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In the mix: Replication studies to test the effectiveness of ochre in adhesives for tool hafting

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CHAPTER ONE: *Introduction*

This research investigates the creation of simple adhesives using ingredients that would have been available in KwaZulu-Natal more than 60 000 years ago. Ochre and a variety of other materials are used experimentally as aggregates in tree resin to make adhesives with which to haft stone tools. The aim of this research is to determine how effective ochre is as an aggregate in resin compared to other materials that would have been readily available (specifically in the Middle Stone Age (MSA) environment at Sibudu Cave, KwaZulu-Natal). This research was inspired by a need to explain why some MSA stone tools in Africa and Upper Palaeolithic stone tools in Europe have ochre residues on them (e.g. Audouin & Plisson, 1982; Allain & Rigaud, 1986; Williamson, 1997; Tomlinson, 2001; Gibson *et al.* 2004; Wadley *et al.* 2004; Williamson, 2004; Lombard, 2002, 2004a, 2004b, 2005). These residues, and use-wear traces, indicate that these tools were hafted. This study involves an in-depth examination of the physical and chemical attributes and processes that are involved in the creation of adhesive and the influence different materials have on the resultant adhesive. This research will aid in understanding why certain materials were chosen above others when making adhesives for hafting tools.

Chapter 2 reviews some African (but mainly South African) archaeological sites where ochre pieces have been found, and discusses some possible functional uses of these pieces. This helps us to understand why ochre is ubiquitous on many South African sites. Thereafter, the archaeological and ethnographic evidence for stone tool hafting and hafting methods is examined (with reference to specific sites), followed by a discussion of the Sibudu Cave evidence for stone tool hafting and ochre use. Thereafter, experimental and replication studies carried out on tool hafting by other researchers is discussed.

In Chapter 3, the basic terminology used in this paper is discussed, including a discussion of the discrepancy that often exists in the labelling of ochre and hematite. Included in this discussion is a description of the main materials used in these hafting experiments. The

experiments are divided into two main groups: Hafting Experiments 1 and Hafting Experiments 2. Hafting Experiments 2 involve fewer variables than Hafting Experiments 1, and they are based on the lessons learnt from tests performed during Experiments 1. Both sets of experiments look at and are enhanced by an understanding of the physical and chemical processes involved in commercially produced concrete, and in geological cementation.

Scientific testing done on the ingredients of the adhesives, and the adhesives themselves are discussed in the Chapters 4, 5, 6, 7 and 8, and are considered in relation to the results of both sets of hafting experiments. A discussion and conclusion follows (in Chapters 9 and 10), followed by some suggestions for further research that can be done on the topic (Chapter 11).

CHAPTER TWO: *Literature Review*

2.1 Ochre

The earliest evidence of ochre use in Africa is at Twin Rivers in Zambia where ochre pieces and some ochre crayons were found associated with the Lupemban Industry, which dates to about 300 000 BP (Barham, 2002). Backed tools and colouring materials were found together in the Lupemban Industry layers, which seem to have been made by *Homo heidelbergensis* (Barham, 2002). At GnJh-15, in Kenya, ochre was systematically used at 285 000 BP (McBrearty, 2001), while at Enkapune Ya Muto, also in Kenya, traces of ochre and an ochre-stained grindstone were found (Ambrose, 1998). At Lion Cavern, in eastern South Africa, tons of specular hematite were mined at 40 000 BP (Beaumont, 1973; Boshier & Beaumont, 1972).

Ochre has been found at many South African sites:

- Hematite 'crayons' were found throughout the Border Cave sequence (Beaumont *et al.* 1978; Beaumont, 1980).
- Crayons, some with incised lines on them, as well as large amounts of unworked ochre were found (in the Howiesons Poort layers) at Klasies River Mouth (Singer & Wymer, 1982).
- Crayons, ochre plaques with engraved lines, over 8000 pieces of unworked ochre, and areas where ochre was ground were found at Blombos Cave (Henshilwood, 2002; Henshilwood *et al.* 2001b; 2002; 2004; d'Errico, 2003).
- An ochre coated grindstone, some ochre crayons, and many pieces of specularite were found at Olieboompoort (Mason, 1962; Watts, 1998).
- Crayons and some unworked ochre were found at Die Kelders (Thackeray, 2000).
- Unworked and worked ochre were found at Rose Cottage Cave (Wadley, 2001a).
- Large amounts of worked and unworked ochre, ochre crayons, and ochre-stained grindstones were found at Sibudu (Wadley, 2001b).

Interpretations of the meaning of ochre on archaeological sites are highly varied. Some archaeologists believe that the mere presence of ochre, especially worked, red ochre, is an indicator of symbolic thought (e.g. Marshack, 1981; 1989; Knight *et al.* 1995; d'Errico & Nowell, 2000; Henshilwood *et al*. 2001a; d'Errico & Soressi, 2002; Watts, 2002; d'Errico, 2003; Henshilwood & Marean, 2003).

However, ochre has many secular functions:

1) Ochre can be used to aid in the **working and tanning of hides**. Mandl (1961) and Velo (1984) have shown that ochre has an antibacterial effect on hides. Ochre (since it is a metal ion) inhibits the decay of hide collagenase, an enzyme produced by bacteria, therefore making ochre ideal for tanning and softening (as well as colouring) leather (Audouin & Plisson, 1982). Audouin & Plissons' experiments with tanning showed that red ochre was more successful than yellow ochre because it enhances the drying process, makes the hides thinner and softer, and also helps preserve the hide through its astringent properties.

Ethnographically, ochre is also a useful tanning agent: Brandt and Weedman (2002a, 2002b) observed the hide-working process of the Konso in southern Ethiopia, and although plain water is sometimes used (Kimura *et al*. 2001), some tanners use a mixture of caster beans, ochre and water (Brandt & Weedman, 2002a, 200b). Volman (unpublished manuscript: 15) lists other tanning or curing agents he has found mentioned in ethnographic literature. Some are: urine, moss, grease-liver mixtures, brains-grease-fat or marrow mixtures, bark, seeds and seed oil.

The use of ochre in the final process of hide-preparation is well documented. The extinct /Xam from north-western South Africa used red ochre to colour leather bags (Bleek & Lloyd, 1911); Steinman (in Audouin & Plisson, 1982) observed the Tehuelches in Argentina tanning hides with ochre and fat; and Sollas (in Audouin & Plisson, 1982) observed that, in Tasmania, skins are rubbed with a fat and ochre mixture, which makes the cloaks waterproof. Keeley (1978, as cited in Volman, unpublished manuscript) states

that the easiest way of performing the finishing process (of hide-working) involves the rubbing of fat or grease into a hide. This grease may be mixed with a pigment to give the hide a desired colour, or mixed with a mineral pigment, which causes more grit to be present inbetween the hide and the scraping tool, therefore allowing for a greater degree of abrasion. Keeley's statement also has archaeological support because some tools (from three Magdalenian sites) that he examined microscopically showed abrasions and striations as well as traces of ochre.

While Watts (2002) agrees that ochre is often used in the final stages of hide preparation, he states that it is not vital to the actual hide working process, and is most often used for colouring the hides. He argues (Watts, 2002) that ochre *can* be used during the tanning process but there is no reason why other red (ferruginous) materials, and other-coloured (ferruginous) materials, may not be used, since ethnographic studies show that this is the case and that other successful ways of tanning hides do not necessarily use ochre.

Traces of ochre on the working edges of scrapers and flakes, in conjunction with abrasions and fractures on these tools, could be indicators that ochre was used in the hide-tanning process. At Sibudu, the small proportion of ochre residues found on scrapers implies either that ochre was not used in the hide tanning process at Sibudu, or that scrapers were not used to tan hides (Williamson, 2004). The high proportion of other residues found on scrapers, together with polishes and worn edges, suggests that they may have been used for various other activities (Williamson, 2004). Henshilwood *et al.* (2001a) found eight MSA ochre-stained, polished bone tools at Blombos Cave. Experimental studies by d'Errico (Henshilwood *et al.* 2001a) support the idea that ochre was used in the hide working process. His experiments involved using bone awls to pierce ochred hides, and he showed that the bone awls become permanently stained.

Therefore, while ochre is an effective agent in the processing of hides, which aids in making a hide thinner and softer, as well as inhibiting the decaying process, it is not an essential part of hide working since other substances may be used instead. Ochre found on the working edges of flakes and scrapers, as well as micro-wear studies of these tools,

provide evidence of the use of ochre in the hide working process. However, these tools may have just been used to prepare ochre (for a variety of uses) or, the ochre may have been used in the final processing or decorating of the hide.

2) Ochre has **medicinal uses** when used internally or externally (Audouin & Plisson, 1982; Velo, 1984). Ochre has an astringent effect, and has antiseptic and deodorizing properties (Velo, 1984).

3) Ochre (in the form, usually, of an ochre-grease or fat paste) can be **spread over the body as protection** from the sun as well as the cold, and from insects (Bonwick, 1898 & Ling Roth, 1890 both cited in Volman, unpublished manuscript; Pitsi, as cited in Wadley, 2001a: 7; Wadley, 2001a). Any coloured metal oxide with a high iron content (and the combination of vegetal or animal fat) can act as body protection (Watts, 1998). Therefore any red (e.g. hematite), black (e.g. manganese) or yellow (e.g. goethite) iron oxide or hydroxide may have been used. Although black and yellow materials are found on many sites, there are still many more sites on which red ochre is present in much greater quantities. This suggests that there was a preference for the red ochre.

4) Most important to the current study is the use of **ochre in adhesives used to haft tools**. Many archaeological and replication studies have been done concerning hafted tools and the evidence for hafting and hafted tools themselves in (lithic) assemblages (e.g. Allain & Rigaud, 1986; Ambrose, 1998; Tomlinson, 2001; Rots, 2002; Williamson, 1997, 2004; Gibson *et al*. 2004; Lombard, 2002, 2004a, 2004b, 2005; Wadley, 2005a; Wadley, in press; Wadley *et al*. 2004; Volman, unpublished manuscript). This will now be discussed in more detail.

2.2 Hafting

Brandt & Weedman's ethnographic studies (1997, 2002a, 2002b; Brandt, 1996; Weedman, 2002a, 2002b) on the Gurage, Gamo and Konso in southern and central Ethiopia have shed light on a variety of hafting methods. They report many different

ways in which scraping tools are hafted – with and without the use of an adhesive, but from their observations the adhesive-hafted tools have a higher success rate (Weedman, 2002b). One adhesive mixture reported is that of cactus milk, or a mixture of gum, butter and sheep hair (Brandt & Weedman, 1997). Another mixture is made from acacia tree resin and ash or charcoal (Brandt & Weedman, 2002a, 2002b). The adhesive is heated, placed in the socket in the haft, left to harden and then reheated and the stone tool inserted (Brandt & Weedman, 1997). The tool is sometimes bound with twine or rope (Brandt, 1996). The tools are scraping tools used to prepare hides and they have a different structure from the chopping tools that were made in the current study (Fig. 1.1).

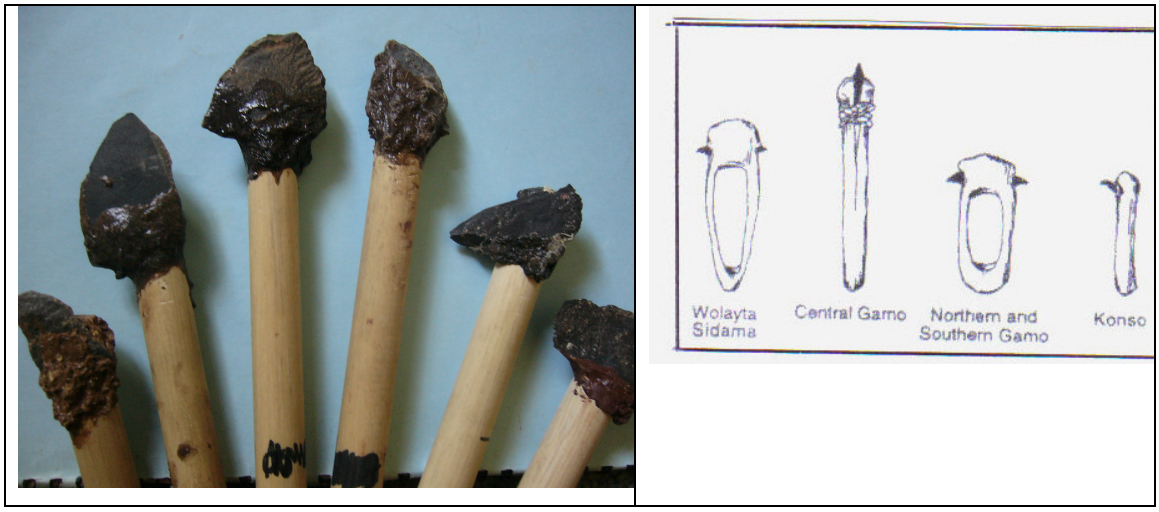


Figure 1.1 Chopping and sawing tools made in the current study (left), as opposed to the scraping tools used in southern Ethiopia (Brandt & Weedman, 1997). The tools on the left are all hafted with plain resin adhesives.

Some other ethnographically documented examples of the use of ochre in adhesives used to haft tools are in the Australian aboriginal and the now extinct Namaqualand San societies. For example, Australian aborigines use a mixture of vegetal fibres, ochre, sand and plant resin to haft tools (Rots, 2002), and the Namaqualand San, in Africa, once used *euphorbid* milk and a 'red clay' to attach feathers to arrows (Webley, 1994). Again, it must be remembered that a hunter-gatherer ethos may be problematic as an indicator of ancient behaviour.

The raw materials chosen to produce a hafted tool influence the tools' strength and durability (Rots, 2002). Each material should be chosen depending on the activity for which the tools will be used, so the desired results may be achieved. For example, if a tool is to be used as a projectile (such as an arrow) to throw at an animal prey, it may be desired that the stone tool remain embedded in the animal while the haft breaks off (Crombé *et al*. 2001). This might be favourable because the embedded stone tool may cause infection and haemorrhaging and the eventual death of the animal (Wadley, 2005a). The best adhesive for this purpose would then be one that keeps the tool in place but crumbles or cracks on impact.

The actual evidence of hafting stone tools is shown through a variety of features on the stone tools:

- Macro and micro fractures, specifically clustered bending fractures, along the proximal laterals of a stone tool. (Ahler, 1977; Barton & Bergman, 1982; Singer & Wymer, 1982; Bergman & Newcomer, 1983; Fisher *et al*. 1984; Odell & Cowan, 1986; Shea, 1988; Holdaway, 1989; Geneste & Plisson, 1993; Lombard, 2002; 2004a; 2004b; 2005). These are indicative of hafting by means of binding, with or without adhesive.
- Use-wear patterns of edge-rounding, edge-damage, polish and striations suggest in what way the tool was held onto the haft and how it was used (Singer & Wymer, 1982; Fisher *et al*. 1984).
- Residue analysis is very important for determining whether a tool was hafted and specifically what adhesives were used (Rots, 2002; Lombard, 2004a, 2004b; Wadley *et al.* 2004; Williamson, 1997, 2000, 2004).
  Firstly, vegetal (especially resinous) residues found mainly on the proximal and medial edges of stone tools are indicative of hafting (Lombard, 2004b). Secondly, epidermal plant tissue and woody residues on the proximal and medial edges show that these places were in contact with wood and possibly, therefore, the haft (Lombard, 2004b). Thirdly, materials found mainly on the proximal and medial edges, e.g. ochre, fat and sand (especially if in conjunction with resin) were likely

to have been used in the adhesive used to bind the stone tool to the haft (Lombard, 2004b). Lastly, residues around the (lateral) working edges away from the proximal end show what materials the tool was used to process (Lombard, 2004b).

Adhesives used to haft tools are also well documented archaeologically. Bitumen has been found on the proximal and medial portions of stone tools found on the Middle Palaeolithic sites, dated to 42 500 BP (Boëda *et al*. 1996; Boëda *et al*. 1998 both cited in Rots, 2002) of *Umm el Tlell* and *Hummal*, which suggests hafting with bitumen. Also at the Mousterian sites (at about 45 000 BP) of *Königsaue* and *Kärlich*, in Germany, resin fragments as well as resin with the imprints of a wooden haft and stone tool were found (Mania & Toepfer, 1973 as cited in Rots, 2002). In the youngest MSA deposits at Apollo 11 in Namibia, a blade with a resin-coated proximal end has been found and this may be evidence of hafting (Wendt, 1974; 1976).

J.D. Clark (1958), while discussing the use of scrapers found in southern Africa (specifically in the Later Stone Age), reported the modern use of hafted scrapers in the Middle Zambezi Valley in 1957. Although, in different regions and in areas of differing vegetation, different adhesives were used and these adhesives were specifically made with resin from the *Commiphora* tree (Clark, 1958). Resin was placed in a hole in the haft, heated and then the scraper was embedded (Clark, 1958). In eastern Zambia, archaeological research (Phillipson, 1976) has shown that a number of backed microliths have adhesive on them – importantly not on the working edges - indicating the use of adhesives in hafting tools.

Backed blades from Enkapune Ya Muto, in layers dated to between 50 000 and 40 000 BP, have red ochre residues on their backed portions (Ambrose, 1998), which Ambrose interpreted as evidence of hafting. A backed blade with ochre residues on its backed edge was found from the Magdalenian Gouy in northern France, and a red ochre and resin mixture was found on some backed bladelets in Lascaux in south-west France (Audouin & Plisson, 1982). Ochre was also found on some of the MSA stone tools from Die

Kelders (Thackeray, 2000). Evidence at Sibudu and Rose Cottage Cave also suggest hafting, and this will be discussed in more detail because both these sites inspired much research into hafting (including the current study).

Residue analysis at Rose Cottage Cave in the eastern Free State was done by Williamson (2000, 2004) and she found that many stone tools have microscopic traces of red ochre on the proximal and medial portions of the tools, as well as white starchy deposit "believed to be cooked starch, resulting from heated, decomposing resin" (Gibson *et al*. 2004: 6). This suggests that the tools were hafted with resin (which was heated) and that ochre may have been added into the adhesive. An investigation of the Howiesons Poort backed tools from the MSA at Rose Cottage Cave (Tomlinson, 2001; Gibson *et al*. 2004) showed that ochre and plant materials are often found together on or near the backed edges, therefore indicating that hafting (with resin and ochre) was occurring. Ochre and vegetal residues are also found on the working edges suggesting that these materials may also have been processed with the stone tool – probably once hafted.

The Rose Cottage Cave sample was small and, due to handling and labelling after excavations in the 1980s, not suitable for in-depth residue work (Wadley, 2005a). Untouched MSA stone tools from Sibudu Cave were then focused on.

2.3 Sibudu Cave

Sibudu is a large rock shelter situated 40km north of Durban on a cliff above the Tongati River. It is in the vicinity of Tongaat, KwaZulu-Natal, and is roughly 15km inland of the coast, and at an altitude of about 100m above sea level. The shelter was formed by the lowering of the river channel and the eroding through the sandstone and shale cliff during the low sea levels of a Pleistocene glacial phase (Maud, as cited in Wadley, 2001b). The shelter is about 55m long and 18m wide, and the floor slopes dramatically from north to south - with a 12m elevation difference (Wadley, 2001b).

The area has high summer and winter rainfalls (750mm and 250mm respectively) with average summer temperatures of 22-25°C and winter temperatures of 17-20°C. Vegetation is a mixture of coastal scarp forest and riverine forest (Wadley, 2001b). On the cliff there is a diversity of woody species, including *Acacia* species (Allott, 2004; Wadley, in press).

The uppermost layers of deposit contain Iron Age occupations, and the layers directly below contain MSA occupations. Iron Age inhabitants had dug some pits into the MSA layers creating a mixture of MSA and Iron Age material culture and food waste (Wadley, 2001b).

An analysis of late MSA tools from Sibudu Cave (Williamson, 2004) found that 27.9% of the (104) points analyzed had ochre residues on them, 36.1% of the (83) scrapers, 30% of the (77) pieces with retouch, and 23% of the (113) flakes analyzed had ochre on them. A high proportion of these tools had the ochre located on the proximal and medial sections of the stone tool, especially the points, which suggests hafting. All tool categories, but especially points and retouched tools, indicate the use of ochre. In conjunction with this is the presence of use-wear traces. Williamson (2004) found that almost half of the tools examined had worn, rounded edges, and about a quarter of the tools had polished edges. Many of these tools also have plant residues on them. She concludes that the activities occurring at Sibudu in the MSA were specific and were concentrated on the processing of plant foods. Interestingly, many tools such as points and scrapers, which are usually associated with hunting, have plant residues on them (Williamson, 2004). She concludes, since this is also the case at Rose Cottage Cave, that specific tool categories were used for multiple tasks.

Lombard (2004a, 2004b) analyzed 24 points from the post-Howiesons Poort layers in Sibudu by looking at both the residues and use-wear traces (in comparison to replicated samples). Her residue analysis shows that vegetal residues are abundant on most of the tools, with a majority of the residues located on the proximal and medial portions. Plant tissue is mainly found on the proximal and medial parts of the points, but also on the

working edges, indicating hafting and also that the tools were used to process plant material. “Epidermal plant cell tissue and clearly distinguishable woody residue” (Lombard, 2004b: 41) are not abundant but are found mainly on the proximal portions of the points, and occasionally also on the medial portions – places which, in hafted stone tools, would have come into contact with wood (from the haft). 85% of the resin exudates found are on the proximal and medial portions, also indicating hafting. Use-wear traces in the form of bending micro-fractures along the lateral edges were found on 52% of the points, from a sample of 50 points. This indicates that the tools were hafted by binding the stone tool to the haft (with some sort of twine), with or without the use of an adhesive.

In addition, the virtual absence of faunal residues (e.g. blood, collagen and hair) on the proximal and medial portions of the points suggests that these areas may have been covered by the haft and adhesive (Lombard, 2004a, 2004b). Fatty residues, however, although also found on the distal edges, are more abundant on the medial and proximal portions than other animal residues. This is evidence that fat may have been used in adhesives (Wadley *et al*. 2004). Replication studies (e.g. Allain & Rigaud, 1986; Wadley, in press, 2005a) and ethnographic evidence (Brandt & Weedman, 1997) show that substances such as fat, grease and wax enhance the adhesive quality by increasing the workability and elasticity of the adhesive.

Ochre, sometimes in conjunction with resin traces, found mainly on the proximal and medial portions of the points indicates that ochre may have been used in adhesives used for hafting (Lombard, 2004a, 2004b). Ochre residues are also found on the distal edges suggesting the points were also used to process ochre (to be used for a variety of possible activities). Residue analyses, use-wear and fracture analyses show that many of the tools from Sibudu were hafted and that ochre was one ingredient that was added to the adhesive (Wadley *et al*. 2004a).

2.4 Previous replication studies on stone tool hafting

Replication studies by Allain & Rigaud (1986) were done to determine whether the success of an adhesive is dependent on the addition of an aggregate, particularly an aggregate in the form of an inert powder. They found that ochre, beeswax and resin (four parts resin, one part ochre, and one part beeswax) was the most successful adhesive recipe (Allain & Rigaud, 1986; Rots, 2002). Small amounts of beeswax (which would have very similar effects on the resin as fat or grease) added in a resin-ochre mixture make the adhesives easier to work with and more homogeneous, as well as results in an adhesive that has fewer visible cracks (Wadley, 2005a). Allain & Rigauds' experiments also show the transforming effect of heat on yellow ochreous powders, which change to red.

Wadley's experiments (2005a, 2005b) confirm Allain & Rigauds' conclusions, and aid in establishing limits and regulations for the current study. Her hafting experiments focused, chiefly, on red ochre as an aggregate. Some tools were also hafted with plain resin; and ochre-beeswax adhesives.

- The red ochre nodules were collected from a quarry on Moletadikgwa, Waterberg.
- Flat sandstone slabs were used as grindstones.
- *Grewia flava* branches were cut and used as handles. Split and L-shaped hafts were used, but only L-shaped hafts will be discussed below.
- *A. karroo* resin was collected on Moletadikgwa and was the only resin used.
- Some of Wadley's tools were bound with either *hypoxis* twine or wool. This will obviously increase a stone tools' stability on a haft. However, it means that the adhesives themselves are not the only variable being tested. Analysis is of the tools that were not bound.
- All adhesives discussed here were heated over an open fire.

Wadley made five tools using only **plain resin** and four were successful. The resin, however, was more brittle than the adhesives that had an aggregate added, and often small pieces of the resin broke off during activities.

Adhesives made with **red ochre** as an aggregate were very successful during Wadley's studies, with 15 successful tools and three unsuccessful tools. These three tools were unsuccessful due to the preparation process and not the ineffectiveness of ochre as an aggregate. Two of the unsuccessful tools had water added to the mixture (after it had been heated). This re-mixing of water to the adhesive prevented the adhesive from setting, therefore if resin does need extra moisture it should be added prior to heating.

Wadley made two tools' adhesives using **yellow ochre** as an aggregate. Neither of these tools were successful.

The addition of **beeswax** into a loaded adhesive was a successful recipe in Wadley's studies, and two of the three tools made with this adhesive recipe were successful. The beeswax makes the adhesive more malleable, flexible and homogeneous. But caution must be exercised not to add too much wax to the adhesive as this prevents the adhesive from setting.

2.5 Conclusion

Allain & Rigaud's and Wadley's experiments have acted as a starting point for the current experiments, and final conclusions take their results into account. Both yellow and red ochre were found to be successful aggregates, but the physical and chemical processes that occur were not explored. Also, they both found that beeswax is an important additive into adhesives because it gives the adhesive some flexibility, i.e. removes, or lessens, one characteristic feature of resin – it's brittleness. The current hafting experiments look further at the success of ochre-loaded adhesives, the effect of beeswax in adhesives, and compare the success of these adhesives to adhesives loaded with a variety of other aggregates. Empirical tests carried out (Chapters 4, 5, 6, 7 and 8) aim to shed some light on this issue, and ultimately discover *why* certain aggregates, when added to resin, produce successful adhesives.

CHAPTER THREE: *Hafting Experiments*

3.1 The Main Materials and Terminology

3.1.1 Resin

Worldwide, plant resin is, and was, one of the most commonly used adhesives. Rots (2002) discusses the two main types of resin used as adhesives: firstly, using resin as it exudes from a plant and loading it with an aggregate or, secondly, obtaining tar by the "destructive distillation" of wood or bark that is resinous (Rots, 2002: 59). The resin used for the current study, and for studies on which this study is based, is plant exudates and was scraped from trees (and did not involve the destruction, or use, of the bark of the tree).

Resin grades in colour from a translucent yellow through to a dark brown-black, depending on a variety of factors such as the species of tree, how deep in the plant the resin exudes from, the season, temperature and rainfall.

Pure resin is very brittle when dry and therefore is often too fragile to use as an adhesive. But past studies (Brandt, 1996; Brandt & Weedman, 2002a; Weedman, 2002a; Wadley, 2005a, in press), and the current study show that, although it is harder to manipulate and may be brittle, it can be successful as an adhesive. This will be discussed in more detail in Chapter 3. To make resin less brittle it can be loaded with an aggregate. This current study deals with these aggregates, and how they can be used to impart different qualities to the adhesives.

Acacia resin is used in this study because it is a widely used adhesive in Africa (Grant & Thomas, 1998; Van Wyk & Gericke, 2000) and *Acacia* species are found near Sibudu Cave - at present and during the MSA (Allot, 2004; Wadley, in press). I used both *Acacia tortilis* and *Acacia karroo* resin.

Acacia tortilis

Acacia tortilis is commonly known as the Umbrella Thorn. It is a widely distributed species in the Free State, Northern Cape, Gauteng, KwaZulu-Natal, Namibia, Botswana and Swaziland (Carr, 1976). It is usually found in the bushveld and lowveld, but is also found in the highveld. The *A. tortilis* tree is quite small (about six meters in height) and has a dense "flattened crown, contorted pods and both hooked and straight thorns" (Carr, 1976: 197). The bark on the trunk varies from grey to black with longitudinal cracks. Flowering, which occurs usually in mid-summer (depending on rainfall), is usually inconspicuous and flowers are cream to white coloured. The pods of the *A. tortilis* roll up into tight circles or coils (Carr, 1976).

Acacia karroo

Acacia karroo has a variety of common names, but the most frequently used is Soetdoring (or sweet thorn). This species can vary considerably in appearance and size but, what Carr (1976: 69) refers to as "the 'typical' *A. karroo*" that is found in the Free State, Gauteng and KwaZulu-Natal, is a single- or several-stemmed tree that is rounded in shape and reaches heights of about five to ten metres. The bark, like the *A. tortilis* bark, has longitudinal cracks but is darker in colour with variations usually from dark brown-grey to jet-black (Carr, 1976). The thorns are usually straight and are white or grey in colour. Flowering usually occurs in summer but is heavily influenced by the weather (specifically rainfall). In favourable conditions the bright yellow, sweet-scented flowers are abundant. Pods are linear, but often twisted, and usually form a tangled mass (Carr, 1976).

3.1.2 Adhesive

Adhesive is the resin-based substance used to 'glue' the stone tool to the haft. Adhesives described here are made up either of plain tree resin or a resin and aggregate mixture, sometimes with the addition of beeswax.

3.1.3 Aggregates

All ingredients used to make adhesives and mixed with tree resin, such as ochre, sand and ash, have been termed ‘aggregates’. Alternative words that may be used are ‘loading agents’ or ‘emulsifiers’. In the creation of industrial concrete all substances (such as stone and sand) added in a cement and water mixture are called aggregates and their function is the same as the aggregates used in resin. The term aggregate is therefore applicable to the substances placed in resin, to form an adhesive. Beeswax is the one exception because its function in the adhesive is different. Beeswax is a plasticizer and makes the adhesive more malleable and flexible and aids in producing an adhesive that is less brittle (Geneste & Plisson, 1986). Beeswax is therefore an additive but will be discussed with the aggregates, because it is always used in conjunction with other aggregates.

3.1.4 Ochre

There are inconsistencies present in archaeological literature concerning the terms colouring material, pigment, ochre, and hematite and this causes confusion.

a) ‘Colouring material’, as the name suggests, includes any kind of rock that may be used in some form (e.g. a powder) as a colouring. It is therefore not necessarily a ferruginous rock.

b) “Pigment is a substance that imparts colour to other materials”(McBrearty & Brooks, 2000: 524). ‘Pigment’ is a more general and inclusive term than ochre. Organic materials, such as flowers, juices of berries and leaves, can be used as pigment but those found archaeologically are mainly metallic oxides, and specifically iron oxides (Masset, 1980; McBrearty & Brooks, 2000). Other pigments found in the archaeological record include rocks that produce streaks of a variety of colours, such as charcoal, manganese and kaolinite (McBrearty & Brooks, 2000).

c) ‘Ochre’ is a term that is used to describe any ferruginous rock (i.e. a rock containing a high amount of iron oxide or iron hydroxide) or geological materials containing iron minerals that leave a red or yellow streak (Wreschner 1983; Volman, unpublished

manuscript). Technically, the term does not imply an artefactual status, even though it is often applied as such. Ochre comes in a variety of forms depending on the conditions under which it was formed and, scientifically, ochre has a variety of names depending on the mineralogy. Iron oxides and iron hydroxides are formed during the process of rock weathering (Schwertmann & Cornell, 1991). Iron (Fe) is the fourth most abundant element present in the earth's crust (Schwertmann & Cornell, 1991). "Precipitation, dissolution and re-precipitation" of iron oxides depends on surrounding conditions, such as pH, Eh, temperature and water activity and therefore iron oxides are good indicators of the kind of environment in which they were formed (Schwertmann & Cornell, 1991: 15).

The common iron minerals that form under sedimentary conditions are hematite, goethite, siderite, glauconite, and pyrite (Berner, 1971). Hematite (Fe_2O_3) and Goethite (FeO(OH)) are the most common and widespread in sediments because they are thermodynamically the most stable iron oxides when in aerobic (or oxidizing) conditions (Huber, 1958; Schwertmann & Cornell, 1991). Hematite (Fe_2O_3) is an iron oxide that has a hexagonal crystal system and which has a red to red-brown streak (Ghose *et al*. 1969; Lurie, 1977; Schwertmann & Cornell, 1991). Hematite can have different crystal forms. For example, when the flakes are arranged in a "foliated micaceous mass" it has a brilliant quality and is called specular hematite or specularite (Hurlbut & Sharp, 1998). If there is no crystal form, but rather an earthy botryoidal mass that is often dull in lustre, it is commonly called ochre and this is the form often used to make paint (Hurlbut & Sharp, 1998; Wenk & Bulakh, 2004). Hematite and ochre are often considered to be the same thing – separated by using the geological or everyday terms (respectively). Chapter 4 discusses the mineralogical properties of ochre in more detail.

Goethite (FeO(OH)) is a hydrated iron oxide (i.e. an iron hydroxide) that has an orthorhombic crystal system and which has a yellow to orange-brown streak (Berry & Mason, 1959; Ghose *et al*. 1969). When there is no crystal structure and the substance is amorphous, it is called limonite ($FeO(OH) \bullet {}_nH2O$). Both of these forms are used to make paint. Although quantities of iron vary greatly, goethite generally has a lower iron content than hematite. Goethite dehydrates when heated to temperatures of between 80°C and 800°

C to form hematite (Schwertmann & Cornell, 1991; Pomiès *et al*. 1999). During this process, and at this wide range of temperatures, water is driven off, which means that the end product (hematite) is lighter than the starting product (goethite). The hematite that results from the heating of goethite can be identified (through a scanning electron microscope) by "non-uniform broadening of x-ray diffraction reflections" and a porous nanostructure (Pomiès *et al*. 1999: 279).

Ochre can come in various crystal forms, and with varying mineralogical make-ups. Some ochre have very porous structures, some have flat plates that form uniform, flat surfaces, and others have tabular particles (Hughes & Solomon, 2000). Iron is present in varying quantities – between different pieces as well as within a single piece.

The main pigmenting agents in ochre are iron and manganese. However, the colour of iron oxides is not solely determined by the amount of iron present although iron (and often manganese) quantities will give an indication of the colouring potential (Hughes & Solomon, 2000). The colour depth also depends on factors such as crystal size and structure, the degree of cementation and the amount of cation substitution (Schwertmann & Cornell, 1991; Schwertmann, 1993). Goethites are usually yellow and hematites red, but there is considerable amount of colour variation within each mineral. Hematite has a greater pigmenting capability than goethite and therefore small quantities in rocks and soils can have an effect on the colour thereof, even if large quantities of goethite are present (Schwertmann & Cornell, 1991), and will result in rocks and soils being preferentially stained red.

Changes in crystal/particle size and morphology can cause differences in these mineral-specific colours of the solid (Winter, 1979 as cited in Schwertmann & Cornell, 1991). A decrease in particle size (i.e. a higher surface area) of goethite results in a browner colour than yellow, and a more blue tint in hematite, rather than a bright red when the particles are larger (Schwertmann & Cornell, 1991).

In this study, all pigments used do contain some iron, and have red to yellow streaks. Many of the pieces collected are earthy varieties of hematite or goethite, but the general term 'ochre' will be used to describe these colouring materials, whether they are iron oxides or iron hydroxides. They are distinguished by their colour – red or yellow – and, where necessary, the geological form in which they came, such as from the non-fissile Pietermaritzburg Formation (Ecca) shale (i.e. snuff-box shale; Hughes & Solomon, 2000), will be mentioned.

Grinding ochre

The most practical and easy way to produce ochre powder is by grinding a piece of ochre against a coarse grindstone. During this process the ochre is worked on several different facies where fine striations are aligned with the direction of rubbing (Wadley, 2005b). The pieces often become shaped like crayons (after grinding), but many pieces resemble the shape in which they originally came. Preliminary analysis by Wadley (2005b) shows that since there are no obvious differences between types of polish and striations on archaeological and experimentally produced 'crayons', then the archaeological 'crayons' (specifically at Sibudu Cave) are waste products of grinding, and not tools themselves, used, for example, as crayons for drawing on a surface. Work on the Sibudu ochre, which is currently being completed by Sunshine Clark, will allow for more conclusive results on this issue. The snuff-box shale pieces have pockets of colouring inside hard shale, and so grinding on slabs to obtain powder is difficult. A more effective way to extract the powder out of these pockets is to use stone flakes or points. Archaeological evidence of these types of modifications is found on some ochre pieces from Qafzeh (Hovers *et al.* 2003).

3.2 Cementing properties

Concrete is made by mixing cement (which is most commonly composed of lime, iron oxide, silica and alumina), water and mineral aggregates, such as sand and stone (Elvery, 1958; Lea, 1970; Benson, 2005). The cement and water mixture covers the surfaces of the aggregate (fine and coarse) and through a chemical reaction, called hydration, the

mixture hardens ands binds them all together and forms concrete. The process therefore involves mixing together materials that have the correct physical and chemical properties (Elvery, 1958). The cement quality is ultimately what determines the character (not success) of the concrete (Portland Cement Association, 2005). The materials and quantities need to be carefully considered and selected depending on the use of the final product. The strength of the aggregate, optimum size of the aggregate, the bond that forms between the aggregate and cement, and the surface characteristics of the aggregate are all important and any of these could limit or enhance the ultimate strength of the concrete.

