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Reviewed Article:

Does the Addition of Manganese Dioxide Aid in The Production of An Ember when Using Strike-A-Light Technology With Horse Hoof Fungus? A Potential Neanderthal Technology

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Recent archaeological and experimental work suggests that Neanderthals may have been purposefully gathering manganese dioxide to aid in their fire lighting. Given the evidence for complex Neanderthal pyro-technology, this appears to be a plausible hypothesis. In this paper, we add to the experimental testing of this hypothesis by adding manganese to horse hoof tinder fungus and then generating embers using a flint tool and an iron sulphide strike-a-light. However, our results show that adding manganese dioxide in this way did not improve spark capture or confer any perceptible advantage in fire lighting.

> Our findings provide contrast to those of Sorensen (2020) who claimed that the addition of manganese dioxide to tinder improved its ability to capture sparks, regardless of tinder type.

Introduction

Fire is a "nexus of human evolution" (Gowlett, 2010, p.158) being connected to many important aspects of our evolution. While the initial stages of this relationship were probably responsive, with humans interacting with wildfires, at some point, a change occurred, and humans became able to keep fires going and then finally to kindle fire at will (Gowlett, 2010). This final kindled stage requires the most developed techno-cultural repertoire, with traditional fire lighting methods being highly challenging to learn and achieve (Lombard and Gärdenfors, 2023).

Fire can traditionally be kindled in two ways: wood-on-wood friction and striking iron sulphide nodules with a hard rock to produce sparks (Lombard and Gärdenfors, 2023). The wood-on-wood method requires specific, completely dry, woods to be used and is extremely sensitive to environmental conditions, such as low temperature and moisture (Lombard and Gärdenfors, 2023). The use of iron sulphide, known as strike-a-light technology, has fewer constraints, requiring only dry tinder and being more reliable in colder damper conditions (Lombard and Gärdenfors, 2023). It would seem logical, therefore, that occupation of colder, higher latitude environments, such as Europe, would require not only a well-developed understanding of fire, but also a reliable technology or ignition potentially reliant on mineral strike-a-lights. There is good evidence for both in the material record associated with Neanderthals (Koller et al., 2001; Henry, 2017; Sorensen et al., 2018). An intriguing discovery from Pech de l'Azé I in the Dordogne, France, shows that along with being able to light fires, Neanderthals may have been exploiting manganese dioxide (MnO_2) to reduce ignition temperatures to aid their fire making (Heyes et al., 2016).

Heyes et al., (2016) experimentally showed that adding MnO_2 to wood shavings reduced the ignition temperature by approximately 100 degrees C. They attributed this to the thermal decomposition of MnO_2, which releases oxygen and subsequently aids combustion. Further work by Sorenson (2020) suggests that a similar advantage exists in adding MnO_2 to specific tinders to produce an ember when using pyrite-based strike-a-light technology. However, a set of experiments by Langley and Needham (2021) challenge these findings. In their experiments, a modern ferrocerium rod, producing sparks of up to 3000 degrees C, appeared unable to ignite either MnO_2 or powdered birch bark with Mn02 added to it. The use of modern high temperature strike-a-light technology by Langley and Needham (2021) appears to indicate that adding MnO_2 provides no advantage at initial ignition.

It is, however, the case that primitive strike-a-light technology employing iron sulphide and flint, does not result in a flame being produced like modern strike-a-lights and birch bark. Indeed, the primitive iron sulphide method does not produce sparks generally hot enough to ignite birch bark. In this case, slow burning tinders, such as horse hoof fungus (*Fomes fomentarius*), are prepared into a fluffy mass. When this catches a spark, it does not result in a flame but rather a smouldering ember. It is this ember which is applied to larger tinder to result in flame.

In this paper, we extend the work of Heyes et al. (2016), Sorensen (2020), and Langley and Needham (2021) to investigate whether the addition of MnO_2 confers advantages in the production of an ember using primitive iron sulphide and flint strike-a-light technology and an appropriate tinder.

Two sets of experiments were performed to explore the possibility of MnO_2 conferring advantages in ember production from the more primitive form of strike-a-light technology. The first experiment employed a radial structure iron sulphide shown by XRD to be iron pyrite and tested horse hoof fungus both with, and without MnO_2. The second experiment used a non-radial iron sulphide nodule with a massive structure (referred to throughout as pyrite) which was shown by XRD to be composed of primarily iron pyrite, with traces of marcasite present. The second experiment also tested horse hoof fungus with, and without the addition of MnO_2. This second pyrite nodule was much less effective at producing sparks than the first and was included to see if the addition of MnO_2 would be beneficial when using materials with sub optimal performance.

Neanderthals: Strike-a-lights and Manganese dioxide

There is limited direct evidence of iron sulphide strike-a-lights in the Middle Palaeolithic because iron sulphide is highly reactive and susceptible to oxidative decomposition (Sorensen, 2014). There is, however, a halved nodule which appears to be radial nodule, found at Drachenloch Cave (Switzerland) in association with a hearth feature that has been dated to cal. 50,000 BP, with what have been interpreted as linear use wear traces. It must, however, be noted that many other actions could create linear marks, including the possibility that the researcher who discovered the nodule may have tested it to see if it was effective at producing sparks (Weiner and Floss, 2014).

While the direct evidence for strike-a-light technology in the form of preserved iron sulphide faces serious preservation issues (Rickard et al., 2007), strike-a-light technology leaves diagnostic wear patterns on the stone tools used to strike or abrade the iron sulphide. Use-wear analysis has shown that Neanderthals at several sites (e.g. Chez-Pinaud, Jonzac) were using the faces of bifacial tools to abrade iron sulphide in this way and that in some populations, they had mastered strike-a-light technology (Sorensen et al., 2018).

Originally, it was thought that Neanderthals were using ground Manganese dioxide as a black pigment, potentially serving a ritual purpose (Bordes, 1961; Soressi and D'Errico, 2007). The ready supply of easier sources of black pigment, such as charcoal, led Heyes et al. (2016) to formulate the alternate hypothesis that the manganese had a different functional role. As discussed above, experiments performed by Heyes et al. (2016), and Sorensen (2020) show that thermal decomposition of manganese dioxide may confer advantages in fire lighting, and that this is why Neanderthals were gathering it. As also noted, the work of Langley and Needham (2021) suggests this is not the case.

Methods and Materials

To test whether the addition of MnO_2 aids in fire lighting when using primitive iron sulphide based strike-a-light technology, we performed 4 separate experiments, which each included approximately 30 runs.

