ELSEVIER

Journal of Archaeological Science 31 (2004) 1715–1734

Journal of Archaeological SCIENCE

http://www.elsevier.com/locate/jas

The decomposition of starch grains in soils: implications for archaeological residue analyses

Michael Haslam

School of Social Science, University of Queensland, Brisbane, QLD 4072, Australia

Received 2 January 2004

Abstract

Recent research involving starch grains recovered from archaeological contexts has highlighted the need for a review of the mechanisms and consequences of starch degradation specifically relevant to archaeology. This paper presents a review of the plant physiological and soil biochemical literature pertinent to the archaeological investigation of starch grains found as residues on artefacts and in archaeological sediments. Preservative and destructive factors affecting starch survival, including enzymes, clays, metals and soil properties, as well as differential degradation of starches of varying sizes and amylose content, were considered. The synthesis and character of chloroplast-formed 'transitory' starch grains, and the differentiation of these from 'storage' starches formed in tubers and seeds were also addressed. Findings of the review include the higher susceptibility of small starch grains to biotic degradation, and that protective mechanisms are provided to starch by both soil aggregates and artefact surfaces. These findings suggest that current reasoning which equates higher numbers of starch grains on an artefact than in associated sediments with the use of the artefact for processing starchy plants needs to be reconsidered. It is argued that an increased understanding of starch decomposition processes is necessary to accurately reconstruct both archaeological activities involving starchy plants and environmental change investigated through starch analysis.

Keywords: Starch grains; Soil; Residue analysis; Archaeology; Taphonomy; Transitory starch

1. Introduction

Analysis of biologically derived microscopic archaeological residues is a rapidly growing field, concerning itself with both the analysis of artefact residues (on stone and ceramics, and to a lesser extent bone and wood) and the recovery of residues from archaeological soils. Increasingly, much of this research has involved the identification and interpretation of microscopic components of plants (e.g. starch grains, cellulose, lignin, phytoliths, pollen, and lipids), particularly in the assessment of artefact use and environmental reconstruction (e.g. [10,43,54,91,138,144,176,183,220]). This research has paralleled the investigation of microscopic faunal and macrobotanical materials, and ongoing studies of soil chemistry at archaeological sites (e.g. [58,143,169,175,226,238]). There has been little discussion in the archaeological literature, however, of the mechanisms and consequences of plant component breakdown relating specifically to residue analysis, to match that concerning the preservation of bone or carbonised plant macroremains (e.g. [98,99,100,146]).

Barton et al. [15], drawing on concerns as to the validity of archaeological residue analyses expressed by Grace [83], noted two issues to be addressed, one of possible contamination of artefacts by non-use-related residues, the other a 'failure of researchers to describe the mechanisms by which residues had been preserved' [15:1231]. Both these concerns are the subject of this paper, through the integration of residue results from a variety of archaeological studies on artefacts and in soils with experimental results from the plant physiological and soil biochemical literature. This synthesis is presented with the needs and interests of both the archaeological residue analyst and the wider archaeological community in mind. In particular, owing mainly to the specific interests of the author, the literature relevant to archaeological starches is addressed. Where

E-mail address: m.haslam@uq.edu.au.

0305-4403/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jas.2004.05.006

discussions of other archaeologically important plant constituents exist, the reader is directed to these (e.g. [16,17,22,23,37,56,61,92,119,175,191]).

As regards starch decomposition, three main problems emerge from current studies: (1) the archaeological literature does not adequately consider the mechanisms and consequences of the breakdown of starch grains; (2) the relationship between starches on artefacts and in associated soils has not been adequately explored; and (3) there has been insufficient discussion in the archaeological literature of the differences in the synthesis, character and degradation of 'transitory' starch (otherwise known as 'transient' or 'leaf' starch) compared to 'storage' starch grains. This paper aims to provide a framework within which each of these issues can be discussed, with a view to encouraging further discussion. In order to keep the review focused, methods for extraction and separation of plant residues from artefacts and soils, and the variety of approaches to artefact use-wear (e.g. [14,38,73,97,118,127,137,139,170,172,201,205]) will not be examined here. Additionally, this paper concentrates on aspects of microscopic rather than chemical compositional residue analyses (e.g. [7,104,109,149]), as historically microscopy has been the more commonly employed tool in starch residue studies.

2. Starch

Starch is the major food reserve of higher plants, although it is also found in fungi, algae and other organisms. Detailed descriptions of the composition, appearance and genetics of starches have been provided elsewhere [8,12,71,72,203] and the following summary is drawn from these studies. Two main forms of starch are important for archaeological analyses, classified by their function and location within the plant: *transitory* starch, which is found chiefly in leaves and acts as an ongoing plant energy source, and *storage* starch. Storage starch is formed in granules within specialised plastids known as amyloplasts, which are found in seeds, roots, tubers, corms, fruits and rhizomes [156]. In these parts of the plant starch acts as a long-term energy storage device, a source of nutrients that allows a plant to survive during unfavourable conditions and a carbon source during such processes as germination. Transitory starch is discussed in greater detail in a later section of this review.

Apart from minor non-carbohydrate components, all starch is composed of glucose molecules (as is cellulose, the structural component of wood) and intact granules are insoluble in cold water. The glucose molecules are formed into two different chains within starch, a linear chain (amylose) and a highly branched chain (amylopectin), with amylopectin typically forming 70–80% of storage starch. Each granule is laid down in concentric layers around a central growth point or hilum, which may or may not be in the physical centre of the grain, in a fairly densely packed (1.4–1.5 g/ml) arrangement [12,43,165]. The layers alternate between semi-crystalline and amorphous composition, with each layer a few hundred nanometres thick [243]. In turn, each of the semi-crystalline layers is composed of stacks of alternating crystalline and amorphous lamellae, with a repeat distance in all starches (storage and transitory) of nine nanometres [111]. These factors, all of which are influenced by the branched amylopectin, give starch granules a quasi-crystalline structure, and birefringence with a characteristic extinction cross under cross-polarised light. The sizes of storage starches range from 1 to more than 100 μm, with shapes typically spherical to ellipsoidal.

Besides the appearance of granules of various species, which has been discussed by others (e.g. [105,162,182,186]), the characteristics of starch of most interest to archaeologists are its behaviour under various conditions of moisture and heat and its ability to be chemically stained. Starch will swell in water, but return to its original shape upon drying provided the swelling is not too severe and the temperature remains below a certain level [112]. Once a specific temperature is reached in the presence of water, individual starch grains will undergo irreversible, pronounced swelling, lose their extinction cross and ultimately their granular features, beyond which point they are not easily identifiable by light microscopy without chemical treatment. This process is known as gelatinisation, and occurs at different temperatures for different species, although 60 °C is common for many plants. In the absence of water, starch is destroyed by heat, and does not survive intact processes such as seed charring [101].

Many have noted that Congo Red stain will turn damaged or gelatinised starch grains a red-pink colour [8:86; 43:178; 91:146; 150:147; 164:8; 223], which may aid in identification once gelatinisation has occurred. The most widely used stain for undamaged starches, however, is iodine [222]. Iodine typically stains starch grains a deep blue colour, although it is in fact amylose which is stained blue, while amylopectin stains a red/brown/purple colour [151,245]. The overall blue appearance is due to the much greater affinity amylose has for iodine (due to the low frequency of branching in amylose), binding on average 20% of amylose weight at 20 °C, whereas amylopectin binds only 0.2% (w/w) [236]. Iodine staining can be misleading if the starch involved has a proportion of amylopectin chains with less branching than usual, but high-amylopectin starches (such as some waxy maize varieties) will stain red/brown rather than blue. This important distinction is considered further in the discussion on transitory starch, as a possible means of differentiating transitory from storage starch grains.

3. Archaeological starch residue analysis

Microscopic plant residues have been detected on Acheulian artefacts dating back to the early Pleistocene [54], and through the Palaeolithic [3,94] up to modern times [230]. There can be no doubt therefore that such residues can survive for considerable periods of time. That they survive on artefacts recovered from a range of environmental contexts (from dry rockshelters to the humid tropics) has also been demonstrated. This ubiquity of plant residues on artefacts in part reflects the importance of starchy plants in the human diet throughout human history [12,64,98,236,240]. The obvious nutritional value of the sugars in starch, along with the presence of large quantities of starch in the seeds, roots, corms, rhizomes and tubers of plants such as potatoes, maize, rice, and yams has contributed to the dominance of starches in many past and present diets.

Because of their importance, starchy plants have received a high degree of attention from archaeological residue analysts. Likewise, the geographical concentration of archaeological starch researchers in Australia and the Americas (although see [114,194,195]) has resulted in an increased understanding of starchy plants from these regions. On artefacts, Piperno, Pearsall, Perry and others in the New World have found starches from plants including maize, potatoes and manioc [7,97,176,177,178,181,182,183], while in the Pacific Fullagar, Loy, Torrence, Barton and others have concentrated on the tuberous starchy plants prevalent in this region [15,74,75,142].

Currently, the most widespread and accessible of the various techniques available for starch residue identification is light microscopy. Microscopy can in some cases provide identifications not attainable by, for example, chemical analysis (although the reverse is also true). Hillman et al. [104] argue that chemical studies are advantageous to morphological microscopic research, even though in some cases the best result that can be obtained chemically is a description such as 'cellulosics', which applies to both cellulose and starch [103:227] (cf. [18:114]). If intact, these two residues would be difficult to confuse using visible morphological characteristics. Doubts have also been expressed over the use of crossover immunoelectrophoresis (CIEP) to identify plant residues [136]. Even scanning electron microscopy (SEM) can in some cases be less useful than light microscopy in correctly identifying starch grains, as characteristic extinction crosses cannot be observed [21]. Visual identification emphasises criteria such as starch granule size, shape and extinction properties, either in situ on the artefact surface or following removal to a microscope slide. The growing literature suggests that these morphological criteria are in fact sufficient for distinguishing starch assemblages of various botanical origins, provided reference collections of economically important species are comprehensive [4].

The role of non-use-related residues in muddying interpretations of artefact use was highlighted by Briuer [20], often cited as one of the more important pioneering studies in the analysis of archaeological residues, and in particular plant residues, on stone artefacts. This concern with 'contamination' has extended from Briuer's [20:482] examination of non-cultural rock surfaces to include the sediment in which the artefacts are discovered. It is now standard practice for artefact residue studies to include a corresponding analysis of a portion of the sediment from the site, as a means of controlling for any possible transfer of residues from the soil to an artefact (e.g. [15,93,118,144,183,231]). The rationale behind the sampling of control soil samples is most simply expressed as an argument that if residues found on artefacts are not present in the soil, then the residue most probably results from use of the artefact. A variation on this notion was employed by Atchison and Fullagar [5], who used differences in the appearance of starches recovered from artefacts and associated sediments to rule out contamination. Criticism of the reasoning behind these approaches has begun to grow, however, and centres largely on the unknown factors involved in post-deposition decomposition of organic residues. Perry [177:184–186] has presented a cogent case for not relying on such indicators of possible contamination, as differences in decomposition factors and rates between artefact surfaces and in sediments have not been investigated.

To date, very few experimental analyses involving starch residues on artefacts have been published. Lu [145] is an exception, using microscopy to calculate the percentage of portions of stone artefacts covered by starch before and after exposure to a variety of soil and environmental conditions. Three main contexts (buried, surface and sheltered surface) and four types of starch (taro, rice, yam and foxtail millet) were used in an effort to discern differential preservation dependant on exposure conditions and starch source. Starch survival varied considerably both between artefacts and between observation points on the one artefact, ranging from 1.6 to 98.6% (in open and sheltered contexts, respectively). Average survival, in terms of percentage covered by starch of a marked observation area on the artefact, was found to be around 80% for sheltered artefacts, 75% for buried artefacts, and 35% for exposed surface artefacts. While the experiment only ran for 71 days with 13 artefacts, and data on the comparative starch content of associated soil samples was not presented, this study represents a positive step towards the larger taphonomic analyses necessary to better understand starch survival. The percentage areas retaining starch after 10 weeks are in fact much higher than would be expected from experiments into starch

degradation in soils as discussed below. An assessment of the representativeness of these results awaits further experimental testing.

The newest area for archaeological starch research involves the analysis of sediments to reconstruct environmental histories or human activity areas [10,106,108,138,171,220]. While these studies may be conducted in association with artefact residue analyses from the same site, they are intended to act as stand-alone reconstructions, in much the same manner as has been employed in pollen research [36,102,175]. The burden of providing evidence for non-differential starch survival must be even greater for these studies than for artefact residue studies, which can rely on use-wear as a means of residue verification (e.g. [11]). Differential preservation through time of starch grains due to species or size-specific variations in starch degradation, or intra-site variations in soil properties, are issues that have not been given necessary attention. A combination of the two could result in biases in the recovered starch assemblage for which no controls have been established.

Only Therin et al. [220] (cf. [218]) have attempted to measure starch change in archaeological soils through time. Balme and Beck [10] recorded starch in the top 3 cm of sediment at the Petzkes Cave rockshelter site, Lentfer et al. [138] collected modern samples from the top 4 cm of sediment in a study from Papua New Guinea (PNG), and Iriarte et al. [108] used the presence of starch grains from sites in Uruguay to infer dietary and horticulture practices. More recently, Parr and Carter [171] recovered an extremely limited number of grains from sites in the Torres Strait, and Horrocks et al. [106] used starch to infer sweet potato cultivation using stone mounds in New Zealand. While Balme and Beck recorded variables including soil moisture, pH and trampling, these data were not presented for the other cited studies. It is becoming increasingly apparent that without consideration of differential decomposition biases, the only reliable statements to be made with regard to soil starch analyses are those identifying the presence of a particular species in a particular sample. Quantitative analyses, and those drawing conclusions from the absence in soils of starch grains of certain sizes, shapes or species, have not at this stage given sufficient attention to possible influences of soil properties and constituents on decomposition to produce defensible reconstructions of the archaeological past.