There are some more specific guidelines in the creation of industrial concretes that apply to and are useful in the creation of adhesives. The physical and chemical nature of the aggregate affects the workability and final product of concrete. Fine and coarse aggregates need to be present. Quartz sand is the most common aggregate used in concretes because it has a medium and varied range of particles sizes, has rounded particles, and a high silica content (Elvery, 1958; Lea, 1970; Addis, 1986). Silica plays an important role in the chemical changes that occur in the concretes when going through the process of hydration (Elvery, 1958). Sand also often contains small quantities of iron ores and mica (Lea, 1970), which are valuable in the process of creating concrete. Coarse aggregates, such as crushed rock and gravel add to the strength of the concrete but also act as a bulk filler (Benson, 2005). Aggregates are often made of hard materials, such as granite, but soft aggregates, such as lime, are also successful and give the concrete different qualities (Elvery, 1958). Rough-textured, angular and elongated particles require more water to be added to the mixture (and therefore more cement, as will be discussed below) than smooth, rounded aggregate particles (Portland Cement Association, 2005).

Silts and clays, often in the form of dirty residues on the sand and gravel particles, must not be present in large amounts because the particles are very fine, and form a film around the sand and gravel particles, which results in a reduction of the strength of the concrete (Benson, 2005). The presence of fine particles also often results in too much water being added, which in turn results in a mixture that is too sticky or that does not

harden (Elvery, 1958; Addis, 1986). The amount of water added changes depending, also, on the moisture content of the aggregates themselves, as well as the particle type of the aggregate. Water is a vital factor in the creation of concretes and too much water is the most common cause of unsuccessful concrete (Elvery, 1958). Excessive impurities, especially chlorides, sulfates, solids and alkalis, in the water may affect the strength and setting time of the concrete, but almost any water that is drinkable is suitable for use in concrete (Portland Cement Association, 2005).

The quantity of aggregate added – or cement to aggregate ratio – must be regulated depending on the water content and depending on the desired application of the concrete. Although mixing quantities vary depending on the materials used, a typical mix is about 10 to 15 percent cement, 60 to 75 percent aggregate, and 15 to 20 percent water (Portland Cement Association, 2005).

3.3 Hafting Experiments

Ninety-seven tools have been hafted with resin or a resin and aggregate mixture during the course of both hafting experiments. Different adhesive recipes were made and used: different kinds and quantities of aggregates were added into resin, and the adhesives heated for differing times. The time that the tools took to dry was noted as well as any physical changes or effects the heating process had on the adhesives. The success of the adhesives was tested by using the tool for chopping and sawing activities.

There were two sets of hafting experiments. The second set built on previous experience of the hafting process. By the second set of experiments I had a better understanding of the physical and chemical processes occurring in the adhesives. The two sets of tests will be discussed separately. Before discussing the results of the experiments, I will discuss the hafts, adhesive ingredients used and preparation techniques employed.

3.3.1 Hafts

The hafts were made using dowel sticks. Dowel sticks were chosen to reduce the number of variables during experimentation. L-shaped hafts were used because Wadley's studies showed that split hafts were fragile and often broke during sawing and chopping activities (Wadley, pers. comm; Wadley, 2005a). Split hafts would also interfere with the aim to test the adhesives, since the haft strength would be tested and not necessarily the adhesives' effectiveness. The dimensions of the hafts were chosen for practical reasons, that is, that the platform is wide enough for the flake to rest on and the handle is long enough to hold comfortably during activities.

3.3.2 Stone flakes

Stone flakes were collected from debris made during previous stone tool knapping experiments. In order not to introduce another variable into the experiments, hornfels flakes of relatively similar sizes and bulb sizes were chosen. Many of the Sibudu MSA tools are made out of hornfels, and so hornfels is a logical choice of raw material for this study. The sizes and shapes of the stone flakes, however, does become problematic because all flakes vary to a certain degree. An alternative would be to use identical glass triangles, but finally it was found to be unnecessary since it is the stress under which the adhesive is placed and the manner in which the tool is used, that is both controllable and more relevant here.

3.3.3 Resin

Resin was collected from *Acacia* trees, specifically *Acacia karroo* and *Acacia tortilis*. Initially, only *Acacia karroo* resin was going to be used, but such proved difficult to obtain in the quantities needed. Therefore, it was decided that *Acacia tortilis* resin would also be used. The resins collected contain some unavoidable impurities such as sand particles and small pieces of bark. These are likely to have existed in resins collected and used during the MSA.

Another facet of resin quality that needs to be considered is that of how the resin was prepared. Some resin used was still liquid enough to use when it was collected from the

tree. Other resin had hardened, or did not have enough liquid in it to be useful for making adhesives (Figure 3.3.1). This resin was then placed in water and, due to its solubility, it was restored to a wet resin (Figure 3.3.2) that looked very similar to the resin collected wet from the tree, but had a less syrupy texture. This resin, when used as an adhesive, initially appears to have the same qualities as resin that is collected and used wet from the tree. The effects of the water to the chemical and physical nature of the adhesive will be looked into in Hafting Experiments 2.



Figure 3.3.1 Ball of hardened resin. Water is then added and the resin becomes reconstituted (Fig. 3.2.2).



Figure 3.3.2 Hardened resin that has been reconstituted.

3.3.4 Aggregates

The different aggregates chosen are materials that are likely to have been readily available to the MSA tool-maker. The aggregates (which are used in Hafting Experiments 1 and 2) are ochre, commercially produced ferric oxide, gypsum, charcoal, kaolinite, ash, sand, burnt bone, and fine wood shavings. Beeswax is also used in conjunction with some of these aggregates.

- Ochre was collected in January and February 2004 from a slate quarry, that is

about 1km from Sibudu Cave. None of the ochre pieces collected are archaeological in origin. Some of the ochre was found within snuff-box shale (and was therefore only discovered once the shale was broken open). This ochre is very powdery or chalky and each rock shows great colour variation, with colours ranging from dark browns to red to yellows (Fig. 3.3.3). Other ochre comes in the form of small, compact and smooth rocks. These are less chalky than the snuff-box shale but also show large colour variations (Fig. 3.3.4). The iron and silica contents of these pieces also vary greatly, with iron percentages ranging from about 7% to about 74%, and silica percentages from about 8% to about 13%. This is discussed in Chapter 4.

All ochre pieces were photographed and catalogued. Pieces were then ground on sandstone slabs (Fig. 3.3.5), which had been collected from Sibudu Cave roof fall. Grinding times between the different pieces varied greatly, since some are more powdery and others are compact and very hard. Grinding did not follow any uniform method but was rather based on the easiest way in which the powder could be produced. Most of the ochre pieces were rubbed hard against the flat sandstone but when certain areas of the ochre became very hard and consequently difficult to grind, the corners of the sandstone slab were more effective grinding surfaces. This produced a ground ridge in the ochre (as opposed to a flat, smooth surface) and the resultant left-over ochre forms a variety of shapes, some of which are crayon-like forms (Fig. 3.3.6, Fig. 3.3.7). The snuff-box shale proved more difficult to grind because small pockets of colouring are found within the hard shale. The easiest way to get the powdery colouring material out is to use a pointed stone flake or a similarly shaped object. Ground pieces were given to Sunshine Clark, for her studies on the ground ochre crayons from Sibudu, and added to her comparative samples.

- Commercially produced ferric oxide (which will be called, for ease of reference, 'ferric oxide') was obtained from the Wits Chemistry Department. This is 85% Fe_2O_3.



Figure 3.3.3 Snuff-box shale piece showing 'pockets' of soft yellow and red colouring.



Figure 3.3.4 Two examples of the smooth, compact pieces of ochre.



Figure 3.3.5 All ochre was ground on sandstone slabs.



Figure 3.3.6 Some ground ochre pieces.



Figure 3.3.7 Ochre pieces and the powder produced from them. Note the snuff-box shale on the left, from which both red and yellow colouring was obtained (by scraping it out of the 'pockets').

- The gypsum was collected during digging MSA levels at Sibudu. The gypsum, or calcium sulphate, is very crumbly and contains some minute pieces of bone.

- Charcoal was collected (a variety of woods were used) and then crushed to a fine powder using a rock.

- Kaolinite was collected from towns in the surrounds of Sibudu - in Verulam and Ndwedwe. The kaolinite comes in red and white, and both colours are used by locals, to colour the skin. The local term for the material is "*ibomvu"* (which means red in isiZulu) and the particles are very fine when ground. Initially it was uncertain whether the colouring material was kaolinite, or just a clayey soil. Components were identified through Fourier Transform Infrared Spectroscopy (FT-IR) using KBr pellets by Solvieg Schiegl (pers. comm. to L. Wadley) at the University of Tüebingen in Germany. The test confirmed that this material is kaolinite. Kaolinite is a colourless material, therefore the red colouring in the kaolinite used for the present experiments suggests that iron oxide is present in the sample (Schwertmann, 1985). This is likely considering that the soils of the region are lateritic, and the lateritic soils of the Table Mountain Sandstone (T.M.S.) are composed, almost entirely, of iron oxides (Maud, 1965; McBrearty & Brooks, 2000). Iron oxides and iron hydroxides are not, however, detectable in the FT-IR spectrum of this sample (Schiegl, pers. comm.). Therefore, Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) analysis was done (Chapter 4).

- The wood used to make the charcoal is the same as that used to produce the ash.

- The sand was collected in Johannesburg and is silica-rich, and ICP-OES tests (Chapter 4) established that this sand has an iron content of about 4%, and a silica content of about 13%.All sand was collected from the same area.

- The burnt bone is from a modern bovid. The bone was burnt in a fire then crushed

into a fine powder with a rock.

- The wood shavings are the by-products of sawing the hafts into shape.

- Natural beeswax was an additive used in some adhesives. To use in adhesives it has to be heated until it becomes soft.

3.3.5 Mixing Quantities

Different resin to aggregate ratios (in volume, not mass) were tried in order to determine which quantities were the most successful (Fig 3.3.8). Unlike commercial concrete mixing ratios, adhesive mixtures were too dry if such large amounts of aggregate were added, especially since the only water used was that already in the resin. Also, the very coarse aggregate or bulk filler, which is usually gravel, is not present in the adhesive because of how the adhesive is being applied and used, i.e. in small amounts and for a delicate and intricate purpose.

Most of the adhesives (31 tools) were made with a resin to ochre ratio of 2:1, that is, two parts resin to one part ochre (Fig 3.3.9), but a number of adhesives (19 tools) were made with equal amounts of resin and ochre, i.e. 1:1 adhesives. A few other ratios (2:3, 4:1, 4:3, 4:3:1) were also experimented with. The adhesives were not mixed for a fixed period but rather until the aggregate was completely mixed in and the mixture looked homogeneous.

3.3.6 Heating

Adhesives were placed on the end of a stick (for ease of reference and clarification this will be called a heating stick) and held close to the fire so that a high temperature could be obtained. The adhesive could not be held too close to the fire or it would burn or a thick outer skin would form. Since a natural open fire is used, temperatures vary greatly and adhesives are therefore likely to be exposed to inconsistent temperatures. Because of the consistency of the adhesive the heating stick has to be turned continuously so that the adhesive does not fall, or drip, off the stick. A variety of heating times were experimented

with to find out whether this influenced the quality and effectiveness of the adhesive as well as the colour of the adhesive (specifically if changes occurred when yellow ochre was used as an aggregate).



Figure 3.3.8 Measuring and mixing the adhesive ingredients.

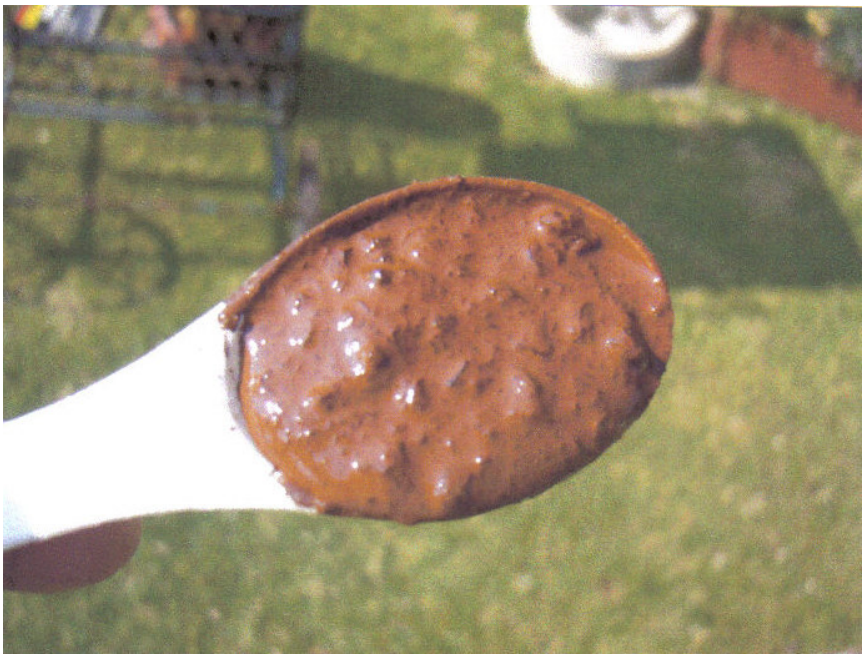


Figure 3.3.9 The adhesive prior to heating.

Most of the tools were heated for one to one and a half minutes. Adhesive was then placed on the haft and the stone tool embedded within the adhesive. None of the tools were reheated after the stone tool had been embedded. Tools were then placed near the fire to dry (Fig. 3.3.10). The distance from the fire is dependent on the heat of the fire. Drying times varied between one hour and five hours.

3.3.7 **Tool activities** (Appendix 2 and 4)

All tools were used to saw and chop branches in order to test the strength and effectiveness of the adhesive (Fig. 3.3.11). Each tool was used for five minutes at the most, but many fell off before then. The first two minutes were spent sawing wood, and the last three minutes involved chopping activities, therefore more impact and more force was used in the last three minutes. The tools that stayed intact for the whole five minutes have been termed 'successful'. Tools that had their stone tools fall off before or during the activities have been termed 'unsuccessful'.



Figure 3.3.10 Drying the tools next to the fire.



Figure 3.3.11 Chopping and sawing branches to test the strength and effectiveness of the hafting adhesive.

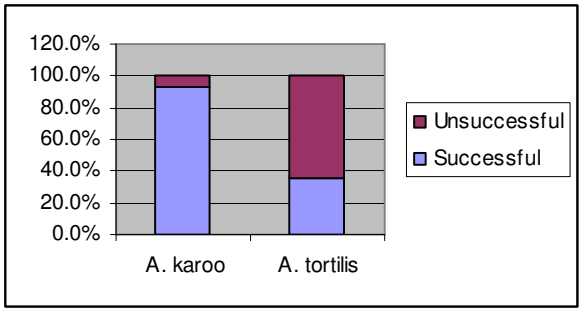
3.4 Hafting Experiments 1

Tools made during Hafting Experiments 1 were made to test different adhesive recipes, but also to test different resin species, adhesive mixing quantities and heating times. Unfortunately, individual analyses of these aspects is difficult (especially in Hafting Experiments 1) because there are many variables involved. The results of the discussions below, on the different species of resin, mixing quantities and heating times (3.4.1, 3.4.2, 3.4.3), although important, are problematic on their own. The implications of these variables are discussed in Chapter 9.

Appendix 1 gives a list of Hafting Experiments 1 results and shows the tools made, the resin and emulsifiers used, quantities used (and ratios), heating times, the reaction of the adhesives to the heat, and the functional effectiveness of the adhesive as a binding material. Where moulds were made (for hardness tests and SEM analysis) a mould number has been given.

A full list of activities done is given in Appendix 2. Five tools, Tools 29 to 33, have been excluded from the following discussion as the resin was of a poorer quality (as it contained large amounts of sand and small wood pieces as well as maggots) and this visibly influenced the adhesive quality prior to and after heating.

3.4.1 Resin



Key to Figure 3.4.1

Resin	Successful	Unsuccessful
A. karoo	92.9% (13)	7.1% (1)
A. tortilis	35% (14)	65% (26)

Note: (n) = quantity of tools made.

Figure 4.3.1 Success rate of adhesives made with two resin species.

Experiments were done with plain resin to see if it is successful on its own as an adhesive used to bind hafted tools, as well as to see if there is any difference in the quality of *Acacia karroo* and *Acacia tortilis* resins when used as adhesives (with or without aggregates). Nearly all (92.9%) of the *A. karroo* resin adhesives were successful, whereas only a minority (35%) of the *A. tortilis* resin adhesives were successful (Fig. 3.4.1). This would seem to imply that *A. karroo* resin is definitely better as a binding agent. However, when one looks closer at the hafting experiments and the other variables involved (including resin *quality*), it becomes clear that the resin species is not the only the deciding factor.

- Four tools were made with plain resin (i.e. no aggregate was used). Tools 22 and 27 were made with *A. karroo* resin and heated for 1:30 minutes and one minute respectively. Tools 35 and 41 were both made with *A. tortilis* resin and heated for one minute and 1:30 minutes respectively. The only unsuccessful tool was Tool 35 – the adhesive was too moist and runny and would not hold the stone tool in place. It therefore cannot only be that the heating time was slightly less since Tool 27 was heated for the same time yet was successful. In this case, then, the resin species was a deciding variable, or the different moisture content was significant.

- Tools 5 and 6 were made with yellow ochre as an aggregate and the same mixing quantities (2:1). Tool 5 was made using *A. tortilis* resin and was heated for four minutes, whereas Tool 6 was made using *A. karroo* resin and was heated for 1:30 minutes. The adhesive on Tool 5 was crumbly and did not stick on the heating stick, and after four minutes of heating the adhesive got considerably drier. In this case, the heating times affected the resultant adhesive quality. However, before heating, the adhesive on Tool 5 was already drier. Moisture content is therefore important.

- Tools 25, 37 and 49 were made with burnt bone as an aggregate and all with the same mixing quantities (2:1). Tool 25 was made with *A. karroo* resin adhesive and heated for one minute, whereas Tools 37 and 49 were made with *A. tortilis* resin and heated for one minute and 1:30 minutes respectively. Tools 25 and 49 were successful. Tool 37 was

unsuccessful. The only difference between Tool 25 and Tool 37 is the resin species, and the one made with *A. karroo* resin was successful. However, Tool 49, although heated for longer, was successful.

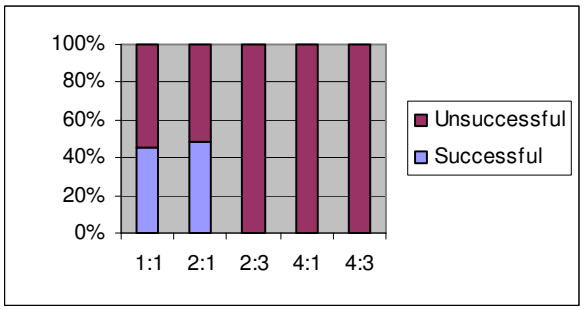
It is likely that the moisture content in the *A. tortilis* resin varies since most of the *A. tortilis* resin had water added to re-soften it, and in the case of Tool 49 the extra heat dried up excess moisture making the adhesive better and therefore successful.

- Tools 26 and 50 were made with wood as an aggregate and the same mixing quantities (2:1). Tool 26 was made with *A. karroo* resin and heated for one minute, whereas Tool 50 was made with *A. tortilis* resin and heated for 1:30 minutes. Tool 26 was successful and Tool 50 was not. Tool 50, when heated, formed a skin. This may again be due to the varying moisture content in the resin, or higher temperatures that the adhesive was exposed to.

The main problem with these results is that there are too many variables involved and it cannot be established whether it is the resin species, the aggregate, the mixing ratios or the heating period that causes an adhesive to be successful.

These contradictory results do, however, not only raise questions about the resin species and moisture content but also about the inconsistency of the heat from the fire and the heat to which the adhesives are exposed. Fire heat is inconsistent and temperatures can vary greatly within the same fire. Adhesives can then be heated slightly differently from one another even at the same fire. In Wadley's studies (2005a, 2005b) and the current study, heating of plain resin was problematic because it was more runny. Heat appears to have a greater immediate effect on the plain resin than it does on the resin that has an aggregate mixed into it. This is shown through the drying up of the resin, the colour change of the plain resin to a lighter, white colour, and the formation of visible cracks, and the consequent brittleness of the resin as an adhesive. Resin that has an aggregate added does not show these signs.

3.4.2 Mixing Quantities



Key to Figure 3.4.2

Ratios	Successful	Unsuccessful
1:1	45.4% (5)	55.6% (6)
2:1	48.4% (15)	51.6% (16)
2:3	0%	100% (2)
4:1	0%	100% (1)
4:3	0%	100% (1)

Note: (n) = quantity of tools made.

Figure 3.4.2 Success rate of adhesives made with different ratios of ingredients (not considering aggregate type).

Most of the successful adhesives were made with 2:1 mixing ratios, but 1:1 mixing ratios were also relatively successful (Fig. 3.4.2). Most of the tools that completed the sawing and chopping activities were made with adhesives that had 2:1 mixing ratios, i.e. twice the amount of resin to aggregate. The 1:1 adhesives were, on the whole, drier and it was harder to mix the aggregate into the resin than with the 2:1 adhesives. It was obvious, at this stage, that some of the 1:1 adhesives were not going to be successful as binding materials for stone tools onto hafts because they were already too dry and crumbly. The 2:1 adhesives were more manageable, easy to mix and form a firm, smooth paste of the desirable consistency.

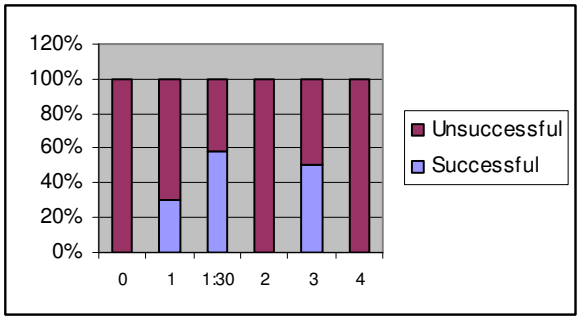
- Two tools, Tool 11 and Tool 15 were made using more aggregate, in this case ochre, than resin (with a mixing ratio of 2:3). On mixing the adhesive it was evident that the adhesive would be too dry because the ochre did not mix easily into the resin. The adhesive was crumbly and the stone tools from both the tools fell off the haft before they were used for any activities. The extra one minute of heat that Tool 15's adhesive was exposed to caused the adhesive to be much too dry and crumbly, and consequently it was a very unsuccessful adhesive. Again, there are two variables being tested here, and so results are insecure.

- Tools 2, 24 and 48 were made with charcoal as an aggregate and were heated for 1:30 minutes. Tools 2 and 48 were made using *A. tortilis* resin and had 2:1 adhesives, whereas Tool 24 was made using *A. karroo* resin and 1:1 adhesive. All three tools were unsuccessful. The only obvious difference is that the mixing quantities may have influenced these tools because during heating the adhesive for Tool 24, a very thick skin formed. Also, Tools 2 and 48 had more moisture (than Tool 24) in their adhesives before and after they were heated. Again, there are many variables involved here.

- Tools 19 and 40 were made with gypsum as an aggregate, *A. tortilis* resin and both were heated for 1:30 minutes. Tool 19 was made with 1:1 adhesive and was successful, whereas Tool 40 was made with 2:1 adhesive and was unsuccessful. Strangely, it was the adhesive used for Tool 40 that was not easy to mix and the adhesive became quite dry and a bit crumbly.

The mixing quantities of ingredients are important in determining adhesive qualities because they influence the moisture available in the adhesive and therefore determine whether the adhesive will be too crumbly or too runny. However, quantities of ingredients must be considered in conjunction with the amount of moisture present in the resin.

3.4.3 Heating times



Key to Figure 3.4.3

Minutes	Successful	Unsuccessful
0	0%	100% (1)
1	30.8% (4)	69.2% (9)
1:30	58.3% (21)	41.7% (15)
2	0%	100% (1)
3	50% (1)	50% (1)
4	0%	100% (1)

Note: (n) = quantity of tools made.

Figure 3.4.3 Success rates of adhesives heated for different times.

1:30 minutes of heating resulted in the largest number of successful tools, regardless of the ingredients used (Fig. 3.4.3). Three minutes of heating also has a relatively high success rate but this is due to small sample size – there were only two tools (Tools 4 and 55) made with adhesive that was heated for three minutes. More were not tried because this heating time resulted in much of the adhesive drying out and forming a thick skin. Tool 55 was made using yellow ochre as an aggregate, and was heated for three minutes to see if a colour change would occur (to a redder shade), but no change occurred. 1:30 minutes was decided upon as a sufficient and useful heating time.

- Tools 3 and 4 were made with the same aggregates (ochre and charcoal), 1:1 adhesives, but were heated for 1:30 minutes and three minutes respectively. Tool 4 ended up having less adhesive on the tool because much of the adhesive dried out during heating. Both tools were, however, unsuccessful because of the dryness of the adhesive, largely due to the ratio of resin to aggregate (as discussed above). As would be expected, Tool 4 dried quicker than Tool 3.

- Tools 5 and 6 were made with the same types of aggregate and the same quantities of resin and aggregate (2:1) but with different resin qualities. Tool 5 was heated for four minutes and Tool 6 for 1:30 minutes. The effects of this were evident during heating, where the adhesive used for Tool 5 became so dry that it would not stay on the heating stick. The adhesive became crumbly and dried after an hour, at which time the stone tool fell from the haft. The adhesive on Tool 6, on the other hand, was smooth and very successful.

- Tools 42 and 55 were made in order to test the resin quality after different heating periods, but also to test if the yellow ochre used as an aggregate changed colour during heating. The adhesive used for these tools was made with the same types and quantities of resin and aggregate (2:1), but the adhesive was heated for 1:30 minutes and 3 minutes respectively. As aforementioned, no colour change occurred, but the differing adhesive qualities were obvious. Tool 55 (the tool with the adhesive that was heated for a longer

period) was surprisingly the tool that was successful and lasted all the activities, whereas Tool 42 lasted just over a minute of its activity.

- Tool 11 was made with *A. tortilis* resin and red and yellow ochre as aggregates, and using a 2:2:1 adhesive or, since both aggregates are ochre, a 2:3 adhesive. The adhesive was then heated for one minute. The adhesive was quite dry and the tool was unsuccessful. Tool 15 was made with the same adhesive but was reheated for 1:30 minutes before the stone tool was embedded, 40 minutes after it was initially heated. The reheating of the adhesive caused it to become very dry and crumbly and the adhesive was unable to hold the stone tool to the haft. The extra heat made the adhesive unusable. Too many variables are involved here to make conclusions on the influencing factors.

Heating times of the adhesives on the heating stick affect the visible qualities of adhesive to a lesser degree than resin moisture, and mixing quantities. Heating times affect the adhesives mainly when heated for long periods, since this results in the drying out of the adhesives, resulting in crumbly or brittle adhesive.

3.4.4 Aggregates

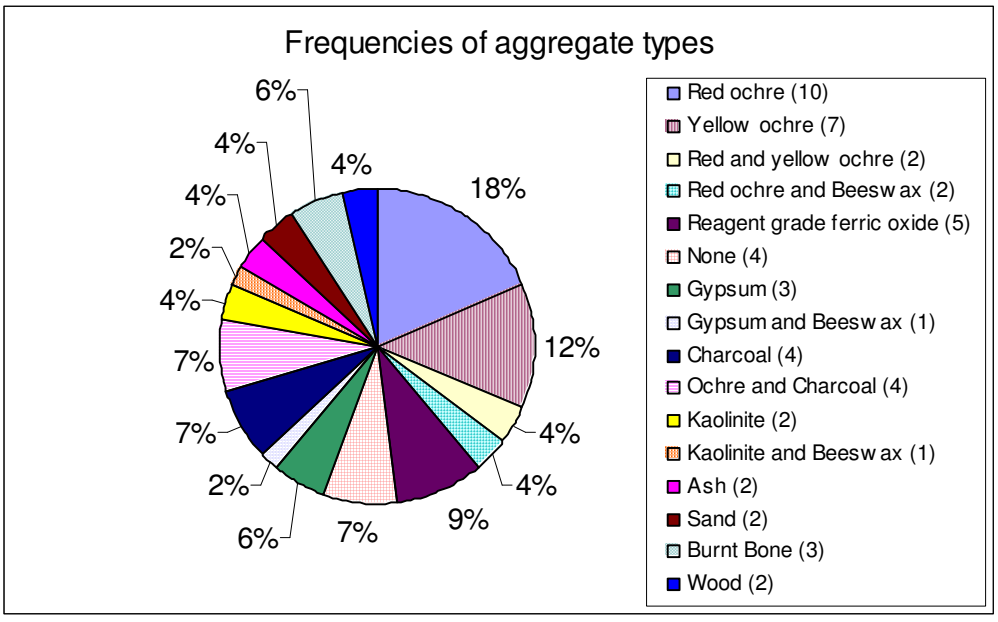


Figure 3.4.4 Frequencies of tools made with each aggregate in Hafting Experiments 1.
Note: (n) = Number of tools made with each aggregate.

i) Ochre

Nineteen tools (35% of all tools made) were made with adhesive made of **resin and ochre.** Of all the tools made with adhesives made of resin and ochre, eleven were successful and eight were unsuccessful (Fig. 3.4.5).

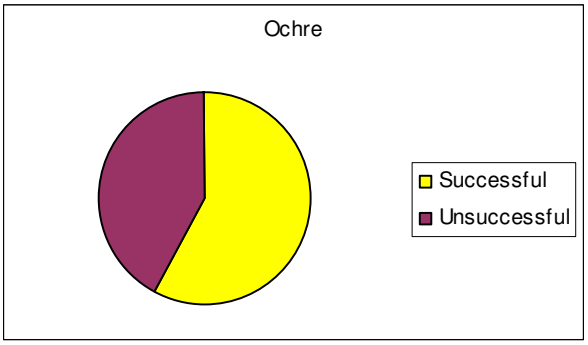
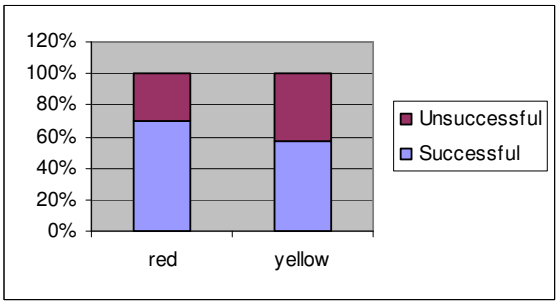


Figure 3.4.5 Success rate of tools made with ochre as an aggregate.

Red versus yellow ochre



Key for Figure 3.4.6

	Successful	Unsuccessful
red	70% (7)	30% (3)
yellow	57.2% (4)	42.8% (3)

Note: (n) = quantity of tools made.

Figure 3.4.6 Success rate of tools made with different colour ochre.

More adhesives made with red ochre as an aggregate were successful than those made using yellow ochre as an aggregate (Fig. 3.4.6). Adhesives made with red ochre as an aggregate have a 70% success rate, whereas adhesives made with yellow ochre have a 57.1% success rate.

-Tools 6 and 8 were made with the same resin (*A. karroo*), the same mixing quantities (2:1) and heated for the same time (1:30 minutes). The only difference between the adhesives was the aggregate. Both were made with ochre from the same rock but the rock had been broken in half and one half was heated prior to grinding. This piece became a

redder colour, whereas the original colour (and colour of the remaining piece) was yellow (Fig. 3.4.7). Tool 6 was made with ochre from the unheated piece, and Tool 8 from the heated piece. Both tools were successful.



Figure 3.4.7 Two examples of the colour changes that occur when ochre is heated. The unheated pieces are those on the left side of each picture. The heated pieces are darker, but sometimes only slightly.

- The aggregate used in Tool 10 and 12's adhesives was ochre (from the same rock), but the ochre used for Tool 10 was from a red section, whereas the ochre used for Tool 12 was from a yellow section. Both adhesives were made with *A. tortilis* resin and were heated for one minute. Tool 10 used a 1:1 adhesive, and Tool 12 a 2:1 adhesive. Both tools were unsuccessful. When the adhesive used on Tool 10 was heated a thick skin formed.

- Tools 16 and 17 were made with *A. karroo* resin, 2:1 adhesive and both were heated for 1:30 minutes. The only difference between the adhesives is the aggregate. Both were made with ochre from the same rock but the rock had been broken in half and one half

had been heated. The heated piece had became a redder colour, whereas the original colour (and colour of the remaining piece) was yellow. Both tools were successful.

- Tools 42 and 43 were made with ochre as an aggregate. Tool 42 was made using powder ground from a yellow section of the rock, and Tool 43 from a red section of the rock. Both were made in exactly the same way – *A. tortilis* resin, 2:1 adhesive and heated for 1:30 minutes. Tool 43 was successful and Tool 42 was unsuccessful.

Based purely on colour, there is a difference between the effectiveness of yellow versus red ochre when used as an aggregate. But all the tools discussed above have many differing variables, such as different mixing quantities, different resin species and differing heating periods. It therefore cannot be said that this is definitely because of the aggregate added. Hafting Experiments 2 investigate more ochre adhesives wherein there are not so many variables involved.

ii) Commercially produced ferric oxide

Five tools were made using adhesives made from **resin and ferric oxide** (Tools 56-60).

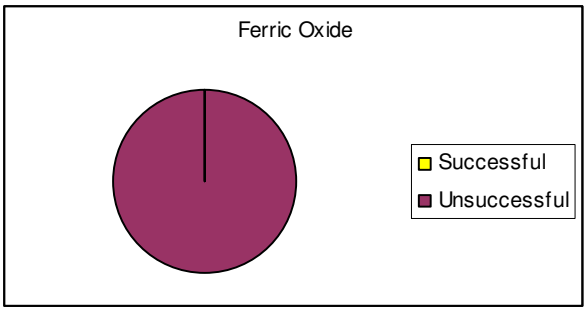


Figure 3.4.8 Success rate of tools made with ferric oxide as an aggregate.

These adhesives were all made to be mounted tested for hardness, to see whether a chemical reaction (that affects the hardness of the adhesive) occurs when large amounts of iron are present. All were made with *A. tortilis* resin. Different mixing ratios were used (4:1, 2:1, 4:3 and 1:1). One of the 2:1 adhesives was also left unheated, all the others were heated 1:30 minutes. All the tools were unsuccessful (Fig. 3.4.8).

iii) Ochre and charcoal

Four tools were made using adhesives made from **resin, ochre and charcoal** (Tools 3, 4, 7, 9). Two of these tools were successful (Fig. 3.4.9).

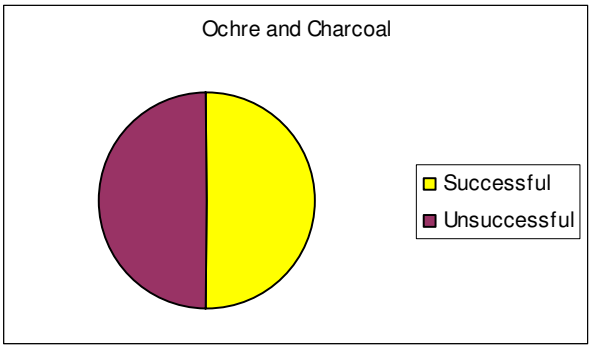


Fig. 3.4.9 Success rate of tools made with ochre and charcoal as aggregates.

- Tools 3 and 4, which were made with red ochre, charcoal and resin were unsuccessful. Both the tools were made with *A. tortilis* resin, 1:1 adhesive, but were heated for 1:30 minutes and three minutes respectively.

- The adhesives used to make Tools 7 and 9 were made with 2:1 adhesives, *A. karroo* resin and were heated for the same time (1:30 minutes). Both were made with charcoal and ochre as aggregates, but Tool 7 was made with unheated yellow ochre and Tool 9 with ochre from the same stone as that used for Tool 7, but the section had been broken off and placed in the fire (and turned red). Both tools were successful.

iv) Beeswax

Four tools were made with beeswax as an additive. Three of these tools were successful (Fig. 3.4.10). They will be discussed separately below.

