Striking Light:
Experimental methods for the production, characterization, and description of iron disulphide pyrodebitage

by

Matthea C. Wiebe

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Approval

Name: **Matthea C. Wiebe**

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Title: **Striking Light: Experimental methods for the production, characterization, and description of iron disulphide pyrodebitage**

Examining Committee: **Chair:**   Michael Richards
Professor

Francesco Berna
Senior Supervisor
Associate Professor

Dennis Sandgathe
Supervisor
Senior Lecturer

April Nowell
External Examiner
Professor and Chair
Department of Anthropology
University of Victoria

Date Defended/Approved: January 24, 2020

Abstract

The adoption of fire into the lives of hominins is widely held to be one of our genus' most significant technological advances. The ability to start fire at will and therefore control when and where fire was available may have been a key factor for survival during the Palaeolithic. However, archaeologists have few methods for identifying fire-starting activities in context. Based on archaeological, anthropological, and mineralogical literature, experimental procedures were developed to identify, describe, and collect microscopic debitage from the strike-a-light fire-starting technique. In these experiments, iron disulphide debitage was the primary focus of study. The experiments produced promising qualitative, quantitative, and semi-quantitative base-line data with great potential for identifying strike-a-light fire-starting in the archaeological record and for advancing our knowledge of the prehistory of fire.

Dedication

This thesis is dedicated to my Oma, Catherine Verkley, whose quiet strength and subtle artistry have knitted themselves into my life without my noticing.

Acknowledgements

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List of Acronyms

IDP   Iron Disulphide Pyrodebitage

CIDA   Chert with Iron Disulphide Adhering

Chapter 1.

Introduction

Developing control over fire is considered one of the most significant technological advancements of our species. The story of that control, what it signifies, and what it looks like archaeologically is still a subject of discussion and debate. Warmth, light in dark places or during the night, protection, manufacturing tools, social gathering, and food preparation are among the uses of fire by contemporary fire users as well as those of the past. Therefore, studying hominin interactions with fire may help to establish a greater understanding of how our cultural and social world developed. Scholars now largely agree that the development of controlled, habitual use of fire was a long, iterative, and punctuated process (Gowlett, 2016; Chazan, 2017; Sandgathe, 2017; Rolland, 2019). The presence of combustion features in one site does not imply an abrupt adoption of all uses of fire, and one population's use, control, or ability to create fire does not signal the same traits in other populations. An important focal point in this long process, and the topic of this thesis, is the at-will production of fire as opposed to its collection from the landscape (Sandgathe et al., 2011a; Sandgathe et al., 2011b; Ronen et al., 2014; Sorensen et al., 2014; Dibble et al., 2018). The material culture associated with fire-starting activities must be described and studied in order to build and share our understanding of how and when anatomically modern humans and/or other hominins began using these technologies.

Collection of flame or embers from naturally started fires in order to build and sustain combustion features is a practice that does not require the possession of fire-starting technologies (McCauley et al. in press; Hough, 1926). It is possible that individuals, populations, or hominin species in the past could have used fire without creating it. For example, whether or not Neanderthals possessed the knowledge and/or capability to create fire at will is currently in debate, as this potential lack of technology could have been a contributing factor in their extinction (Sandgathe et al., 2011a; Sandgathe et al., 2011b; Dibble et al., 2018). The intricacies of fire use by species, populations, or individuals could have had significant influence on the trajectory of human adaptation. In order to address questions of fire starting in the deep past, it is

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necessary to develop tools and procedures to identify and analyze fire starting activities in the archaeological record (Mallol et al., 2013; Aldeias, 2017).

This thesis will focus on strike-a-light fire starting, a technique that consists of hitting or rubbing iron disulphide nodules or agglomerates and chert together to create sparks (Figure 1.1). Research into Palaeolithic fire starting has focused on this technique rather than wood-on-wood combustion methods because of the preservation potential of mineral artefacts and the extreme unlikeliness of the survival of wooden fire-making tools (Sorensen and Rots, 2014). However, research into this activity has been limited to the identification and analysis of residues or use-wear left on chert tools (Stapert and Johansen, 1999; Sorensen and Rots, 2014; Sorensen et al., 2018), to ethnographic accounts of the activity applied analogously (Mccauley et al., in press; Hough, 1890a, 1890b, 1926; Spikins et al., 2010), or to the cursory mention of iron disulphide nodules found at sites (see Sorensen and Rots, 2014 for a comprehensive list of iron disulphide finds in Eurasian Lower and Middle Palaeolithic sites). In order to gain a greater understanding of this technique and, in turn, of the fire-starting capabilities of Palaeolithic populations, this thesis investigates the microscopic mineral artefacts produced by the process of strike-a-light, termed here Iron Disulphide Pyrodebitage (IDP).

Figure 1.1.   Strike-a-light activity with pyrite and chert.

The project includes a discussion of the archaeological literature related to strike-a-light fire-starting, as well as a description of the relevant geochemical aspects of iron disulphide mineral artefacts. Finally, this thesis proposes a novel protocol for producing

and characterizing IDP in order to aid and encourage further research into this important class of artefacts. Broadly, it is my aim to address a gap in the archaeological literature; that is, the identification of strike-a-light fire-starting techniques from their residues. The thesis is organized in the following manner:

Chapter 2 is a discussion of the state of archaeological research into fire-starting technologies. This will include a discussion of how the study of fire can inform our understanding of past lifeways and behaviours, and how fire as a technology contributed to the evolutionary success or survival of different hominin species or populations. This chapter includes an overview of archaeological literature on the adoption of fire as a survival tool and addresses the current debate regarding the hypothesis that at least some Neanderthals were unable to create fire at will. The chapter also includes a definition of the strike-a-light fire-starting technique and an overview of associated archaeological literature. Finally, I will discuss several methodological approaches to the archaeological study of fire and fire-starting that are relevant to this thesis.

In Chapter 3, I will review the study of iron disulphides (pyrite and marcasite) in archaeology as they relate to the strike-a-light fire-starting technique. A mineralogical overview of iron disulphides will be followed by an in-depth discussion of the properties of iron disulphides that are of interest to archaeologists, namely their ability to generate sparks when struck with a hard object and their propensity to "decay," or oxidize, posing problems for their archaeological recovery.

Chapter 4 is a description of two experiments undertaken for the purpose of developing a procedure for the production and analysis of iron disulphide pyrodebitage (IDP). These are the Iron Disulphide Pyrodebitage Production Experiment and the Iron Disulphide Weight Loss Experiment. The experiments were conducted with the intention of setting a foundation for further research and should be considered preliminary. Scanning Electron Microscopy was performed on the debitage resulting from the Iron Disulphide Pyrodebitage Production Experiment to obtain qualitative and semi-quantitative results. Quantitative weight values were collected from both experiments. This chapter includes the methods and results of these experiments.

Chapter 5 includes a discussion of experiment results, as well as a discussion of the procedures developed for them. Results and procedures are discussed separately

as they provide their own specific contributions to the field. Additionally, limitations of the procedures and results are explained, as well as confounding variables.

Finally, Chapter 6 provides an overview of the thesis and discusses the significance of the research to the field at large.

Chapter 2.

Background

In this chapter I will examine the current archaeological literature regarding fire-starting technologies in the past. First, I discuss the archaeology of fire starting in a Paleolithic context and the significance of identifying fire-starting activities in the archaeological record. Secondly, I discuss the theoretical and practical background of my research, including fire-related experimental archaeology, geoarchaeology, and microarchaeology.

2.1. Fire-starting in Archaeology

This thesis is concerned specifically with the potential for identifying fire-starting activities in the archaeological record. Identification of such activities will allow archaeologists to distinguish between fire production and fire collection in the Palaeolithic. First, it is necessary to provide a brief overview of the broad discussion of fire in the discipline.

2.1.1. Fire and the Hominin Past

Evidence of fire in an anthropogenic context has been identified as early as 1.5 to 1 million years ago (Berna et al., 2012; Hlubik et al., 2017), though some have suggested that at least some use of fire was present in Africa associated with the emergence of *Homo erectus*, closer to 2 million years ago (Wrangham et al., 1999; Wrangham, 2009, 2017; Wrangham and Carmody, 2010; Parker et al., 2016). Whether fire at these times was regularly or opportunistically used is subject to some debate, as the development of fire is considered to have been a long process with multiple stages including opportunistic collection of fire from the landscape and creation of fire at will (Dennis M. Sandgathe et al., 2011; Roebroeks and Villa, 2011; Ronen et al., 2014; Gowlett, 2016; Chazan, 2017). Current evidence overwhelmingly supports a much later date for *regular* hominin use of fire, with most researchers agreeing that the oldest incontrovertible evidence for regular fire use dates to ~300-400 kya (Sandgathe et al., 2011a; Sandgathe et al., 2011b; Roebroeks and Villa, 2011; Ronen et al., 2014;

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Shimelmitz et al., 2014; Shahack-Gross et al., 2014; Roebroeks and Soressi, 2016). However, it is difficult to understand the nature of this fire use because the available evidence for patterns of fire use in the Palaeolithic are time compressed in the archaeological record. Some use the term "habitual" to describe continuous or high frequency evidence of fire use (E.g., Roebroeks and Villa, 2011), however Sandgathe (2017) makes the important point that this term is in need of clarification, as what is considered continuous in archaeological contexts can still realistically represent very long intervals between periods of use.

Recently, scholars have emphasized the need for more substantial evidence to support claims of fire related technological advancements in both Neanderthal and modern human contexts (Sandgathe et al., 2011a; Sandgathe et al., 2011b; Roebroeks and Villa, 2011). While the presence of hearths and fireplaces *in situ* provides strong evidence for the *use* of fire by associated peoples, the difference between *use* of fire and fire *production* may signal important differences between the cognitive abilities, technological advancements, or survival advantages of different populations. In order to understand these differences through the archaeological record it is necessary to identify, describe, and study the material culture of fire-starting techniques. Further development of refined archaeological techniques is needed to fill out our picture of the development of fire use by hominins (Aldeias, 2017; Sandgathe, 2017).

Fire-starting technologies are of special significance to the study of Palaeolithic hominins. The ability or inability to produce fire at will has recently been considered to be a contributing factor in Neanderthal extinction (Sandgathe et al., 2011a; Dibble et al., 2018). Hypotheses explaining Neanderthal extinction include competition with anatomically modern humans for resources and territory, as well as the increasingly cold climatic conditions of the Last Glacial Period (MIS 3), to which some argue Neanderthals were ill-adapted (Belmaker and Hovers, 2011; Delagnes and Rendu, 2011; Hallin et al., 2012; Orain et al., 2013; López-García et al., 2015). However, micromorphological analyses from Pech de l'Azé and Roc de Marsal in Southwest France suggests that while Neanderthals readily used fire during warm interglacial periods, evidence for the use of fire during colder times is extremely slight (Dibble et al., 2018; Goldberg et al., 2012; Aldeias et al., 2012; Sandgathe et al., 2011a; Sandgathe et al., 2011b; Dibble et al., 2015). In other words, combustion features were created in times when natural fires started by lightening strikes would have been widely available for harvesting, but when

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lightening storms would have subsided, no fires were made. It is indeed possible that populations can use fire by collecting it from the landscape and curating it in combustion features, and it has been suggested that this was the practice of Neanderthals in Southwest France (Sandgathe et al., 2011a; Sandgathe et al., 2011b; Dibble et al., 2018). This hypothesis is posited to explain the lack of evidence for combustion activity during colder periods as discussed above. The observation that Neanderthal hearths in Southwest France are associated only with warm, relatively humid periods, and that evidence for fire use decreases significantly during cold, dry periods, challenges the assumption that Neanderthals needed and used fire to stay warm during these colder times. These observations raise the question of whether Neanderthals were able to create fire at will, or if they were simply collecting fire from wildfires which would be much more frequent during warm and interglacial periods. If similar connections between combustion features and climatic conditions are confirmed elsewhere in Europe or Asia, they may reveal the existence of an overlooked factor contributing to the physical and genetic replacement of Neanderthals by *Homo sapiens*.

It has, however, conventionally been assumed and asserted in recent literature that Neanderthals were able to produce fire at will (Sorensen, 2017). This is supported by evidence of habitual fire use such as birch bark pitch hafting technologies, where it is argued that the evidence of fire use in tool manufacture suggest that Neanderthals had control over fire to the extent of possessing fire-starting capabilities (Mazza et al., 2006; Cabanes et al., 2010; Douka et al., 2010; Villa and Roebroeks, 2014; Groom et al., 2015; Sykes, 2015). It is suggested that extremely regular use of fire would have been necessary for the development of pitch hafting, though this is difficult to substantiate without proper methods for identifying fire starting in the archaeological record. Additionally, direct evidence of regular fire-starting by Neanderthals in France has recently been posited by analyzing usewear patterns on chert strikers (one material used in the strike-a-light fire-starting technique) (Sorensen et al., 2018). The ability to make fire at will may have been an important adaptation for any hominin group, but while fire is assumed to be one of the greatest technological advancements in prehistory, it is unclear whether the ability to start it at will had an effect on the behavior or survival of either Neanderthals or Anatomically Modern Humans.

The study of fire use in the Palaeolithic has the potential to shed light on behaviours, survival strategies, and lifeways of past peoples (Daniau et al., 2010; Vidal-

Matutano et al., 2015; Aarts et al., 2016). For example, recent scholarship has investigated the use of fire as a tool to extend daylight, and therefore prolong social interactions beyond the work of the day (Wiessner, 2014). Wiessner observed that, among modern hunter-gatherers, topics of conversation differed between daytime and nighttime interactions. In short, nighttime conversations served to reify a social identity among groups. Nowell extends this analysis, concluding that interactions in the night include an added heightening of emotion, serving to further connect members of a group (2014). In a Palaeolithic context, therefore, it is useful to consider the fire as a node of cultural identity expression and reification, from which we stand to learn about the intricacies of Palaeolithic lives.

2.1.2. Fire-Starting

Ethnographic and archaeological research into fire use and fire starting have identified two main fire-starting techniques whose materials would have been available in the Lower and Middle Palaeolithic (Hough, 1926; Mohr and Sample, 1983; Djuricic, 1997; Davidson, 2004; Cobb and Pope, 2006; Watson, 2009; Axel et al., 2015; Fitzhugh, 2016; Teather and Chamberlain, 2016; Runnels, 2018). These are wood-on-wood friction used to create intense heat that ignites fine tinder, and percussive stone-on-mineral techniques used to produce sparks that are caught by fine tinder. One such stone-on-mineral technique involves the use of an iron disulphide nodule or agglomerate in conjunction with a hard, sharp stone (usually chert) and is called the strike-a-light technique. While it has been cited that other silica rich materials such as quartzite and even bamboo can be used as strikers (e.g. Hough, 1890; Cave-Browne, 1992; Bernatchez et al., 2009; Brumm, 2012), chert is the main focus of this study given its ubiquity in the Palaeolithic record. Chert is the general name for very fine-grained siliceous rocks from a variety of origins, and includes variants such as flint and jasper and is commonly used as a stone tool material because of its conchoidal fracture habit (Tucker, 2001). While the term "flint" is often used in discussions of strike-a-light tools, "chert" will be used here because represents a more inclusive group of rocks.

It is possible that Neanderthals or other early hominins were producing fire using either wood or stone methods. Unfortunately, organic material, such as wood, very rarely preserves in Palaeolithic contexts, so if the wood friction method was being used, we have little chance of finding evidence of this activity. If the strike-a-light method was

being used, we are more likely to find evidence of this activity since there is a reasonably good chance that the associated mineral artefacts or residues will preserve. For this reason, some archaeologists have elected to focus on looking for evidence of the strike-a-light fire-starting technique and its associated material culture (Stapert and Johansen, 1999; Sorensen and Rots, 2014).

2.1.3. Strike-a-Light Fire-starting: The Archaeological Literature

In addition to its potential for preservation, the use of the strike-a-light technique as an indicator of fire-starting activity in Palaeolithic contexts is supported by ethnographic and archaeological examples strike-a-light in a wide variety of locations and time periods (Mccauley et al., in press; Weiner, 2003; Brumm, 2012). The two raw materials used in strike-a-light fire starting are a pyrogenic material, either iron or iron disulphide rich rock, as well as the striker, which is used to break pieces of the pyrogenic material from the cortex. Before the invention of steel, the pyrogenic material used would likely have been an iron disulphide (pyrite or marcasite) (Stapert and Johansen, 1999; Weiner, 2003; Brumm, 2012; Sorensen and Rots, 2014; Sorensen, 2017).

Because of their association with fire starting, marcasite and pyrite nodules found in archaeological contexts are often interpreted as fire-starting tools, especially when striations attributed to striking are present (Sorensen and Rots, 2014). Given that the strike-a-light technique produces debris from both the striker and nodule, it is possible that microscopic evidence in the form of debitage will be present in site substrates, especially within or near hearths. Debris less than 1 mm in length derived from making stone tools are defined by Fladmark (1982) as "microdebitage" and have been shown to be important markers of past stone tool making activity *in situ* (Fladmark, 1982; Sonnenburg et al., 2013; Frahm, 2016).

Experiments with chert strikers on iron disulphide nodules are known to produce significant and characteristic retouch and wear patterns on both the chert and the nodules observable at both micro- and macroscopic scales. These include significant edge rounding, linear scratches, and microscopic striations on both the working edge and on tool faces (Stapert and Johansen, 1999; Sorensen and Rots, 2014; Sorensen 2018). Thus, the focus of strike-a-light investigations have been on the macroscopic artefacts themselves, rather than debitage associated with the activities. In Sorensen

and Rots' 2014 article detailing experimental work on the effects of strike-a-light on chert artefacts, the authors report "the removal of numerous small angular-blocky fragments, occasional micro-flakes, and some larger flakes" (482). In this and other experimental publications, however, the main analysis was restricted to the usewear traces left on the tools themselves. Expanding such experimentation to include debitage associated with the strike-a-light technique, both at the micro- and macroscopic levels is necessary for further development of strike-a-light investigations. This thesis aims to address this gap, specifically focussing on the iron disulphide debitage created from strike-a-light fire starting.