4. Decomposition of starch

The first of the three key issues outlined in the introduction concerns the mechanisms of starch breakdown in archaeological contexts. For all archaeological residue analyses, these contexts involve two specific environments—artefact surfaces and the general soil environment. Although some advances in understanding have been made regarding the survival of animal-derived blood, protein and bone components [34,40,44,62,110,226], the corresponding archaeological plant residue literature reveals a lack of investigation (although see [56]), leading in some cases to confusion and misinformation. In particular, it is necessary to address views such as those expressed by Therin et al. [220:447], that 'in plants and animals starch is broken down through the use of specific enzymes which are not normally present in soils'. This statement runs contrary to the current state of knowledge regarding soil enzymes (see for example papers in Burns [25]), and taking it at face value could lead to inaccurate interpretation of archaeological data. Organic decay is one of the most important processes affecting the composition of the archaeological record, and an appreciation of the variety of mechanisms by which such decay occurs is crucial to the production of informed re-creations of the archaeological past.

The factors influencing the degradation of plant components in soils can be divided into two broad categories: soil properties such as pH, temperature, texture and moisture content, and soil constituents including enzymes, bacteria, fungi and earthworms [87]. Unfortunately, it is not usually feasible for archaeologists to quantitatively measure most of these factors, beyond simple pH testing and the recording of soil appearance and macroscopically visible faunal activity. Even where long-term experimental projects to measure biological decomposition have been developed with archaeological needs in mind, it has not always been possible to include microbial measurements in the tests conducted (e.g. [133:284]). This is less a reflection on archaeological practice as it is a reality of the time, expense and expertise required to perform such tests. Nevertheless, if residue analysts wish to make informed decisions when interpreting their data, some consideration of the burial environment must be included.

4.1. Enzymes

Both bacterial and fungal decomposition of plant components is achieved through the action of enzymes. Enzymes are biological catalysts, proteins capable of lowering the activation energy required for certain chemical reactions [85,185:896]. Performing this function does not alter an enzyme, which is therefore able to catalyse over and over again, making them effective even at low concentrations. Enzymes are designated by the suffix -ase (from the Greek *diastasis*, separation) added to a prefix derived from the *substrate*, the material

catalysed by the particular enzyme. The enzymes related specifically to the breakdown of starches are therefore known as amylases, from the prefix amylo- (starch; technically, this renders the study of ancient starch palaeoamylology, or more succinctly palaeoamylogy). The amylases form a component of the broader category of polysaccharidases, which includes other enzymes such as cellulase (which breaks down cellulose). Polysaccharidases are found in every type of organism including plants, mammals, algae, bacteria, and moulds [192].

In soils, enzymes are derived from a number of different sources, including active plant, animal or microbial cells, fungal spores, bacteria, enzymes enclosed within dead cells or cell debris, or as extracellular proteins in the soil solution or bound to organic and inorganic soil particles [26,130,173:65;216]. Effectively, these can be distinguished into intracellular enzymes which reflect ongoing microbial activity, and extracellular enzymes, which form the greater part of soil enzymes and reflect previous organismal activity [39:45;189]. Kiss et al. [123:118] note: 'Under natural soil conditions the polysaccharidases, like other enzymes, are continuously being synthesised and accumulated, inactivated and decomposed'. Most soils therefore contain a 'background' level of accumulated enzymes, the exact composition of which will depend on both the history and current condition of the soil.

Apart from the ubiquity of enzymes in soil capable of degrading starch, cellulose, lignin and other plant components, the key attribute of interest to archaeologists is the ability of enzyme-producers to remain in an inactive state, awaiting reactivation by the appropriate substrate. Most of the microbial soil community is dormant owing to limited mobility or restricted access to food [87:C109]. Soil microorganisms depend on water for survival and mobility, although bacteria and fungi exploit this differently in their modes of growth. Bacteria live on surfaces, exist in clustered colonies occupying only a few cubic millimetres of soil, and are dependent largely on episodic events such as rainfall, root growth, tillage or faunal ingestion for movement. Fungi, on the other hand, are able to grow hyphae to extend into microhabitats where they secrete enzymes to decompose organic matter, translocating nutrients back through the hyphal network [39:35;87]. Soil microbiologists have classified bacteria into two classes based on their response to soil substrates: *autochthonous* organisms grow slowly and predominate when there is little oxidisable substrate; *zymogenous* organisms respond to substrate addition by rapidly increasing in numbers and activity, with the majority then dying out following substrate exhaustion [33,87]. Even if little evidence in the form of vegetation or obvious fungal/microbial activity is present, therefore, there may still be inactive enzymes and enzyme-producers awaiting re-activation by the appropriate substrate.

4.2. Enzymatic degradation of starch

Starch grains are typically degraded in a multi-stage process, involving first the disruption of the grain through gelatinisation or hydrolysis, followed by enzymatic conversion of starch polysaccharides into component sugars (see Warren [237] for a comprehensive review). Other stages or catalysts may be involved, for example the presence of salts may allow for gelatinisation at a much lower temperature than normal [12:264–267;187], and both mechanical and oxidative damage make granules more susceptible to enzymatic attack [71,239:223]. The initial stage of enzyme action is formation of an enzyme–substrate complex, after which the addition of water elements to the D-glucosidic bonds enables hydrolysis [126,174]. Eventually, the breakdown products of starch may be further decomposed into carbon dioxide and water. Of the many enzymes which are necessary for the complete degradation of starches, it is currently thought that only two, endoamylase (α-amylase) and α-glucosidase, are capable of direct attack on native starch granules, acting either singly or in synergy [79:575;211,212]. Other enzymes are then able to begin catalysis, for example phosphorylases utilise the resultant glucans as a substrate [210], and β-amylase reduces amylose to maltose [173:133]. In many cases, a suite of enzymes may be responsible for this secondary process of degradation, in part because starch granules are not only composed of amylopectin and amylose, but also contain small amounts of proteins, lipids and non-starch polysaccharides [42,72,84,213:24–26]. Different enzymes (for example endo- and exo-polysaccharidases) possess varied mechanisms by which to catalyse their preferred substrate [59,60,173:64;192:143], and the physical structure of the starch granule (for example the presence or absence of 'surface pores') may also contribute to differential degradation [63].

On current evidence, transitory starch grains present in leaf chloroplasts are much more readily hydrolysed than those from storage organs ([9]; see also discussion below), however, both processes are extremely rapid on an archaeological time-scale. In vitro experiments exposing starch granules directly to a variety of starch-degrading enzymes demonstrate this rapidity. When storage starch from major food plants was exposed to bacterial α-amylase, between 18% (potato) and 55% (tapioca) of the starch was decomposed within 24 h [135]. Even faster degradation has been recorded: 5% of potato starch and approximately 52% of maize and rice starch was digested by bacterial α-amylase within 2 h of enzyme addition [76]. After 24 h exposure to glucoamylase, potato starch was degraded 14%, and maize and rice starch grains 94 and 97%, respectively [76]. In other words, almost all the maize and rice starch granules were catalysed to form simple sugars (a state unrecognisable via microscopy) within one day of exposure. Similar

results have been observed in many other studies (e.g. [148,157,210,212,242], with the initially quick degradation rate in almost every case following an asymptotic curve approaching 100% decomposition [135:38;179]. As enzyme activity is stimulated by the presence of suitable substrate, then the rates displayed in these experiments could well be approached in specific localities within soils. The implications of these results for residue analyses of artefacts and soils is that without a mechanism of protection from enzymatic attack, it is difficult to see how any starch could survive the long periods of burial experienced in archaeological contexts.

In addition to studies which evince rapid degradation of starches derived from both chloroplasts and amyloplasts, research into the effects of amylases on storage starch has revealed species-specific differences in enzyme attack patterns and rates. In part, these are caused by changes in enzymatic susceptibility due to differing granule structure and sizes, amylopectin/amylose ratios, and crystal types [126,148]. Several researchers have used these differences to create ordered lists, which show the susceptibility of storage starches from various plants to bacterial α-amylase [42,76,77,135]. These lists have been collated in Table 1, along with data on granule size, amylose content, and gelatinisation temperature of the starches involved. The plants are ordered from the most to the least susceptible to starch hydrolysis, and the results show a general trend towards a greater degree of degradation as both amylose content and starch granule diameter decrease. Similarly Franco et al. [69] (see also [70]) analysed cassava and maize starch grains of various size fractions, and concluded that enzymatic susceptibility increased with both decreased granule size (and therefore increased relative surface area) and decreased amylose content. That granule size and amylose content both within and between species may in fact be linked is suggested by data in Franco et al. [69:424] and Shannon and Garwood [203:34] (cf. [125]). This is also a factor in the development of transitory starches, as discussed later in this review. Gelatinisation temperature does not appear to display any clear correlation with degradability, however Tester and Sommerville [217] have shown that water content can play an important role in degradation, through regulation of swelling and gelatinisation. Once gelatinisation begins, increased enzyme access to the easily degradable amorphous regions of the granule leads to an increased rate of starch decomposition, although the presence of a high level of branched amylopectin may restrict swelling and therefore hydrolysis.

4.3. Decomposition of starch in soils

Cases of exceptional preservation of archaeological starch grains have been recorded. The stomach contents of Iron Age bog bodies found at Tollund and Graubelle yielded starch 'which has kept its specific agglomerate structure and ability to stain with iodine' [101:208]. Loy et al. [144] reported starch on artefacts from a cave site in the Solomon Islands dating back 28,000 years. Numerous other studies have recovered starch grains from artefacts several thousand years old (e.g. [7,65, 97,183]). Survival of starch on artefacts therefore appears to be a justifiably accepted occurrence. The recovery of starch grains from archaeological sediments has not proved as successful, however, and several researchers have questioned the ability of starches to survive for any length of time as discrete entities in soils [5:121;177:185;183:896].

Within soils (as opposed to in vivo degradation of starch), carbohydrates are utilised in two main ways; to produce energy through oxidation to CO_2, and as a means of obtaining monosaccharides for further polysaccharide synthesis [33:128]. The cycling of soil organic matter is one of the more crucial components of the biogeochemical cycles, returning carbon fixed by photosynthesis back into the atmosphere [87:C107]. As plant residues contribute the largest fraction of organic carbon entering the soil [173], this turnover is essential for continuation of the carbon cycle. Unfortunately for archaeological residue analyses, once a component such as starch has entered the soil and begun to be broken down, it is rarely possible to determine just how much was originally present, owing to biochemical similarities in the make-up of all living things [31]. Compounding this problem is the fact that the ready availability of

Table 1
Susceptibility of storage starches to enzymatic degradation, ordered from most to least susceptible

	Starch	Granule size range (μm); average (μm)	Amylose content (%)	Gelatinisation temperature (°C)	References
Increasing susceptibility ==========>	Rice	3–8; 5	17–22.7	68–78	[42,213,214]
	Tapioca	3–28; 14	17–20	59–69	[42,206,213]
	Sorghum	3–26; 15	28	68.5–75	[134,213]
	Wheat	2–35; 15	25–28	58–64	[42,77,213]
	Maize	3–26; 15	24–29	62–72	[42,77,213]
	Sago	5–65; 30	27	60–72	[135,213]
	Arrowroot	5–70; 30	20–27	62–70	[135,162,213]
	Potato	5–100; 33	21–31.9	58–68	[42,213]

sugars in starch, along with the large quantities added to soils as part of either leaf litter or from storage organs, means that many bacteria and fungi have evolved to produce the extracellular enzymes necessary for starch degradation. As noted by Cheshire et al. [32:495], 'it is clear … that polysaccharide-decomposing bacteria are present at all times in soils and, as in the current experiment, may account for 20 to 30 percent of the bacterial population'.

Starch-hydrolysing enzymes have been found in practically every soil type studied, from forested areas to open grasslands, agricultural areas, river sediments, subantarctic semi-frozen soils and peat bogs [128,131, 188,189,193,235]. Viable cell-bound and extra-cellular amylases are even produced by alkaliphilic bacteria in soils from Ethiopian soda lakes in the Rift Valley area, where the ambient alkalinity is over pH 10 [154]. Enzyme activity tends to be higher closer to the soil surface, concentrated especially in the rhizosphere (the area immediately surrounding plant roots), but also surrounding earthworm burrows and other areas where organic materials are readily available [39]. Salam et al. [193] found that enzyme activity was greater at 0–20 cm depth than 20–40 cm in soils from several different land-use systems, correlated with soil nitrogen content. Similarly, a study of agricultural soils down to 3 m (in sand) and 4.2 m (in clay) revealed microbial, fungal and enzymatic activity was much higher near the surface than at mid-points and the base of the examined soil columns [216]. Fungal activity was absent from the deepest measured soils, however both microbial and enzyme activity (including that of starch-hydrolysing enzymes) was present throughout the soil profiles, with a strong positive correlation between microbes and enzymes, and between enzymes and soil organic matter. Taylor et al. [216:399] concluded that even at depth the two soils, 'with sharply contrasting physical and chemical composition and properties, are metabolically active and contain substantial numbers of microorganisms'. There is no reason, therefore, to expect archaeological sites within this depth range, and even deeper, to be free of starch-degrading agents. Furthermore, microbial decomposition can be expected to continue at most depths until all available substrate is consumed.