1. Lighting prepared horse hoof fungus with massive **pyrite** and flint (n = 31).
2. Lighting prepared horse hoof fungus with added **MnO_2** with massive **pyrite** and flint (n = 34).
3. Lighting prepared horse hoof fungus with **radial pyrite** and flint (n = 38).
4. Lighting prepared horse hoof fungus with added **MnO_2** with **radial pyrite** and flint (n = 30).

Experimental set up

The experiments were conducted in the Experimental Archaeology Research and Training Hub (EARTH) workshop within the department for Archaeology, Classics, and Egyptology, at the University of Liverpool. Prior to data collection, striking technique and ember formation were practiced to ensure consistency.

The tinder was weighed at the beginning of each condition and placed onto a piece of tanned leather (grain side facing up) with 4 stones under the leather, creating a depression.

In the conditions without MnO_2, 8 g of hoof fungus tinder was used. In the experiments with added MnO_2, 4 g of hoof fungus was used with the addition of 4 g of MnO_2, which was mixed in with gloved hands to create a homogenous mixture of manganese dioxide and hoof fungus.

The percussion method, rather than the scraping method, was selected to strike the flint tools against the sulfuric iron nodules, as this allowed for a quick succession of strikes and thus we found this to be more effective at spark production. In this method, the left wrist was kept approximately 20 cm above the table, with the right hand holding the experimental strike-a-light. The experimental strike-a-light was struck down onto a groove within the iron sulphide longitudinally to the working edge. The lateral edges of the stone tool, near the base where the tool is thickest, were used as the striking edge, as this is less subject to edge failure. When an ember was produced, it was removed from the tinder, and a pinch of tinder (with or without added MnO_2) was added to replace it.

Experiments were recorded with an iPhone 13 camera attached to the table with a holder angled to capture a full view of hand position and the tinder (See Figure 1). This video footage was then used to find the time taken to form an ember in each run. The stopwatch was paused whenever striking was stopped in a run to check for ember formation and restarted upon resuming strikes. The number of strikes needed to generate an ember was also counted.

Horse hoof fungus

Hoof fungus was used as this is arguably the best tinder for readily capturing a spark (Weiner and Wescott, 2003). It commonly occurs on hardwood standing trees, with the host species varying by geographical region (Schmidt, 2006, p.142) and is widely geographically distributed in Europe (Schwarze et al., 2000, p.59) and Africa, Asia and North America (Schmidt, 2006, pp.195-197). Hoof fungus has been found in sites as old as 11,555 ± 100 BP (Peintner et al., 1998), most notably in 'The Iceman's' girdle bag, alongside a larger and smaller flint blade as a mass of clumped hyphae, with traces of pyrite (Sauter and Stachelberger, 1992) which has been radiocarbon dated through analysis of the Copper Age mummy's tissue and bone to 5300 - 5160 BP (Prinoth-Fornwagner and Niklaus, 1995).

To produce enough Hoof fungus tinder, dried hoof fungus was scraped with a flint 'scraper' type tool (See Figure 2), in line with the tool industry available to Neanderthals during the Middle Palaeolithic (Bisson, 2001).

Iron sulphide identification

Two forms of iron sulphide with different spark producing characteristics were used in this experiment to provide extended testing of the effects of adding MnO_2 to the tinder. The nodule with a radial structure performed much better with much more frequent sparks which also visually looked brighter in colour, indicating a higher temperature. To establish the nature of each iron sulphide nodule, structural analysis via Xray diffraction (XRD) and elemental composition using a portable X-ray fluorescence Analyzer (pXRF) was performed on one of the radial nodules and the pyrite nodule.

XRD analysis involved representative sub-samples being pre-crushed dry in a steel disc mill for 5 seconds. Fine crushing was carried out with a steel ball mill, using 7x 10mm diameter balls, for 5 minutes at 400 rpm to achieve a powder <50μm. Samples were backloaded into cavity holders as random powders. A Copper X-ray tube was used, with Ni filter to select for Cu k-α radiation. Scans covered the 2Theta range of 4-70°2θ. The XRD software used was "HighScore Plus" analysis software, quantifying by the Relative Intensity Ratio (RIR) method. With reference patterns from: International Centre for Diffraction Data, Powder Diffraction File-4+ Release 2023. A bulk compositional analysis was conducted with a Niton XL3 Xray-fluorescence analyser using the test all geo function. Average readings from 30 tests on each nodule are included in Tables 1 and 2, displaying elements considered as present, with readings more than 3 times the relative error (See Figures 3 and 4).

Element	ppm	Error (±2σ)
Si	13512.08	3455.236
Ca	7446.764	741.0639
Cl	800.4932	264.2148
Bal	188166.0829	7052.067419
S	363923.3806	13265.74
V	173.8687097	52.55193548
Cr	419.9993548	52.07516129
Fe	382160.3852	14764.76
Zn	483.8235484	55.44709677
As	245.7609677	32.11258065
Mo	54.54903226	8.708387097
Te	301.3080645	60.78741935
Cs	583.99	67.30870968
Pb	56.95	17.04

TABLE 1. AVERAGE BULK COMPOSITION OF RADIAL PYRITE NODULES DISPLAYING PRESENT ELEMENTS (WITH PPM MORE THAN 3 TIMES THE ERROR) FROM 30 RUNS USING PXRF.

Element	(ppm)	Error (±2σ)
Si	16668.128	3329.432667
Cl	967.4613333	252.805
Bal	206701.4929	6794.656129
S	369463.316	11426.262
Cr	415.4393548	89.12483871
Fe	359596.1613	11872.1929
Zn	579.936129	83.56967742

Mo	38.41193548	9.995806452
Te	314.131	62.88133333
Cs	583.399	69.12533333

TABLE 2. AVERAGE BULK COMPOSITION OF THE PYRITE NODULE DISPLAYING PRESENT ELEMENTS (WITH PPM MORE THAN 3 TIMES THE ERROR) FROM 30 RUNS USING PXRF.

The grooves in the radial pyrite nodules were measured with a digital vernier calliper and varied from 10.6- 21.6 mm wide, and approximately 8mm deep, which is narrower in width but around the same depth relative to the pyrite nodule.

Flint tools

Two small bifacially knapped flint stone tools, approximately 8-9 cm x 4.5- 5.5 cm wide were used throughout the experiments to strike the different iron sulphide nodules (See Figure 5). The flint tools were retouched between experimental runs to ensure a comparably sharp edge for each experimental run. The flint was acquired from Norfolk, UK, and can be described as medium to fine-grained.

MnO_2

The manganese dioxide (MnO_2) selected for use was commercially manufactured with over 96% purity and came as a fine powder. This is because manganese dioxide does not naturally occur in pure form and is found in combination with mineral and chemical impurities. Use of a chemical grade manganese dioxide thus allows for greater control of composition related to replication. No further preparation was carried out other than mixing with the tinder.

