Characterising Chumash Rock Art Pigments Using Portable XRF Technology

by

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Abstract

The aims in this examination were to explore the viability of using XRF technology to gather information on raw materials and preparation techniques used, to differentiate between pigments and painting events, and to discuss the social implications of this information. Five Chumash rock art sites in the Windwolves Preserve, California were examined using X-Ray fluorescence analysis in order to characterise the range of pigments used. Most of the pigments were red in colour but black, grey, blue and white pigments were also included in the study. The findings showed that this technique is viable, particularly as a quick method of identifying different pigments and painting events, and provides information from which it is possible to infer preparation techniques.

The results showed that multiple pigments were used within each rock art panel and within individual elements. It is also possible to infer from the data that some pigments were directly applied raw ochres and some had been processed, thus indicating different techniques being applied to the same panel. As such it is likely that rock art sites were revisited with rock art being added to at various times indicating that it may have been much less exclusive than has previously been suggested. This project also opened up a number of questions relating to rock art research in terms of the identification of pigment binders from the data and the possibility of utilising other analytical techniques in order to glean more information.

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INTRODUCTION

South Central California is home to many fine examples of rock art, the exact nature, purpose and chronology of which is not known with any certainty, and as such is the subject of great debate (Blackburn 1977; Hyder 1989; Hyder and Oliver 1986; Insoll 2012; Lee and Hyder 1991; McCall 2007; Quinlan 2000; Robinson 2010; Whitley 1987).

Figure 1. An example of California rock art at Three Springs in the Windwolves Preserve

The work presented in this thesis builds on the many analyses already performed on California rock art. These analyses have largely focused on typology (Blackburn, T. 1977; Lee, G. and Hyder, 1991) and symbolism (Keyser and Whitley 2006) within rock art, and have used interpretations of form to establish chronologies (Hyder and Oliver 1986) and discuss the significance and social role of rock art.

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This project will add a new perspective to the current debate by using portable X-Ray Fluorescence (pXRF) techniques to characterise the chemical composition of pigments used in Chumash rock art in the Windwolves Preserve in South Central California. Portable XRF is a method which uses temporary irradiation by X-Rays to identify the chemical elements that make up a material. Portable XRF has developed from lab based XRF devices but does not need the sample preparation that is required by lab based instruments. The portable devices can therefore be used *in situ* without causing any damage to the material being examined. Such non-destructive analysis of *in situ* rock art has not previously been performed in the Windwolves Preserve or in South Central California, and has only been applied to a small number of rock art sites globally. The application of portable XRF technology will provide information about the chemical composition of materials used in the rock art elements at each site.

There are two main aims in this project. The primary aim is to establish a method for the use of portable XRF to examine *in situ* rock art, and the secondary aim is to apply this method to five rock art sites in the Windwolves Preserve in order to contribute to the existing debate about the social significance of Chumash rock art.

The Current Debate

There is currently much discussion about the nature, purpose and production of Californian rock art (McCall, G.S. 2007; Insoll, T. 2012) and specifically Chumash rock art (Whitley, D. 1987; Robinson, D.W. 2010; Blackburn, T. 1977; Lee, G. and Hyder, 1991; Quinlan, A.R. 2000). Many of the arguments regarding this focus upon interpretations of iconography to determine chronology, exclusivity and potential links to states induced by the use of hallucinogens (Blackburn, T. 1977 p93).

In Whitley's (1987) earlier work he states that rock art is a product of ritual and ceremony and played a part in the socio-religious lives of its creators and users (Whitley 1987:159). In particular he argues that California rock art, including that of the Chumash is ceremonial in nature with restricted iconography (Whitley 1987:159). He argues that this was largely restricted to a small number of individuals but in some cases may have been in public view, or produced during rituals that involved members of the public.

Shortly after this his view changed and Whitley (1998; Keyser and Whitley 2006) adopted a view that rock art was produced by Shamans or in 'Shamanistic' rituals performed by other individuals (Insoll 2012:311; Keyser and Whitley 2006:5). This view is largely based on ethnographic examples of rock art relating to visionary imagery (Whitley 1998:24). According to Whitley (1998) rock art preserves supernatural experiences and depicts imagery from 'hallucinations of trance' (Whitley 1998:22). Such trance states would be experienced by Shamans or by people involved in Shamanistic rituals such as life-crisis rituals, vision quests and both male and female puberty rites (Whitley 1998:24). Whitley (1998) argues that the depiction of visionary imagery is the 'unifying characteristic of Native Californian rock art' (Whitley 1998:25). He is also part of a group including Blackburn (1977) and Lee (1991) who argue that some rock art production was likely to be influenced by the use of *Datura inoxia* which is known to be a hallucinogen (Blackburn 1977:93; Lee 1991: page).

McCall (2007) criticises the Shamanistic view of rock art as he feels it relies upon the view that Shamanism is universal and unvarying (McCall 2007: 224). Quinlan (2000) however argues that the ethnographic examples on which Whitley's (1998) arguments are based do not sufficiently support the idea that California rock art was only produced by Shamans, given that most of the few Yokut natives interviewed stated that this was not the case (Quinlan 2000:95-6). Hyder (1989) questions the view that rock art was ceremonial or private in nature. He argues that rock art occurs at a wide variety of sites and has a significant association with occupation sites and that there should be further investigation in public rock art (Hyder 1989:15). In addition to this Hyder and Oliver (1986) challenge the widely held view that rock art is no older than 1000 years old. Hyder and Oliver (1986) propose that Chumash rock art is at least 5000 years old and have established different styles of rock art which they have used to establish a chronology in particular rock art panels. These styles overlay one another indicated that they were produced at different times at Painted Cave (Hyder and Oliver 1986:88). Some of these styles have been identified at other sites and are associated with archaeological materials which known dates (Hyder and Oliver 1986:92).

Robinson (2006; 2010a; 2010b; 2011) challenges the view that rock art was private and Shamanistic in nature. He observes that there is a close relationship between rock art and bedrock mortar stations (BRMs), which were used for the processing of acorns as well as other places involved in ordinary activities.

Figure 2. A bedrock rock mortar station in the Pinwheel bedrock mortar complex overlooking the Windwolves Preserve

These BRMs were seasonal centres of acorn processing which would provide staple food for most of the year. BRMs are considered to have been women's work spaces, but all members of the community would contribute to the gathering of acorns before the processing began. Robinson (2010b) therefore argues that most of the community would have been aware of the rock art at these sites, rather than it being exclusive to a restricted group of people (Robinson 2010b:810).

Robinson (2010) argues that rock art is found in the sphere of day to day activities and would therefore be publicly accessible (Robinson 2010b:793). He argues that these sites are conspicuous on internal route ways and form a type of ideological media for communication within a community (Robinson 2010b:811). This view contrasts starkly with the idea that rock

art was a restricted ritual phenomenon formed during a particular event, and suggests rather than rock art was more involved in social practices.

Little native knowledge is available about Chumash rock art tradition and we are therefore dependent on archaeological evidence (Quinlan 2000: 96). This archaeological material must be examined carefully in order to attempt to draw any conclusions about the nature of Chumash rock art and its relationship to Chumash communities. In order to contribute to such an examination and add to our knowledge about this rock art tradition I will examine archaeological pigments by analysing *in situ* readings taken from Chumash rock art from five sites on the Windwolves Preserve, which are described below.

Examining rock art in the Windwolves Preserve

Figure 3. A view over the Windwolves Preserve from Pinwheel looking North

In order to accomplish the aims of this research, five sites on the Wind Wolves Preserve in South Central California (fig. 4) were visited with a portable XRF and readings were taken from

the rock art elements within them. The Preserve covers 100,000 acres and is positioned in the San Emidgio Hills (fig. 5).

Figure 4. Map showing the location of the Windwolves Preserve within California (www.thefluiddruid.com)
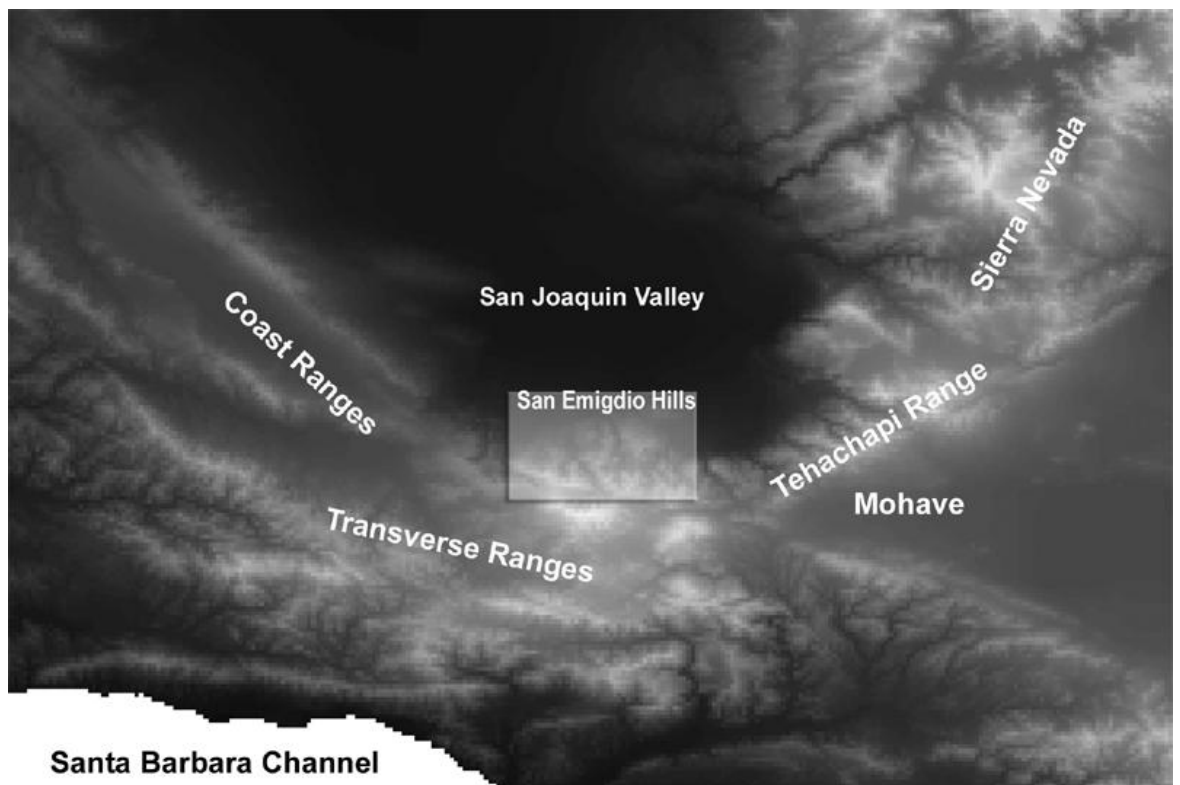
Figure 5. Map showing the mountain ranges surrounding the San Emigdio Hills (Robinson, 2008)

These nestle in amongst the Coastal and Tehachapi ranges and sit above the San Joaquin Valley (Robinson 2009). Within the preserve are a variety of sites including BRM sites and lithic scatters as well as the ethno historically known settlements of Tecuya, Tashlipun and Matapuan (Robinson 2010a: 278). Seventeen pictograph sites have been discovered within the Windwolves Preserve but they are not all included in this project. The five sites which are the focus of this project are spread across the preserve as shown in the map below.
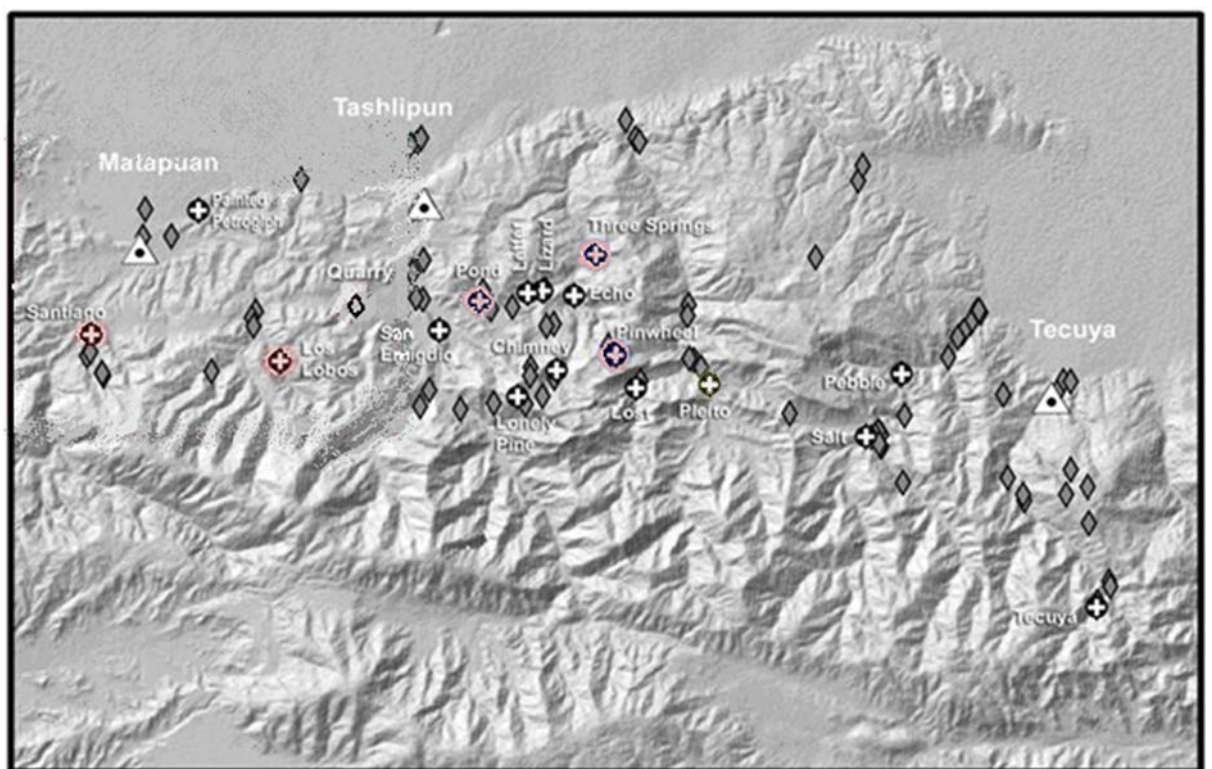
Figure 6. Map showing the relative positions of sites within the Windwolves Preserve

The sites selected for this study are Pinwheel, Pond, Three Springs, Los Lobos and Santiago. Each of them was selected for this analysis because it has been excavated as part of the Enculturating Environments Project. During these excavations a range of archaeological artefacts indicating different types of activity were found, as is detailed in the following sections. These include Bedrock Mortars, or BRMs, which were used predominantly by women to pound acorns (Robinson 2010b:802). At each site is at least one rock art panel. These contain rock art elements which are mostly monochrome red or black, although some sites also display polychrome elements. These elements take a number of forms which include

zoomorphic and anthropomorphic images, linear, curvilinear, finger smears and brushed lines in red, black, blue, grey or white.

Figure 7. Examples of rock art elements from the sites examined. Clockwise from top left; black linear aquatic motif, complex polychrome 'Blueboy', red fine linear aquatic motif, complex red curvilinear 'Pinwheel' motif, black and red figure eight motif with red dots.

Pinwheel

Figure 8 View of Pinwheel Cave from its associated BRM station (Robinson 2008:8)

Fig 8 shows Pinwheel cave as viewed from its associated BRM station. It is located downhill from its associated BRM complex which overlooks the central part of the preserve. Of all the sites chosen for this study, Pinwheel cave is the furthest from its BRM stations. The rock art elements at Pinwheel are mostly on the walls and roof of the cave. Three further elements can be found at Pinwheel's second locus, in a panel on a rock next to the cave. The elements within the cave include a Pinwheel motif, after which the site was named (Robinson 2006), an anthropomorphic figure, circle, dots and red fragments and all are red in colour. Most of the cave geology consists of a varied conglomerate rock (Robinson 2006). This rock may prove to be problematic when attempting to assess fluctuations in particular chemicals in the applied pigments as it may be difficult to determine which fluctuations are in the rock and which are in the pigment material.