Several case studies have shown rapid degradation of starch in soils to be a normal process [67]. Martin [153:34], for example, notes 'individual polysaccharides such as starch … may be almost entirely decomposed in a few weeks'. Lahdesmaki and Piispanen [131] examined the concentration of several plant components, including starch, in fresh, recently fallen, and humus layer needles and leaves from spruce (*Picea abies*) and aspen (*Populus tremula*). They found that starch originally constituted some 1.5–4% of the plant dry weight, but that this fraction entirely degraded within a period of a few months to two years. Similar results were recorded by Fioretto et al. [66]. An in vitro experiment using fallow loam soil with an added wheat starch substrate showed that carbohydrate content of the soil returned to the level observed prior to starch addition after only 28 days [33], indicating complete degradation of the starch by this time. The same study noted a very rapid initial development of microbial activity upon addition of starch to the soil, with both fungal and bacterial elements acting to decompose the starches to their component sugars. Adu and Oades [2] found that more than half the carbon in starch in both sandy loam and clay soils was converted to carbon dioxide within 24 days of starch addition, with over 20% converted in the first 3 days. An asymptotic decay rate is typical for starch decomposition in soils, as for in vitro studies, with growing evidence suggesting that a large proportion of starch substrate may be lost in the first three days following incorporation into a soil [2,35,89]. Although the exact rate does vary (for example, Cheshire et al. [32] found 10% of wheat starch added to soil remained after 8 weeks), again the implications for residue analyses are that unprotected survival of starch grains in soils should be rare over archaeological time scales.

Apart from biotic attack by enzyme-producing fungi and bacteria, other factors can influence starch degradation in soils, although usually to a lesser degree. Variations in soil pH, temperature and moisture are the most important, both for their direct effect on starches and for their influence on soil flora and fauna. In most cases, however, it is the interplay between soil conditions and local enzyme-producing species which most dramatically alter starch preservation, through greater accessibility provided to soil microorganisms by the weakening or damage of starch granules. For example, a decrease in soil moisture could cause drying of starch grains, which substantially increases susceptibility to amylase attack [135:43]. Starches (particularly the amorphous component) are also vulnerable to hydrolysis in acidic or alkaline conditions, although this process is much slower than enzymatic decomposition, and slower again in granular rather than dispersed starch [31,71:291]. Overall soil pH is not as important to amylase activities as it is to other enzymes such as invertase [189:353], and while microorganisms prefer slightly acidic soils, the example of amylase-producing bacteria from soda lakes over pH 10 shows the adaptability of microbes to their environmental conditions. Temperature is similarly less of a concern than moisture levels, except where freezing soils physically damage grains [6] or fermenting soils reach temperatures close to the gelatinisation point. Many α-amylases lose activity over 50 °C, but this is not universal and deactivation may be moderated, for example, by the presence of calcium ions in the soil [85]. The presence of surface vegetation may play a small additional role—roots from living plants have been shown to

stimulate organic matter decomposition by inducing higher microbial activity [30]; see also [130]. Soil composition factors which may in fact help in starch preservation are considered later in this paper.

5. Transitory starch

Archaeological references to starch rarely discuss the important distinction between starch grains produced in the amyloplasts of major storage organs, and those produced in chloroplasts at the locations of photosynthesis (leaves and green stems). Most archaeologists who note the distinction do so in passing, and usually in the context of dismissing the diagnostic potential of small starch grains. For example, Loy [142:89] only mentions 'transient' starches as being one of the two main starch types, while Therin, Torrence and others [15:1234;138:695;220,221:451] interpret starch grains less than 5 μm as typically indicating general vegetation rather than plant foods. The size overlap between transitory and small storage starch grains has led to a situation in which starch grains less than 5 μm were not even counted in one Papua New Guinean study [15], despite the known presence in the area of food plants containing storage starch grains typically less than this size [13,74,75,144,209,241]. A greater understanding of transitory starches would therefore both allow the identification of 'background' starch levels and provide increased recognition to the role played by plants with small storage starch grains.

The mechanisms of production and destruction of chloroplast-formed starch have not been addressed in any detail in the archaeological literature. This situation should not be surprising, as even the plant physiological literature provides little information. One recent article [28:294] notes:

> Indeed, there is a relatively small literature on the transitory starch of leaves in general. Benchmark data for the rates and magnitude of reserve accumulation in leaves, even in plants which are primarily starch-accumulating species (SAS) are sparse and where data are available, the range of units in general usage makes comparisons between studies difficult. Most reports of synthesis and regulation have been restricted to the more experimentally amenable sink systems for storage of starch in seeds and tubers.

While the bias towards starches produced in storage organs is understandable given the increased diagnostic potential of larger grains, consideration of the nature of smaller grains is important at this stage of archaeological starch research to allow for more concrete conclusions than those currently offered to be drawn.

5.1. Transitory starch synthesis and in vivo degradation

Various names have been used in the plant physiological literature to describe the small starch grains formed in chloroplasts, including *assimilation* [158:4;196:83], *leaf* [71:275;166,184,208], and *transitory* [8:70;80,165,211,224,244], of which the latter currently has the most common usage. Although 'transient' has also been sporadically employed in both the archaeological and physiological literature (e.g. [142:89;161:974;236:486]), in order to maintain consistency, the term 'transitory' will be employed in this paper to describe starches originating in chloroplasts. Chloroplasts are the sites of photosynthesis in plants, and are so named for the green chlorophyll pigments they contain, which act as light energy receptors. As with all plastids, chloroplasts are internally differentiated into a system of membranes (the thylakoids) and a more or less homogenous matrix (the stroma) [185:48]. Starch formation in these plastids is via enzymes located in the stroma [8:71;234]. Chloroplasts are typically ellipsoidal in shape, and individually measure between 3 and 10 μm in diameter [47:7;88:11;129:1801;132:58]. The surface of a leaf may contain some 500,000 chloroplasts per square millimetre [185:49]. In higher plants, the ability to lay down transitory starch is manifested long before chloroplast pigmentation [152:29], and in at least some species the starch level exhibits seasonal variation [95,140,197].

Transitory starch grains are a temporary form of carbohydrate storage produced only when a plant is actively photosynthesising [185:49]. They are exhibited by many higher plants, however, the proportion of newly assimilated carbon allocated by different plants to starch production varies considerably, and a number of species do not accumulate starch in their chloroplasts at all under normal growth conditions [225:206]. Although the most common and commonly studied transitory starches are present in leaves, they may also be present in green stems and shoots [71:277]. The regulatory mechanisms involved in transitory starch synthesis and degradation within the chloroplast are currently incompletely understood [80]; for a detailed discussion of the enzymes and possible pathways involved, see Trethewey and Smith [225] (cf. [79]). The following summary represents the state of current understanding of these processes.

The daylight hours during which starch is formed are generally referred to as the photoperiod [165:20249;244], with the synthesis of new starch granules in chloroplasts beginning shortly after exposure to light [28:297;200:1170]. It is likely that new starch grains continue to be initiated throughout the photoperiod [165]. Over the course of a single day, starch content in the leaves of a plant may rise at a rate of up to 41 mg/h per g of fresh plant weight (in *Phaseolus vulgaris* leaves;

[204]), although the majority of reported rates are less than 4 mg/h per g of fresh weight [28:301, Table 1]. As an example, *Bryophyllum calycinum* leaves accumulated approximately 20 mg/g fresh weight over the course of a day, at a rate of 1–2 mg/h per g of fresh weight [232:371]. Similarly, starch in the leaves of *Arabidopsis thaliana* (mouse-ear or thale cress) accumulated from almost zero to around 13 mg/g fresh weight over a 12 h period [244:1704].

Other plants exhibit lower total transitory starch levels and synthesis rates: *Pisum sativum* (pea) leaf starch reached between 3.6 and 4.5 mg/g fresh plant weight after an approximately 15 h photoperiod [224], starch in leaves of *Lolium temulentum* (ryegrass) reached 7.5 mg/g fresh weight at a rate of 0.6 mg/g per h [27:223;28:297], and *Zea mays* (maize) leaves accumulated starch at a rate of 0.34 mg/g per h [29:143]. Comparable rates have been observed in spinach, soybean and sugar beet leaves [29]. Accumulation of starch in ryegrass was noted despite the limited capacity shown by fructan-accumulating grasses to polymerise and mobilise transitory starches [27]. The initial synthesis of starch is controlled in at least some higher plants by the regulatory action of photosynthesis-driven pH changes in the stroma [80,211:215], with an initially slow rate of starch production until pH inhibition of hydrolysing enzymes allows synthesis to exceed degradation. It has been shown, however, that starch degradation in the chloroplast is not a significant factor over the course of the synthesising photoperiod [68:676;243].

Following a return to darkness, transitory starch loss from leaves is typically immediate and rapid as carbon stores are mobilised [199], corresponding to a doubling in the activity of the chloroplastic amylose enzyme [80] and proceeding at an essentially linear rate [244]. In this manner, transitory starch enables the leaves to continue exporting sugars during the night period [165]. There have been reported exceptions to the immediate loss of starch, in which barley [82] and sugar beet [68] leaves exhibited a lag in mobilisation upon commencement of the dark period, owing to high sucrose levels in the chloroplast. Similarly, recent studies show that *Panax quinquefolius* (American ginseng) is unable to mobilise its transitory starch reserves to anywhere near the same extent as *Panax ginseng* (Korean ginseng), spinach or pea leaves [161:975]. Instead, *P. quinquefolius* synthesises transitory starch at a high rate early in leaf development and maintains starch at a high level in both light and dark conditions. These cases are not considered typical, however [82:845].

5.2. Transitory starch appearance and structure

Attributes of transitory starches which may be of use in the microscopic differentiation of archaeological starch residues include grain size, appearance and structure. As for transitory starch synthesis, the appearance and physicochemical composition of transitory starch granules is an issue still under investigation [27:228;224:32]. It is, however, generally agreed that, in keeping with their transitory nature, the grains themselves are smaller than those produced by most plants for long-term starch storage (e.g. [71:275;184]). The few reports detailing the microscopic appearance of these granules show that they range in size from 0.2 to 7 μm, with the largest range represented within the leaves of the sunflower, *Helianthus annuus* [184]. Broken down into size classes, the maximum diameter of 70–80% of sunflower transitory starch is between 1.5 and 2.5 μm, while 1–2% of grains fall between 4 and 5.5 μm. The larger grains possess centric hila, while the smallest grains (0.2–1.0 μm) did not exhibit any hila. These findings are reported by Radwan and Stocking [184:682] to be comparable with grains isolated from potato leaves by Meyer and Heinrich [159].

The general shape of the sunflower starch grains is discoid, although some tend towards a more spherical appearance [184:682]. A similar flattened discoid shape, with distinctly irregular margins, was noted for the transitory leaf starch of *L. temulentum*, *A. thaliana* and *Ipomoea cordatotriloba* (a wild relative of sweet potato). In the former two species, *L. temulentum* possessed grains averaging 1.7 μm in diameter (range 0.9–3.5 μm), and *A. thaliana* grains 1–2 μm in diameter and 0.2–0.5 μm in thickness ([27,243,244]; see also [8:71]). The leaf starch of *I. cordatotriloba* is somewhat larger at 3–7 μm [124]. Despite the paucity of information available on the subject, it is reasonable to suggest at this stage that transitory starch grains should therefore generally be discoid in shape, have irregular margins, and typically be less than 4–5 μm in diameter, with some grains up to 7 μm.

In terms of internal structure, transitory starch grains contain both branched and unbranched glucose polymers which correspond to the amylopectin and amylose fractions seen in storage starch [225:209]. Importantly, several researchers have discovered that the ratio of these two polymers appears to differ from that found in the reserve organs, with lower percentages of amylose found in transitory starch (e.g. [27:225;55:1767;155:253;224:36]). The amylose percentages for various transitory leaf starches and their corresponding storage starch percentages in non-mutant plants are shown in Table 2. Plants which have not had their transitory starch analysed for amylose content have been included to show typical values for storage starch granules. A notable exception to the general rule is the leaf starch of *I. cordatotriloba*, which has an atypically high amylose fraction, perhaps due to long-term starch storage in the leaves, as has been observed in tobacco leaves [155].

Amylopectin dominance in transitory grains means that they retain the semi-crystalline and birefringence

Table 2
Amylose percentage in transitory and storage starches of selected plants

Species	Common name	Amylose %		References
		Transitory starch	Storage starch	
Solanum tuberosum	Potato	9.8–14.1	21–31.9	[42,105,107,213]
Oryza sativa	Rice	12.6	17–22.7	[196,213,214]
Ipomoea cordatotriloba	Wild sweet potato relative	25.3	19.0	[124]
Pisum sativum	Pea	<5	30–43.5	[42,224]
Lolium temulentum	Ryegrass	14	29	[27]
Arabidopsis thaliana	Mouse-ear (or thale) cress	6	–	[243]
Triticum aestivum	Wheat	–	25–28	[77,213]
Zea mays	Maize	–	24–29	[42,77,213]
Hordeum vulgare	Barley	–	26–29.2	[116,215]
Colocasia esculenta	Taro	–	14–21.4	[105,162]
Dioscorea esculenta	Lesser yam	–	14–30	[105,162]
Canna edulis	Queensland arrowroot	–	38	[207]

properties typical of larger storage grains, including the 9-nm thick lamellae seen in storage starch [165]. Use of iodine staining to differentiate the amylose (blue stain) and amylopectin (red to purple) fractions have shown that in sunflower transitory starch, the amylose fraction is concentrated more towards the centre of the grain [184:682]. Along with a trend towards increasing percentages of amylopectin during the photoperiod, this may suggest that it is amylopectin which is preferentially synthesised and degraded as part of the diurnal cycle [225]. In terms of archaeological investigation, staining smaller grains with iodine and observation of colour should help in the differentiation of starches derived from transitory versus storage contexts. Much more work needs to be done in this area, however, to test the viability of this method and its applicability to archaeological starches.