A complicating factor for the study of iron disulphide is its rapid oxidation, sometimes termed "pyrite decay", which may cause residues of these minerals to break down much more quickly than surrounding minerals or rocks (Pugh et al., 1984; Doner and Lynn, 1989; Chandra and Gerson, 2010; Mees and Stoops, 2010). However, the diagenesis of these minerals may result in the formation of iron oxides such as hematite and goethite, as well as different forms of iron sulfate, such as jarosite (Doner and Lynn, 1989; Schwertmann and Taylor, 1989). Additionally, degrading pyrite may form minerals that appear as pyrite pseudomorphs, meaning they maintain the external crystalline habit of the parent mineral (i.e., pyrite and marcasite) despite transformation into another mineral (e.g., hematite or jarosite). The possibilities and limitations of using iron disulphide pyrodebitage as a marker for fire-starting activity will be discussed more thoroughly in Chapter 3.

2.2. Methodological Approaches to the Study of Fire

The study of Prehistoric fire can be approached through several methodological frameworks. The research and experiments conducted here rely on the theoretical and practical bases of experimental archaeology, geoarchaeology, and microarchaeology (see Weiner, 2010) and the microcontextual approach (Goldberg and Berna, 2010).

2.2.1. Experimental archaeology

Lab based controlled or semi-controlled experimentation has advanced many subfields of archaeology. It has been exceptionally beneficial for investigating characteristics of combustion features such as fuel types, temperature ranges, and

residues left by various activities (E.g., Berna et al., 2007; Mallol et al., 2013; March et al., 2014; Mentzer, 2014; Aldeias, 2017). Our ability to interpret what is found in archaeological contexts is dependent on our understanding of which specific behaviours or actions could result in what we find in archaeological sites. Experimentation is at times the only or least destructive method for creating or testing hypotheses to explain these findings. In many cases, it is advantageous to test the viability of already formed hypotheses using experimentation (E.g., Henry, 2017). Additionally, experimental archaeology can be used to generate hypotheses through observation of processes, behaviours, or events analogous to those in the past (E.g., March et al., 2014). Finally, experimentation can be used to test methods or protocols created for the extraction and observation of archaeological material (E.g., Stepka et al., 2018). The experiments presented in Chapter 4 fall within the latter two categories. To best of my knowledge, to date, no systematic investigations of the debitage associated with the strike-a-light technique have been conducted. Such investigations are needed to make identification in archaeological and paleoanthropological contexts possible. First, strike-a-light pyrodebitage must be described and defined using controlled experimentation.

2.2.2. Geoarchaeology

Iron disulphides are included in archaeological literature about fire starting because of their pyrogenic properties, but they are rarely discussed in depth from a mineralogical perspective. In order to make use of their potential as markers of past fire-starting activities, it is important for archaeological investigations of fire starting to consider the intricacies of such important mineral artefacts through a geoarchaeological lens. Geoarchaeology is the application of the methods and concepts of the earth sciences to archaeological questions (Renfrew, 1976). Geoarchaeologists often work with the sedimentary context of archaeological sites to determine site formation processes and diagenetic factors affecting site interpretation. In addition, geoarchaeological methods such as micro-excavation, loose sediment analysis, and soil micromorphology can be used to determine artefacts' source locations, to understand artefact use, and to analyze the use and origin of combustion features (Goldberg and Berna, 2010; Mallol et al., 2013; Mentzer, 2014; Sorensen and Rots, 2014; Ortiz et al., 2016; Reidsma et al., 2016; Aldeias, 2017). In the context of combustion features, geoarchaeological methods allow specific observation of combustion feature inclusions,

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fuel, and deposition events such as cleaning, covering, or re-use of features (Mallol et al., 2013; Mentzer, 2014). Additionally, these methods can allow identification of combustion features that may not be visible to the naked eye or evaluate whether sediment is burned or altered diagenetically (Goldberg and Berna, 2010; Mentzer, 2014). This study is informed by the breadth of combustion feature experimentation; however, pyrodebitage is not necessarily deposited within combustion features, as tinder can be ignited away from exact locations of fire curation.

Applying a geoarchaeological framework to the study of strike-alight fire-starting includes understanding the mineralogical nature of the artefacts in question, as well as the sedimentological and environmental context in which these artefacts are likely to be deposited, altered, and found (Figure 2.1). It also considers the possible impacts that these artefacts may have on the surrounding sediments. Current geoarchaeological theory considers archaeological sediments themselves to be artefacts (Shahack-Gross, 2017). The integrated study of cultural and environmental impacts on archaeological deposits, and how these factors interact within a sedimentary system, has been termed geo-ethnoarchaeology (Shahack-Gross, 2017). Figure 2.1 represents Shahack-Gross's visualization of the relative study concerns of ethnoarchaeology and geo-ethnoarchaeology as they apply to archaeological formation processes.
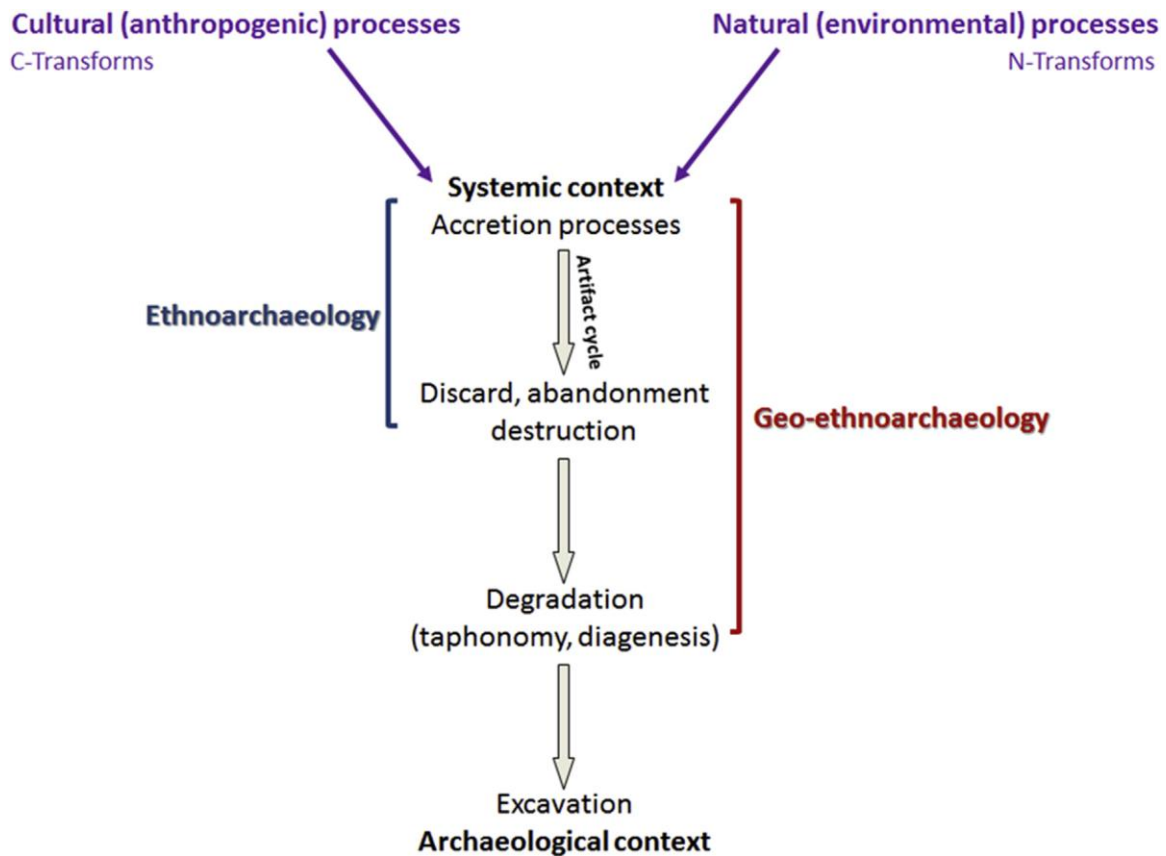
Figure 2.1. **"Schematic representation of the formation processes building the archaeological record, from the systemic context in the past to the archaeological context in the present."**
From Shahack-Gross 2017 p.41.

2.2.3. The Microcontextual Approach and Microarchaeology

In order to interpret archaeological finds, it is necessary to understand the microscopic context of artefact deposition and the taphonomic processes that affect artefacts. The experiments outlined in Chapter 4 set up a foundation for the identification of iron disulphide pyrodebitage (IDP) in the field. The protocols and results developed add to microarchaeological and geoarchaeological methods already in use. Application of the findings will add to the microcontextual analysis of sites or features where fire starting is of interest.

Over the last decade, a microcontextual approach to excavation and analysis of archaeological materials has been demonstrated to be particularly effective for the study of the archaeology of fire (E.g. Goldberg and Berna, 2010; Mentzer, 2014; Aldeias, 2017; Sandgathe and Berna, 2017). Mentzer (2014) defines the approach as "integrated,

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multidisciplinary studies of intact sediment blocks and petrographic thin sections,"
however, the term is not restricted to the techniques of micromorphology in more recent
publications (E.g., Aldeias, 2017; Sandgathe and Berna, 2017), but rather speaks to
integration and multidisciplinary studies of the microscopic geoarchaeological aspects
associated with artefacts or features of interest. These include palaeoclimatological data,
depositional factors, and taphonomy related factors. This approach is tightly linked to the
tenets of both geoarchaeology and microarchaeology.

Microarchaeology includes the use of microscopic analytical techniques to
understand archaeological deposits and their contexts (Weiner, 2010). This can include
analysis of microscopic artefacts such as phytoliths, secondary minerals, and pyrogenic
calcite identifiably by optical microscopy or infrared spectrometry (Weiner, 2010).
Microarchaeological methods have greatly increased the amount and types of data
available to archaeologists (Karkanas et al., 2002; Mentzer, 2014). Microarchaeological
and microcontextual methods allow for fine grained analyses of depositional and post-
depositional factors that might affect the preservation and nature of deposited artefacts
(Aldeias, 2017; Weiner, 2010). Use of these approaches is especially useful when the
artefact in question, in this case iron disulphide, is microscopic and dynamic in nature
and therefore receptive to small changes in environment or soil chemistry over time. To
understand mineral artefacts such as iron disulphide strike-a-light debris, it is essential to
form a picture of their histories from creation to excavation, including their exposure to
the elements and diagenetic transformations.

Chapter 3.

Iron Disulphides and the Archaeology of Fire-Starting

This chapter outlines the characteristics of iron disulphides relevant to strike-a-light fire starting, and examines the archaeological literature concerned with iron disulphides as a pyrogenic artefact.

3.1. Iron Disulphides in Fire starting: The Strike-a-Light Technique

3.1.1. Spark Production with Iron Disulphides

The technique of striking iron disulphide nodules or agglomerates together with a hard material such as chert to produce sparks is known in the archaeological literature as the "strike-a-light" fire-starting technique. Ethnographic research shows that friction force and percussive force are both used to produce sparks using these materials (Hough, 1890a, 1926; Stapert and Johansen, 1999; Williams, 2002). Percussive force is used by striking the materials together with the hands starting from about a foot apart, while friction force applies great pressure from the chert striker onto the iron disulphide nodule from a static position, scraping across the nodule's surface (Figure 3.1).
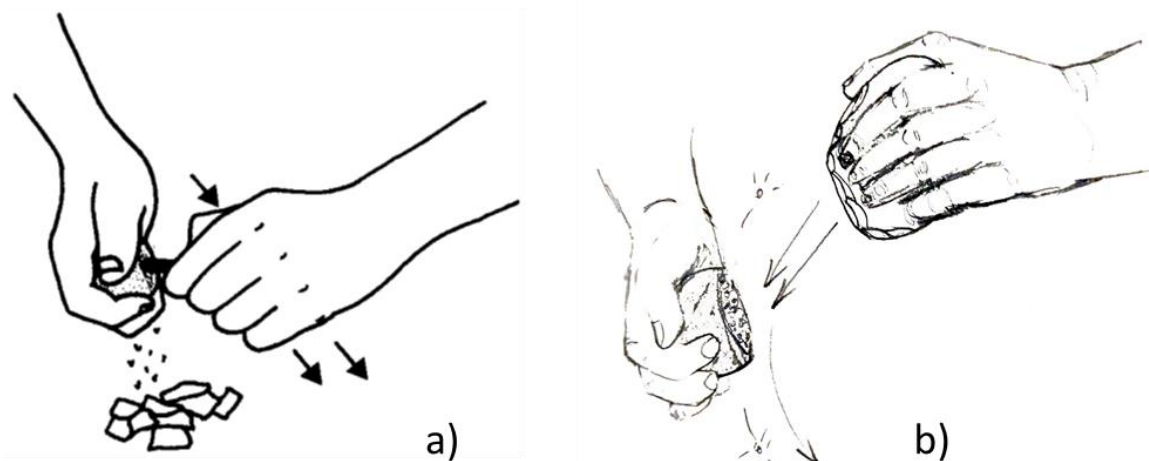
Figure 3.1.   Force types. A) Friction force strike-a-light from Stapert and Johansen 1999. Image by Lykke Johansen. B) Percussion force strike-a-light. Image by Matthea Wiebe.

Strike-a-light fire starting in more recent periods was carried out with chert and steel. According to Hough (1890), sparks in this version of the technique are created when small bits of steel, scraped off of the steel striker, react with oxygen upon exposure to the atmosphere and the addition of the energy of friction or percussion. It is assumed that strike-a-light with iron disulphide minerals happens in a similar manner, where particles are broken from the main nodule and ignited through the combination of exposure to oxygen and the addition of force energy. Strike-a-light with iron disulphide results in the release of sulphur gas and accompanying sulphurous smell, as well as dull, red-orange sparks. When dislodging nodules of pyrite by striking it against the sharp edge of a chert tool, the reaction can be written as

$$2FeS_2 + 11/2\ O_2 \rightarrow Fe_2O_3 + 4SO_2 + 411kcal$$

Where FeS_2 is pyrite, Fe_2O_3 is hematite and SO_2 is sulphur dioxide (see: https://ilblogdellasci.wordpress.com/2016/08/03/la-chimica-della-pietra-focaia/).

While the sulphur dioxide gas evaporates, it is logical to assume that hematite or other iron oxides may precipitate as microscopic and submicroscopic particles. The identification of such particles from iron disulphide nodules has yet to be documented. However, hematite particles struck from chert and steel strike-a-light activity (Figure 3.2) were visualized for the first time by Robert Hooke during his first microscope

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observations in the late 1600s (Hooke, 1780). During preliminary experiments for this thesis, similar spherules as well as unignited steel ribbons were produced using a magnesium strike-a-light (Figure 3.3) and chert and steel (Figure 3.4). It is not yet known whether similar spherules would form with the use of iron disulphides in the place of steel.
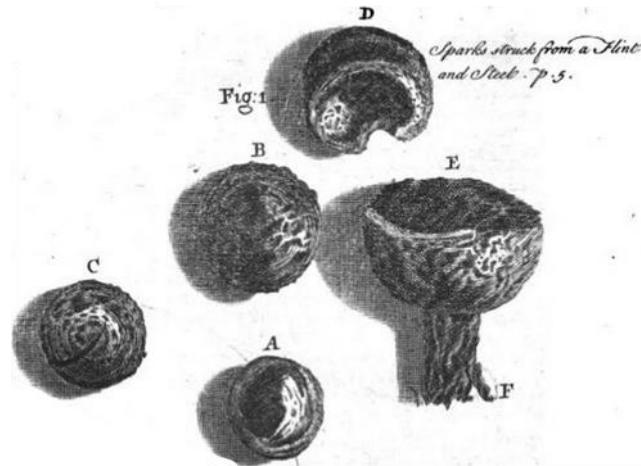
Figure 3.2. **Sparks Struck from Chert and Steel (Hooke 1780, Plate III -- Fig:1)**
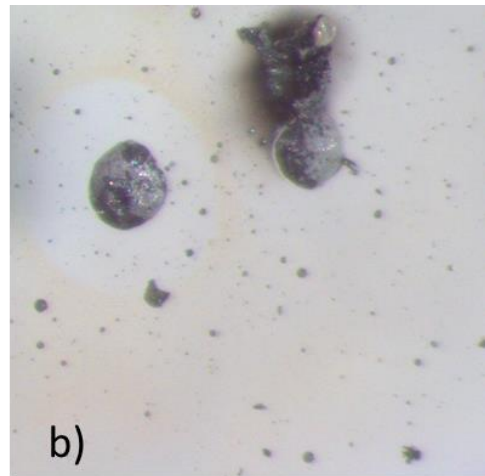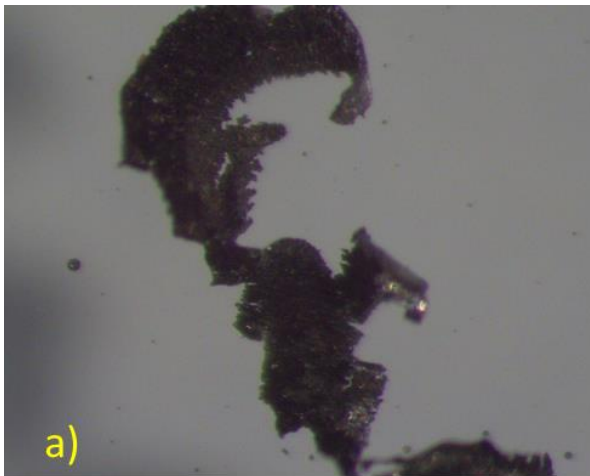
Figure 3.3. **Ribbon (a) and globule (b) struck from a magnesium strike-a-light.**
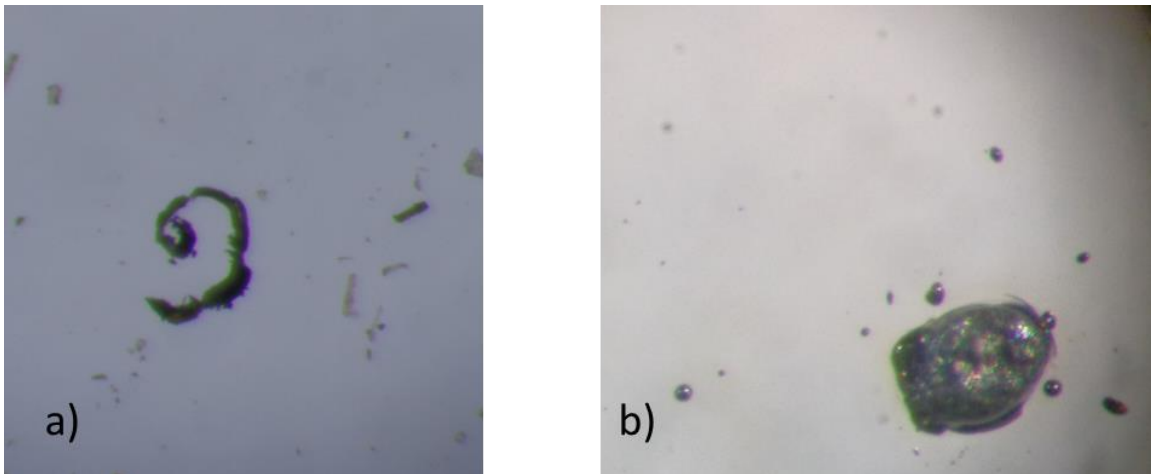
Figure 3.4.   A) Steel ribbon (~2.5X) and b) globule (~5X) from chert and steel strike-a-light trials.