Results

There is a high correlation between the number of strikes and the time taken to achieve an ember when considering all the data (Spearmans $r = 0.98$, $p < 0.01$), which indicates a consistent speed of striking across the experiments (See Figure 6).

Comparing Iron sulphide nodules

As noted in the introduction, the two iron sulphide nodules were characterised by XRD and pXRF.

Results from XRD showed that the iron sulphide nodule with a radial structure was pyrite and the iron sulphide nodule lacking the radial structure was primarily pyrite with some marcasite present (See Figure 7).

The radial pyrite took significantly less time and number of strikes in comparison to the pyrite to form an ember, (Wilcoxon rank sum $p < 0.05$). The mean average of all pyrite was 48 seconds, SD. 38, and all radial pyrite 19 seconds, SD 11.9 (See Figures 8 and 9).

Radial pyrite experiments

There was a statistically significant difference between both the number of strikes used and the time taken to generate an ember between tinder and tinder with MnO_2 added when using the radial pyrite (Wilcoxon test $p < 0.05$). In both cases, however, the addition of MnO_2 made achieving an ember harder, not easier (See Figure 3, 10 and 11). The mean average number of strikes without MnO_2 was 71 (sd. 41.7), increasing to 112 (sd. 58) when MnO_2 was added. A similar pattern is observed with the average time taken to achieve an ember rising from 15 seconds (sd. 10) when no MnO_2 was present to 23.8 seconds (sd. 12) when MnO_2 was added.

For tinder without MnO_2 and using the radial pyrite, there was no correlation between either the run and the time taken to achieve an ember ($r = -0.265$, $p = 0.11$) or the run and number of strikes needed to achieve an ember ($r = -0.2$, $p = 0.21$). This general pattern was not altered by adding MnO_2 to the tinder, with no correlation between the run and the time taken to achieve an ember ($r = -0.1$, $p = 0.59$) or the number of strikes ($r = -0.13$, $p = 0.49$).

Pyrite experiments

For experiments using pyrite, there was no statistically significant difference in the time taken to achieve an ember between tinder with no MnO_2 and the tinder with MnO_2 (Wilcoxon test $p > 0.05$), or in the number of strikes (Wilcoxon test $p > 0.05$) (See Figures 12 and 13).

For tinder without MnO_2 and using pyrite, there was no correlation between either the run and the time taken to achieve an ember ($r = 0.04$, $p = 0.79$), or the run and number of strikes needed to achieve an ember ($r = 0.01$, $p = 0.94$). This general pattern was not altered by adding MnO_2 to the tinder, with no correlation between the run and the time taken to achieve an ember ($r = -0.19$, $p = 0.25$), or the number of strikes ($r = -0.19$, $p = 0.26$).

Discussion

Our results show that for iron sulphide and flint strike-a-light technology using horse hoof fungus as a tinder, the addition of MnO_2 confers no advantages in the formation of an ember.

While there was some variability introduced with the use of two flint tools which were retouched throughout, and the use of more than one type of iron sulphide nodule, the sample sizes are considered large enough for us to be confident in our findings.

Our findings provide contrast to those of Sorensen (2020) who claimed that the addition of manganese dioxide to tinder improved its ability to capture sparks, regardless of tinder type. Our varying results could be the result of different ratios of tinder to MnO_2. Sorensen (2020) used a 1:3 ratio of MnO_2 to tinder, while in this research we used a 1:1 ratio of tinder and

MnO_2. It is possible that the MnO_2 ratio we used was too high and that in some way it was preventing the sparks from finding the tinder. Sparks would often fall onto 'black' areas and fail to ignite, indicating that high concentrations of manganese dioxide or poor mixing of the tinder and MnO_2 were having an effect. It could also be that we had half as much tinder present in the condition with MnO_2 present, 4 grams compared to 8 grams. We do not, however, think this would have had a strong effect as 4 grams still provided the same surface area when laid out to ensure sparks always landed on the tinder.

Given that MnO_2 is listed as an oxidising agent with thermal decomposition beginning at 530 degrees C, a more probable answer is that the sparks produced were not hot enough to initiate oxidation and thermal decomposition. The failure of Langley and Needham (2021) to ignite MnO_2 with a modern ferrocerium rod indicates, however, that high temperatures alone are insufficient and that a more sustained energy is needed to initiate the thermal decomposition and release of oxygen. This is achieved in the experimental work of Hayes et al. (2016) as they use a heat pad which provides a sustained heat source. It seems that the spark from strike-a-light technology is not hot enough for long enough to cause the thermal decomposition of MnO_2 and the subsequent release of Oxygen capable of aiding combustion.

Once again, in contrast to the findings of Sorensen (2020), our experiments did not show changes in the time taken for an ember to form as the experiments progressed with no correlations between time or strikes needed to form an ember and the experimental run. Sorensen (2020) found that in three types of tinder (tinder fungus, black poplar, and creeping thistle), all tinders became more effective in the capture of sparks over time. This was attributed to the deposition of a thin layer of sulfuric iron dust (Sorensen, 2020). Throughout our experiment runs, however, the amount of tinder was 'topped up' incrementally, which will have decreased the amount of iron sulphide powder on the top of the spark-capturing area.

Conclusions

Our experiments support the work of Langley and Needham (2021) and show that the addition of MnO_2 to horse hoof fungus tinder does not aid in combustion when using iron sulphide and flint strike-a-light technology. Our experiments also show that the presence of marcasite in the iron sulphide nodule is less important than the overall structure of the nodule in terms of successful use as strike-a-light, although more work would need to be done to explore this.

Our results suggest that Neanderthals were not gathering Mn02 to aid in the initial and most challenging stages of fire making, that of ember production. The possibility remains that they were using it to help with later stages of fire lighting. Future experimentation should look at what environmental conditions make the use of MnO_2 in fire lighting most advantageous. Could it be that the benefits are much more significant in wetter or colder conditions when fire is always more difficult to light and maintain?