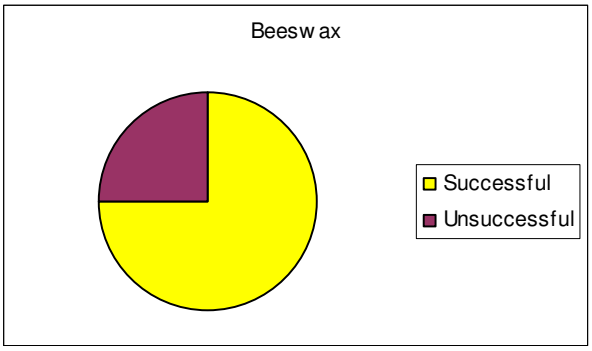


Figure 3.4.10 Success rate of tools made with an aggregate and beeswax.

a) Ochre and Beeswax

Two tools were made with adhesives made of **resin**, **red ochre and beeswax** (Tools 20 and 51). They were both heated for the 1:30 minutes, made with *A. tortilis* resin, but had slightly different mixing quantities – Tool 20 had a 4:3:1 (resin:ochre:beeswax) adhesive, and Tool 51 had a 4:2:1 adhesive. Tool 20 therefore had more aggregate in its adhesive. The tools were made with different 'qualities' of ochre – Tool 20 was made with light red ochre, whereas Tool 51 was made with red, heated (formerly yellow) ochre. This and the slight differences in mixing quantities did not seem to change the two adhesives greatly. Both tools were successful.

b) Kaolinite and Beeswax

One tool was made using **resin, kaolinite and beeswax** (Tool 21). A 4:3:1 adhesive was used, *A. tortilis* resin, and the adhesive was heated for 1:30 minutes. Some beeswax lumps were apparent in the adhesive. This tool was unsuccessful. This was the only tool made with resin, an aggregate and beeswax that was unsuccessful.

c) Gypsum and Beeswax

One tool was made using **resin, gypsum and beeswax** (Tool 23). A 4:3:1 adhesive was used, *A. tortilis* resin and the adhesive was heated for 1:30 minutes. This tool was successful.

A problem with beeswax is the melting thereof, as lumps of beeswax can still be seen in most of the adhesives. Success rates could therefore have been influenced by the amount that the wax was melted and the resulting homogeneity of the adhesive. If well mixed then the adhesive becomes easy to work with and is more flexible (Rots, 2002; Wadley, 2005a, in press). Very small amounts of beeswax should be used, otherwise the tool will not set and the adhesive will shrink, which causes the stone tool to come loose (Allain & Rigaud, 1986; Wadley, 2005, in press). Therefore, very small amounts of beeswax were added into the adhesives.

v) Gypsum

Three tools were made using adhesive made of **resin and gypsum** (Tools 19, 36 and 40).

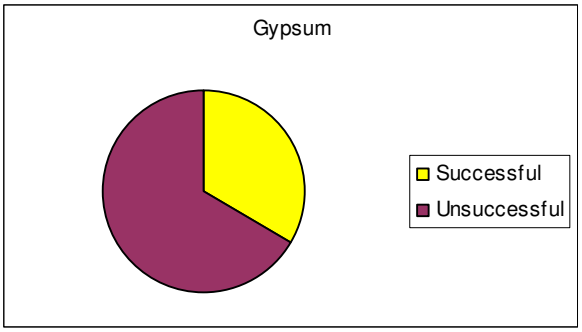


Figure 3.4.11 Success rate of tools made with gypsum as an aggregate.

Different mixing ratios were used (1:1, 2:1, and 2:1 respectively) and different heating times were experimented with (1:30 minutes, one minute, and 1:30 minutes respectively). Tools 36 and 40 were unsuccessful but Tool 19 was successful (Fig. 3.4.11), therefore it appears that the mixing quantities influenced the resultant adhesive – with the 1:1 adhesive being successful. But from prior research (Wadley, pers. comm.; Koursaris, pers. comm.), gypsum would be expected to be unsuccessful as an aggregate because when heating gypsum the molecules line up and therefore form a weaker crystalline structure (Miller, pers. comm.).

Gypsum and Beeswax: As discussed above, one tool was made using adhesive made of **resin, gypsum and beeswax** (Tool 23). Experiments with beeswax and gypsum were

carried out to see if beeswax could influence how the gypsum reacts under heat. This tool was successful.

vi) Charcoal

Four tools were made using adhesive made of **resin and charcoal** (Tools 2, 24, 34 and 48).

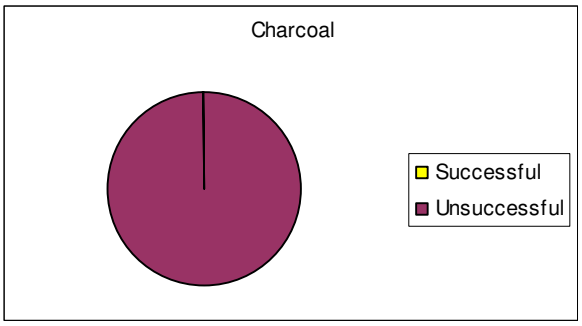


Figure 3.4.12 Success rate of tools made with charcoal as an aggregate.

Tools 2, 34 and 48 were made with 2:1 adhesives (with *A. tortilis* resin) and Tool 24 with *A. karroo* resin and a 1:1 adhesive. All the tools were heated for 1:30 minutes. All these tools were unsuccessful (Fig. 3.4.12). These differences and changes do not appear to have influenced the effectiveness of the adhesive. Charcoal is therefore not a good aggregate in hafting adhesives.

Charcoal and Ochre: When ochre and charcoal were used as aggregates there was a 50% success rate. All adhesives had a 1:1 (or 2:1:1) mixture and were heated for 1:30 minutes, except for Tool 4, which was heated for three minutes. The two successful tools were both made with *A. karroo* resin, whereas the two unsuccessful tools were made with *A. tortilis* resin. Tool 7 (which was made with yellow ochre and charcoal as aggregates) and Tool 9 (which was made with red ochre and charcoal as aggregates) were both successful. Tools 3 and 4 made with red ochre from the same piece were both unsuccessful.

vii) Kaolinite

Two tools were made using adhesive made of **resin and kaolinite** (Tools 18 and 52).

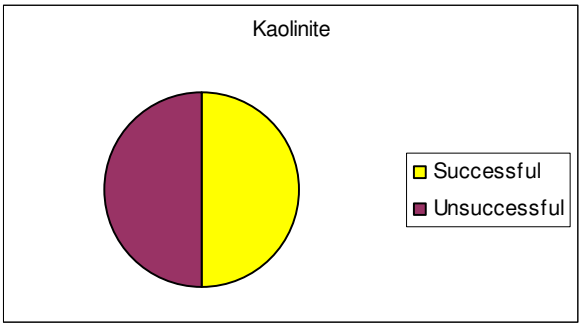


Figure 3.4.13 Success rate of tools made with kaolinite as an aggregate.

Both tools were made with *A. tortilis* resin and heated for 1:30 minutes. Tool 52, which was successful, had a 2:1 adhesive, whereas Tool 18 had a 1:1 adhesive and was unsuccessful (Fig. 3.4.13). The successful kaolinite mixture was very smooth and homogeneous (prior to and after heating) when compared to that of Tool 18. Tool 18 could not have just had too much aggregate, as the mixture was still spongy and moist. Kaolinite and beeswax: One tool was made using adhesive made of **resin, kaolinite and beeswax** (Tool 21). As discussed earlier, this tool was unsuccessful. The addition of beeswax did not have any noticeable effect on the adhesive's effectiveness.

viii) Ash

Two tools were made using adhesive made of **resin and ash** (Tools 39 and 53).

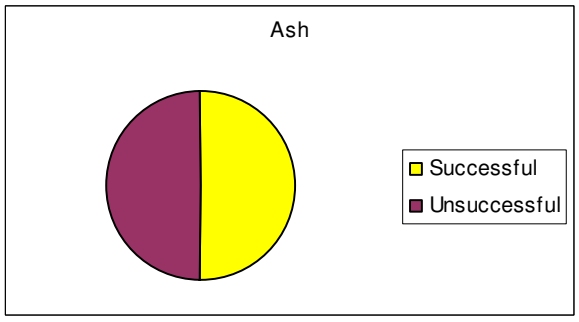


Figure 3.4.14 Success rate of tools made with ash as an aggregate.

The tools were made with 2:1 adhesives and *A. tortilis* resin. The only difference is that Tool 53 was heated for 1:30 minutes and Tool 39 for one minute. Tool 53 was successful, Tool 39 was not (Fig. 3.4.14). Although Tool 53 was successful, the adhesive taken to be mounted for hardness tests and SEM and EDS analyses was too crumbly to even mount and it broke into small, powdery pieces. Adhesives using ash as an aggregate seem to dry out and crumble more and sooner than other adhesive recipes used.

ix) Sand

Two tools were made using adhesive made of **resin and sand** (Tools 38 and 54).

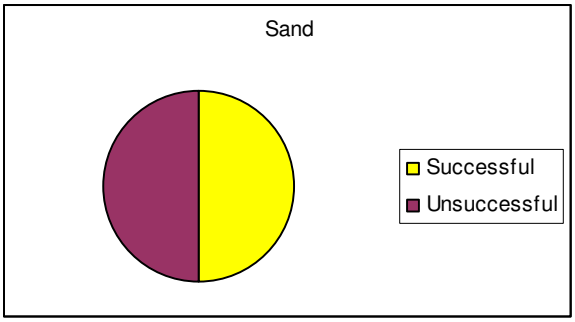


Figure 3.4.15 Success rate of tools made with sand as an aggregate.

Both were made with 2:1 adhesives and *A. tortilis* resin. Tool 38 was heated for one minute and Tool 54 for 1:30 minutes. The successful tool was Tool 54 and its adhesive was very strong and, as shall be shown later, very hard too (Fig. 3.4.15).

x) Bone

Three tools were made using adhesive made of **resin and burnt bone** (Tools 25, 37 and 49).

Tool 25 was made with *A. karroo* resin and was heated for one minute. Tools 37 and 49 were made with *A. tortilis* resin and heated for one minute and 1:30 minutes respectively. All three tools were made with 2:1 mixing ratios. Tools 25 and 37 were unsuccessful and Tool 49 was successful (Fig. 3.4.16). Tool 49 was made with the adhesive that had been heated for slightly longer. As with the ash, the mounting of the resin-bone adhesive (the

same adhesive as that used for Tool 49), for SEM/EDS and hardness tests, was problematic because the adhesive was crumbly.

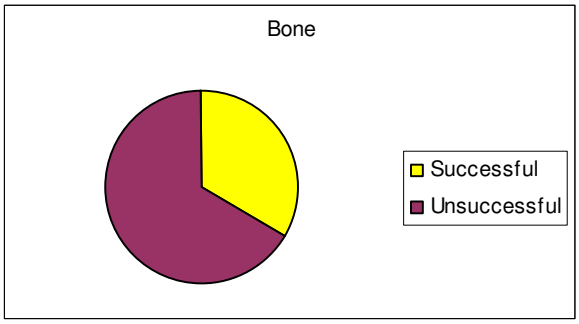


Figure 3.4.16 Success rate of tools made with burnt bone as an aggregate.

xi) Wood

Two tools were made using adhesive made of **resin and fine wood shavings** (Tools 26 and 50).

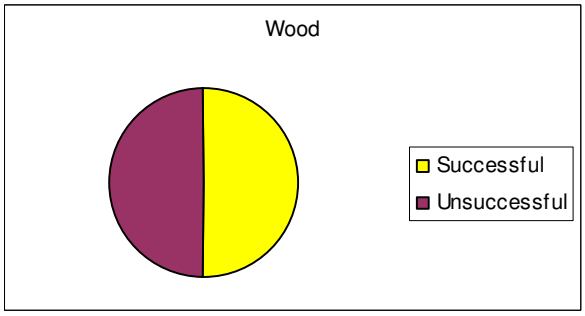


Figure 3.4.17 Success rate of tools made with wood shavings as an aggregate.

Tool 26, which was successful, had an adhesive that was made with a 2:1 mixing ratio, *A. karroo* resin and was heated for one minute. Tool 50's adhesive was made with 2:1 mixing ratio, *A. tortilis* resin and was heated for 1:30 minutes. This adhesive was unsuccessful (Fig. 3.4.17).

xii) Plain resin/no aggregate

Four tools were made with adhesives made of **plain resin** (Tools 22, 27, 35, 41).

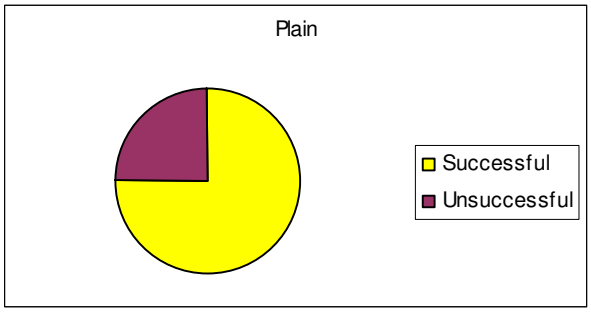


Figure 3.4.18 Success rate of tools made with no aggregate, i.e. plain resin.

Three of the tools made with plain resin (Tools 22, 27 and 41) were successful (Fig. 3.4.18).

3.4.5 Lyn Wadley's hafting experiments

Lyn Wadley's hafting experiments (2005a, in press) focused, chiefly, on red ochre as an aggregate. Some tools were also hafted with plain resin; and ochre-beeswax adhesives. Results were discussed in Chapter 2. What is clear from both her experiments and the current study is that plain resin is a successful adhesive for hafting tools, but that it is less easy to work with and manipulate, more sensitive to surrounding conditions (e.g. heat and moisture) and is consequently likely to be a more brittle adhesive than one that contains an aggregate. Also, moisture content is vital to an adhesive's success but can be varied and rectified by adding different amounts of aggregate.

Adhesives made with red ochre as an aggregate were very successful during Wadley's experiments. The current study does not have as high a success rate with red ochre, but red ochre is one of the more successful aggregates.

Wadley made two adhesives using yellow ochre as an aggregate; both of which were unsuccessful. Her adhesives did show a colour change when heated but to a brown (not redder) colour. My studies showed that no colour change occurred, even when yellow aggregates with large amounts of iron were used (e.g. Tool 55 with 43.9% Fe). Therefore,

although in cases it might be due to low iron quantities, the heat from a fire is not high enough to cause the ochre to change colour, i.e. change goethite to hematite, without the adhesive burning.

As in the current study, the addition of **beeswax** into a loaded adhesive was a successful recipe in Wadley's studies. The beeswax makes the adhesive more malleable, flexible and homogeneous.

3.4.6 Texture and Particle Size

Texture (that is the size of the particles) of the aggregates was considered as a possible explanation to why certain aggregates are successful in adhesives used to haft tools. Based on techniques of creating industrial concretes, the texture, and specifically grain size, of the aggregates is a vital factor in producing a successful adhesive. Many of the aggregates used in the hafting adhesives are composed of different sized particles and inclusions, and simple preparation techniques (such as grinding on sandstone slabs) add to this rough texture. All ochre was ground on sandstone slabs and during this process small pieces of the silica-rich sandstone are rubbed off and included in the ochre powder. These inclusions enhance the adhesive quality and cohesive properties because of the texture of the particles present in the aggregates and also because of the silica inclusion (Elvery, 1958; Lea, 1970; Baker, 2001). The sand, too, has a high success rate due to the mix of large and small sized particles and also because of the silica and iron content (this will be explored further in Chapter 4).

On the other hand, commercially produced ferric oxide and ash adhesives were largely unsuccessful. Both these aggregates consist of very fine particles and they do not need to be prepared in any way (e.g. by grinding), therefore no inclusions are present and it is likely to be the small particle size that is responsible for their ineffectiveness as aggregates, regardless of their mineralogical make-up. The specific quantities of iron oxide and silica present in the different aggregates are determined through ICP-OES analysis. Results will be discussed in the following section and in Chapter 4.

3.4.7 Conclusion

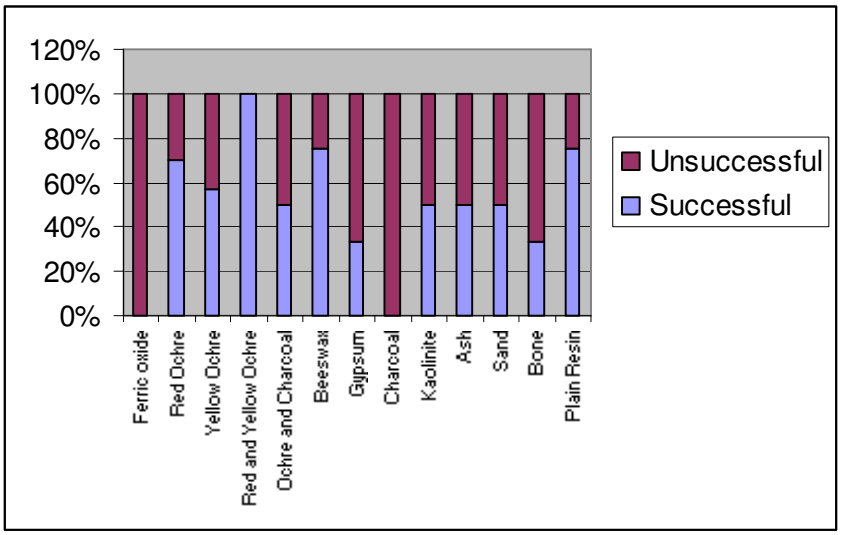


Figure 3.4.19 Success rate of aggregates used in Hafting Experiments 1.
Note: All adhesives made with resin, beeswax and an aggregate have been grouped under 'Beeswax'.

Conclusions on which aggregates produce the most successful adhesives are difficult to make due to the numerous variables involved and also due to small sample sizes of some aggregate-loaded adhesives, such as the kaolinite, ash and sand adhesives (which each were used to make only two tools). Therefore, some of the percentages represented in Fig. 3.4.19 are not necessarily good indicators of which adhesives are the most successful. For example, the combined red and yellow ochre adhesive was only made for one tool, which was successful but was not necessarily the most successful adhesive recipe as the graph shows. The most successful aggregates, all of which were used to make the adhesive for at least four tools, were red ochre, the adhesives which had beeswax added (with various aggregates) and the plain resin adhesives. The least successful aggregates were charcoal, ferric oxide, gypsum and bone.

Hafting Experiments 1 results alone offer insufficient evidence for the success, or lack thereof, of different aggregates. There are many uncontrollable variables involved in the hafting process, from heat variations to unexpected inclusions in the resins, and any of these variables may affect the resultant adhesive. These variations also make it hard to compare tools and determine why they are successful or unsuccessful.

An understanding of the chemical and physical properties of the adhesive ingredients, and processes occurring in the adhesives is important in the creation of successful adhesives. Physical properties (such as texture and water content) have been explored in Hafting Experiments 1. Hafting Experiments 2 were done after some of the scientific tests (Chapters 4, 5, 6, 7 and 8) were completed and so were done with more knowledge of the chemical attributes of and processes occurring in the adhesives. Additionally, awareness of the principles of geological cementation aids in a more complete understanding of the chemical and physical processes occurring in the adhesives.

Hafting Experiments 2 therefore aimed to investigate a few key elements in adhesive production. First, to determine whether differing silica and iron contents of the aggregates influence the success of the adhesives, and whether this can be seen through changes in pH. Secondly, to explore both the physical (textural etc) and chemical attributes of the ingredients in terms of successful mixtures and unsuccessful ones. Thirdly, to establish whether the processes of geological cementation and industrial concrete production relate to adhesive production, in terms of what attributes determine a successful mixture.

3.5 Geological binding agents

3.5.1 Diagenesis of Sedimentary Rocks

The formation of sedimentary rocks and the cementation processes undergone during their formation is important in understanding the chemical and physical changes that occur in different adhesive recipes.

Diagenesis, in the AGI glossary, is defined as “the physical, chemical, and biological changes and modifications, or transformations undergone by sediment after its initial deposition” (Jackson, 1997: 174). These changes, which include the replacement of original material, can greatly modify the composition of sediments and sedimentary rocks (Berner, 1971; Baker, 2001). The processes are:

- Compaction
- De-watering
- Cementation
- Replacement
- Recrystallization

The first three stages will be discussed below.

Compaction or compression of sediments occurs because of the increased weight of the overlying sediments and results in the reduction of pore space (Berner, 1971; Blatt *et al*. 1972). Most sandstones have a porosity of about 26% to 48% (Prothero & Schwab, 1996 as cited in Baker, 2001), and the minerals are geometrically packed (Berner, 1971). Clay-rich sediments, on the other hand, have a reduced porosity and are basically impermeable because the (fine-sized) grains are flattened and aligned and consequently very cohesive (Baker, 2001: 2). Compaction changes sedimentary rocks and sediments by reducing the porosity and permeability, and results in de-watering (Baker, 2001).

Dewatering accompanies compaction, wherein compaction causes physical changes, and de-watering (and the movement of water through sediments) can cause chemical changes to occur (Baker, 2001: 2). The minerals in the pore waters then become (re-)deposited or precipitated and cementation may occur if the appropriate minerals are present.

Cementation of sediments involves the deposition of precipitated mineral matter in the pores of sediment (Berner, 1971; Blatt *et al*. 1972; Baker, 2001). Cementation depends on the minerals present in the water moving through the pore spaces.
The three most common cements or geological binding agents, which are also important in this cementation process, are:

- Iron Oxides
- Silica
- Calcium Carbonate (or Calcite)

Different minerals and conditions influence the speed at which precipitation and compaction occurs and therefore how long the initial cementation process takes. For example, silica and iron oxide precipitation is usually slow because they have a low solubility (James, 1966; Baker, 2001) and so sometimes pore spaces are not completely filled. Terrestrial pore waters are generally acidic and consequently are often richer in slowly soluble minerals, such as iron and silica (Baker, 2001). Therefore, most terrestrially formed rocks have cements rich in silica and iron oxides. Marine pore waters are basic and richer in calcite, salts (such as gypsum) and siderite – which are highly soluble in the higher pH of marine waters (Berner, 1971; Baker, 2001). They then neutralize acidic solutions and contribute to the higher pH. Due to diffusion of minerals and groundwater flow, chemical elements are usually dispersed in a sediment or sedimentary rock, but can be found in layers or nodules (Lepp & Goldich, 1964; Garrels & Mackenzie, 1971). This segregation of elements is often due to decomposing organic matter (Berner, 1971).

The inter-related geological conditions that promote cementation are:

- Changes in the pressure of sediments through compaction, which results in the desiccation of sediments (Blatt *et al*. 1972). Pore waters migrate to areas higher up in the sediment, where there is less pressure. This pressure release can promote precipitation.
- Changes in the temperatures of the sediments (Blatt *et al*. 1972). Sediments deeply buried are not only under more pressure but also have an increased temperature, as do the surrounding pore waters. This forces pore waters into areas higher up in the sediment where temperatures are lower and desiccation of sediments again occurs though precipitation (Baker, 2001).
- Changes in the chemistry of pore waters, i.e. the changes in the concentrations of pH. Any changes of pH can force pore waters to become over-saturated, which may result in the precipitation of mineral cements in pore spaces (Baker, 2001).

In short, heat and/or pressure and surrounding acidic pH levels cause the desiccation of sediments. This in turn causes chemical changes to occur in the sediment. If the

appropriate minerals are present, i.e. those listed above, then cementation may occur. This process of cementation causes the surrounding pH to become more alkaline.

3.5.2 Adhesives and cementation

A combination of both the desirable chemical and physical properties is needed.

Chemical properties: Firstly, it is important that the adhesives have the correct mineralogy, i.e. that there are geological binding minerals present. In the current experiments that means that it is important that they contain certain amounts of iron oxide and/or silica. In Hafting Experiments 2 these different aspects are explored and discussed in detail. Secondly, the resin used needs to be acidic, which allows chemical reactions to occur when certain minerals are present. pH tests 1 and 2 investigate the acidity of the resin and adhesives. Thirdly, the effects that the heating of the adhesive has on its success, in terms of chemical and physical changes, is important and is likely to play an important role in the de-watering of the adhesives. Hafting Experiments 2 look into this.

Physical properties: Firstly, as in the creation of industrial concretes, it is vital that the quantities and qualities of aggregate and cement are carefully monitored. Secondly, the moisture content in the resin must be noted and quantities of aggregate varied accordingly. Experience is important here as it allows one to know what consistency is desirable.

3.6 Hafting Experiments 2

All ingredients and hafts were prepared in the same way as those in Hafting Experiments 1. There are fewer kinds of aggregates used in these experiments. All tools were made with L-shaped hafts, *Acacia tortilis* resin, adhesives were made with 2:1 mixing ratios (variations exist with adhesives made with beeswax) and were heated for 1:30 minutes The only addition to the process is the testing of the pH of the adhesives before and after heating.

Thirty-eight tools were made in Hafting Experiments 2, making the total number of tools made 97 (only 92 tools were analyzed since five had to be excluded from Hafting Experiments 1). The results of Hafting Experiments 2 will be shown and discussed below. An analysis of combined Hafting Experiments 1 and Hafting Experiments 2 results will be discussed in Chapter 9.

3.6.1 **Aggregates** (Appendix 3)

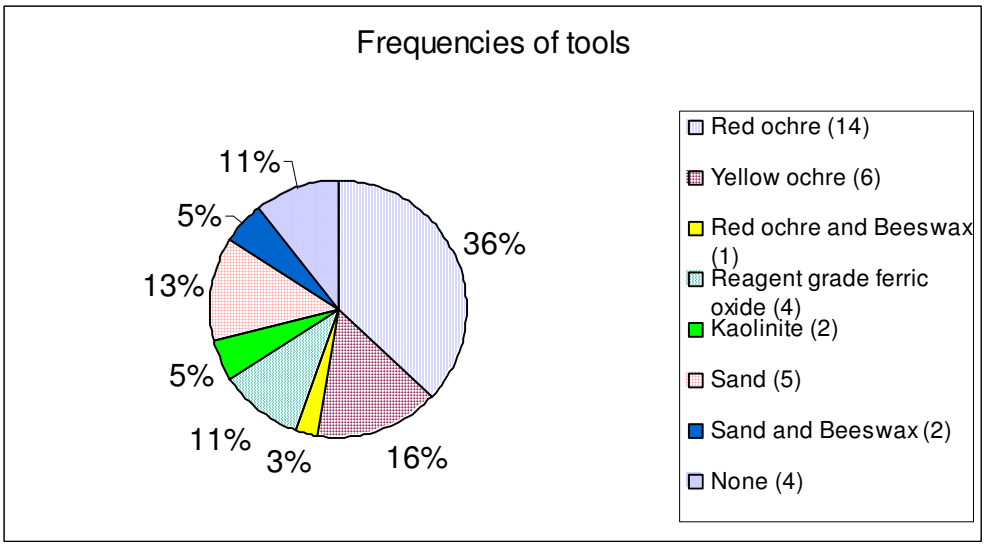


Figure 3.6.1 Frequencies of tools made with each aggregate in Hafting Experiments 2.
<u>Note:</u> (n) = Number of tools made with each aggregate.

i) <u>Ochre</u>

Twenty tools were made with adhesives made of **resin and ochre** (Tools 64-67, 72-80, 83-85, 92-95). Of these tools, nine were successful and eleven were unsuccessful (Fig. 3.6.2). This is a large percentage of unsuccessful tools.

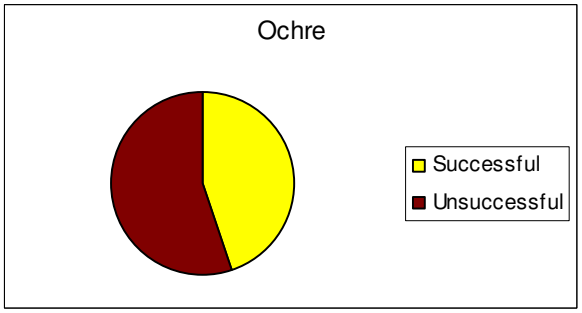
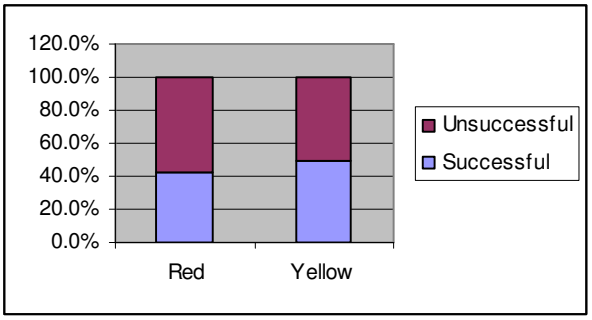


Figure 3.6.2 Success rate of tools made with ochre as an aggregate.

Red versus yellow ochre

Six adhesives were made with yellow ochre, and fourteen adhesives were made with red ochre as an aggregate.



Key for Figure 3.6.3

	Successful	Unsuccessful
Red	42.9% (6)	57.1% (8)
Yellow	50% (3)	50% (3)

Note: (n) = quantity of tools made.

Figure 3.6.3 Success rate of tools made with different colour ochre.

Results are different from results obtained in Hafting Experiments 1, with a higher (although not much higher) percentage of successful yellow ochre adhesives than successful red adhesives – 50% versus 42.9% (Fig. 3.6.3). Unlike Hafting Experiments 1, all these adhesives were made in the same way and so comparison between them does not involve so many variables.

ii) Commercially produced ferric oxide

Four tools were made with **resin and ferric oxide** adhesives (Tools 61-62 and 71). None of these tools were successful (Fig. 3.6.4).

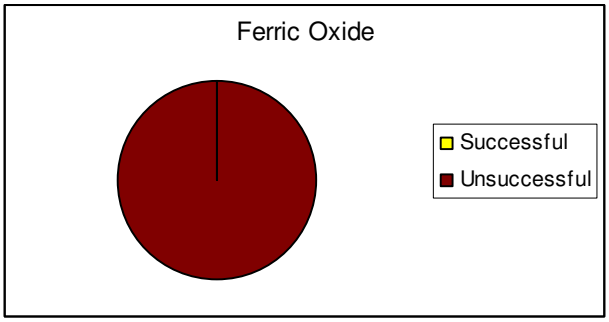


Figure 3.6.4 Success rate of tools made with ferric oxide as an aggregate

iii) Beeswax

Three adhesives were made with resin and an aggregate, and beeswax as an additive (Tools 96, 97, 98). All the tools were successful (Fig. 3.6.5). It was ensured that the beeswax was well melted in these experiments, so that no lumps remained (as was problematic in Hafting Experiments 1).

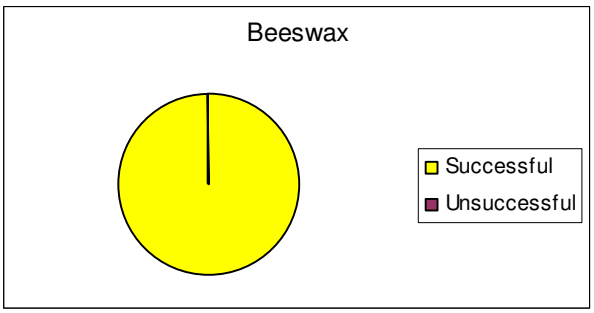


Figure 3.6.5 Success rate of tools made with an aggregate and beeswax.

a) Ochre and Beeswax

The one adhesive was made with ochre and beeswax (Tool 96). This adhesive looked strong and cohesive. It had a more lumpy texture than the plain ochre and resin adhesives. The consistency was very different as it was very sticky and greasy.

b) Sand and Beeswax

Two tools were made with resin, sand and ochre adhesives (Tools 97 and 98). Both these adhesives looked very grainy and appeared to be unsuccessful. They were, however, very strong.

iv) Kaolinite

Two tools were made with resin and kaolinite adhesives (Tools 81 and 82). As in Hafting 1 there was a 50% success rate (Fig. 3.6.6).

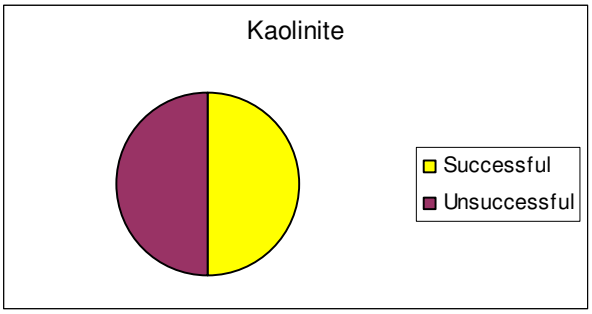


Figure 3.6.6 Success rate of tools made with kaolinite as an aggregate.

v) Sand

Five tools were made with resin and sand adhesives (Tools 86- 90). Only one of these tools was unsuccessful (Fig. 3.6.7) - Tool 87. One tool (Tool 90) was made using an unheated adhesive. This tool was still successful.

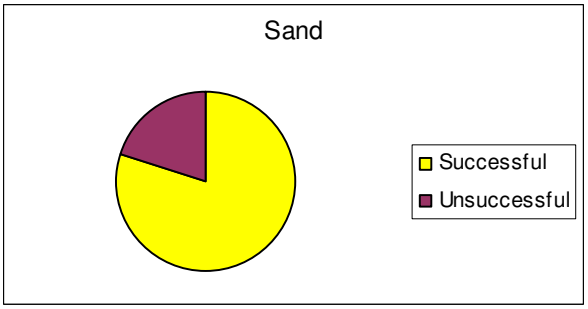


Figure 3.6.7 Success rate of tools made with sand as an aggregate.

The most obvious feature of these adhesives is that they are very rough in texture due to the relatively large size and range of particles in the sand itself. The adhesives do not appear to be very cohesive and often look like they will crumble when dry. But clearly this is not the case.

vi) Plain resin/no aggregate

Four tools were made with plain resin adhesives (Tools 68, 69, 79, 91). Only one of these tools was unsuccessful (Tool 68). The adhesives used for Tools 69 and 91 were not heated, both were still successful (Fig. 3.6.8).

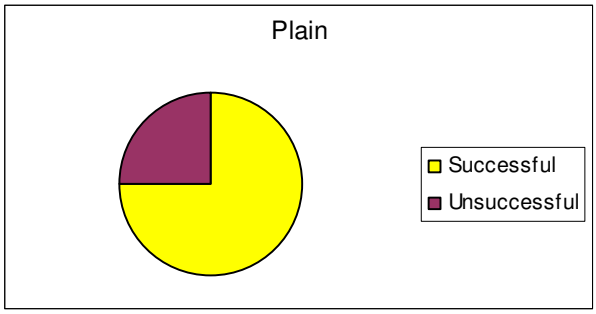


Figure 3.6.8 Success rate of tools made with no aggregate, i.e. plain resin.

3.6.2 Conclusion

The results of Hafting Experiments 2 involve fewer variables than Hafting Experiments 1, making analysis simpler. Results also reflect the influence of the aggregate more so than elements such as mixing ratio or heating times. That said, the variable moisture content in the resin, as well as variations in resin quality make resin quality difficult to predict or control. This influences the resultant adhesive. When creating an adhesive, this needs to be monitored and amounts of aggregate added should vary accordingly.

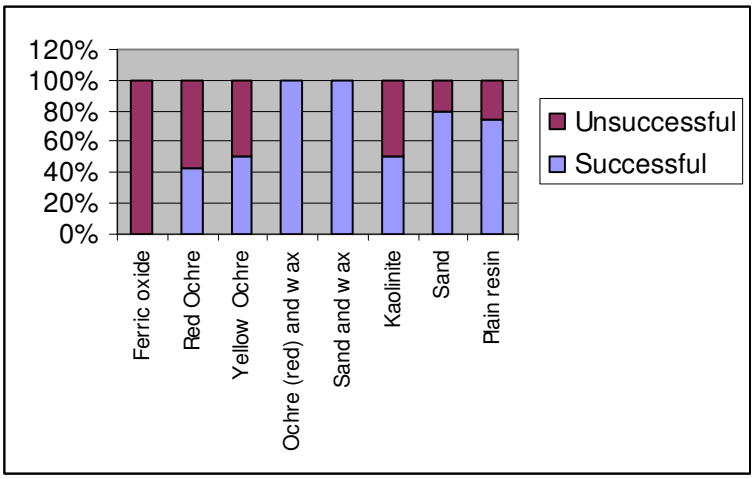


Figure 3.6.9 Success rate of all tools made in Hafting Experiments 2.

As in Hafting Experiments 1, the ferric oxide adhesives were the least successful. Also, the adhesives that had beeswax added were highly successful (in this case there was a 100% success rate) as were the plain resin adhesives (Fig. 3.6.9). Surprisingly, the red ochre adhesives were less successful than the yellow ochre, sand and kaolinite adhesives - the sand adhesives, especially, having a very high success rate (Fig. 3.6.9).

Hafting Experiments 1 and Hafting Experiments 2 suggest that certain physical characteristics (such as particle size) is important in creating an effective adhesive. In the following chapters, the chemical nature of the aggregates, and resin, will be investigated to determine how the aggregates influence the success of an adhesive, i.e. what chemical attributes are important in an aggregate to be used in resin to make adhesive.

CHAPTER FOUR : *Iron Quantities: Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)*

4.1 ICP-OES 1

Twelve samples were taken for Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) tests to determine the quantities of iron in different ochreous materials that were used as aggregates. The large quantities of iron in ochre is its distinctive feature and it was deemed necessary to determine, firstly, whether the ochre pieces obtained are all iron-rich, and secondly, whether the iron quantities have any direct effect on the effectiveness of the adhesive.

4.1.1 Preparation

Twelve pieces of ochre were analyzed for iron quantities. Choices were made based on morphology and a variety of ochreous rocks were chosen, e.g. red and yellow pieces from snuff-box shale and slate-like pieces. The pieces were then prepared by grinding on sandstone slabs.