It is highly unlikely that reacted IDP (i.e. the "spark" itself) will be successfully identified from archaeological contexts. For one, images and descriptions of reacted iron disulphide sparks have yet to be published. More importantly, so few sparks are created with every strike-a-light event that finding one sparked particle in an archaeological site would be improbable. However, strike-a-light activity produces debitage including chert flakes and microflakes, iron disulphide dust, and larger particles of iron disulphide. It is possible that these materials are diagnostic of strike-a-light activity, and that they could be identified in archaeological contexts. Table 3.1 shows the parent and byproduct materials expected to be found in the archaeological record if fire were started by striking iron disulphides with chert or other sharp materials. The debitage materials associated with strike-a-light activities will be referred to from here on as pyrodebitage, while the iron disulphide particles in particular will be called iron disulphide pyrodebitage (IDP).

Table 3.1. **Minerals associated with iron disulphide spark production and their relevant properties. Jarosite, goethite, amorphous iron, and iron oxides are potential byproducts of the decomposition of iron disulphide minerals.**

Name	Formula	Crystal system	Crystal class	Specific gravity (g/cm^3)	Crystal habit	Hardness
Parent Minerals						
Marcasite	Fe(II)S$_2$	Orthorhombic	Dipyramidal	4.875	Tabular with twinning	6-6.5
Pyrite	Fe(II)S$_2$	Isometric	Diploidal	5.01	Cubic and twinning	6-6.5
Pyrrhotite (marcasite may form after pyrrhotite)	Fe(II)S to Fe(II)$_{0.8}$S$_{0.2}$	Monoclinic	Prismatic	4.58-4.65	Tabular or prismatic in hexagonal prisms; massive to granular	3.5-4.6
Byproduct minerals						
Jarosite	KFe(III)$_3$(OH)$_6$(SO$_4$)$_2$	Trigonal	Rhombohedral	2.9-3.3	Pseudocubic or tabular, granular crusts, nodules, fibrous masses, concretionary	2.5-3.5
Goethite	α-FeO(OH)	Orthorhombic	Dipyramidal	3.3-4.3	Radial acicular, mammillary, botryoidal, stalactitic, massive	5.0-5.5
Hematite	Fe(III)$_2$O$_3$	Trigonal	Hexagonal scalenohedral	5.26	Commonly in rosettes	5.5-6.5
Magnetite	Fe(II, III)$_3$O$_4$	Isometric	hexoctahedral	5.175	Octahedral	5-6.5

3.1.2. Iron Disulphides in Archaeology

Iron disulphides from archaeological contexts have been noted in associated literature for some time, especially as they relate to fire starting (E.g., Hough, 1890). Iron disulphides are mentioned in anthropological literature on fire-starting activities, though their specific properties are rarely if ever detailed. Iron disulphide nodules or agglomerates have been interpreted as strike-a-light material culture in archaeological literature as well. See Sorensen and Rots (2014) for a detailed list of these finds in Lower, Middle, and Upper Palaeolithic Eurasia. Iron disulphide nodules, especially with characteristic wear patterns, are often interpreted as strike-a-light tools. Iron disulphides may also appear in archaeological contexts as pigments (Pomiès et al., 1998; Huntley et al., 2015) or dental inlays (Fastlicht, 1962). Of course, the mere presence of iron disulphides in archaeological contexts does not prove use of strike-a-light fire-starting.

3.2. Iron Disulphides: Mineralogical Perspective

Despite the importance of iron disulphides to the study of fire-starting in the past, there is little discussion of its variable phases, expressions, and diagenetic pathways within archaeological literature. In order to appreciate the potential of iron disulphide artefacts to advance our understanding of fire-starting behaviours in the past, methods and procedures must be developed that take into consideration the properties of these mineral artefacts from deposition to excavation. Here I will discuss significant factors of iron disulphides relevant to archaeological production of fire.

Iron disulphides form in sedimentary, metamorphic, and igneous contexts. Formation of either pyrite or marcasite may be dependant on the pH values of their formation environments, and often the two disulphides will form within the same deposit (Thomas et al., 1998; Chandra and Gerson, 2010; Kitchaev and Ceder, 2016). Nodules or agglomerates of iron disulphides can be found in various environments, including eroding from limestone or clay cliffsides or on beaches (having eroded from sedimentary formations). Thus, iron disulphide nodules and chert can be found in close proximity, though iron disulphide would be significantly more rare than chert (Sorensen et al., 2014).

3.2.1. Relevant Properties

Pyrite and marcasite share the same chemical formula (FeS_2) but are structurally different. Pyrite has an isometric crystal system and a simple cubic structure. It forms several crystal habits (Figure 3.5 a), namely cubic, pyritohedral (dodecahedral shapes with pentagonal faces), octahedral, and radial (Figure 3.5 b). Pyrite cuboid crystals can also form in clusters called framboids (Figure 3.5 c). Marcasite forms in an orthorhombic structure with tabular, spearhead, and cockscomb habits (Figure 3.6). Pyrite and marcasite fracture unevenly, though pyrite can fracture conchoidally.
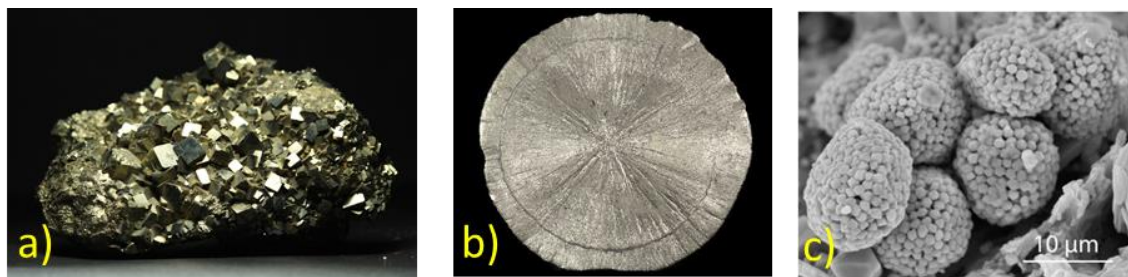
Figure 3.5. **Common pyrite crystal habits: a) cubic; b) radial; c) framboids.**
a) (University of Hong Kong, 2020); b) (Fossilera, 2020) c) (Rickard, 2019)
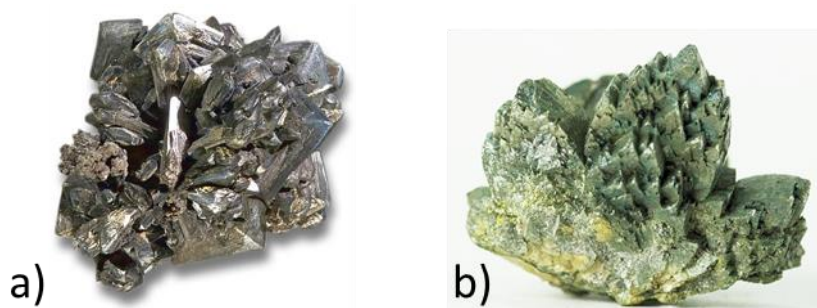
Figure 3.6. **Common marcasite crystal habits: a) spearhead; b) cockscomb.**
a) (Maggie's Science Connection, 2020); b) (Mineral Auctions, 2020)

The structure and habits of iron disulphides are of value in discerning between the two disulphides and identifying them in sediments. Crystal habit is of particular interest because of the potential formation of pseudomorphs after pyrite and marcasite (Doner and Lynn, 1989). Iron disulphides can be oxidized more rapidly than other minerals, and as such may not preserve in all Palaeolithic contexts. Because this oxidation happens at the surface, particles with greater surface area to volume ratios (i.e. smaller particles) are more susceptible to full oxidation (Chiriță and Schlegel, 2017). However, pseudomorphs after pyrite and marcasite are known to be made up of iron oxides such as goethite (Doner and Lynn, 1989), a material that is more stable than its precursor in several depositional environments (Chandra and Gerson, 2010). It is therefore possible to assume that IDP may be found in archaeological contexts as goethite but with pyrite or marcasite habits. Developing a detailed body of knowledge about IDP morphologies (i.e., habits) may be the key to their identification as pseudomorphs in Palaeolithic contexts, especially in depositional environments where iron disulphide is less likely to preserve. Determining under what habit(s) IDP is

deposited is an important first step in studying the morphologies and the diagenesis of this important archaeological material.

3.2.2. Iron Disulphide Oxidization

Iron disulphide oxidation (also termed pyrite decay, pyrite oxidation, pyrite disease, or pyrite rot) is a well-known but not fully understood process that presents as the relatively rapid break down of iron disulphide objects through oxidation. This process poses significant issues for geological, paleontological, and archaeological curated collections (Nordstrom, 1982; Wiersma and Rimstidt, 1984; Rimstidt and Vaughan, 2003; Leduc et al., 2012; Baars et al., 2018), where entire specimens containing or made up of pyrite or marcasite can be lost as a result of oxidation. The problem is also significant for mining operations where iron disulphide is a byproduct or an associated mineral. In this case, oxidizing iron disulphides causes extreme acidity in surrounding sediments and water outflow, which can become toxic (known as *acid mine drainage*).

Due to its known propensity to decay, the iron disulphide archaeological record has been dismissed by most researchers dealing with Prehistoric fire use. However, some larger nodules have been documented in a few archaeological contexts (Sorensen, 2014). Thus, differences in sedimentological and pedological contexts may change the intensity and extent of the diagenesis of archaeological iron disulphide deposits. Indeed, the exact conditions that allow iron disulphides to preserve over such long periods rely on a variety of factors. These will be discussed below. Additionally, iron disulphide oxidation may result in the production of more stable minerals that contain signatures of their origins (i.e. crystal habit and isotope composition). Thus, it is imperative to investigate the various diagenetic pathways of iron disulphides to avoid overlooking this important archaeological resource.

Iron disulphide oxidation takes place in several steps. From Brown and Jurinak, 1989:

"The stoichiometry of the reaction with each [Aqueous Fe^{3+} and O_2] is shown in Eq. 1 and 2:

[1] $FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$

$$[2]\ FeS_2 + 7/2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$
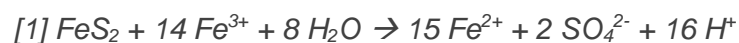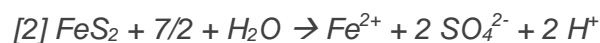
Solution Fe2+ in reactions [1] and [2] is oxidized by O2 (aq) as shown in reaction [3].

$$[3]\ Fe^{2+} + 1/4\ O_2\ (aq) + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O$$
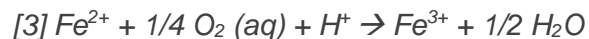
The Fe^{3+} can be recycled as pyrite oxidant as shown in Eq. [1]."

The oxidation process can therefore result in acidification of the system and the formation of ferrous iron and iron oxides, as well as the redeposition of sulphates (Chandra and Gerson, 2010). The dissolution of pyrite and marcasite would result in the redeposition of different iron and sulphur minerals and compounds.

Iron disulphide oxidation rates are affected by environmental moisture content, amount of available oxygen, temperature, availability of electrons in the system (eH), acidity of the environment (pH), and the presence of iron oxidizing bacteria (Nordstrom, 1982; Jerz and Rimstidt, 2004; Chandra and Gerson, 2010; Baars et al., 2018). In particular, as shown in the Sulphur Eh-pH diagram in Figure 3.7, sulphides will be stable only in subalkaline peat soil. Ideally, iron sulphide will be preserved as such only in extremely acid soils with moderate reducing conditions. Sulphur in the quasi totality of soils will form sulphate (SO_4) compounds. Iron disulphides deposited in the quasi totality of the soils will tend to transform into reduced iron sulphates such as Melanterite ($FeSO_4 \cdot 7H_2O$) and Rozenite ($FeSO_4 \cdot 4H_2O$).
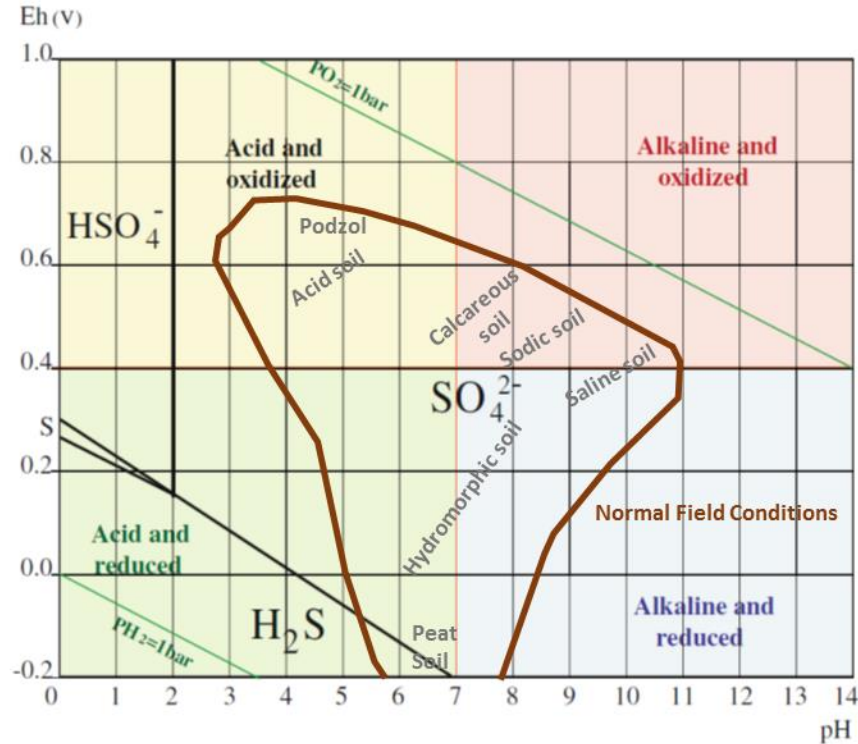
Figure 3.7. Modified figure from Husson, 2013 showing the stability fields of the different sulphur species in in different soil environments. Sulphides are stable in acid and reduced soils. The brown line defines the most common soil Eh pH conditions found in nature

As Fe(II) sulphates are prone to dehydration, oxidation, and dissolution, iron sulphates will normally transform into iron oxy-hydroxides such as goethite and hematite or in presence of abundant sulphate in solution into jarosite ($KFe(III)_3(OH)_6(SO_4)_2$). However, due to the complex nature of this series of reactions, which often involve the action of specialized bacteria, it is difficult to predict where, how, and after how long iron disulphides will preserve. This complexity is illustrated by Nordstrom (1982) as seen in Figure 3.8.
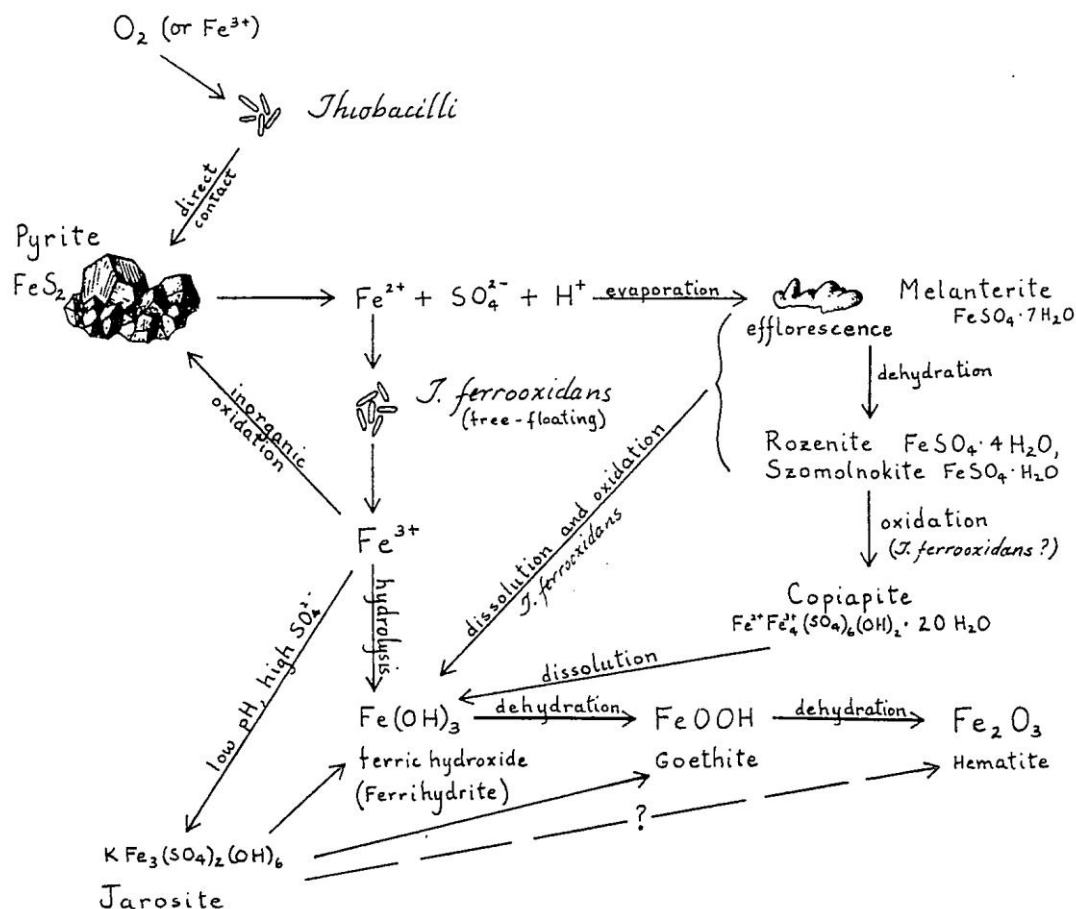
Fig. 3. The overall sequence of mineral reactions for pyrite oxidation showing the relationships between oxidizing agents, catalysts, and mineral products.

