fig. 2c and d) with high enough birefringence to produce low order white and grey interference colours even at micron and submicron crystal sizes.

3. Plant composition

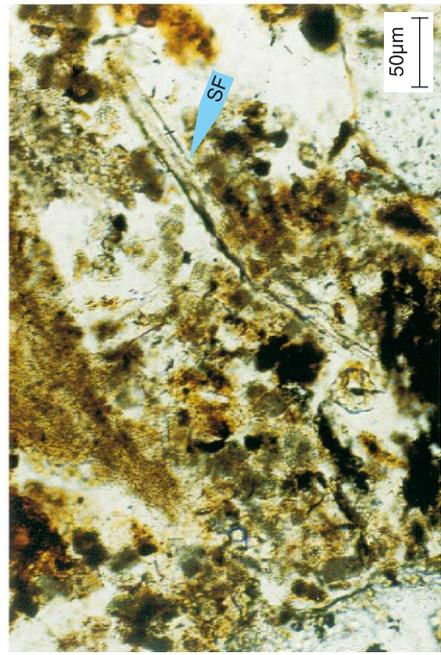
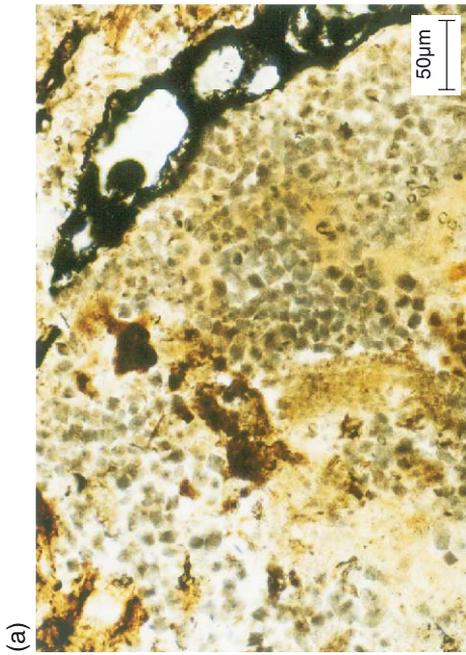
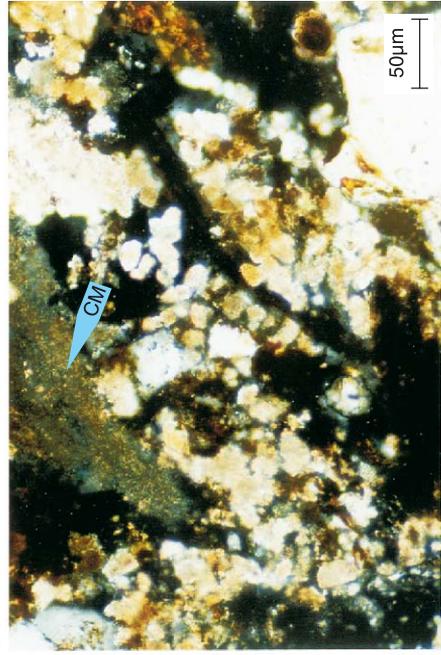
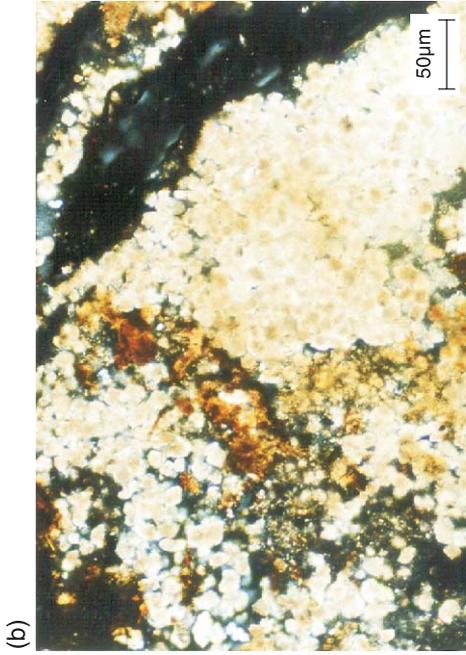
Plants are complex organomineral structures. As well as the compounds of carbon, oxygen, hydrogen and nitrogen, which make up the carbohydrates and proteins, plants also contain variable amounts of organic and inorganic salts. These occur in a number of different forms.

3.1. Cell wall calcium

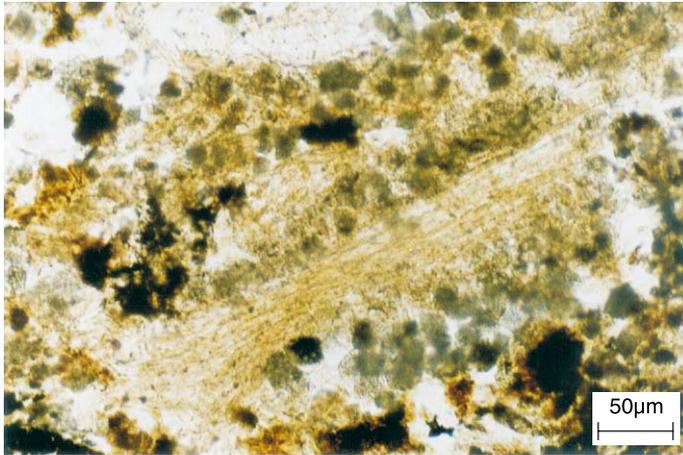
The plant cell wall contains pectin—a negatively charged polysaccharide which tends to attract Ca^{2+} and other positively charged ions (Cooper, 1997). This material is often referred to as ‘calcium pectate’ and is particularly concentrated in the middle lamellae of the cell walls (Lodish et al., 1995).

3.2. Dissolved nutrients

Nutrients with mineral cations are dissolved in the sap and protoplasm—e.g. sodium and potassium chlorides, sulphates, phosphates, tartrates, malates and citrates (Weier et al., 1982; Arnott and Pautard, 1970).



(e)



(f)

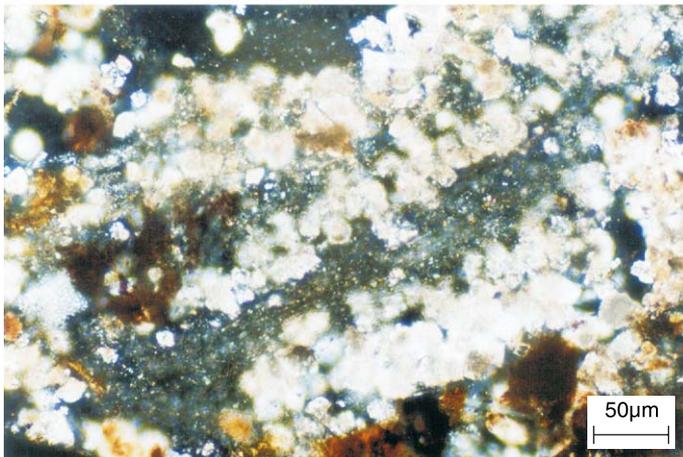


Fig. 2. Mixed plant ashes. (a) Mass of calcium carbonate aggregates in plane polarised light (PPL) and (b) in XPL. Note dirty vesicular glass fragment to the right of the frame; (c) silica remains of plant fragment (SF) in PPL; (d) same in XPL. Note also the low order white and grey submicroscopic mass of fine crystalline material (CM) at the top middle of the photograph; (e) layered silica remains and calcium carbonate aggregates in PPL and (f) XPL.