Keywords fire

Country United Kingdom

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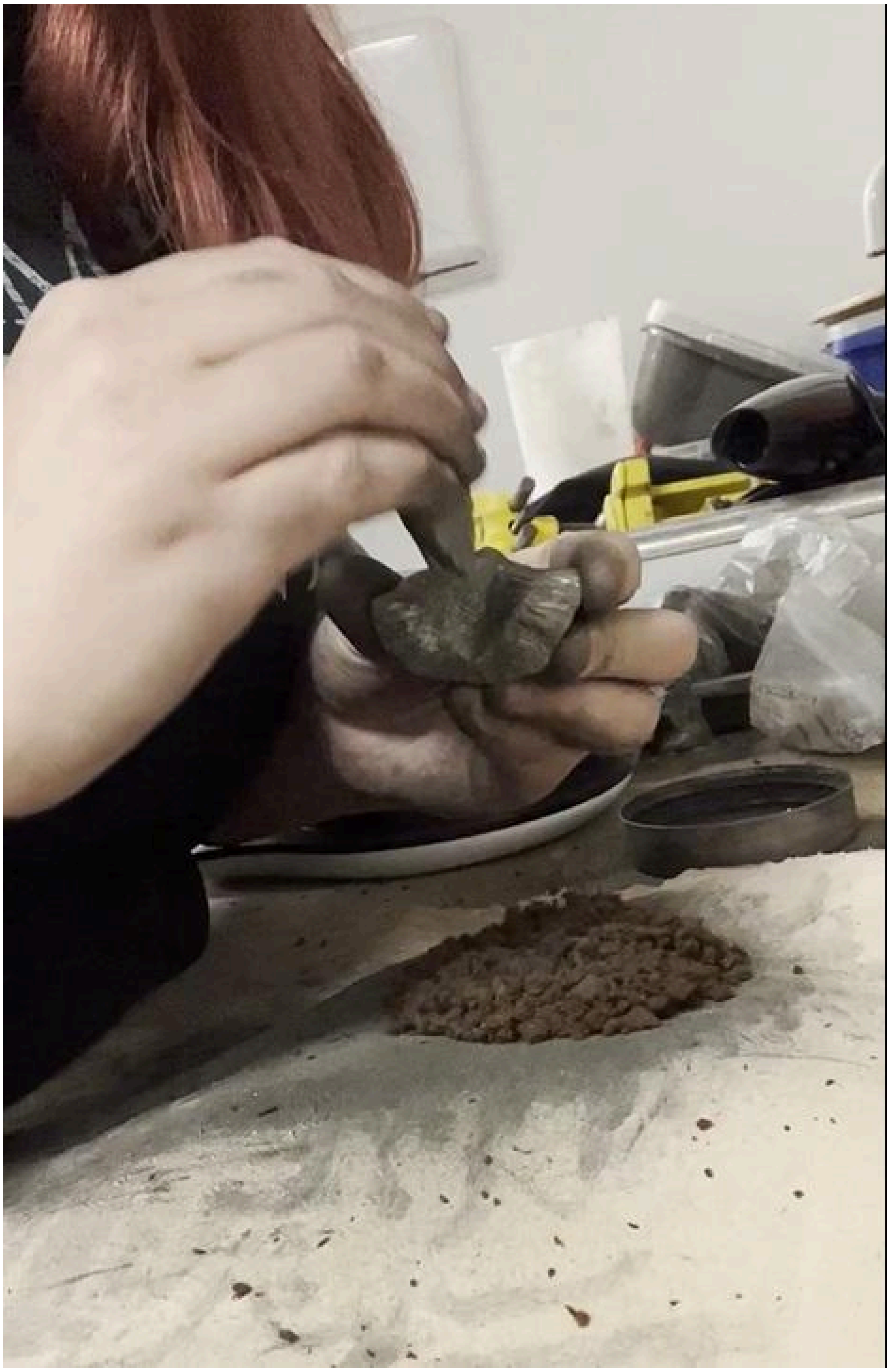

FIG 1. PHOTOGRAPH OF THE EXPERIMENTAL SETUP. PHOTO BY CHARLOTTE CLARKE.

FIG 2A. PHOTOGRAPH OF THE FLINT ‘SCRAPER’ USED. PHOTO BY CHARLOTTE CLARKE.

FIG 2B. DRIED HOOF FUNGUS PRIOR TO PROCESSING INTO TINDER. PHOTO BY CHARLOTTE CLARKE.

FIG 2C. DRIED HOOF FUNGUS AFTER PROCESSING INTO TINDER. PHOTO BY CHARLOTTE CLARKE.

FIG 3. RADIAL PYRITE NODULE. PHOTO BY CHARLOTTE CLARKE.

FIG 4. PYRITE NODULE. PHOTO BY CHARLOTTE CLARKE.

FIG 5. EXPERIMENTAL REPLICA BIFACIALLY FLAKED FLINT TOOLS. PHOTO BY CHARLOTTE CLARKE.

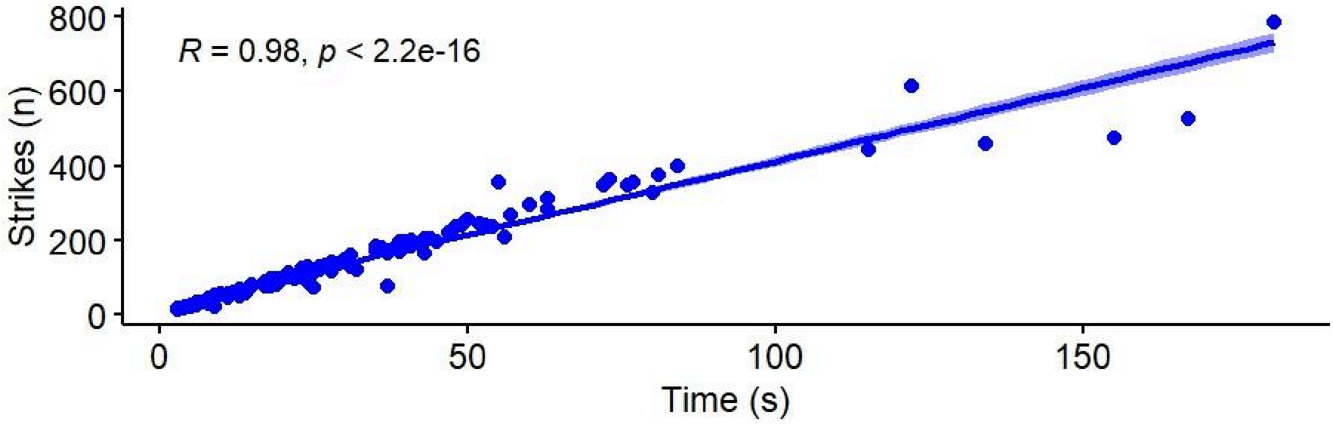

FIG 6. CORRELATION BETWEEN STRIKES AND TIME TAKEN TO FORM AN EMBER IN ALL EXPERIMENTAL CONDITIONS. GRAPH BY CHRISTOPHER SCOTT.