4.1.2 Procedure: The ICP-OES Process

0.1 gram of the powder of each sample was placed in test tubes. And each sample was mixed with 5ml Nitric acid and 2ml Hydrofluoric acid. ICP-OES analysis was then performed on each of the samples:

The samples are placed in a Multiwave 3000 V1.27 Microwave and after heating they are placed in the ICP-OES instrument. Argon gas is directed through a torch that consists of three concentric tubes, usually made of quartz (Alnatour, 2005). A Radio Frequency (RF) power, of 1300 watts, is then applied to a copper coil, which is around the top end of the

torch, and a current then moves back and forth within the coil at a frequency of 27 to 40 megahertz (Alnatour, 2005). This oscillation causes electric and magnetic fields to be set up, and a spark is applied to the argon gas, which causes some electrons to be stripped of their argon atoms, and the electrons are then caught in the magnetic field (Alnatour, 2005). This adds energy to the electrons, and this process is called inductive coupling. Gradually, through this process, inductively coupled plasma discharge is formed. The light emitted by the excited atoms and ions in the plasma is measured so that information about the sample can be obtained (Alnatour, 2005). Light is emitted at several different wavelengths and is therefore polychromatic; this polychromatic radiation is separated (using a monochromator) into individual wavelengths so that the emission from each individual excited species can be identified and its intensity measured (Alnatour, 2005). Quantitative information is then obtained by plotting emission versus concentration called calibration curves.

4.1.3 Results

Table 4.1 Iron quantities present in each sample

Sample #	Ochre piece and tool number (as referred to in Appendix 1)	Success of tool	Unheated or heated	Colour	Fe (ppm)	Percentage of Fe in sample
A	17 (Tool 95*)	S	Unheated	Yellow	209400	20.9%
B	16 (Tool 94*)	S	Unheated	Red	172150	17.2%
C	8 (Tools 42, 55, 77*, 78*)	U, S, U, U	Unheated	Yellow	154500	15.5%
D	8 (Tool 43, 76*)	S, U	Unheated	Red	439000	43.9%
E	9 (Tool 44)	U	Unheated	Red	319000	31.9%
F	10 (Tool 45, 83-85*)	S, U, S, S	Unheated	Yellow	67650	6.8%
G	-	-	Unheated	Red	175350	17.5%
H	11 (Tool 46)	S	Unheated	Red	219950	22.0%
I	13 (Tools 73-75*, 96*)	U, S, U, S	Unheated	Red	514000	51.4%
J	-	-	Heated	Red	408000	40.8%
K	12 (Tools 47, 51, 64-67*, 71*)	S, S, U, U, S, U, U	Heated	Red	516500	51.7%
L	-	-	Heated	Red	126250	12.6%

Notes: * These tools are discussed in Hafting Experiments 2.

The lowest iron quantity is Sample F with 6.8%, and the highest is Sample K with 51.7%. Both these samples were ground from snuff-box shale but Sample F is yellow, and Sample K is red. Other snuff-box shale samples were C, D, G, I and J. Sample I has the second highest percentage of iron, with 51.4%.

- Samples C and D were taken from the same rock, but different sections (according to colour). The iron quantities reflect a significant difference between the two with Sample C, which is yellow, having a relatively low iron content of 15.5% Fe, while Sample D, which is red, has a high percentage of 43.9% Fe.
- This is not the case, however, with Samples F and G, which were taken from the same rock. Sample F, as aforementioned, is yellow and has a low iron content (6.8%), and Sample G is red but also has a relatively low iron content (17.5%).
- Samples I and J are both red. They both have quite high iron contents: Sample I has 51.4% Fe, and Sample J has 40.7% Fe.

Snuff-box shale

On the whole, the snuff-box shale samples have higher iron contents than the other ochreous rocks. The snuff-box pieces have an average of 32.5% Fe, whereas the other pieces have an average of 20.9% Fe. The red areas of the snuff-box shale seem to usually, but not exclusively, have higher iron contents than the yellow areas of the rocks. The red snuff-box shale samples have an average of 41.1% Fe, and the yellow samples have an average of 11.2% Fe.

Colour

Looking at the iron percentages and the colour of the samples, it becomes clear that there is a correlation between the two. The overall red samples from all the tested pieces have readings between 12.6% Fe and 51.7% Fe, with an average of 32.1% Fe. The yellow samples, on the other hand, have readings between 6.8% Fe and 20.9% Fe, with an average of 14.4% Fe. Therefore the red ochre generally, but not exclusively, has a higher iron content than the yellow ochre.

4.1.4 Conclusion: Iron Quantities, Colour and Hafted Tools

What do the abovementioned percentages mean, then, for the success of adhesives? Thirteen of the tools made with adhesives using red ochre as an aggregate were successful and eleven were unsuccessful. There were seven successful tools made with adhesive using yellow ochre as an aggregate, and six unsuccessful. Red ochre (as confirmed above) has a higher iron content than yellow ochre, but, in the same breath, it is impossible to judge, even estimate, the iron content of a piece of ochre from its colour alone. Since not all the ochre pieces that were used as aggregates in adhesives underwent ICP-OES analyses, only the analyzed pieces will be discussed below.

Seven tools were made with the ochre that had undergone ICP-OES analysis: Tools 42 – 47 and Tool 55. All these tools were made in the same way with regard to resin (*A. tortilis*), mixing ratios (2:1) and heating times (1:30 minutes), except Tool 55, which has been discussed earlier, and which was heated for three minutes to see whether the yellow adhesive would change colour. Two of these tools were unsuccessful – Tool 42 and Tool 44. Tool 42 was made with Sample C (15.5% Fe, which is yellow) and Tool 44 was made with Sample E (31.9% Fe, which is red).

The aggregates used in the adhesives of the successful tools have a wide range of iron content percentages – Tool 43 (Sample D) has 43.9% Fe and is red; Tool 45 (Sample F) has 6.8% Fe and is yellow; Tool 46 (Sample H) has 22% Fe and is red; Tool 47 (Sample K) has 51.7% Fe and is red; Tool 55 (Sample C) has 15.5% Fe and is yellow.

Some adhesives made with low iron content ochre were successful and some made with high iron content ochre were unsuccessful. Therefore, the iron content (and colour) of the ochre used as an aggregate in the resin does not necessarily have an influence on the success of adhesive. But again, the problem of the presence of different variables such as resin type, heat, mixing ratios, the degree of moisture and the amount of coarse material in the mixture could influence the results. Its seems that, under some conditions (and if other physical conditions are right), only small amounts of iron are sufficient to act as

binding agents, since some adhesives made with aggregates that had only 6% Fe were successful.

4.2 ICP-OES 2

Six samples were taken for a full elemental analysis by ICP-OES. These results (Appendix 7) were problematic and inconsistent with results obtained from ICP-OES 1 tests. However, they do show what elements are present in the samples (but the quantities are unreliable). They show that all the samples (commercially produced ferric oxide, red ochre, yellow ochre, sand and kaolinite) contain some iron and silica. They also contain small amounts of aluminium, sodium and calcium and very small amounts of manganese.

What is important is that all samples contain some iron and silica (which are the elements that will be focused on). Also, the presence of aluminium aided in interpreting the EDS results. The same six samples that underwent full elemental ICP-OES analysis, and an additional ochre sample (ICP-OES 2 Sample 4) were then taken for further ICP-OES tests to determine the exact iron and silica quantities they contain. Iron and silica are main geological cementing minerals and are present in all the samples. Specific quantities needed to be ascertained to determine whether quantities influence the success of the adhesive in which they are used.

4.2.1 Preparation

Ochre powder was obtained in the same way as the ochre powder used in hafting experiments, i.e. it was ground on sandstone slabs. All other samples did not need to be prepared by grinding. The samples are labelled according to Table 4.2 below, which is a continuation of the labelling system used for the ICP-OES 1 tests. The samples are:

M) Ferric oxide (commercially produced Fe_2O_3). This was an unsuccessful aggregate and all nine tools made with it were unsuccessful.

N) Yellow Ochre. This ochre was tested in the previous tests – it is piece 10 (in Appendix 1 and 3) and Sample F from ICP-OES 1 tests (the previous set of tests),

which found that the sample contained 6.8% Fe. It is yellow and was used as an aggregate in four adhesives, only one of which was unsuccessful as a binding material to haft tools.

O) Red Ochre (1). This ochre was tested in the previous tests - it is piece 12 (in Appendix 1 and 3) and Sample K from ICP-OES 1 tests, which found that the sample contains 51.7 % Fe. It is a red sample and was used as an aggregate in seven adhesives (one with beeswax), four of which were unsuccessful.

P) Red Ochre (2). This ochre piece is from Moletadikgwa in the Limpopo Province. This piece was used by L. Wadley as an aggregate in her adhesives – all of which were successful. This ochre was used as an aggregate in Hafting Experiments 2, piece 15 (Appendix 3) and was chosen to be analyzed for iron and silica contents to determine whether there is a significant mineralogical difference between this ochre and the other ochre used in the current study. The two adhesives made with this ochre as an aggregate were both successful as binding agents.

Q) Kaolinite. Kaolinite tested here is the same as that used for all tests and experiments. It is therefore the red kaolinite. Four tools (excluding that made with beeswax added) were made with kaolinite and there was a 50% success rate.

R) Sand. The sand that was collected and used for all tools, tests and moulds, was from Emmarentia, Johannesburg. This area is on the Witwatersrand quartz ridge and therefore the sand is silica-rich. Eight tools were made with this sand used as an aggregate in the adhesive, including two made with the addition of beeswax (Appendix 1 and 3). Only two tools were unsuccessful (neither of which were those made with the addition of beeswax).

S) Sand. This sand is taken from B5b Light Brownish Grey II at Sibudu. No tools were made with this sand.

4.2.2 Procedure

0.25g of each sample powder was placed into a container and 5ml Nitric acid, 4ml Hydrofluoric acid and 0.5ml Hydrochloric acid was then added. The ICP-OES process is the same as that discussed in ICP-OES 1, but only iron and silica quantities were examined on this occasion.

4.2.3 Results

Table 4.2 Quantities of iron and silica present in the seven tested samples. The numbering of the samples is the same as (and linked to) that from ICP-OES 1 (Table 4.1.)

Sample #	Sample	Tool #	Fe (ppm)	Fe%	Si (ppm)	Si%
M	Ferric oxide	56-63, 71	839000	83.90%	118000	11.80%
N / F *	Yellow ochre	45, 55, 83-85	212700	21.27%	134100	13.40%
O / K *	Red ochre 1	47, 51, 64-67, 72	569000	56.90%	102600	10.26%
P	Red ochre 2	92, 93	743000	74.30%	84900	8.49%
Q	Kaolinite	18, 21, 52, 81, 82	124100	12.41%	114000	11.40%
R	Sand	38, 54, 86-90, 97, 98	39800	3.98%	125800	12.58%
S	Sibudu Sand	-	17800	1.78%	93900	9.39%

Notes: * The last letter is the Sample from ICP-OES 1. That is, these two pieces (N / F and O / K) were tested in ICP-OES 1 and ICP-OES 2.

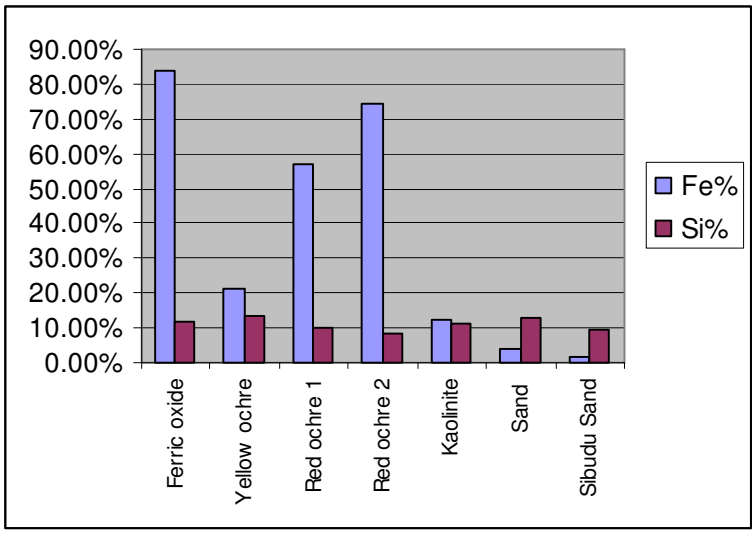


Figure 4.2 Percentages of iron (Fe) and silica (Si) found in each sample.

Iron quantities, colour and hafted tools (Table 4.2 and Fig. 4.2)

As would be expected, the ferric oxide contains the most iron (83.9%), followed by the red ochre from the Waterberg (with 74.3 % Fe), then the red ochre from the quarry near Sibudu (with 56.9 % Fe). All these quantities are significantly high. The yellow ochre has

much less iron, with 21.27% Fe. Both the sand samples and the kaolinite sample contain iron but it is in low percentages.

Of all the adhesives made only with aggregates that contain a high iron percentage (i.e. ferric oxide, ochre 1 and ochre 2 - 83.9%, 56.9% and 74.3% respectively) only 23.1% were successful. The ineffectiveness of the ferric oxide adhesives is expected due to the physical properties thereof (the very fine grain size). When looking only at the adhesives made with the two ochre samples, there is a 42.3% success rate. This is still quite low.

The adhesives made with aggregates that have low iron percentages (i.e. yellow ochre, kaolinite, sand – 21.3%, 12.4% and 4% respectively) have a 68.8% success rate. This is significantly higher than the success rate of the adhesives made with aggregates that have high iron contents.

The expected positive effect of the high iron content of the aggregate does not appear to determine the success of the adhesive. ICP-OES 1 analysis showed the same results but because there were many different variables involved in the creation of those adhesives, they were not conclusive. However, now that adhesives were created in the same way with fewer variables introduced into the adhesive-making process, it can be seen that the iron content is not the only thing that determines a successful adhesive, although the presence of some iron, even small quantities, is important in the creation of adhesives (based on geological binding principles). The influence of other physical variables, specifically texture (grain size), and other mineralogical variables, specifically silica content, also needs to be considered.

Silica quantities and hafted tools (Table 4.2 and Fig. 4.2)
Unlike the iron quantities, the silica quantities show less variation between samples, with the highest amounts being in the yellow ochre (with 13.4% Si) and the Johannesburg sand (with 12.58% Si), and the lowest amount being in the red ochre from the Waterberg (with 8.49% Si). The quantities are all lower than expected.

All silica quantities show very little variation between samples, but all samples do contain some silica. As with the iron quantities, the presence of some silica, even if in small quantities, is still important and plays a part in determining the success of the adhesive – as it does geologically.

4.2.4 Conclusion

The iron and silica content in the aggregates is an important and vital factor in the creation of successful adhesives. However, the higher the amount of these minerals (or the other main geological cementing agent, calcium carbonate) does not necessarily mean that the aggregate is better or that the adhesive made with that aggregate will automatically be successful. There are other variables involved. Geologically and industrially, cement (with the correct mineralogy, pH and water content) binds sands and gravel together to form a rock conglomerate or concrete. It is a combination of having the correct minerals present (that is iron, silica and/or calcium carbonate) even in relatively small quantities, as hafting and ICP-OES show, and aggregates of the correct texture (i.e. particle size must be mixed, and particles must not be too small) as well as the correct amount of moisture and an acidic pH. Initial pH tests determined that all resin used is acidic, and looked at whether heating results in a change of pH. All adhesives made during Hafting Experiments 2 had their pH levels taken to determine whether the adhesive was acidic and at which stage the pH changes (i.e. when does a chemical reaction take place) – when the aggregate is added or when the adhesive is heated.

CHAPTER FIVE : *pH Tests*

5.1 pH Tests 1

These tests were done specifically to establish whether the adhesives themselves are acidic, and to find out whether heating the sample, and specifically the resin, changes the pH of the sample. This indicates a chemical change and therefore sheds some light on how the resin acts with the aggregates and how this influences the success of certain adhesives.

5.1.1 Preparation

pH tests were carried out at by the Protein Structure and Function Research Program in Wits' Biochemistry Department. The department's pH probe is unsuitable for testing a sample of this consistency, so pH tests were done using pH indicator papers. All samples were made using *A. tortilis* resin, 2:1 mixing ratios, and were heated for 1:30 minutes (three samples were, however, not heated). Two samples (1 and 4) did not have any aggregate added (Table 5.1.1).

The samples:

- Commercially produced ferric oxide, which is 85% Fe_2O_3.
- A yellow piece of non-archaeological ochre (piece 10), which ICP-OES 1 analysis found to have 6.8 % Fe.
- A red piece of non-archaeological ochre (piece 12), which ICP-OES 1 analysis found to have 51.7% Fe.

5.1.2 Procedure

In the laboratory each sample was mixed with 5ml de-ionized water so that the sample would become more liquid, and so that impurities that may exist in tap water are not present. The samples were then left for a few minutes. With all samples, except the plain

resin samples, the mixture dissolved into the water with only a few pieces of the original adhesive that did not get dissolved. With both the plain resin samples, however, the water was absorbed into the resin resulting in a more spongy resin and no liquid left in the canister. This shows that the aggregate changes the qualities of the resin (in both the heated and unheated samples). Also, this would have been a desirable attribute of adhesives for people living in open-air sites, since adhesives would otherwise dissolve in the rain.

The pH indicator papers were then dipped into each sample and after a few minutes results were received (Table 5.1.1).

5.1.3 Results

Table 5.1.1 Results of pH Tests 1

Sample #	Recipe	Heating	pH
1	Plain resin	Unheated	**3 - 3.5**
2	Resin and ferric oxide	Unheated	**6**
3	Resin and #6 ochre, 6.8% Fe	Unheated	**5 - 5.5**
4	Plain resin	Heated 1:30 min	**3.5 - 4**
5	Resin and ferric oxide	Heated 1:30 min	**5.5 - 6**
6	Resin and #6 ochre, 6.8% Fe	Heated 1:30 min	**4.5 - 5**
7	Resin and #11 ochre, 51.7% Fe	Heated 1:30 min	**4 - 4.5**

All the samples with an aggregate added have significantly higher pH readings than the plain resin samples – with an average of 5 versus 3.5.

Unheated versus heated resin (no aggregate): The heated resin has a slightly higher pH – 3.5 to 4 (Sample 4) as opposed to 3 to 3.5 (Sample 1). This difference is very slight but shows that a change is occurring, where heating makes the adhesive more alkaline.

Resin with ferric oxide: the heated adhesive has almost the same pH – 6 (Sample 2) as opposed to 5.5 to 6 (Sample 5) in the unheated adhesive.

Resin with ochre (6.8% or 51.7%): The heated adhesives (Samples 6 and 7) have a higher pH than the unheated adhesives (Sample 3) – 5 to 5.5 as opposed to 4.5 to 5. The difference is the same as that with the plain resin.

5.1.4 Conclusion

The addition of an aggregate to resin increases the pH of the resin. This suggests that a chemical reaction does occur when the aggregates are added to the resin. The geological binding minerals present in the adhesive are likely to be the cause for this reaction. Interestingly, heating the (loaded) adhesives does not cause any further pH changes, as would have been expected. The pH of the plain resin, however, does increase when heated. The aggregates therefore change both the chemical and physical properties of the resin, making it react differently to heat. pH tests 2 will discuss these pH changes in more depth, as well as deal with a wider variety of aggregates.

5.2 pH Tests 2

These tests were done simultaneously with Hafting Experiments 2. The aim of these tests was to discover when and what chemical changes occur in the adhesives during their production. They further aim to establish whether the same binding processes that occur geologically are occurring in the adhesives. The chemical changes that occur during the cementation process are detectable through changes in pH levels.

5.2.1 Preparation and Procedure

The adhesives made during Hafting Experiments 2 were tested to determine their pH. All adhesives were tested before and after heating. The adhesives were tested using de-ionized water and pH indicator papers. The basic procedure was the same as that used in pH tests 1. All adhesives were made with *A. tortilis* resin and were heated for 1:30 minutes. Some samples did not have any aggregate added. The aggregates used are those used in Hafting Experiments 2, and not only ochre samples, as in pH tests 1. All of the aggregates underwent ICP-OES analysis, but the ones tested during ICP-OES 1 test did not have their silica contents determined. Therefore, silica quantities are only available for the samples that were tested during ICP-OES 2.

The aggregates tested for pH are:

- **Ferric oxide** (Fe_2O_3) with an iron content of 83.9%.
- **Red ochre**: Piece 8, ICP-OES 1 Sample D with an iron content of 43.9%.
  Piece 12, ICP-OES Sample O / K with average iron content of 54.3%, and a silica content of 10.3%.
  Piece 13, ICP-OES 1 Sample I with an iron content of 51.4%.
  Piece 14, ICP-OES 1 Sample H with an iron content of 22%.
  Piece 15, ICP-OES 2 Sample P with an iron content of 74.3% and a silica content of 8.5%.
  Piece 16, ICP-OES 1 Sample B with an iron content of 17.2%.
- **Yellow ochre**: Piece 8, ICP-OES 1 Sample C with an iron content of 15.5%.
  Piece 10, ICP-OES Sample N / F with and average iron content of

14% and silica content of 13.4%.
Piece 17, ICP-OES 1 Sample A with an iron content of 20.9%.

- **Kaolinite**: ICP-OES 2 Sample Q with an iron content of 12.4% and a silica content of 11.4%.

- **Sand**: ICP-OES 2 Sample R with an iron content of 3.9% and a silica content of 12.6%.

5.2.2 Results (Table 5.2.1)

The pH levels were taken at different stages of the making of each adhesive, before the adhesive was used to haft the stone tool. Each pH reading is therefore linked to the tools hafted with that adhesive, and separate sample numbers are not used (Table 5.2.1).

As with pH tests 1, the main pH changes do not occur during the heating process but rather when the aggregate is added – when the average pH increases from 4 to between 4.5 and 6. The changes in pH indicate that there are chemical changes occurring when the aggregates are added.

5.2.3 Conclusion

The adhesives made with aggregates that have relatively lower iron contents (e.g. kaolinite, yellow ochre and sand) show less change in pH than adhesives made with aggregates that have high iron contents (e.g. red ochre and ferric oxide). The changes in pH indicate that chemical changes are occurring in the adhesives and the principles that govern the geological binding process are in operation here too. Geologically, the presence of iron, silica and calcium carbonate cause chemical changes in the presence of moisture, heat or pressure, and some of these conditions are met in the creation of adhesives. Importantly though, the chemical changes alone do not result in an adhesive that is necessarily successful, because other physical conditions are also vital to a successful adhesive.

Table 5.2.1 The pH of resin, and pH of adhesives before and after heating

Aggregate	Tool #	pH of resin prior to adding aggregate	pH before heating	pH after heating	Success of tools
Reagent grade ferric oxide	61-63, 71	4	6	6	U *
Ochre, 8, Red and Yellow	76-78	4	6	6	U *
Ochre, 10, Yellow	83-85	4	5	5.5	U, S, S
Ochre, 12, Red	64-67, 72	4	6	6	U, U, S, U, U
Ochre, 13, Red	73-75	4	5.5 - 6	6	U, S, U
Ochre, 14, Red	79, 80	4	6	6	S, U
Ochre, 15, Red	92, 93	4	5.5 - 6	5.5 - 6	S **
Ochre, 16, Red	94	4	4.5	4.5	S
Ochre, 17, Yellow	95	4	4	4.5 - 5	S
Kaolinite	81, 82	4	5	5.5	S, U
Sand	86-90	4	4.5 - 5	5 - 5.5	S, U, S, S, S, S
Ochre (13, Red) and Beeswax	96	4	4.5	5	S
Sand and Beeswax	97, 98	4	4.5	4.5 - 5	S **
None	68-70, 91	4	4	4.5 - 5	U, S, S, S

Note (to Table 5.2.1): *** The tools listed are *ALL* unsuccessful (U).**
**** The tools listed are *ALL* successful (S).**

CHAPTER SIX : *Hardness Tests*

Two sets of hardness tests were done to answer slightly different questions. The first tests, on 16 samples, aimed to look at whether certain aggregates make adhesives harder and whether hardness correlates with the success of the adhesive. The second tests, on five samples, aimed to find out: a) whether the combination of large quantities of iron (oxide) mixed with resin results in a chemical reaction, and b), whether iron affects the adhesive's hardness. Commercially produced ferric oxide was used so that a high percentage of iron is in the sample and so that the possibility that other elements, which may affect the result, do not enter the equation.

6.1 Preparation: Mounting samples

All adhesive samples were prepared in the same way that their corresponding tools (Appendix 1) were made: aggregate and resin was combined with 2:1 mixing ratios, and heated on a heating stick for 1:30 minutes, except for Sample 16, which was heated for three minutes.

The adhesives were then placed into bottle tops that had been lined with wax paper. Wax paper was used so that the adhesive could be taken out of the bottle tops without sticking. Once the adhesives were placed into the bottle tops they were not reheated, but were placed near the fire to dry. These adhesive moulds took long to dry, even longer than the same adhesives used to haft tools. The hafted tools usually took four to five hours to dry, but these adhesive moulds took up to seven hours to dry. This is because the adhesive is thicker than that used on the tools and is insulated from the heat by the metal of the bottle top.

Samples were mounted for hardness tests, as well as SEM and EDS work, using the Wits Process and Materials Engineering School's mounting press. The moulds were made

using Lucite and Bakelite powder. The black bakelite powder is not as conductive as Lucite powder under the electron beam; therefore, it is vital to use Bakelite powder on the surface of the samples that will be looked at under the SEM/EDS. The moulds have a diameter of 30mm and vary in depth (depending on how much Lucite and Bakelite powder is used) (Fig. 6.1). Heat is used for 20 minutes and pressure is used throughout the heating and cooling process (cooling takes six minutes). Pressure is pumped up to 4000 PSI and maintained at that pressure for the whole process. Pressure and heat allow the powders to solidify.

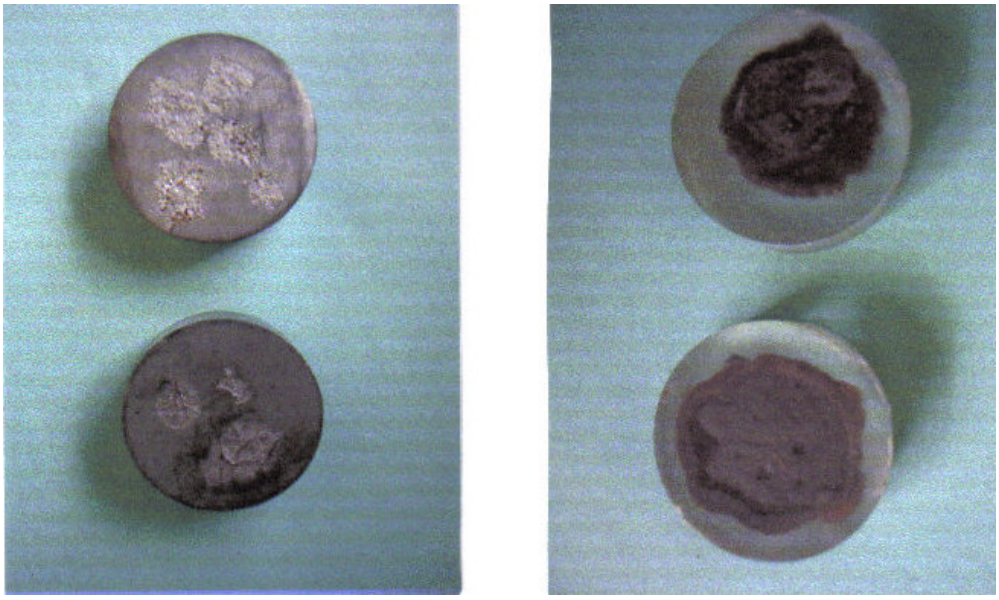


Figure 6.1 The moulds made for hardness tests, SEM and EDS analysis.

The amount of adhesive used and the amount that shows on the surface of each mould varies depending on the quality of the adhesive, for example Sample 10 (burnt bone) was very crumbly and brittle and therefore there was only a small area on the surface that could be tested. All adhesive samples had to be ground down prior to mounting so that a flat surface could be obtained. It is this surface on which the hardness tests are done and the same surface is viewed through the SEM. It was often during this initial grinding process that the samples broke up.

Moulds are then polished using a silicon-based sandpaper. All polishing is done wet. Different grains of sandpaper are used – 220, 600 and 1000 are the coarser papers used. The final polishing stage is done using an electric polishing machine and an aluminium-based liquid. The liquid is placed on the sandpaper wheel while polishing.

6.2 Procedure: Rockwell T Hardness Tests

Hardness tests were done by Andre Jooste and Mandla Mbatha at M & S Metrology Services (Pty) Ltd.

Initially experiments were performed on unmounted adhesive samples to see if the adhesive would break when weight is exerted. The adhesive, however, crumbled under a 3kg pre-load. Consequently, only the mounted samples were used.

Thereafter, experiments were done to see which hardness test would be the most suitable and give the most accurate readings for the sample type. Firstly, a Rockwell A was used, which had a 60kg full load and a diamond cone indenter. This was unsuccessful as the adhesive is too soft and the cone penetrates the surface, under the 10kg preload, which results in an inaccurate reading.

Then a Superficial Rockwell T Hardness Tester (HR15X) was tried, which had a 15kg full load, a 3kg pre-load, and a ball indenter. This proved to be suitable. Then different ball indenters were investigated. First an eighth of an inch ($^1/_8$") steel ball was used, but it proved to be too small for the kind of sample being used. This was visible as the sample reading was not yielding, i.e. the load and nature of the ball resulted in the adhesive getting constantly compacted under the weight as the ball penetrated the surface. Then a quarter of an inch ($^1/_4$") steel ball indenter was tried, and found to be the most satisfactory. HR15X tests have an average error norm of 3 HRT (Hardness Rockwell T), but because of the quality of the adhesive there would be an uncertainty norm of about 8 HRT.

6.3 Results

Table 6.3 Results of Hardness Tests

Sample #	Tool #	Aggregate	Mixing ratio	HR15 X readings	Average	Success as a tool
1	**40**	Gypsum	2:1	11, -20, 20, 49, 17	**16**	**U**
2 *	**41**	None		17¤ , 28, 36, 48, 57◘	**37.3**	**S**
3	**42**	Yellow ochre	2:1	68, 72, 71, 74, 64, 64	**68.8**	**U**
4	**43**	Red Ochre	2:1	59, 57, 57, 43¤, 61, 52¤, 61	**57.2**	**S**
5	**44**	Red Ochre	2:1	58, 68, 49, 56, 64, 58, 58	**58.8**	**U**
6	**45**	Yellow Ochre	2:1	64.5, 65, 67◘, 57, 72, 60, 68¤ 63, 62, 73	**65.2**	**S**
7 *	**46**	Red Ochre	2:1	48¤, 65, 66, 56, 64	**61.7**	**S**
8	**47**	Red Ochre	2:1	49, 53, 32¤	**49**	**S**
9	**48**	Charcoal	2:1	66, 71, 58¤, 65, 55, 69	**65.8**	**U**
10	**49**	Burnt bone	2:1	54 **	**40**	**S**
11	**50**	Wood dust	2:1	41, 54, 52, 43, 68◘, 59, 46	**50.8**	**U**
12	**51**	Ochre and beeswax	4:2:1	18, 43, 38, 39, 43, 9	**32.3**	**S**
13	**52**	Kaolinite	2:1	58, 68.5, 70, 70, 72, 76, 73	**70.9**	**S**
14	**53**	Ash	2:1	Sample very crumbly, no suitable surface available	**-**	**S**
15	**54**	Sand	2:1	68, 71, 72, 70, 72	**71**	**S**
16	**55**	Yellow Ochre	2:1	48, 65, 68.5, 70◘	**66.8**	**S**
17	**56**	ferric oxide	4:1	96, 96.5, 93◘, 91¤, 71	**93.3**	**U**
18	**57**	ferric oxide	2:1	83, 77, 81¤, 80.5◘, 80	**80.5**	**U**
19	**58**	ferric oxide	4:3	94, 92.5, 95.5, 81, 90, 84¤	**90.1**	**U**
20	**59**	ferric oxide	1:1	92, 99◘, 94, 90, 94.5	**93.5**	**U**
21	**60**	ferric oxide	2:1	99.5◘, 93¤, 79, 93, 86	**90.7**	**U**

Notes: * **Samples 2 and 7 were both very cracked samples.**

** **Sample 10 was a very brittle sample and mounted pieces of adhesive were very small.The reading could only be taken near the edge of the sample and mounting resin. The reading obtained is probably high because of the hardness of the mounting resin.**

¤ **All readings marked with this symbol were taken on or right next to cracks in the adhesive. The readings could be slightly low.**

◘ **All readings marked with this symbol were taken near the edge of the adhesive and mounting resin. The readings could be slightly high.**

1) **Mounting resin has a reading of about 90 HRT**
2) **Some samples had more readings done because the surface area was larger.**
3) **The highest and lowest readings have been excluded when calculating the averages.**
4) **The adhesive of Sample 16 (Tool 55) was heated for three minutes.**
5) **The adhesive of Sample 21 (Tool 60) was not heated.**

1) Results for Samples 1 to 16 (Table 6.3):

The sample that is the hardest is Sample 15, with an average reading of 71 HRT. This sample was made of resin and sand.

The sample that is the softest is Sample 1, with an average reading of 16 HRT. This sample was made of resin and gypsum.

The combined average for the samples that have ochre as an aggregate (Samples 3, 4, 5, 6, 7, 8, and 16) is 61.1 HRT. The readings themselves vary (for the ochre samples) from 49 HRT to 66.8 HRT.

2) Results for Samples 17 - 21 (Table 6.3):

All the hardness readings in this set were high compared to the first set of hardness tests done. All these samples have commercially produced ferric oxide as an aggregate. The only difference between the samples is the quantities of aggregate added to the resin, and one sample had not been heated (the others were heated for 1:30 minutes).

The hardest sample is Sample 20, which has a reading of 93.5 HRT. This sample was made using equal amounts of resin and ferric oxide.

The softest sample was Sample 18, which has a reading of 80.5 HRT. This sample was made using the normal 2:1 ratio that was used for most tools (and tested samples).

The aim of this set of tests, to determine whether a chemical reaction (which results in a harder adhesive) takes place when larger amounts of ferric oxide are added, was achieved, although the results themselves were different from what had been expected. All the samples have considerably higher hardness readings then the other samples. This is largely due to ferric oxide's distinctive feature (and the reason why it was experimented with as an aggregate) - the very high amount of the geological binding mineral, iron. However, hardness is not increased by the resin to ferric oxide mixing ratio. The hardest sample (Sample 20), with a reading of 93.5 HRT, is the sample with

the most ferric oxide, yet the sample with the least ferric oxide (Sample 17) is the second hardest sample, with a reading of 93.3 HRT. The softest sample (Sample 18) had half the amount of aggregate to resin. Therefore, there is no gradual progression of hardness as more ferric oxide is added, and/or no sudden rise in hardness of the adhesives that have larger amounts of ferric oxide. Therefore, the drop in hardness of Sample 18, which has a reading of 80.5 HRT, cannot be because of a chemical reaction caused by the addition of more or less ferric oxide, but is rather because the sample was perhaps more cracked and fragile. This could be due to a number of possible reasons, e.g. the adhesive was exposed to more heat (when originally heated), or perhaps more moisture was used when polishing the mount surface causing the sample to get moist and then re-harden with cracks forming. The physical, textural properties of the aggregate used in these five adhesives are the same since the ferric oxide is commercially produced and all the particles are very fine.

Sample 21 was the unheated sample and it has a relatively high average hardness reading of 90.7 HRT. Overall, therefore, it appears that the heating of the adhesives does not affect the hardness thereof. Heating of the adhesives aids in making the adhesives more manageable during the hafting process but too much heat can affect adhesives by drying them out, but heating itself does not appear to have a significant and lasting affect on the physical quality of the adhesive (as far as hardness is concerned). All these samples have much higher HRT readings than those tested in the first set of tests, suggesting that the high iron content influences hardness but, as established earlier, not necessarily the success of the adhesive itself (other physical attributes, such as particle size, excluded).

Problems with results

What becomes problematic with these readings is a result of the quality and nature of the materials used to make the adhesive. The resin itself is very porous and has many air bubbles present (Fig. 6.3). The heating of the adhesive, during preparation, results in more bubbles forming, and consequently the production of weaker and softer sections. Therefore, although the surface of the mounted adhesive is seemingly homogeneous to the naked eye, it is still difficult to say whether the areas tested on each sample has

flaws/air-bubbles underneath the surface. This would result in a significantly softer reading. To help lessen this degree of error, all samples were tested at least three times, and calculated averages excluded the highest and lowest readings.



Figure 6.3 The adhesives left on the hafts of Tools 51, 21 and 68. Tool 51 was successful, but broke months afterwards, whereas Tools 21 and 68 broke during the activities. The bubbles, and inconsistent and crumbly nature of the adhesives, especially those on Tools 21 and 68, are clearly visible.

<u>Note:</u> The adhesives used for Tools 21 and 68 did not adhere well to the haft, whereas, the adhesive used for the successful tool (Tool 51) formed a good bond with the haft. This is another important element in hafting, and concerns the cohesiveness and consistency of the adhesive (Grant, pers. comm.)