At the associated BRM site of Pinwheel Cave are nine BRM stations with 19 BRMs and at least 12 cupules. Excavations also uncovered debitage, bone, burnt bone, lithic tools (flakes), shells, beads (shell and glass), points and some fire affected rock (Robinson *et al.* 2008: 9). Investigation of the cave site revealed a possible sandstone hopper, as well as fibrous

materials crammed into hollows in the ceiling, which may be chews or quids (Robinson *et al.* 2010a:10).

Pond

Figure 9. View of Pond Window-box from nearby Frog Rock.

The site of Pond is shown in fig. 9 and rests between San Emigdio and Pleitito Canyons and gets its name from the sag pond which is visible beyond the rocky outcrop in the picture above (Robinson *et al.* 2008). The site includes 5 pictograph locations, and up to 100 BRMs. During excavation work at Pond dozens of cupules, an extensive midden with lithics and groundstone, manos, pestles, a Tembler chert bifacial point and a Monterey chert scraper were found. It was a major food-processing site, possibly for the inhabitants of Tashlipun (Robinson *et al.* 2008:8).

The rock art here is not particularly distinct and occurs on three panels called the 'Window box', 'Boulder' and 'Alcove'. The 'Window box' is the small cave on top of the highest point of the outcrop shown in fig. 9, and the alcove is below this. Most of the pigments at Pond are red in colour but the element in the alcove appears to have a white pigment within it.

Three springs

Figure 10. View from Three Springs wetland from BRM

Three Springs is located on a terrace high above Pleitito creek next to a wetland area which is shown toward the bottom of fig. 10 and is named after the three converging springs at the site (Robinson *et al.* 2008). On the terrace are 5 stations with 36 BRMs (Robinson *et al.* 2008:24). Excavations have revealed midden material which includes local basalt and Tembler chert flakes and cores, burnt bone, anadonta flecks, fragments of stone bowls and lithic debitage (Robinson *et al.* 2008).

There are two rock art loci here. The first of these is located in a raised cave close to the BRMs and contains polychrome rock art. This is more complex than the rock art seen at the other four sites involved in this study. There are the two panels within the main cave and another element in the small cave underneath one of the BRMs at the site (pictured below). There are a variety of forms of rock art within the cave at Three Springs including anthropomorphic and two zoomorphic figures, aquatic elements, radial bursts and red smears and linear elements. These include a 'birdman' which is called 'Blueboy' for the purposes of this project. This element displays four different colours of pigment including blue, black, red and grey. There is

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another bird figure which consists of black linear markings and a black zigzag with red dots (Robinson *et al.* 2008:24).

Figure 11. BRM station at Three Springs

Figure 12. Cave at Three Springs containing polychrome rock art

Los Lobos

Los Lobos is located between the excavated settlement of Tashlipun and the area containing the historically recorded settlement of Matapuan which has not yet been specifically identified archaeologically (Robinson 2010a:798). At this site with BRMs and midden, excavations found numerous projectile points, shell beads, burnt faunal remains and a complete pestle (Robinson, 2009). There are two rock shelters, shelter A and shelter B which are shown in fig. 13 (Robinson *et al.* 2009: 7). There are eleven BRM stations which have 26 BRMs between them and are located at the top of the slope on which the rock shelters rest. There are also 29 cupules at the site (Robinson *et al.* 2009:5).

Figure 13. Overview of Los Lobos showing the two shelters (Robinson *et al.* 2009:7)

Both rock shelters contain a number of rock art elements in both red and black. Shelter A is shown in fig. 14 and is sits toward the top of the slope, and within it are elements including 5 finger-smears in red, a red spoke element, red dots, red curvilinear elements and a black linear grid. At the lower Shelter B there are fewer elements, including two black radial spoke elements, one black linear element and a red oval (Robinson *et al.* 2009:6)

Figure 14. Shelter A at Los Lobos (Robinson 2010a)

Santiago

Santiago is located on the eastern side of Santiago Creek at the western boundary of the Preserve. There are two rock art loci at Santiago which are the Monolith and Lonely Boulder, shown in figs 15 and 16. Each locus has two panels. The Monolith has nineteen elements between its two panels and most of these use red pigments although there are some black pigments here. The rock art elements here are largely linear or curvilinear.

Figure 15. Santiago – The Monolith   **Figure 16.Santiago – Lonely Boulder**

Figure 17. Santiago Monolith rock shelter, containing most of the rock art elements at this site.

Excavations next to the Monolith at Santiago revealed large numbers of chert flakes, projectile points and beads (including glass beads), and what may be a shell pendant. Within two metres of the main rock art panel here is a BRM at which a pestle was found in one of the mortars. The site includes 13 BRM stations and 49 BRMS (Robinson 2006:204). Four of the BRM stations are located very close to the rock art shelter.

The rock art elements from each of these sites will be analysed using portable XRF to examine the pigments used. I will then discuss the significance of the results of this analysis in terms of the usefulness of this approach, techniques of rock art production and the people involved in this, as well as the significance of rock art in Chumash society.

Primary aim – Establishment of a methodology

As previously stated the primary aim is to establish a method for examining *in situ* rock art in order to examine rock art within the Windwolves Preserve and to inform future researchers who wish to perform such an analysis elsewhere. To do this I will examine pXRF data which I have gathered from five sites within the Windwolves Preserve, and assess the scope of this technique in terms of chemical characterisation by addressing the following research questions:

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- Can XRF be used to effectively characterise the chemical composition of *in situ* rock art pigments?
- Can these pigments be differentiated from one another using this method?
- Can this method be used to infer pigment preparation techniques?
- Can XRF data be used to establish a chronology for rock art?

Can XRF be used to effectively characterise the chemical composition of *in situ* rock art pigments?

I will determine the extent to which pXRF can be used to reliably establish the chemical composition of pigments used in *in situ* rock art at the five sites chosen for this study, by identifying their main chemical constituents, and by examining the proportions any trace elements which are detected. These will then be used to establish a specific chemical fingerprint for each element which can be used to identify each pigment used in the rock art panels. In order to establish a method for doing this I will of course draw on the experience of other researchers who have used XRF to examine archaeological materials as outlined in the next chapter.

Can these pigments be differentiated from one another using this method?

Once the chemical composition of each pigment is established these will be compared in order to determine how reliably and clearly pigments can be differentiated from one another. Pigments will be compared within each panel, site and if possible between sites. Doing this will allow the identification of differences and consistencies in materials used across the study area, and to determine the number of painting events at each site.

Can this method be used to infer pigment preparation techniques?

There is also a question of the technology used to process raw materials in order to apply them to the rock. As mentioned above, the ability to identify source material would allow us to infer treatment given to ochre in order to achieve its final colour. For example goethite, which is a yellow iron compound, has a different composition to haematite but will adopt the same colour if it is sufficiently heated (Gialanella *et al.* 2011:9).

Some pigments may have been applied directly, almost like using a piece of chalk to apply a pattern, whereas others will have been ground into a powder and then mixed with a binder. This binder is likely to consist of cucumber extract or blood (Scott and Hyder 1993:157-158). Any ingredients added to the ochre will of course affect the resultant spectrum, as will grinding and heating. This study will examine how far it is possible to infer such preparation techniques using XRF data.

Can XRF data be used to establish a chronology for rock art?

Portable XRF examination of rock art has the potential to contribute to chronologies in two ways. Firstly it can be used to expand on existing chronologies. Some rock art elements or pigments can be seen to overlay one another indicating that one was applied at a later date as was observed by Hyder (1989) at Painted Cave. Some rock art chronologies have been established by looking at different forms of rock art within a panel (Hyder, W.D. and Oliver 1986). By identifying elements that share their chemical composition with those already established in a chronology a common production period for these elements can be inferred.

In addition to this, a number of raw ochre samples have been excavated in the Windwolves Preserve. As these are from known archaeological contexts any parallels drawn between their chemical composition and that of in situ rock art would indicate a date for the rock art. During the course of this project I will assess the extent to which pXRF can be used to link rock art to such existing chronologies.

Second aim – pXRF applied to regional questions

The second aim is to use this method to examine the chemical composition of the pigments used in Chumash rock art in the Windwolves Preserve. The application of XRF analysis to sites in the Windwolves Preserve will be used to establish the number of pigments used within each rock art panel and to identify the chemical structure of different pigment materials which were used within each rock art panel. I will then discuss the significance of varying composition and numbers of pigments in terms of technology, chronology and social significance of California rock art. Specifically the second aim is to address the following questions:

- Were the same pigments used on a number of sites and were different pigments used within rock art elements, panels or sites?
- Based on this information, how many painting events occurred at each site?
- What is the significance of these results in terms of technology and chronology?
- Was rock art exclusive in nature, and how much can we tell about who was producing it?

Were the same pigments used on a number of sites and were different pigments used within rock art elements, panels or sites?

By examining pXRF data from the rock art in the Windwolves Preserve I will establish the number of different pigments used within each element, panel and site, by identifying those which clearly contrast chemically with each other. This data will also be used to identify any common pigment materials used in a number of elements in the same panel, in different panels or between sites.

Based on this information, how many painting events occurred at each site?

Once common and contrasting pigment materials are established, the number of different pigments used within a site can be determined. Each change of pigment material will be treated as a different painting event, which is potentially at a different time or by a different hand. These constitute a minimum number of painting events as the same material may have been used on more than one occasion, and there may have been other painting events which are no longer identifiable.

What is the significance of these results in terms of technology and chronology?

As described above, the chemical composition of *in situ* rock art pigments can provide very useful information relating to the processing of ochre and for the establishment of a relative chronology. During this thesis I will examine how the specific data from my selected sites reflect upon the processing technology used here and the time frame within which the rock art production took place.

How do these results reflect on the social role of rock art?

The establishment of a minimum number of painting events at each site informs us on the minimum number of visits received by each rock art panel. As well as this, the number of pigments in a specific rock art element will indicate whether this element was produced as a single event or was revisited and added to over time. This information is very important in determining the extent to which members of Chumash communities interacted with rock art and how much of a conspicuous role rock art played in Chumash society.

Was rock art exclusive in nature, and how much can we tell about who was producing it?

The use of pXRF has the potential to contribute to discussions about the role of rock art in Chumash society as described above. One of the debated issues relating to the role Chumash rock art played in society is that of the exclusivity of rock art which is discussed in more detail in the following section.

Conclusion

As described earlier, the aims of this project are to establish a method for using pXRF to examine *in situ* rock and to apply this method to specific Chumash rock art, thereby contributing to this wider debate surrounding the role of rock art in Chumash society. The ability to identify different and shared chemical compositions between applied pigments would allow us to address a number of broad questions relating to rock art. As outlined earlier these include questions about who was producing rock art, how many times the sites were revisited, which pigment preparation techniques were used and how much of a connection there was between rock art sites. The examination of the data may allow us to discuss ideas about the potential role of communities in rock art production and question whether rock art was exclusive and produced by high status individuals, or whether it was much more involved in ordinary lives of Chumash people.

Portable XRF is a widely used technique in analysis of archaeological materials as can be seen in the following chapter. One of its major advantages is its non-destructive nature which allows analysis of unique or fragile items from which samples cannot be taken (Pollard *et al*. 2007:107). The details of this technique will be outlined further in the methodology section. The following chapter discusses the applications of XRF in archaeology and the advantages and limitations of the technique.

CHAPTER 1 – PORTABLE XRF IN ARCHAEOLOGICAL RESEARCH: DETAILING ITS POTENTIAL IN *IN SITU* ANALYSES

XRF has been used extensively to look at various archaeological materials including bone, ceramics, obsidian, lithics, glass, metal and pigments. Portable XRF has been very useful for performing non-destructive analysis of items which cannot be sampled or transported to a laboratory. The following sections outline the applications of XRF with these materials with a particular focus on portable XRF and its potential in the examination of *in situ* rock art pigments. Reading about the techniques and applications described below has informed the methodology which is describe in the next section.

Bones

It is perhaps surprising that XRF is able to provide useful data about chemical composition of teeth and bones. However, Martin *et al.* (2007), Kyle *et al.* (1986) and Piga *et al.* (2009) all used XRF to examine bones or teeth. The results gathered from these studies have highlighted the usefulness of XRF in examining trace elements and the importance of considering taphonomic effects on XRF results. When dealing with pigments from known archaeological contexts it will be important to look at the potential mineralogical changes in order to allow a meaningful comparison with the pigments within rock art.

Martin *et al. (2007)* looked at the cementum rings in modern human teeth from a U.S. surgery which removes teeth for cosmetic reasons, and other human teeth excavated from various archaeological sites on the north coast of Peru. They found metals in these rings which were indicative of human activity (Martin *et al.* 2007:936). These include lead which was found in modern teeth and was probably a result of using lead water pipes and the levels of bromine found in two of the teeth would be consistent with a marine diet. Kyle *et al.* (1986) similarly found bones and teeth in burials in Papua New Guinea that were enriched in strontium, magnesium and barium which are thought to be the result of a high shellfish intake (Kyle *et al.* 1986:403).

Piga *et al.*(2009) used XRF to supplement XRD analysis looking at human and animal bone fossils ranging from present day to the Middle Triassic in order to try to reconstruct the mineralization process (Piga *et al.* 2009:1857), highlighting the importance of considering the process by which palaeological and archaeological materials reach their present state.

Ceramics

XRF has been similarly useful in allowing archaeologists to examine details of ceramic materials, both to source the materials used in the main fabrics of ceramics, and to identify and differentiate between types of decoration. This technique has been useful to Terenzi *et al.* (2010) and Tschegg *et al.*(2009) who used XRF with other techniques to source ceramic fabrics. Terenzi *et al.* (2010) used XRF and NMR to characterise two groups of similar medieval ceramic fragments. Elementally they were homogenous as shown by XRF, suggesting a common source material, but NMR analysis showed differences in structure indicating different firing techniques (Terenzi *et al.* 2010:1403).

Contrastingly, Tschegg *et al.* (2009) looked at the bulk composition of Late Cypriot Bronze Age Plain Wheel made ware from Cypriot excavation sites and identified several workshops. They concluded however that the raw materials used were available around ancient Enkomi in East Cyprus (Tschegg *et al.* 2009:1103). The ability to differentiate between workshops using raw materials from the same area demonstrates the potential usefulness of XRF in identifying subtle differences between preparation techniques, which may be useful in pigment examination.

Culbert *et al.* (1987) examined a range of ceramic materials from Tikal including unslipped, polychrome and red-slipped wares. They identified differences in fabric composition between slipped and unslipped wares, and in the materials from different periods (Culbert *et al.* 1987:635). Papachristodoulou *et al.* (2010) also found that variation in slips supported the fabric based groupings of local and imported red slipped pottery in NW Greece. These groups were also established using chemical characterisation by XRF (Papachristodoulou *et al.* 2010:2146).

Odriozola and Hurtado (2009) used XRF to examine white incrustations on 3rd millennium BC pottery from the Guadiana River basin in Spain. These incrustations were usually calcium carbonate but in this case XRF showed that they were made of burnt bone, contrasting with the tradition on the Iberian Peninsula (Odriozola and Hurtado Perez 2009:1794).

One important trend in the use of XRF in ceramics is that the XRF was often used in conjunction with other techniques which look at trace elements, although XRF has been shown to be good for bulk analysis, group characterisation and provenance identification. This does

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present the possibility that the use of a different analytical instrument to perform secondary analysis may be worth considering in rock art study.

Obsidian

XRF has been extensively used in provenance studies of obsidian, a naturally occurring volcanic glass. This is largely because the high level of internal consistency within each obsidian source allows obsidian artefacts to be linked to their geological source with a high degree of confidence (Hancock *et al.* 2010:243). This demonstrates the potential for pXRF in sourcing materials which are suitably internally consistent.