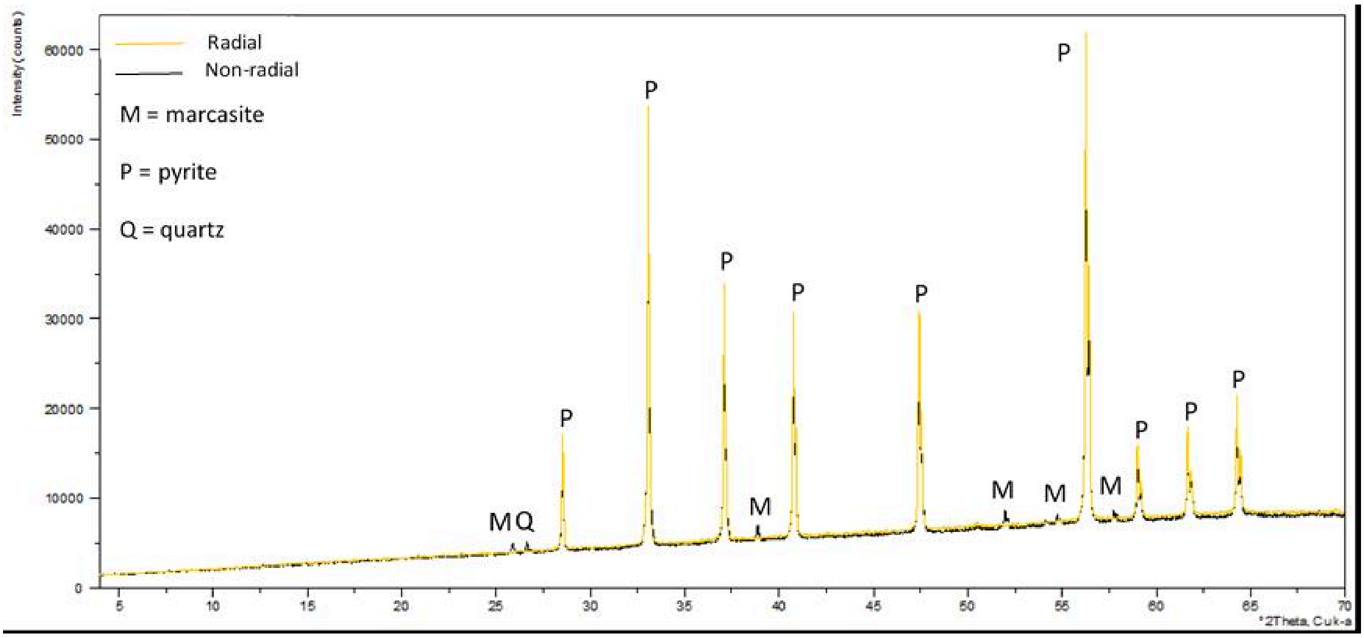

FIG 7. XRD RESULTS FOR THE IRON SULPHIDE NODULES USED. GRAPH BY JAMES UTLEY.

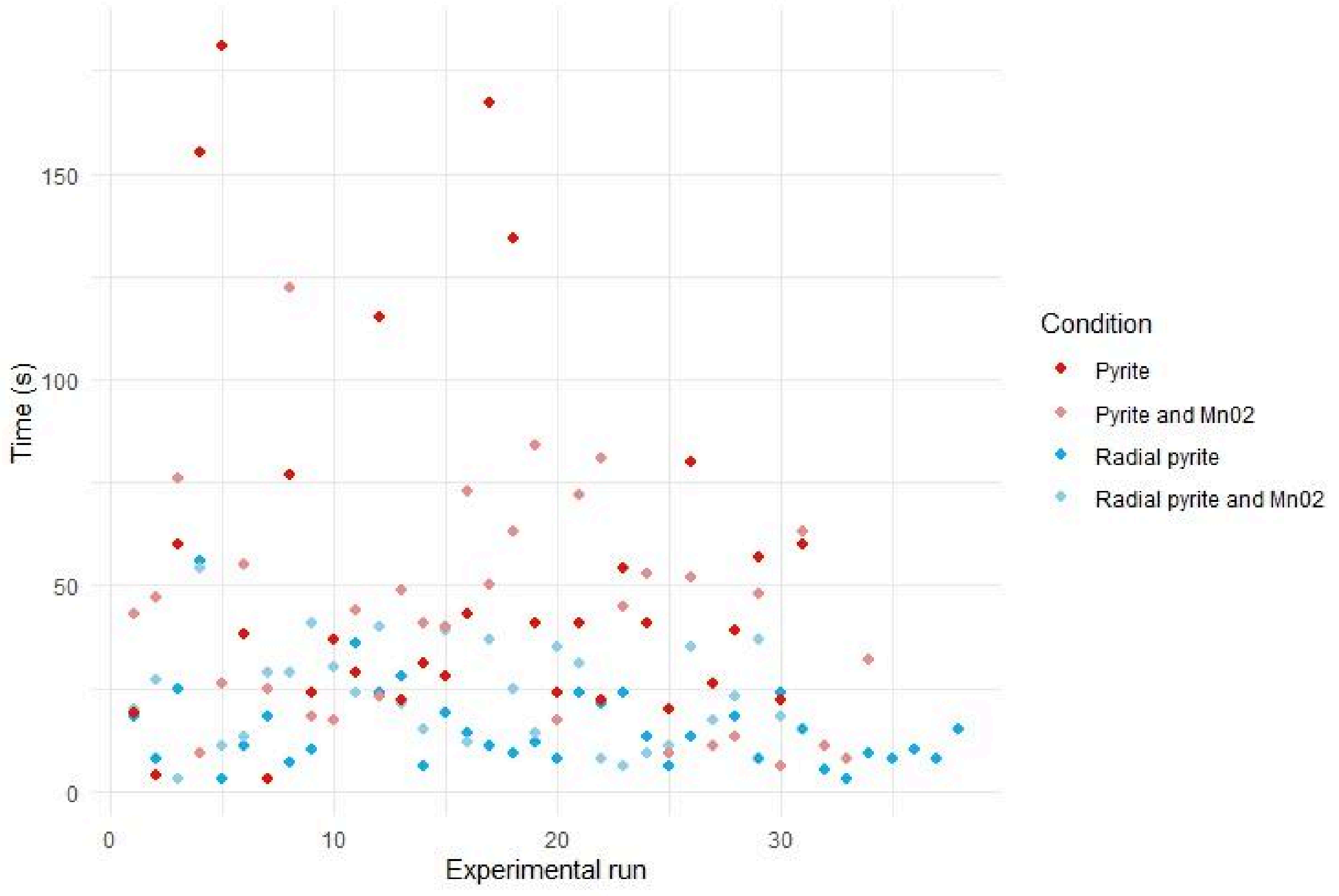

FIG 8. TIME TAKEN TO FORM AN EMBER FOR ALL EXPERIMENTAL CONDITIONS. GRAPH BY CHRISTOPHER SCOTT.