6.4 Discussion: Aggregates, Hardness and Iron and Silica Quantities

6.4.1 Aggregates and Hardness (Table 6.4.1 and Fig. 6.4.1)

On the whole, the successful adhesives have a lower average hardness (55.1 HRT) and the unsuccessful adhesives have a higher average hardness (70.8 HRT). If one excludes the hardness of the adhesives made with ferric oxide (all of which were unsuccessful), however, then the average hardness of the successful and unsuccessful adhesives are very similar - 55.2 HRT versus 52 HRT– with the successful adhesives being slightly harder. But, a hardness as low as 32 HRT can be successful (Sample 12) since the addition of beeswax reduces the hardness but increases flexibility.

Table 6.4.1 Aggregates and hardness. Adhesives are listed in order of hardness

Aggregate	Sample #	HRT	Tool # and success of tool
Ferric oxide	20	93.5	59 - U
Ferric oxide	17	93.3	56 - U
Ferric oxide	21	90.7	60 - U
Ferric oxide	19	90.1	58 - U
Ferric oxide	18	80.5	57 - U
Sand	15	71	54 - S
Kaolinite	13	70.9	52 - S-S
Yellow Ochre	3	68.8	42 - U
Yellow Ochre	16	66.8	55 - S
Charcoal	9	65.8	48 - U
Yellow Ochre	6	65.2	45 - S
Red Ochre	7	61.7	46 - S
Red Ochre	5	58.8	44 - U
Red Ochre	4	57.2	43 - S-S
Wood	11	50.8	50 - U
Red Ochre	8	49	47 - S-S
Burnt Bone	10	40	49 - S-S
None	2	37.3	41 - S
Red Ochre and Beeswax	12	32.3	51 - S-S
Gypsum	1	16	40 - U

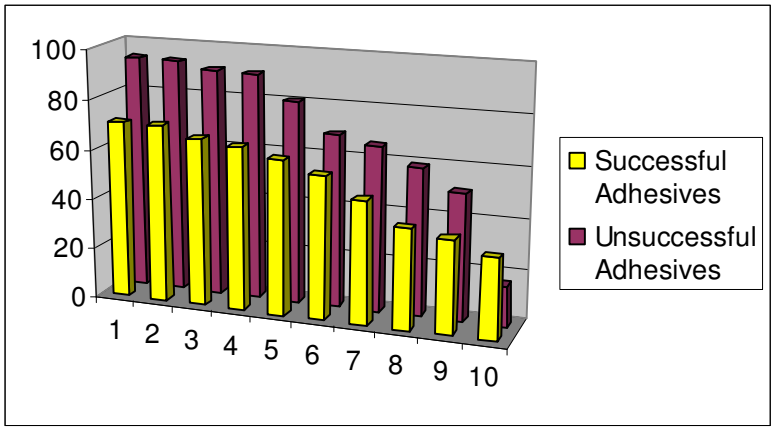


Figure 6.4.1 Successful versus unsuccessful adhesives in order of hardness. Each adhesive has been grouped firstly as successful or unsuccessful , and secondly, in order of hardness.
Note: y-axis is HRT readings, x-axis is aggregates ordered from hardest to softest (according to HRT readings).

6.4.2 Iron Quantities and Hardness (Table 6.4.2 and Fig. 6.4.2)

The samples with the largest amounts of iron, which are Samples 17 to 21 (Tools 56 to 60), i.e. those that were made with ferric oxide, have the highest HRT readings. However, Sample 15, an adhesive made with sand as an aggregate, has a very low iron percentage (1.78%) but is one of the harder adhesives. As known, the texture of the aggregates is a vital factor that determines the success of an adhesive. It could be the larger particle size of the sand that aids in making sand-loaded adhesives harder, whereas the very large amount of iron present in the ferric oxide is what aids in making ferric oxide adhesive harder (and this makes up for the very small particle size). However, when it comes to the actual success of the adhesive, then hardness alone is not an indicator of success and a mixture of the correct chemical and physical attributes is important. Therefore, iron quantity does correlate with hardness but other attributes of the adhesive ingredients (and the resulting processes that occur within the adhesive) can influence the hardness and it may not just be the iron that is the influential factor.

Table 6.4.2 Iron quantities and hardness readings

Sample #	Aggregate	ICP-OES # and Fe %	Hardness (HRT)
3	Yellow Ochre	C - 15.5%	68.8
4	Red Ochre	D - 43.9%	57.2
5	Red Ochre	E - 31.9%	58.8
6	Yellow Ochre	F / N – 14% *	65.2
7	Red Ochre	H - 22%	61.7
8	Yellow Ochre	K / O – 54.3% *	49
16	Yellow Ochre	C - 15.5%	66.8
13	Kaolinite	12.4%	70.9
15	Sand	1.78%	71
17	Ferric oxide	83.9%	93.3
18	Ferric oxide	83.9%	80.5
19	Ferric oxide	83.9%	90.1
20	Ferric oxide	83.9%	93.5
21	Ferric oxide	83.9%	90.7

Notes: * These were tested in ICP-OES 1 and 2. Percentages are averages from the two sets of results.

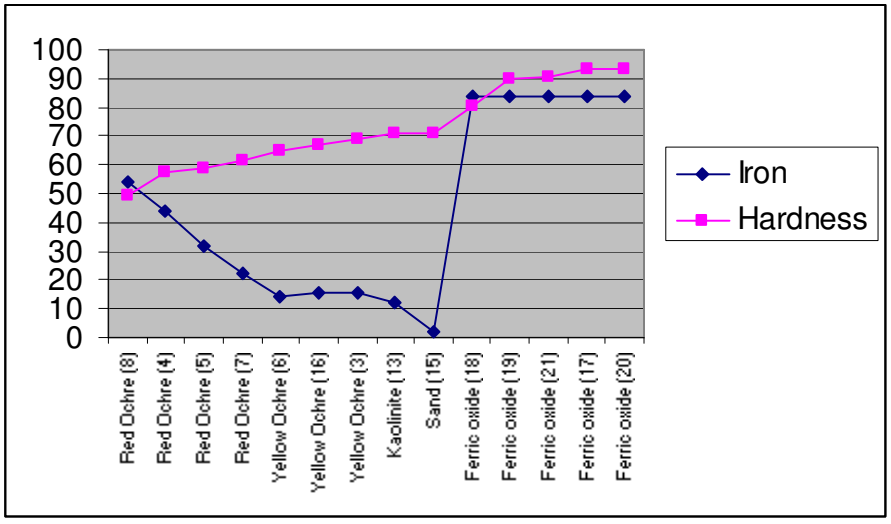


Figure 6.4.2 HRT readings versus percentage of iron (in the aggregates). Hardness test sample numbers are given after the aggregate.

6.4.3 Silica Quantities and Hardness (Table 6.4.3 and Fig. 6.4.3)

Table 6.4.3 Silica quantities and hardness readings

Sample #	Aggregate	ICP-OES # and Si%	Hardness (HRT)
8	Red Ochre	O - 10.26%	49
6	Yellow Ochre	N - 13.4%	65.2
13	Kaolinite	Q - 11.4%	70.9
15	Sand	R - 12.58%	71
18	Ferric oxide	M - 11.8%	80.5
19	Ferric oxide	M - 11.8%	90.1
21	Ferric oxide	M - 11.8%	90.7
17	Ferric oxide	M - 11.8%	93.3
20	Ferric oxide	M - 11.8%	93.5

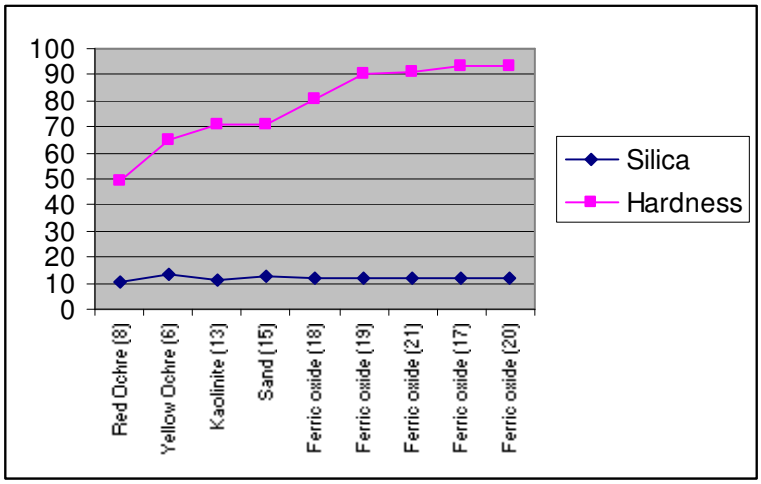


Figure 6.4.3 HRT readings versus percentage of silica (in the aggregates). Hardness test sample numbers are given after the aggregate.

All silica quantities are quite small, but there is no correlation between silica quantities and the hardness of the samples. Therefore the amount of silica, at least in small quantities, in a sample does not affect the hardness.

6.5 Conclusion

There is great variation between the hardness of the different adhesive samples. The hardness tests show, firstly, that the hardness of the adhesive alone does not necessarily correlate with the success of the adhesive as a binding agent on hafted tools. There are unsuccessful tools made with adhesives that have high readings (e.g. 93.5 HRT and 68.8 HRT) and successful tools made with adhesives that have low readings (e.g. 37.3 HRT). As well as successful tools made with adhesives that have high readings (e.g. 71 HRT and 66.8 HRT), and unsuccessful tools made with adhesives that have low readings (16 HRT).

Secondly, the ferric oxide adhesives, which contain very large amounts of iron, are very hard (although unsuccessful as binding agents for tools). This may suggest a chemical reaction is occurring between the resin and the aggregate (because of the large quantities of iron perhaps), but this reaction does not mean that the adhesive will be successful – there are other attributes, such as the rough texture of the aggregate, that are lacking. Thirdly, small amounts of silica do not affect the hardness of the adhesive, even though these quantities may have a positive effect on the success of the adhesive. And lastly, neither the iron nor the silica contents of the aggregate can be used alone to determine the hardness (or the success) of an adhesive because there are other chemical and physical attributes that come into the mix.

CHAPTER SEVEN: *Scanning Electron Microscope (SEM)*

SEM images enable an in-depth analysis of the topography of a sample at various magnifications. SEM allows for a nearly 3-dimensional picture therefore enabling one to examine surface contours and features. These images have a depth focus that is improved 300 times and resolution that is at least 10x than that which is offered by a light microscope (Oatley, 1972). A limitation of SEM images is that they are only in black and white.

7.1 Preparation

Samples used are those that had been mounted and had undergone hardness tests. Mounted samples were then coated with a carbon coating for SEM and EDS work. This coating is necessary as it prevents the sample from getting charged but still allows for x-rays to flow through it.

7.2 Procedure

Each sample was looked at under various magnifications (from 18 000x to 950x). Photographs were taken at different magnifications depending on the material and what magnification captured the over-all surface appearance. The SEM made it obvious how much the samples vary (within each sample as well as between the samples), from the homogeneity or heterogeneity, to the cracks, pits, bubbles and flows that exist on the surface of the samples. Heterogeneity (such as a heap or clump of aggregate that has not been mixed into the resin properly) and features such as cracks, pits and bubbles are likely areas of weakness in the adhesives, and SEM imagery allowed us to see these characteristics and determine whether they correlate with the success of an adhesive. Not all the samples have images due to difficulties with the reflective nature of the samples.

7.3 Results

Table 7.3 Observations made during SEM analysis

Sample #	Tool #	Aggregate	Success of tool	Observations
1	40	Gypsum	U	Many very small cracks. Also granular sections Not homogeneous. Adhesive uneven and varied. Some bubbles. See flow of resin.
2	41	Plain resin	S	Few cracks, some are big. Still particles present - cannot be aggregate (as was thought). See some bubbles. Generally smooth surface.
4	43	Ochre (red) (43.9% Fe)	S	Some large and small cracks. Not very homogeneous. Some pits and holes evident.
6	45	Ochre (yellow) (6.8% Fe)	S	Large cracks, and few small cracks. Quite homogeneous.
8	47	Ochre (red) (51.7% Fe)	S	Minute cracks and some large cracks. See flow of resin. Not very homogeneous.
10	49	Bone	S	Many large cracks, some small cracks too. Not very homogeneous.
12	51	Ochre (red) (51.7% Fe) and Beeswax	S	Very few cracks, but some big and small. More cracks on smoother sections. Quite homogeneous.
13	52	Kaolinite	S	More cracks on smoother sections. Quite homogeneous.
15	54	Sand	S	Large and small cracks. See the flow of resin. Quite homogeneous.

7.3.1 Cracking

The SEM images (Appendix 6) make it extremely apparent that all the samples are fragile because they all showed some degree of cracking whether on a small or large scale. What causes these cracks to form is not entirely evident but there are a few possible explanations:

a) The nature of resin when it dries, wherein the natural drying process causes cracks to form, especially when the drying process is sped up by additional heat (fire).
b) The pressure and temperature the samples are placed under when the moulds are made. All moulds were made with the same pressure and temperatures, therefore all samples were treated in the same way.

The adhesive samples with many large cracks are Samples 4, 6,10 and 15 (Fig. 7.3.5, Fig. 7.3.6, and Fig. 7.3.10 in Appendix 6). All these adhesives were successful on hafted tools during the initial activities (Table 7.3). All the samples have many minute cracks but the samples with minute cracks over most of the surface are Samples 1, 4, 8 and 15 (Fig. 7.3.1, Fig. 7.3.2, Fig. 7.3.5, Fig. 7.3.6, Fig. 7.3.7, Fig. 7.3.8, and Fig. 7.3.10 in Appendix 6). Samples 4, 8 and 15 (Fig. 7.3.5, Fig. 7.3.6, Fig. 7.3.7, Fig. 7.3.8, and Fig. 7.3.10 in Appendix 6) were successful as binding agents during hafting activities.

The amount and size of cracks evident, on the sample surface at least, is important because it would seem logical that more or larger cracks would mean a more fragile and unsuccessful adhesive recipe and therefore an unsuitable adhesive recipe to be used to haft tools. However, it appears that this may not be the case in some of the samples. Some very cracked samples were successful as binding agents for hafted tools. The photographs show this (Appendix 6). All samples show many (both large and small) cracks and successful and unsuccessful samples cannot be morphologically distinguished from each other when looking at the surface topography.

7.3.2 Homogeneity

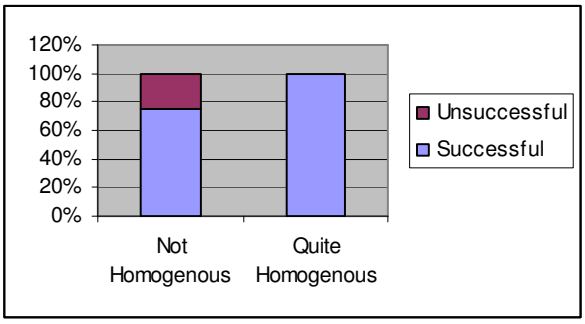
Homogeneous adhesives have the same texture over the whole surface. SEM analysis allowed me to see that many of the samples, or sections thereof, are not homogeneous, but rather that clear sections of smooth, featureless resin and granular masses of aggregate are visible. This find initially raised the question of whether adhesives need to be mixed for a much longer period than seems necessary, to ensure that the aggregate is fully mixed in. The expected result of under-mixing of the aggregate and the resin would be that the adhesive would be less successful as a binding agent due to the likelihood that

areas without aggregate or with too much aggregate may become more weak and cracked (and also that possible chemical reactions that occur are inhibited from occurring due to insufficient mixing). If further replication studies are performed then mixing times should be recorded and standardized, in order to remove this variable, even if the influence thereof is very slight.

Most of the adhesives have sections that are homogeneous, some areas that are smooth, seemingly plain resin areas and other areas that are granular accumulations of aggregate (Fig. 7.4). When looking at the images of the plain resin sample (Fig. 7.3.3 and Fig 7.3.4 in Appendix 6) particles can be seen within the resin. They are quite evenly spread but still show evidence of some clustering. Therefore, not all the particles visible in the other samples are necessarily the aggregate but unavoidable inclusions present in the resin. It is likely that the large clusters in the other samples (e.g. Fig 7.3.2 in Appendix 6) are aggregate. The inclusions present in the resin may be important and could explain some of the plain resin adhesive's success.

Samples 12 and 13 are the most homogeneous. From the backscatter images of Sample 13 (Fig. 7.3.11 in Appendix 6), the resin and kaolinite adhesive, this homogeneity is clearly visible, however the regular SEM image (Fig. 7.3.12 in Appendix 6) shows that there are obvious sections that are granular and sections that are smooth. The photograph of Sample 12 (Fig. 7.3.9 in Appendix 6), the resin, ochre and beeswax adhesive, was taken to show a section with distinct ball-shaped features, which appear to be beeswax, and it is difficult to see the general homogeneity of the sample. Both Samples 12 and 13 were successful as adhesives on the hafted tools.

The adhesive samples that appear the least homogeneous are Samples 1, 4, 8 and 10. This lack of homogeneity is obvious in the images (Fig.7.3.1, Fig. 7.3.2, Fig.7.3.5, Fig. 7.3.6, Fig. 7.3.7 and Fig. 7.3.8 in Appendix 6) and clear granular clumps can be distinguished from smooth (often cracked) areas. Samples 4, 8 and 10 were successful as binding materials on the hafted tools, whereas Sample 1 was unsuccessful.



Key for Figure 7.4

	Not Hmgn	Quite Hmgn
Successful	75% (3)	100% (5)
Unsuccessful	25% (1)	0%

Note: (n) = quantity of tools made.

Figure 7.4 Percentages of successful and unsuccessful tools and how they relate to the homogeneity of the surface of the sample (as seen through an SEM).

Figure 7.4 shows that there is a relation between the homogeneity of the sample and the success of the tool, with successful tools generally more homogeneous adhesives. However, there are still many successful tools that are not homogeneous and a homogeneous sample does not necessarily mean that it will be unsuccessful as an adhesive with which to haft tools.

Problems with the samples

The samples are made of resin, which is an insulating material. This causes the samples to be charged with electrons, which in turn results in the image being very reflective, therefore making it appear very light on the screen; making the image difficult to photograph. It causes the beam to move around on the sample and this makes it very difficult to focus on one point. This becomes especially problematic with the EDS (as shall be discussed later).

7.4 Conclusion

All samples show some degree of cracking on their surfaces. Surprisingly, the degree of cracking does not correlate with the success of the adhesive on the hafted tool. Perhaps this is because SEM involves only looking at the surface of the sample, which has been (wet-) ground and coated – creating cracks on the surface that are not necessarily representative of the whole sample. Because of the nature of the samples, all these processes could affect the samples' surfaces. Many of the samples have areas or clumps

of granular material and others have small spread out granular inclusions. The plain resin sample also has small particles in it therefore showing that no sample would appear completely homogeneous and smooth, because unknown inclusions exist in the resin. This is expected because bark, plant tissue, sand and even insect parts can naturally be incorporated in the resin. The aggregates can be seen, in most samples, as large granular sections. Some samples with large granular inclusions evident were successful suggesting that, although there is a correlation between homogeneity and success of the adhesive as a binding agent, homogeneity does not necessarily mean that the adhesive *will be* successful.

The morphology of the ochre, or any of the aggregates, were not looked at since the main aim was to determine the general surface morphology of the adhesive. A higher magnification than that in images (Appendix 6) is needed to see aggregate morphology. From what can be seen, all aggregates have similar shaped particles – quite round in shape, sometimes with angular edges. The (red and yellow) ochre pieces that Hughes & Solomon (2000: 22) analyzed were "angular and platy" in nature, except for two goethite samples, which had a tubular structure. Further morphological analysis of the aggregates, in conjunction with hafting experiments, would be useful and informative specifically in terms of the texture.

SEM imagery can be useful but the surface features and contours are not necessarily an indication of the internal structure and form of the adhesive. More in-depth investigation into the internal chemical and physical structure of the adhesives is necessary to establish their potential success.

CHAPTER EIGHT : *Energy Dispersive Spectrometer (EDS)*

Energy Dispersive Spectrometry (EDS) analysis was performed on six of the adhesive samples. EDS allows one to ascertain the (qualitative and quantitative) chemical make-up of specimens. EDS images are taken on certain, specific areas of the sample so that SEM observations about the different features on the sample surface can be supported.

8.1 Preparation

Samples used were those that had been mounted and had undergone hardness tests and SEM analysis. Mounted samples were coated with the carbon coating that had been used for the SEM.

8.2 Procedure

In order to find out the chemical make-up of the samples, different areas were chosen on which EDS analysis would be done i.e. homogeneous, featureless or granular areas. A 'spot mode' area analysis was used wherein the beam focuses on a single point on the sample and only that point is analyzed.

8.3 Results

The analysis done was a qualitative identification of the elements present in the sample. Therefore, no precise abundances of the minerals present are established. Data are then processed by a computer system, called a Multi-channel analyzer (Oatley, 1972), and displayed on the screen as a spectrum (Appendix 7). The spectrum shows peaks of the elements present. The peaks do not indicate the quantity of the elements present in the sample but correspond to the strength of the pulses, and therefore energy, from each of the x-rays that are emitted from the sample. Most elements produce K x-rays that are in

the 1.0 to 10.0 KeV (energy voltage) range. All samples analyzed using the EDS were done with 4 KeV. Two types of K x-rays are generated and both of these produce peaks on the spectrum. Therefore, when looking at the spectrum one element will produce two peaks, with one always being smaller than the other (Appendix 7).

Table 8.3 Observations and analysis of EDS spectrum

Sample #	Tool #	Aggregate	Success of Tool	Comments - Area on sample on which EDS done, and results	Figure *
1	40	Gypsum	U	On smooth, dark section No Aluminium. Calcium- and sulphur-rich (as would be expected with gypsum).	8.3.1
1	40	Gypsum	U	On granular area Some iron, potassium, magnesium, sulphur, chlorine and aluminium. Lots of calcium, silica and manganese.	8.3.2
2	41	Plain resin	S	On smooth, featureless area. Calcium and aluminium dominate the reading.	8.3.3
6	45	Yellow ochre (piece #10) 6.8% Fe	S	On granular area Iron reading is very low. Lots of aluminium and calcium.	8.3.4
8	47	Red Ochre (piece #12) 51.7% Fe	S	On granular area Mainly iron. Some aluminium, silica, sulphur and calcium. Tiny amounts of copper (probably an intrusion).	8.3.5
8	47	Red Ochre (piece #12) 51.7% Fe	S	On smooth, featureless area Mainly calcium. Very little anything else.	8.3.6
12	51	Red Ochre (piece #12) 51.7% Fe and Beeswax	S	Mixed area, so some granules are visible. Mainly calcium. Quite a lot of iron and silica. Very small amounts of aluminium.	8.3.7
12	51	Red Ochre	S	On smooth, featureless area	8.3.8

		(piece #12) 51.7% Fe and Beeswax		Little iron. Mainly calcium.	
12	51	Red Ochre (piece #12) 51.7% Fe and Beeswax	S	On granular area Lots of iron, silica and aluminium. Little calcium.	8.3.9
13	52	Red Kaolinite	S	On smooth, featureless (but not shiny) area high aluminium and calcium. Others all very low.	8.3.10
13	52	Red Kaolinite	S	On granular area Lot of iron, aluminium and silica. Tiny amounts of titanium (probably an intrusion).	8.3.11

Note: * **Figures are in Appendix 7.**

The EDS readings taken on granular areas show more variation in elements present (Fig. 8.3 in Appendix 7). Sample 1 (gypsum) has a high calcium, silica and manganese reading. Samples 8, 12 and 13 all have high iron readings (on the granular areas). This correlates with the aggregates added and the iron in them: ochre was the aggregate used in Samples 8 and 12; kaolinite was the aggregate used in Sample 13. Therefore, the granular clumps evident on the surface of these samples are, in fact, particles of aggregate.

Readings on areas that are smooth and featureless all have high calcium readings, and the plain resin sample also contained calcium (Fig. 8.3 in Appendix 7). This obviously suggests that the resin itself contains calcium. This is important when the geological binding agent, calcium carbonate, is considered. This will be discussed in Chapter 9. The EDS on the smooth section of Sample 1 (gypsum) shows the area contains calcium and sulphur. The presence of the sulphur suggests that, even though there are still many sections with granular clumps of gypsum, some of the gypsum has been dissolved in the resin. A degree of dissolving of an aggregate is expected but with gypsum it may perhaps be more so than the other samples and their aggregates, because when EDS was done on

the smooth, featureless areas on the other samples, the minerals in the aggregate used in the sample are not always found. This might be an explanation for why gypsum is not very successful as aggregates in adhesives.

The aluminium in Samples 6, 8, 12 and 13 was initially thought to be a contamination from the polishing process. All the polishing of the materials was done wet using fine-grained sandpaper. Fine polishing is done mechanically and with an aluminium-based liquid. Since the adhesive is water-soluble, this process makes the surface of the adhesive soft and it is likely that some aluminium particles present in the liquid will be incorporated into the adhesive. However, the ICP-OES results show that the aggregates themselves contain aluminium. The results of the full ICP-OES analysis were unreliable (as discussed in Chapter 4) but importantly they show that many of the samples *do* contain some aluminium.

Problems with the samples

The insulating and reflective nature of the adhesive results in the beam moving around constantly making the focusing on one point for EDS very difficult. A suggested solution is that a gold or gold-palladium alloy coating be used. The carbon coating has a lower density and so most of the x-rays pass through it. (Heywood, 1971; Oatley, 1972) The gold coating, on the other hand, because of its high density, prevents the escape of some characteristic specimen x-rays at the specimen surface (Heywood, 1971; Oatley, 1972). Gold coatings were not used in this study because other complications arose – that of suspected Aluminium contamination. The EDS was not working when initial SEM work was performed and so not all samples have EDS readings. It was decided that, due to difficulties with viewing the sample (and movement of the beam due to the type of sample), it was not necessary to do further EDS work on the other samples. ICP-OES results were deemed sufficient.

8.4 Conclusion

There are not many unexpected results, except for the aluminium and calcium contents. Quite a few of the samples have aluminium in them, although some could be intrusions (from the preparation process). But the aluminium in the ochre and kaolinite samples is consistent and is likely to be in the aggregate (and not from the preparation process). The role of aluminium in the adhesives is unknown, but because of its close relationship with iron, it is likely to be another important and influential element in cementation (Taylor & Schwertmann, 1978). Nearly all samples show high calcium readings whether on smooth or granular sections of the samples. This suggests that calcium is in the resin (as well as possibly in some aggregates, such as gypsum), which is important because calcium (carbonate) is a main geological binding agent. The two tests that lacked or had low calcium readings were on the granular sections of Samples 12 and 13. This reiterates the evidence of these granular areas being masses of aggregate.

CHAPTER NINE : *Discussion*

The replication studies aid in a better understanding of the properties and qualities of adhesives and their aggregates, so that a more complete awareness and understanding of the MSA tools and people can be obtained. Hafting experiments answer questions about which aggregates are successful, as well as the attributes that make aggregates ineffective and effective. Importantly, they also demonstrate that there are many controllable and uncontrollable variables that play a role in the making of adhesives and hafted tools. An understanding of these variables, and learning to work around them or control them (where possible), will result in a successfully hafted tool.

Hafting Experiments 1 determined that the best way to make a successful adhesive is by using a two parts resin, one part aggregate (2:1) mixing ratio. When beeswax is added a good ratio is four parts resin, to two parts ochre (i.e. the same 2:1 mixing ratio as used above), to one part beeswax (4:2:1). Depending on the moisture content in the resin, a 4:3:1 ratio can also be used. The mixing of the aggregate with the resin is important and mixing procedures used in Hafting Experiments 1 and 2 could account, in some way, for the Scanning Electron Microscope (SEM) results, which showed that many of the adhesives were not completely homogeneous but had separate areas of aggregate and resin. In future studies, adhesives should be mixed for fixed periods and for longer than seems necessary because this will ensure a complete particle mixing of the aggregate and resin, i.e. a more homogeneous adhesive.

Once the adhesive has been well mixed, it is then heated for 1:30 minutes, and it must be ensured that all the adhesive is heated, and not just the outside sections. The adhesives that were heated for more than one and a half minutes had a number things happening to them: a skin formed, the adhesive started to burn slightly at the areas closest to the heat (and these parts then became hard and could not be used in the adhesive in which the stone tool was set), and/or the moisture in the adhesive evaporated leaving little wet adhesive left to be used to haft the tool.

Heating makes it easier to manipulate the adhesive, and may help with the geological cementation process (however, this was not demonstrated in the current study). After heating, the adhesive is placed on the haft, the stone tool inserted and the rest of the adhesive placed around the tool. The adhesive must be completely dry before using the tool – this takes from one to five hours if near a fire. Adhesives made with the addition of beeswax take longer.

9.1 Resin

Experiments were done with two resin species, *Acacia karroo* and *Acacia tortilis.* Most tools were made with *A. tortilis* resin, and few tools were made with *A. karroo* resin. On the whole, the *A. karroo* adhesives were more successful than the *A. tortilis* adhesives. Additionally, Wadley's (2005a, in press) adhesives were all made with *A. karroo* resin and she had a very high success rate. What is a problematic with the success rates here is that, as discussed in Chapter 3, there are many variables involved in the creation of each adhesive that it is impossible to know whether it is the resin type and species that is the determining variable. Further investigation into this is vital. Importantly though, both the resin types have acidic pH readings of 4, and they both have similar consistencies.

Moving on past the issue of the resin species, the mineralogical make-up of the resin is important. EDS spectra (Fig. 8.3.3 in Appendix 7) showed that the resin is calcium-rich. Calcium (carbonate) is one of the three main geological binding agents and therefore it is likely that resin would be a good 'cement' into which aggregates are added. It is likely that the calcium content also plays a role in explaining why the plain resin adhesives were so successful.

The adhesives containing water (i.e. those that had been hard and were softened by adding water) had similar success rates to the ones without water, but they were more likely to dry out and break a few months after use. The life of the adhesive is therefore changed by the amount of water added and the condition of the resin. But importantly, the addition of water does not have a positive or negative effect on the adhesive if it used

soon after the tool is hafted. The best quality resin is one that is moist and sticky without being runny.

The quality of the resin used plays an important role in all hafting and was a constant concern in the current experiments. The specific qualities of the resin (aspects such as pH, mineralogy, moisture content, and the inclusions present in the resin) are very difficult to control. Further tests would be necessary for the resin alone, to insure that specific parameters are met. Some characteristics are easy to change – such as the consistency and water content of resin. This varies greatly due to rainfall and temperature, but if resins and adhesives do need more moisture then water can be added (as long as it is added prior to heating). If the resin is runny, then more aggregate must be added. Heating times also need to be varied depending on the consistency of the adhesive being worked with, with wet adhesives needing longer heating times than drier adhesives. An experienced adhesive-maker, as with a concrete specialist, can control some of the deficiencies of the ingredients through varying the type and quantities of aggregates and through varying the heating times and temperature of the fire.

Further, M. Lombard (2004a, 2004b) analysed 24 stone points from Sibudu. She found that vegetal residues are abundant on many of the tools. 73.96% of the stone tools have the vegetal residues, including resin, on the proximal and medial portions and 26.03% have vegetal residues on the distal portions of the stone tools (Lombard, 2004a, 2004b). This is evidence that resin was used as a binding material for hafted tools (and also, the stone points may have been used to process vegetal matter)

9.2 Beeswax

The addition of beeswax into adhesives has been proven to be successful (Allain & Rigaud, 1986; Wadley, 2005a, in press) and the results of the present study support this, because a majority (85.7%) of the adhesives made with the addition of beeswax were successful (Fig. 9.3). Adding too much beeswax must be avoided as this may hinder the setting of the adhesive and also, due to uncontrollable shrinkage over time, will cause the

stone tool to come loose (Wadley, 2005a, in press). Beeswax, on the whole, makes adhesives more flexible and easier to use, and counters the property of resin to dry into a brittle and crumbly material.

Beeswax needs to be heated before it is mixed into an adhesive or it will not mix in completely. Wadley's (2005a) microscopic studies of adhesives showed that fatty wax globules can still be seen in the adhesives, but that generally the waxy adhesives have a more opaque appearance suggesting the presence of the wax distributed in the adhesive. Any fatty or greasy substances are likely to have the same effect as beeswax on adhesives (Brandt & Weedman, 1997).

9.3 Aggregates

The use of aggregates in adhesives is not a necessity because plain resin used as an adhesive in the current study had a 75% success rate – the second highest success rate of all the adhesive recipes, after the adhesives that had beeswax added (Fig 9.3). Wadley's studies (2005a, in press) had a 80% success rate with plain resin adhesives. However, these adhesives are not ideal due to a number of reasons. Firstly, because plain resin is quite runny, it is difficult to manipulate and this makes placing the tool onto the haft difficult. Secondly, plain resin is a lot more sensitive to heat and can crack and get very brittle if held too close to the fire, or for too long. If this happens, the resin is unusable as a binding agent with which to haft tools. Crombé *et al*. (2001) suggest that since plain resin adhesive is generally more brittle than loaded adhesive, and that tools using plain resin as an adhesive may have been made with the intention that the stone tools would become dislodged in an animal, inducing haemorrhage. Thirdly, the addition of an aggregate into adhesives helps to prevent the adhesive from absorbing water in wet weather and resulting in the stone tool coming loose from the haft (Wadley, pers. comm.). This would have been an important factor for people living in open-air sites.

Evidence at Sibudu, in the form of stone tools (backed tools and points) that have plain resin residues on their proximal edges (Gibson *et al*. 2004; Lombard, 2004a, 2004b),

supports the fact that plain resin was used to haft tools. But such resin-coated stone tools are a minority, suggesting that resin hafting may have been used only for a specific kind of tool, with a specific purpose.

Another important aspect of hafting with plain resin, is the natural inclusions, such as bark, sand and possibly insects. These inclusions are visible in the SEM images (Fig. 7.3.3 and Fig. 7.3.4 in Appendix 6) and look like the aggregates that are visible in the other samples. These influence the adhesive (depending on the kind of inclusion) because they would function in the same way as the aggregates would. But inclusions do not necessarily mean the adhesive will be successful.

Mixing an aggregate with resin can produce a variety of different quality adhesives. The addition of an aggregate can aid in making the adhesive more malleable, making the hafting process easier by creating a less runny adhesive – therefore it is easier to heat and will not drip off the tool and haft when drying. But more importantly, the aggregate changes the quality of the resin and can result in a stronger and longer-lasting adhesive. The success of different adhesive recipes, from Hafting Experiments 1 and 2 are discussed below.

The adhesives with the highest success rate are the beeswax adhesives – with a success rate of 85.7%. Thereafter the plain resin adhesives, with a 75% success rate. The sand adhesives have a 71.4% success rate. This is substantially higher than the success rate of the ochre adhesives, which is 54%. However, there were only seven tools made with sand-loaded adhesives, compared to the 39 ochre adhesives. The adhesives that were all unsuccessful are the ferric oxide adhesives and the charcoal adhesives. The one tool hafted with a kaolinite and beeswax adhesive was also unsuccessful. As expected the burnt bone and gypsum adhesives also do not have high success rates. Most of the adhesive recipes have average success rates.

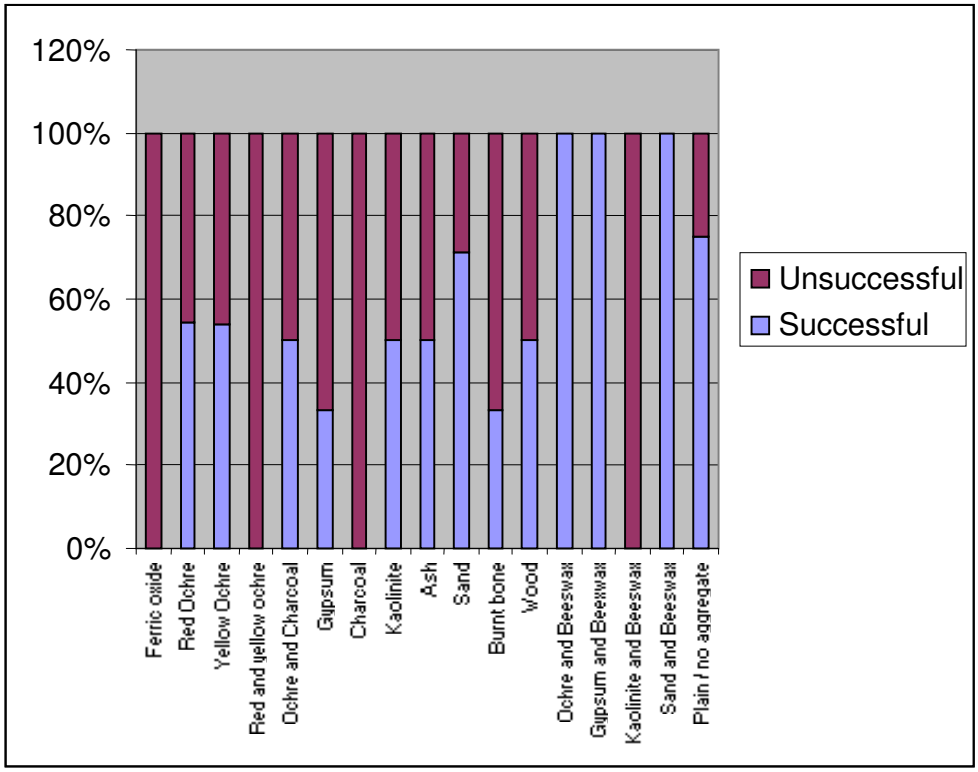


Figure 9.3 Success rates of different adhesive recipes.