Figure 3.8.   From Nordstrom 1982. Diagram of iron disulphide oxidation.

In conclusion, the preservation of iron disulphide can take different paths: in acid and reducing conditions, pyrite and marcasite are expected to preserve best. In the other conditions, pyrite and marcasite are expected to transform, partially or totally into other minerals such as iron sulphates (i.e. jarosite) or iron oxy-hydroxides (goethite and hematite). In some conditions these secondary minerals will maintain the crystal habit of pyrite or marcasite forming pseudomorphs. Normally the original habit will be lost. The diagenetic path and the composition and morphology of the mineralogical end-products can be predicted by analyzing the mineralogical composition of the archaeological deposits and used as a proxy for eH, pH, and humidity of past depositional environments (Weiner, 2010).

Chapter 4.

Experimental Production and Analysis of Iron Disulphide Pyrodebitage (IDP)

In order to begin a discussion on the characteristics of iron disulphide pyrodebitage (IDP), a protocol for the production of experimental IDP was developed. This was necessary for the controlled testing of hypotheses related to strike-a-light fire starting. The results include an initial description of IDP particles using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) to create a reference material collection for the study of the micro- and macroscopic archaeological record.

4.1. Objectives

The broad objective of the current research is to develop an experimental protocol to produce, characterize and quantify iron disulphide pyrodebitage (IDP) resulting from the strike-a-light fire-starting technique in order to identify these artefacts in a variety of archaeological contexts, including Palaeolithic ones.

The specific objectives are as follows:

i. Produce and collect microscopic iron disulphide pyrodebitage using a reproducible method

ii. Describe the morphological characteristics of microscopic iron disulphide pyrodebitage

iii. Determine whether iron disulphide particles adhere to chert microdebitage particles

iv. Compare the amount of material produced by percussive and friction force strike-a-light actions.

v. Estimate conservatively the amount of iron disulphide produced per strike of the strike-a-light fire-starting technique

vi. Estimate the ratio of iron disulphide to chert introduced into the sediment system by the strike-a-light fire-starting technique

4.2. Materials and Methods

Two groups of experiments were conducted in order to address the objectives above:

1. Strike-a-Light Pyrodebitage Production Experiments

2. Iron Disulphide Weight Loss Experiments

The methods by which they were executed are discussed here.

4.2.1. Strike-a-Light Pyrodebitage Production Experiment

Aims

The strike-a-light pyrodebitage production experiment addresses objectives i, ii, iii, iv, vi, and vii. The specific aims of this experiment are as follows:

a. produce microdebitage associated with the strike-a-light technique (objective i)

b. explore effective ways of collecting this microdebitage for further analysis (i.e., imaging and weight)

c. explore high-speed imaging capabilities for pinpointing sparked material

d. develop a protocol for the collection and observation of microscopic iron disulphide pyrodebitage (IDP)

Experimental Set-Up

In order to observe the physical and chemical characteristics of debitage produced from strike-a-light fire-starting activities, the experiments were performed using the following set-up.

• A 45 x 45 cm square was drawn on large white poster paper and subdivided into a 5 x 5 cm square grid (see **Error! Reference source not found.**).

• The poster paper was taped to a lab table to form the experimental surface. Two 20 cm wide transparent 75' Reynolds® wax paper sheets were cut to 45

cm long and laid over the grid to be used as removable collection surfaces for each experiment.

- The wax paper sheets were secured to the table with removable tape on each corner.

- Two sheets of wax paper were necessary to cover the 45 x 45 cm grid and were placed in an overlapping fashion to match the edges of the grid.

- Each wax paper sheet was numbered and weighed before the experiments three times using a precision scale.

After some preliminary experimentation with different collection materials, wax paper proved to be the most satisfactory for the aims of this experiment. Aluminium foil was tested but ruled out because of its propensity to crease and therefore hold onto the finest iron disulphide dust. Additionally, foil was torn when stabs with carbon paper stickers were lifted from the collection surface. Acid free tissue paper was also ruled out due to its similar propensity to tear when SEM stabs were applied. A thicker paper may have been more successful; however, it was not tested due to the assumption that it would be too fibrous at the microscopic level and hold onto fine iron disulphide particles. Wax paper was chosen for experiments because of its smoothness, durability, light weight, and foldability.
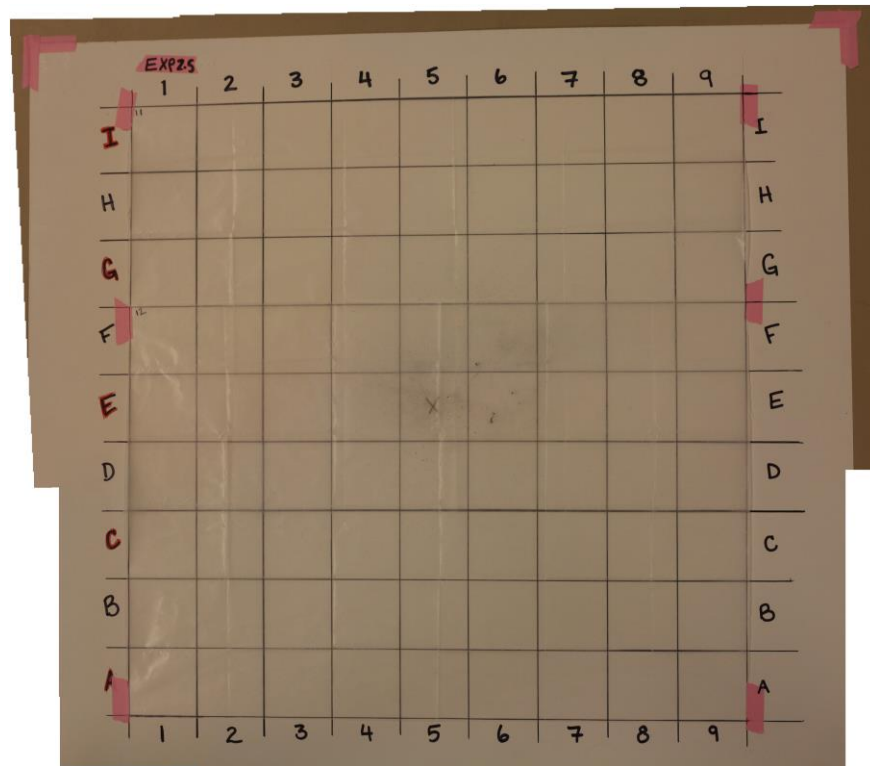
Figure 4.1. Experiment setup: wax paper collection material on poster paper grid.
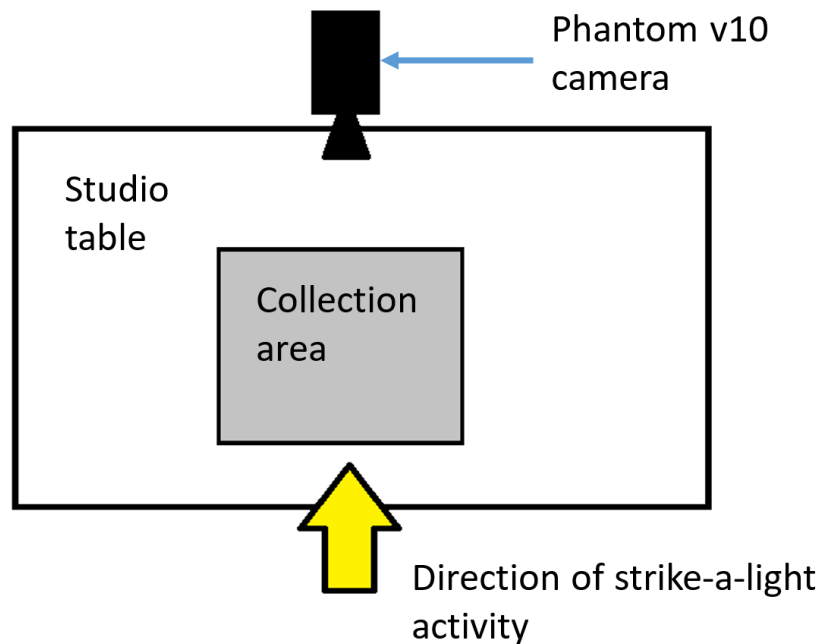
Figure 4.2. Experiment setup: diagram of the experiment area showing the slow-motion camera, wax paper collection area on the studio table, and the position of the experimenter shown by the arrow indicating the direction of strike-a-light activity.

To record as much information about the striking events as possible and to monitor the trajectories and landing spots of the sparks on the 45 cm x 45 cm grid, every experiment was recorded using two high-speed cameras, a Phantom v10 and a Chronos 4.7. After several experiments, the Chronos 4.7 was deemed insufficient for our purposes due to a lower storage capacity. In addition to high-speed recording, photographs were taken of the experimental surface with a Canon Rebel after the striking event and after sample collection. A simplified diagram of the experimental setup is shown in Figure 4.2.

Experiments

One chert biface was struck 50 times against one iron disulphide nodule (marcasite) to simulate spark production in the strike-a-light style (See Figure 4.3 for images of raw materials). Because marcasite nodules commonly contain both pyrite and marcasite crystals, experimentation with marcasite allowed observation of both minerals. The experiments were performed over the collection surface and the striking motion was aimed at the centre of the 9 x 9 grid (i.e., square E5 in **Error! Reference source not found.**). The experiment (50 strikes) was repeated 3 times with percussive force and 3 times with friction force. Friction and percussion are the two types of force applied in the strike-a-light technique (Stapert and Johansen, 1999; Sorensen and Rots, 2014). Between each repetition, the chert biface was washed with a toothbrush in soap and water, rinsed with acetone, and allowed to air dry.
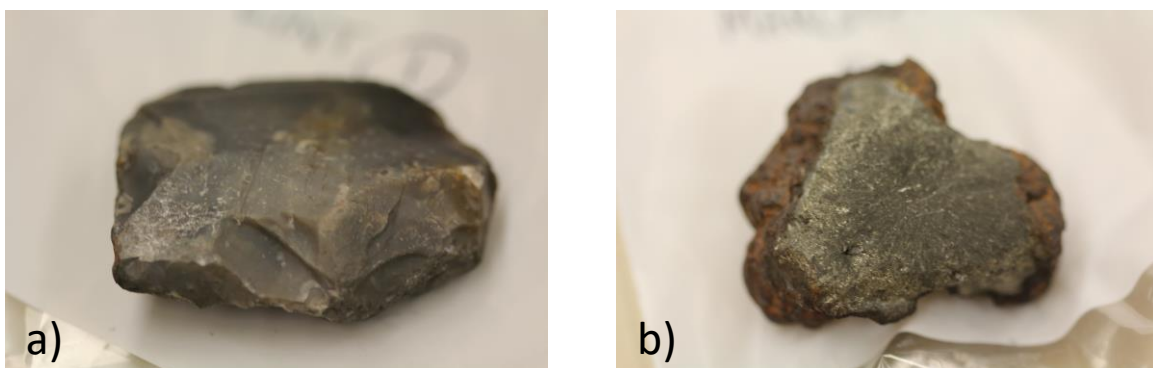
Figure 4.3.   **A) chert biface used in strike-a-light experiments. B) marcasite nodule used in strike-a-light experiments.**

After striking the chert biface against the marcasite nodule 50 times, the high-speed video from the Phantom v10 was played back at framerates between 20 to 60 frames per second to count the number of sparks produced during each striking experiment and to record their exact landing location on the grid.

The microdebitage produced by each fire-starting experiment was collected for Scanning Electron Microscopy (SEM) imaging. For each experiment, ten 1 x 1 cm circular aluminium stabs were prepared using circular PELCO™ carbon conductive tabs labeled with a unique sequential number using a permanent marker. Samples of the microdebitage that landed on the 45 x 45 cm grid were collected by pressing aluminium stabs prepared with carbon conductive tabs in the grid locations shown in Figure 4.4 and 4.5.

Table 4.1.   **Sample collection locations**

Stab Number	Location of Sample Collection
Stab x.**1**	Center of the grid's central square (E5)
Stab x.**2** to x.**4**	In proximity of 3 sparks landing locations
Stabs x.**5**-x.**9**	Along the grid transect from the centre of the grid to the square closest to the experimenter, in the centre of each square (D5, C5, A5, F5).
Stab x.**10**	Finest residual material adhering to the wax paper after large material is shaken from the collection paper.
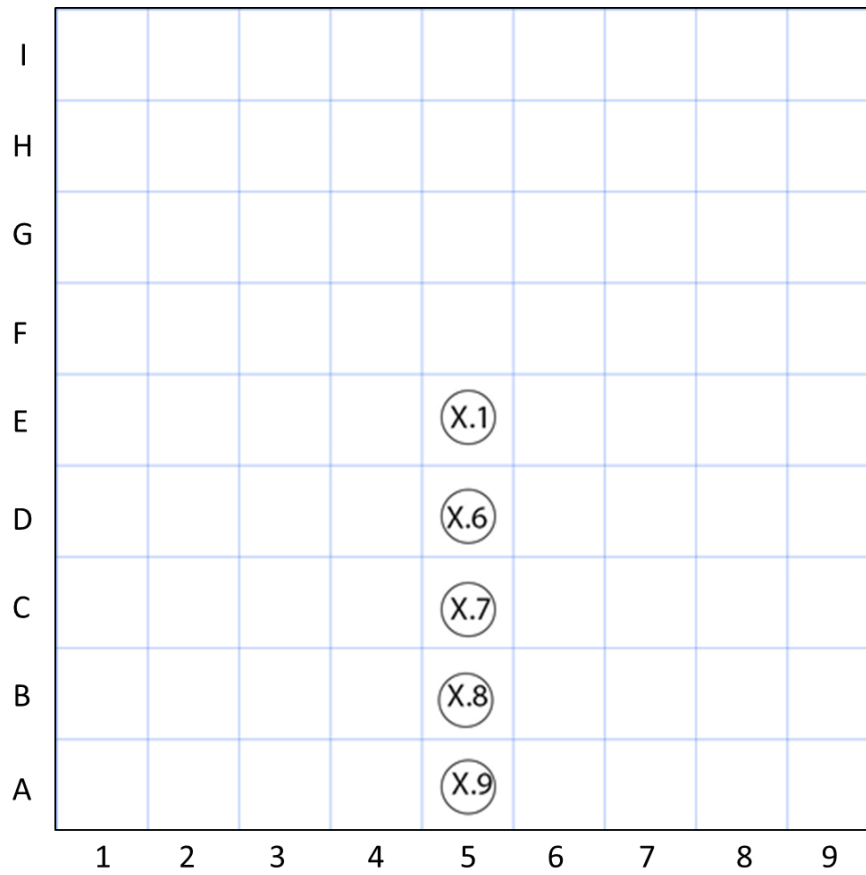
Figure 4.4. Sample collection map. Circles represent locations of stab sample collection.
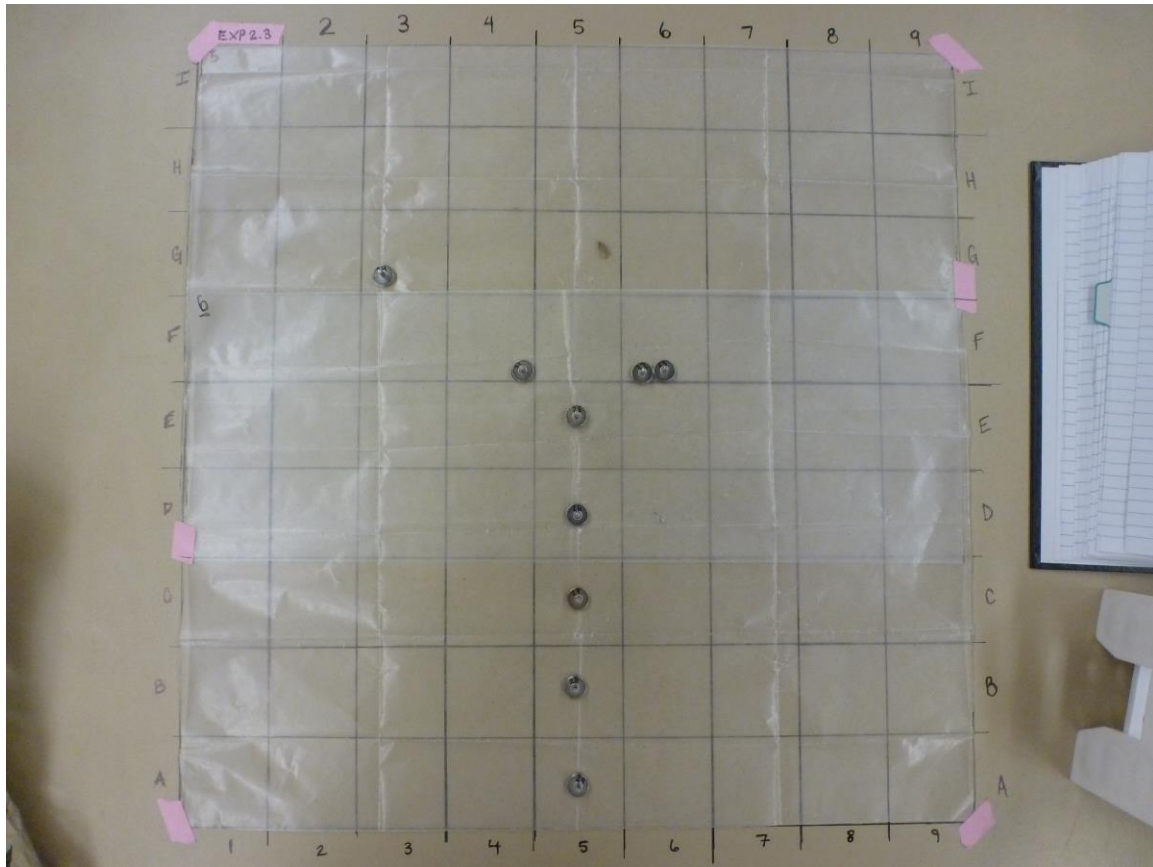
Figure 4.5.   Photograph of sample collection process before stabs are collected.

        To minimize contamination and iron disulfide oxidation, the aluminium stabs containing sampled material were stored in a covered container placed under vacuum in a desiccator with silica gel desiccant.