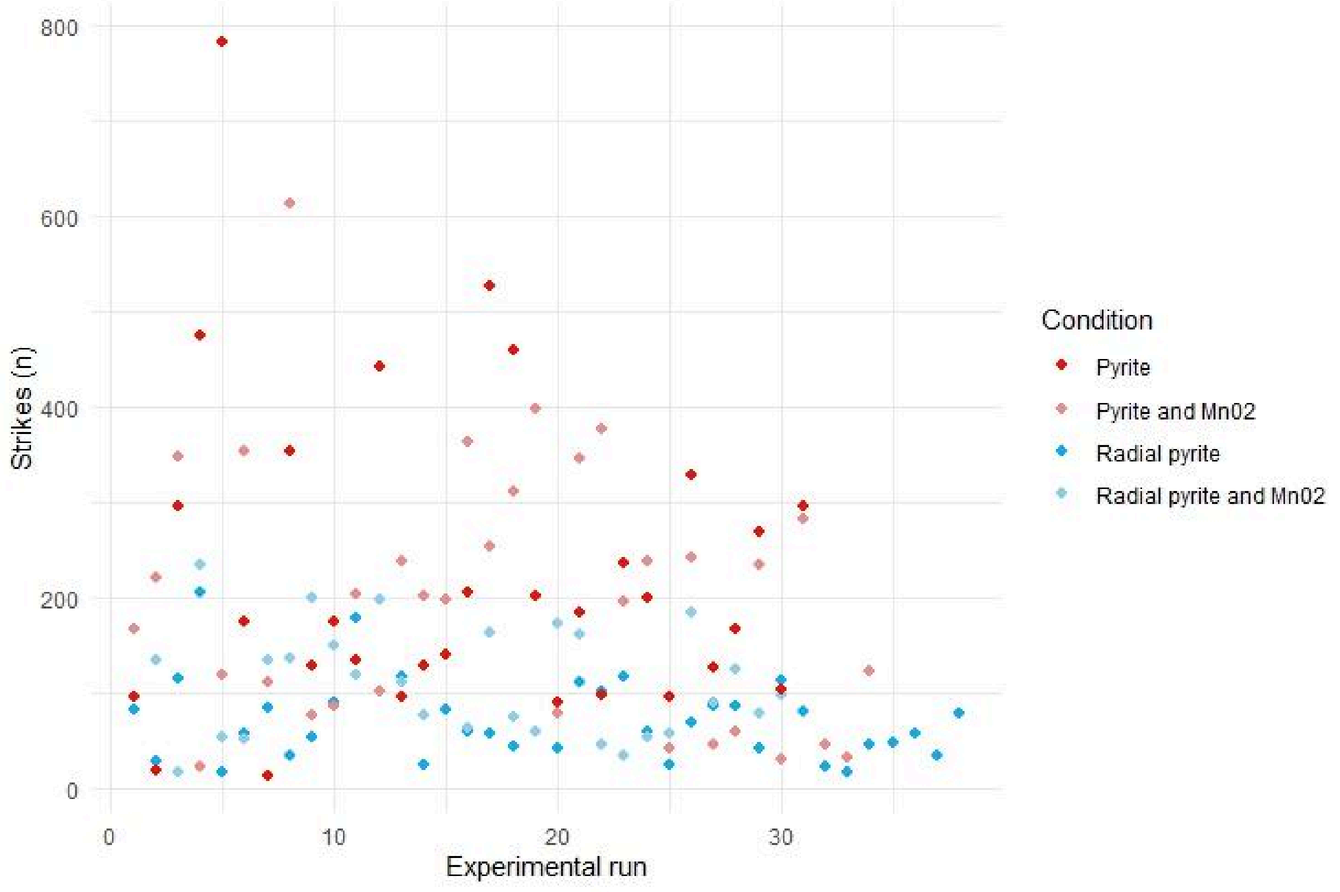

FIG 9. STRIKES NEEDED FOR AN EMBER TO FORM FOR ALL EXPERIMENTAL CONDITIONS. GRAPH BY CHRISTOPHER SCOTT.