3.3. *Calcium oxalate*

Many plants contain cellular calcium oxalate crystals, usually concentrated in the leaves. Quantities can be very large in special cases; for instance more than 60% of dry weight in some lichens (Syers et al., 1967), and 85% in *Cactus senilis* (Cheavin, 1938). Amongst herbaceous and tree species, quantities are usually smaller but still significant (e.g. 15% of dry weight in autumn *Rheum raponticum* leaves—personal observation).

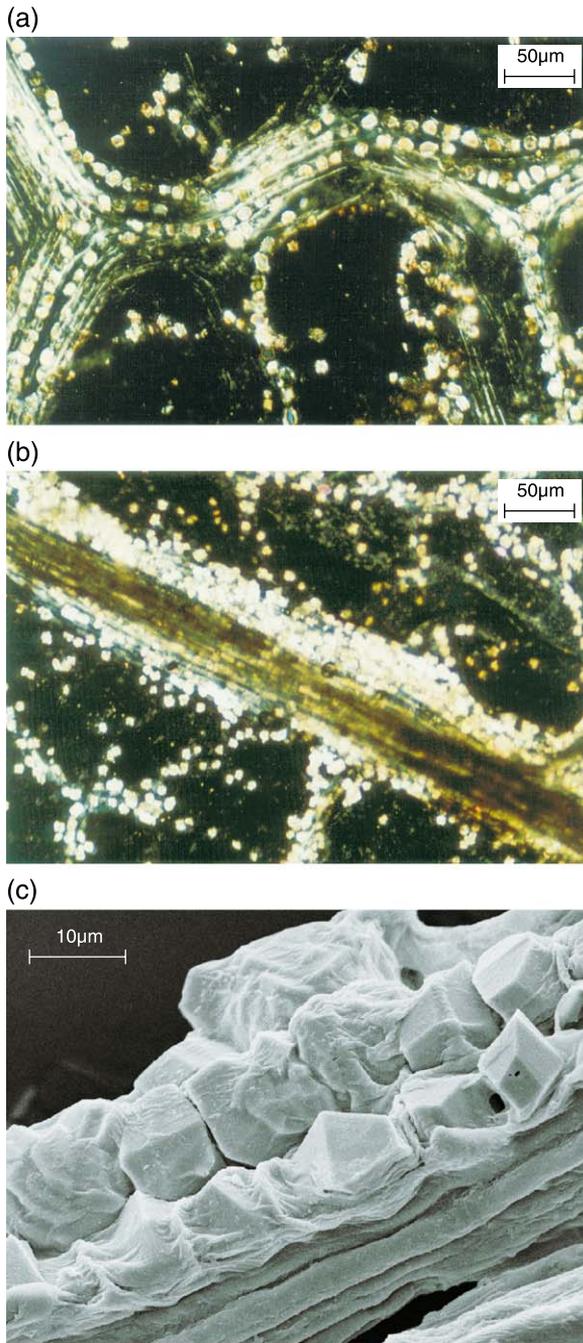


Fig. 3. Leaves of (a) oak (*Quercus robur*) and (b) birch (*Betula pendula*) bleach-treated to remove cellulose and reveal the various types of calcium oxalate crystals present (XPL); (c) SEM photograph of prismatic crystals from oak (*Q. robur*) in situ.

The most widespread forms are the druse—a cluster of radially aligned crystals, and various types of prismatic crystal, sometimes twinned. Rarer, extremely elongated crystals (raphides and styloids) are found in some plants (especially non-grass monocotyledons), as is a very fine dust referred to as ‘crystal sand’ (Pobeguín, 1943; Arnott and Pautard, 1970; Franceschi and Horner, 1980; Horner and Wagner, 1995; Brochier, 1996b).

The ubiquity and abundance of this near-insoluble salt in plants cannot be overstressed. Leaves of most common trees, for example, contain large amounts of prismatic oxalate crystals apparently armouring the veins (Fig. 3), as well as druse crystals (Figs. 6a, 7a and b) in the parenchyma.

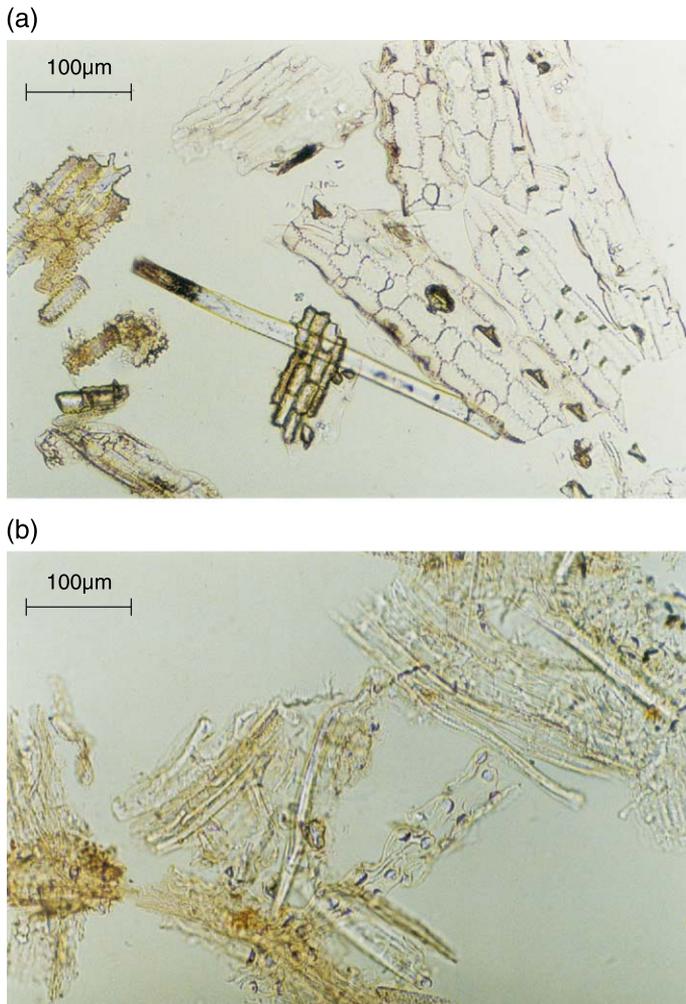


Fig. 4. (a) Encrustations of silica from maize (*Zea mays*) and (b) phytoliths from mixed grasses (Poaceae). Both PPL.