6. Discussion

6.1. Implications for soil residue studies

As the evidence reviewed so far suggests that starch grains are rapidly decomposed in most soils, how then can the recovery of any grains from archaeological soils be explained? There are a number of possible answers to this question, each of which approaches the problem from a different angle. First, starches may survive through sheer weight of numbers. It has been estimated that 1 kg of corn starch comprises some 1,000,000,000,000 individual starch granules [213:22]. Similarly, the presence of half a million chloroplasts for every square millimetre of a leaf can lead to the creation of an enormous number of transitory starch grains every day. Under the influence of the asymptotic decomposition rate seen in most starch degradation experiments, through pure chance at least a few grains might therefore survive to be recovered archaeologically. In addition, the simultaneous addition to soils of large numbers of grains (from a decaying tuber or seed, for example) results in starch clusters rather than individual separated granules. In turn the decreased available surface area of clustered granules, and the interaction of starch with other plant components such as cellulose and lignin, can be expected to result in much lower levels of initial degradation [56,126]. Even within whole barley grains preserved by extreme aridity in Egyptian Nubia, however, starch components showed a significant decrease after 600 years when analysed by pyrolysis-gas chromatography/mass spectrometry [18]. Further observations of vegetable decay processes in starch-bearing organs are necessary to determine just how starch decomposition relates to other tissues.

Survival of starch due to high numbers or clustering is likely to be a species specific occurrence, given the evidence for differential degradation by amylases discussed above. In such cases, diachronic quantitative studies of archaeological starch should include estimated quantities of starch produced by the plant or process which is suggested as the cause of the residue. The various sources of starch can then be ranked in terms of both initial abundance of starch grains and predicted survival rate based on grain characteristics (amylose content, size, shape, etc.), and this ranking compared to recovered starch quantities. Quantitative synchronic starch patterning (e.g. [10]) should be less affected by differential survival as all grains have been in the ground for the same period of time, although any qualitative study involving grain sizes or identification will be affected. Obviously, starch recovery techniques will also be a factor in any quantitative study.

The stability of the starch granular structure has been cited by some archaeological researchers as contributing to its longevity in soils (e.g. [220:447]). Cheshire et al. [32:497] on the other hand suggest ‘that the stability of

the polysaccharide in soil is caused by inaccessibility or insolubility as a result of its relationship with other soil components, and not by a biologically stable molecular structure *per se*'. Dimbleby [51:1] noted that pollen survival in land sites is only possible if some factor exists which inhibits microbiological decay, and the same reasoning applies to starch grains. In the soil protective mechanisms do exist, for example, starches may be protected from enzymatic attack by the presence of soil aggregates, clays, or heavy metals.

The formation of soil aggregates and the effect of this process on starch has been studied by Guggenberger et al. [89]. They found that once starch was added to a soil, stimulation of fungal hyphae growth in the areas of highest substrate concentration led to the creation of soil aggregates greater than 250 μm (macroaggregates) from smaller soil particles, held together by fungal exudates and hyphae. Starch that remained associated with smaller microaggregates (<53 μm and 53–250 μm) was then subjected to a slower decay rate and a shorter overall period of attack than that incorporated into the new macroaggregates, as both fungi and bacteria retained access to the larger accumulations. Fungi (with an average hyphal width of 2.3–2.4 μm) were unable to access the starch in the smaller aggregates as readily. While starch therefore triggers the formation of the macroaggregates which permit continued and rapid degradation, any starch which is incorporated into a smaller soil structure has a better chance of stabilisation and survival. This physical protection of starch and other organic material, either through aggregation or small soil pore size, has been recorded by several authors [2,81,86,115]. Starch may be released from aggregates and become available for decomposition, however, either by mechanical disruption (including archaeological excavation) or repeated drying and wetting of the soil [1,57]. Fungal activity is not the only factor in aggregate formation, either, and the contribution of other components of soil organic matter to aggregate formation has also been noted [117,153].

Clay soils have been discussed in relation to the preservation of animal-derived organic proteins (e.g. [41,48,90,168]; see also [180]), and evidence suggests they can play a role in the prevention of starch decomposition as well. Two processes working in conjunction have been suggested as means of clay influence on organic matter survival: (1) inactivation of enzymes by clays, and (2) adsorption of the substrate by clay minerals and subsequent protection from degradation [130,147]. Ross [190] clearly demonstrates the marked effect of both clays and clay fractions obtained from soils in reducing the activity of α-amylase and β-amylase. In particular montmorillonite and kaolinite clays almost totally stopped amylase activity. The exact mechanism of the adsorption of enzymes is a matter still under examination, but the existence of both external and internal (owing to expanding clay lattices) adsorption surfaces provides abundant area for entrapment [24]. The same situation applies of course to organic substrates such as starch. Lynch and Cotnoir [147] found that soluble substrates showed little reduction in decomposition in the presence of clays, but insoluble substrates were to some degree protected, in particular by the expandable montmorillonite. They postulated that a combination of intermediate breakdown products being adsorbed and therefore protected against enzyme activity, and enzymatic inactivation were responsible for organic survival.

The effect of heavy metals such as lead, copper, aluminium, iron, and zinc on lowering rates of organic decomposition has been established over the past 50 years and more [19,52]. Studies involving amylase, cellulase and invertase in particular have shown that the presence of metals in soils inhibits enzyme activity by a combination of inhibiting enzyme synthesis by soil microorganisms and disrupting the normal interaction of enzymes with available substrate [49,53]. Inhibition of an enzyme by metals results from the capacity of metals to form stable complexes with proteins, affecting the enzyme's active sites [78]. Each of these factors slows down the degradation of starch by reducing the level of contact between enzymes and starch grains. A practical demonstration of the effect this can have on decomposition is provided by Joshi et al. [113], who examined leaf litter from alder and pine trees located next to a highway, and compared degradation of cellulose, starch, and sucrose to leaf litters from a forest away from any pollutants. They discovered that microbial population numbers, and therefore bacterial enzyme activity levels, were consistently lower in the site next to the highway owing to metal accumulation in the soil. Concentrations of lead, zinc and copper were up to six times higher in the roadside soils than the unpolluted soils.

Aluminium has been found to have a significant effect in lowering decomposition rates of both cellulose and non-cellulosic polysaccharide [160], because of the high affinity of organic materials for aluminium hydroxide. Once bound to the metal, substrate is unavailable for interaction with enzymes, thus retarding decomposition. In addition, copper artefacts have been shown to have a preservative effect on nearby organic materials including seeds, grass, wood, pollen, linen, flax and hemp due to the biocidal effect of the cupric salts [122,133]. It should be noted that unless metals are continually added to a soil through dumping, pollution or metal artefact decay, the inhibitory effect will slowly dissipate, however this process may take several years.

A further possible explanation for starch survival is that protection in archaeological contexts may in fact be provided by artefacts, and starch grains recovered from soils therefore represent 'contamination' of the surrounding soil by starch dislodged from the shelter of an

artefact [5]. This issue is discussed in further detail below, although the survival of any starch grain once separated from the protective environment could be expected to be short. Any starch recovered from sediments located near a starch-covered artefact should only have been in that sediment for a period of not more than a few years, provided none of the other protective mechanisms mentioned have continued to shield the grain following its dislodgement.

Finally, it is possible that starch grains are able to move within the soil profile in greater numbers than currently proposed. Grains from deep archaeological sites therefore may not be contemporaneous with the cultural layer in which they are found. That some starch grains do move under the influence of groundwater has been proven by results obtained in limited experimental studies [75,219], but this movement has been suggested to involve chiefly the smaller grains [219:70]. Comparisons with palynological studies, where calculated downward percolation rates average around 1 cm per 4–30 years for a portion of the pollen record [51:59; 120,121], and phytolith movement research [96] also lend weight to the supposition that at least some starch will move in sediments. Research into this subject is ongoing, however at this stage large scale movement of starch grains through a natural soil appears unlikely. Archaeological field estimates of soil porosity and permeability (e.g. [167]; see [16] for other tests) would aid in any starch movement calculations. As our knowledge currently stands, degradation of starch following initial introduction into the soil is expected to play a much more important role in determining starch content of any soil (recent or buried) than percolation of grains through groundwater or soil movement.

Even at this early stage in the investigation of archaeological starch survival in soils, there is cause for guarded optimism. Studies such as those of Therin et al. [220], showing a clear decrease in numbers of starch grains less than 5 μm in diameter from the earliest to later levels of the FAO site in PNG, interpreted as a vegetation change coincident with early use of the site, are promising. Similarly encouraging are the results obtained by Iriarte et al. [108], in demonstrating the likely presence of maize and other cultivars at various sites in Uruguay through starch analysis. Caution is required, however, regarding reports dealing specifically with starch in soils which do not include an assessment of at least some of the variables affecting starch survival. Insufficient attention has been given to decompositional factors to assume that starch recovered is necessarily reflective of starch deposited at a site over a period of thousands of years. This is especially true when absolute starch counts number only in the hundreds (or less) per gram of sediment, as acknowledged [220:457].

6.2. Implications for artefact residue studies

Starch residues appear to survive for long periods of time provided they are in some manner sheltered or occluded from the typical processes of natural decomposition. The literature concerning starch residues on artefacts shows that artefact surfaces constitute one such protective mechanism. Increasingly, organic residue studies have found that artefacts of different materials create a ‘microenvironment’ which acts to prevent decomposition through restricted access to the residue. Researchers examining artefacts for general plant remains [3:394;104:96], pollen [121], wood [93], and starch [177,181,183], as well as blood, proteins and DNA [202] have all credited a protective role played by the artefact itself as a factor in the survival of residues.

Kelso et al. [121] provided one of the clearest examples in their analysis of pollen from a seventeenth-century refuse pit in Virginia, USA. In this study, pollen was found in two contexts: in the sediment filling the pit, and immediately under artefacts (including floor tiles, bricks and bottle glass) found in the pit. Pollen was recovered from all samples taken under artefacts, while the deepest pollen found in the pit sediments, representing a normal percolation profile undergoing decay, was 25 cm above the most shallow pollen associated with an artefact. Kelso et al. [121:52] interpret this sterile 25 cm gap as evidence that the artefact-associated pollen was deposited contemporaneously with, and owed its preservation to the shelter provided by, those artefacts. There is no biochemical reason why a similar situation should not be possible for starch, although the exact preservative process is not yet understood. One cause postulated by many researchers is that residues become trapped in crevices and cracks in an artefact’s surface. Although it is rarely explicitly discussed, this entrapment may limit access to starch and other organic remains by microorganisms and enzymes, as well as protecting them to some extent from fluctuations in soil moisture, temperature and pH.

Consistently across all studies, starch grain frequencies in control sediments are significantly lower than those on artefact surfaces. As Kelso et al. [121] have shown that the concept of an artefact-based ‘microenvironment’ may be extended from residues on an artefact’s surface to those in immediately neighbouring soils, the absence of starch grains in sediments outside the protective influence of starch-bearing artefacts, so often taken as proof of residue authenticity, may therefore just as likely represent the preferential decay of unprotected starch in soil. In a study from Papua New Guinea, Fullagar et al. [75] noted much higher numbers of starch grains in soil actually adhering to artefacts than in background sediment samples. This is precisely what would be expected if such preferential decay was occurring. Ongoing research at the Mayan

site of Copán also supports this hypothesis. Obsidian artefacts from a pit context at Copán analysed for use-wear and residues contained large numbers of starch grains in portions of the adhering sediment [97], although associated soil samples were not available for comparison at the time the study was undertaken. Subsequently, soil samples have been analysed from the pit, and preliminary results suggest that starch is present in much lower numbers in the soil samples than was observed in the attached soil. In this case, the high starch levels in the sediment adhering to the artefacts are taken to be a much truer reflection of starch levels in the sediment at the time of pit in-fill than those seen in the archaeological soil samples, owing to differential decay in the two contexts.

Concerns over the contamination of artefacts by starch residues unrelated to artefact use following deposition should be eased by the findings of this review. Any starch found on an artefact should represent either authentic contact-residue (either from use or incidental contact) or sediment transfer within the first months of deposition. By incorporating use-wear into the analysis of such artefacts, information can therefore be gleaned about either the processing of starchy plants (if residues are positively correlated with use-wear) or the environment at the time of deposition (if residues are not associated with use-wear). The integration and discrimination of transitory starch grains into artefact studies will aid in distinguishing cultural and natural influences on the starch assemblage at a site. In either case, the negative connotations often associated with the term 'contamination' should be less of a concern, provided the focus is instead on examining starch residues within a framework of revealing the 'life-history' of the artefact [198]. Out-of-hand dismissal of any artefact residue, related or not to actual tool use, can only serve to limit the environmental and depositional information available.

6.3. Transitory starch

One focus of current research into archaeological starch residues is on the identification of tuber and root starches where other tuberous remains are poorly preserved (e.g. [14,45,144,177,178,220,227,228,229]). An issue arising out of this investigation is the very small size of the starch grains from some of these plants. Potentially, this could lead to uncertainty or misidentification of transitory grains as belonging to storage organs (or vice versa). Both *Colocasia esculenta* (taro) and *Dioscorea esculenta* (yam) have been included in Table 2 because of the small size of the starch grains located in their underground storage organs. *C. esculenta* has storage starch grains measuring 1–10 μm, with the majority of grains <4 μm in diameter [105:254;141, 163,162:563]. Likewise, numerous studies have shown *D. esculenta* to have storage grains measuring 1–5 μm [105:254;162:563], with the typical granule shape for both species being round/polygonal/oval. The overlap in size with all transitory starch grains currently characterised is clear, although granule shape and amylose fraction (determined through iodine staining) may provide an avenue for discrimination. Moorthy et al. [163] note that of the 10 cultivars of taro they examined the largest granules were found in the cultivar with the highest amylose content, although this relationship was not consistent for the remainder of the cultivars. Despite the relatively low amylose content of *C. esculenta* and *D. esculenta* when compared to other storage starches, this content is still higher than that seen in all but one of the transitory starches characterised to this point.