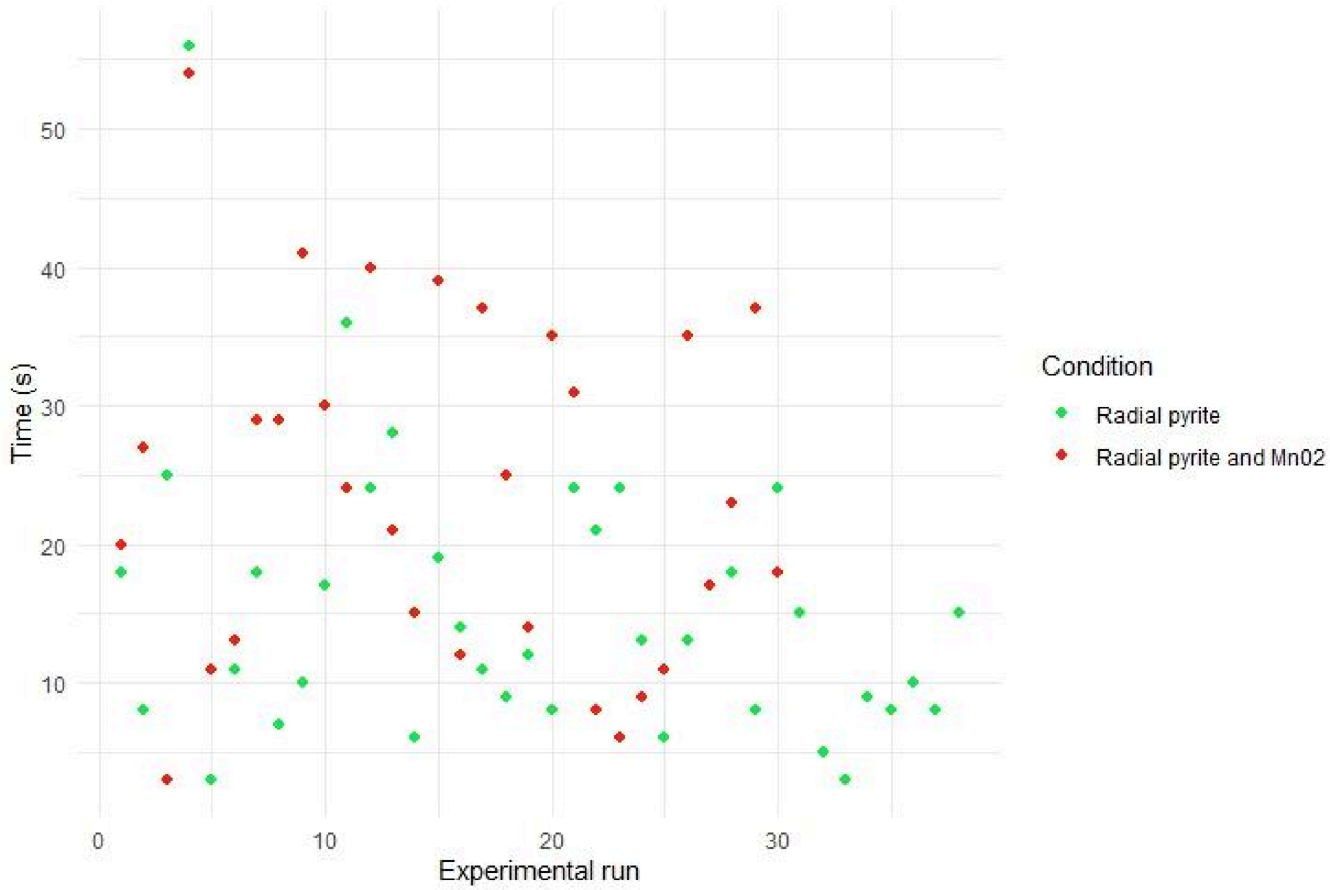

FIG 10. TIME TAKEN FOR EMBER FORMATION USING RADIAL PYRITE WITH AND WITHOUT THE ADDITION OF MNO2. GRAPH BY CHRISTOPHER SCOTT.

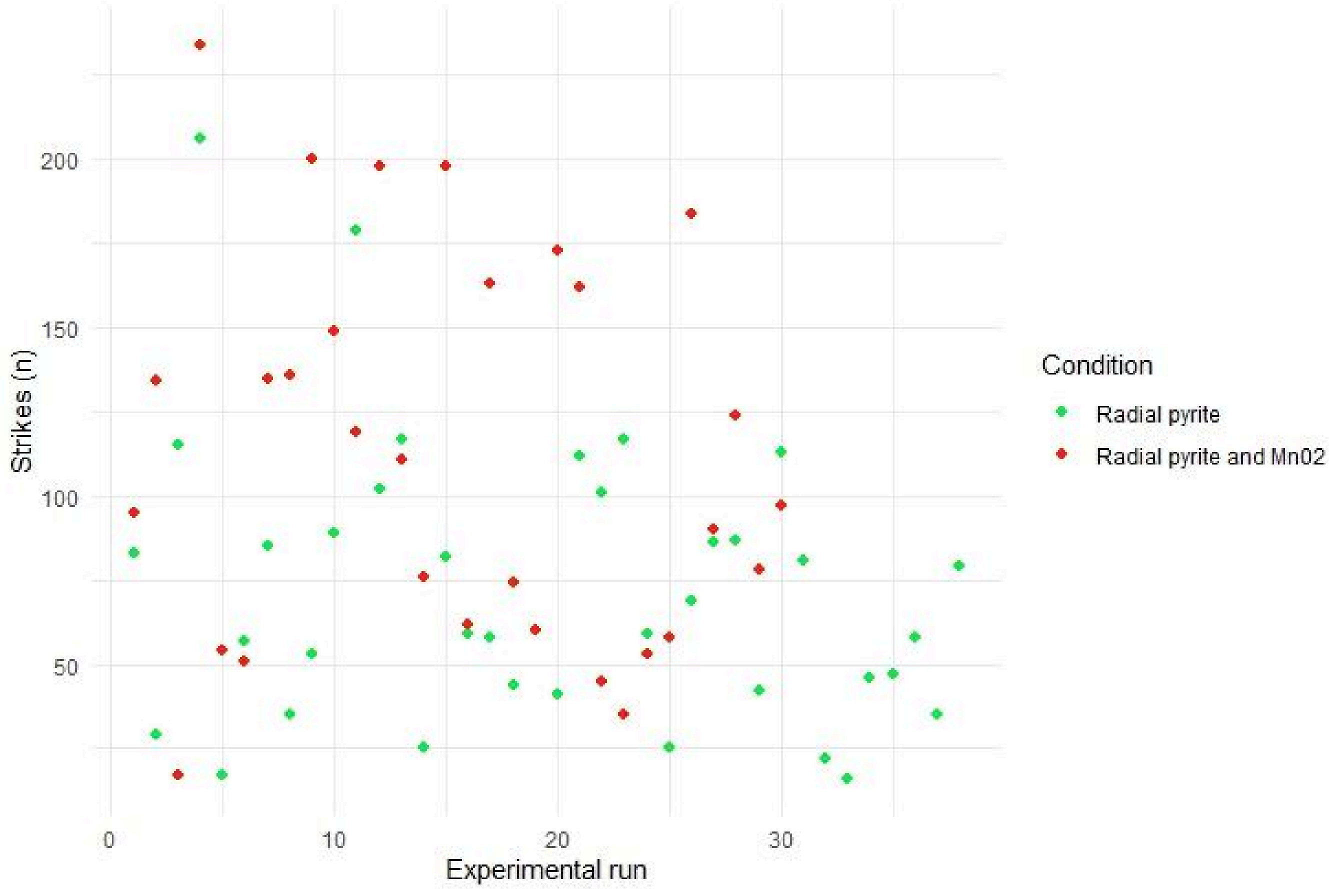

FIG 11. STRIKES NEEDED FOR EMBER FORMATION USING RADIAL PYRITE WITH AND WITHOUT THE ADDITION OF MNO2. GRAPH BY CHRISTOPHER SCOTT.