3.4. Silica

Silica (as opal) is widespread in the plant kingdom and particularly rich in the grasses (Sangster and Parry, 1981). It is also found in appreciable quantities in the wood of many tree species. Silica occurs in various forms, usually either as single or aggregate grains in the parenchyma cells; as dense fillings of the lumina; and as encrustations (Fig. 4) of the vessels and fibres (Scurfield et al., 1974; Piperno, 1988; Richter, 1980). The quantity of silica produced by the same species varies by as much as a factor of four, under different growing conditions (Geis, 1973).

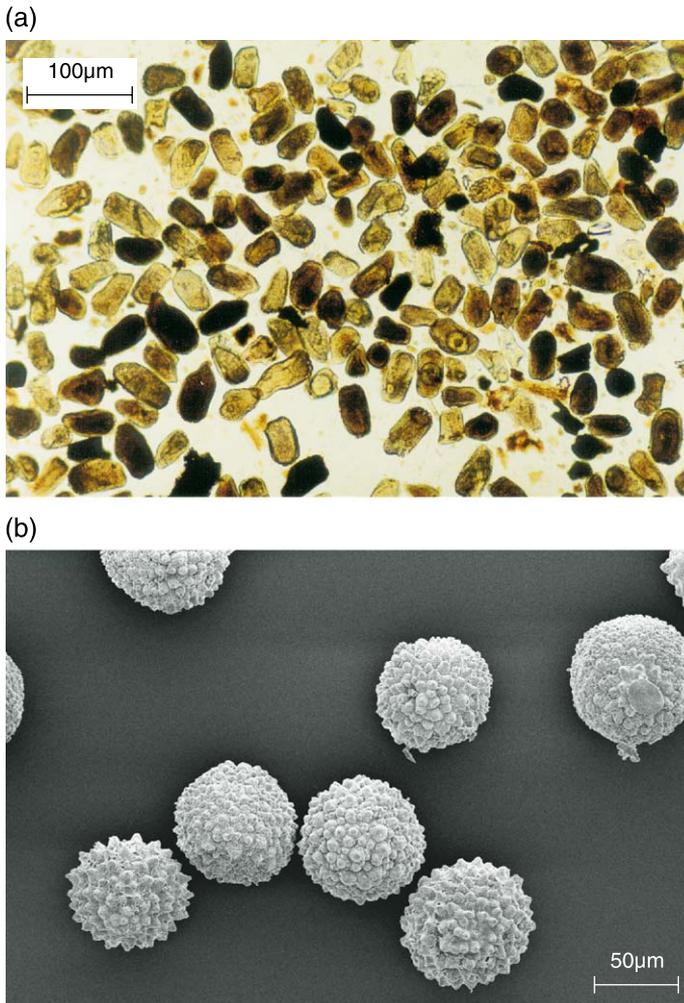


Fig. 5. Cystoliths from (a) stinging nettle (*Urtica dioica*) (PPL); (b) *Parietaria diffusa*. Scanning electron microscope photograph (SEM).

3.5. Carbonates

Two main forms of crystalline CaCO_3 are found in plants. Firstly, there are the large silica and calcium carbonate cellular ingrowths known as cystoliths (Fig. 5) which occur in a wide range of families, particularly Urticaceae, Moraceae, Ulmaceae, Acanthaceae and Boraginaceae (Haberlandt, 1914; Fahn, 1982; Pireyre, 1961; Piperno, 1988; Setoguchi et al., 1989). Secondly, crystals of CaCO_3 are found in some tree heartwoods (Pobeguín, 1954; Janin and Clément, 1972) and a few other terrestrial plants (Scurfield et al., 1973; Arnott and Pautard, 1970; Smith et al., 1971).

3.6. Other minerals

In terms of the practical results of burning, fine soil material trapped on the outside of the plant should also be included here. Even when thoroughly washed, plant matter will always have a fine residue of local soil grains trapped in hairs or waxes on the cuticle. There must also be minute amounts of submicroscopic mineral material brought osmotically into the plant with the soil–water.

3.7. Relative quantities of mineral components in plants

If the plant still has adherent soil when burnt, this will obviously be the major influence on ash composition. However, assuming a fuel mixture of clean plants, then by far the most significant contributors to the final ash percentages are the three main inter- and intracellular mineral deposits—oxalates, silica and (amongst a few plants) carbonates. The proportions of these mineral components vary greatly, and a few plants concentrate some of them in certain organs (for example, the sepals of *Geranium pratense* in which every cell contains an oxalate druse). These differences must be reflected in the final ash composition.

4. Ash formation and composition

When plant matter is completely burnt, the organic components are driven off as gaseous oxides and the relatively small quantities of mineral materials described above start to take on a far greater significance in the proportional make-up of the residue. Some (e.g. chlorides, sulphates and the organic salts) alter due to their anions denaturing or disappearing as gases; some (silica in conjunction with alkaline salts) undergo melting processes to form glassy slag; some (e.g. calcium and potassium) oxidise and remain as solids; a small proportion (e.g. silica on its own) are unchanged. The net result of these interactions is a mix of partly new and partly old compounds with elemental percentages (see, for example, Etiégni and Campbell, 1991) broadly reflecting the non-volatile elements in the original plants. The proportions of these compounds vary greatly, even in ashes from similar types of material (Sanderson and Hunter, 1981). However, the most abundant constituents are usually the silica and the carbonates that re-form from the unstable alkaline oxides on cooling and rewetting. Thus, after burning, all the calcium from the cellular minerals (carbonates or oxalates) and the cell walls ('pectate') will end up

recrystallised as carbonate once the ash has absorbed enough moisture and CO₂ from the air.

4.1. Component morphological change on burning

The morphological transformations that affect each component depend partly on temperature and length of burn, and partly (in the case of silica) on the other ash