9.3.1 Ochre

Ochre adhesives do not have a very high success rate (54%) (Fig. 9.3).

There are two basic groupings for the ochreous materials used in my study – snuff-box shale, and smooth, compact ochre pieces (Fig. 3.3.3 and Fig. 3.3.4). ICP-OES 1 analysis showed that the snuff-box shale generally has higher iron contents than the other compact ochre pieces, with the shale having an average of 32.5% Fe and the other pieces having an average of 20.9% Fe. Further, all red samples from ICP-OES 1 have an average of 32.1% Fe and yellow samples have an average of 14.4% Fe. The pieces tested in ICP-OES 2 samples all had larger amounts of iron, with the yellow ochre containing 21.27% Fe (although ICP-OES 1 found only 6.8% Fe in the same piece) and the red ochre samples having a average of 65.6% Fe. Both the tests show that there is a correlation between colour and iron content, even though there are other factors that also influence the colouring of the material – factors such as crystal size and structure, the degree of

cementation and the amount of cation substitution (Schwertmann & Cornell, 1991; Schwertmann, 1993).

Based purely on colour, there is no significant difference between the effectiveness of yellow and red ochre when used as an aggregate. Ochre pieces that were placed into a fire prior to grinding, and mixing into resin, showed colour changes to darker shades of red (Fig. 3.4.7). Tools 6 and 8 were hafted with adhesives made with unheated (yellow) ochre and heated (now red) ochre, and the same quantities of resin and aggregate (2:1), and were heated for the same time period (1:30 minutes). Both adhesives were successful and strong and, although there were colour differences, they looked the same (texturally). These results apply to Tools 16 and 17 (these had identical adhesives but were made with heated versus unheated ochre from the same stone). Therefore, the heating of yellow ochre pieces, prior to grinding and mixing with resin, appears not to affect the end quality of the adhesive. That is, iron hydroxides and iron oxides react in the same way (in adhesives), providing that heat is applied at the same stage in the process. The conditions necessary for colour change in goethite and hematite are complex, and depend on many variables such as the crystal structure, the elements present (such as aluminium and magnetite), the amount of organic matter and the amount of water present (Taylor & Schwertmann, 1978; Schwertmann, 1985; Grant, pers. comm.).

The prolonged heating of the adhesives made with yellow ochre powder as an aggregate (as done with Tools 5 and 55) does not cause any colour change. This lack of colour change may be due to an unknown geological or mineralogical factor (such as one of those mentioned above), since Audouin and Plisson (1982) did have colour change to red, and Wadley's yellow ochre adhesives changed to a more brown colour (Wadley, in press). Temperatures from the fire are probably too low to cause colour change, i.e. a chemical change in the ochre, and the resin probably also inhibits these changes. ICP-OES results confirm that there is a correlation between iron quantity and colour, but hafting experiments show that iron content alone is not accountable for the success of an adhesive.

The correct physical properties of a good aggregate, namely a mixture of particle sizes, is likely to have been deficient in many of the ochre adhesives. The ochre, although containing silica-rich inclusions (with a larger particle size) from being ground on sandstone slabs, is still quite fine in texture. Some ochre will be more so than others. The combination of the correct textural properties and the correct mineralogy is important, and if one element is lacking (which is hard to tell without doing individual and numerous tests on the mineralogical and textural properties of the ochre as well as the resin) it is likely that the adhesive will be unsuccessful. Additionally, the ochre pieces used are very different from each other – in terms of readily visible differences in colour, texture and form, as well as in terms of the crystal structures and mineralogy.

9.3.2 Sand

Sand is a very successful aggregate in adhesive, and hafting experiments showed this – with sand adhesives having a 71.4% success rate (Fig. 9.3). ICP-OES analysis of the sand shows that it contains very small amounts of iron – 3.98%. Surprisingly, it is does not contain large amounts of silica, only 12.5%, but compared to the other samples is quite high with only the yellow ochre sample having a higher silica content (of 13.4%).

The sand adhesives look different from all the other adhesives because of the larger particle size of the sand. They have a rough texture and the adhesives sometimes appear to be too dry, but they are very strong. Although hardness tests, in conjunction with hafting experiments, showed that the hardness of an adhesive is not necessarily related to its success, the sand adhesive tested was one of the hardest adhesives (after the ferric oxide adhesives). Sand is an important aggregate used to create concrete because of its range of particle sizes, rounded particle shape, and because of the silica content in most sands (Elvery, 1958; Lea, 1970; Addis, 1986). There is not a very large amount of silica or iron in the sand used in the current study, and because sand also has the desired physical properties of a range of particles size and rounded particles, these adhesives are strong, well concreted and hard. They are also not too rigid and inflexible whereby they cannot resist high impact pressure.

9.3.3 Other Aggregates

Gypsum, charcoal and burnt bone were the least effective aggregates experimented with (Fig. 9.3). Some of these aggregates were only used to haft a few tools and so success rates from hafting alone are not conclusive. The quality of some of these samples becomes evident when looking at SEM imagery (Appendix 6). However, ethnographic studies (Brandt & Weedman, 2002a, 2002b) have shown that some hafters do use materials such as charcoal and ash in resin. The current study, though, did not find them successful as aggregates. Both the burnt bone and ash adhesives were very crumbly and brittle, and mounting was problematic.

Wood shavings is an aggregate that is unlikely to have been used in the MSA, because for it to be effective, it needs to be made into a fine wood dust, which would have hard to do in the MSA considering the tools available. Wood-loaded adhesives have a 50% success rate (Fig. 9.3), but since only two tools were made it is hard to say whether this is a valid representation. The adhesive was quite hard and compact and was, unlike some of the other organic aggregates, not crumbly, and was therefore easy to mount for hardness tests and SEM/EDS analysis.

Kaolinite adhesives had a 50% success rate (Fig. 9.3), but unlike the ash and burnt bone adhesives, the adhesives were quite homogeneous. ICP-OES results did not reveal any interesting data concerning the make-up of kaolinite: it contains 12.4% iron (which gives it the red colour), and similar amounts of silica to the other samples. Kaolinite, since it is a clay, is not expected to be a successful aggregate – according to both geological binding principles and methodology employed in the creation of concretes – because of the very fine particle size. But it is quite an effective adhesive, and has a success rate that is only marginally lower than the ochre adhesives. Since both the kaolinite and ochre are relatively fine-grained (although the ochre does have the silica inclusions from grinding) , but they both contain iron and silica, it is probable that their percentage of successful tools would be significantly raised if more coarse grains (such as sand) were added.

9.4 Physical and Chemical Properties

Knowing the physical and chemical properties of the ingredients involved in the adhesive-making process is vital in resolving the issue of the processes occurring in the adhesives, and therefore why certain adhesive recipes are successful and others are not. Elemental analysis, pH tests, hardness tests and SEM and EDS work shed some light on both the properties of the individual ingredients, and also on the processes that occur within the adhesives. Understanding the principles employed when creating industrial concretes, and the processes involved in and conditions necessary for geological cementation give an awareness of what attributes are likely be important when creating adhesives for hafting.

For geological cementation to occur, there are some important conditions. Firstly, the correct minerals need to be present (in the pore waters). These are one or more of the geological binding agents – iron oxides, silica and calcium carbonate. These minerals are deposited in the surrounding sediment once the soils have become desiccated, and they are vital in the cementation process (Baker, 2001). EDS spectra show that calcium is present in the resin (Fig. 8.3.3), so already without adding an aggregate (and especially if there are certain inclusions in the resin to which the resin can adhere) there is a good possibility of success.

Secondly, the surrounding pH needs to be acidic so that precipitation can facilitate cementation. All the resins used in the current experiments are acidic – with a pH of 4. The addition of an aggregate usually causes the pH to rise, making the adhesive more alkaline and perhaps (if the alkalinity gets too high) interferes with or prohibits proper cementation. The pH of the adhesives (in Hafting Experiments 2) increased when the aggregate was added to the adhesives, but did not rise further when the adhesives were heated. This is the time when pH change would occur geologically. This is an important facet of creating a successful adhesive, and it perhaps needs to be more closely controlled and explored.

The addition of an aggregate into the resin has many advantages (as mentioned in 9.1), but the aggregates need to fit certain requirements (based largely on the process of creating industrial concrete). The texture of the aggregate is important, with a larger particle size being preferable in combination with a range of particle sizes. Sand is the most common aggregate used industrially because it has the right particle sizes, spherical particles, and because it usually contains high amounts of silica. Sand proved to be one of the most successful aggregates when used on its own (and when beeswax was added) in the hafting experiments. However, ICP-OES analysis showed that the sand used for my replications contained small percentages of silica and iron, suggesting that the physical attributes of the aggregate, together with the chemical attributes, are important in both cementation and adhesive production.

This importance of the physical attributes of the ingredients is supported by evidence from other adhesive recipes. The ochre adhesives have a lower success rate than was expected. Success rates are much lower than previous hafting experiments (Wadley, 2005a, in press). Even the adhesives made with ochre that contained high amounts of iron had a low success rate. Ochre was prepared on sandstone slabs and during this process pieces of the silica-rich sandstone are rubbed off and included in the ochre powder. These inclusions add to the texture as well as enhance the already rich (in iron) mineralogical make-up by adding silica.. The ochre and sand have different mineral percentages, with the ochre usually containing a higher percentage of iron than the sand. However, this is not always the case since some ochre pieces only had very small quantities of iron.
The main reason for the lower success rate of the ochre adhesives is likely to be the lack of larger particles. There is a vast difference between the appearance of the sand and ochre adhesives – with the ochre adhesives being very smooth, and the sand adhesives looking very rough and coarse.

These results are, however, only what the current study found. Wadley (2005a, in press) found that nearly all the adhesives she made with ochre as an aggregate were successful. Her ochre was prepared also by grinding on a sandstone slab, and would have been roughly the same texture (and would have had some silica-rich inclusions). Her adhesives

were made with a 1:1 mixing ratio. Perhaps the larger quantities were more successful with the moisture content present in the resin she used, whereas the current experiments found a 2:1 mixing ratio to be more effective.

The ferric oxide is a prime example of the importance of the physical qualities of the aggregates. The ferric oxide is produced in a laboratory and therefore the powder is very fine. It contains very high amounts of iron (83.9%), a small quantity of silica (11.8%) and has minute quantities of other minerals. The two main elements are therefore iron and silica – both two of the main geological binding agents. All of the (nine) adhesives made with ferric oxide as an aggregate were unsuccessful. Therefore, although the ferric oxide adhesives have the correct chemical properties and the low surrounding acidic pH levels, ferric oxide is unsuccessful as an aggregate because it lacks the necessary physical attributes – a rougher texture.

CHAPTER TEN: *Conclusion*

The maker of hafted tools clearly needs to possess a considerable amount of experience with the hafting process. In addition, the artisan must have extensive knowledge of the way in which the ingredients react with each other. Specific heating times and quantities of ingredients are vital to a successful adhesive, and they are both determined directly by the amount of moisture present in the resin in the first place. Adhesives must be well-mixed in order to eliminate flaws and weaknesses, which may cause the adhesive to break and the stone tool to come loose.

Different aggregates possess different qualities and these need to be considered in conjunction with the task for which the tool is being used. The chemical and physical processes that occur in the adhesives are complex and this research has only touched the surface of the issue. These properties of the ingredients were obviously not known to the MSA stone tool hafter, but experience would have resulted in the use of ingredients that achieved optimum results.

A good quality resin is essential, because resin, being the main cement-like substance in the 'concrete' is one ingredient that has the most influence on the success of an adhesive. Having said that, a poor quality resin can still be a successful adhesive depending on the type of aggregates added (and the quantities used) and the way in which the adhesive is made. It is therefore also the pH and water component of the resin, and the chemical and physical properties of the aggregates (and how they react with the resin) that determine the success of an adhesive.

Also, the MSA hafter would obviously not have known about the mineralogical and chemical potentials of the ingredients but would have learnt, through experience, that the ochre or sand (for example) from a certain area or of a certain colour or texture is a good aggregate, especially if prepared in a certain way – such as grinding on a sandstone grindstone.

To sum up, the most successful adhesives were those made with beeswax as an additive. These tools had different aggregates added, but both the presence of the aggregate and the beeswax is important. The beeswax adhesives are also easier to manipulate and have an added level of flexibility. The plain resin adhesives were very successful, but are not ideal due to resin's sensitivity to certain preparation processes (such as heat and the addition of water) and also because plain resin is very difficult to manipulate. The sand adhesives also have a high success rate. The iron and silica contents in the sand are relatively low but, importantly, there is iron and silica present. The sand also has the desirable physical attributes (larger and varied particle size), which is likely to be the main factor influencing the sand adhesives success. Future work could be done on this.

Ochre is a successful aggregate but, unlike Allain & Rigaud's (1986) and Wadley's (2005a, in press) experiments, it did not produce the most successful adhesive in the hafting experiments reported here. The different types of ochre all embody different attributes (such as particle size, mineralogical make-up) and these are not known in advance without conducting tests on each specimen. As a result, there are many unknown variables in adhesives where the ochres have not been analysed. These varying attributes of ochre could change the outcome of manufactured adhesives. Since not all these variables were tested in my experiments, there is a large degree of variability within each sample, which in turn influences the result of the adhesive in some way. The (chemical and physical) properties of all the aggregates used needs to be known and to be held constant for all experiments in order to achieve more reliable results. Sand grains play a crucial role in the adhesive, due mainly to the larger particle size, and also since most sands will have the necessary mineral(s) present (namely silica, and also iron). These larger particles, whether present naturally in the aggregate or introduced by the addition of sand or during the process of grinding, are very important in the success of any adhesives, including ochre adhesives.

Ochre can be successful as an aggregate in adhesives since ochre always contains some iron (although amounts vary greatly) and often does have coarse particles, especially if ground on sandstone slabs (as are found with ochre residues on them at many MSA sites,

including Sibudu). The ochre traces found on the proximal portions of stone tools, in conjunction with use-wear patterns, are highly likely to be from adhesives, particularly when with fatty residues on them because beeswax (and other such greasy or fatty substances) are such effective additives in adhesives. Ochre has many practical uses and archaeological evidence and results from this study suggest that ochre is likely to have been used as an ingredient in hafting adhesives together with coarser aggregate materials.

CHAPTER ELEVEN: *Future Research*

This research has answered many questions on the chemical and physical processes involved in adhesive production. Yet, it also raises many questions; questions that require large amounts of inter-disciplinary research to answer. How the ingredients of adhesives react with each other (and how they bind to the haft), and why, needs to be understood fully in order to answer the question of why some MSA tools were hafted with ochre-loaded adhesives, when so many other easily-obtainable ingredients are available. The procedure of hafting tools involves so many variables, and all of the variables need to be fully investigated so that their contribution to the success or failure of an adhesive can be fully viewed and quantified. Also, it needs to be kept in mind that adhesive ingredients are likely to be regionally different (and have different mineral and/or organic inclusions present) resulting in regional-specific preferences for certain materials.

The influence of the quality of resin on an adhesive is obviously very large. The species of tree from which the resin was obtained must first be identified. The moisture content and pH of the resin, as well as the inclusions present, need to be identified and the effects of variations in these quantities needs to be investigated. Also, the best way of combining aggregates and resin should be experimented with. SEM analysis in the current study showed that the adhesives have sections of unmixed aggregate and S. McCarthy at Wits University Geology Department suggested an alternative way to ensure a homogenous adhesive – that dry resin be ground and mixed with the dry aggregate, then as much water (or moisture, in whatever form) as is needed is added in order to get the desired consistency. Importantly, the pH of the water needs to be monitored as this may influence the results.

Ethnographic studies done by Brandt (video shown at PAA conference, 2005; Brandt & Weedman, 1997, 2002a, 2002b) on the Konso of southern Ethiopia, show this technique being used. The video documents the entire hide working process, including the making of the hafted stone tool scrapers. Although different hide workers have different

techniques, in one instance, dry resin used to make adhesive was crushed on a grindstone or earthenware sherd, and various aggregates were then added. In this case, the ochre used was more clayey and was collected in a powdery form and therefore did not need to be ground. However, with different forms of ochre (such as those found at Sibudu and many other archaeological sites) the grinding of resin and ochre on a grindstone is highly feasible.

Microscopic studies of three ochre 'crayons' from Sibudu (Wadley *et al.* 2004) showed that all three had starch grains on them, which suggests that they were used in conjunction with plant materials. Wadley *et al*. (2004) further suggest that the ochre itself could have been rubbed with sticks to produce powder. Additionally, one ochre 'crayon' from Sibudu had resin on it, suggesting that it was ground on a grindstone on which resin had been ground previously (Wadley, pers comm.; 2005a, 2005b). Some Sibudu points also have resin residues on the distal portions, which possibly indicates that the way of processing resin in the way mentioned above, was occurring. Perhaps this method of grinding dry resin to make adhesives can be attempted in future studies.

There are still so many unknowns regarding the nature of iron and silica and how they react in resin. Slight variations in conditions, such as moisture content, heat and specifically pH, could influence how the iron and silica react. Furthermore, the quantities of the geological binding agent (iron oxide, silica and calcium carbonate), that are necessary for cementation to occur in adhesives, should be explored and the effects thereof further understood. Also, the role of aluminium (even though it is not a geological binding agent) may be quite large and should be further explored.

Then specifically with ochre: there are many different types of ochre, all with different mineralogical make-ups, and different crystal sizes and structures. All these factors could influence an adhesive, or at least, how the ochre reacts with the resin. It would be interesting and informative to discover which attributes of the ochre influence the final product. SEM analysis of the structure of the ochre, like that done by Hughes & Solomon (2000) should be done in the future. Also, the chemical make-up of different ochre (with

specific attention to iron, silica, and possibly even aluminium contents) can be explored further.

Different sands from different geological backgrounds need to be tested and used as aggregates in adhesives - as do sands with different particle sizes. The texture of the aggregates was found to be an essential attribute of a successful aggregate. Particle size, in terms of size and shape, of all aggregates should be analysed in future studies. Also, the degree that particle size versus the chemical make-up influences the success of an adhesive should be further explored. This could be done by experimenting with sand that contains none of the geological binding agents, and therefore only the physical properties will be tested.

Lastly, the role of other elements and inclusions, such as organic materials, clay and aluminium, needs to be determined, since they may have a significant affect on an adhesive's success (Schwertmann & Cornell, 1991; Lewis & Schwertmann, 1979).

APPENDIX ONE: *Hafting Experiments 1*

Tool #	Mould #	Resin	Aggregate	Amounts/Ratios	Time heated	Comments	Result
1		*A. tortilis*	**Ochre**: 1, Red	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Started to blacken with heat	U
2		*A. tortilis*	**Charcoal**	resin: 1 tsp char: 0.5 tsp 2:1	1:30 mins	Bubbled on heat	U
3		*A. tortilis*	**Ochre**: 1, Red **Charcoal**	resin: 1 tsp ochre: 0.5 tsp char: 0.5 tsp 2:1:1 / 1:1 *	1:30 mins	Started blackening with heat	U
4		*A. tortilis*	**Ochre**: 1, Red **Charcoal**	resin: 1 tsp ochre: 0.5 tsp char: 0.5 tsp 2:1:1 / 1:1 *	3 mins	Mastic evaporated - little used on tool	U
5		*A. tortillis*	**Ochre**: 2, Yellow	resin: 1 tsp ochre: 0.5 tsp 2:1	4 mins	Very crumbly - didn't stay on stick, hard to mix in ochre	U
6		*A. karoo*	**Ochre**: 2, Yellow	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Got smooth and formed a skin.	S
7		*A. karoo*	**Ochre**: 2, Yellow **Charcoal**	resin: 1 tsp ochre: 0.5 tsp char: 0.5 tsp 2:1:1 / 1:1 *	1:30 mins	Got smooth and formed a skin.	S
8		*A. karoo*	**Ochre**: 2, Red-Brown	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Got smooth and formed a skin.	S

9		*A. karoo*	**Ochre**: 2, Red-Brown **Charcoal**	resin: 1 tsp ochre: 0.5 tsp char: 0.5 tsp 2:1:1 / 1:1 *	1:30 mins	Smooth and formed a skin	S
10		*A. tortilis*	**Ochre**: 3, Red	resin: 1 tsp ochre: 1 tsp 1:1	1 min	Bubbled a bit and darkened on outside. Skin formed	U
11		*A. tortilis*	**Ochre**: 3, Red **Ochre**: 3, Yellow	resin: 1 tsp r ochre: 1 tsp y ochre: 0.5 tsp 2:3	1 min	Quite dry, and hard to mix	U
12		*A. tortilis*	**Ochre**: 3, Yellow	resin: 1 tsp ochre: 0.5 tsp 2:1	1 min		U
13		*A. karoo*	**Ochre**: 4, Red	resin: 1 tsp ochre: 1 tsp 1:1	1 min	Hard to mix. Heat caused bubbles and skin formed	S
14		*A. karoo*	**Ochre**: 4, Red	resin: 1 tsp ochre: 1 tsp 1:1	1:30 mins	Also hard to mix. Bubbled a lot	S
15		REHEATED # 11 (AFTER 40 MINS)			1 min	Very dry and crumbly	U
16		*A. karoo*	**Ochre**: 5, Light Red	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins		S
17		*A. karoo*	**Ochre**: 5, Yellow	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins		S

18		*A. tortilis*	**Kaolinite**	resin: 1 tsp Kaolin: 1 tsp 1:1	1:30 mins	Very mushy, tool kept falling off during heating	U
19		*A. tortilis*	**Gypsum**	resin: 1 tsp gyp: 1 tsp 1:1	1:30 mins		S
20		*A. tortilis*	**Ochre**: 6, Light Red **Beeswax**	resin: 1 tsp ochre: 0.75 tsp wax: 0.25 tsp 4:3:1	1:30 mins		S
21		*A. tortilis*	**Kaolinite** **Beeswax**	resin: 1 tsp kaolin: 0.75 tsp wax: 0.25 tsp 4:3:1	1:30 mins	Pieces of beewax apparent	U
22		*A. karoo*	**None**	resin: 1 tsp	1:30 mins		S
23		*A. karoo*	**Gypsum** **Beeswax**	resin: 1 tsp gyp: 0.75 tsp wax: 0.25 tsp 4:3:1	1:30 mins		S
24		*A. karoo*	**Charcoal**	resin: 1 tsp char: 1 tsp 1:1	1:30 mins	Bubbled and formed very thick skin	U
25		*A. karoo*	**Burnt bone**	resin: 1 tsp bone: 0.5 tsp 2:1	1 min	Formed quite thick skin	U
26		*A. karoo*	**Wood**	resin: 1 tsp wood: 0.5 tsp 2:1	1 min		S
27		*A. karoo*	**None**	resin: 1 tsp	1 min	Very runny	S
28		*NO TOOL, NO TOOL, NO TOOL, NO TOOL*					

29		*A. karoo* poor	**Ash**	resin: 1 tsp ash: 0.5 tsp 2:1	1 min	Crumbly appearance	U
30		*A. karoo* poor	**Ochre**: 7, Yellow	resin: 1 tsp ochre: 0.5 tsp 2:1	1 min	Crumbly appearance but still runny.	U
31		*A. karoo* poor	**Kaolinite**	resin: 1 tsp Kaolin: 0.5 tsp 2:1	1 min	Crumbly appearance	U
32		*A. karoo* poor	**Gypsum**	resin: 1 tsp gyp: 0.5 tsp 2:1	1 min	Formed a solid ball, fell of stick (not dripped)	U
33		*A. karoo* poor	**Sand**	resin: 1 tsp sand: 0.5 tsp 2:1	1 min	Formed a solid ball, fell of stick (not dripped)	U
34		*A. tortilis*	**Charcoal**	resin: 1 tsp char: 0.5 tsp 2:1	1 min		U
35		*A. tortilis*	**None**	resin: 1 tsp	1 min	Runny	U
36		*A. tortilis*	**Gypsum**	resin: 1 tsp gyp: 0.5 tsp 2:1	1 min	Formed a solid ball, fell of stick (not dripped), but not very crumbly.	U
37		*A. tortilis*	**Burnt bone**	resin: 1 tsp bone: 0.5 tsp 2:1	1 min		U
38		*A. tortilis*	**Sand**	resin: 1 tsp sand: 0.5 tsp 2:1	1 min		U
39		*A. tortilis*	**Ash**	resin: 1 tsp ash: 0.5 tsp 2:1	1 min		U

40	1	*A. tortilis*	**Gypsum**	resin: 1 tsp gyp: 0.5 tsp 2:1	1:30 mins	Hard to mix, crumbly	U
41	2	*A. tortilis*	**None**	resin: 1 tsp	1:30 mins	Not very runny, glassy look	S
42	3	*A.tortillis*	**Ochre**: 8, Yellow 15.5% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Not very runny, glassy look. Quite solid.	U
43	4	*A. tortilis*	**Ochre**: 8, Red 43.9% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Not very runny, glassy look	S
44	5	*A. tortilis*	**Ochre**: 9, Red 31.9% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Not very runny, glassy look	U
45	6	*A. tortilis*	**Ochre**: 10, Yellow 6.8% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Not very runny, glassy look	S
46	7	*A. tortilis*	**Ochre**: 11, Red 22% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Not very runny, glassy look	S
47	8	*A. tortilis*	**Ochre**: 12, Red 51.7% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Marshmallow-like, skin formed	S
48	9	*A. tortilis*	**Charcoal**	resin: 1 tsp char: 0.5 tsp 2:1	1:30 mins	Marshmallow-like, skin formed	U
49	10	*A. tortilis*	**Burnt bone**	resin: 1 tsp bone: 0.5 tsp 2:1	1:30 mins	Marshmallow-like, skin formed	S
50	11	*A. tortilis*	**Wood**	resin: 1 tsp bone: 0.5 tsp 2:1	1:30 mins	Marshmallow-like, skin formed	U

51	12	*A. tortilis*	**Ochre**: 12, Red 51.7% Fe **Beeswax**	resin: 1 tsp ochre: 0.5 tsp wax: 0.25 tsp 4:2:1	1:30 mins	Smooth but sticky. Can see pieces of wax. Very smooth when heated.	S
52	13	*A. tortilis*	**Kaolinite**	resin: 1 tsp kaolin: 0.5 tsp 2:1	1:30 mins	Very smooth. Bright red	S
53	14	*A. tortilis*	**Ash**	resin: 1 tsp ash: 0.5 tsp 2:1	1:30 mins	Marshmallow-like, skin formed	S
54	15	*A. tortilis*	**Sand**	resin: 1 tsp sand: 0.5 tsp 2:1	1:30 mins	Marshmallow-like, skin formed. Smooth.	S
55	16	*A. tortilis*	**Ochre**: 8, Yellow 43.9% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	3 mins	Done to see if colour change: none apparent. Thick skin formed.	S
56	17	*A. tortilis*	**Ferric Oxide** (red) 83.9% Fe	resin: 1 tsp ochre: 0.25 tsp 4:1	1:30 mins	Quite sticky but not extremely so. Very smooth mixture.	U
57	18	*A. tortilis*	**Ferric Oxide** (red) 83.9% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Easily holds the stone tip onto the haft. Very smooth mixture.	U
58	19	*A. tortilis*	**Ferric Oxide** (red) 83.9% Fe	resin: 1 tsp ochre: 0.75 tsp 4:3	1:30 mins	Hard to mix. Quite sticky although the mixture is quite compact.	U
59	20	*A. tortilis*	**Ferric Oxide** (red) 83.9% Fe	resin: 1 tsp ochre: 1 tsp 1:1	1:30 mins	Very compact mixture and hard to mix in. Quite hard to work with. Not very sticky.	U
60	21	*A. tortilis*	**Ferric Oxide** (red) 83.9% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	Unheated	Very sticky - difficult to place stone tip onto haft as sticks to my fingers.	U

Notes:

1) In Results column: **S = Successful**; **U = Unsuccessful.**
2) Resin that has been termed 'poor' has been done so because it contained much sand and plant matter, as well as maggots. These tools have not been included in the analysis.
3) All ochre pieces were numbered and these numbers have been given in the table, e.g. "Ochre: **1**, Red, Unheated."
4) One teaspoon of resin = 5ml.

* Mixing ratios of 2:1:1 mean two parts resin to one part of one aggregate, and one part of another aggregate, therefore there are two parts resin to two parts of combined aggregate.

APPENDIX TWO: *Hafting Experiments 1 – Tool Activities*

Haft #	Activity Times and the time at which stone tips broke off
1	2 mins: still strong, not wobbling. Small pieces of adhesive coming off. 3 secs: still seemingly sturdy but pressed hard and stone tip came off. Resin itself is hard
2	Already broken
3	Already broken
4	Already broken
5	2 mins: still strong, using quite a lot of force 1 min: came off after much force. Adhesive is hard but a little crumbly
6	2 mins: still strong 3 mins: still strong
7	2 mins: still strong 3 mins: still strong
8	2 mins: still strong 3 mins: still strong
9	2 mins: still strong, few pieces of adhesive coming off 3 mins: still strong
10	2 mins: still strong 1:30 mins: came off, adhesive dry
11	Came off straight away, adhesive crumbly but dry
12	Came off straight away, adhesive crumbly but dry
13	2 mins: still strong 3 mins: still strong
14	2 mins: still strong 3 mins: still strong
15	Already broken
16	2 mins: still strong 3 mins: still strong
17	2 mins: still strong 3 mins: still strong
18	Already broken
19	2 mins: still strong 3 mins: still strong
20	2 mins: still strong 3 mins: still strong

21	Was still soft inside (after a day) and came off straight away.
22	2 mins: still strong 3 mins: still strong
23	2 mins: still strong 3 mins: still strong
24	2 mins: still strong 1 min: feel off
25	2 mins: still strong 3 mins: still strong, small pieces of adhesive coming off
26	2 mins: still strong 3 mins: still strong
27	2 mins: still strong 3 mins: still strong
28	NO TOOL
29	Already broken
30	Already broken
31	Already broken
32	Already broken
33	Already broken
34	Already broken
35	Already broken
36	2 mins: fell off
37	Already broken
38	30 secs: fell off
39	2 mins: still strong 3 mins: still strong
40	2 mins: still strong, some pieces coming off 10 secs: came off
41	2 mins: still strong 3 mins: still strong
42	1:30 mins: came off
43	2 mins: still strong 3 mins: still strong
44	2 mins: still strong

	30 secs: tool fell off, adhesive hard and not crumbly
45	2 mins: still strong 3 mins: still strong
46	2 mins: still strong, a few pieces of adhesive coming off 3 mins: still strong, stone chipped off
47	2 mins: strong, half of the main working edge of the tool was chipped off 3 mins: still strong
48	2 mins: still strong, few small pieces of adhesive coming off 10 secs: came off
49	2 mins: still strong, lots of adhesive coming off, quite big pieces, but tool completely sturdy 3 mins: tiny pieces of adhesive coming off. Thought stone tip would loosen but is very sturdy
50	2 mins: still strong (appearance of adhesive looked like it would be weak) 2:30 mins: fell off after much force, had chipped the stone tip
51	2 mins: still strong. Tip of tool broke off 3 mins: still strong
52	2 mins: still strong 3 mins: still strong, tiny pieces of adhesive coming off
53	2 mins: still strong 3 mins: still strong, stone chipped off a little
54	Chipped the tool - couldn't use tool as no available edge. Stone tip is very sturdy
55	2 mins: still strong 3 mins: still very strong, no adhesive coming off
56	Already broken
57	Already broken
58	Already broken
59	Already broken
60	Already broken

Note: **Activities Performed to test the strength of adhesives:**

1) First 2 minutes involved sawing and scraping activities. Medium amount of pressure.

2) Second 3 minutes involved chopping and sawing activities. Large amount of pressure.

All activities carried out on dry and wet branches.

Time entered after two minutes is an addition to the two minutes, therefore the successful tools were used for five minutes in total.

APPENDIX THREE: *Hafting Experiments 2*

Tool #	pH (unheated)	pH (heated)	Resin	Aggregate	Amounts	Time heated	Comments	Result
61	6	6	*A. tortilis*	**Ferric Oxide** 83.9% Fe 11.8% Si	resin: 1 tsp Fe_2O_3: 0.5 tsp 2:1	1:30 mins	Started to harden before heating. Looked a bit crumbly. Hard to manipulate. Dried fast.	U
62	6	6	*A. tortilis*	**Ferric Oxide** 83.9% Fe 11.8% Si	resin: 1 tsp Fe_2O_3: 0.5 tsp 2:1	1:30 mins	Started to harden before heating. Could see pieces of resin. Looked a bit crumbly.	U
63	6	6	*A. tortilis*	**Ferric Oxide** 83.9% Fe 11.8% Si	resin: 1 tsp Fe_2O_3: 0.5 tsp 2:1	1:30 mins	More cohesive than the others. Less crumbly looking. Dried fast.	U
64	6	6	*A. tortilis*	**Ochre**: 12, Red About 54.3 % Fe 10.3% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Quite cohesive, bit crumbly.	U
65	6	6	*A. tortilis*	**Ochre**: 12, Red About 54.3 % Fe 10.3% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Started to harden before heating. Looked a bit crumbly. Hard to manipulate. Dried fast.	U
66	6	6	*A. tortilis*	**Ochre**: 12, Red About 54.3 % Fe 10.3% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Started to harden before heating. Looked a bit crumbly. Hard to manipulate. Dried fast.	S
67	6	6	*A. tortilis*	**Ochre**: 12, Red About 54.3 % Fe 10.3% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Started to harden before heating. Looked a bit crumbly. Hard to manipulate. Dried fast.	U
68	4	5.5	*A. tortilis*	**None**	resin: 1 tsp	1:30 mins	Mushy and hard to manipulate.	U
69	4	unheated	*A. tortilis*	**None**	resin: 1 tsp	1:30 mins		S
70	4	5	*A. tortilis*	**None**	resin: 1 tsp	1:30 mins	Used wetter resin as others seemed a bit dry. Very runny and hard to control. Not very sticky.	S
71	6	6	*A. tortilis*	**Ferric Oxide** 83.9% Fe 11.8% Si	resin: 1 tsp Fe_2O_3: 0.5 tsp 2:1	1:30 mins	With wetter resin (water added). Drips but easier to insert tip.	U

72	6	6	*A. tortilis*	**Ochre**: 12, Red About 54.3 % Fe 10.3% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Resin more wet. Not very sticky.	U
73	6	6	*A. tortillis*	**Ochre:** 13, Red 51.4% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Runny. Set nicely. Looks smooth.	U
74	5.5	6	*A. tortillis*	**Ochre:** 13, Red 51.4% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Not as runny as # 73.	S
75	5.5	6	*A. tortillis*	**Ochre:** 13, Red 51.4% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Quite runny. Not very sticky. Didn't hold tip easily.	U
76	6	6	*A. tortillis*	**Ochre**: 8, Red 43.9% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Quite runny. Not very sticky. Didn't hold tip easily.	U
77	6	6	*A. tortillis*	**Ochre**: 8, Yellow 15.5% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Formed a ball. Easy to heat. Easy to place tip and keep it in place.	U
78	6	6	*A. tortilis*	**Ochre**: 8, Yellow 15.5% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Formed a ball. Easy to heat. Easy to place tip and keep it in place.	U
79	6	6	*A. tortilis*	**Ochre**: 14, Red 22% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Formed a ball but still a bit runny. Dripping while drying.	S
80	6	6	*A. tortilis*	**Ochre**: 14, Red 22% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Dripping while drying.	U
81	5	5.5	*A. tortilis*	**Kaolinite** 12.4% Fe 11.4% Si	resin: 1 tsp kaolin: 0.5 tsp 2:1	1:30 mins	Formed a ball but still a bit runny. Held tip well.	S
82	5	5.5	*A. tortillis*	**Kaolinite** 12.4% Fe 11.4% Si	resin: 1 tsp kaolin: 0.5 tsp 2:1	1:30 mins	Formed a ball but still a bit runny. Held tip well.	U
83	5	5.5	*A. tortillis*	**Ochre**: 10, Yellowish About 14% Fe 13.4% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Formed a ball but still a bit runny. Didn't hold tip easily.	U

84	5	5.5	*A. tortillis*	**Ochre**: 10, Yellowish About 14% Fe 13.4% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Formed a ball but still a bit runny. Held tip well.	S
85	5	5.5	*A. tortillis*	**Ochre**: 10, Yellowish About 14% Fe 13.4% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Held tip well. Not too runny.	S
86	4.5 - 5	5	*A. tortillis*	**Sand** 3.9% Fe 12.6% Si	resin: 1 tsp sand: 0.5 tsp 2:1	1:30 mins	Sand very coarse and grainy. DIdn't hold tip easily. Dried very quickly.	S
87	5	5.5	*A. tortillis*	**Sand** 3.9% Fe 12.6% Si	resin: 1 tsp sand: 0.5 tsp 2:1	1:30 mins	Less coarse sand. More runny when heated. Dried very quickly.	U
88	5	5.5	*A. tortillis*	**Sand** 3.9% Fe 12.6% Si	resin: 1 tsp sand: 0.5 tsp 2:1	1:30 mins	Less coarse sand. More runny when heated. Dried very quickly.	S
89	5	5.5	*A. tortillis*	**Sand** 3.9% Fe 12.6% Si	resin: 1 tsp sand: 0.5 tsp 2:1	1:30 mins	Less coarse sand. More runny when heated. Dried very quickly.	S
90	5	Unheated	*A. tortillis*	**Sand** 3.9% Fe 12.6% Si	resin: 1 tsp sand: 0.5 tsp 2:1	1:30 mins	Runny.	S
91	4	Unheated	*A. tortillis*	**None**	resin: 1 tsp	1:30 mins	Runny.	S
92	6	6	*A. tortillis*	**Ochre:** 15, Red 74.3% Fe 8.49% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Held tip well. Looks cohesive. Ochre has a strong colouring ability.	S
93	5.5	5.5	*A. tortillis*	**Ochre:** 15, Red 74.3% Fe 8.49% Si	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Held tip well. Bit runnier than Tool 92.	S
94	4.5	4.5	*A. tortillis*	**Ochre:** 16, Red, 17.2% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Looks cohesive. Bit runny and lumpy.	S

95	4	4.5 - 5	*A. tortillis*	**Ochre:** 17, Yellow 20.9% Fe	resin: 1 tsp ochre: 0.5 tsp 2:1	1:30 mins	Looks cohesive. Bit runny.	S
96	4.5	5	*A. tortillis*	**Ochre:** 13, Red 51.4% Fe **Beeswax**	resin: 1 tsp ochre: 0.5 tsp wax: 0.25 tsp 4:2:1	1:30 mins	Very sticky. Different consistency Very waxy and greasy. Hard to place tip	S
97	4.5	5	*A. tortillis*	**Sand** 3.9% Fe 12.6% Si **Beeswax**	resin: 1 tsp sand: 0.5 tsp wax: 0.25 tsp 4:2:1	1:30 mins	Very grainy (i.e. rough texture of sand). Quite dry.	S
98	4.5	4.5	*A. tortillis*	**Sand** 3.9% Fe 12.6% Si **Beeswax**	resin: 1 tsp sand: 0.5 tsp wax: 0.25 tsp 4:2:1	1:30 mins	Very grainy (i.e. rough texture of sand). Quite dry.	S

Notes:

1) In Results column: **S = Successful**; **U = Unsuccessful.**
2) All ochre pieces were numbered and these numbers have been given in the table, e.g. "Ochre: **1**, Red, Unheated."
3) Where iron percentages are given, they are the results obtained either during ICP-OES 1 or ICP-OES 2 tests. The average iron percentage has been given for pieces that were tested in both sets of tests, e.g. About 14% Fe.
4) One teaspoon of resin = 5ml.