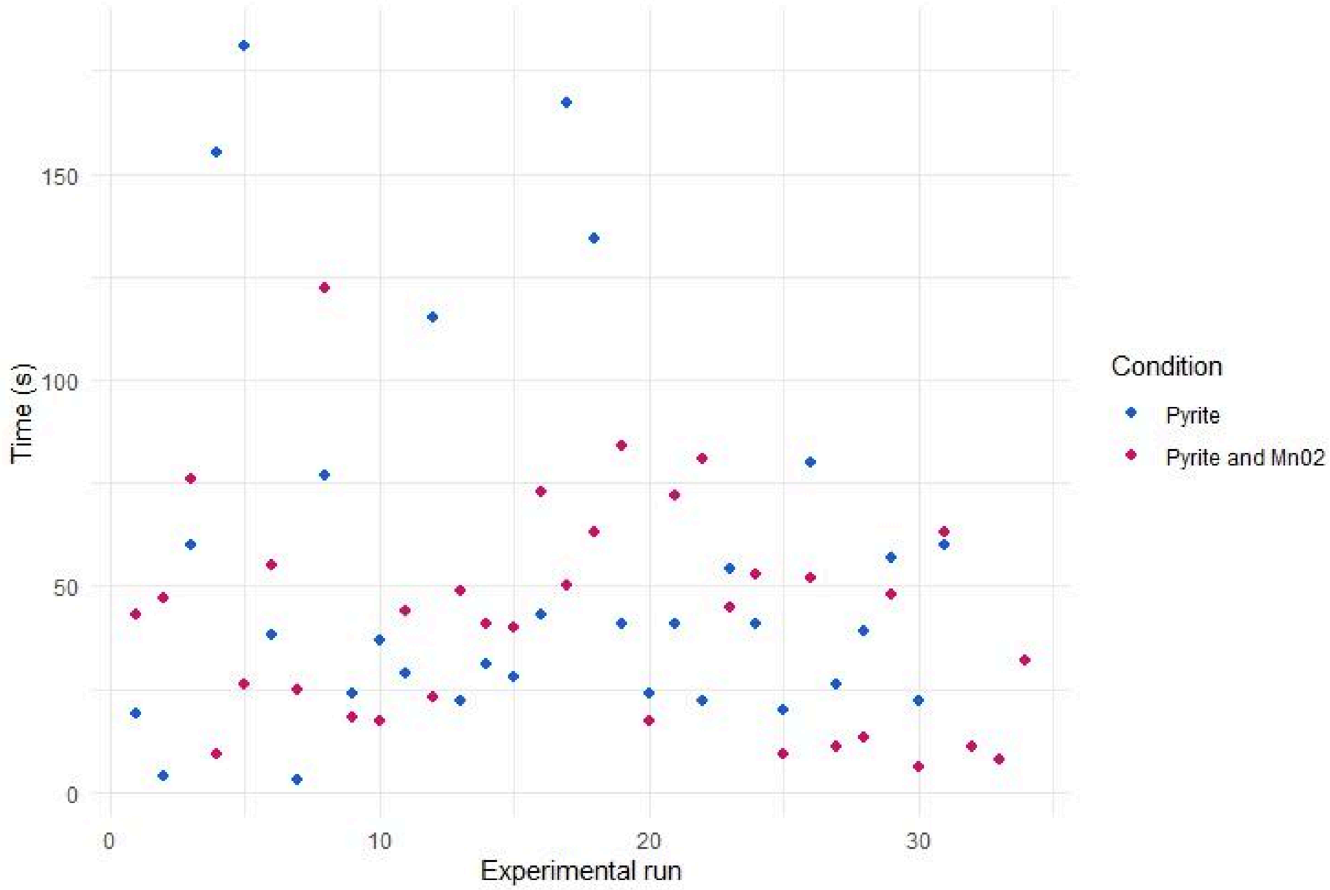

FIG 12. TIME TAKEN FOR EMBER FORMATION USING PYRITE WITH AND WITHOUT THE ADDITION OF MNO2. GRAPH BY CHRISTOPHER SCOTT.

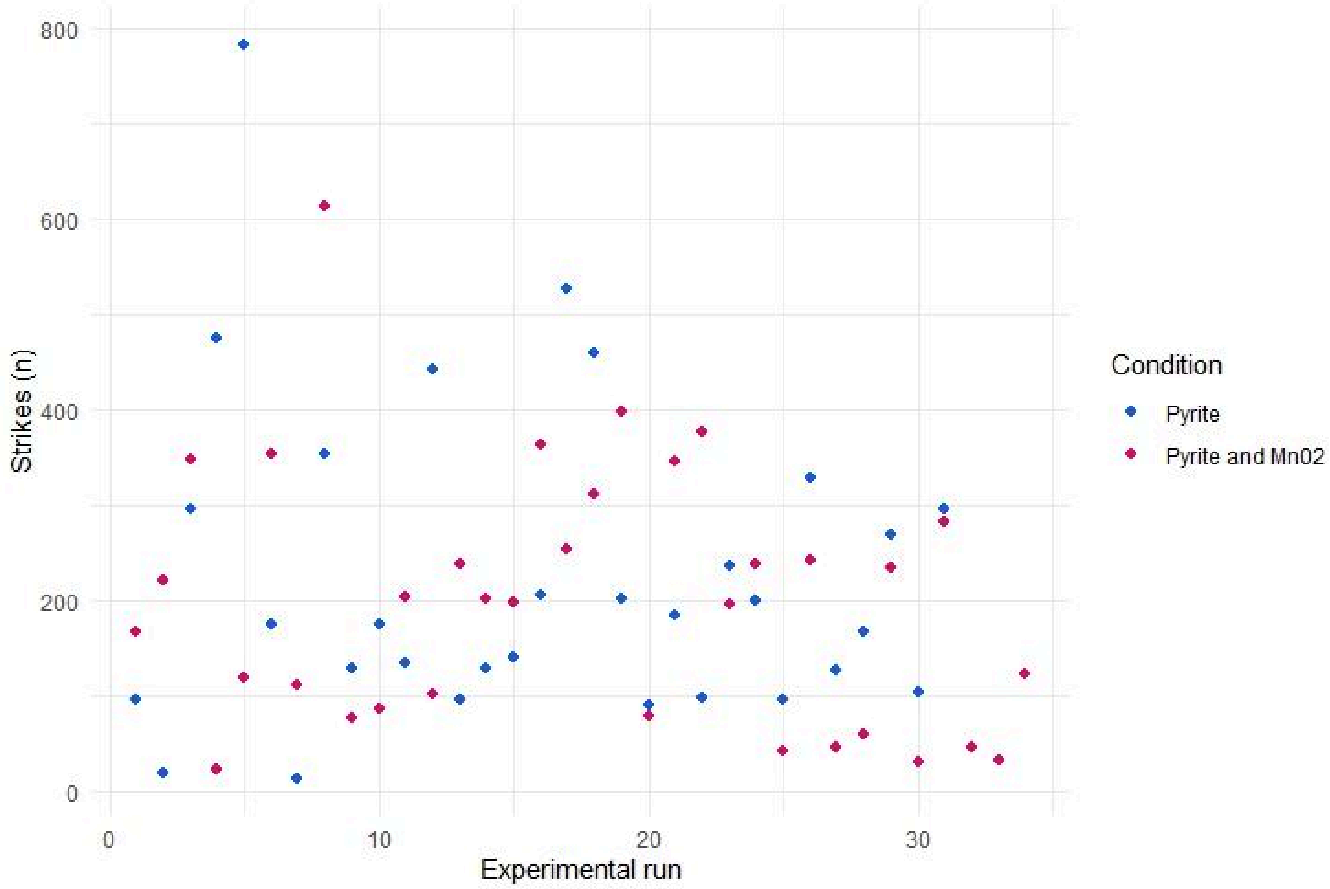

FIG 13. STRIKES NEEDED FOR EMBER FORMATION USING PYRITE WITH AND WITHOUT THE ADDITION OF MNO2. GRAPH BY CHRISTOPHER SCOTT.