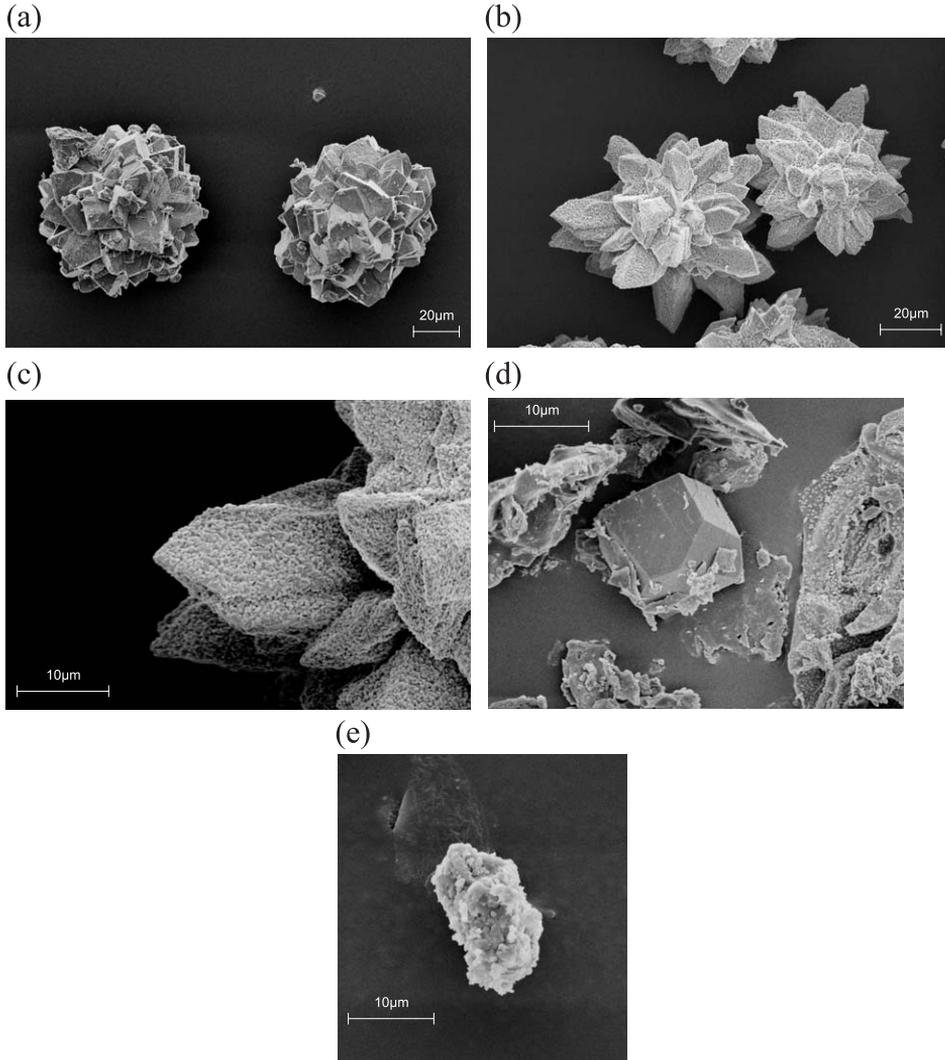


Fig. 6. (a), (b) and (c): SEM photographs of rhubarb (*R. raponticum*) druses (a) unheated; (b) heated to 700 °C and left in air for 2 days; (c) close-up of (b). (d) and (e): oak (*Q. robur*) prismatic crystal (d) unheated; (e) heated to 700 °C and left in air for 2 days.

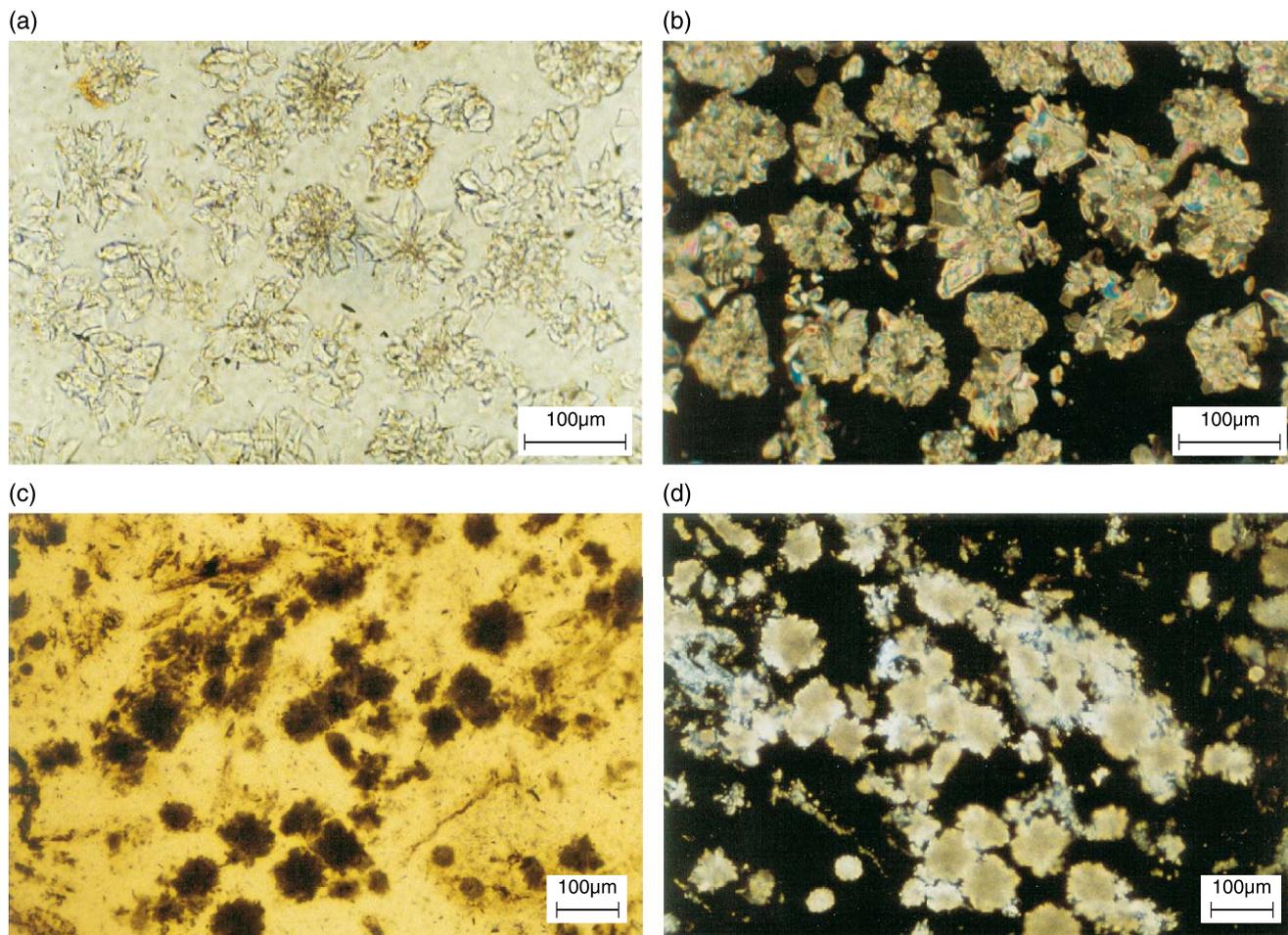


Fig. 7. Rhubarb (*R. raponticum*) druses (a) unheated (PPL); (b) unheated (XPL); (c) heated to 700 °C and left in air for 2 days (PPL); (d) same material in XPL.

constituents. The druse and prismatic forms of calcium oxalate both undergo molecular re-arrangements as they pass through CaO and CaOH phases before finally ending up as CaCO₃ (Fig. 6). These transformations do not change the gross oxalate shapes, and the crystals are still recognisable as calcite pseudomorphs in the ash (Brochier, 1983a,b, 1999). The surface morphology is, however, radically altered. Previously smooth oxalate crystal faces (Fig. 6a and d) become deeply undulating or fissured (Fig. 6c). It is not easy to determine how the neoformed calcite is arranged in these structures. Some individual crystals can be seen under the highest magnification, but the remainder must be submicron sizes. These smaller crystals lead to a higher proportion of the microscopic view being taken up by the dark crystal outlines. The pseudomorphs are thus darkened in plane polarised light due to compound relief produced by multiple overlying crystals (Fig. 7c). Under crossed polars, the compound birefringence of the stacked submicron crystals produces high order interference colours but the opacifying effect of the compound relief acts to strongly reduce the overall brightness (Fig. 7d).