APPENDIX FOUR: *Hafting Experiments 2 – Tools Activities*

Haft #	Activity Times and the time at which stone tips broke off
61	Alr eady broken
62	Already broken
63	Already broken
64	2 mins: still strong 1 min: came off after much force. Adhesive stuck very fast on tool.
65	Already broken
66	2 mins: still strong 3 mins: still strong, small pieces of adhesive coming off. Looks unstable but is not.
67	Already broken
68	Already broken
69	2 mins: still strong 3 mins: still strong
70	2 mins: still strong 3 mins: still strong
71	1 min: Looked very homogenous. But fell off with just a little force.
72	Already broken
73	Already broken
74	2 mins: still strong 3 mins: still strong, but a bit cracked.
75	Already broken
76	Already broken
77	Already broken
78	Already broken
79	2 mins: still strong 3 mins: still strong
80	Already broken

81	2 mins: still strong 3 mins: still strong
82	Already broken
83	Already broken
84	2 mins: still strong 3 mins: still strong, small pieces of adhesive coming off
85	2 mins: still strong 3 mins: still strong, some cracks
86	2 mins: still strong 3 mins: still strong
87	Already broken
88	2 mins: still strong 3 mins: still strong
89	2 mins: still strong 3 mins: still strong
90	2 mins: still strong 3 mins: still strong
91	2 mins: still strong 3 mins: still strong
92	2 mins: still strong 3 mins: still strong
93	2 mins: still strong 3 mins: still strong
94	2 mins: still strong 3 mins: still strong
95	2 mins: still strong 3 mins: still strong
96	2 mins: still strong 3 mins: still strong
97	2 mins: still strong 3 mins: still strong
98	2 mins: still strong 3 mins: still strong

Note: **Activities Performed to test the strength of adhesives:**

1) First 2 minutes involved sawing and scraping activities. Medium amount of pressure.

2) Second 3 minutes involved chopping and sawing activities. Large amount of pressure.

All activities carried out on dry and wet branches.

Time entered after two minutes is an addition to the two minutes, therefore the successful tools were used for five minutes in total.

APPENDIX FIVE: *Full Elemental ICP-OES analysis*

Sample #	Loading agent	Na	Mg	Al	Si	P	S	K	Ca	Cr	Mn	Fe	Cu	Sr	Ba
1	Reagent grade Fe_2O_3	3.26	0.05	0.49	10.84	0.009	0.14	0.31	2.47	0.003	0.09	18.9	0	0.006	0.002
2	Yellow, unheated Ochre (piece 6)	0.49	0.06	2.14	14.16	0.1	0.005	1.55	0.09	0.008	0.02	11.9	0.005	0.003	0.14
3	Red, heated Ochre (piece 11)	0.48	0.03	1.34	10.5	0.36	0.03	0.22	0.08	0.01	0.1	17.06	0.0007	0.002	0.009
4	Sand	1.08	0.34	1.44	14.74	0.08	0.06	0.63	0.75	0.008	0.04	2.6	0.003	0.007	0.27
5	Kaolinite	2.02	0.96	4.21	13.76	0.008	0.03	0.61	1.37	0.04	0.05	9.28	0.0006	0.006	0.52
6	Sibudu Sand	0.37	0.82	1.04	11.58	4.05	0.11	1.39	5.74	0.002	0.3	0.83	0.007	0.04	0.03

APPENDIX SIX: *SEM Images*

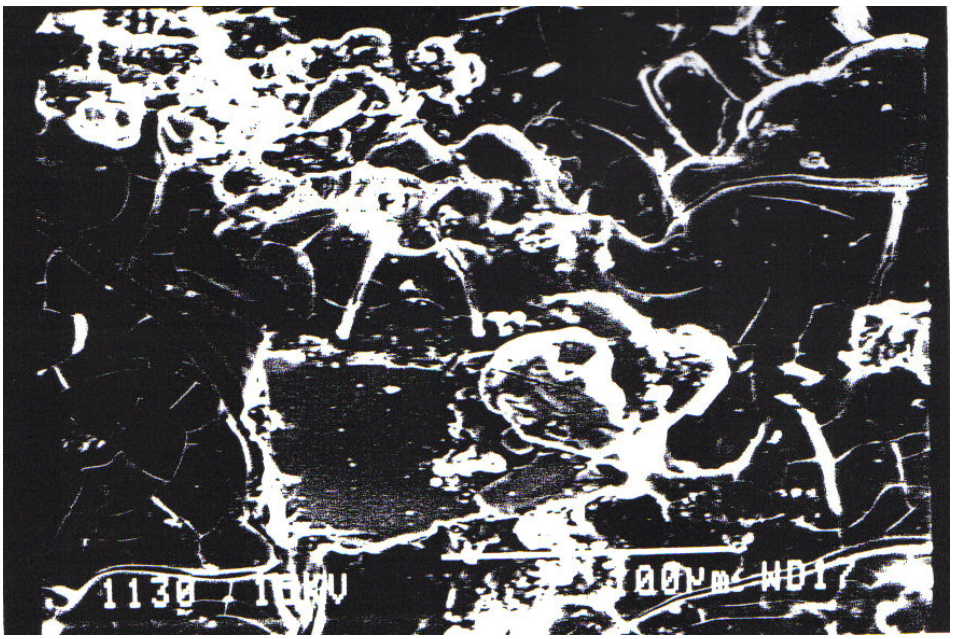


Figure 7.3.1 SEM image of Sample 1 (Tool 40). Gypsum. Unsuccessful.

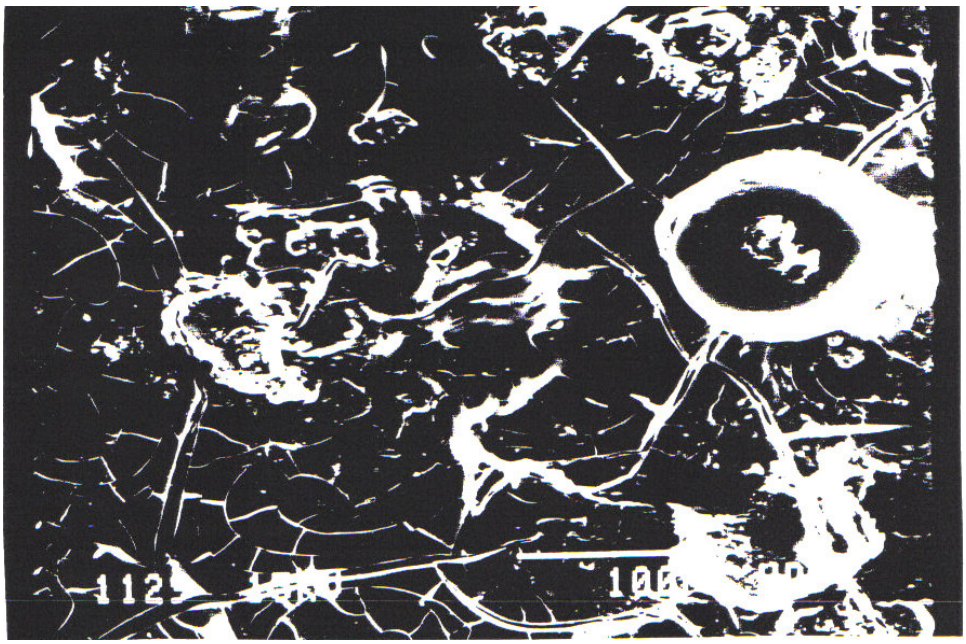


Figure 7.3.2 SEM image of Sample 1 (Tool 40). Gypsum. Unsuccessful.

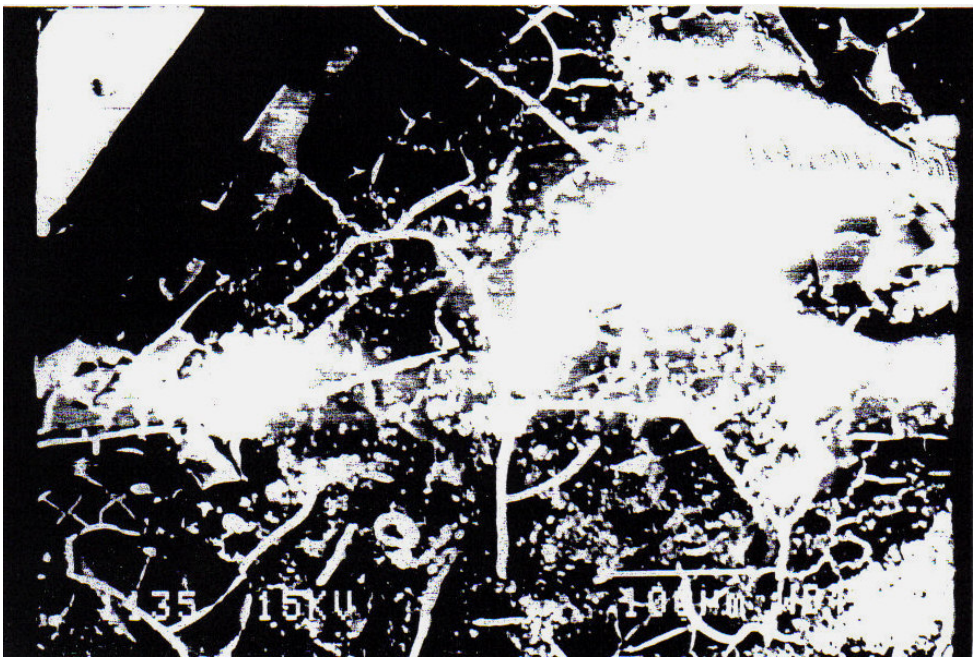


Figure 7.3.3 SEM image of Sample 2 (Tool 41). Plain Resin. Successful.

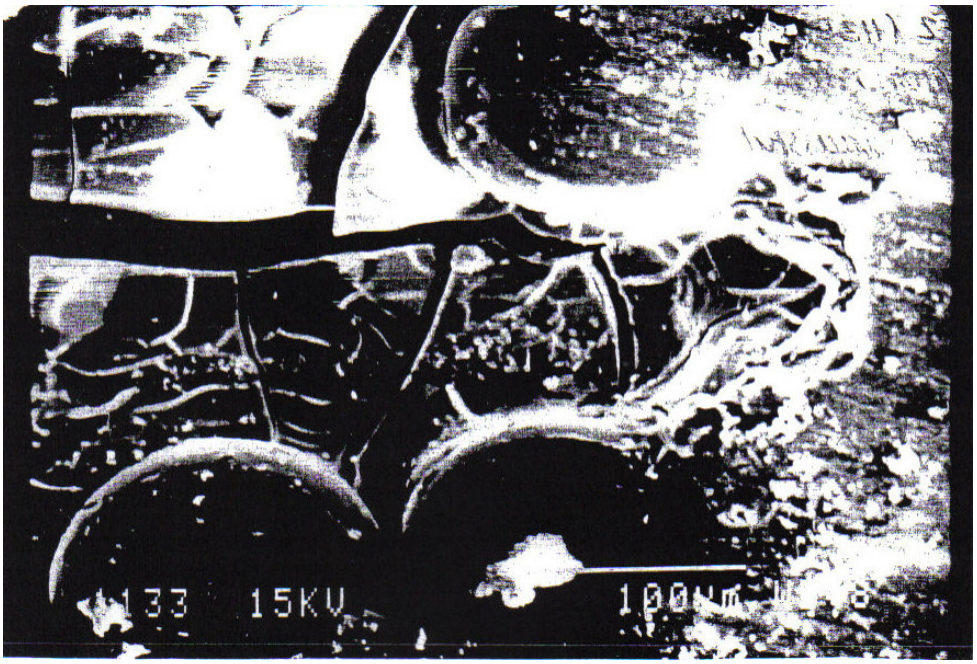


Figure 7.3.4 SEM image of Sample 2 (Tool 41). Plain Resin. Successful.

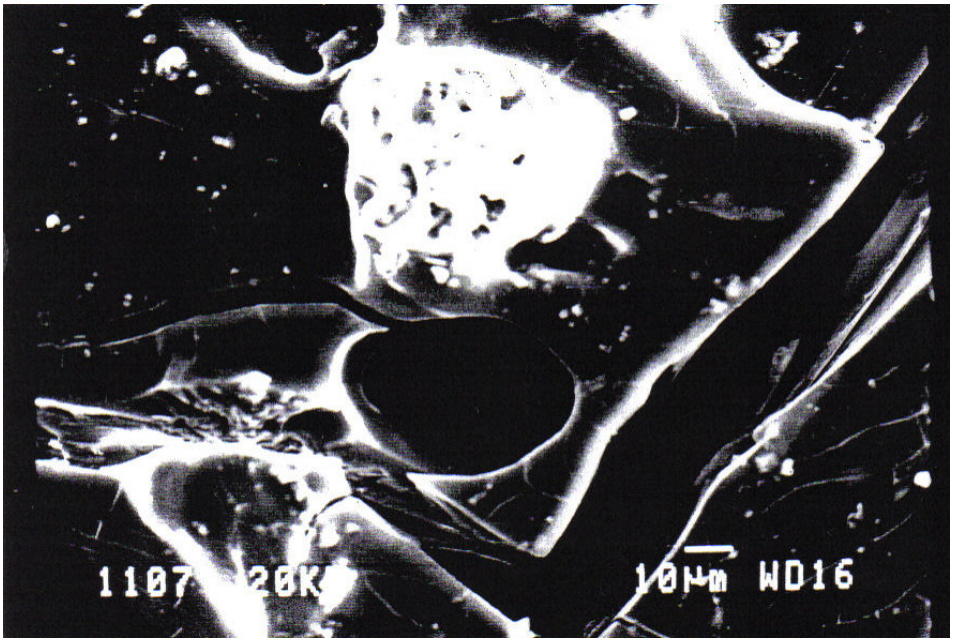


Figure 7.3.5 SEM image of Sample 4 (Tool 43). Red Ochre. Successful.

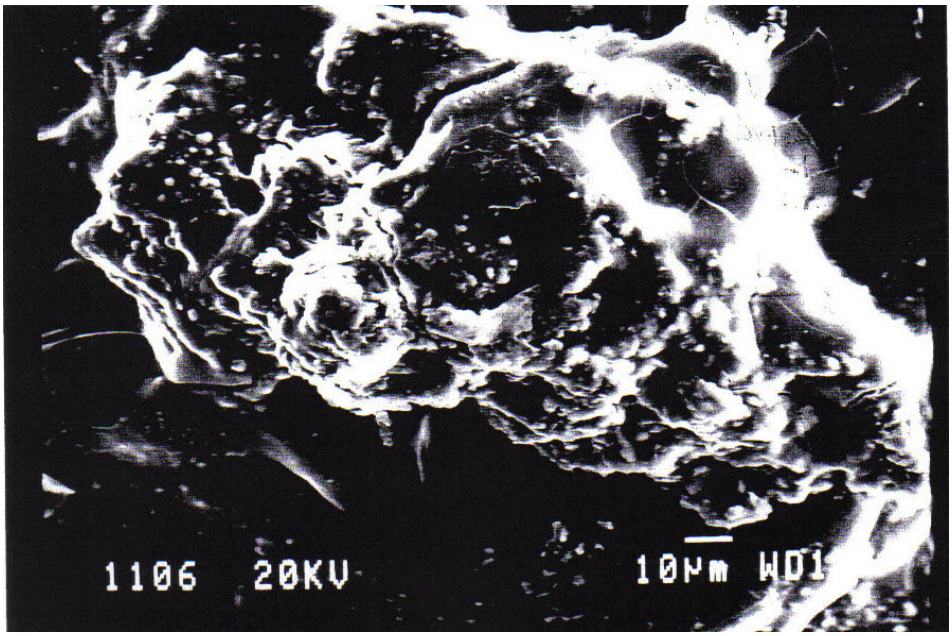


Figure 7.3.6 SEM image of Sample 4 (Tool 43). Red Ochre. Successful.

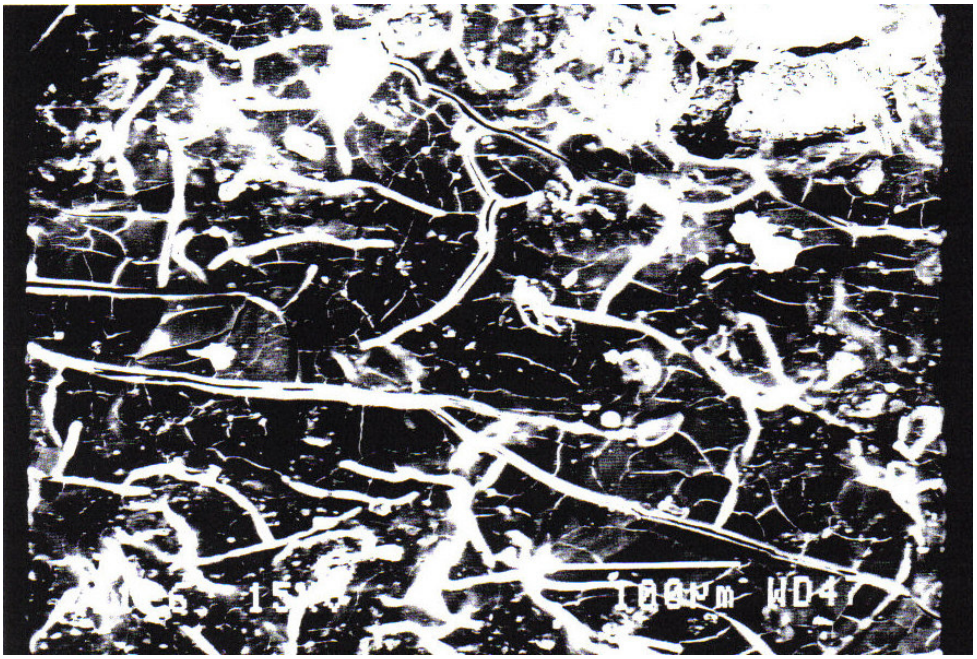


Figure 7.3.7 SEM image of Sample 8 (Tool 47). Red Ochre. Successful.

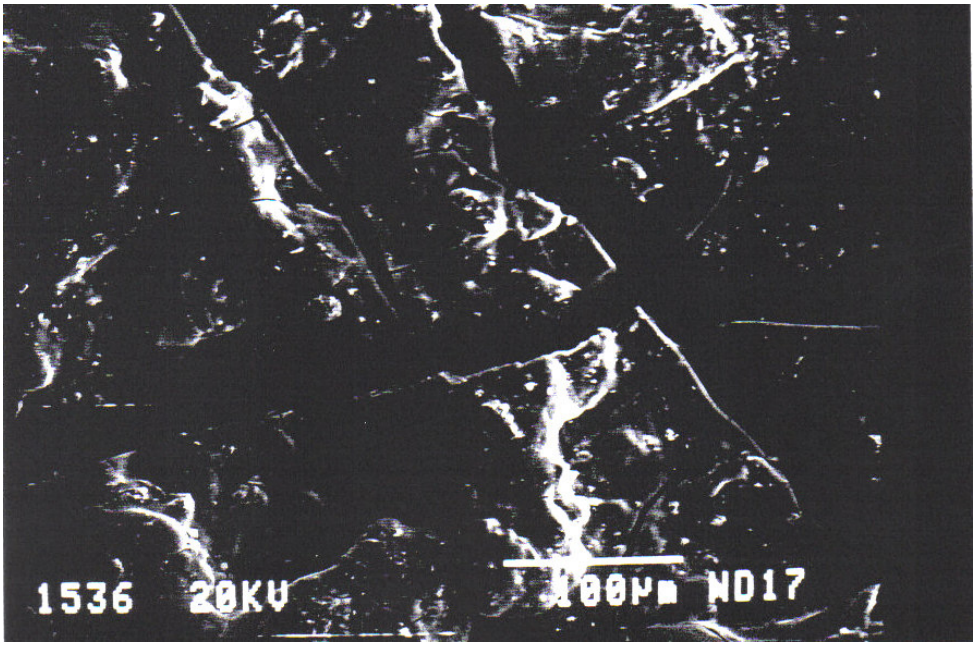


Figure 7.3.8 SEM image of Sample 8 (Tool 47). Red Ochre. Successful.

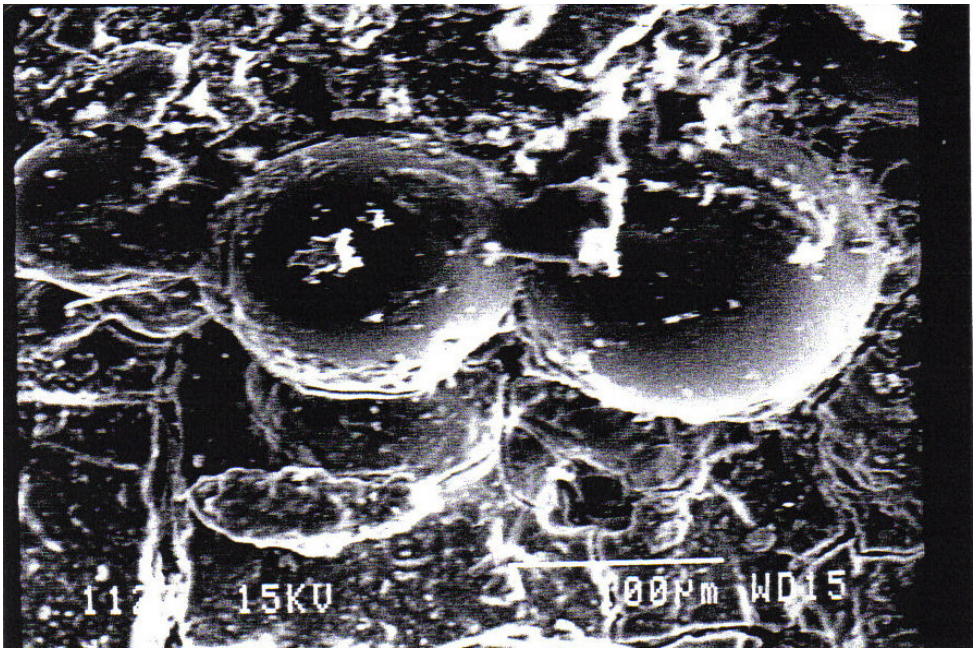


Figure 7.3.9 SEM image of Sample 12 (Tool 51). Red Ochre and Beeswax. Successful.

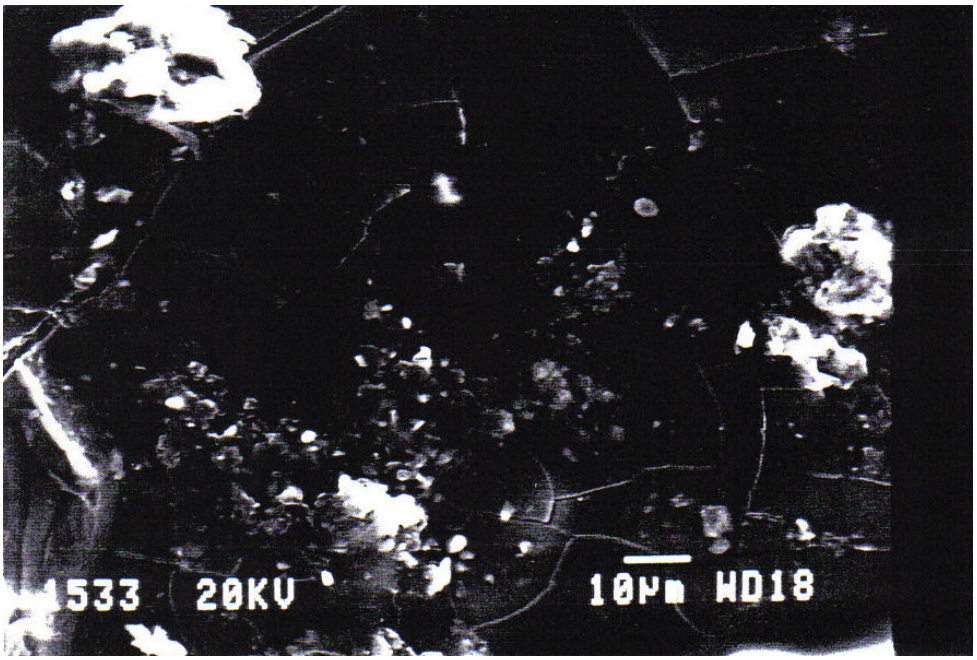


Figure 7.3.10 SEM image of Sample 15 (Tool 54). Sand. Successful.

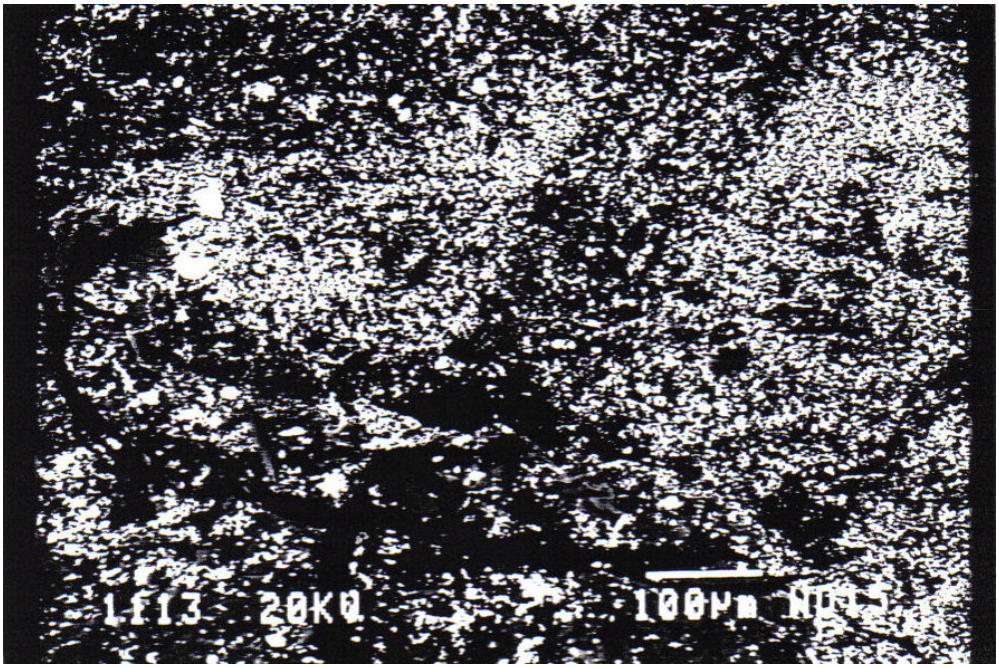


Figure 7.3.11 SEM image of Sample 13 (Tool 52). Kaolinite. Successful.

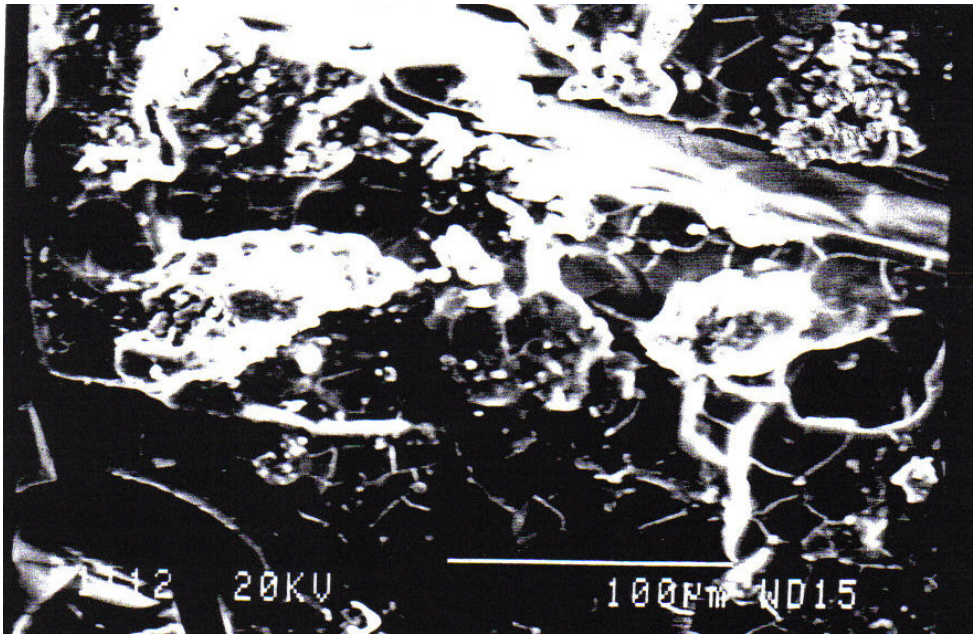


Figure 7.3.12 SEM image of Sample 13 (Tool 52). Kaolinite. Successful.

APPENDIX SEVEN: *EDS Spectra*

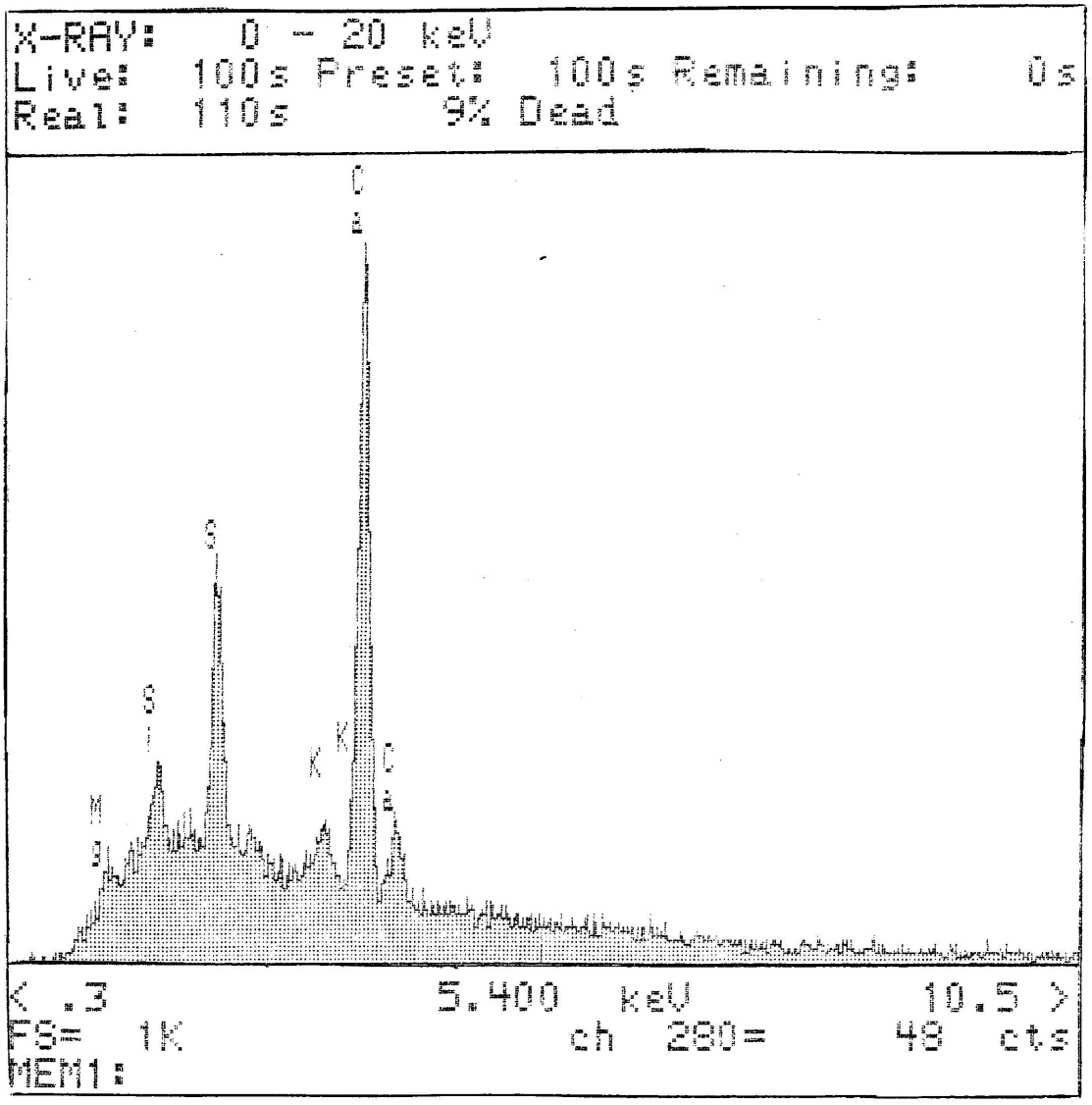


Figure 8.3.1 EDS Spectra I: Gypsum. Smooth, featureless section.