This characteristic of obsidian has allowed Glascock *et al.* (1999) to successfully identify and source obsidian using a combination of XRF and Instrumental Neutron Activation Analysis (INAA) (Glascock *et al.* 1999:861). Jia *et al.* (2010) demonstrated the interpretative potential of this technique in examining social relationships by using portable XRF to characterise obsidian artefacts from NE China and Far East Russia. The chemical signatures of these indicated two-way movement of artefacts between these regions (Jia *et al.* 2010:1670).

Craig *et al.* (2007) and Nazaroff *et al.* (2010) compared the effectiveness of portable XRF to that of lab based analytical techniques, an important consideration when deciding how useful the method can be for examination of both trace elements and bulk materials (Nazaroff *et al.* 2010:885). Craig *et al.* (2007) looked at 68 obsidian artefacts from Jiskairumoko in Peru using both lab based and portable XRF and found that there were some small differences which could be explained by calibration differences, but that both methods connected the artefacts to the same geological sources (Craig *et al.* 2007:2012).

Similarly Nazaroff *et al.* (2010) found that portable XRF was not equivalent to lab based XRF in terms of quantification of chemical composition but was a valid technique for provenance questions (Nazaroff *et al.* 2010:885). So too did Poupeau *et al.*(2010) who compared XRF to two other lab based methods and found that all three divided 100 artefacts from Catal Huyuk into the same compositional groups and linked them to the same geological sources (Poupeau *et al.* 2010:2705).

Similar to the study of ceramics, trace element detection techniques have been used alongside XRF in obsidian analysis. However, some of these studies directly compared the effectiveness of XRF with other techniques and found that it was a valid method for characterising groups and provenance study. It is encouraging that both obsidian and ceramics have been successfully grouped and sourced using XRF as both of these materials contain elements which can be expected in rock art pigments, such and iron, strontium and zirconium.

Lithics (other than obsidian)

XRF has been used to characterise a number of other lithic materials other than obsidian. It has been found to be particularly useful for major element analysis as discovered by Jones *et al.* (1997) and Williams-Thorpe *et al.* (1999). These major elements can be used to identify source materials (Jones init *et al.*, 1997 p1997). Williams-Thorpe *et al.* (1999) compared portable XRF with lab based WDXRF and found that portable XRF gave reliable results on fresh surfaces but was less consistent on weathered surfaces (Williams-Thorpe *et al.*1999:215).

Major element determination by XRF has been used to source lithic materials from other sites. Lebo *et al.* (2007) compared 7 rock specimens and 6 stone artefacts from the Hawaiian islands of Nihoa and Necker and found a major element distinction between the two (Lebo *et al.*, 2007 p858). Warashina (1992) compared Jasper artefacts from sites around Tokyo, Kobe city and Awaji Island with natural sources of Jasper, and successfully sourced the artefacts to Kasenzan and Tamatani (Warashina 1992:357).

Tripati *et al.* (2010) were able to identify the major elements in 269 stone anchors from sites on the Indian coast and this alongside petrography was used to identify possible sources for the stone. The source information can then be used to discuss ancient maritime trade contacts (Tripati *et al.* 2010:1999). Similarly Gluhak (2009) examined 13 Roman basaltic lava quarries in order to source the material used to make millstones and to recommend a standard procedure for millstone provenance studies (Gluhak *et al*. 2009:*1774*).

These studies have also shown that examination of bulk elements can provide information on provenance even if the lithic material is not as homogeneous as obsidian. Lithic studies have also highlighted the potential effect of weathering on XRF results. This is a factor that could affect the reliability and usefulness of the readings from rock art elements and is important to consider when analysing the results.

Glass

Studies of various glasses found XRF to be very effective for differentiating between contemporary types of glass, and glasses from different periods. The ability to differentiate between materials will be very important when examining the number of different pigment materials present in Chumash rock art. It was also possible for inferences to be made about sourcing materials used, the use of recycling and different glass working techniques.

Kato *et al.* (2009) found that plant ash glass from the site of Raya on the Egyptian Sinai Peninsula could be characterised into three compositional groups using portable XRF on site (Kato *et al.* 2010:1381), and found distinct chemical differences between glass from the 8th and 9th centuries (Kato *et al.* 2009:1698).

Similarly Silvestri (2008) used XRF and found compositional differences between low status vessels and bottles which involved varied raw materials and recycling, and higher status vessels which seemed to use more strictly controlled raw materials and were more consistent (Silvestri 2008:1489).

As with obsidian, XRF has been used to examine the provenance of glass. Salviulo *et al.* (2004) used XRF to look at the bulk composition of early medieval glass from the Po Valley in northern Italy. The chemical composition allowed the samples from Monte Barro and Brescia to be differentiated from those from Monselice. These differences were interpreted as showing different provenances or glass working techniques (Salviulo *et al.* 2004:293).

Garcia Heras *et al.* (2005) also characterised second century BC glass beads from Numantia in Spain using XRF in order to look at production processes, provenance, and to assess corrosion and decay processes. From the XRF results it was concluded that the presence of glass beads at the site was probably the result of trade rather than local production (Garcia-Heras *et al.* 2005:272).

Degryse *et al.* (2005) looked at glass chunks found with fuel ash slag and kiln fragments at Sagalassos dating from the imperial to early Byzantine periods, as well as local vessels. WD-XRF was used for trace analysis. The results indicated a change in the raw materials used in vessels made from coloured glass over time, but no such change in colourless glass. The analysis also

showed that the composition of the fragments was the same as the local vessels indicating they relate to the production of the vessel glass (Degryse *et al.* 2005:287).

Not all of these projects made use of portable XRF, but they all show that XRF can be used to identify small chemical differences confidently in glass. This includes the study which did use a portable device (Kato *et al.*2009), and supports the results from the previously mentioned materials in indicating that this method could be very effective in identifying subtle differences in pigment materials.

Metals

Both ferrous and non-ferrous metals have been examined using XRF, although studies of iron are much less common than those of non-ferrous metals. The identification of non-ferrous metals would be applicable to blue and green pigments which may consist of copper or cobalt compounds. Portable XRF devices are also used to sort between iron based scrap metals and clearly can differentiate between different iron based materials. The ability to do this is particularly important to this project as the red pigments being examined are likely to be made of iron ore.

Non-ferrous metals

Dungworth (1997) examined 1200 artefacts from the Roman period in Britain using XRF. The results gained were found to be comparable with those obtained using other techniques. The results demonstrated a decline in unleaded brass and an increase in leaded bronze and gunmetal over time. They also showed a level of consistency in the alloys used for particular purposes which led to the conclusion that smiths had a great understanding of the raw materials they were using even when recycling (Dungworth 1997:910). This demonstrates the potential of XRF to shed light upon the processing techniques used to produce materials, which may also prove to be very valuable to this project.

Friedman *et al.* (2008) and Renzi *et al.* (2009) both used XRF to identify the bulk composition of artefacts in provenance studies. Friedman *et al.* found that 7 bronze bangles from Tell en-Nasbeh in Northern Judah were made of leaded tin bronze which were likely to have been produced in the neighbouring region of Edom (Friedman *et al.* 2008:1951). Renzi *et al.* (2009) looked at 22 samples from the Phoenician site of La Fonteta. XRF was used to establish their

bulk composition then lead isotopes were identified to shed light on the provenance of the samples (Renzi *et al.* 2009:2584).

These studies show the potential for XRF to provide information that is useful in determining the techniques used to prepare materials by looking at the ratios of certain elements, including identification of recycling processing, and identifying materials which are likely to be made from raw materials from different sources.

Ferrous metals

Mentovich *et al.* (2010) used hand held XRF to examine the proportions of iron, silicon, manganese and phosphorus in cannonballs from the Akko 1 shipwreck site in Israel. This analysis combined with petrographic techniques allowed Mentovich to infer the date of the shipwreck and the type of vessel (Mentovich *et al.* 2010:2520).

The application of portable XRF to ferrous metals demonstrates the potential for the device to identify particular ferrous metals by identifying proportions of its constituent elements, but also shows some of the technique's limitations. Although it can be useful in looking at minor elements included in ferrous metals, and can infer the presence of carbon but cannot be used to directly measure carbon levels which would be needed to characterise types of ferrous metal.

Sediments and soils

When looking at sediments and soils XRF has been useful in identifying areas of specific activity on archaeological sites, and has been shown to be useful both on its own and in conjunction with other analytical methods. It has been calibrated using other methods but the comparison with these methods has shown the XRF results to be reliable for these purposes, showing that XRF can produce reliable results.

Berna *et al.* (2007) looked at sediments from Tel Dor in Israel and used XRF to characterise their metal content and calibrated the results using ICP-OES. This, combined with other evidence of structural changes resulting from exposure to high temperature indicated sites used for metal working in the middle bronze age to Roman period (Berna *et al.* 2007:358).

Similarly, Cook *et al.* (2010) used XRF elemental metal analysis to distinguish between domestic and industrial copper alloy working sites in the Roman town of Calleva Atrebatum, Silchester (Cook *et al.* 2010:2010). Gallo *et al.* (2011) used XRF to examine material from magnetic anomalies in Tavoliere in lowland southern Italy. Magnetic susceptibility testing was used to map buried structures and XRF analysis bulk analysis showed that the material related to activity from Mount Vesuvius (Gallo *et al.* 2011:399).

Nodarou *et al.* (2008) look at the chemical composition of mud bricks from Bronze Age Crete. This was compared with the composition of local raw materials in order to identify potential sources. XRF was used for major element characterisation. The results suggested that there was a degree of standardisation of recipes and manufacturing processes but selection of raw materials was largely led by local availability (Nodarou *et al.* 2008:2997).

Pigments

The use of portable XRF in pigment analysis is becoming increasingly widespread. These analyses include raw pigment materials and pigments which have been applied to objects, rock faces, frescoes and murals as detailed below. XRD, INAA and ICP-MS have often been used alongside XRF as they are useful for examining chemical characteristic that XRF, and particularly portable XRF, cannot look at such as lighter organic elements (Pollard *et al.* 2007:107). X-Ray Diffraction (XRD) can determine the compounds in which elements are present within a material, and Neutron Activation Analysis (INAA) and Induction Couple Plasma Mass Spectrometry (ICP-MS) can identify organic materials and ICP-MS can identify isotopes as well as elements (Pollard *et al.* 2007:201).

Examination of ochres

Nuevo *et al.* (2011), Roldan *et al.* (2010) and Olivares *et al.* (2012) show that portable XRF can be extremely valuable in the study of *in situ* rock art. They also agree that red pigments tend to be iron oxides and black pigments are likely to be either charcoal or manganese (Nuevo *et al.* 2011:4; Olivares *et al* 2012). It is also useful that Nuevo *et al.* (2011) identify potential identification of different pigments on the basis of different iron levels, and that Roldan *et al.* (2010) discuss the possibility of using the presence or absence of manganese in ochre to differentiate between different sources and different preparation techniques in rock art production (Roldan *et al.* 2010:243).

Nuevo *et al.*(2011) employed pXRF to examine pigments in Neolithic rock art paintings in the Abrigo dos Gaivoes and Igreja dos Mouros Caves in Portugal. Most of the figures examined were red, some black and one was white. The red pigments were found to be predominantly iron oxides and displayed higher levels of iron than the bare rock on which they were applied (Nuevo *et al.* 2011:3).

Nuevo *et al.* (2011) state that the usual source of black pigment is manganese oxide (Nuevo *et al.* 2011:4). The absence of manganese in the black pigments was concluded to be an indication that the black colour consisted of organic material such as charcoal (Nuevo *et al.* 2011:4). The white pigment displayed less iron than the bare rock and was deemed to be a layer of organic material.

The anthropomorphic figure which was identified in the Abrigo dos Gaivoes Cave appeared to display less iron than the other pigments and so Nuevo *et al.* (2011) suggest that this may have been applied differently or at a different time. This idea is supported by the superimposition of a zoomorphic figure over this. Otherwise the red pigments are described as being similar between panels (Nuevo *et al.* 2011:3). Nuevo *et al.*(2011) conclude that portable XRF is a very useful tool for studying elemental composition *in situ*.

Roldan *et al.* (2010) similarly studied *in situ* pigments in rock art, but in 3 of 9 rock shelters at the Saltadora site in Spain. These pigments were red and black (Roldan *et al.* 2010:243). Here however it was concluded that the black pigments were based on manganese rather than being organic materials. The red pigments here were also deemed to be iron oxides with trace elements including sulphur, potassium, calcium, titanium, arsenic, strontium and barium (Roldan *et al.* 2010:247). According to Roldan *et al.* (2010) these trace elements are typical of prehistoric red pigments such as ochres.

Manganese is discussed here as an impurity of iron oxides in ochre. Roldan *et al.* (2010) suggest that fluctuating levels of manganese within red pigments therefore could indicate different preparation techniques, whereas the absence of manganese in one pigment could indicate a different ochre source (Roldan *et al.* 2010:248).

Olivares *et al.* (2012) examined *in situ* rock art in La Pena Cave in San Roman de Candamo (Spain) using pXRF and portable Raman spectroscopy. Using these techniques they were able

to identify the chemical components of red, black and yellow pigments. PXRF provided information about trace elements within pigments and Raman spectroscopy was able to identify carbon in black pigments as well as different types of iron oxides in red pigments (Olivares *et al* 2012*)*.

Sawczak *et al.* (2009) mapped the pigments in murals and frescoes from Gdansk in Poland using portable XRF. Carbon black could not be identified by the device, but ochre was identified and was found to contain barium, strontium, antimony and molybdenum (Sawczak *et al.* 2009:5542).

Desnica and Schreiner (2006) examined the mural on the wall of the church of St Nicholas in the village of Winkl near Vienna (Desnica and Schreiner 2006:280). Portable XRF was used for *in situ* analysis, but its capabilities were compared with lab based XRF. The iron peaks were found to be smaller using the portable device which turned out to be useful as high levels could be measured without exceeding the point on the instrument at which they become less accurate (Desnica and Schreiner 2006:284).

Daniilia *et al.* (2008) carried out a similar study on the wall paintings of the 15th century central church of the monastery of Christ Antiphontis in Kyrenia on Cyprus. Many pieces of these wall paintings were looted in order to be sold but 32 were returned. Ten of these were examined using a variety of methods including Raman spectroscopy, FTIR, optical microscopy and SEM-EDS. Using these techniques, eight pigments were identified including red and yellow ochres. By examining these pigments Daniilia *et al.* (2008) suggested that two artists, possibly in different periods were responsible for the artwork (Daniilia *et al.* 2008:1695). They also identified important chemical changes over time, which have caused significant changes in the colours exhibited by the pigments. These include changes in lead oxides which have caused the change from orange to black (Daniilia, S. *et al.*, 2008 p1695).

Jercher *et al.* (1998) examined Australian Aboriginal Ochres in order to try to establish sources for red and yellow ochre materials (Jercher *et al.* 1998:383). The samples examined were from the South Australian Museum and included two samples from the quarry sites of Pukartu and Wilgie Mia. Only a single sample was available from each quarry, and the problems caused by this demonstrate one the limitations in ochre sourcing. The issue is that ochre occurs in pockets of varying quality (Jercher *et al.* 1998:386) and therefore when comparing ochre

samples to a source it needs to be determined whether they fall significantly into a compositional range. Without a sufficient number of samples from a source it is difficult to establish this range (Shennan 1997:365). It is dangerous to view one reading as being typical as it may not be representative and thus would render comparisons meaningless.

These Australian samples were examined by looking at both mineralogical and geochemical characteristics of the material (Jercher *et al.* 1998:386). The geochemical analysis used both XRF and XRD, with XRF being used to look at trace elements in bulk material. Using these methods Jercher *et al.* (1998) characterised the yellow ochre as being either goethite or jarosite based and the red ochres as haematite based. In each case they were fine grained highly coloured materials which would be used in powder form and possibly mixed with water (Jercher *et al.* 1998:387).