Cystoliths undergo the same recarbonation processes as the oxalates, and are morphologically unchanged up to at least 900 °C (Fig. 8).

Pure silica melts at 1713 °C (Drees et al., 1989), so biogenic opal is frequently left unchanged by burning. However, the presence of alkaline salts in the ashes means that these high melting points can be strongly reduced where the right silica/alkali ratio occurs in powdered form. If such a mixture occurs in a higher temperature zone of the fire, glass-forming conditions will prevail, at least for a short period. This is usually quite a small-scale phenomenon in fires, and leads to the deposition of millimetre or occasionally centimetre scale lumps of glassy slag (Vélain, 1878; Baker and Baker, 1963; Baker, 1968; Folk and Hoops, 1982; Robinson and Straker, 1991). The slag is characteristically

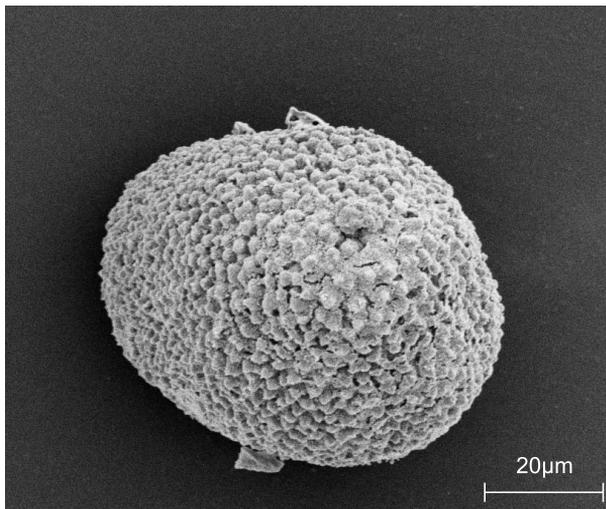


Fig. 8. Stinging nettle (*Urtica dioica*) cystolith heated to 900 °C (SEM).

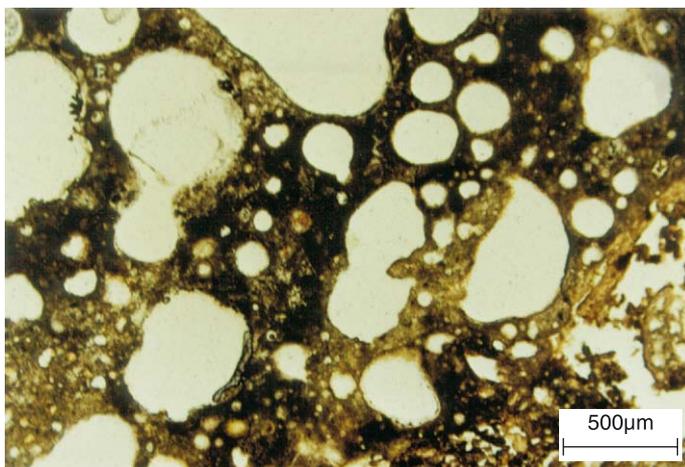


Fig. 9. Vesicular glassy slag from Saxon ash layers at Flixborough, UK (PPL).

vesicular, resulting from gas bubbles failing to escape as the melt cools down. It is found commonly in micromorphological samples of ash layers or occupation horizons where ash has been present (Fig. 9).

The cell wall calcium ('pectate') is present in small amounts relative to the other constituents described above. Once ashed therefore, the derived calcite can only be seen in situations where the major mineral bodies are rare or absent. Some heartwoods, for example, contain little oxalate or silica. Their ash is mainly submicroscopic

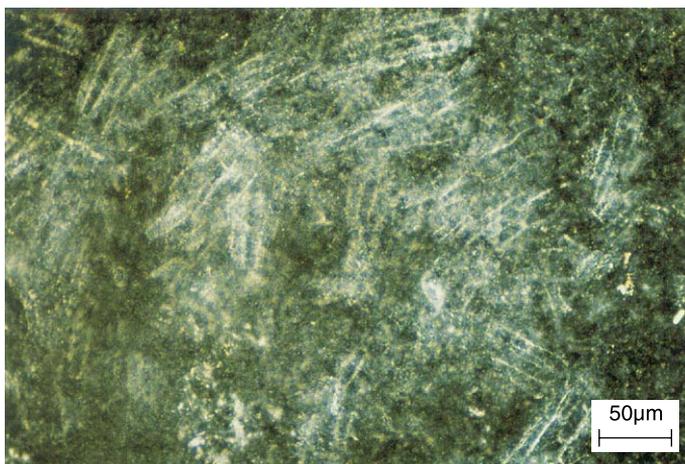


Fig. 10. Ultra-fine calcite crystals (XRD-tested) following the original shape of fibres from the ash of the heartwood of Douglas fir *Pseudotsuga menziesii* (XPL).

crystals of calcite arranged in long fibres replacing the original vessels of the wood (Fig. 10).

4.2. Chemical make-up

Understanding the chemical make-up of ash requires some form of diagrammatic simplification. The numerous components make this difficult, and no single method is