The small size of certain storage starches means that once methods for differentiating between these and transitory grains are developed, species such as *C. esculenta* and *D. esculenta* can be re-incorporated into studies where they might otherwise have been overlooked. Blanket statements such as 'previous work has shown that grains below 5 μm are rarely diagnostic to taxa and merely represent plant tissue' [15:1234] can then be refined, and specific differences examined. The inclusion of comments such as the one quoted creates further confusion when at least three of the five references provided to support the statement [46,144, 164] in fact contradict it, as each of the three studies provide evidence for storage starches below 5 μm in size (in *Hordeae* sp.; *C. esculenta* and *D. esculenta*; and rice, wheat and barley respectively). Additionally, identification of taro starch via 'size, shape, surface morphology, clustering and co-occurrence of raphides' on three artefacts from Kuk Swamp, PNG, has recently been announced by one of the authors of the Barton et al. study [50:191]. Incorporation of techniques designed specifically to target distinguishing characteristics of transitory grains will lend added weight to any future claims concerning residues of small storage starch.

6.4. Future directions

Several avenues must be pursued to gain a more complete understanding of the relationship between observed archaeological residues and the behavioural, social and environmental contexts in which they were produced. One of the key areas to be addressed concerns the impact of human activity on starch preservation [6,10,16]. Compaction of sediments in living areas, agricultural activities including soil tillage, the impact of fires and food processing techniques, and trash disposal all have an effect on either soil properties or soil microorganisms, and on residue survival. Preservation should therefore be greater in a compacted soil by restricting biotic access to organic residues, while it should be decreased in soils where aggregates are

mechanically disturbed by agricultural curation. The creation of a project dedicated to the observation of starch survival under a variety of circumstances has been considered (for example at the Ancient Starch Research Group meeting in February 2000 in Sydney), but as yet such projects are still under development. Nonetheless, knowledge about archaeological starches is increasing at an accelerating rate, and the efforts of a comparatively small group of researchers over the past 20 years have already given us important insights into ancient subsistence activities and the spread of agriculture which cannot be attained through other techniques. Continued recognition and investigation of the processes affecting archaeological starch degradation will provide us with even more confidence in the reconstruction and interpretation of ancient starch use.

7. Conclusion

Many of the issues currently confronting archaeological starch residue analysts are not new. Sixty-five years ago, Walter Von Stokar [233] commented on organic residues found on artefacts throughout Europe. He advocated control sampling of soils surrounding ceramic pots being chemically tested for residues, and the examination of artefacts with at least a magnifying glass prior to cleaning. He also pointed out a crucial aspect of any residue study: 'Not until one began to study systematically the decomposition phenomena of organic fragments was a successful advance possible' [233:83]. Despite significant technological advances made in the intervening years, the practical bases for undertaking residue analysis (examination of uncleaned artefacts, control soil samples, and a thorough understanding of the composition and decomposition of the residues analysed) remain the same today as then. This review represents one step towards the goal of comprehensive understanding of archaeological starch, by incorporating biochemical, physiological and archaeological literature, and by suggesting further avenues of research.

The interaction between soil organic matter, soil microorganisms and soil structure and properties is extraordinarily complex. It is also the environment in which archaeological materials spend the vast majority of their existence, and it can be ignored only at the cost of the faithfulness of archaeological reconstruction to past reality. Concern over biases created by differential decomposition is perhaps even more applicable to microscopic plant components than macroscopic elements of the archaeological record, as the smallest particles are interacting with bacteria, fungi and soil changes which can destroy them entirely within a very short period of time if they are not protected. As numerous archaeological starch studies have shown, however, protective mechanisms do exist, and residue studies can continue to fill the important niche they currently occupy provided those protective forces are acknowledged and potential biases accounted for.

Acknowledgements

I would like to thank Jay Hall, Richard Fullagar, Tom Loy, Sean Ulm and Alison Crowther for informative comments and criticisms of various manuscript drafts, and colleagues in the Archaeological Science Laboratory at the University of Queensland for their support. Fieldwork in Copán was facilitated by the Honduran Institute of Anthropology and History and Dr Rene Viel. Funds were supplied in part by an Australian Postgraduate Award.

References

[1] J.K. Adu, J.M. Oades, Physical factors influencing decomposition of organic materials in soil aggregates, Soil Biology and Biochemistry 10 (1978) 109–115.
[2] J.K. Adu, J.M. Oades, Utilization of organic materials in soil aggregates by bacteria and fungi, Soil Biology and Biochemistry 10 (1978) 117–122.
[3] P. Anderson-Gerfaud, Aspects of behaviour in the Middle Palaeolithic: functional analysis of stone tools from southwest France, in: P. Mellars (Ed.), The Emergence of Modern Humans: An Archaeological Perspective, Cornell University Press, Ithaca, NY, 1990, pp. 389–418.
[4] J. Atchison, Analysis of food starch residues at the Jinmium archaeological site, Northern Territory, unpublished BEnvSc (Hons) thesis, University of Wollongong, Wollongong, 1994.
[5] J. Atchison, R. Fullagar, Starch residues on pounding implements from Jinmium rock-shelter, in: R. Fullagar (Ed.), A Closer Look: Recent Australian Studies of Stone Tools, Archaeological Computing Laboratory, University of Sydney, Sydney, 1998, pp. 109–125.
[6] M.d.P. Babot, Starch grain damage as an indicator of food processing, in: D.M. Hart, L.A. Wallis (Eds.), Phytolith and Starch Research in the Australian-Pacific-Asian Regions: The State of the Art. Papers from a conference held at the ANU, August 2001, Canberra, Australia, 2001, Pandanus Books, Canberra, 2003, pp. 69–81.
[7] M.d.P Babot, M.C. Apella, Maize and bone: residues of grinding in Northwestern Argentina, Archaeometry 45 (1) (2003) 121–132.
[8] N.P. Badenhuizen, Occurrence and development of starch in plants, in: R.L. Whistler, E.F. Paschall (Eds.), Starch: Chemistry and Technology, Academic Press, New York, 1965.
[9] R.W. Bailey, J.C. Macrae, Hydrolysis of intact leaf starch grains by glucamylase and alpha-amylase, FEBS Letters 31 (2) (1973) 203–204.
[10] J. Balme, W. Beck, Starch and charcoal: useful measures of activity areas in archaeological rockshelters, Journal of Archaeological Science 29 (2002) 157–166.
[11] J. Balme, G. Garbin, R. Gould, Residue analysis and palaeodiet in arid Australia, Australian Archaeology 53 (2001) 1–6.
[12] W. Banks, C. Greenwood, Starch and its Components, Edinburgh University Press, Edinburgh, 1975.
[13] J. Barrau, Subsistence Agriculture in Melanesia, Bernice P. Bishop Museum Bulletin No. 219, Bernice P. Bishop Museum, Honolulu, HI, 1958.
[14] H. Barton, Raw material and tool function: a residue and use-wear analysis of artefacts from a Melanesian rockshelter,

unpublished BA (Hons) thesis, University of Sydney, Sydney, 1991.
[15] H. Barton, R. Torrence, R. Fullagar, Clues to stone tool function re-examined: comparing starch grain frequencies on used and unused obsidian artefacts, Journal of Archaeological Science 25 (1998) 1231–1238.
[16] W. Beck, The taphonomy of plants, in: W. Beck, A. Clarke, L. Head (Eds.), Plants in Australian Archaeology, Tempus, vol. 1, Anthropology Museum, University of Queensland, Brisbane, 1989, pp. 31–53.
[17] R.A. Blanchette, T. Nilsson, G. Daniel, A. Abad, Biological degradation of wood, in: R.M. Rowell, R.J. Barbour (Eds.), Archaeological Wood: Properties, Chemistry and Preservation, American Chemical Society, Washington, DC, 1990, pp. 141–174.
[18] H.A. Bland, P.F. van Bergen, J.F. Carter, R.P. Evershed, Early diagenetic transformations of proteins and polysaccharides in archaeological plant remains, in: B.A. Stankiewicz, P.F. van Bergen (Eds.), Nitrogen-Containing Macromolecules in the Bio- and Geosphere, American Chemical Society, Washington, DC, 1998, pp. 113–131.
[19] J.M. Bremner, R.L. Mulvaney, Urease activity in soils, in: R.G Burns (Ed.), Soil Enzymes, Academic Press, London, 1978, pp. 149–196.
[20] F.L. Briuer, New clues to stone tool function: plant and animal residues, American Antiquity 41 (4) (1976) 478–484.
[21] J.E. Brochier, M. Thinon, Calcite crystals, starch grains aggregates or … POCC? Comment on 'calcite crystals inside archaeological plant tissues', Journal of Archaeological Science 30 (9) (2003) 1211–1214.
[22] V. Bryant, S. Hall, Archaeological palynology in the United States: a critique, American Antiquity 58 (2) (1993) 277–286.
[23] V. Bryant, R. Holloway, The role of palynology in archaeology, in: M.B. Schiffer (Ed.), Advances in Archaeological Method and Theory, Academic Press, New York, 1983, pp. 191–224.
[24] R.G. Burns, Enzyme activity in soil: some theoretical and practical considerations, in: R.G. Burns (Ed.), Soil Enzymes, Academic Press, London, 1978, pp. 295–340.
[25] R.G. Burns (Ed.), Soil Enzymes, Academic Press, London, 1978.
[26] R.G. Burns, Enzyme activity in soil: location and a possible role in microbial activity, Soil Biology and Biochemistry 14 (1982) 423–427.
[27] A.J. Cairns, P. Begley, I.M. Sims, The structure of starch from seeds and leaves of the fructan-accumulating ryegrass, *Lolium temulentum* L., Journal of Plant Physiology 159 (2002) 221–230.
[28] A.J. Cairns, A. Cookson, B.J. Thomas, L.B. Turner, Starch metabolism in the fructan-grasses: patterns of starch accumulation in excised leaves of *Lolium temulentum* L., Journal of Plant Physiology 159 (2002) 293–305.
[29] N.J. Chatterton, J.E. Silvius, Photosynthate partitioning into leaf starch as affected by daily photosynthetic period duration in six species, Physiologia Plantarum 49 (1980) 141–144.
[30] W. Cheng, D.C. Coleman, Effect of living roots on soil organic matter decomposition, Soil Biology and Biochemistry 22 (6) (1990) 781–787.
[31] M.V. Cheshire, Nature and Origin of Carbohydrates in Soils, Academic Press, London, 1979.
[32] M.V. Cheshire, M.P. Greaves, C.M. Mundie, Decomposition of soil polysaccharide, Journal of Soil Science 25 (1974) 483–498.
[33] M.V. Cheshire, C.M. Mundie, H. Shepherd, Transformation of ^{14}C glucose and starch in soil, Soil Biology and Biochemistry 1 (1969) 117–130.
[34] A.M. Child, Towards an understanding of the microbial decomposition of archaeological bone in the burial environment, Journal of Archaeological Science 22 (1995) 165–174.
[35] J.L. Chotte, J.N. Ladd, M. Amato, Sites of microbial assimilation, and turnover of soluble and particulate ^{14}C-labelled substrates decomposing in a clay soil, Soil Biology and Biochemistry 30 (2) (1998) 205–218.
[36] K.H. Clary, Appendix C: Exploratory pollen studies from contemporary maize (*Zea mays* L. ssp. *mays*) processing facilities, the Puuc region, Northwestern Yucatan, Mexico, in: M.P. Smyth (Ed.), Modern Maya Storage Behaviour: Ethnoarchaeological Case Examples from the Puuc Region of Yucatan, University of Pittsburgh, Pittsburgh, PA, 1991, pp. 129–150.
[37] J. Coil, Design, methods and initial results for microfossil research in Kahikinui, Maui, Hawaiian Islands, in: D.M. Hart, L.A. Wallis (Eds.), Phytolith and Starch Research in the Australian-Pacific-Asian Regions: The State of the Art. Papers from a conference held at the ANU, August 2001, Canberra, Australia, Pandanus Books, Canberra, 2003, pp. 55–68.
[38] J. Coil, M.A. Korstanje, S. Archer, C. Hastorf, Laboratory goals and considerations for multiple microfossil extraction in archaeology, Journal of Archaeological Science 30 (2003) 991–1008.
[39] D.C. Coleman, D.A. Crossley, Fundamentals of Soil Ecology, Academic Press, San Diego, CA, 1996.
[40] M.J. Collins, M.S. Riley, A.M. Child, G. Turner-Walker, A basic mathematical simulation of the chemical degradation of ancient collagen, Journal of Archaeological Science 22 (1995) 175–183.
[41] M.J. Collins, D. Walton, A. King, The geochemical fate of proteins, in: B.A. Stankiewicz, P.F. van Bergen (Eds.), Nitrogen-Containing Macromolecules in the Bio- and Geosphere, American Chemical Society, Washington, DC, 1998, pp. 74–87.
[42] J.W. Cone, M.G.E. Wolters, Some properties and degradability of isolated starch granules, Starke 42 (1990) 298–301.
[43] A.R. Cortella, M.L. Pochettino, Starch grain analysis as a microscopic diagnostic feature in the identification of plant material, Economic Botany 48 (2) (1994) 171–181.
[44] O.E. Craig, M. Collins, The removal of protein from mineral surfaces: implications for residue analysis of archaeological materials, Journal of Archaeological Science 29 (2002) 1077–1082.
[45] A. Crowther, Pots, plants and Pacific prehistory: residue analysis of plain Lapita pottery from Anir, New Ireland, c. 3300BP, unpublished BA (Hons) thesis, University of Queensland, Brisbane, 2001.
[46] A. Czaja, Structure of starch grains and the classification of vascular plant material, Taxon 27 (1978) 463–470.
[47] S.M. Danks, E.H. Evans, P.A. Whittaker, Phtosynthetic Systems: Structure, Function and Assembly, Function and Assembly, John Wiley & Sons, Chichester, 1983.
[48] A. De Cristofaro, A. Violante, Effect of hydroxy-aluminium species on the sorption and interlayering of albumin onto montmorillonite, Applied Clay Science 19 (2001) 59–67.
[49] S.P. Deng, M.A. Tabatabai, Cellulase activity of soils: effect of trace elements, Soil Biology and Biochemistry 27 (7) (1995) 977–979.
[50] T.P. Denham, S.G. Haberle, C. Lentfer, R. Fullagar, J. Field, M. Therin, N. Porch, B. Winsborough, Origins of agriculture at Kuk Swamp in the Highlands of New Guinea, Science 301 (2003) 189–193.
[51] G.W. Dimbleby, The Palynology of Archaeological Sites, Academic Press, New York, 1985.
[52] P. Doelman, L. Haanstra, Effects of lead on the decomposition of organic matter, Soil Biology and Biochemistry 11 (1979) 481–485.
[53] P. Doelman, L. Haanstra, Effects of lead on the soil bacterial microflora, Soil Biology and Biochemistry 11 (1979) 487–491.
[54] M. Dominguez-Rodrigo, J. Serralonga, J. Juan-Tresserras, L. Alcala, L. Luque, Woodworking activities by early humans: a plant residue analysis on Acheulian stone tools from Peninj (Tanzania), Journal of Human Evolution 40 (2001) 289–299.