When using XRF goethite and haematite are unfortunately difficult to separate, as only the iron content will be detected. However, the jarosite pigments contain sulphur which is detectable even by portable XRF (Pollard *et al.* 2007:113). Jercher's study did not allow the pigment samples to be sourced but did provide criteria by which such source characterisation may be possible. 'Cell parameters' or a range of readings for particular minerals may be used to find their origin (Jercher *et al.* 1998:403). This study also established that ochres are in fact very complex materials to be dealing with, similar to soils. They contain carbonates, clays and gypsums and are affected by phases of activity and moisture changes (Jercher *et al.*1998).

Studies by d'Errico *et al* (2010) and Gialanella *et al.* (2011) both address the issue of the heating of ochres and the effect this can have on their colour. It is also important in understanding the process of pigment production, its level of complexity and the amount of work involved. Gialanella *et al.* (2011) created artificial haematite samples by heating local goethite from the area around Palaeolithic sites of Riparo Dalmeri. These were compared with recovered archaeological samples using XRD, SEM, TEM-EDX and Raman spectroscopy (Gialanella *et al.* 2011:4).

Very little naturally occurring haematite is available yet large amounts were found on the archaeological sites. Apart from a slightly elevated level of impurities in the artificial haematite the samples were observed to be very similar and so Gialanella *et al.* (2011) suggests that haematite was being produced in order to use as pigment material, and points out that even in

small proportions haematite is a very effective pigment, and can be produced from goethite by heating it to 800˚C (Gialanella *et al.* 2011:8).

D'Errico *et al* (2010) used a variety of techniques including SEM and TEM-EDX alongside XRD to examine Middle Palaeolithic fragments from the Es-Skhul shelter at Mount Carmel in Israel. XRD provided structural information differentiating between material which had been heated and that which had not. It was concluded that the red pigments that had not been heated were from a natural haematite source whereas those which had been heated were probably from a different goethite source (d'Errico *et al.* 2010:3099).

Calza *et al.* (2004) used a portable EDXRF to look at the palette of Brazilian artists and identified ochre and black iron oxide amongst other pigments (Calza *et al.* 2010:866). Papparlardo *et al.* (2004) used portable XRF to examine trace elements non-destructively in ceramic glazes on Della Robbia sculptures (Papparlardo *et al.* 2004:183). Rosi *et al.* (2008) used non-invasive XRF to look at the principal components in pigments used by Cezanne. Ochre was one of the materials identified (Rosi *et al.* 2008:1655).

Darchuk *et al.* (2011) used SEM-XRF along with FTIR and micro-Raman spectroscopy to examine prehistoric rock painting pigments used in the Gilf Kebir area in Egypt (Darchuk *et al.* 2011:34). Deneckere *et al.* (2009) similarly used XRF in conjunction with Raman spectroscopy to investigate vault paintings in Antwerp Cathedral *in situ*. Haematite and gypsum were both identified (Deneckere *et al.* 2009:511).

McGil *et al.* (2007) looked at red and yellow ochres in geological sources. The intention was to examine the chemical and mineralogical distinctiveness of natural pigment sources, and establish a connection between natural sources and the pigments used in murals (McGil *et al.* 2007:728). This study found that iron ores contained six times the iron level than other areas of the earth's crust, and identified a number of chemical elements which could be used to provide a chemical fingerprint for pigments. These include lead, arsenic, copper and zinc (McGil *et al.* 2007:728).

Similarly Civici (2006) used Total Reflection XRF to identify ochres in pigments in five Albanian icons (Civici N. 2006 p339). Galvan Josa *et al.* (2010) used SEM-XRF along with XRD to look at the chemical composition of white and reddish pigments used on Argentinean pottery. This

study found that these techniques could be used for small amounts of pigment, particularly when the Rietveld method was applied to the analysis (Galvan Josa *et al.* 2010:259).

Aquilia *et al.* (2011) used handheld EDXRF to perform initial chemical characterisation of pigments on Hellenistic painted plasters from Licata in Sicily (Aquilia *et al.* 2011). This was then quantified using SEM-EDX. Desnica *et al.* (2008) similarly used portable XRF for preliminary characterisation of pigments on a wooden inventory in the Trski Vrh Church in Croatia (Desnica *et al.* 2008). Other techniques requiring sampling were only used if the XRF results were unsuitable. The only limitations in this case seemed to be with organic materials which the portable XRF cannot measure, and identification of ultramarine (Desnica *et al.* 2008).

XRF has also been useful in analysing other colours of pigments such as blacks, greens and blues, indicating that it could be used to examine complex polychrome rock art. For example Uda *et al.* (2005) used a portable XRD device with XRF capability to simultaneously perform both analyses non-destructively on a bronze mirror (Uda *et al.* 2005:77). The XRF results demonstrated that an underlying layer was painted with emerald green, thus demonstrating its potential usefulness in identifying the composition of layers of material. Uda (2004) also used a portable XRD and XRF device to identify materials used in the plaster and pigments in Amenhotep III's tomb (Uda M. 2004:75). Yoshinari Abe (2009) used portable XRF and XRD to identify materials used in blue, red and black pigments from Saqqara in Egypt. Some of the blue pigments were identified as cobalt blue, and the results suggested the possibility of compositional transitions over time (Yoshinari Abe 2009).

Tite *et al.* (2009) used SEM-EDS to look at the chemical composition of faience objects. 15 objects from the Middle Minoan IIIA to the Late Minoan IA period on Crete were examined. These were compared with replica beads produced in the lab using manganese, copper and iron as colorants (Tite *et al.* 2009:370). The 15 objects in the present day exhibit tones of grey, brown and subtle greens and blues. However, the results of this study suggest that they were originally bright turquoise, purple, pale yellow and greenish, and the colours that we see are in part a result of weathering processes (Tite *et al.* 2009:370). This demonstrates the importance of considering the effect of weathering on the materials that we examine.

Aliatis *et al.*(2009) used SEM-EDX to look at green pigments from Pompeii, and was able to identify green earths, malachite, Egyptian blue and yellow ochre which were all contributing to

the green colour (Aliatis *et al.* 2009). Hajjaji *et al.* (2011)found that cobalt and manganese enhance the blackness of inorganic black pigments (Hajjaji *et al.* 2011). Hoseini-Zori *et al.* (2008) examined the effect of heat on ceramic pigments, and found that haematite/silica pigments were good reds for fast firing cycles. Ochre was one of the materials identified (Hosseini-Zori *et al.* 2008:491). Similarly Rosi *et al.* (2009) used non-invasive XRF to look at the principal components in pigments used by Cezanne (Rosi *et al.* 2009:1655).

Potential damage to rock art and taphonomic influences.

A number of other studies have highlighted the importance of considering the effects of weathering on the results of analysis.

Gialanella *et al.* (2011) examined ochres using SEM and found that grain morphology gave an indication of formation processes and some peculiar grain formations appeared to result from natural precipitation processes (Gialanella *et al.* 2011:10).

Moussa *et al.* (2009) looked specifically at the factors affecting deterioration of pigments on wall paintings in Al Qurna in Egypt. This study used XRD and ICP-AES to evaluate the effect of soluble salts and climate. The study found that different pigment materials were affected differently by external factors and that gypsum is 200 times more soluble than calcites, making it more susceptible to weathering. Moussa *et al.* (2009) found that the porosity of the surface and variations in environmental temperature were very important in degradation processes. Also, photochemical processes had an influence on the appearance of brown pigments and on the reaction between gypsum and red haematite (Moussa *et al.* 2009:292). These factors are useful to consider when examining surviving pigments and inferring their original appearance.

Conclusion

In examining all of the materials described above a few themes appear. Portable XRF has been found to be comparable with lab based techniques in terms of its effectiveness in provenance (Craig *et al.* 2007; Nazaroff *et al.* 2010; Poupeau *et al.* 2010; Warashina 1992), comparative and qualitative analysis (Poupeau *et al.* 2010; Kato *et al.* 2010), but is not as accurate for quantitative analysis of trace elements (Nazaroff *et al.* 2010). It is however a useful technique for comparing levels of some trace elements between samples, and is very valuable for

evaluating and reducing the necessity for any destructive sampling on archaeological materials (Desnica *et al.* 2008).

Portable XRF provides important information when used on its own as well as in conjunction with other techniques (Aquilia *et al.* 2011; Desnica *et al.* 2008). Although it is limited by its inability to detect organic materials, it is a quick, reliable and non-destructive method which has been shown to be effective for *in situ* ochre analysis (Roldan *et al.* 2010; Nuevo *et al.* 2011; Olivares *et al*. 2012). The results of various studies cited here present useful ideas concerning methodology and raise a number of issues which need to be considered for this project.

It is clear that XRF can be used to look at relative proportions of elements which can be used to characterise different materials, and to look at trace elements which can potentially verify any materials identified (Roldan *et al.* 2010). It is important, however to consider that over time weathering may have affected the composition and colour of pigments, (Tite *et al.* 2009:370) and that at a later point it may be useful to supplement this analysis another technique such as XRD to identify compounds used in pigment, and assist with quantitative analysis. These studies provide results which have helped to inform the following methodology for this project.

CHAPTER 2 – P-XRF AND IN SITU PICTOGRAPHS, A METHODOLOGY

As mentioned in the introduction the main aims of this project are to establish a method for p-XRF analysis of rock and then to apply this to the five selected sites in the Windwolves Preserve. The many studies cited in the last chapter show that p-XRF can provide data about main constituent and trace elements that is accurate and reliable enough to allow differentiation between different materials (Kato *et al.* 2010; Silvestri 2008; Nuevo *et al*. 2011; Roldan *et al.* 2010). Nuevo *et al.* (2011) and Roldan *et al.* (2010) have demonstrated that iron based pigments can be differentiated and that the detection of trace elements such as manganese can help with the identification of different red and black pigments (Roldan *et al.* 2010:243; Nuevo *et al.* 2011:4).

Based on the experience of these researchers, as well as advice from Dr Bruce Kaiser of Bruker who provided the XRF instrument, I have developed a method which will allow the observation of differing iron levels and the detection of trace elements which may indicate different source materials.

Background to the theory of p-XRF analysis

Five rock art sites of Pinwheel, Pond, Three Springs, Los Lobos and Santiago on the Wind Wolves Preserve in south Central California were examined using a handheld or portable XRF spectrometer. XRF devices work by temporarily irradiating samples using X-Ray radiation, causing the chemical elements within them to fluoresce. Each chemical element has its own characteristic radiation and can therefore be identified by the detector within the device. XRF instruments are either Wavelength dispersive (WXRF) or Energy dispersive (EDXRF).

WXRF detects elements within a selected range of wavelengths, which is selected using prisms within the instrument, whereas EDXRF can detect elements across the whole range of the instrument by measuring the energy level of the emissions, but is slightly less accurate. There are many lab based XRF devices which can analyse samples once they are ground into powder. Such preparation is often necessary for chemical analysis using laboratory instruments but it is not needed when using portable XRF. As no sample preparation is needed, portable XRF can be used to examine *in situ* archaeological remains, as shown in figs 18 and 19, and it does not cause any damage to the materials being examined.
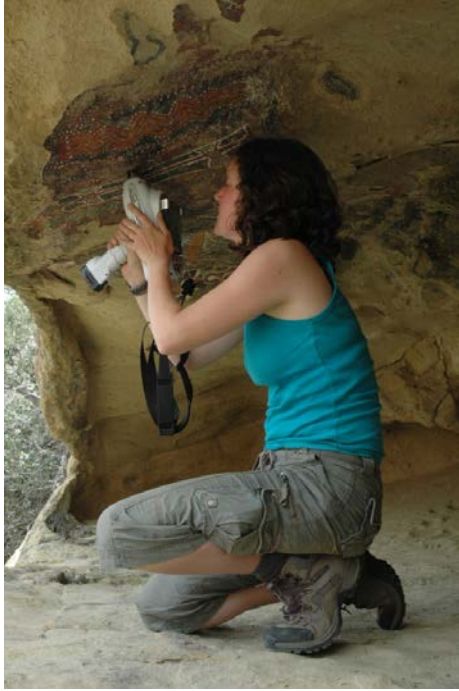
Figure 18. Portable XRF in use on *in situ* rock art **Figure 19. Close up of Portable XRF device in use**

When materials are examined *in situ* only the surface of that material is examined which can limit the scope of the examination, particularly where surface coatings have been applied to a different core material (Pollard *et al.* 2007:107). There is also more interference from the air when such devices are used *in situ*, which obscures chemical signatures from lighter elements such as carbon and oxygen. As a result this particular device can identify any chemical elements between magnesium and uranium, but not lighter organic materials such as carbon, oxygen or nitrogen (Pollard *et al.* 2007:107). However, this method only provides elemental data and does not identify chemical compounds. Chemical elements are the individual chemical components which make up pigment materials. I will also refer to 'rock art elements' throughout this study. This term describes single images, icons or motifs used to produce rock art.

A description of the pigment colours to be analysed

Initially red pigments were examined. As red pigments tend to be made from ochre which is iron based, this analysis took the form of a comparison of relative iron levels. Pigments using different ochre sources may also be identifiable by analysis of other trace elements as shown by Roldan (Roldan *et al.* 2010:248) and according to Roldan *et al.,* (2010) it is possible that different levels of manganese may result from different preparation techniques. Any variation

in trace elements such as calcium, strontium, zirconium, arsenic and rubidium are also discussed in the following results section.

Black, white, blue and grey pigments at these sites were also examined using portable XRF. Black pigments may be produced using either charcoal (carbon) or manganese (Roldan *et al.* 2010:243; Olivares *et al.* 2012). Unfortunately carbon cannot be measured using portable XRF but if manganese is present this can be detected. White pigments tend to be calcium based.

Calcium can be detected with this device but also occurs in large and fluctuating levels in many types of rock and may therefore be difficult to distinguish from the readings from the rock itself. Grey pigments would be produced using a mixture of black and white pigments.

A type of blue can also be produced by layering black and white pigments (Scott *et al.*2002:190), but blues can also be produced using copper ores which are available with the Windwolves Preserve. The aim here will be to identify which method was used to produce the blue pigment used at Three Springs.

Technical details of the sampling strategy and analysis in the Windwolves Preserve

Individual rock art elements were identified and up to five readings were taken for each of these, as well as up to five readings from the bare rock around each rock art element. This analysis was undertaken using a Bruker Tracer III handheld X-Ray fluorescence spectrometer. S1PXRF software was used to gather the spectra and the device was set at 40kV and 3.4uA and was run for one minute for each reading. The analysis compared the relative number of counts per second of particular elements at this voltage setting by using ARTAX software to calculate the net area under each elemental peak and converting in total counts which were examined using Microsoft Excel. This analysis is a study of relative ratios but not of quantitative element concentrations.