        After collecting the material for SEM analysis, photos of the sampling area were taken, and the residual dust was folded into the wax paper collection sheets. Each numbered wax paper sheet with remaining debitage residue was weighed. The difference between the weights of the wax paper sheets with and without the residue was recorded as the produced *microdebitage weight*. These recorded weights are an underrepresentation of the accurate debitage weight produced in each experiment since small portions of debitage were sampled with aluminium stabs for SEM analysis, and because some debitage was observed scattering outside the 45 cm x 45 cm collection area.

Alternate Experimenter

In order to explore the differences in pyrodebitage production created by different individuals, the experiment was repeated by a second experimenter, Dr. Sem Scaramucci. During these iterations of the strike-a-light debitage production experiment, one friction and one percussion event were recorded using the same materials and number of strikes.

Scanning Electron Microscopy Image Collection

Scanning Electron Microscopy (SEM) was undertaken at 4D Labs using a FEI Aspex Explorer SEM microscope equipped with Energy-dispersive X-ray spectroscopy (EDX).

The specific aims of SEM analysis were as follows:

a. Make general observations of IDP particles at the microscopic level

b. Develop and trial a protocol for semi-quantitative analysis of IDP amounts using representative images

c. Determine whether IDP particles show crystal morphologies typical of pyrite and marcasite

d. Determine whether chert microflakes can be soon to have iron disulphide particles adhering (CIDA)

e. Produce reference materials for future IDP research

One sample stab from each experiment was selected for systematic analysis. The centre of each of stab was located using map navigation through the SEM console and a secondary electron image (SEI) and a corresponding back scattered electron (BSE) image were taken at 100X magnification. BSE images were combined with elemental composition obtained with EDX spot analysis to determine the appearance of the iron disulphide and chert microparticles. In BSE images, iron disulphide particles typically appear whitish gray while chert particles appear medium gray.

Next, a 250X magnification BSE image mosaic was created by collecting 9 partially overlapping BSE images taken at 250X magnification and merged using Adobe Photoshop ™ (Figure 4.6). The 250X magnification image mosaic was determined to be the minimum magnification at which the smallest visible particles occupied at least one

pixel. This strategy was the most efficient way to collect high enough resolution photos to observe every particle adhering to the stab.

Scanning Electron Microscopy Image Analysis

Two major types of image analysis were performed on the 250X image mosaics: 1) qualitative analysis to identify specific crystal shapes and determine their size ranges, and 2) semi-quantitative analysis to estimate the relative proportions of iron disulphide and chert particles produced.

Qualitative analysis

By using BSE and EDX, particles were identified to be either iron disulphide or chert and their dimensions were measured. Chert particles with iron disulphide adhering (CIDA) were also measured. The morphology of the different particles of iron disulphides were described and identified according to standard terminology used in mineralogy and petrography (Stoops, 2003; Mees and Stoops, 2018).

Semi-quantitative Analysis

Since the particles were found clustered over one another, the decision was made to count "features" rather than individual particles. A "feature" is any number of particles within two pixels of one another. Iron disulphide features were circled with pink ellipses, and chert features were circled with yellow ellipses (Figure 4.7). If chert and iron disulphide overlapped within a feature, they were each counted as separate features. The chert particles also have a different shape and texture when large enough to discern. When particles were less than 1 µm across they were too small to identify visually due to lack of focus. In these cases, the particles were counted as iron disulphide. Features were then counted and the amounts of chert and iron disulphide were compared for each mosaic.
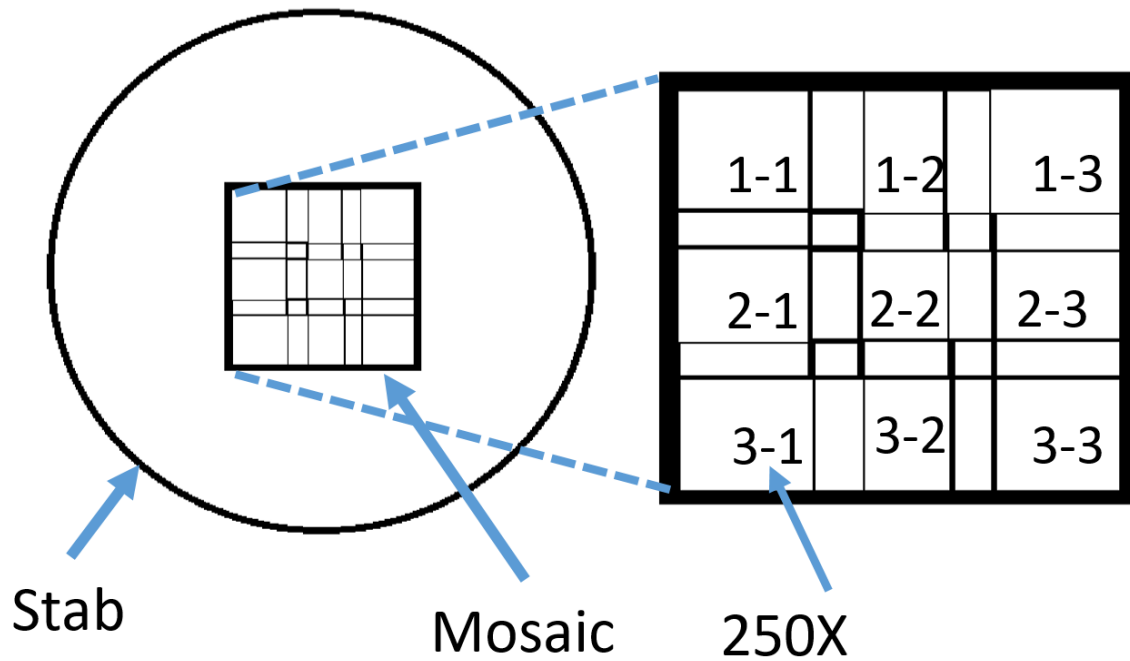
Figure 4.6.   Diagram of mosaic photomicrograph process.
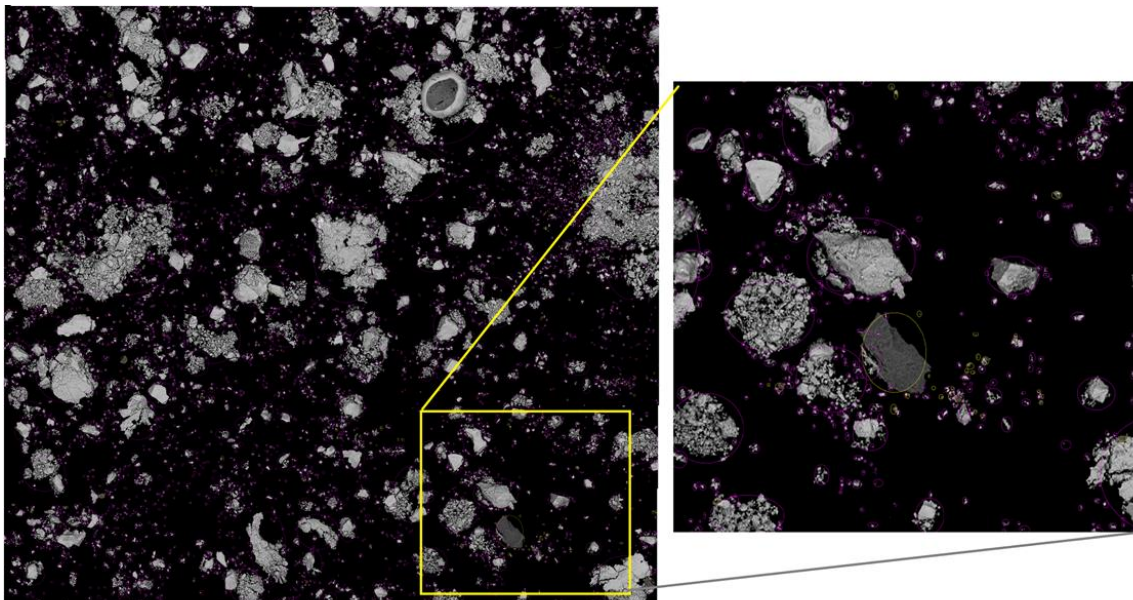
Figure 4.7.   Mosaic created from photomicrographs of stab 51 with features marked in Adobe® Photoshop®.

4.2.2. Iron Disulphide Weight Loss Experiment

In order to obtain an estimate of the amount of material lost during a fire-starting event, a weight loss experiment was conducted. The set up was as follows.

- A marcasite nodule was struck 50 times with a chert flake to simulate a fire-starting event.

- The debitage from the striking was collected in a stainless-steel receptacle.

- The marcasite nodule and chert striker ("raw materials") were weighed prior to and after striking to determine the amount of debitage removed from each during striking.

- The debitage collected in the stainless-steel receptacle was weighed. In order to minimize measurement error, all weighing was repeated three times. The mean of these measurements constituted the final recorded weight.

- The experiment was repeated a total of 10 times, five with percussion force and five with friction force.

- To calculate the total amount of debitage produced, the post striking weights of the raw materials were subtracted from their pre-striking weight. This produced the known weight of the debitage produced during a strike a light event of 50 strikes.

- The amount of marcasite and chert lost in the event were each divided by 50 to yield the average amount of each material produced by each strike.

- The average material produced per strike was averaged across the 5 percussive and 5 friction repeats.

- The collected weight was subtracted from the known weight to produce the amount of potentially lost debitage. The weight of the potentially lost debitage was also represented as a percentage of the weight of the known debitage produced.

Due to the limitations of the precision scale used to weigh raw specimens in the weight loss experiments, it was necessary to use raw materials that were significantly smaller than those used in the strike-a-light debitage production experiments. The chert flake used for the weight loss experiments was ~4 cm long and 3 cm wide. The iron disulphide nodule was ~3 cm in diameter.

4.3. Results

The results will be presented by first describing the qualitative and semi-quantitative data obtained in the strike-a-light pyrodebitage production experiments, followed by the quantitative data obtained from the iron disulphide weight loss experiments.

4.3.1. Strike-a-Light Pyrodebitage Production Experiment

Six spatially controlled strike-a-light experiments were conducted using the percussion and friction techniques and were monitored with high-speed cameras. SEM photomicrograph analysis was used to analyse the debitage produced by these experiments. Several sparks were produced in each experiment, and their landing locations were recorded using slow motion replay (Figure 4.8, Figure 4.9).

The landing spots of 41 sparks produced in six experiments were monitored. The cumulative spatial distribution of the sparks' landing spots produced in six experiments is presented in the diagram in Figure 4.10. The qualitative and semi-quantitative SEM observation of the pyrodebitage produced in the experiments provided new and important data. A total of 90 stabs were analyzed, producing over 300 images and 10 merged mosaics from which the semi-quantitative data was extracted. See abstract for images of these mosaics.
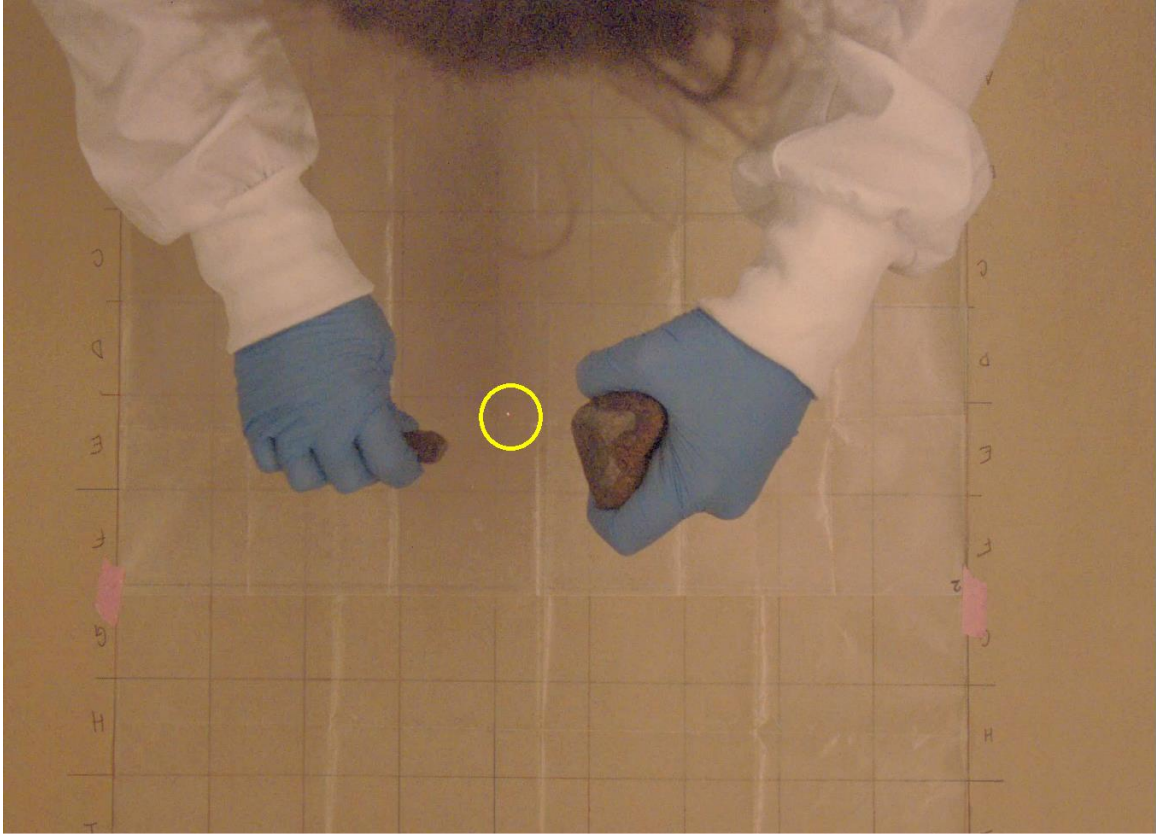
Figure 4.8. Top view of spark production using percussion force. Still image taken from Chronos 1.4.
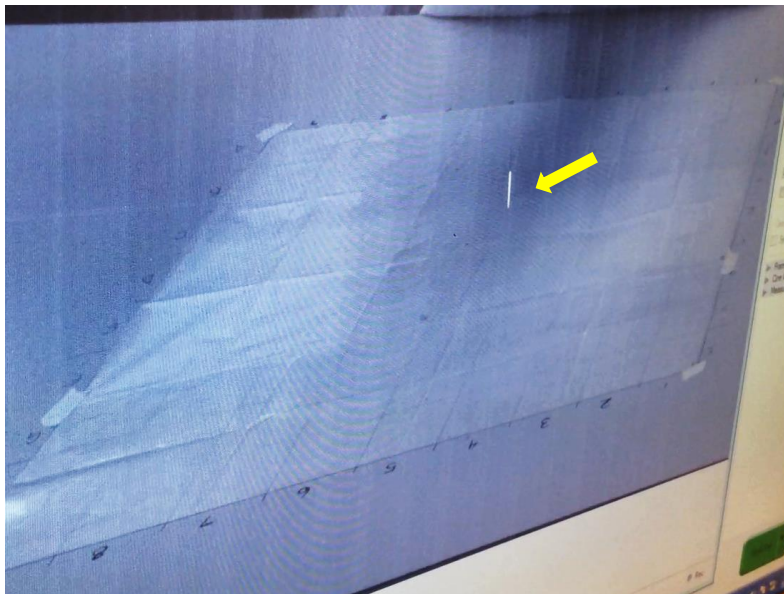
Figure 4.9. Screenshot of high-speed camera video capturing the exact trajectory (arrow) and landing spot of a spark produced using iron disulphide and chert (square F4).
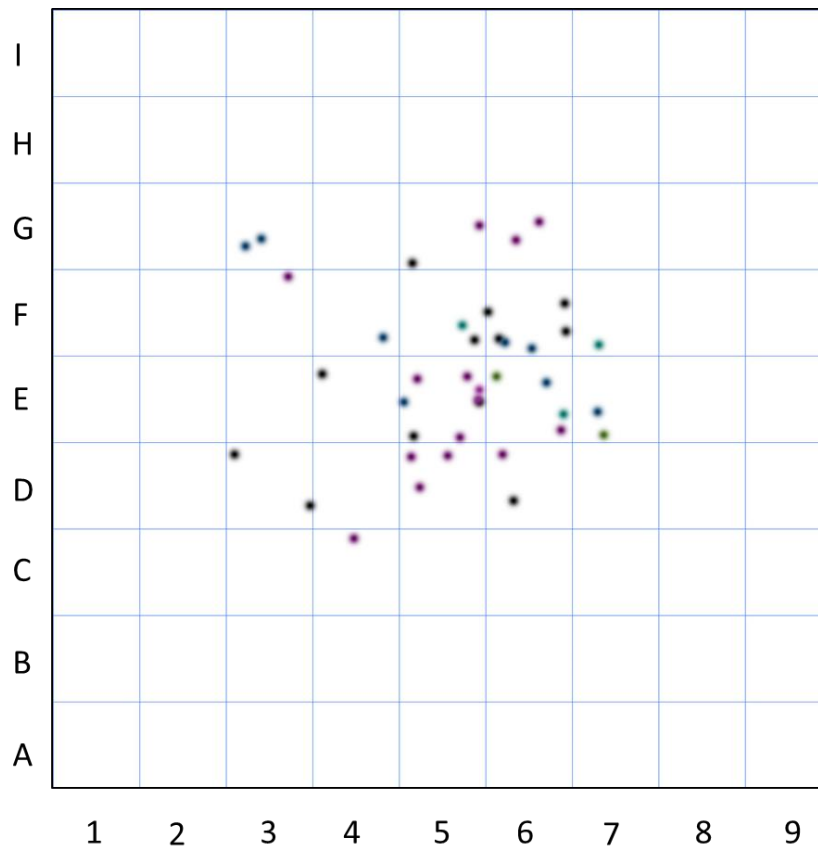
Figure 4.10. Cursory spatial analysis of spark landing. 5 cm grid with plot of spark landing spots observed during Exp 2.1 (black); exp 2.2 (purple), exp 2.3 (blue); exp 2.4 (green); exp 2.5 (teal); exp 2.6 (pink).