[55] A. Edwards, J-P. Vincken, L.C.J.M. Suurs, R.G.F. Visser, S.C. Zeeman, A.M. Smith, C. Martin, Discrete forms of amylose are synthesised by isoforms of GBSSI in pea, The Plant Cell 14 (2002) 1767–1785.
[56] G. Eglinton, G.A. Logan, Molecular preservation, Philosophical Transactions of the Royal Society of London Series B 333 (1991) 315–328.
[57] E.T. Elliott, Aggregate structure and carbon, nitrogen, and phosphorous in native and cultivated soils, Soil Science Society of America Journal 50 (1986) 627–633.
[58] J.A. Entwistle, P.W. Abrahams, R.A. Dodghson, The geo-archaeological significance and spatial variability of a range of physical and chemical soil properties from a former habitation site, Isle of Skye, Journal of Archaeological Science 27 (2000) 287–303.
[59] A.D. Evers, B.M. Gough, J.N. Pybus, Scanning electron microscopy of wheat starch, IV. Digestion of large granules by glucoamylase of fungal (Aspergillus niger) origin, Starke 23 (1971) 16–18.
[60] A.D. Evers, E.E. McDermott, Scanning electron microscopy of wheat starch, II. Structure of granules modified by aplha-amylosis—preliminary report, Starke 22 (1970) 23–26.
[61] R.P. Evershed, Biomolecular archaeology and lipids, World Archaeology 25 (1) (1993) 74–93.
[62] R.P. Evershed, G. Turner-Walker, R.E.M. Hedges, N. Tuross, A. Leyden, Preliminary results for the analysis of lipids in ancient bone, Journal of Archaeological Science 22 (1995) 277–290.
[63] J.E. Fannon, R.J. Hauber, J.N. Bemiller, Surface pores of starch granules, Cereal Chemistry 69 (3) (1992) 284–288.
[64] FAO, Maize in Human Nutrition, FAO Food and Nutrition Series, 25, Food and Agriculture Organisation of the United Nations, Rome, 1992.
[65] J. Field, R. Fullagar, Grinding and pounding stones from Cuddie Springs and Jinmium, in: R. Fullagar (Ed.), A Closer Look: Recent Australian Studies of Stone Tools, Archaeological Computing Laboratory, University of Sydney, Sydney, 1998.
[66] A. Fioretto, S. Papa, G. Sorrentino, A. Fuggi, Decomposition of *Cistus incanus* leaf litter in a Mediterranean maquis ecosystem: mass loss, microbial enzyme activities and nutrient changes, Soil Biology and Biochemistry 33 (2001) 311–321.
[67] M.L. Fogel, N. Tuross, Transformation of plant biochemicals to geological macromolecules during early diagenesis, Oecologia 120 (1999) 336–346.
[68] B.R. Fondy, D.R. Geiger, Diurnal patterns of translocation and carbohydrate metabolism in source leaves of *Beta vulgaris* L., Plant Physiology 70 (1982) 671–676.
[69] C.M.L. Franco, C.F. Ciacco, B. Geraldo, Factors that affect the enzymatic degradation of natural starch granules—effect of the size of the granules, Starke 44 (1992) 422–426.
[70] C.M.L. Franco, C.F. Ciacco, D.Q. Tavares, The structure of waxy corn starch: effect of granule size, Starke 50 (5) (1998) 193.
[71] D. French, Chemistry and biochemistry of starch, in: W.J. Whelan (Ed.), Biochemistry of Carbohydrates, Butterworths, London, 1975, pp. 267–335.
[72] D. French, Organisation of starch granules, in: R.L. Whistler, J.N. Bemiller, E.F. Paschall (Eds.), Starch: Chemistry and Technology, Academic Press, New York, 1984, pp. 183–247.
[73] R. Fullagar, Use-wear and residues on stone tools: functional analysis and its application to two southeastern Australian archaeological assemblages, unpublished PhD thesis, La Trobe University, 1986.
[74] R. Fullagar, Flaked stone tools and plant food production: a preliminary report on obsidian tools from Talasea, West New Britain, PNG, in: P.C. Anderson, S. Beyries, M. Otte, H. Plisson (Eds.), Traces et Fonction: Les Gestes Retrouvés, ERAUL, Liège, 1993, pp. 331–337.
[75] R. Fullagar, T. Loy, S. Cox, Starch grains, sediments and stone tool function: evidence from Bitokara, Papua New Guinea, in: R. Fullagar (Ed.), A Closer Look: Recent Australian Studies of Stone Tools, Archaeological Computing Laboratory, University of Sydney, Sydney, 1998, pp. 49–60.
[76] H. Fuwa, M. Nakajima, A. Hamada, D.V. Glover, Comparative susceptibility to amylases of starches from different plant species and several single endosperm mutants and their double-mutant combinations with *Opaque*-2 inbred 0h43 Maize, Cereal Chemistry 54 (2) (1977) 230–237.
[77] D. Gallant, C. Mercier, A. Guilbot, Electron microscopy of starch granules modified by bacterial alpha-amylase, Cereal Chemistry 49 (1972) 354–365.
[78] G. Geiger, M.P. Livingston, F. Funk, R. Schulin, Beta-glucosidase activity in the presence of copper and geothite, European Journal of Soil Science 49 (1998) 17–23.
[79] G. Geiger, J.C. Servaites, M.A. Fuchs, Role of starch in carbon translocation and partitioning at the plant level, Australian Journal of Plant Physiology 27 (2000) 571–582.
[80] C. Ghiena, M. Schulz, H. Schnabl, Starch degradation and distribution of the starch-degrading enzymes in *Vicia faba* leaves, Plant Physiology 101 (1993) 73–79.
[81] A. Golchin, J.M. Oades, J.O. Skjemstad, P. Clarke, Study of free and occluded particulate organic matter in soils by solid state ^{13}C CP/MAS NMR spectroscopy and scanning electron microscopy, Australian Journal of Soil Research 32 (1994) 285–309.
[82] A.J. Gordon, G.L.A. Ryle, G. Webb, The relationship between sucrose and starch during dark export from leaves of uniculum barley, Journal of Experimental Botany 31 (1980) 845–850.
[83] R. Grace, Use-wear analysis: the state of the art, Archaeometry 38 (2) (1996) 209–229.
[84] R. Gracza, Minor constituents of starch, in: R.L. Whistler, E.F. Paschall (Eds.), Starch: Chemistry and Technology, Academic Press, New York, 1965, pp. 105–131.
[85] C.T. Greenwood, E.A. Milne, Starch degrading and synthesizing enzymes: a discussion of their properties and action pattern, Advances in Carbohydrate Chemistry 23 (1968) 281–366.
[86] E.G. Gregorich, C.F. Drury, B.H. Ellert, B.C. Liang, Fertilization effects on physically protected light fraction organic matter, Soil Science Society of America Journal 61 (1997) 482–484.
[87] E.G. Gregorich, H.H. Janzen, Decomposition, in: M.E. Sumner (Ed.), Handbook of Soil Science, CRC Press, Boca Raton, FL, 2000, pp. C107–C120.
[88] R.P.F. Gregory, Biochemistry of Photosynthesis, John Wiley & Sons, London, 1977.
[89] G. Guggenberger, E.T. Elliott, S.D. Frey, J. Six, K. Paustian, Microbial contributions to the aggregation of a cultivated grassland soil amended with starch, Soil Biology and Biochemistry 31 (1999) 407–419.
[90] D.M. Gurfinkel, U.M. Franklin, A study of the feasibility of detecting blood residue on stone artifacts, Journal of Archaeological Science 15 (1988) 83–97.
[91] J. Hall, S. Higgins, R. Fullagar, Plant residues on stone tools, in: W. Beck, A. Clarke, L. Head (Eds.), Plants in Australian Archaeology, Tempus, Anthropology Museum, University of Queensland, Brisbane, 1989, pp. 136–160.
[92] S. Hall, Deteriorated pollen grains and the interpretation of Quaternary pollen diagrams, Review of Palaeobotany and Palynology 32 (1981) 193–206.
[93] B.L. Hardy, G.T. Garufi, Identification of woodworking on stone tools through residue and use-wear analyses: experimental results, Journal of Archaeological Science 25 (1998) 177–184.
[94] B.L. Hardy, M. Kay, A.E. Marks, K. Monigal, Stone tool function at the paleolithic sites of Starosele and Buran Kaya III. Crimea: behavioral implications, Proceedings of the National Academy of Sciences 98 (19) (2001) 10972–10977.

[95] U. Harms, J.J. Sauter, Changes in content of starch, protein, fat and sugars in the branchwood of *Betula pendula* Roth during fall, Holzforschung 46 (6) (1992) 455–461.
[96] D.M. Hart, G.S. Humphreys, Plant opal phytoliths: an Australian perspective, Quaternary Australasia 15 (1997) 17–25.
[97] M. Haslam, Evidence for maize processing on 2000 year old obsidian artefacts from Copan, Honduras, in: D.M. Hart, L.A. Wallis (Eds.), Phytolith and Starch Research in the Australian-Pacific-Asian Regions: The State of the Art. Papers from a conference held at the ANU, August 2001, Canberra, Australia, Pandanus Books, Canberra, 2003, pp. 153–161.
[98] J.G. Hather, The identification of charred root and tuber crops from archaeological sites in the Pacific, in: J.G. Hather (Ed.), Tropical Archaeobotany: Applications and New Developments, Routledge, London, 1994, pp. 51–64.
[99] R.E.M. Hedges, A.R. Millard, A.W.G. Pike, Measurements and relationships of diagenetic alteration of bone from three archaeological sites, Journal of Archaeological Science 22 (1995) 201–209.
[100] R.E.M. Hedges, Bone diagenesis: an overview of processes, Archaeometry 44 (2002) 319–328.
[101] H. Helbaek, Palaeo-ethnobotany, in: D.R. Brothwell, E. Higgs (Eds.), Science in Archaeology, Thames and Hudson, London, 1969, pp. 206–214.
[102] J.N. Hill, R.H. Hevly, Pollen at Broken K Pueblo: some new interpretations, American Antiquity 33 (2) (1968) 200–210.
[103] G. Hillman, Late Palaeolithic plant foods from Wadi Kubbaniya in Upper Egypt: dietary diversity, infant weaning, and seasonality in a riverine environment, in: D. Harris, G. Hillman (Eds.), Foraging and Farming: The Evolution of Plant Exploitation, Unwin Hyman, London, 1989, pp. 207–239.
[104] G. Hillman, S. Wales, F. McLaren, J. Evans, A. Butler, Identifying problematic remains of ancient plant foods: a comparison of the role of chemical, histological and morphological criteria, World Archaeology 25 (1) (1993) 94–121.
[105] R. Hoover, Composition, molecular structure, and physiochemical properties of tuber and root starches: a review, Carbohydrate Polymers 45 (2001) 253–267.
[106] M. Horrocks, G. Irwin, M. Jones, D. Sutton, Starch grains and xylem cells of sweet potato (*Ipomoea batatas*) and bracken (*Ptridium esculentum*) in archaeological deposits from northern New Zealand, Journal of Archaeological Science 31 (2004) 251–258.
[107] J.H.M. Hovenkamp-Hermelink, J.N. De Vries, P. Adamse, E. Jacobsen, B. Witholt, W.J. Feenstra, Rapid estimation of the amylose/amylopectin ratio in small amounts of tuber and leaf tissue in potato, Potato Research 31 (1988) 241–246.
[108] J. Iriarte, I. Holst, J.M. Lopez, L. Cabrera, Subtropical wetland adaptations in Uruguay during the Mid-Holocene: An archaeobotanical perspective, in: B.A. Purdy (Ed.), Enduring Records: The Environmental and Cultural Heritage of Wetlands, Oxbow Books, Oxford, 2001, pp. 61–70.
[109] A.H. Jahren, N. Toth, K. Schick, J.D. Clark, R.G. Amundson, Determining stone tool use: chemical and morphological analyses of residues on experimentally manufactured stone tools, Journal of Archaeological Science 24 (1997) 245–250.
[110] M.M.E. Jans, C.M. Nielsen-Marsh, C.I. Smith, M.J. Collins, H. Kars, Characterisation of microbial attack on archaeological bone, Journal of Archaeological Science 31 (2004) 87–95.
[111] P.J. Jenkins, R.E. Cameron, A.M. Donald, A universal feature in the structure of starch granules from different botanical sources, Starke 45 (1993) 417–420.
[112] L. Jing-ming, Z. Sen-lin, Scanning electron microscope study on gelatinization of starch granules in excess water, Starke 42 (3) (1990) 96–98.
[113] S.R. Joshi, G.D. Sharma, R.R. Mishra, Microbial enzyme activities related to litter decomposition near a highway in a subtropical forest of North East India, Soil Biology and Biochemistry 25 (12) (1993) 1763–1770.
[114] J. Juan-Tresserras, La cerveza prehistórica: investigaciones arqueobotánicas y experimentales, in: J.L. Maya, F. Cuesta, J. López Cachero (Eds.), Genó: un Poblado del Bronce Final en el Bajo Segre (Lleida), Universitat de Barcelona, Barcelona, 1998, pp. 241–252.
[115] N.G. Juma, Interrelationships between soil structure/texture, soil biota/soil organic matter and crop production, Geoderma 57 (1993) 3–30.
[116] E.N. Kalistratova, A.V. Persikov, A.N. Danilenko, V.A. Protserov, V.P. Yuryev, The generalized heat capacity/amylose content function for barley and maize starches, Starke 51 (5) (1999) 160–162.
[117] B.D. Kay, D.A. Angers, Soil structure, in: M.E. Sumner (Ed.), Handbook of Soil Science, CRC Press, Boca Raton, FL, 2000, pp. A229–A276.
[118] L. Kealhofer, R. Torrence, R. Fullagar, Integrating phytoliths within use-wear/residue studies of stone tools, Journal of Archaeological Science 26 (1999) 527–546.
[119] G.K. Kelso, Pollen-record formation processes, interdisciplinary archaeology, and land use by mill workers and managers: the Boott Mills Corporation, Lowell, Massachusetts, 1836–1942, Historical Archaeology 27 (1) (1993) 70–94.
[120] G.K. Kelso, Pollen percolation rates in Euroamerican-era cultural deposits in the northeastern United States, Journal of Archaeological Science 21 (1994) 481–488.
[121] G.K. Kelso, S.A. Mrozowski, D. Currie, A.C. Edwards, M.R. Brown III, A.J. Horning, G.J. Brown, J.R. Dandoy, Differential pollen preservation in a seventeenth-century refuse pit, Jamestown Island, Virginia. Historical Archaeology 29 (2) (1995) 43–54.
[122] J.E. King, W.E. Klippel, R. Duffield, Pollen preservation and archaeology in eastern North America, American Antiquity 40 (2) (1975) 180–190.
[123] S. Kiss, M. Dragan-Bularda, D. Radulescu, Soil polysaccharides: activity and agricultural importance, in: R.G. Burns (Ed.), Soil Enzymes, Academic Press, London, 1978, pp. 117–147.
[124] K. Kitahara, I. Imamura, Y. Omae, T. Suganuma, Characterization of molecular structure of starch granules in suspension-cultured cells from *Ipomoea cordatatriloba* Denn, Bioscience Biotechnology and Biochemistry 62 (10) (1998) 1962–1967.
[125] C.A. Knutson, U. Khoo, J.E. Cluskey, G.E. Inglett, Variation in enzyme digestibility and gelatinization behavior of corn starch granule fractions, Cereal Chemistry 59 (6) (1982) 512–515.
[126] B.-W. Kong, J.-I. Kim, M.-J. Kim, J.C. Kim, Porcine pancreatic alpha-amylase hydrolysis of native starch granules as a function of granule surface area, Biotechnology Progress 19 (4) (2003) 1162–1166.
[127] M.A. Korstanje, Taphonomy in the laboratory: starch damage and multiple microfossil recovery from sediments, in: D.M. Hart, L.A. Wallis (Eds.), Phytolith and Starch Research in the Australian-Pacific-Asian Regions: The State of the Art. Papers from a conference held at the ANU, August 2001, Canberra, Australia, Pandanus Books, Canberra, 2003, pp. 105–118.
[128] S. Kshattriya, G.D. Sharma, R.R. Mishra, Enzyme activities related to litter decomposition in forests of different age and altitude in North East India, Soil Biology and Biochemistry 24 (3) (1992) 265–270.
[129] J. Kutik, L. Natr, H.H. Demmers-Derks, D.W. Lawlor, Chloroplast ultrastructure of sugar beet (*Beta vulgaris* L.) cultivated in normal and elevated CO2 concentrations with two contrasted nitrogen supplies, Journal of Experimental Botany 46 (293) (1995) 1797–1802.
[130] J.N. Ladd, Origin and range of enzymes in soil, in: R.G. Burns (Ed.), Soil Enzymes, Academic Press, London, 1978, pp. 51–96.