Approximately five readings were taken from each element of each rock art panel in the five study sites. Between three and five readings were also taken from the rock on which each element was painted. At each site between 10 and 20 elements were examined. Each reading contained numbers of counts for a range of chemical elements which are displayed as seen in the chart below:
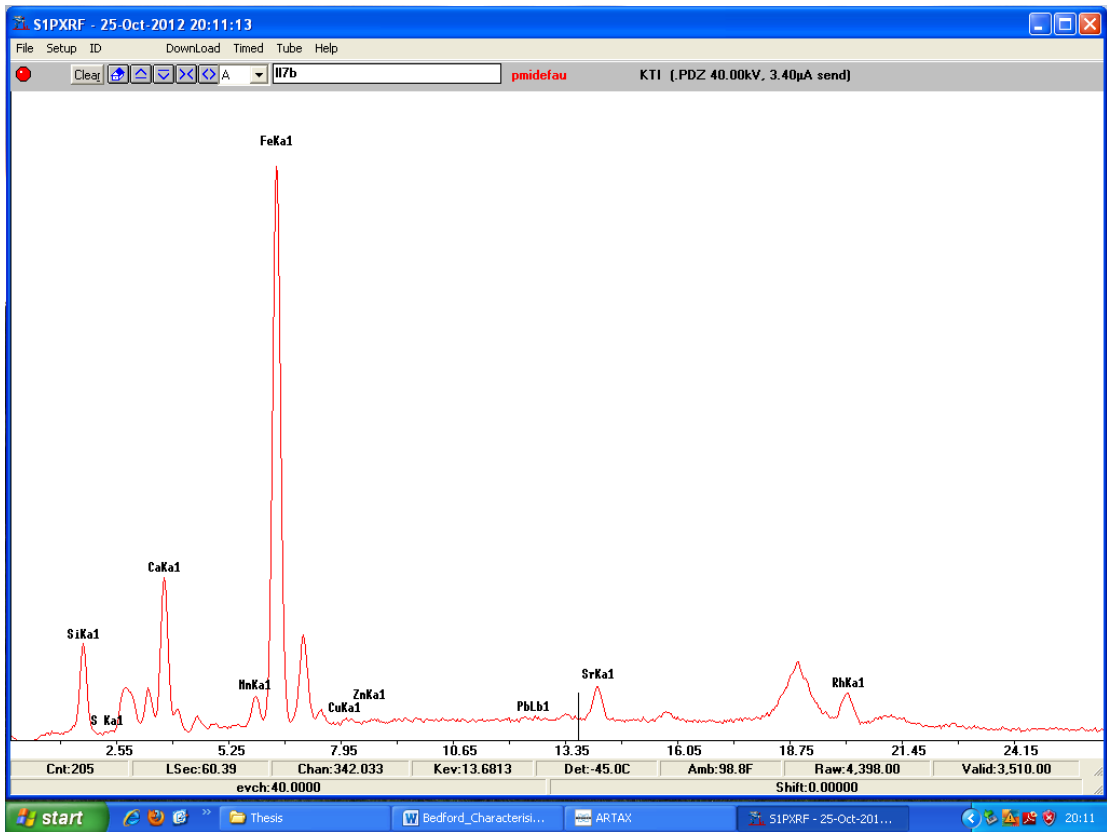
Figure 20. Raw spectrum obtained by pXRF instrument
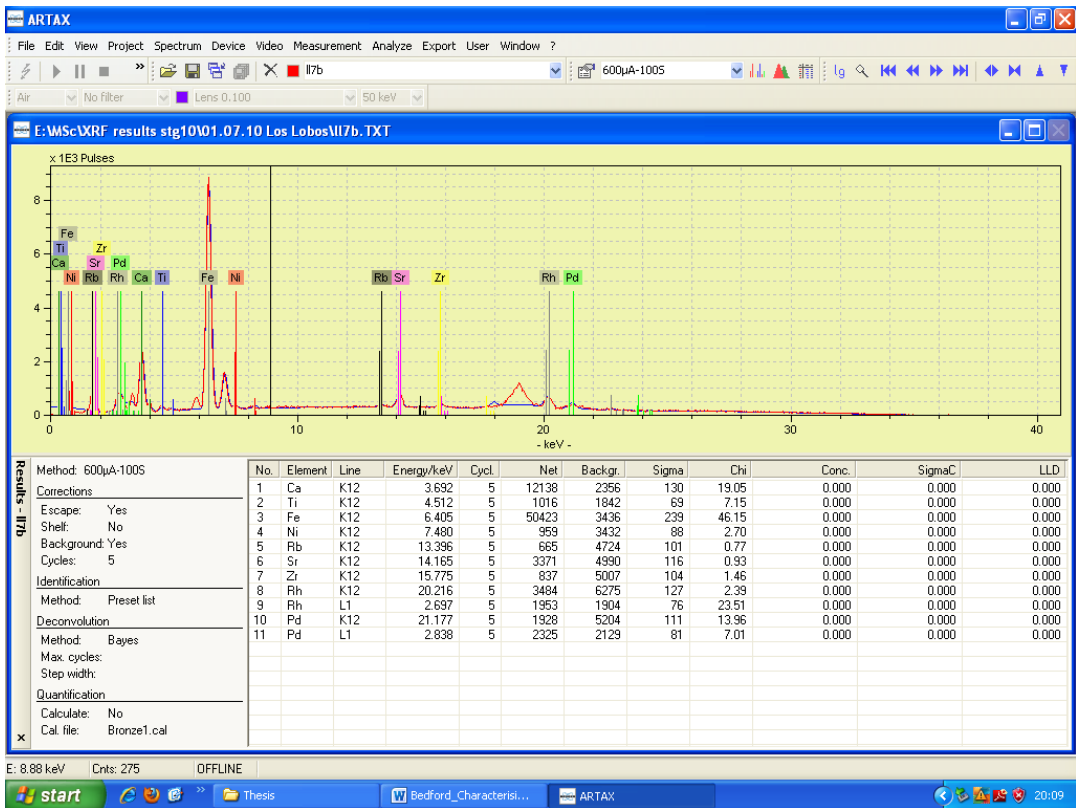
Figure 21. Spectrum once converted in Artax data

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These results were then converted into Excel spread sheet format using Artax. The readings for individual chemical elements can then be examined and compared. As these results have not been calibrated to provide absolute quantities of chemical elements the relative levels of iron were examined by comparing them to strontium, an element which maintains a consistent level throughout both pigment and rock readings. Strontium counts were used as a baseline against which to compare relative iron levels in the XRF readings. Strontium and iron were plotted against each other to produce a scatter graph for each rock art element, including readings from the background rock to which pigment was applied. The resultant graph appears as below:
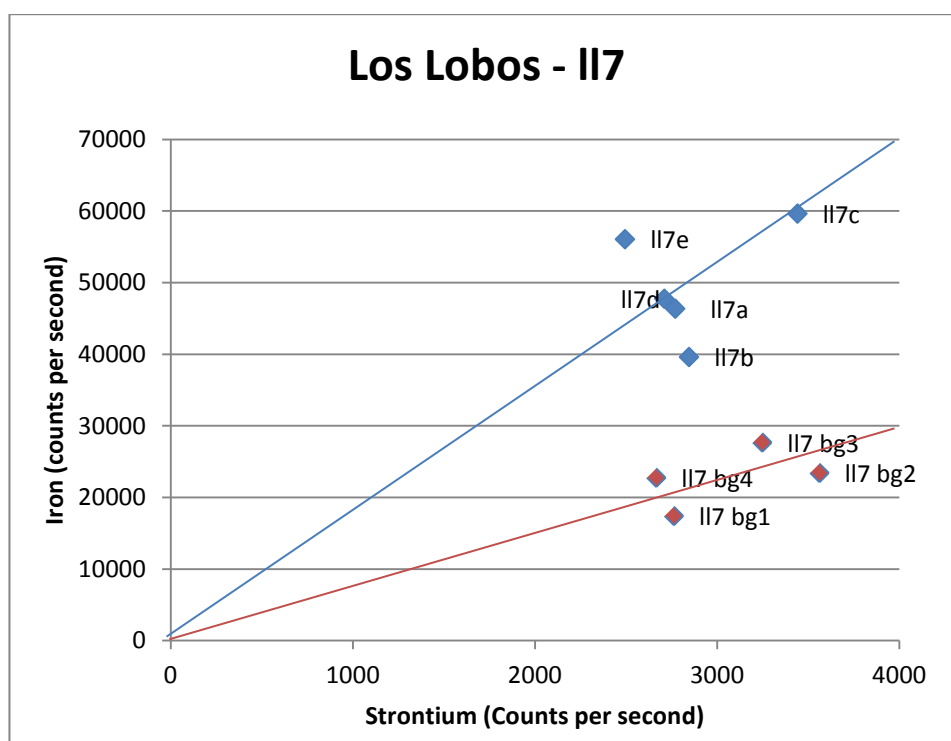
Figure 22. Iron and strontium readings from spectrum plotted against one another

Statistical analysis

Using these scatter graphs linear groups of pigment readings which were distinctly different to the background rock were identified. These groups represent readings which fall on the same axis as one another have the same proportion of iron to strontium as each other, and therefore are most likely to consist of the same material. By doing this the areas of different elemental composition become clear as they form groups within the scatter, and these groups

of readings fall on or close to the axis shown in each scatter graph. Pigment readings are represented by blue axes on the scatter graphs, and the red ones show background readings.

Groups of readings which showed clear differences to one another were then also identified. The groups identified were tested using variance analysis. As the readings appear to be normally distributed an ANOVA test was performed to test the statistical validity of the groups identified within each element.

The ANOVA test is performed using a package called PAST (Hammer *et al.* 2001) which is a statistical package designed for use by archaeologists and palaeontologists. When groups of figures are put into this package the ANOVA test calculates the probability that the figures are likely to represent the same group of readings. In this case I am using this to identify groups that are likely to represent the same pigment material, and also using this test to identify which groups are significantly different to others.

Only those with less than 5% probability of being the same material are described as being significantly different. Similarly only those with over a 95% chance of belonging to the same group are described as being the same.

Interpretation of results

Those groups of results which are statistically different are considered to consist of different pigment material, an idea supported by Nuevo *et al.,* (2011) and the implications of this are discussed further in the following chapters. It is likely that pigments containing differing levels of iron were either from different sources or had been prepared in different ways.

Using the number of contrasting pigments the number of painting events for each site was calculated. The implications of these will be discussed in chapter 4. As well as looking at the number of painting events the results also give indications of different preparation and application techniques, which are discussed for each element in the next chapter.

In addition to this *in situ* analysis a number of ochre pieces were examining using the same technique. These were collected during excavations at Pinwheel, Pond, Three Springs and Los Lobos. Approximately five readings were taken for each and their iron and strontium levels

were plotted against each other. These do not form a core part of this study but I will make references to the distribution of these readings. For this reason these results are included in appendix 2.

Conclusion

The many studies described in the previous chapter demonstrate the potential for pXRF to be used to gather useful readings from, and differentiate between, *in situ* archaeological materials. These have assisted in the establishment of the method described above. The following chapter details the results obtained from the five selected sites using this method of portable XRF analysis in the Windwolves Preserve. Readings were taken from individual rock art elements within each panel. The XRF readings for these show the levels of particular chemical elements within them. In the following chapter I examine the chemical composition of each element, compare these elements with each other and start to discuss the significance of any variations seen in this chemical composition.

CHAPTER 3 - A PXRF ANALYSIS OF *IN SITU* PICTOGRAPHS: DETAILS AND RESULTS.

Rock art at the sites of Pinwheel, Three Springs, Pond, Los Lobos and Santiago was analysed using the method described in the previous chapter. Also analysed were a number of ochre samples from excavations at these sites. The data from these samples is in Appendix 2 and is referred to occasionally in this chapter.

The following sections detail the results from each rock art site and briefly discuss interpretations and explanations of the chemical compositions observed. In each section the number of painting events per site is determined, and the significance of these, as well as any variations in chemical composition will be discussed further in Chapter 4.

This work forms the key component of this research and is central to addressing the key aims laid out in chapter 1, the first of which was to assess the viability of pXRF in analysing rock art *in situ*, and to develop a method for its use, and the second to apply this method in order to discuss the technological and social aspects of rock art at these sites.

Pinwheel

The site of Pinwheel has two rock art loci each with one rock art panel. The first is inside the main cave, and the second is the rock surface next to this cave. Here this second locus is called 'Pinwheel rocks'.

The cave at Pinwheel contains 6 rock art elements, most of which consist of red pigments. Readings were taken from the pigments and the rock to which they were applied. Below are images of each rock art element showing the points from which each of these readings was taken. As described in the methodology section the relative proportions of iron and strontium are examined and compared between readings from each element. The results are shown in the scatter graphs which accompany each element here.

Rock art element 1

Figure 23. Pinwheel rock art element 1 ('Pinwheel'). Labelled are the points from which 8 pigment readings a-h were taken, and 5 background readings bg1-5.
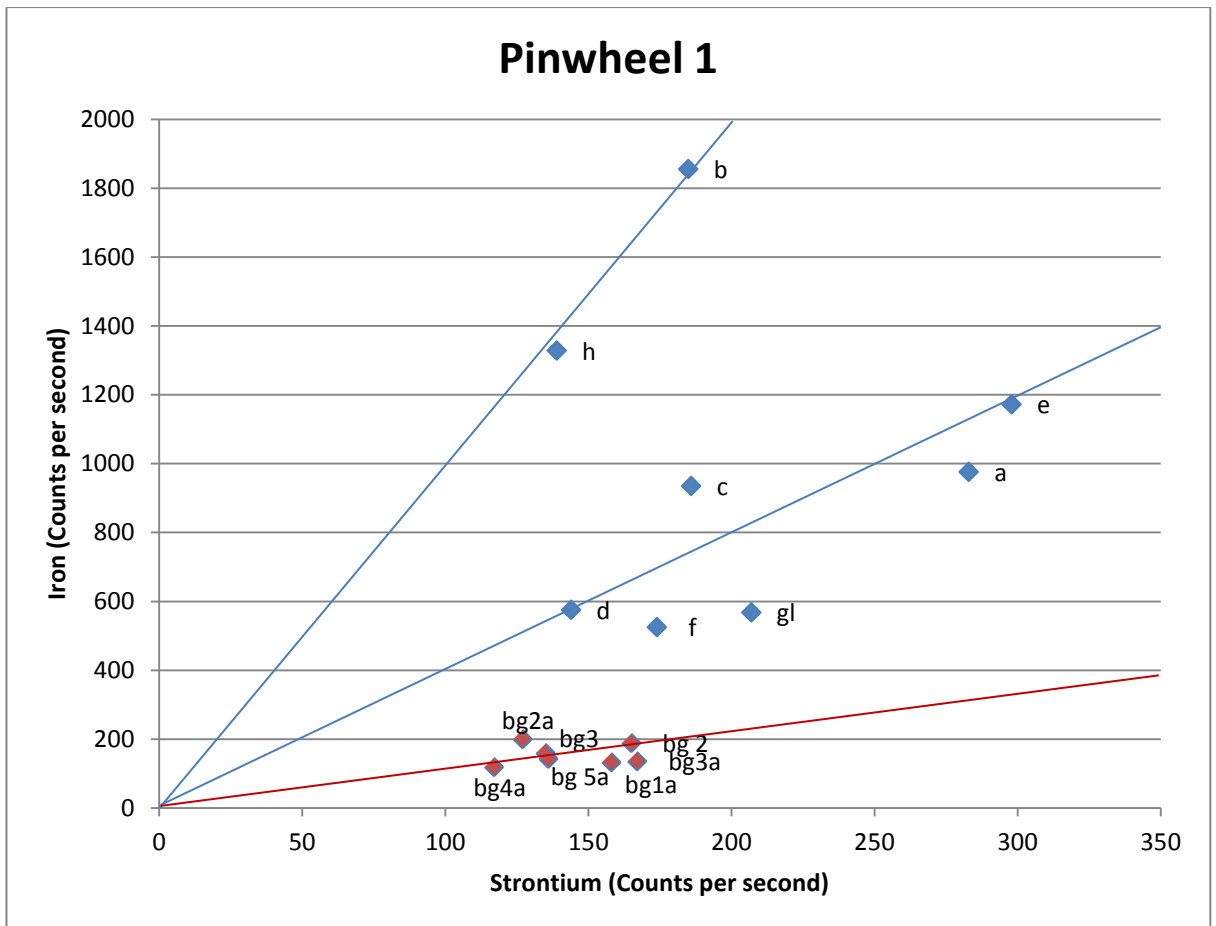
Figure 24. Scatter graph of strontium plotted against iron in rock art element 1.

Fig 23 shows the first rock art element at the Pinwheel site, which is a Pinwheel motif. As shown if fig 23, readings were taken from each 'spoke' in the rock art element.

As shown in fig 24 the XRF results for this rock art element form 3 distinct groups, two groups of pigment readings and one from the background rock. These groups follow the three axes shown. Of these the background readings are on the red axis and the pigment readings follow the blue lines. The pigment readings contrast well with the background reading from the rock to which the pigment has been applied.

Within the pigment there appear to be two different groups, one formed by a, c, d, e, f and g (pnw1a), and the other consisting of b and h (pnw 1b). Variance analysis confirms that these groups are different to each other as well as the background rock (see Appendix 1). This indicates it is likely that at least two pigments were used here.