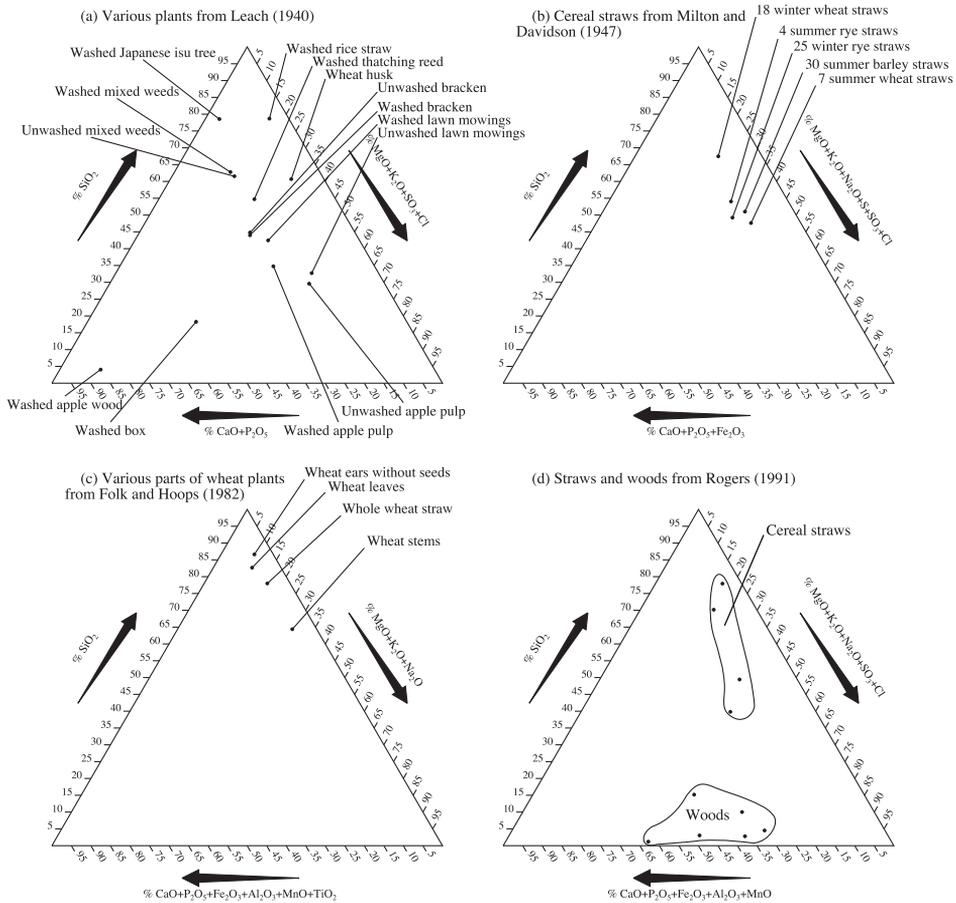


Fig. 11. Ternary diagrams of the various components of fresh ash showing high-solubility components (right-hand axis), low-solubility components (bottom axis) and silica (left-hand axis): (a) from Leach's (1940) data; (b) from Milton and Davidson (1946); (c) from Folk and Hoops (1982); (d) from Rogers (1991); (e) and (f) from Thorpe and Whiteley (1937); (g) from Witting (1851) and Böttinger (1844); (h) from Will and Fresenius (1844), Leuchtweiss (1844) and Poleck (1844). Note the differences in the axes due to varying types and degrees of analysis. All values have been rebased to 100%. In (d) 0.05% of CuO in one oak sample was ignored before rebasing the data. In (a) and (g), carbonate values were similarly treated.

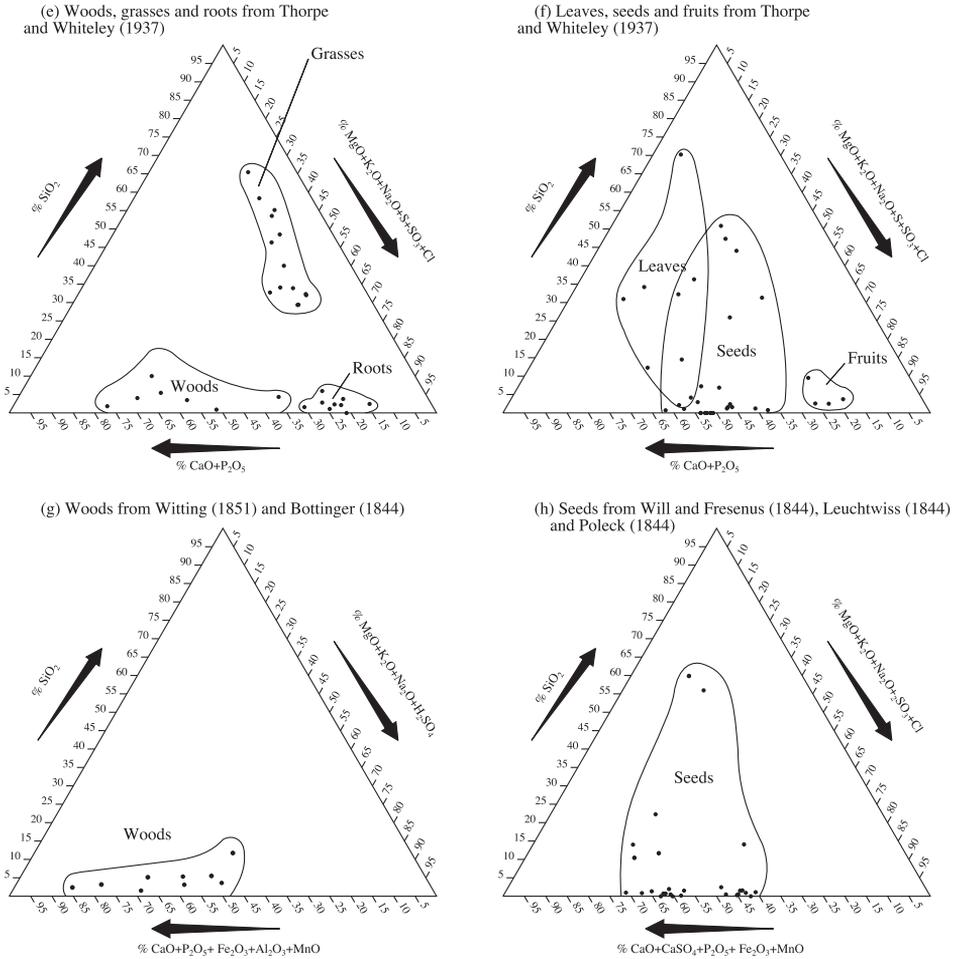


Fig. 11 (continued).

universally applicable. Furthermore, different authors present the results in different forms; some show oxide-equivalents only, for example, while others also show anions. Fig. 11 shows ash analyses from a variety of sources plotted to emphasise both biological and solubility differences. The right-hand axis is composed of those constituents most likely to be very soluble; the bottom and left-hand axes show the low solubility components, split so that silica alone is on the left, and the other low-solubility components (chiefly calcium but with variable additional constituents) are put along the bottom axis. This approach successfully highlights three groupings in the data set, namely woods with high calcium/low silica in the bottom left, dried monocotyledons with high silica/low calcium in the top right, and edible roots and seeds, both with high solubles and low silica in the bottom right. Leaves and seeds also have characteristic