[131] P. Lahdesmaki, R. Piispanen, Degradation products and the hydrolitic enzyme activities in the soil humification processes, Soil Biology and Biochemistry 20 (3) (1988) 287–292.
[132] D.W. Lawlor, Photosynthesis: Molecular, Physiological and Environmental Processes, Longman Scientific and Technical, Harlow, 1993.
[133] T. Lawson, D.W. Hopkins, J.A. Chudek, R.C. Janaway, M.G. Bell, The experimental earthwork at Wareham, Dorset after 33 years: 3. Interaction of soil organisms with buried materials, Journal of Archaeological Science 27 (2000) 273–285.
[134] H.W. Leach, Gelatinization of starch, in: R.L. Whistler, E.F. Paschall (Eds.), Starch: Chemistry and Technology, Academic Press, New York, 1965, pp. 289–307.
[135] H.W. Leach, T.J. Schoch, Structure of the starch granule, II. Action of various amylases on granular starches, Cereal Chemistry 38 (1961) 34–46.
[136] J.D. Leach, A brief comment on the immunological identification of plant residues on prehistoric stone tools and ceramics: results of a blind test, Journal of Archaeological Science 25 (1998) 171–175.
[137] C. Lentfer, W.E. Boyd, A comparison of three methods for the extraction of phytoliths from sediments, Journal of Archaeological Science 25 (1998) 1159–1183.
[138] C. Lentfer, M. Therin, R. Torrence, Starch grains and environmental reconstruction: a modern test case from West New Britain, Papua New Guinea, Journal of Archaeological Science 29 (2002) 687–698.
[139] C.J. Lentfer, W.E. Boyd, Simultaneous extraction of phytoliths, pollen and spores from sediments, Journal of Archaeological Science 27 (2000) 363–372.
[140] H. Lepedus, V. Cesar, N. Ljubesic, Chloroplast ultrastructure and chlorophyll levels in vegetative buds and needles of Norway spruce (*Picea abies* L. Karst.), Periodicum Biologorum 103 (1) (2001) 61–65.
[141] S.T. Lim, T. Kasemsuwan, J. Jane, Characterization of phosphorus in starch by 31p nuclear magnetic spectroscopy, Cereal Chemistry 71 (1994) 468–472.
[142] T.H. Loy, Methods in the analysis of starch residues on prehistoric stone tools, in: J.G. Hather (Ed.), Tropical Archaeobotany: Applications and New Developments, Routledge, London, 1994, pp. 86–114.
[143] T.H. Loy, E.J. Dixon, Blood residues on fluted points from Eastern Beringia, American Antiquity 63 (1) (1998) 21–46.
[144] T.H. Loy, M. Spriggs, S. Wickler, Direct evidence for human use of plants 28,000 years ago: starch residues on stone artefacts from the northern Solomon Islands, Antiquity 66 (1992) 898–912.
[145] T. Lu, The survival of starch residue in a subtropical environment, in: D.M. Hart, L.A. Wallis (Eds.), Phytolith and Starch Research in the Australian-Pacific-Asian Regions: The state of the art. Papers from a conference held at the ANU, August 2001, Canberra, Australia, Pandanus Books, Canberra, 2003, pp. 119–126.
[146] R.L. Lyman, Vertebrate Taphonomy, Cambridge Manuals in Archaeology, Cambridge University Press, Cambridge, 1994.
[147] D.L. Lynch, L.J. Cotnoir, The influence of clay minerals on the breakdown of certain organic substrates, Proceedings of the Soil Science Society of America 20 (1956) 367–370.
[148] A.W. MacGregor, D.L. Ballance, Hydrolysis of large and small starch granules from normal and waxy barley cultivars by alpha-amylases from barley malt, Cereal Chemistry 57 (1980) 397–402.
[149] M.E. Malainey, R. Przybylski, B.L. Sherriff, The effects of thermal and oxidative degradation on the fatty acid composition of food plants and animals of western Canada: implications for the identification of archaeological vessel residues, Journal of Archaeological Science 26 (1999) 95–103.
[150] R. Manelius, E. Bertoft, The effect of Ca^{2+} ions on the alpha-amylosis of granular starches from oats and waxy-maize, Journal of Cereal Science 24 (1996) 139–150.
[151] D.J. Manners, Enzymic synthesis and degradation of starch and glycogen, Advances in Carbohydrate Chemistry 17 (1962) 371–430.
[152] I. Manton, Some possibly significant structural relations between chloroplasts and other cell components, in: T.W. Goodwin (Ed.), Biochemistry of Chloroplasts, Academic Press, London, 1966, pp. 23–47.
[153] J.P. Martin, Decomposition and binding action of polysaccharides in soil, Soil Biology and Biochemistry 3 (1971) 33–41.
[154] R.F. Martins, W. Davids, W.A. Al-Soud, F. Levander, P. Radstrom, R. Hatti-Kaul, Starch-hydrolyzing bacteria from Ethiopian soda lakes, Extremophiles 5 (2001) 135–144.
[155] N.K. Matheson, The chemical structure of amylose and amylopectin fractions of starch from tobacco leaves during development and diurnally-nocturnally, Carbohydrate Research 282 (2) (1996) 247–262.
[156] P.J. Matthews, M. Matsuda, Y. Ochiai, Comments on the classification and naming of root crops and other crop categories, in: S. Yoshida, P.J. Matthews (Eds.), Vegeculture in Eastern Asia and Oceania, Japan Center for Area Studies, Suita City, Osaka, 2002, pp. 331–335.
[157] J.E. Mellon, M.K. Dowd, P.J. Cotty, Time course study of substrate utilization by *Aspergillus flavus* in medium simulating corn (*Zea mays*) kernels, Journal of Agricultural and Food Chemistry 50 (2002) 648–652.
[158] W. Menke, The structure of the chloroplasts, in: T.W. Goodwin (Ed.), Biochemistry of Chloroplasts, Academic Press, London, 1966, pp. 3–18.
[159] K.H. Meyer, F. Heinrich, Recherches sur l'amidon, XXIII. La composition de l'amidon de feuilles, de germes et de tubercules de pommes de terre, Helvetica Chimica Acta 25 (1942) 1038–1046.
[160] A. Miltner, W. Zech, Carbohydrate decomposition in beech litter as influenced by aluminium, iron and manganese oxides, Soil Biology and Biochemistry 30 (1) (1998) 1–7.
[161] J.-A. Miskell, G. Parmenter, J.J. Eaton-Rye, Decreased Hill reaction rates and slow turnover of transitory starch in the obligate shade plant *Panax quinquefolius* L. (American ginseng), Planta 215 (2002) 969–979.
[162] S.N. Moorthy, Physicochemical and functional properties of tropical tuber starches: a review, Starke 54 (2002) 559–592.
[163] S.N. Moorthy, P.K. Thankamma Pillai, M. Unnikrishnan, Variability in starch extracted from taro, Carbohydrate Polymers 20 (1993) 169–173.
[164] G.E. Moss, The microscopy of starch, in: J.A. Radley (Ed.), Examination and Analysis of Starch and Starch Products, Applied Science Publishers, London, 1976, pp. 1–32.
[165] T.H. Nielsen, L. Baunsgaard, A. Blennow, Intermediary glucan structures formed during starch granule synthesis are enriched in short side chains, a dynamic pulse labelling approach, Journal of Biological Chemistry 77 (23) (2002) 20249–20255.
[166] C. Niemann, A.B. Anderson, K.P. Link, The isolation and characterization of a starch polysaccharide from the leaf tissue of the apple tree (*Malus malus*), Journal of Biological Chemistry 116 (1936) 447–455.
[167] A.M. O'Neal, A key for evaluating soil permeability by means of certain field clues, Proceedings of the Soil Science Society of America 16 (1952) 312–315.
[168] L.J. Palmer, Blood residue detection: an Australian appraisal, in: B.L. Fankhauser, J.R. Bird (Eds.), Archaeometry: Current Australasian Research, Occasional Papers in Prehistory, No. 22, Department of Prehistory, Research School of Pacific Studies, The Australian National University, Canberra, 1993, pp. 28–37.