In element Pnw1at Pinwheel the trace elements are mostly very consistent in both pigment and background readings except for calcium manganese and arsenic. Arsenic and manganese levels in this element are higher in pigment readings than the background rock and both trace elements peak significantly in pnw 1a,b,e and h as shown below. It is interesting that these four readings show higher levels of arsenic than the others (see below) when only b and h show significantly different iron levels. Readings a and e, however, do form a discrete group along their axis.

Perhaps these two areas of pigment used the same source material as b and h but were processed differently. If this is the case then it is possible that there are three painting events here. In this case readings a and e form pigment c here, and this may lead us to question the cohesiveness of other pigment groups which are spread along their axes. It is also possible that a and e display characteristics of both of the other pigments and the XRF spectrum reflects and mixing of readings from these as one overlays the other. It is unfortunately difficult to separate layers of pigment using this technique.
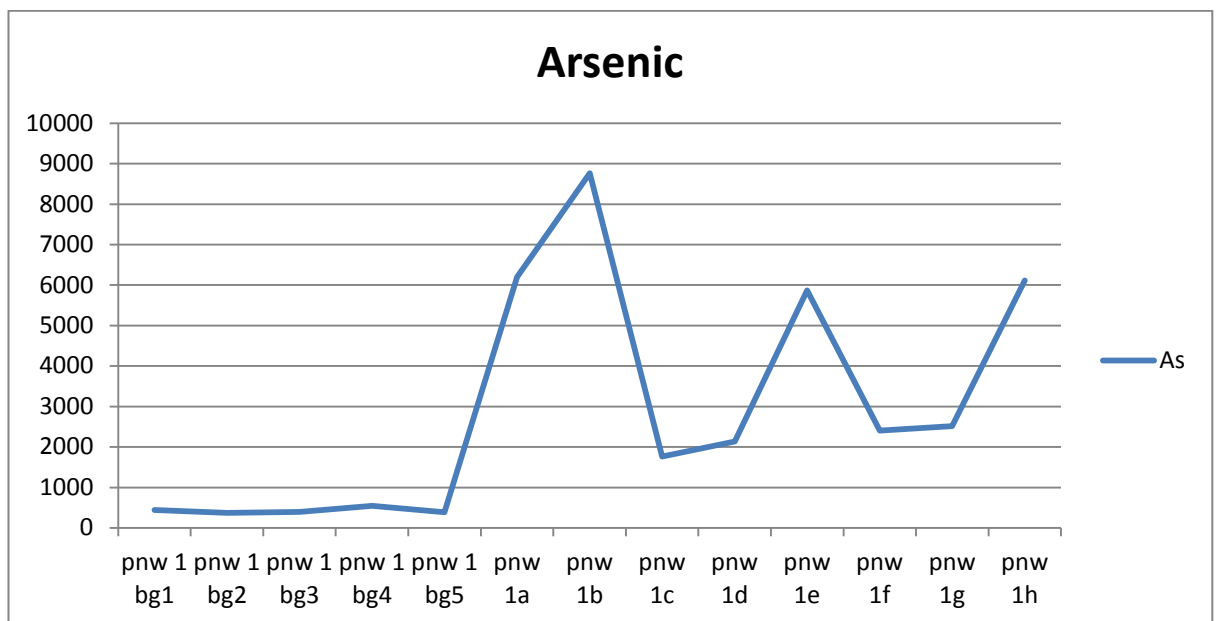
Figure 25. Line graph showing the relative level (Counts per second) of arsenic (As) in readings from Pinwheel element 1.

There is massive variation in all trace chemical elements in all the other rock art elements at Pinwheel. These trace elements include calcium (Ca), strontium (Sr), zirconium (Zr), tin (Sn), antimony (Sb) and barium (Ba).

Members of each group may vary along their axis, reflecting a variation in thickness or density of pigment, but they retain their iron to strontium ratio which is indicative of a particular pigment material. It is possible therefore that different thicknesses of pigment could be examined by looking at their position along this axis, thereby indicating reapplication of the same pigments or the effect of weathering over time. The effect of factors such as density and thickness will be discussed in more detail in the discussion section later.

Element 2

Figure 26. Pinwheel element 2 showing positions of pigment readings a-d and 5 background readings
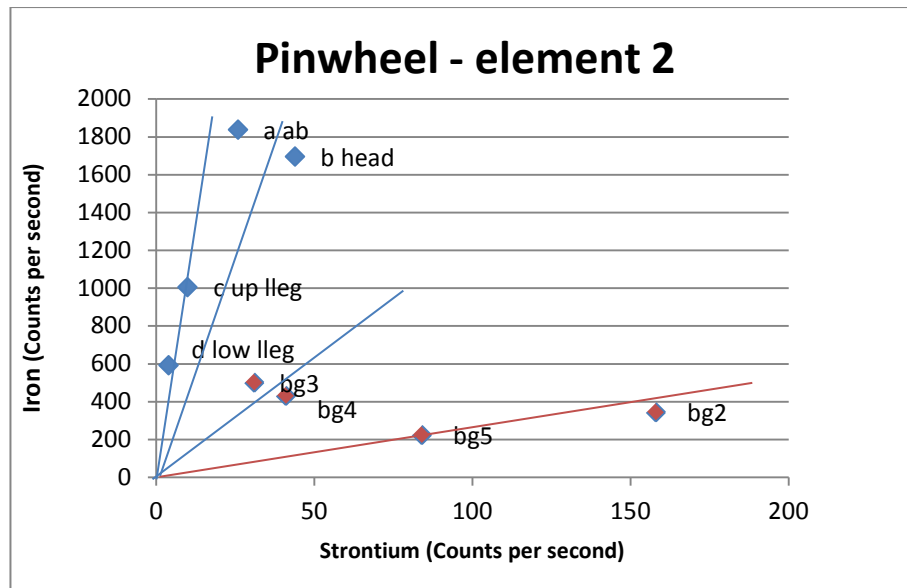
Figure 27. Scatter graph showing iron plotted against strontium in element 2.

Element 2, a zoomorphic figure, also appears to contain contrasting groups of readings. The pigment used for the legs within this element appear to show a different chemical signature to the pigment in the head and abdomen, the head and abdomen readings are very distinctly different to the background readings.

However, although the background readings are distinct from the pigments, there seems to be some variation in the background rock. This variation is particularly striking when examining the trace element readings for the rock. Interestingly such variation is not apparent in the area in which Pinwheel 1 was painted, but is clear in the rest of the cave.

There is also huge variation in the iron to strontium ratio within the groups of pigment and background readings themselves, so much so that these cannot be treated as valid separate groups. Without an accurate way of extracting the pigment readings from the overall readings gained while the pigment is *in situ* these results cannot be used to come to any reliable conclusions.

Elements 3,4,5 and 6

Figure 28. Pinwheel element 3 showing positions of pigment readings a-d and 5 background readings.

The readings from the pigments in these elements vary greatly and are mixed with or overlap the background readings, as shown in figs 29-32. Element 4 has only one reading. It contrasts with the background rock but could be an anomaly. Further supporting readings would be needed for this to be considered reliable. The pigments in elements 3, 5 and 6 show a very strong statistical similarity to the rock to which they were applied, and to each other.

It may be that these areas of pigment were too faint to distinguish from the surrounding rock and therefore it is not possible to discuss their chemical composition.
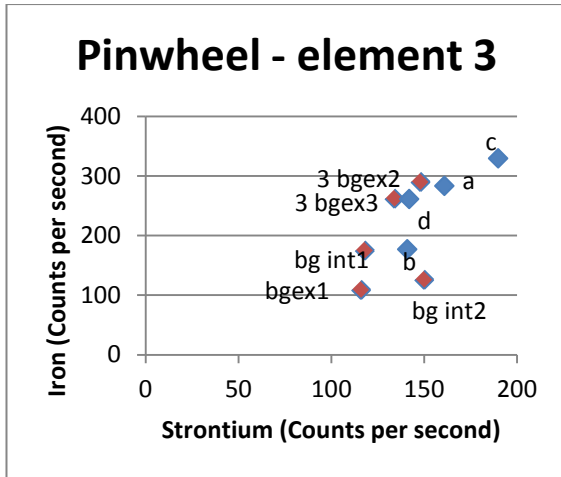
Figure 29. Scatter graph showing relative iron and strontium levels from element 3.
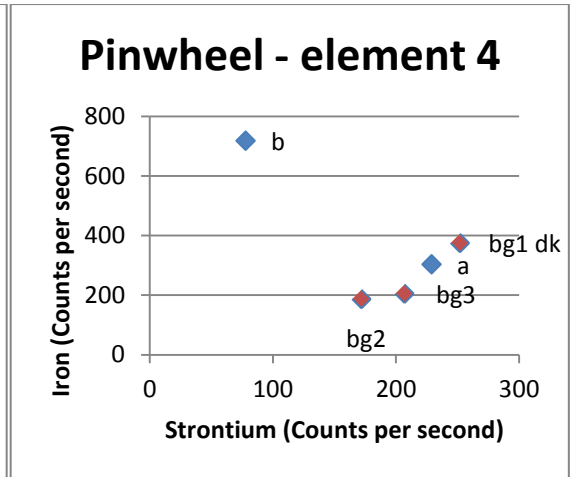
Figure 30. Scatter graph showing relative iron and strontium levels from element 4.
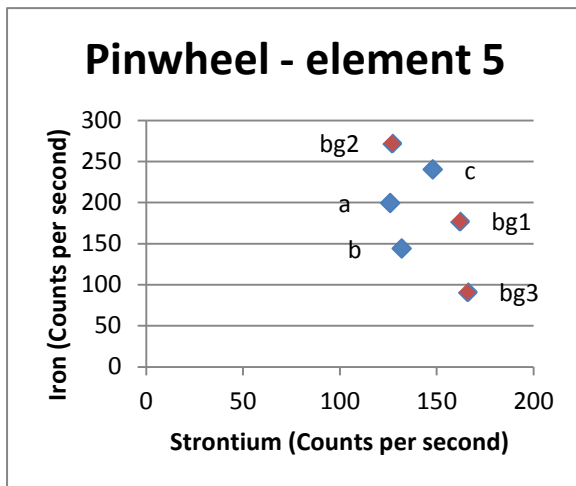
Figure 31. Scatter graph showing relative iron and strontium levels from element 5
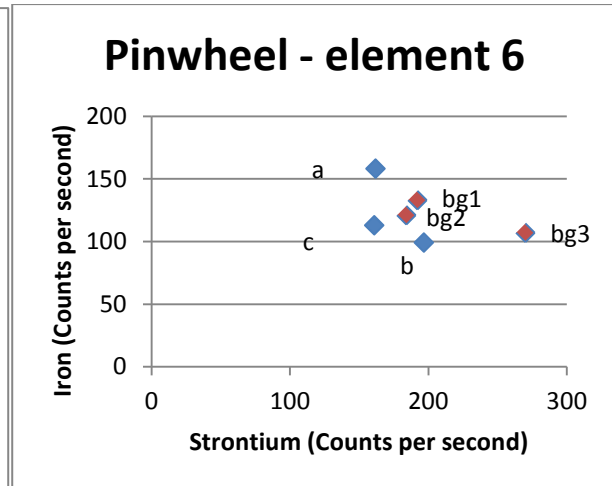
Figure 32. Scatter graph showing relative iron and strontium levels from element 6

Figure 33. Pinwheel element 4 showing positions of readings a and b and three background readings

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Figure 34. Pinwheel element 5 showing positions of readings a, b and c, and three background readings
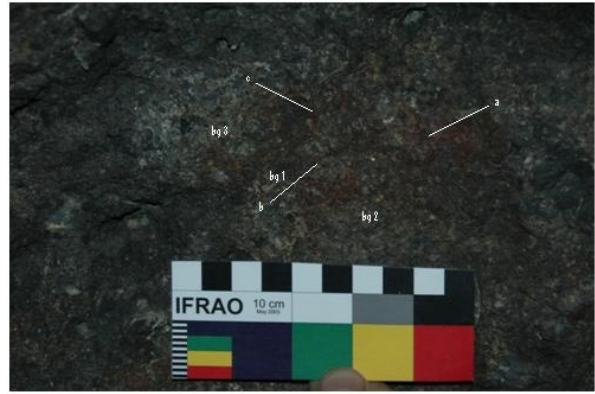
Figure 35. Pinwheel element 6 showing positions of readings a, b and c, and three background readings