Qualitative Results: Imaging the Pyrodebitage using Scanning Electron Microscopy

A survey of photomicrographs and live SEM imaging showed that the iron disulphide particles produced by the strike-a-light pyrodebitage production experiment range in morphology and size. Single particles vary in size from approximately 1 μm to several millimeters. Grain morphologies include angular, subrounded, subangular, and amorphous and irregular shapes (Figure 4.11).
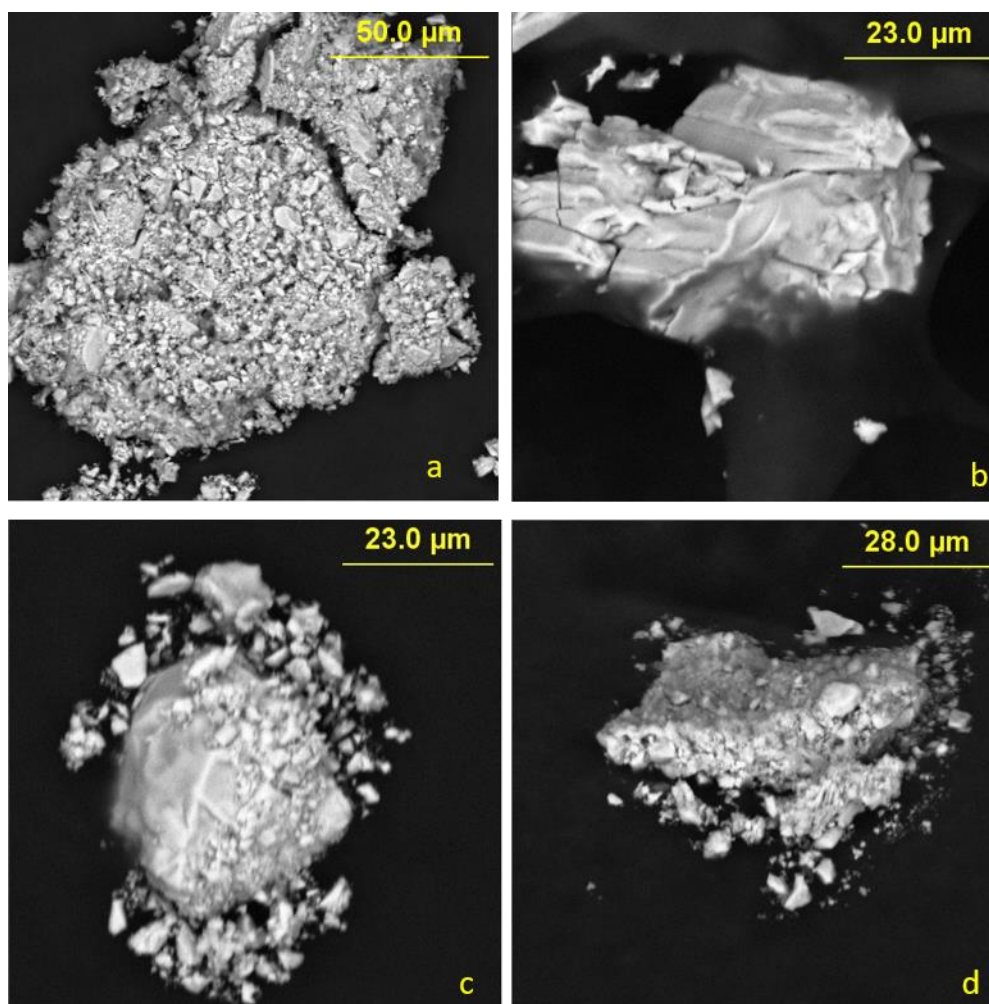
Figure 4.11. **Representative samples of common morphotypes observed in SEM. A) polycrystalline subrounded (possible framboid) B) Monocrystalline subangular C) monocrystalline subrounded D) polycrystalline amorphous.**

Other features observed in electron photomicrographs include conchoidal fracture scars on large monocrystalline iron disulphide particles and iron disulphide crystals with recognizable pyrite and marcasite crystal forms (i.e. cubic, orthorhombic, cockscomb) (Figure 4.12). Additionally, iron disulphide particles adhering to chert microflakes (CIDA) were visible on every mosaic analysed (Figure 4.13). The disulphide particles adhering to chert microflakes have diameters ranging from a fraction of a micron to 5 microns.
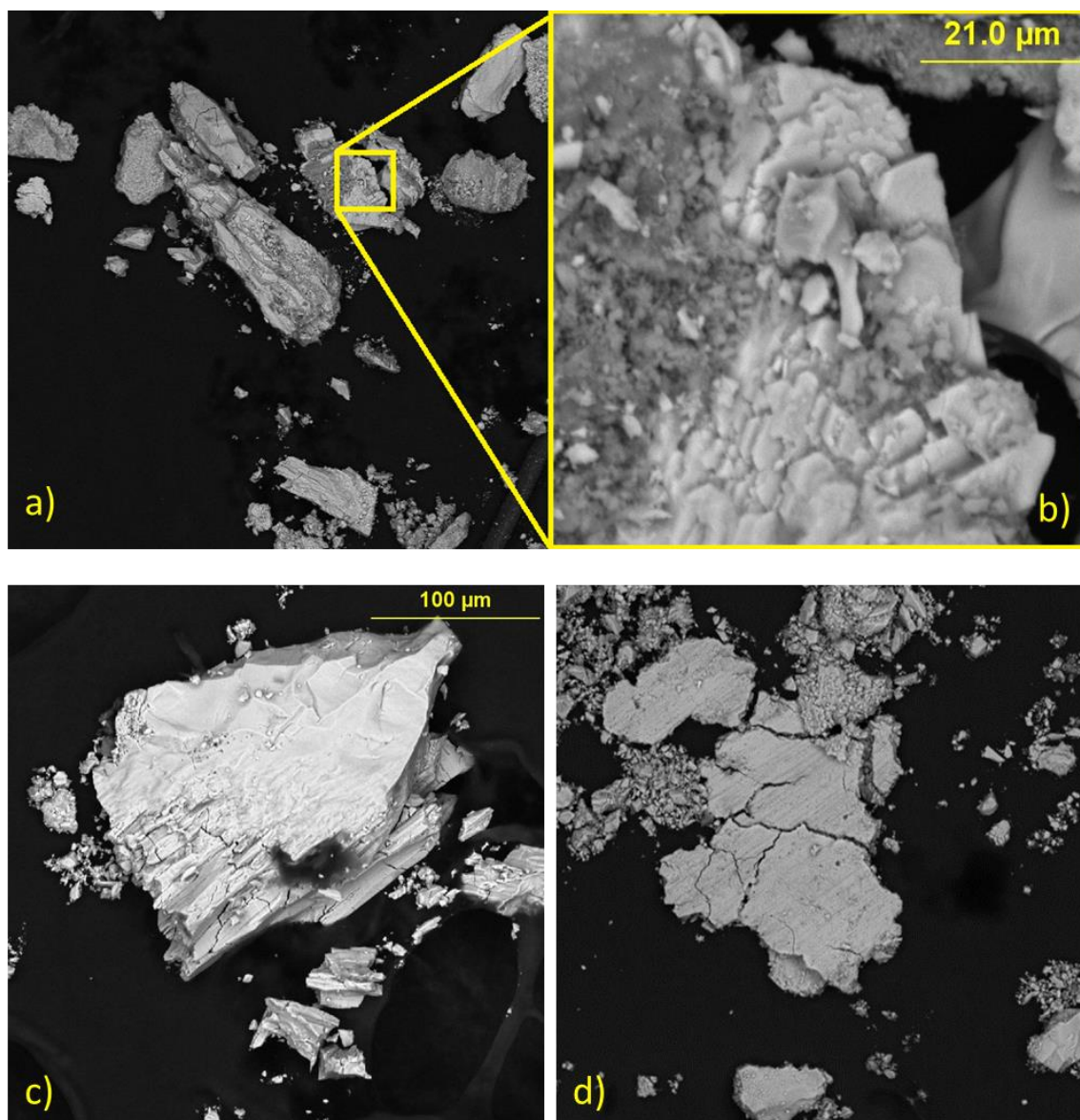
Figure 4.12. Features characteristic of pyrite and marcasite: a) cockscomb crystal shape b) cockscomb crystal shape detail c) conchoidal fracture scar d) twinning seen in SED (pyrite).
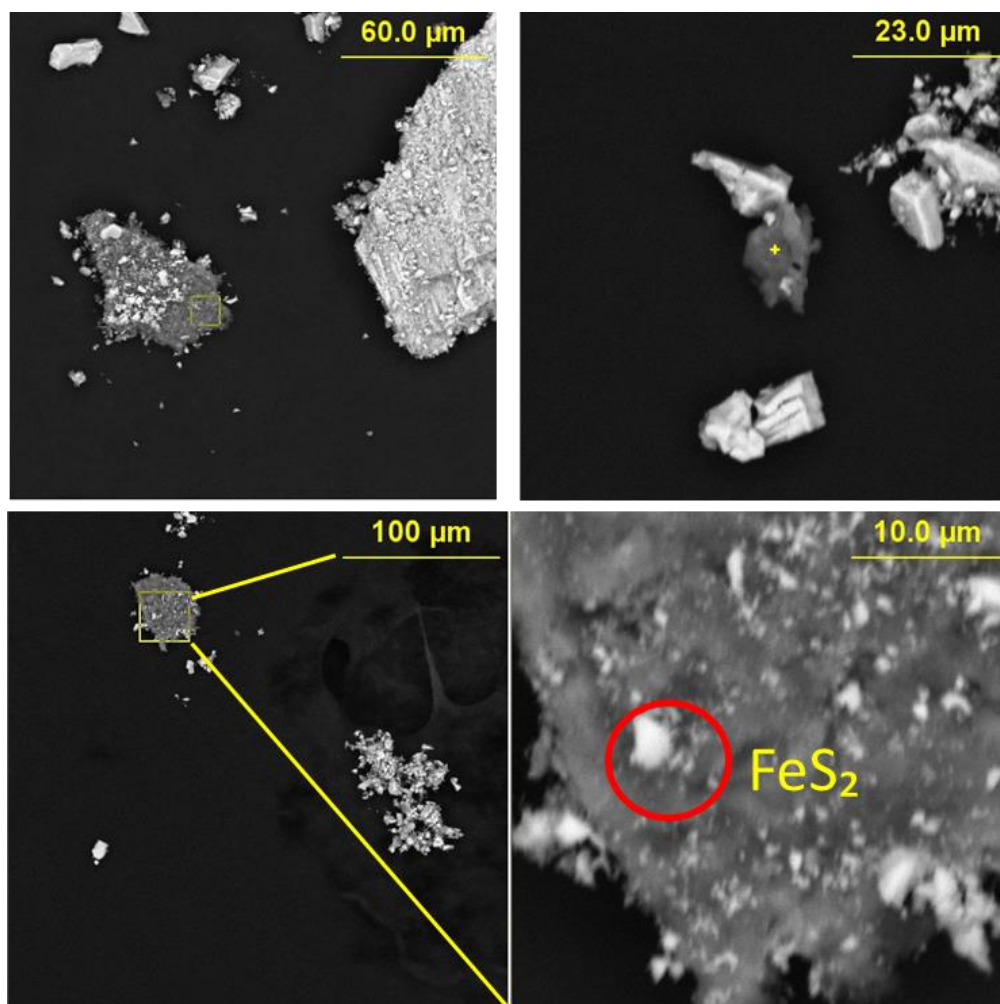
Figure 4.13.   Photomicrographs showing Chert with Iron Disulphide Adhering (CIDA).

In addition to samples of IDP produced in the strike-a-light debitage production experiments, control samples were produced and observed under SEM. Control samples include marcasite (iron disulphide) nodule cortex, marcasite scraped with a dental tool from the inside of the nodule, leather used to wipe marcasite during one experiment performed by Dr. Scaramucci, and *Fomes fomentarius* fibres (a common fine tinder used in strike-a-light fire starting) burned with a spark (Table 4.2).

Table 4.2.   Control Samples

Name	Description	Stab #
C1	Cortex of marcasite used in experiments Some rust coloured, some dark brown	S91
C2	Inside of marcasite used in experiments Grey and sparkling yellow, dark grey when scraped	S92
C3	Hair from leather cleaner and leather piece	S93
C4	*Fomes fomentarius* with ignited spark from same marcasite and chert as experiments.	S94
C5	*Fomes fomentarius* with ignited spark and established burn from same marcasite and chert as experiments	S95

Cortex material appears similar in crystal habit (e.g., cubic pyrite) to the interior scrapings; however, EDX analysis indicates that they are composed only of Fe. The particles have therefore lost sulphur and transformed into iron oxide (Figure 4.14). The oxidized cortex of intact marcasite nodules may be a good representation of what iron oxide pseudomorphs after pyrite and marcasite.   The use of nodule cortexes as analogues for pseudomorphs after iron disulphides may provide visual comparisons for archaeological samples.
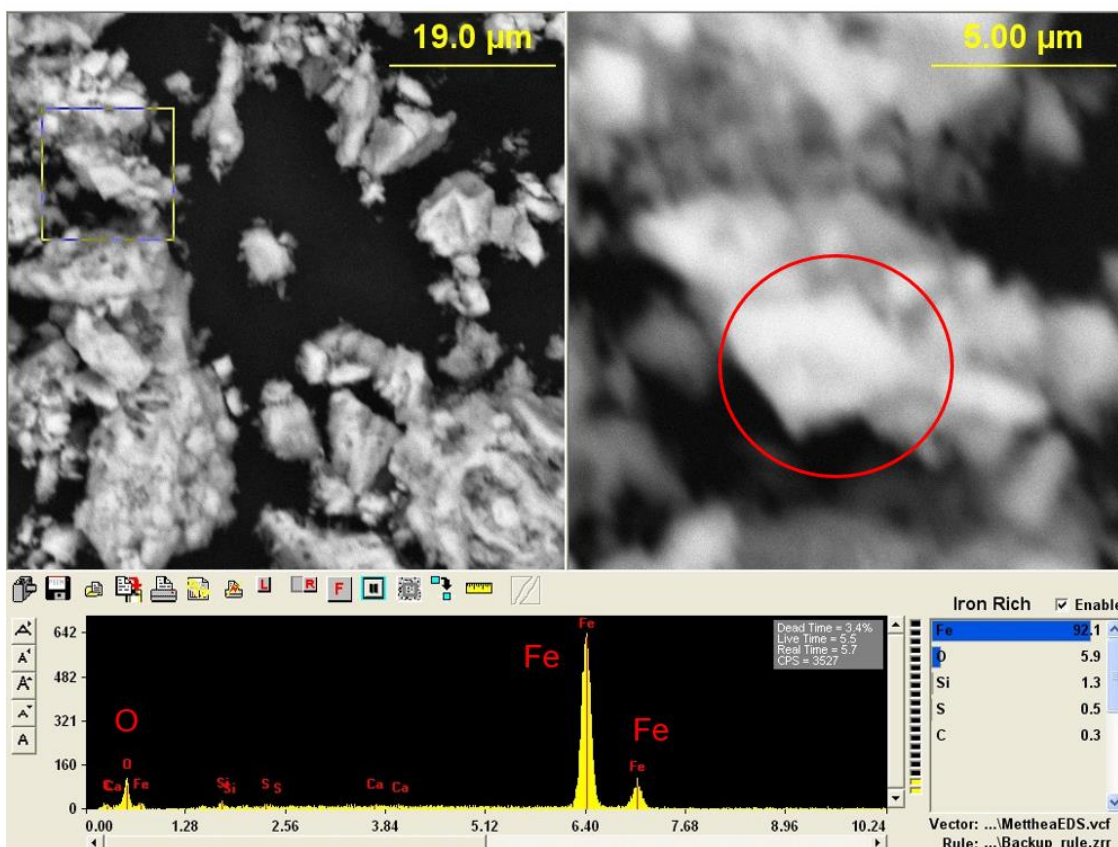
Figure 4.14.   Example of cortex control photomicrographs showing crystal habits comparable to inner marcasite material with iron rich EDX reading.

Semi-quantitative Analysis: counting iron disulphide pyrodebitage features using Scanning Electron Microscopy

Numbers and ratios of iron disulphide determined through analysis of image mosaics created in Adobe® Photoshop® are presented in Table 4.3 and Table 4.4. SEM image mosaics showed a range in total number of features from 524 to 4539. See appendix for all mosaic images.

Table 4.3.   Percussion Experiments: Total chert and iron disulphide features and their percentages of overall debitage counted on stab mosaics. Chert with iron disulphide adhering (CIDA) is also included.

Stab		Total features	Chert features		FeS$_2$ features		CIDA	
ID	Type of material sampled on stab	(n)	(n)	(% of total features)	(n)	(% of total features)	(n)	(% of total features)
1	spark landing location 1.1	524	17	3.2	507	96.8	7	1.3
11	fine material	1321	49	3.7	1272	96.3	16	1.2
10	fine material	2387	79	3.3	2308	96.7	6	0.3
21	fine material	820	55	6.7	765	93.3	10	1.2
20	fine material	2216	71	3.2	2145	96.8	18	0.8
30	fine material	1327	67	5.1	1260	95.0	7	0.5
Percussion Experiment	AVG	1432.5	56.3	4.2	1376.2	95.8	10.7	0.9
	SD	741.5	22.1	1.4	722.9	1.4	5.1	0.4
	%SD	52%	39%	33.6%	53%	1.5%	48%	49%

Table 4.4.   Friction Experiments: Total chert and iron disulphide features and their percentages of overall debitage counted on stab mosaics. Chert with iron disulphide adhering (CIDA) is also included.

Stab		Total features	Chert features		FeS2 features		CIDA	
ID	Type of material sampled on stab	(n)	(n)	(% of total features)	(n)	(% of total features)	(n)	(% of total features)
31	spark landing location 4.1	4539	51	1.1	4488	98.9	10	0.2
40	fine material	3165	170	5.4	2995	94.6	21	0.7
41	spark landing location 5.1	944	71	7.5	873	92.5	16	1.7
51	spark landing location 6.1	5028	110	2.2	4918	97.8	35	0.7
Friction experiment	AVG	3419	100.5	4.1	3318.5	96.0	20.5	0.8
	SD	1828.8	52.4	2.9	1826.8	2.9	10.7	0.6
	%SD	53%	52%	72%	55%	3%	52%	76%

Image analysis of mosaics showed that the chert features made up an average of 4.20% of total features in percussion experiments (Table 4.3) and 4.05% in friction experiments (Table 4.4), while FeS_2 features made up an average of 96.30% in percussion experiments and 95.33% in friction experiments. Additionally, the number of chert features with FeS_2 adhering to their visible surfaces (CIDA) made up from 0.2% to 1.7% of total feature counts at an average of 0.73% from percussion experiments, 0.86% from friction experiments, and 0.79% overall. More experimentation is needed to provide statistically significant figures, though at present little variation between percussion and friction can be observed. Finally, granulometry of the mosaics showed that roughly 70% of IDP in mosaic images was between silt and very fine sand size, though particle size ranged from clay to fine gravel.