[169] J.J. Parnell, R. Terry, P. Sheets, Soil chemical analysis of ancient activities in Ceren, El Salvador: a case study of a rapidly abandoned site, Latin American Antiquity 13 (3) (2002) 331–342.
[170] J.F. Parr, A comparison of heavy liquid floatation and microwave digestion techniques for the extraction of fossil phytoliths from sediments, Review of Palaeobotany and Palynology 120 (2002) 315–336.
[171] J.F. Parr, M. Carter, Phytolith and starch analysis of sediment samples from two archaeological sites on Dauar Island, Torres Strait, northeastern Australia, Vegetation History and Archaeobotany 12 (2003) 131–141.
[172] J.F. Parr, K. Farrugia, Waste reduction and value adding during fossil phytolith extraction and pelaeoenvironmental analysis of volcanic sediments and tephra using microwave digestion and ICP/MS, in: D.M. Hart, L.A. Wallis (Eds.), Phytolith and Starch Research in the Australian-Pacific-Asian Regions: The State of the Art. Papers from a conference held at the ANU, August 2001, Canberra, Australia, Pandanus Books, Canberra, 2003, pp. 19–30.
[173] E.A. Paul, F.E. Clark, Soil Microbiology and Biochemistry, Academic Press, San Diego, CA, 1996.
[174] J.H. Pazur, Enzymes in synthesis and hydrolysis of starch, in: R.L. Whistler, E.F. Paschall (Eds.), Starch: Chemistry and Technology, Academic Press, New York, 1965, pp. 133–175.
[175] D. Pearsall, Paleoethnobotany: A Handbook of Procedures, Academic Press, San Diego, CA, 2000.
[176] D. Pearsall, Integrating biological data: phytoliths and starch grains, health and diet, at Real Alto, Ecuador, in: D.M. Hart, L.A. Wallis (Eds.), Phytolith and Starch Research in the Australian-Pacific-Asian Regions: The State of the Art. Papers from a conference held at the ANU, August 2001, Canberra, Australia, Pandanus Books, Canberra, 2003, pp. 187–200.
[177] L. Perry, Prehispanic subsistence in the Middle Orinoco Basin: starch analyses yield new evidence, unpublished PhD thesis, Southern Illinois University, Carbondale, 2001.
[178] L. Perry, Starch granule size and the domestication of manioc (*Manihot esulenta*) and sweet potato (*Ipomea batatas*), Economic Botany 56 (4) (2002) 335–349.
[179] P. Piacquadio, G. De Stefano, V. Sciancalepore, The effect of heating at subgelatinisation temperatures on enzymatic digestibility of corn starch, Starke 52 (2000) 345–348.
[180] L.A. Pinck, F.E. Allison, Resistance of a protein montmorillonite complex to decomposition by soil microorganisms, Science 114 (1951) 130–131.
[181] D. Piperno, D. Pearsall, The Origins of Agriculture in the Lowland Neotropics, Academic Press, San Diego, CA, 1998.
[182] D.R. Piperno, I. Holst, The presence of starch grains on prehistoric stone tools from the humid neotropics: indications of early tuber use and agriculture in Panama, Journal of Archaeological Science 25 (1998) 765–776.
[183] D.R. Piperno, A.J. Ranere, I. Holst, P. Hansell, Starch grains reveal early root crop horticulture in Panamanian tropical forest, Nature 407 (2000) 894–897.
[184] M.A. Radwan, C.R. Stocking, The isolation and characterization of sunflower leaf starch, American Journal of Botany 44 (8) (1957) 682–686.
[185] P.H. Raven, R.F. Evert, S.E. Eichhorn, Biology of Plants, Sixth ed., Worth Publishers, New York, 1999.
[186] E.T. Reichert, The Differentiation and Specificity of Starches in Relation to Genera, Species etc.: Stereochemistry Applied to Protoplasmic Processes and Products, as a Strictly Scientific Basis for Classification of Plants and Animals, Carnegie Institute of Washington, Washington, 1913.
[187] S.A. Roberts, R.E. Cameron, The effects of concentration and sodium hydroxide on the rheological properties of potato starch gelatinisation, Carbohydrate Polymers 50 (2002) 133–143.
[188] D.J. Ross, Assays of invertase and amylase activities in soil, 1. Influence of buffered and unbuffered systems with soils from grasslands, New Zealand Journal of Science 26 (1983) 339–346.
[189] D.J. Ross, Assays of invertase and amylase activities in soil, 2. Influence of pH with soils and plant materials from tussock grasslands, New Zealand Journal of Science 26 (1983) 347–355.
[190] D.J. Ross, Invertase and amylase activities as influenced by clay minerals, soil-clay fractions and topsoils under grassland, Soil Biology and Biochemistry 15 (3) (1983) 287–293.
[191] I. Rovner, Plant opal phytolith analysis: major advances in archaeobotanical research, in: M.B. Schiffer (Ed.), Advances in Archaeological Method and Theory, Academic Press, New York, 1983, pp. 225–266.
[192] H.J. Ruijssenaars, S. Hartmans, Plate screening methods for the detection of polysaccharase-producing microorganisms, Applied Microbiology and Biotechnology 55 (2001) 143–149.
[193] A.K. Salam, Y. Desiva, E. Sutanto, T. Syam, S.G. Nugroho, M. Kimura, Activities of soil enzymes in different land-use systems in middle terrace areas of Lampung Province, South Sumatra, Indonesia, Soil Science and Plant Nutrition 45 (1) (1999) 89–99.
[194] D. Samuel, Archaeology of ancient Egyptian beer, Journal of the American Society of Brewing Chemists 54 (1) (1996) 3–12.
[195] D. Samuel, Cereal foods and nutrition in Ancient Egypt, Nutrition 13 (6) (1997) 579–580.
[196] K. Sato, Starch granules in tissues of rice plants and their changes in relation to plant growth, Japan Agricultural Research Quarterly 18 (2) (1984) 79–86.
[197] J.J. Sauter, S. Wellenkamp, Seasonal changes in content of starch, protein and sugars in the twig wood of *Salix caprea* L., Holzforschung 52 (3) (1998) 255–262.
[198] M.B. Schiffer, Archaeological context and systemic context, American Antiquity 37 (2) (1972) 156–165.
[199] J. Schleucher, P.J. Vandeveer, T.D. Sharkey, Export of carbon from chloroplasts at night, Plant Physiology 118 (1998) 1439–1445.
[200] J.C. Servaites, B.R. Fondy, D.R. Geiger, Sources of carbon for export from spinach leaves throughout the day, Plant Physiology 90 (1989) 1168–1174.
[201] H. Shafer, R. Holloway, Organic residue analysis in determining stone tool function, in: B. Hayden (Ed.), Lithic Use-wear Analysis, Academic Press, New York, 1979, pp. 385–399.
[202] O.C. Shanks, R. Bonnichsen, A.T. Vella, W. Ream, Recovery of protein and DNA trapped in stone tool microcracks, Journal of Archaeological Science 28 (2001) 965–972.
[203] J.C. Shannon, D.L. Garwood, Genetics and physiology of starch development, in: R.L. Whistler, J.N. Bemiller, E.F. Paschall (Eds.), Starch: Chemistry and Technology, Academic Press, New York, 1984, pp. 25–86.
[204] T.D. Sharkey, J.A. Berry, K. Raschke, Starch and sucrose synthesis in *Phaseolus vulgaris* as affected by light, CO_2 and abscisic acid, Plant Physiology 77 (1985) 617–620.
[205] A.K. Sievert, Root and tuber resources: experimental plant processing and resulting microwear on chipped stone tools, in: P.C. Anderson (Ed.), Prehistory of Agriculture: New Experimental and Ethnographic Approaches, University of California, Los Angeles, 1999, pp. 24–32.
[206] E.M. Snyder, Industrial microscopy of starches, in: R.L. Whistler, J.N. Bemiller, E.F. Paschall (Eds.), Starch: Chemistry and Technology, Academic Press, New York, 1984, pp. 661–673.
[207] P.L. Soni, H. Sharma, H.C. Srivastava, M.M. Gharia, Physiochemical properties of *Canna edulis* starch—comparison with maize starch, Starke 42 (1990) 460–464.
[208] H.A. Spoehr, H.W. Milner, Leaf starch: its isolation and some of its properties, Journal of Biological Chemistry 111 (1935) 679–687.

[209] M. Spriggs, Taro cropping systems in the southeast Asian-Pacific region: archaeological evidence, Archaeology in Oceania 17 (1982) 7–15.
[210] M. Steup, H. Robenek, M. Melkonian, In-vitro degradation of starch granules isolated from spinach chloroplasts, Planta 158 (1983) 428–436.
[211] Z. Sun, S.H. Duke, C.A. Henson, The role of pea chloroplast alpha-glucosidase in transitory starch degradation, Plant Physiology 108 (1995) 211–217.
[212] Z. Sun, C.A. Henson, Degradation of native starch granules by barley alpha-glucosidases, Plant Physiology 94 (1990) 320–327.
[213] J.J.M. Swinkels, Sources of starch, its chemistry and physics, in: G.M.A. van Beynum, J.A. Roels (Eds.), Starch Conversion Technology, Marcel Dekker Inc., New York, 1985, pp. 15–46.
[214] T. Taira, M. Uematsu, Y. Nakano, T. Morikawa, Molecular identification and comparison of the starch synthase bound to starch granules between endosperm and leaf blades in rice plants, Biochemical Genetics 29 (1991) 301–311.
[215] H. Tang, K. Watanabe, T. Mitsunaga, Characterization of storage starches from quinoa, barley and adzuki seeds, Carbohydrate Polymers 49 (2002) 13–22.
[216] J.P. Taylor, B. Wilson, M.S. Mills, R.G. Burns, Comparison of microbial numbers and enzymatic activities in surface soils and subsoils using various techniques, Soil Biology and Biochemistry 34 (2002) 387–401.
[217] R.F. Tester, M.D. Sommerville, Swelling and enzymatic hydrolysis of starch in low water systems, Journal of Cereal Science 33 (2000) 193–203.
[218] M. Therin, Subsistence through starch: the examination of subsistence changes on Garua Island, West New Britain, Papua New Guinea, through the extraction and identification of starch in sediments, unpublished BA (Hons) thesis, University of Sydney, Sydney, 1994.
[219] M. Therin, The movement of starch grains in sediments, in: R. Fullagar (Ed.), A Closer Look: Recent Australian Studies of Stone Tools, Archaeological Computing Laboratory, University of Sydney, Sydney, 1998, pp. 61–72.
[220] M. Therin, R. Fullagar, R. Torrence, Starch in sediments: a new approach to the study of subsistence and land use in Papua New Guinea, in: C. Gosden, J. Hather (Eds.), The Prehistory of Food: Appetites for Change, Routledge, London, 1999, pp. 438–462.
[221] M. Therin, R. Torrence, R. Fullagar, Australian Museum starch reference collection, Australian Archaeology 44 (1997) 52–53.
[222] P. Tomasik, C.H. Schilling, Complexes of starch with inorganic guests, Advances in Carbohydrate Chemistry and Biochemistry 53 (1998) 263–343.
[223] P. Tomasik, C.H. Schilling, Complexes of starch with organic guests, Advances in Carbohydrate Chemistry and Biochemistry 53 (1998) 345–426.
[224] K.L. Tomlinson, J.R. Lloyd, A.M. Smith, Importance of isoforms of starch-branching enzyme in determining the structure of starch in pea leaves, The Plant Journal 11 (1) (1997) 31–43.
[225] R.N. Trethewey, A.M. Smith, Starch metabolism in leaves, in: R.C. Leegood, T.D. Sharkey, S. von Caemmerer (Eds.), Photosynthesis: Physiology and Metabolism, Kluwer Academic Publishers, Dordrecht, 2000, pp. 205–231.
[226] N. Tuross, I. Barnes, R. Potts, Protein Identification of blood residues on experimental stone tools, Journal of Archaeological Science 23 (1996) 289–296.
[227] D. Ugent, T. Dillehay, C. Ramirez, Potato remains from a late Pleistocene settlement in southcentral Chile, Economic Botany 41 (1) (1987) 17–27.
[228] D. Ugent, S. Pozorski, T. Pozorski, Archaeological potato tuber remains from the Casma Valley of Peru, Economic Botany 36 (1982) 182–192.
[229] D. Ugent, S. Pozorski, T. Pozorski, New evidence for ancient cultivation of *Canna edulis* in Peru, Economic Botany 38 (1984) 417–432.
[230] S. Ulm, T. Eales, S. L'Estrange, Post-European Aboriginal occupation of the Southern Curtis Coast, Central Queensland, Australian Archaeology 48 (1999) 42–43.
[231] P. Veth, R. Fullagar, R. Gould, Residue and use-wear analysis of grinding implements from Puntutjarpa Rockshelter in the Western Desert: current and proposed research, Australian Archaeology 44 (1997) 23–25.
[232] H.B. Vickery, The behavior of the organic acids and starch of Bryophyllum leaves during culture in continuous light, Journal of Biological Chemistry 205 (1953) 369–381.
[233] W. Von Stokar, Prehistoric organic remains, Antiquity 12 (1938) 82–86.
[234] D. von Wettstein, On the physiology of chloroplast structures, in: T.W. Goodwin (Ed.), Biochemistry of Chloroplasts, Academic Press, London, 1966, pp. 19–22.
[235] M. Wainwright, J.E. Duddridge, K. Killham, Assay of alpha-amylase in soil and river sediments: its use to determine the effects of heavy metals on starch degradation, Enzyme and Microbial Technology 4 (1982) 32–34.
[236] T.L. Wang, T.Y. Bogracheva, C.L. Hedley, Starch: as simple as A, B, C? Journal of Experimental Botany 49 (1998) 481–502.
[237] R.A.J. Warren, Microbial hydrolysis of polysaccharides, Annual Review of Microbiology 50 (1996) 183–212.
[238] E.C. Wells, R.E. Terry, J.J. Parnell, P.J. Hardin, M.W. Jackson, S.D. Houston, Chemical analyses of ancient paleosols in residential areas at Piedras Negras, Guatemala, Journal of Archaeological Science 27 (2000) 449–462.
[239] W.J. Whelan, Starch and similar polysaccharides, in: W. Ruhland (Ed.), Encyclopedia of Plant Physiology, Springer-Verlag, Berlin, 1958, pp. 154–240.
[240] R.L. Whistler, History and future expectation of starch use, in: R.L. Whistler, J.N. Bemiller, E.F. Paschall (Eds.), Starch: Chemistry and Technology, Academic Press, New York, 1984, pp. 1–9.
[241] D.E. Yen, The development of Sahul agriculture with Australia as bystander, Antiquity 69 (1995) 831–847.
[242] B. Yu, S. Fujii, S. Kishihara, Physicochemical property of Huaishan (*Rhizoma Dioscorea*) and Matai (*Eleocharis dulcis*) starches, Starke 51 (1) (1999) 5–10.
[243] S.C. Zeeman, A. Tiessen, E. Pilling, K.L. Kato, A.M. Donald, A.M. Smith, Starch synthesis in Arabidopsis. Granule synthesis, composition, and structure, Plant Physiology 129 (2002) 516–529.
[244] S.C. Zeeman, T. Umemoto, W-L. Lue, P. Au-Yeung, C. Martin, A.M. Smith, J. Chen, A mutant of Arabidopsis lacking a chloroplastic isoamylase accumulates both starch and phytoglycogen, The Plant Cell 10 (1998) 1699–1711.
[245] H.F. Zobel, Molecules to granules: a comprehensive starch review, Starke 40 (1988) 44–50.