Pinwheel rocks

Figure 36. Rock face adjacent to Pinwheel cave on which 'pinwheel rock' elements were applied
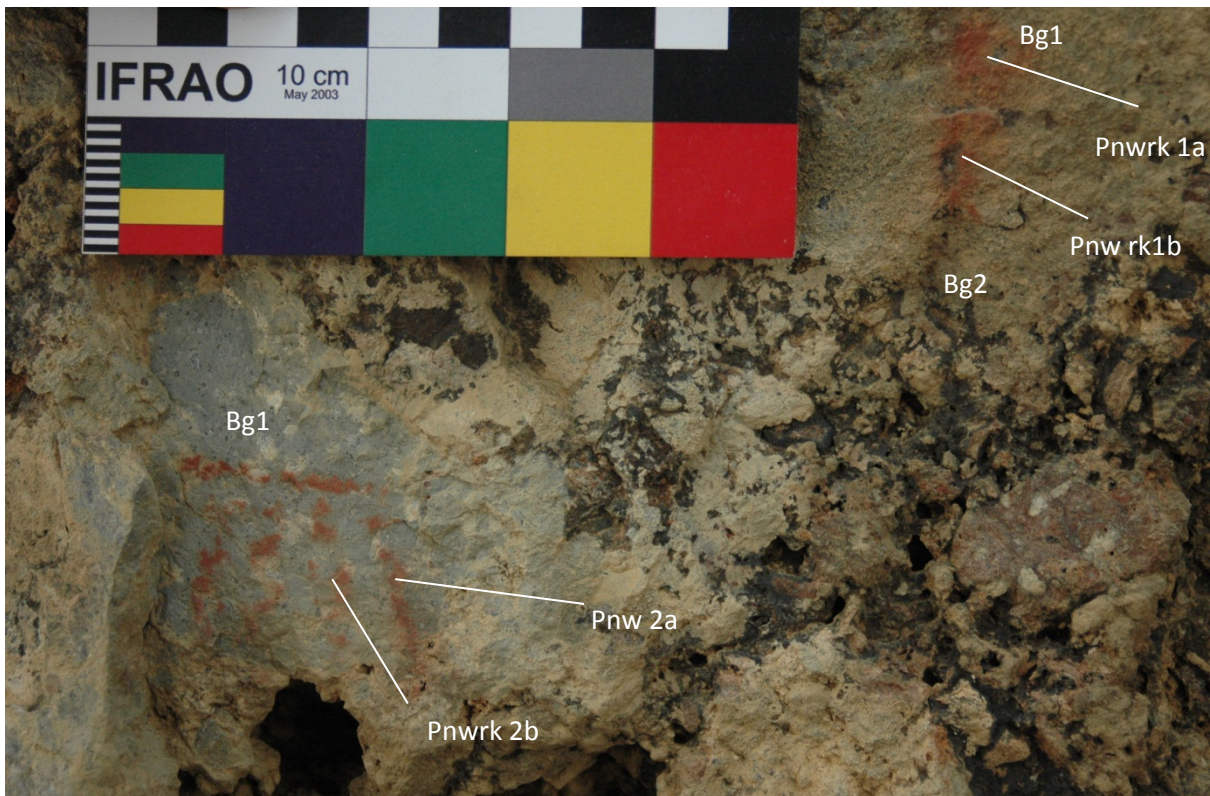
Figure 37. Pinwheel rock elements 1 and 2 showing position of pigment and background readings
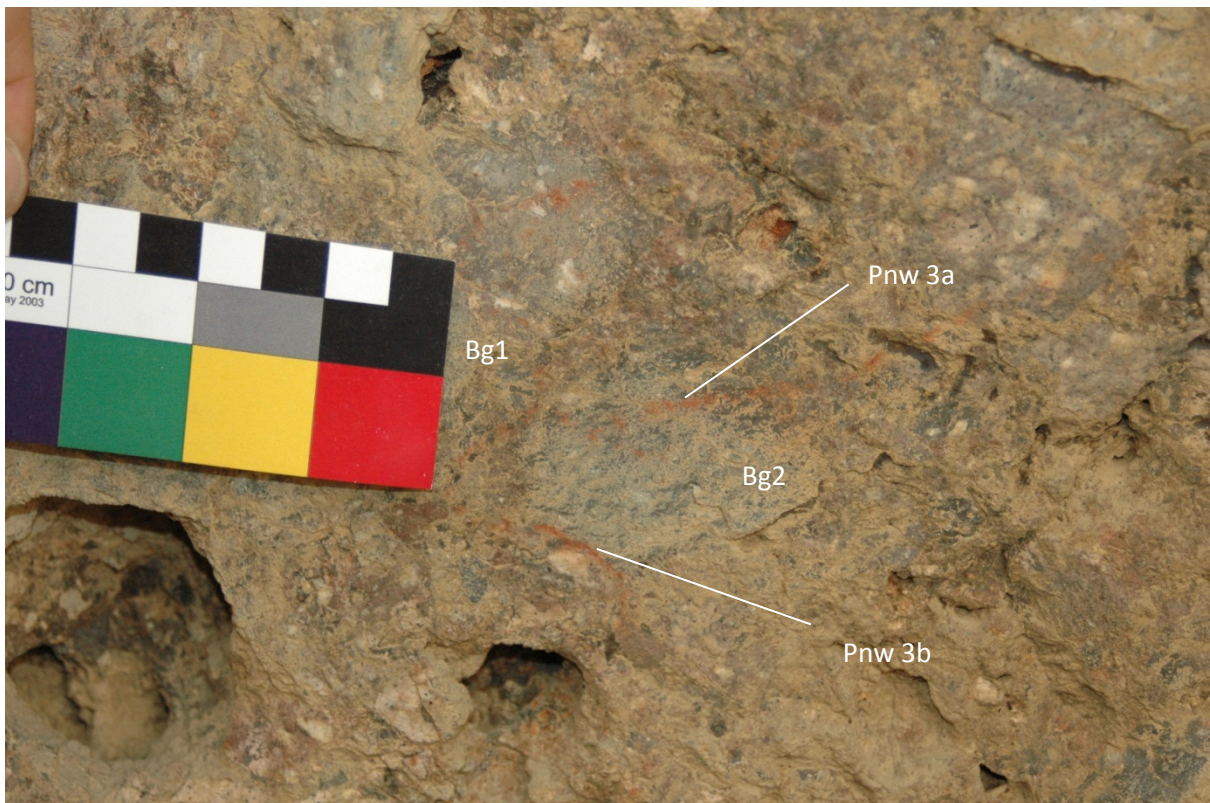
Figure 38. Pinwheel rock element 3 showing positions of pigment and background readings
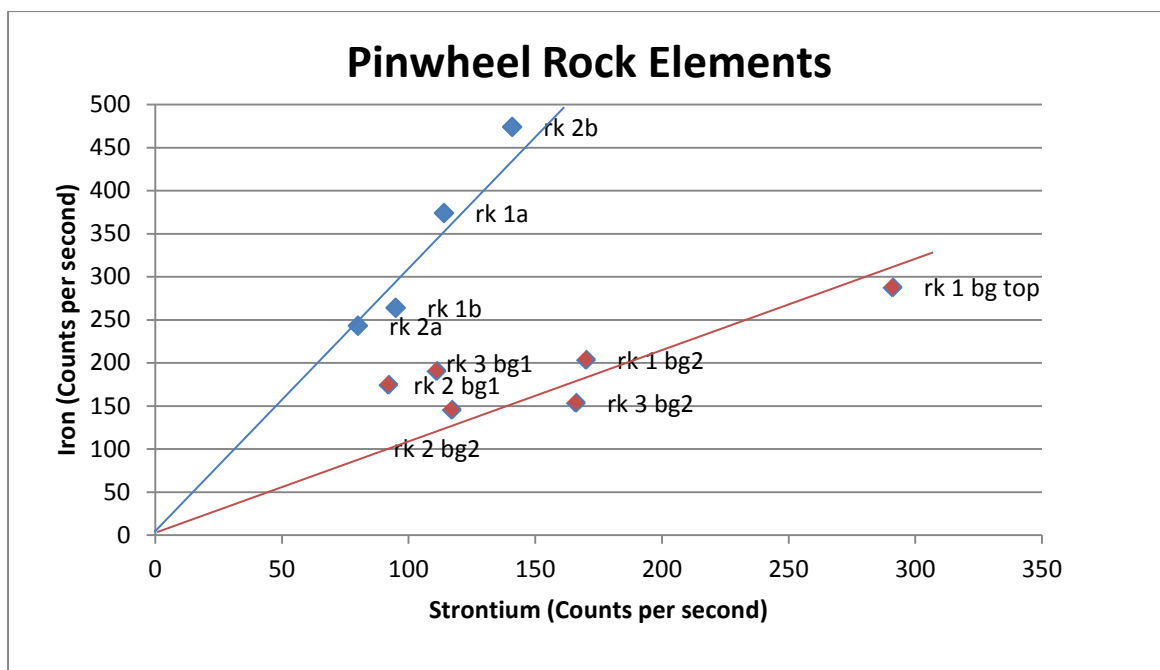
Figure 39. Pinwheel rock elements – scatter graph showing relative proportions of iron and strontium

Three elements on the rock next to Pinwheel cave were analysed. The background readings for these were largely consistent with one another but significantly different to the pigments. The pigment readings were significantly similar to one another suggesting that the same type of pigment was used for all of these.

Comparison of elements within site.

The results from all elements were compared to see how many pigments were used at Pinwheel, and if common pigments can be identified. Below is a scatter graph showing the relative iron and strontium levels in all the readings which were distinguishable from their background readings.
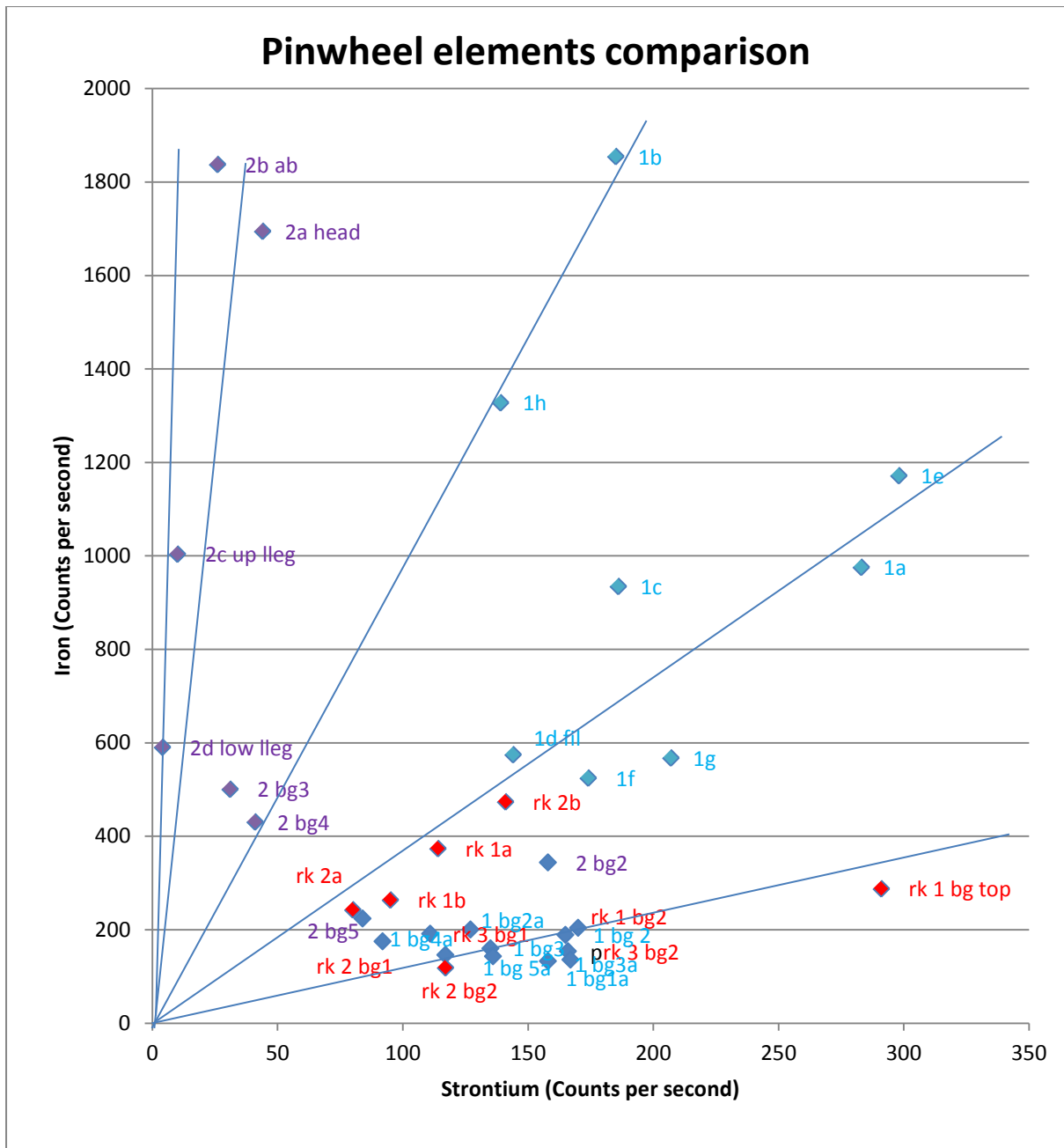
Figure 40. Scatter graph comparing iron to strontium proportions of pnw1 2 and rocks 1=◆ 2=◆ rocks=◆.

This graph shows that the background readings are statistically very similar to one another in all of the rock art elements, apart from those from pinwheel 2. As already mentioned, the great internal variation in pinwheel 2 coupled with the great trace element variation in the rock on which it was painted, prevent its readings from providing reliable information.

The pigments themselves seem to vary more than the background readings. The discrete groups identified above can still largely be seen although some of the readings from the pinwheel rock elements follow the same axis as one group of readings from pinwheel 1.

There are still clearly at least two different pigments in element 1, suggesting that this element was 'touched up' at some point using a different pigment. Pigment group pinwheel 1b appears to have been produced using the same pigment material as the Pinwheel rock elements, which is supported by variance analysis. It looks like pigment pinwheel 1a was added to this element last and so this analysis suggests that the original Pinwheel motif and the Pinwheel rock elements were produced together in an earlier phase. The pinwheel rock elements do not show any arsenic which is consistent with pigment b in element 1 in Pinwheel cave.

This first pigment identified at pnw1 (pigment 1a) appears brighter in colour than the second (1b), and these areas look like more dense areas of pigment, but they show a lower iron level, suggesting that either a different pigment source or binder was used. A change from the use of blood to cucumber extract (Scott and Hyder 1993:157-158) may explain the change in this relative iron reading, but the change in arsenic levels between them suggests the use of a different source material. It is possible of course that both the source material and processing method were changed to produce this new area of pigment.

The variation is arsenic is interesting as the increased arsenic levels do not appear exclusively in either pigment group. Although arsenic appears most in pigment a, there is some in pigment b but only in the readings at the lower end of its axis. It is possible therefore that two different source materials were used were used to produce pigments used to add to the pinwheel motif, but that these were processed similarly and contain the same binder, thereby resulting in a similar spectrum. The effect of the preparation and source material factors needs to be explored in more depth as will be discussed later.

This change may indicate either that the people visiting the site changed their method of pigment production over time, or that different people were using the site. Whatever the cause of this variation, the pXRF results at Pinwheel indicate the use of at least 3 different red pigments.

Three Springs

This site has two loci, Three Springs cave and the BRM site nearby. Readings were taken from 5 rock art elements within the panel in Three Springs cave, and four different colours including red, black white and a type of blue. Measurements were taken for each of these and the iron and strontium levels plotted against each other. XRF readings were taken from each rock art element. Below are images showing where the readings for each element were taken and scatter graphs showing the relative readings of iron and strontium for each.

Blueboy
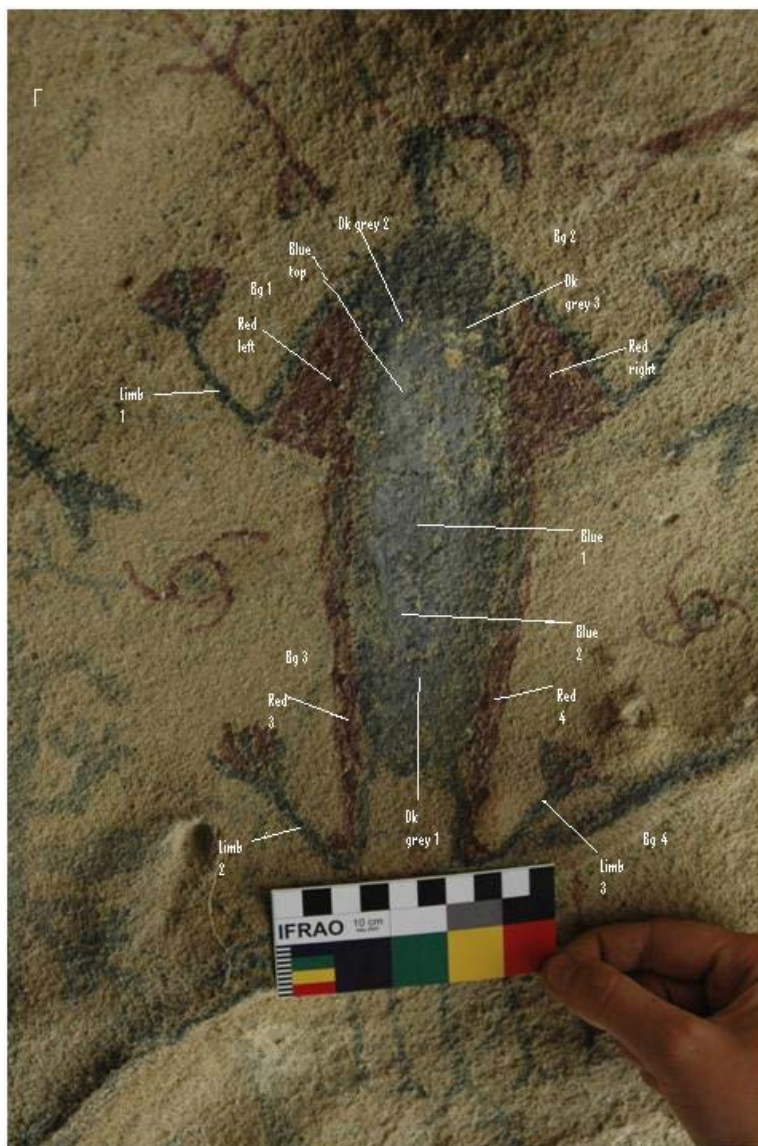
Figure 41. Photograph of Blueboy showing points at which readings were taken.
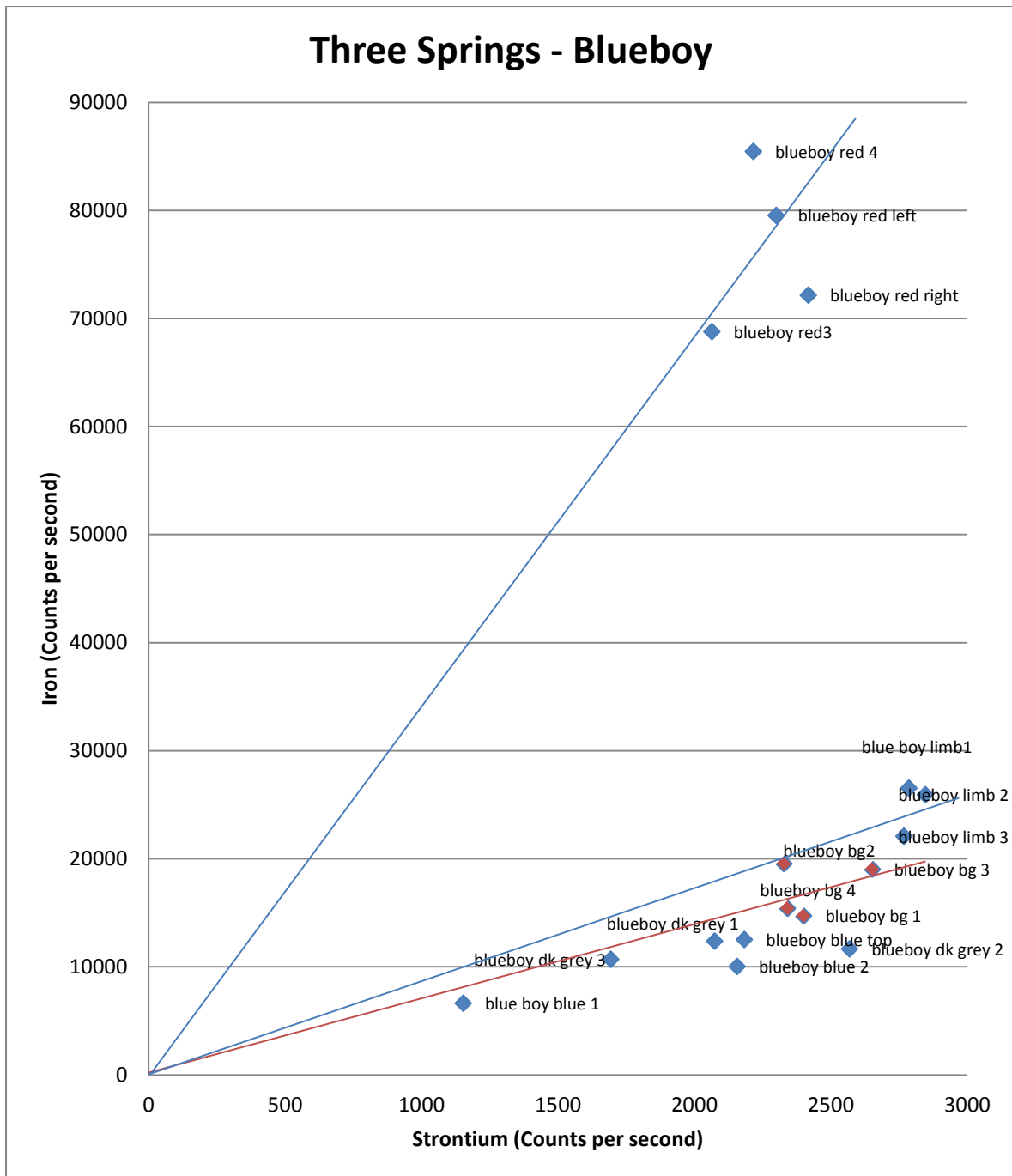
Figure 42. Scatter graph showing relative proportions of iron and strontium in readings from Blueboy