Quantitative Results: Weight Data from Pyrodebitage Production Experiments

Weights of the debitage collected from the strike-a-light debitage production experiments are presented in Table 4.5 and Table 4.6. Weights reflect iron disulphide and chert values together since the two raw materials were not separated before weighing. Weights in percussion experiments ranged from 29 mg to 120 mg (mean = 67 mg, SD = 63%). Weights in friction experiments ranged from 41 mg to 192 mg (mean = 116 mg, SD = 54%).

Table 4.5.   Weight collected from strike-a-light activity in percussion experiments (Strike-a-Light Pyrodebitage Production Experiments).

Percussion	
Exp. #	**Debitage Collected (mg)**
2.4	40
2.6	29
3.4	120
3.3	107
3.5	41
AVG	**67**
SD	**43**
SD%	**63%**

Table 4.6.   **Weight collected from strike-a-light activity in friction experiments (Strike-a-Light Pyrodebitage Production Experiments)**

Friction	
Exp. #	**Debitage Collected (mg)**
2.1	66
2.2	126
2.3	156
2.5	41
3.2	192
AVG	**116**
SD	**63**
SD%	**54%**

4.3.2. Weight Loss Experiment

The weights of the raw materials before and after the weight loss experiment, as well as the average weight of each type of debitage produced per experiment and per strike, are presented in Table 4.7. In percussion force events, the amount of iron disulphide produced ranged from 2.1 mg to 7.4 mg (mean = 5.3 mg, %SD = 41%), and the amount of chert from 0.8 mg to 6.8 mg (mean = 2.7 mg, %SD = 93%). In friction force events, the amount of iron disulphide produced ranged from 1.8 mg to 4.9 mg (mean = 3.7 mg, %SD = 30%), and the amount of chert from 0.1 mg to 8.7 mg (mean = 1.5 mg, %SD = 127%). Iron disulphide percentages of the total weight lost ranged from 23.6% to 89.2% in percussion experiments (mean = 66.1%, %SD = 39) and 36.0% to 96.7% in friction experiments (mean = 70.0%, %SD = 29) (Table 4.8).

Chert production amounts were significantly more variable than iron disulphide amounts. The total weight lost from chert and iron disulphide for each experiment was compared to the weights of materials actually collected from the stainless-steel receptacle. Actual collection weights ranged from 1.4 mg to 6.7 mg (mean = 5.1 mg, %SD = 28%) in percussion events, and from 1.2 mg to 4.7 mg (mean = 3.1 mg, %SD = 40%) in friction events (Table 4.7).

Amount of iron disulphide produced per strike is shown in Table 4.9. Per strike, in percussive events, the amount of iron disulphide produced ranged from 41 μg to 148 μg

(mean = 106 μg, %SD = 41%). In friction events, the amount of iron disulphide produced

per strike ranged from 44 μg to 99 μg (mean = 73 μg, %SD = 30%).

Table 4.7. **Weight loss experiment values by experiment including weight lost from marcasite (FeS$_2$) alone, and weight lost from chert alone, and total weight lost from raw specimens. These values are compared with the actual collection from strike-a-light activity. The difference between the debitage collected and the total weight lost from raw specimens is presented as a percentage.**

Force Type	Experiment ID	FeS$_2$ measured weight loss (mg)	Chert measured weight loss (mg)	Calculated total weight loss (mg)	Recovered weight (mg)	% of total weight that is not recovered
Percussion	Exp. 1.1	4.2	1.2	5.4	3.3	39%
	Exp. 1.2	6.2	1.3	7.6	4.3	43%
	Exp 1.3	6.6	0.8	7.4	4.9	34%
	Exp 1.4	7.4	3.4	10.8	6.4	41%
	Exp 1.5	2.1	6.8	8.9	6.7	24%
	AVG	**5.3**	**2.7**	**8.0**	**5.1**	**36%**
	SD	**2.2**	**2.5**	**2.0**	**1.4**	**7.4**
	SD%	**41%**	**93%**	**25%**	**28%**	**20%**
Friction	Exp 1.6	4.0	4.7	8.7	4.7	46%
	Exp 1.7	2.2	0.4	2.6	1.7	33%
	Exp 1.8	4.9	2.0	7.0	3.9	44%
	Exp 1.9	2.9	0.1	3.0	2.1	31%
	Exp 1.10	4.2	0.5	4.7	3.0	36%
	AVG	**3.7**	**1.5**	**5.2**	**3.1**	**38%**
	SD	**1.1**	**2.0**	**2.6**	**1.2**	**6.8**
	%SD	**30%**	**127%**	**50%**	**40%**	**18%**

Table 4.8. Weight loss experiment data showing iron disulphide percentages of total weight lost in percussion and friction force experiments.

Percussion				Friction			
Exp.#	FeS_2 weight loss (mg)	Total weight loss (mg)	FeS_2/total %	Exp. #	FeS_2 weight loss (mg)	Total weight loss (mg)	FeS_2/total %
1.1	4.2	5.4	78%	1.6	4.0	8.7	46%
1.2	6.2	7.6	82%	1.7	2.2	2.6	85%
1.3	6.6	7.4	89%	1.8	4.9	7.0	70%
1.4	7.4	10.8	69%	1.9	2.9	3.0	97%
1.5	2.1	8.9	24%	1.10	4.2	4.7	89%
AVG	**5.3**	**8.0**	**66%**	**AVG**	**3.6**	**5.2**	**70%**
SD	**2.1**	**2.0**	**26%**	**SD**	**1.1**	**2.6**	**20%**
SD %	**40%**	**25%**	**39%**	**SD%**	**30%**	**50%**	**29%**

Table 4.9. Iron Disulphide Produced Per Strike in Weight Loss Experiment

Experiment Force	Exp #	Iron disulphide produced/ strike (µg)
Percussion	1.1	84
	1.2	124
	1.3	133
	1.4	148
	1.5	41
	AVG percussion	**106**
	SD	**43**
	SD %	**41%**
Friction	1.6	79
	1.7	44
	1.8	99
	1.9	59
	1.10	85
	AVG friction	**73**
	SD	**22**
	SD %	**30%**

Chapter 5.

Discussion

This chapter will first provide a brief summary of the major results achieved through experimentation. Secondly, the archaeological applications for these results and the procedures developed to obtain them will be discussed. Third, the broad significance of these results and procedures to the archaeological field will be discussed. Finally, this chapter will include an overview of possible future directions for strike-a-light experimental research. The objectives laid out in chapter 4 are presented in Table 5.1 alongside the procedures used to address them.

Table 5.1.   Specific objectives and the procedures used to address them

Objective	Procedure
i. Produce and collect microscopic Iron Disulphide Pyrodebitage using a reproducible method	Strike-a-light pyrodebitage production experiments
ii. Describe the morphological characteristics of microscopic Iron Disulphide Pyrodebitage	Strike-a-light pyrodebitage production experiments – Qualitative
iii. Determine whether iron disulphide particles adhere to chert microdebitage particles	Strike-a-light pyrodebitage production experiments – Qualitative
iv. Compare the amount of material produced by percussive and friction force strike-a-light actions.	Strike-a-light pyrodebitage production experiments Weight loss experiments
v. Estimate conservatively the amount of iron disulphide produced per strike of the strike-a-light fire-starting technique	Weight loss experiments
vi. Estimate the ratio of iron disulphide to chert introduced into the sediment system by the strike-a-light fire-starting technique	Strike-a-light pyrodebitage production experiments Weight loss experiments
vii. Provide a starting point for predictions of iron sulphide decay within sediment systems after strike-a-light activity	Literature review (Chapter 3)

5.1. Characterization of the IDP

This project is the first to produce photomicrographs of microscopic IDP, and as such adds great value to the archaeology of fire starting. The images produced can be used as invaluable reference materials to study archaeological samples that potentially contain disulphide particles derived from ancient pyrotechnological activities. Comparison of experiment results shows that percussion and friction forces do not vary in the proportion of iron disulphide to chert produced: an average of 95.8% of the total features counted in image analysis of percussion strike-a-light experiments are iron disulphide (Table 4.3), and 96.0% of total features in friction experiments are iron disulphide (Table 4.4). This is not entirely consistent with an average iron disulfide weight of 66% of the total weight in percussion weight loss experiments and 70% in friction weight loss experiments (Table 4.8). This shows that iron disulphide makes up the majority of strike-a-light pyrodebitage (compared with chert) in both particle number and weight, however, there is some inconsistency between weight and particle count values. This might be due to the small size of IDP particles, or due to poor recovery techniques in the weight loss experiments. Results also show that the total amount of debitage produced (including chert) varies significantly between experiments (Table 5.2).

5.1.1. IDP Size Range and Rough Quantification

The experimentally produced pyrodebitage ranged from approximately 1 cm in length to around 1 micron, though only debitage smaller than 2 mm was collected for analysis with SEM in order to maintain the focus of the present research on iron disulphide microdebitage. Roughly 70% of particles were between silt and very fine sand size (Stoops, 2003). It should be noted that very few pieces of macroscopic debitage were produced, and all of these were derived from the chert raw material. Additionally, debitage scatter was not limited to the 45 x 45 cm square but spanned over a meter. That being said, the densest concentration of material was observed to be inside the defined 45 x 45 cm collection area. Estimates from the measurements of features and single particles collected on the SEM stabs suggest that experiments could have produced between roughly 70 to 168 million iron disulphide particles per experiment. Clearly, this quantification should be considered a conservative estimate.

5.1.2. IDP Morphologies: Single particles, Features, and Clusters

The images of the experimentally produced IDP show that the main morphologies observed were:

1. Identifiable monocrystalline particles,

2. Irregular or undiagnostic monocrystalline particles, and

3. Polycrystalline clusters.

Some characteristic crystal habits associated with both pyrite and marcasite were observed to have preserved immediately after strike-a-light activity. These habits are cockscomb, spearhead, and pyritohedron. The presence of clearly observable habits is promising because it suggests that these minerals, or pseudomorphs after them, may be still observable in archaeological deposits. It is worth noting that simple cubic crystal habits were not observed in these experiments. In addition, several crystalline pyrite particles showed characteristic twinning and conchoidal fractures. Interestingly, no iron oxides ribbons or globules have been observed with the exception of one possible feature (Fig 4.11 and Figure 5.1) imaged in spark landing location Exp 5.1 (stab 51). This feature is strikingly similar to those observed by Hooke (1780) and had an "iron rich" EDX reading with very little sulphur.
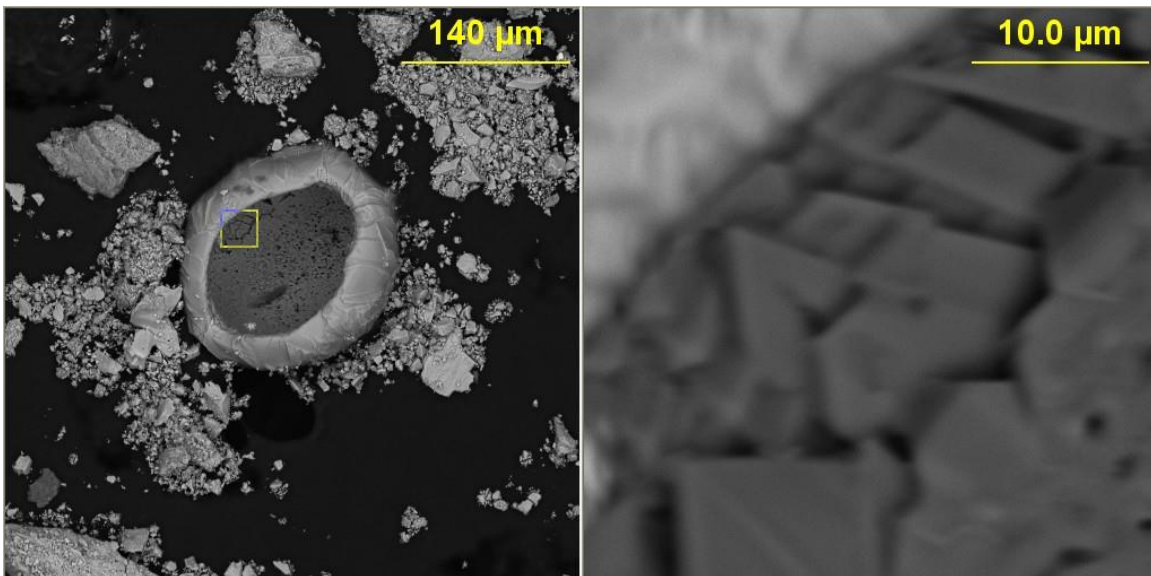
Figure 5.1.   Iron rich particle comparable to globules produced by flint and steel and magnesium strike-a-light materials.

Interestingly, experiments conducted with Dr. Scaramucci produced oblong clusters of iron disulphide particles (Figure 5.2). Specifically, these features were observed only in this experiment in which a leather cloth was used to remove disulphide dust adhering to the marcasite nodule in between strikes. In fact, the disulphide dust hampers the production of sparks and its removal it is of great help to increase the efficiency of the process. The observation of these elongated clusters of disulphide materials is significant: if similar clusters were found in archaeological deposits they could be used as positive evidence of strike-a-light fire-starting technique.
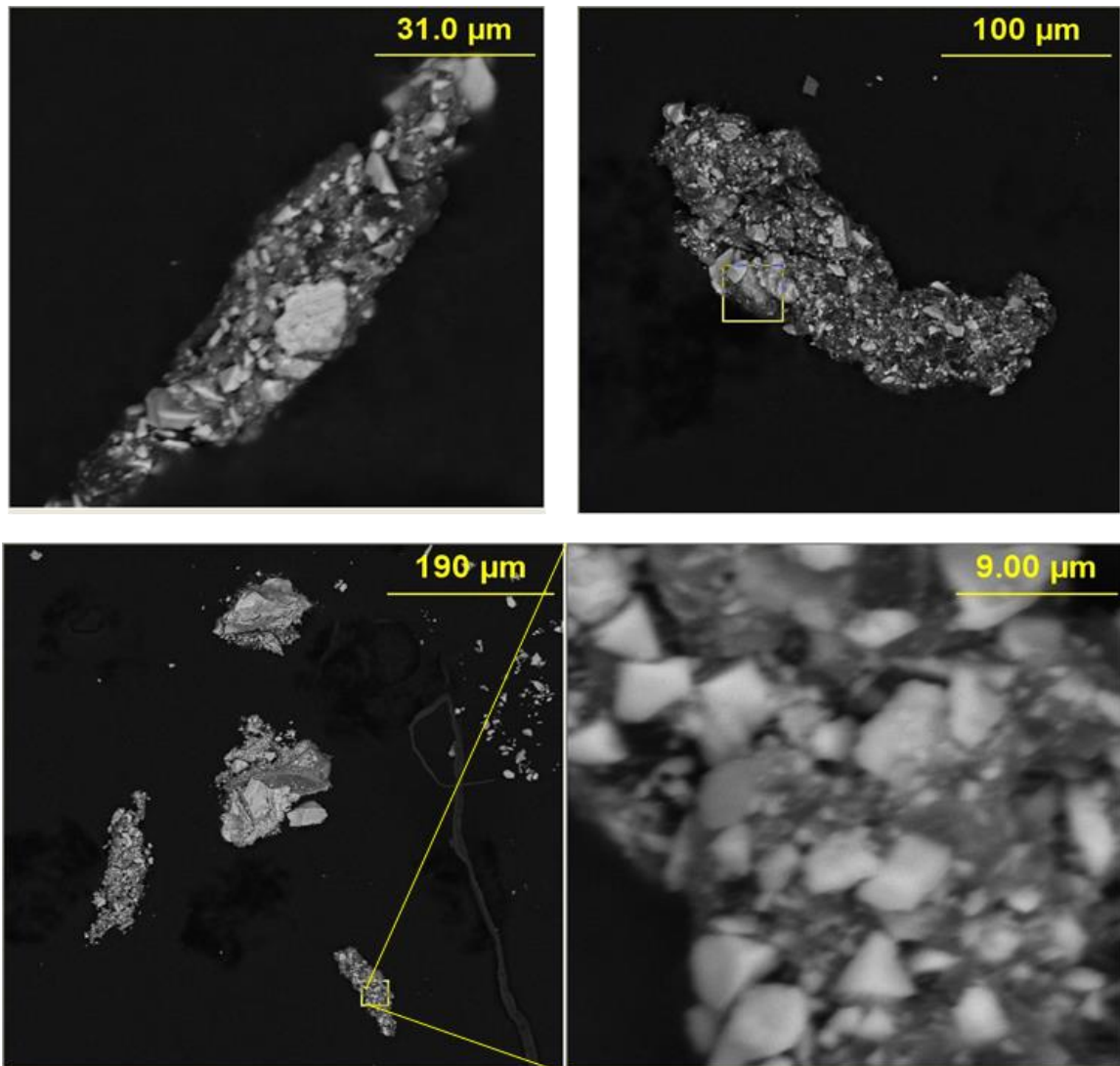
Figure 5.2. **Elongated clusters resulting from rubbing a piece of leather over the marcasite nodule during strike-a-light activity.**

5.1.3. Chert with Iron Disulphide Adhering (CIDA)

It was successfully determined that micrometer-sized iron disulphide particles do adhere to chert microdebitage particles at least temporarily. It is yet undetermined whether the IDP would remain attached over time or when subjected to weathering. Additionally, chert with iron disulphide particles adhering (CIDA) make up about 1% of the total (chert and iron disulphide) observed particles produced through strike-a-light action and thus represent a detectable proportion of the chert microdebitage. Thus, it would be appropriate to look for CIDA among the extracted chert microdebitage from archaeological deposit (see Stepka et al., 2018 for microflint separation technique). For this purpose, any protocol for microdebitage extraction would have to be modified to target and preserve potential iron disulphide particles adhering to chert microflakes. Such protocol modifications would include buffering the pH of the extracting solutions and the density of the heavy liquid used for the separation of the microdebitage.