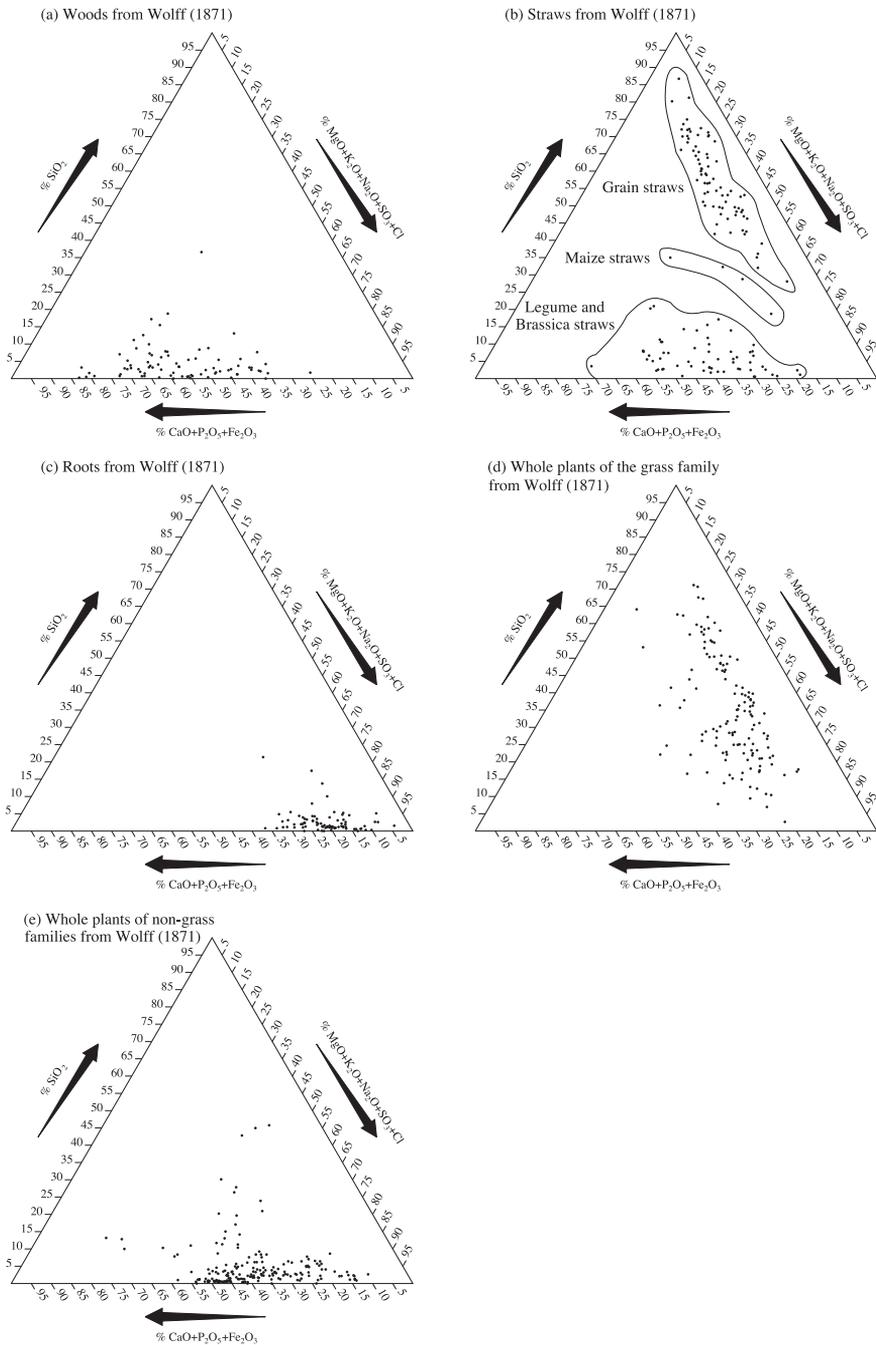


Fig. 12. Ash analyses from Wolff (1871): (a) woods; (b) straws; (c) roots; (d) whole plants of the grass family; (e) whole plants of non-grass families.

positions on the diagram (Fig. 11f and h), although they cover rather large areas and are thus not easily summarised.

Thousands of ash analyses comprising a full range of agricultural and waste materials were collated by Wolff (1871). These can be usefully employed to check some of the inferences described above. Fig. 12 shows the positions on the triangle occupied by woods, straws (of the grasses and non-grasses), roots and whole plants (of all species).