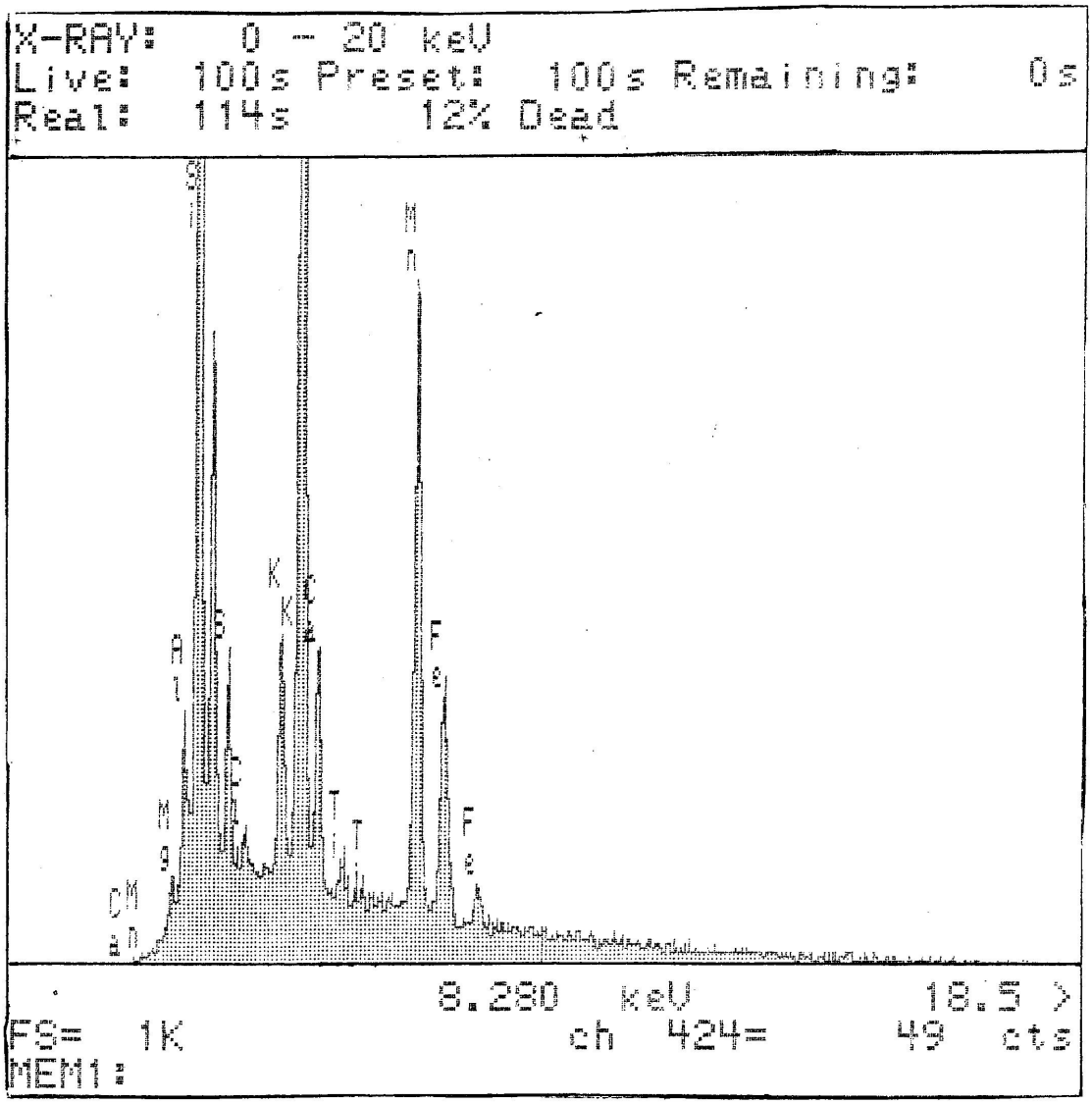


Figure 8.3.2 EDS Spectra II: Gypsum. Granular area.

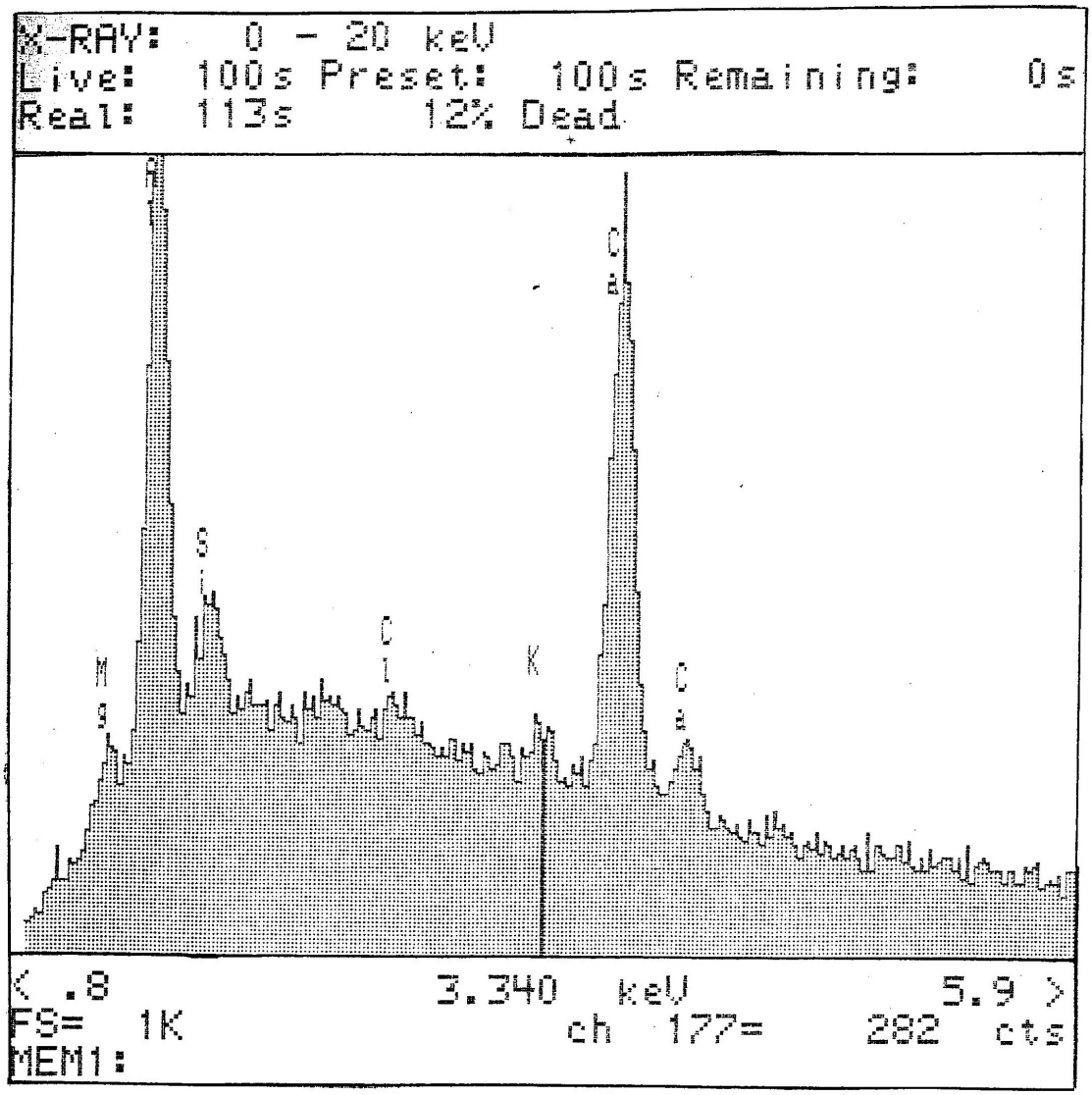


Figure 8.3.3 EDS Spectra III: Plain Resin. Smooth, featureless area.

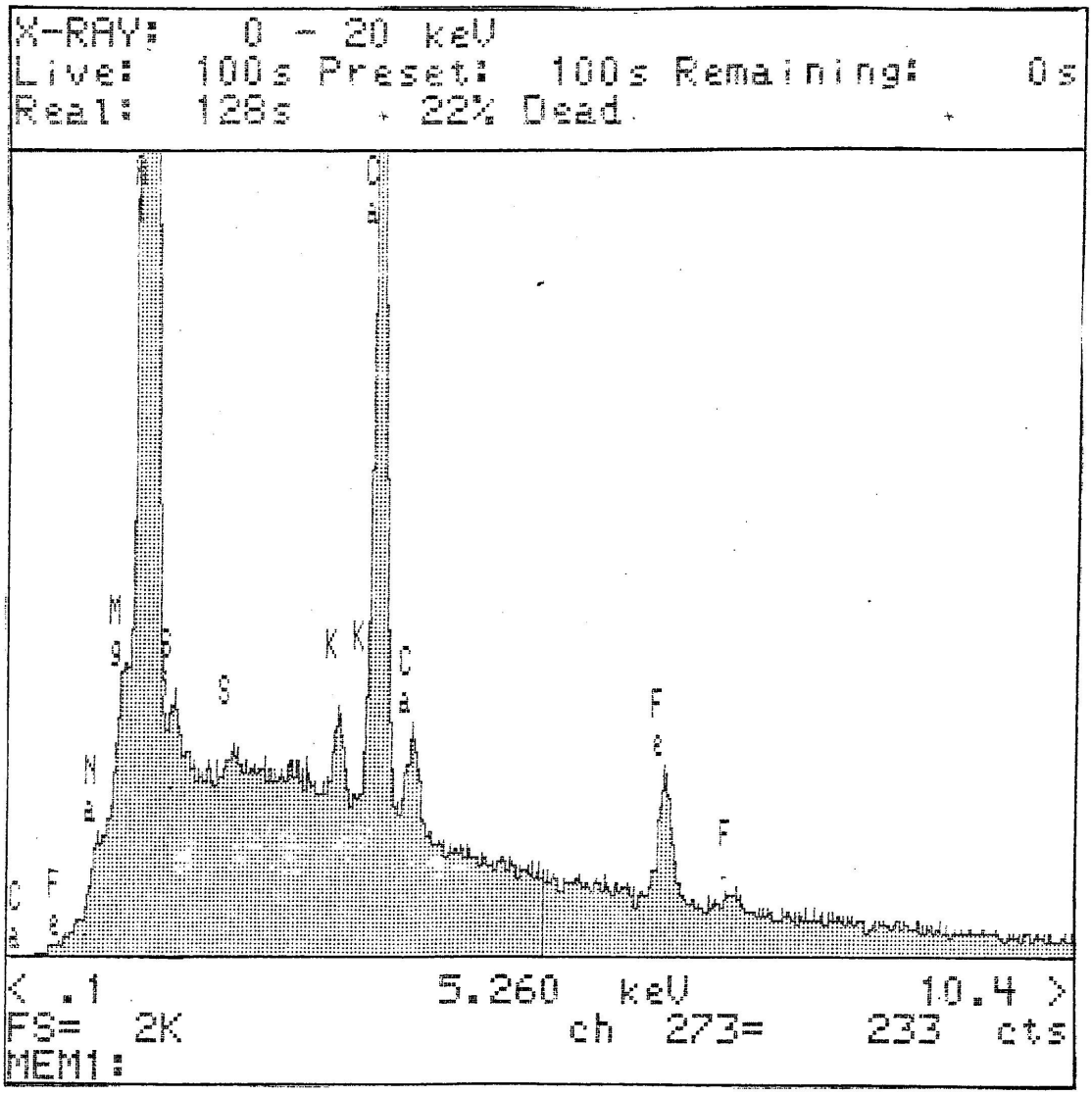


Figure 8.3.4 EDS Spectra IV: Yellow Ochre. Granular area.

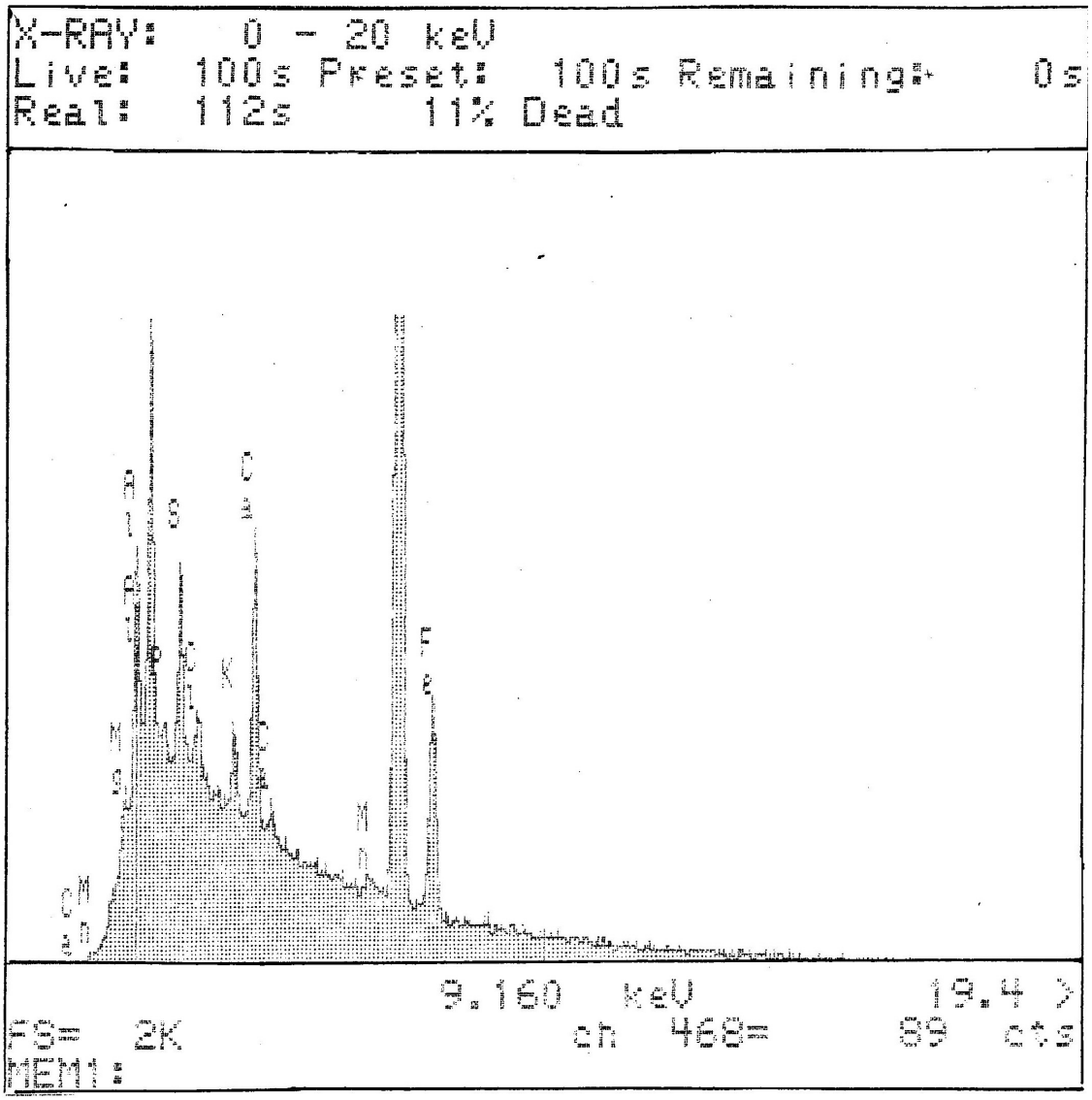


Figure 8.3.5 EDS Spectra V: Red Ochre. Granular area.

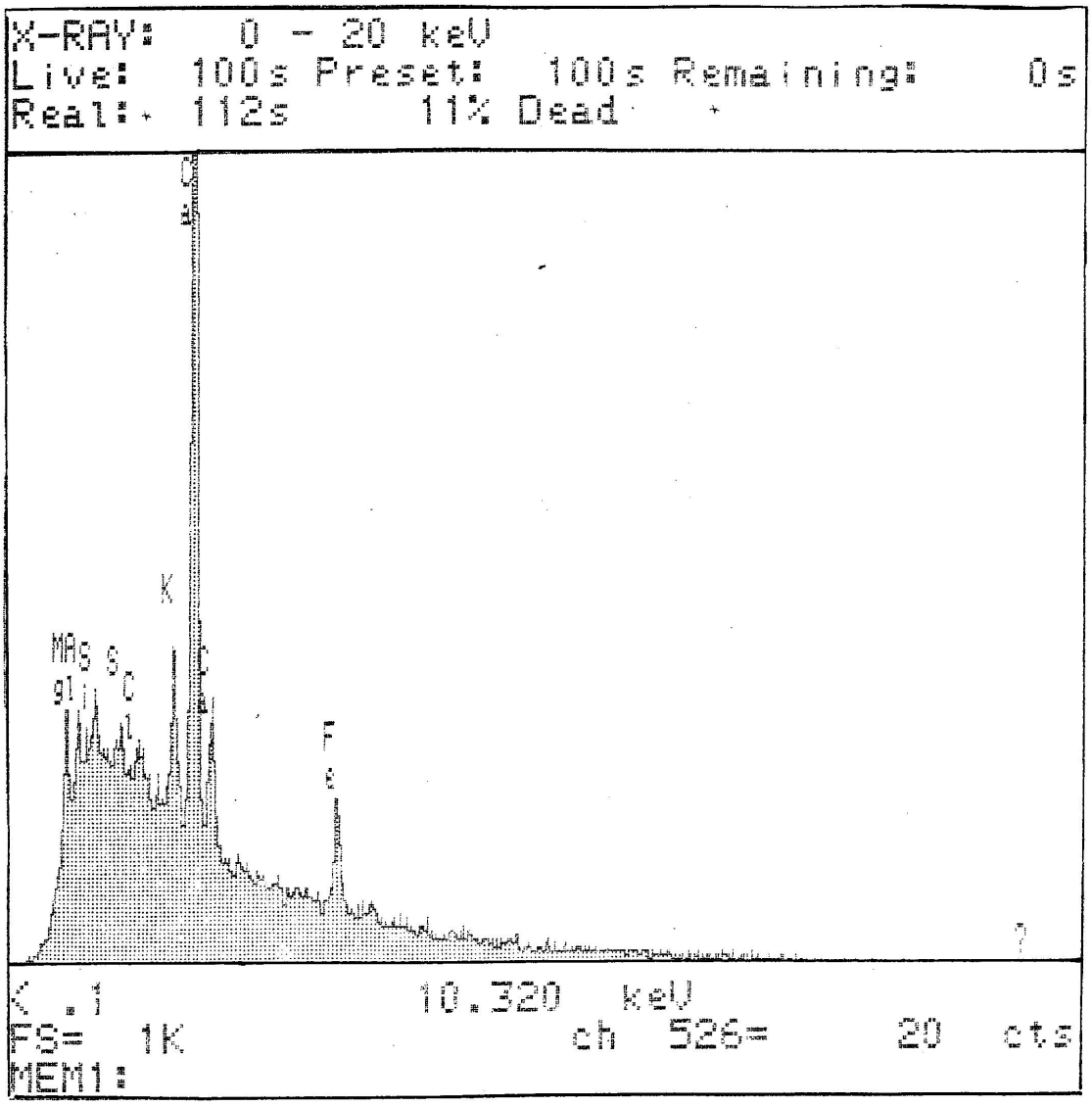


Figure 8.3.6 EDS Spectra VI: Red Ochre. Smooth, featureless area.

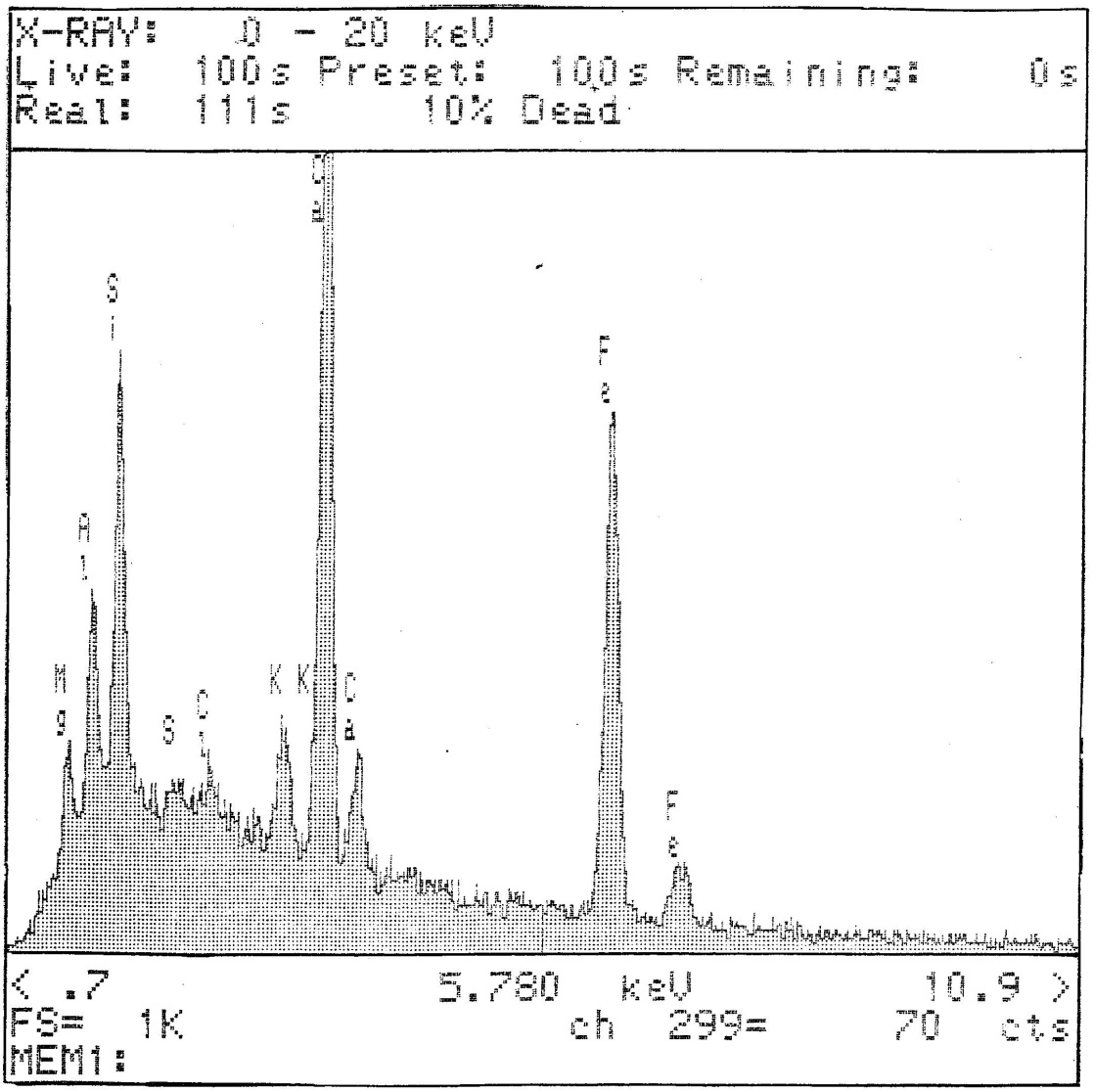


Figure 8.3.7 EDS Spectra VII: Red Ochre and Beeswax. Mixed area, some granules but quite smooth.

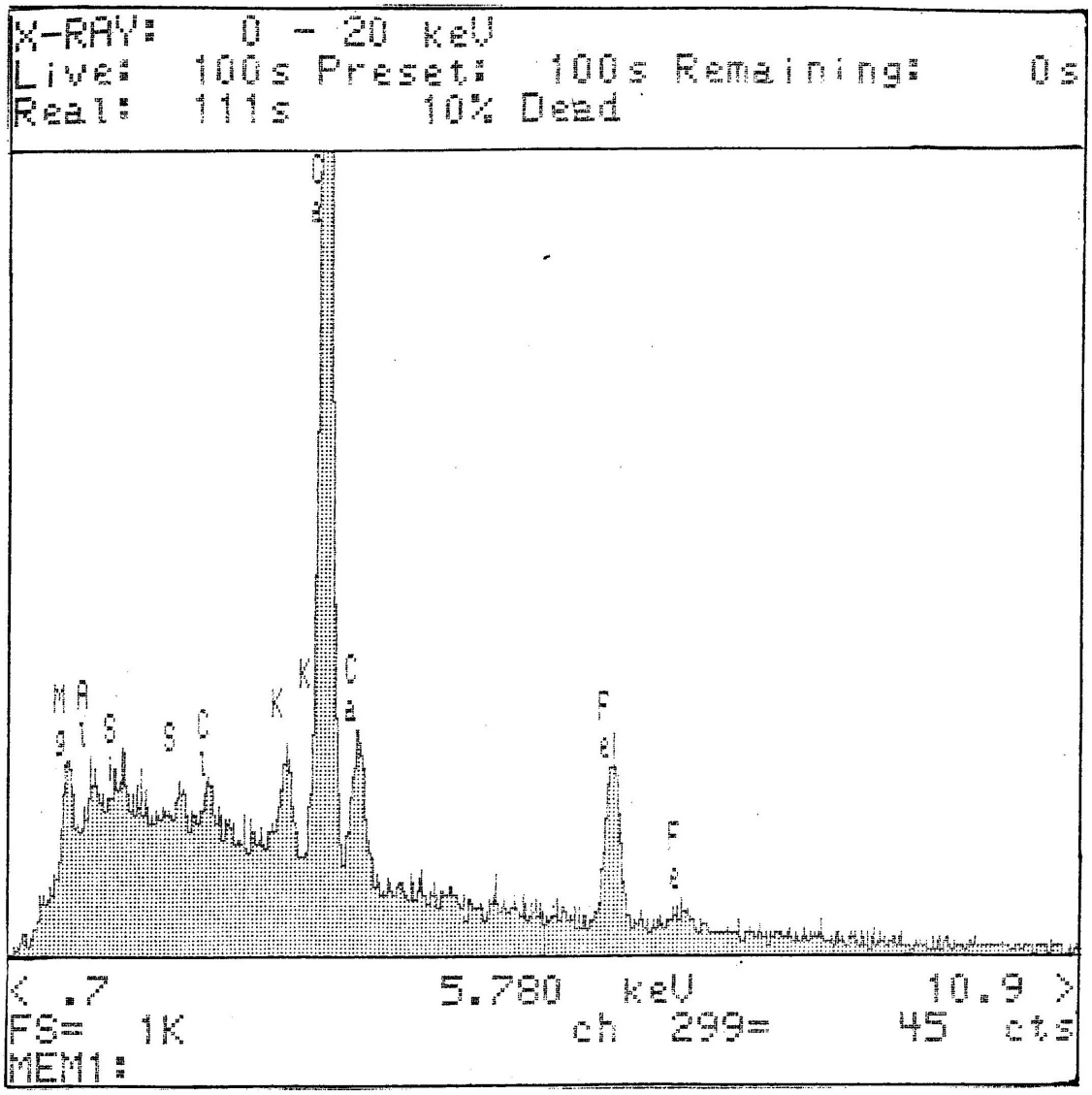


Figure 8.3.8 EDS Spectra VIII: Red Ochre and Beeswax. Smooth, featureless area.

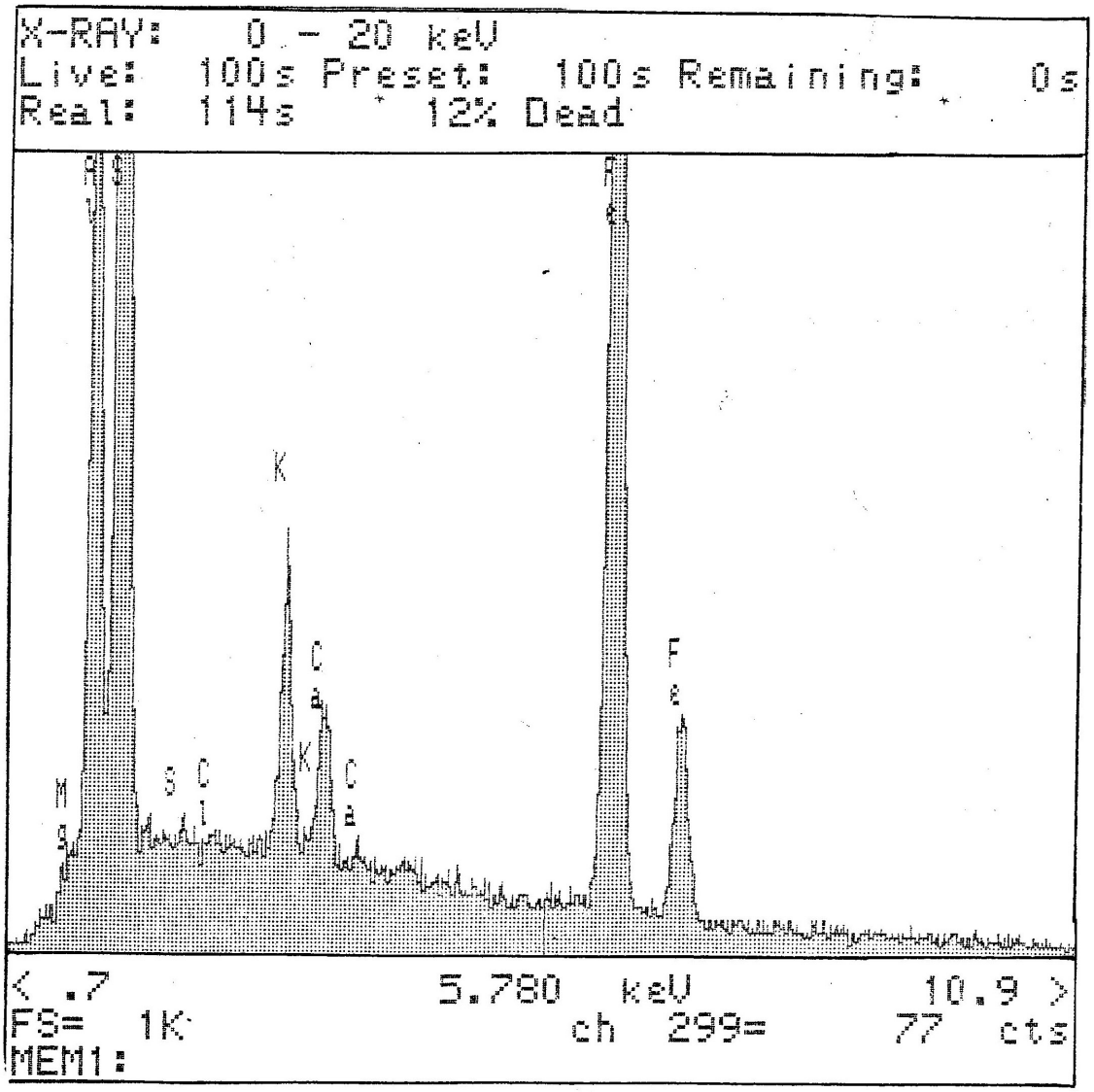


Figure 8.3.9 EDS Spectra IX: Red Ochre and Beeswax. Granular area.

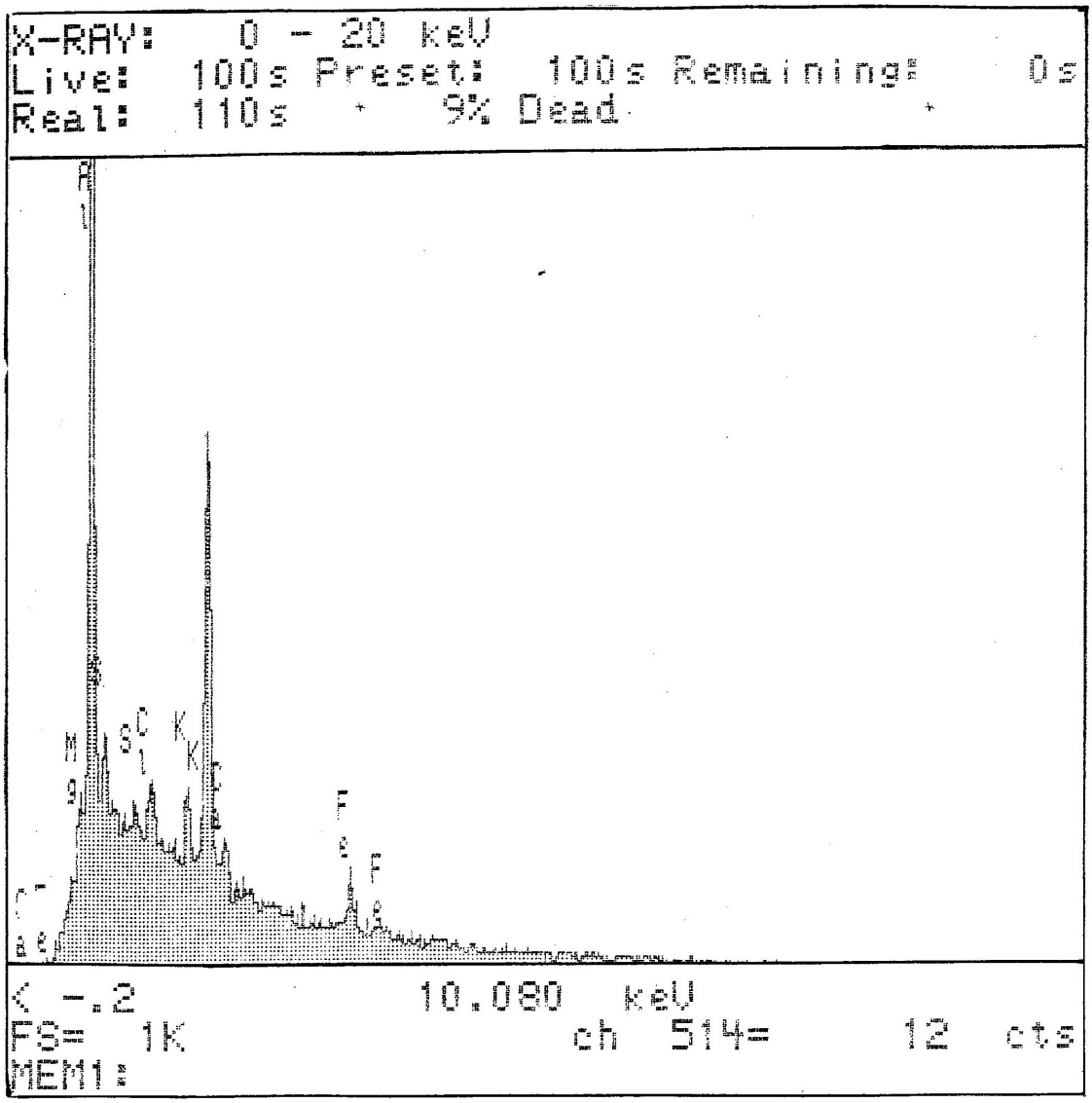


Figure 8.3.10 EDS Spectra X: Kaolinite. Smooth, featureless area.

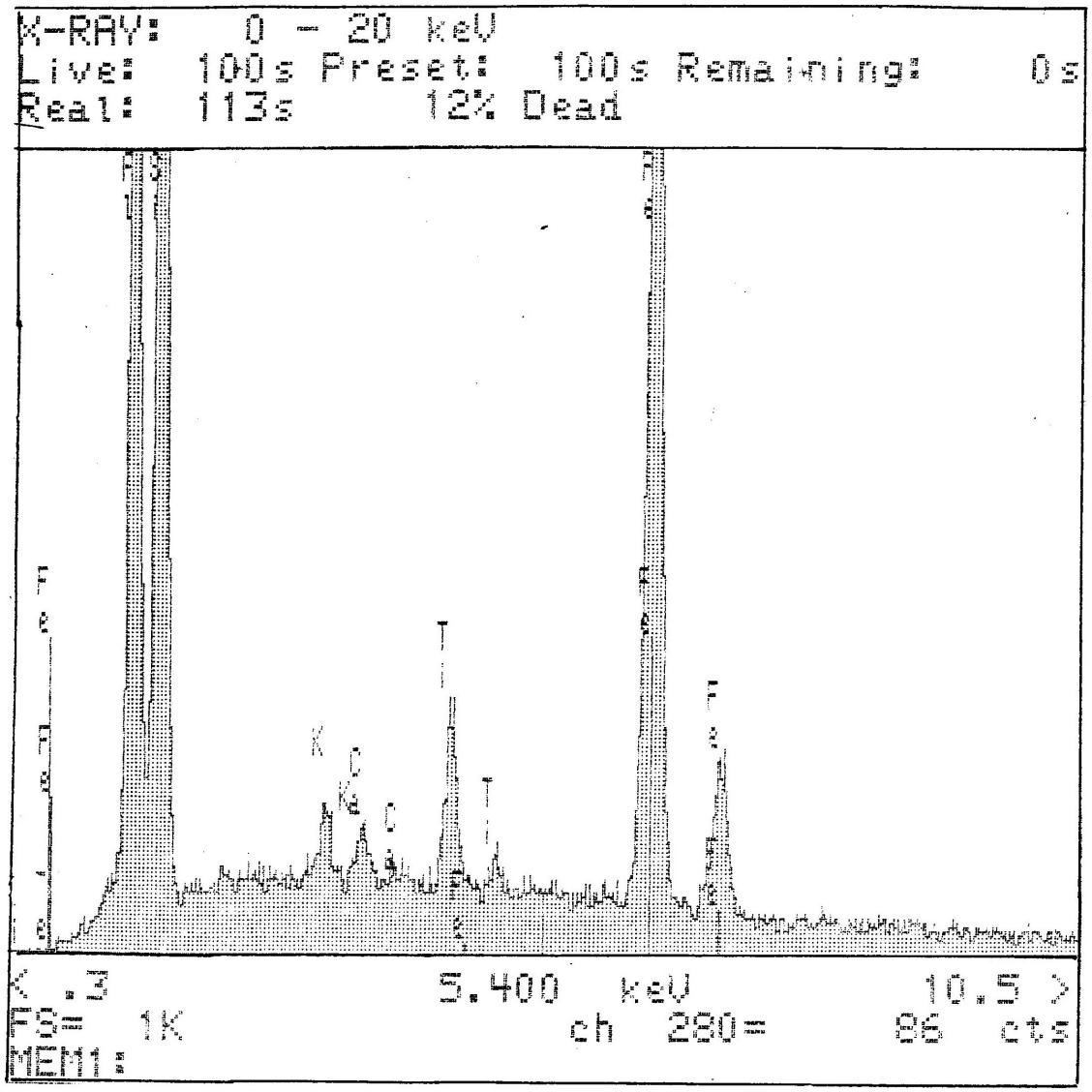


Figure 8.3.11 EDS Spectra XI: Kaolinite. Granular area.

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