5.1.4. Contrasting Percussion and Friction Strike-a-light

Weight loss experiment data (Table 4.7) show that friction force experiments produced lower weight values of total debitage than percussion force experiments. Weight values recovered from the strike-a-light debitage production experiments show that in friction experiments significantly more debitage mass was collected than in percussion experiments, with an average of 67.0 mg produced per percussion experiment compared to an average of 116.0 mg per friction experiment (Table 5.2). This apparent weight discrepancy can be explained by the fact that by using friction as opposed to percussion, the debitage dispersion radius is significantly more restricted. Additionally, the IDP image analysis counts showed that friction force experiments produced on average more than twice the number of features than percussion force experiments (Table 4.3 and Table 4.4). These preliminary data suggest that friction will produce more concentrated and fragmented IDP than percussion. A closer look at the image analysis shows that percussion force experiments yielded a mean of 1432.5 features compared to a mean of 3419 features for friction force experiments. The average number of distinct iron disulphide features in the roughly 2 x 2 mm area observed at the centre of each SEM stab was 1376.2 particles for percussion and 3318.5 particles for friction force experiments. If this is representative of the entire 45 x 45 cm collection zone, the experiments would have produced roughly 69,670,125

distinct particles within that area in percussion events and 167,999,062.5 distinct particles in friction events if there was an even distribution of particles throughout the 45 cm x 45 cm collection area. This is not accurate, but it does give a rough estimate of the amount of particles produced.

Preliminary semi-quantitative analysis also suggests that the mass, the size, and the number of particles of iron disulphide produced are affected by several factors such as raw material used, the individual expertise, and the type and intensity of force applied. Specific techniques appear to be dependent on the individual, the size and shape of the materials, and whether composite tools are used (Sem Scarammucci, personal communication). The protocol developed for this thesis would be an ideal method for testing each variable independently.

Table 5.2. **Comparison of percussion and friction weight or feature number across experiments.**

Experiment Type	Percussion		Friction	
	Amount of Debitage Produced (mean)	% Standard Deviation	Amount of Debitage Produced (mean)	% Standard Deviation
Debitage Production Exp. Weights	67.0 mg	54%	116.0 mg	54%
IDP Photomicrograph Analysis counts	N = 1432.5	53%	N = 3419	53%
Weight Loss Exp. Weights: Recovered weight	5.1 mg	28%	3.1 mg	40%
Weight Loss Exp. Weights: Calculated loss	8.0 mg	25%	5.2 mg	50%

Similar relative distributions were obtained for CIDA particles counts. In the 2 x 2 mm stab surfaces analyzed, an average of 10.7 particles in percussion experiment and 20.5 in friction force experiments were counted. If this is representative of the entire 45 x 45 cm collection surface, the experiments would have produced roughly 541,687.5 particles in the collection zone in percussion events and 1,037,812.5 particles in friction events. While the number of particles differ between friction and percussion events, their percentages of total features are similar (1% in percussion and 0.9% in friction experiments).

Nevertheless, it is important to note that the ratio of iron disulphide to chert production in percussion and friction experiments is nearly identical (95.8% for

percussion and 96% for friction). This suggests that regardless of the amount of material produced, which might vary depending on experience or individual strengths or styles, the proportion of iron disulphide to chert remains constant. This proportion may vary when different nodules and strikers are used, though it was not possible to examine this variable here.

5.1.5. Likelihood of Preservation

Low humidity (<40%)	High humidity (>40%)
Low eH	High eH
Low pH (<7)	High pH (>7)
Lower temperature	Higher temperature

Decreasing likelihood of preservation

Preservation of pristine mineralogy and habit

Preservation of Pseudomorph

Preservation of geochemical signature
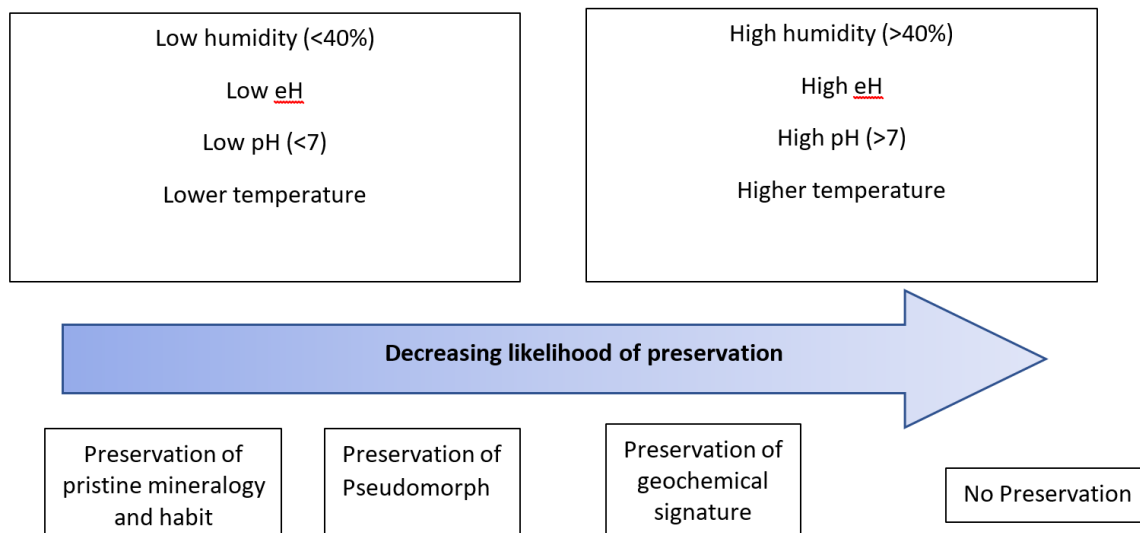
No Preservation

Figure 5.3. **Schematic representing the relative likelihood of IDP preservation affected by environmental conditions and preservation scenarios.**

As presented in Chapter 3, the diagenesis of iron disulphides is complex and dependant on many variables. The rate and intensity of iron disulphide oxidation varies depending on factors such as humidity, eH, pH, and temperature. Based on the review of geochemical literature conducted, Figure 5.3 was developed to represent a simplified diagram of preservation of iron disulphide dependent on depositional environment conditions. Four possible preservation scenarios are presented

1. Pristine preservation, where iron disulphide is preserved in the physical and chemical form in which it was deposited;

2. Preservation as pyrite or marcasite pseudomorph, in which iron disulphide crystal habits are preserved even if chemical and mineralogical changes have occurred;

3. Marcasite and pyrite are dissolved and the only signature preserved is abnormal values in the archaeological deposits of total iron or sulphur and of their isotopes; and

4. Marcasite and pyrite are dissolved, and iron and sulphur are leached away.

In order to make predictions about the preservation potential of IDP artefacts in archaeological contexts, a detailed understanding must first be gained of the environmental contexts from the time of IDP deposition through to the time of excavation. Thus, looking for IDP in archaeological contexts should be a part of integrated, multidisciplinary, microcontextual research projects. Additionally, it is necessary in archaeological applications to obtain background analyses of amounts of iron, iron disulphides, iron oxides, and sulphates within and near sites. It is possible that the identification of IDP may rely on detecting concentrations of iron, sulphides, and the resultant minerals of oxidation in the sediment if distinct particles (i.e., pristine crystal or psudomorphs) cannot be found. Additionally, iron concentrations with isotopes different from background iron isotopes may suggest anthropogenic input of iron disulphides. Therefore, comparison of sedimentary mineral content with background samples may be the only potential evidence of strike-a-light activity. Finally, it is important to consider that a relative humidity below 40% should be maintained where potential IDP sediments and artefacts are stored, since oxidation can occur within minutes of exposure to the atmosphere (Chiriță and Schlegel, 2017; Baars et al., 2018).

5.2. Considerations for Experimental Set-up

The high-speed camera used (Phantom v10) was effective in determining the landing location of sparks to a moderate degree. It was almost always possible to determine the 5 x 5 cm grid square within the 45 x 45 cm collection area that a spark landed in. In some cases, the angle of the camera was such that depth may have been misidentified. This might be alleviated by different or multiple camera angles. Additionally, the model used allowed a long enough buffer time to complete 50 strikes at a resolution of 1920 x 1080 and a sample rate of 30 frames per second. While a higher resolution and frame rate might allow more accurate visuals, this must be weighed against the risk of cutting out important data.

Additionally, the number of iterations (n=3) for each force type (friction and percussion) needs to be increased to improve the statistical significance of the results. The weight loss experiments were conducted in order to address these issues. Overall the strike-a-light pyrodebitage production experiments were designed for obtaining preliminary qualitative and semi-quantitative results than strictly quantitative results.

The experimental procedures produced for this thesis have great potential for the further study of iron disulphide pyrodebitage, as well as other forms of microdebitage. However, the current procedure is limited by collection area size. Depending on collection material, available space, and purpose of the experiment, the collection area can be made larger, however it is unlikely that recovery of 100% of the pyrodebitage produced is possible. This is due to the range of scatter involved in percussive strike-a-light activity, as well as the propensity for iron disulphide powder to adhere to various surfaces including skin, gloves, and raw materials. Therefore, estimates of the amount of material produced using this procedure will always be underestimates.

The main aim of the strike-a-light debitage production experiments was to produce debitage for analysis and description with Scanning Electron Microscopy. This aim was met. The experiments are deemed significant mainly because of the success of the procedure and the descriptive results achieved. While the quantitative data show good preliminary results, the specific experiments conducted were designed to yield good qualitative results first. The procedure developed can be used for both qualitative and quantitative experiments and is not limited to strike-a-light debitage collection. Microdebitage represents an almost ubiquitous component of lithic assemblages that can inform researchers about the production and use of tools, which lead to insights about past behaviours (Fladmark, 1982; Frahm, 2016; Weiner, 2010). In addition to developing a new procedure, this research is the first to focus on strike-a-light debitage. It is therefore of special significance to the study of fire starting with mineral components. Given its mineral nature, products of the strike-a-light technique have the potential to survive for long periods in a variety of environments (Sorensen et al., 2014; Baars et al., 2018). The added complexity of pyrite oxidization should not completely deter researchers, as this study shows that fresh IDP includes diagnostic crystal fracture and habits. Various iron oxides can form pseudomorphs after iron disulphide, so it may be possible to identify IDP even after oxidization of iron disulphide. The results of the

qualitative analysis also show the adherence of submicron- to micron-sized IDP to chert microflakes.

While the results and procedures produced are promising, they represent preliminary development of tools for the identification and analysis of IDP. Further experimentation will bolster results and fine tune procedures. Some directions that should be pursued include

1. Developing and testing techniques to extract IDP and CIDA from sediments;

2. Testing the factors identified in this study that affect the amount of strike-a-light debitage; and

3. Developing experimental thin sections with IDP inclusions to test identification in micromorphological contexts.

5.3. Archaeological Significance

The results produced during the experiments are intended to be applied to archaeological investigations by providing a foundation for future research into IDP, and to show that iron disulphide has potential as a significant mineral artefact and should not be discounted because of its propensity to oxidize under some conditions. Additionally, the qualitative results produced can be used as reference material for further experimental work, as well as for proper archaeological materials. Geoarchaeological methods such as micro-excavation, micromorphology, chemical spectroscopy, and heavy liquid separation stand to be informed by the material presented in this thesis. By providing a representative set of IDP particles at the time of deposition, this research sets the stage for further investigations of fire-starting residues after deposition and through their taphonomic pathways. Therefore, this research represents the first step to understanding the physical and chemical characteristics of IDP artefacts at the time of deposition, which is an important factor for further research into the taphonomy and excavation of fire-starting residues (Shahack-Gross, 2017).

In addition to the results, three novel procedures were produced for this thesis:

1. Strike-a-light pyrodebitage production;

2. IDP photomicrograph analysis; and

3. Iron disulphide weight loss experimentation.

These procedures are intended to address a noted gap in archaeological fire research; that is, ways to identify and understand fire-starting activities in the past (Aldeias, 2017). The strike-a-light debitage production experiments and IDP photomicrograph analysis procedure were successful in that strike-a-light microdebitage was produced, collected, and analysed effectively in a reproducible manner. The iron disulphide weight loss procedure may be more useful for the quantitative comparison of iron disulphide and chert materials produced during strike-a-light activities.

The results and procedures produced for this thesis show potential for developing a more in depth and high definition understanding of how fire-starting technologies have been created and used in any time period or location. The ability or knowledge to start fire at will represents an important node in the long development of fire use by humans (Pruetz and LaDuke, 2010; Chazan, 2017; Sandgathe and Berna, 2017). Thus, the development of research protocols and procedures for identifying and studying the artefacts of fire-starting activities has the potential to inform us about our relationship with one of the most important technological developments in prehistory.

The ability of individuals, populations, or species to start fire without reliance on natural wildfires would have been a significant advantage over those groups who did not possess such an ability. It has been hypothesized that Neanderthals in Southwest France were unable to create fire at will (Sandgathe et al. 2011a, b; Dibble et al., 2018 and 2017). If correct, this could have been a contributing factor to the out-competition of Neanderthals by modern humans. In fact, there is little evidence for fire starting in the Middle and Lower Palaeolithic in both Neanderthal and modern human contexts (Sandgathe et al., 2011a, b; Roebroeks and Villa, 2011; Villa and Roebroeks, 2014; Dibble et al., 2018). Whether this dearth of evidence is due to an absence of the behaviour, issues of preservation, or excavation practices, it is clear that the study of fire starting is dependent on the development of new techniques and procedures created specifically for this purpose.

Chapter 6.

Conclusion

In this dissertation I present the experimental set up and the results for the creation and the characterization of microscopic residue produced by striking iron disulphide rich rocks to produce fire. This method, commonly called the strike-a-light technique, entails the striking of iron disulphide minerals with a sharp rock of suitable hardness to produce sparks. Based on indirect evidence, it has been hypothesized that this fire-starting technique is deeply rooted in the history of humanity and has been used since the Middle Paleolithic by Neanderthals and early modern humans. During that time, the rocks of choice for this type of technique were pyrite and/or marcasite rich nodules and flint and other types of chert. The chert was used to strip fresh particles of iron disulphide from pyrite and marcasite nodules. The iron disulphide molecules would oxidize in contact with air and, with the added energy of friction or percussion, ignite to form sparks. To the best of my knowledge, no data existed to date on the qualitative and quantitative aspects of the microscopic residue derived from strike-a-light fire starting using iron disulphides and chert. My work is thus the first attempt to produce a reference collection of pyrite and marcasite residues derived from strike-a-light fire-starting activities with the intent to identify the presence of these materials as residues in archaeological deposits of all ages and regions.

Three novel procedures were developed to identify and characterize the microdebitage resulting from strike-a-light activity. The strike-a-light pyrodebitage production experiments were a group of partially controlled experiments where a marcasite nodule and chert biface were struck or forcefully rubbed together 50 times per iteration over a collection area of wax paper. The collection area was a 45 x 45 cm square which was underlain with a 9 x 9 grid in order to facilitate the recording of spark landing positions using a high-speed camera. The use of high-speed imaging allowed the collection of microdebitage from areas where sparks landed. Microdebitage was then collected systematically from the collection area using SEM stabs and carbon paper. Remaining debitage was collected in the wax paper collection sheets and weighed.

The microdebitage was then observed using SEM imaging and EDX spectroscopy for elemental analysis, producing qualitative and semi-quantitative results. Samples were surveyed for significant factors such as visible crystal habits of iron disulphides, presence of iron disulphide particles adhering to chert microflakes, and general size ranges and morphologies. Semi-quantitative data was obtained by creating 250x images stitched together using Adobe Photoshop and counting iron disulphide and chert particles. This allowed comparison of relative iron disulphide and chert amounts in strike-a-light debitage.

Finally, a secondary experiment, the iron disulphide weight loss experiment, was conducted to compare the relative weights of iron disulphide and chert introduced into the system from strike-a-light activity. This was done by performing strike-a-light actions over a stainless-steel collection receptacle and weighing the collected debitage as well as weighing the marcasite nodule and chert striker before and after striking. The weight measurement of the nodule and striker allowed comparison of the mass of iron disulphide and chert produced from the actions.

The major results of these procedures are as follows:

- The debitage produced and examined showed angular, subrounded, subangular, and amorphous and irregular morphologies.

- Sizes ranged from ~5 microns to ~1 cm.

- Iron disulphides made up between 70% and 96% of total debitage based on weight and particle count values.

- Iron disulphide debitage showed characteristic crystal habits such as cockscomb, spearhead, and pyritohedral, as well as irregular crystal shapes and clusters.

- Iron disulphide particles were observed to adhere to chert microflakes.

Iron disulphide microdebitage produced from the strike-a-light technique is defined in this dissertation as iron disulphide pyrodebitage (IDP) as it should be considered an important artefact in the archaeology of fire starting. Also defined in this dissertation are chert particles with iron disulphide adhering (CIDA).

Comparison of percussion and friction force striking activity showed that friction force produces more particles in a concentrated area than percussion force. However, it

was also found that the amounts and weights of debitage produced are dependent on the specific tools used as well as the strength and experience of the individual performing the action. Additionally, while amounts and weights of iron disulphide and chert produced vary throughout experiments, the ratio of iron disulphide to chert remains quite similar (96%). Therefore, regardless of the individual creating fire, or the tools or technique they are using, it is clear that IDP represents a significant portion of the residues of fire starting.

This thesis also provides a review of the degradation processes that IDP can incur once it is deposited in sediments. Several possible preservation scenarios are provided, which are dependent on the geochemical characteristics of the depositional environment. Subsequently, the analytical tools for the reconstruction of the history of the geochemical conditions of any given deposit are listed. Specifically, it was found that IDP shows characteristic crystal habits that may be useful in its identification in archaeological contexts and may even survive as pseudomorphs even if the original iron disulphide changes its chemistry and mineralogy. This dissertation therefore offers a novel and powerful framework for the identification and study of the strike-a-light fire-starting technique in archaeological contexts. As the interest in the prehistory of fire and its role in human evolution continues to rise among academics and the general public, this thesis is an important contribution to the advancement of this important topic and anthropology in general. In particular, this work shows that IDP should be considered a promising mineral artefact that should not be overlooked in studies concerning the archaeology of fire starting. On a larger scale, this work contributes a powerful tool for the study of the prehistory of fire use which lead eventually to habituation and manufacture. The possibility of positively identifying direct evidence of fire-starting techniques in archaeological contexts will provide key data for discrimination between fire starting and fire collection in the past. My research therefore adds to the large body of effective experimental archaeology and microarchaeology that has proven integral to addressing archaeological inquiries into past uses of fire and continues to inform conversations about how peoples in the past have created, used, and lived with fire.

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Appendix

Mosaic Images – Supplementary Material

Merged images of image analysis mosaics (250X) are provided as supplementary files.