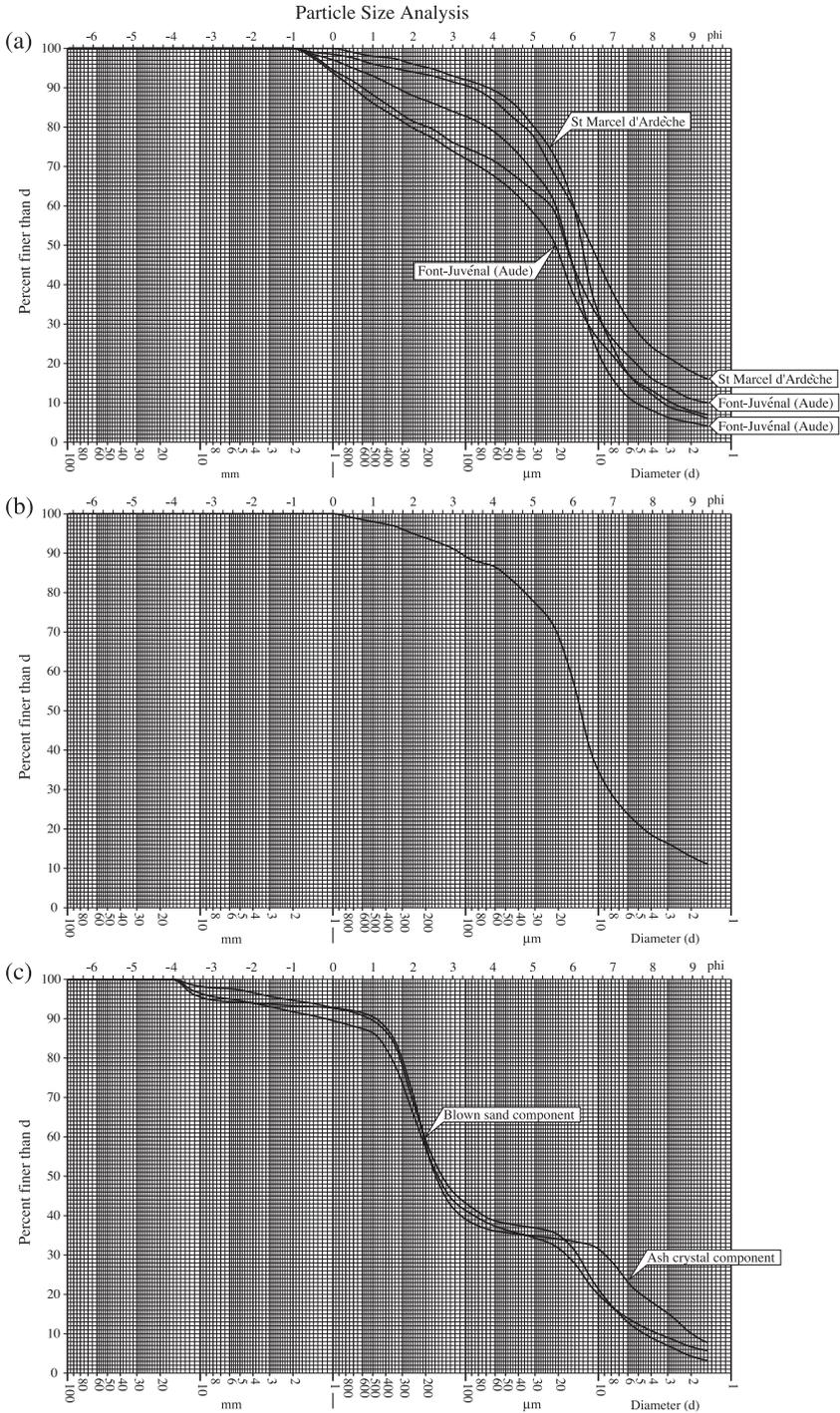
4.3. *Granulometry*

Ash deposits often show distinct peaks in the particle-size curve from about 20–5 μm (Fig. 13, see also Brochier, 1983a; Canti, 1992). This is the predominant size range of the druse and prismatic calcium oxalates pseudomorphed in calcium carbonate. Plant silica bodies are more varied, and contain some larger extracellular forms such as hair-bases and silicified epidermis (Piperno, 1988). However, they are predominantly in the range 100–5 μm and will thus tend to reinforce rather than diminish the 20–5 μm particle size peak. Overall, this peak can be seen as reflecting the size of crystal bodies once lying free within cells; since plant cells are typically 50–15 μm , it is unsurprising that free crystalline bodies within them should range from 20 to 5 μm .

5. Weathering and diagenesis

Fresh ash generally has a high pH owing to the presence of alkaline hydroxides and carbonates (Ulery et al., 1993). The various components have a wide range of solubilities, and therefore leach differentially on most open-air sites. First to go (on a time scale of weeks in temperate climates) will be the highly soluble salts such as carbonates and hydroxides of sodium and potassium. Next, the calcium carbonate and siliceous remains (plant silica and glasses) will slowly dissolve. The rate of this process varies considerably with taphonomic parameters. Silica and glasses are far more soluble in alkaline than acid conditions, so will dissolve relatively quickly while they are still surrounded by calcium carbonate. If all the carbonate goes and the soil solution is naturally acidic, the remaining siliceous components are likely to be preserved for longer. Whether the ash is buried or not thus becomes critical to the outcome, as does the nature of what it is buried by. Both calcium carbonate and the siliceous components are only sluggishly soluble, so the time scales can be a few to many thousands of years (see Alexandre et al., 1994 for rates of phytolith dissolution).

It is these calcium carbonate and siliceous remains (both plant opal and glassy slag) that are recognised as ash in the field. Apart from the usually small proportion of glassy fragments, these two components are both fine grained and white, appearing grey due to contamination by unburnt carbon. They are the largest component of most fresh ashes, and their long period of dissolution provides the window of opportunity for archaeological discovery. Eventually, however, as long as there is some leaching, all that will remain is the charcoal fragments and the tiny quantities of quartz, iron oxides and other minerals burnt with the plant. These have negligible dissolution rates over archaeological time scales.



6. Discussion

Throughout history, ash has been used for a variety of purposes. It was often a key ingredient for glass manufacture (Geilmann and Brückbauer, 1954; Newton, 1985; Turner, 1956a,b; Wedepohl et al., 1975) and for ceramic glazes (Matson, 1986; Rogers, 1991; Leach, 1940); it was used for repairing glass (Theophilus, undated), for washing wool (Forbes, 1955), as a crude alkali in dyeing (Grierson, 1990; Hurry, 1930) and in the preparation of toxic or bitter foods such as acorns (Smith, 1933; Johns and Kubo, 1988). Ash is still used today as a fertiliser or soil neutralising agent (Naylor and Schmidt, 1986; Ohno and Erich, 1990); and as a form of low-technology cement in parts of Asia (Smith, 1981). In New Guinea, the Anga people extract a range of useful salts from the ash left after deliberate burning of different tree species (Lemonnier, 1984).

Human production of ash can be copious. In some areas of the world, such as parts of South India and Botswana, ash has built up to such an extent over time that it actually forms the modern topsoil. This phenomenon seems to be strongly associated with the cattle cultures found in these areas, and the ash layers probably result from long-term dung-burning (Allchin, 1963; Zeuner, 1959) or lightning strikes (Thy et al., 1995).

Clearly, understanding more about archaeological ash layers is desirable from an interpretative standpoint. In particular, a knowledge of what was burnt and why could be a valuable adjunct to cultural information retrieved from artifacts. At the moment, the most obvious separation running through the analyses and morphological descriptions presented here is between the *high silica–low calcium* grass/cereal ashes, which contain no calcite pseudomorphs of oxalate, and the *high calcium–low silica* wood ashes, which are composed mostly of oxalate pseudomorphs or calcium ‘pectate’ remains. Given the right burial conditions, these two are clearly distinguishable ash types.

Could identification be taken further? The possibility of separating individual species used as fuel would rest on the presence of identifiable mineral bodies in different plants. J.E. Brochier has discovered a few such cases amongst calcium oxalates of *Tilia*, *Pinus* and *Vitis*, successfully using their presence to enhance palaeoenvironmental interpretations (Brochier, 1990, 1996a). Further work may be worthwhile to extend this range. However, it seems unlikely that specific identifiable crystal pseudomorphs will turn out to be a widespread phenomenon. The majority of plant species appear to contain druse and prismatic crystals of very similar morphology. Equally, although silica and cystoliths occur in many plant families, their morphologies are generally too close to allow identification to species level.

Subdivision into plant parts could have potential. There is very little data available on the mineral content of different parts of the same species, and it would seem from the chemical analyses presented here that variation may be systematic. From the morphological point of view, different plant organs show clear differences of mineral quantity. The density of prismatic crystals in tree leaves (see Fig. 3), for example, is in strong contrast to

Fig. 13. Particle size curves of (a) ash-rich cave sediments from Font-Juvénal and St. Marcel d’Ardèche, France; (b) fresh wood ash. Both (a) and (b) redrawn from Brochier, 1983a; (c) ash and blown sand deposits Flixborough, Humberside (Canti, 1992) showing clear 20–5 μm peak.

the more general case of plant tissues which typically have just one or two druses scattered amongst many empty cells.

7. Conclusion

The varieties of ash, and the complexities of its taphonomy combine to form an extensive range of morphologies that need to be examined archaeologically. Many of these materials could benefit from further application of both chemical and micromorphological techniques. We now have a relatively clear understanding of the major plant-derived types, but this needs to be further extended. Suggestions for achieving greater detail amongst ordinary plant ashes have been presented above, but as archaeology becomes more geographically widespread and more temporally inclusive, there will be a need for intensive investigation of other ash types as well. Very little work appears to have been done on coal ash, for example, despite the widespread burning of this material since Roman times. Peat ash has become more significant in northern European archaeology recently as a result of the burgeoning growth of archaeology in Iceland, Scotland, and the UK's northern Isles where it was a major source of fuel (Carter, 1998).

To achieve this extension of knowledge, the growth in range of archaeological analysis will need to be matched by greater detail in the pedological approaches used, and a parallel improvement of scientific discipline on the part of practitioners. Ash, through its complex origins and intricate diagenesis, provides a perfect springboard for such discipline to emerge and flourish.

Acknowledgements

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