The Blueboy element is more complex than the others at this site. There are five different colours within it, including red, black, grey, white and blue. Once again the background readings form a close group.

The red pigments are particularly distinct from all the others, and when subjected to variance testing they show a 99.9% probability of being different to the other pigments and background readings

within this rock art element. They seem to form one discrete group, suggesting that they were produced using the same pigment.

The close grouping of these readings may indicate that the pigment was processed and homogenised by grinding into a powder. It also is in the form of fine lines suggesting it was applied with a brush, supporting the idea that it was processed before being applied. Its high iron content may also indicate the addition of blood as a binder (Scott and Hyder 1993:157-158).

The blue and grey pigments display the same ratio of iron to strontium as the background readings. This could be explained by the use of carbon in these pigments, as carbon is too light to be detected by portable XRF and would not show up in the results (Pollard *et al.* 2007:107). The blue and grey pigments seem to have a weaker signal than the background readings which would also be explained by the presence of a material which was interfering with the XRF signal produced by the rock, but which is not detectable by the device, such as carbon.

There has been much discussion about the materials used in Chumash blue pigments such as the one seen here, (Scott *et al.* 2002:190; Reeves et al 2009) and whether it is the result of the addition of metals such as copper or cobalt to the mix, or a particular combination of black and white pigments which refract light in a way which appears blue. Scott *et al.* (2002) analysed a similar blue pigment produced by the Chumash and found it to consist of white gypsum (a sulphur compound), and a finely ground charcoal black which combined to produce a blue appearance (Scott *et al.* 2002:190). This was described as 'optical blue', which can also be produced using calcite as the white component (Scott *et al.* 2002:190).

Here the blue pigment appears to consist of the same material as the grey pigment, and there is no copper present. There are traces of sulphur present in both the blue and grey pigment, although this is also present in the rock so may not be part of the pigment itself. The lack of any blue colouring mineral elements here suggest that it is most likely that optical blue that was used here.

Fig 8

Figure 43. Photograph of 'fig 8' element showing points from which readings were taken.
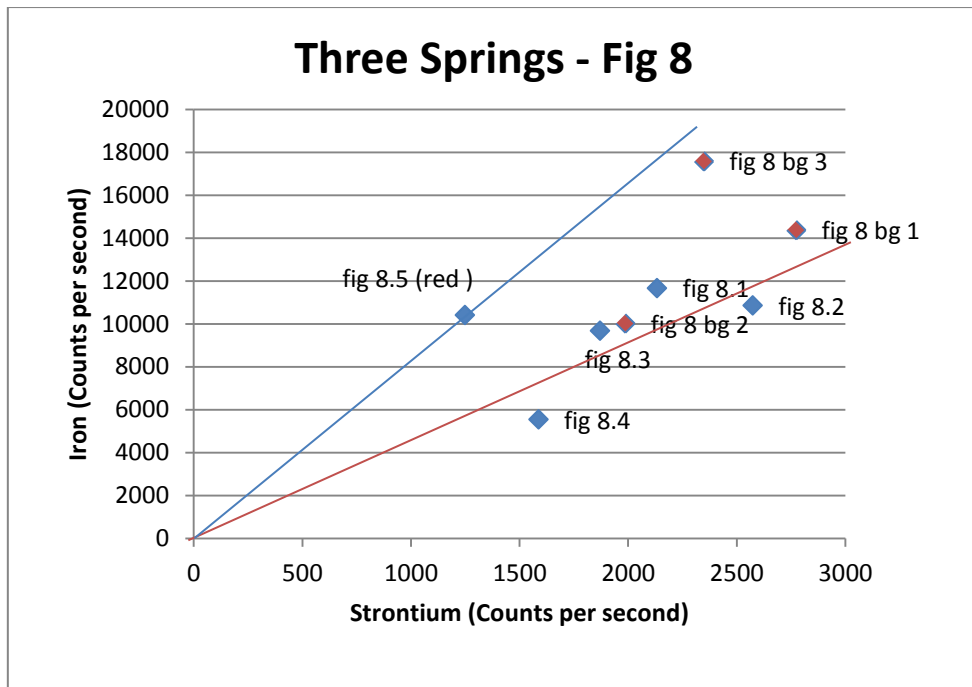
Figure 44. Scatter graph showing relative amounts of iron and strontium in results from 'fig 8'

Once again the background readings here showed the same ratio of iron to strontium as most of the pigment readings which were from black pigments. This suggests that these are also carbon based black pigments.

The single red pigment reading ('fig 8.5' in fig. 44 above) seems to show a different ratio of iron to strontium to most of the other readings within this element. Unfortunately, as there is only one reading for the red pigment this could not be tested using the ANOVA test, or used to draw any reliable conclusions. It is therefore unclear if this reading contrasts significantly with either the background material or the black pigment and more readings from the red part of the element would be needed to determine this.

Zoomorph

Figure 45. 'Zoomorph' at Three Springs showing points from which readings were taken
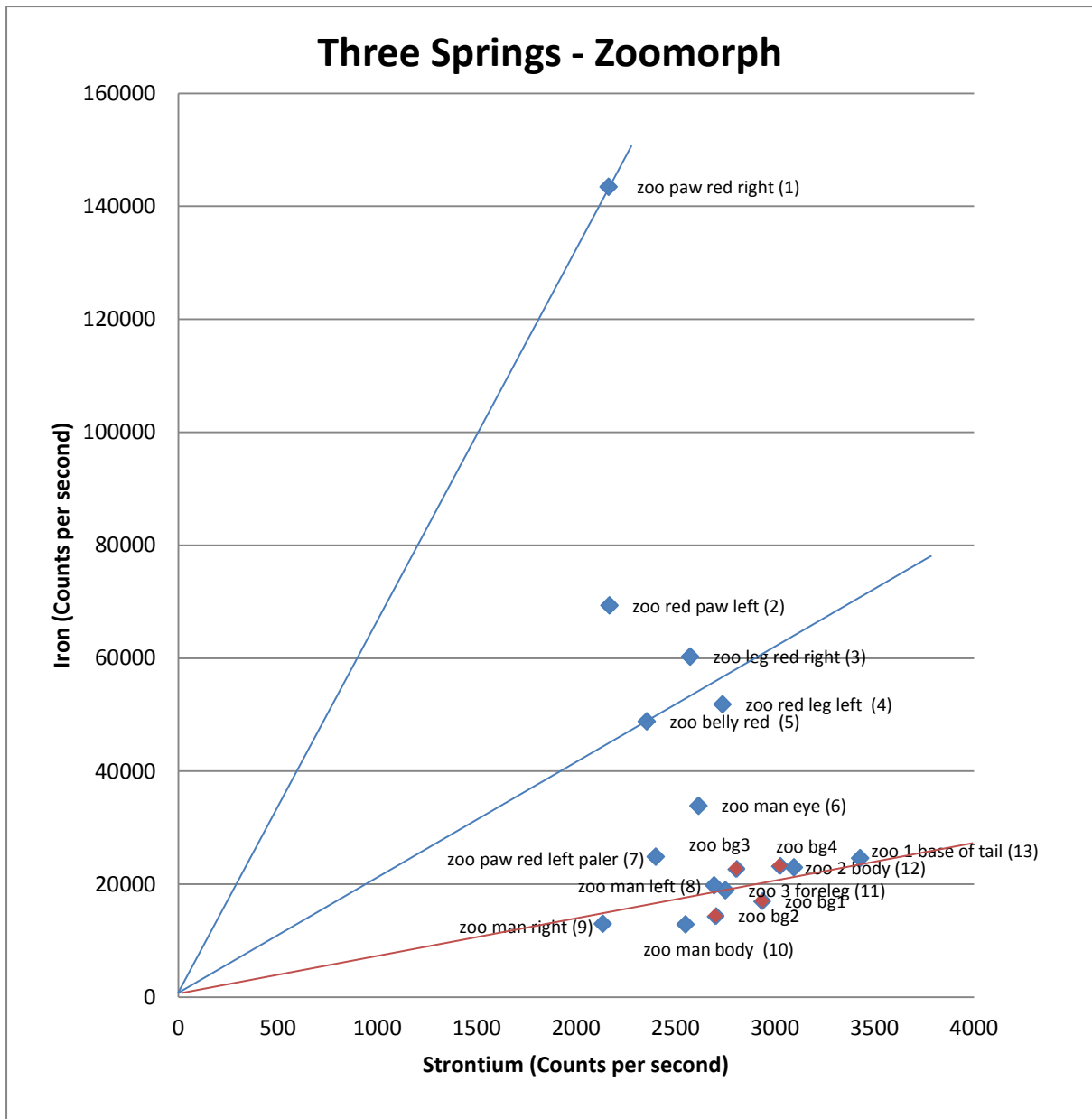
Figure 46. Scatter graph showing relative iron and strontium readings from 'Zoomorph' at Three Springs

The background readings in the zoomorph element form a close group. The red pigment in the body of the zoomorph is very distinct from the other colours and from the background readings.

Once again the black pigments in the 'zoomorph man' element show similar proportions of strontium and iron to background rock, possibly indicating the use of charcoal for these parts of this element.

The red pigment in the man and the left paw of the zoomorph are not statistically different to the background or the black pigments, which may be because they are too faint or too thinly applied to contrast sufficiently with these.

The readings for most of the red legs and paws (2,3,4 and 5) form a discrete group. This group may include the eye of the man figure incorporated into the zoomorph, and the zoomorph's left paw. This sort of wide internal variation may indicate direct application of raw pigment which would be consistent with the visual appearance of the red parts of this element. The right paw (1) shows a significantly higher proportion of iron to strontium.

It is possible therefore that this area was retouched after it was originally produced using a pigment either made from a different source material or produced using a different binder. For example, the addition of blood to the mix here would explain a significant rise in the proportion of iron. Unfortunately there is only one reading from this part of the element. It is therefore hard to say if this is just an anomalous reading, and this reading cannot be compared statistically with the others

Zigzag
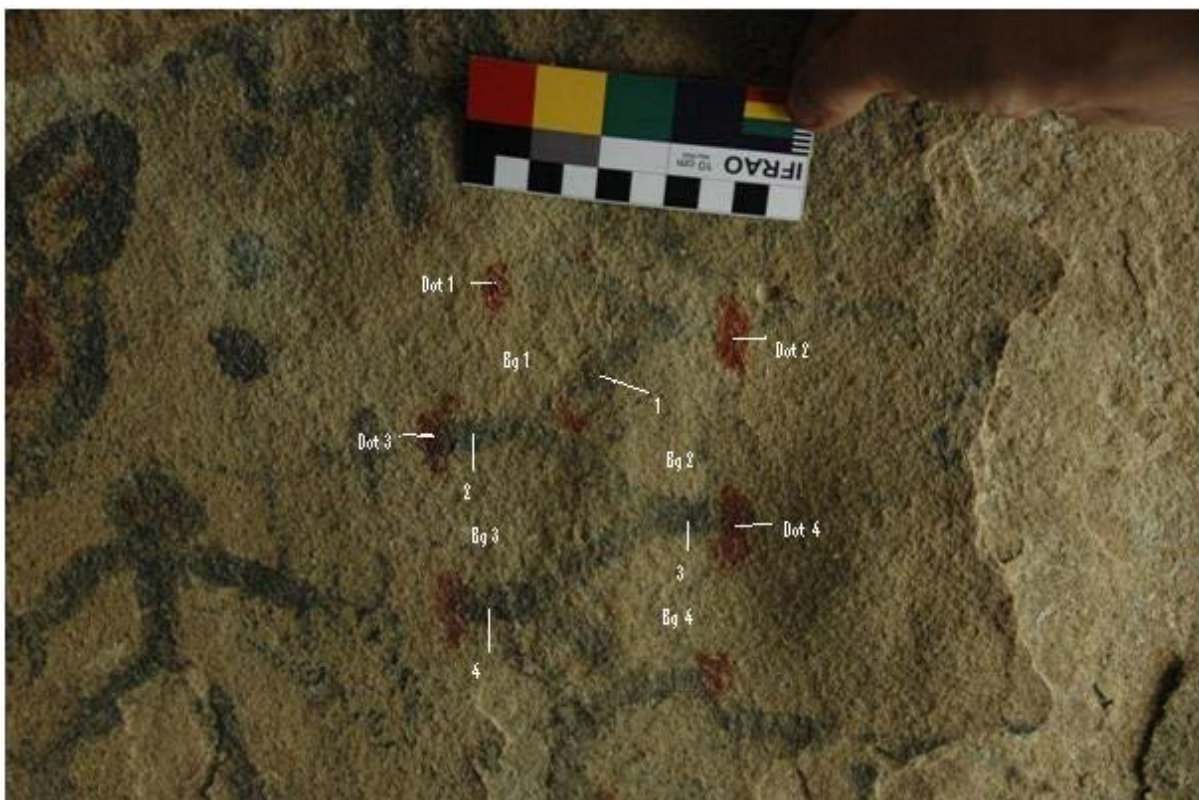
Figure 47. 'Zigzag' at Three Springs showing points from which readings were taken
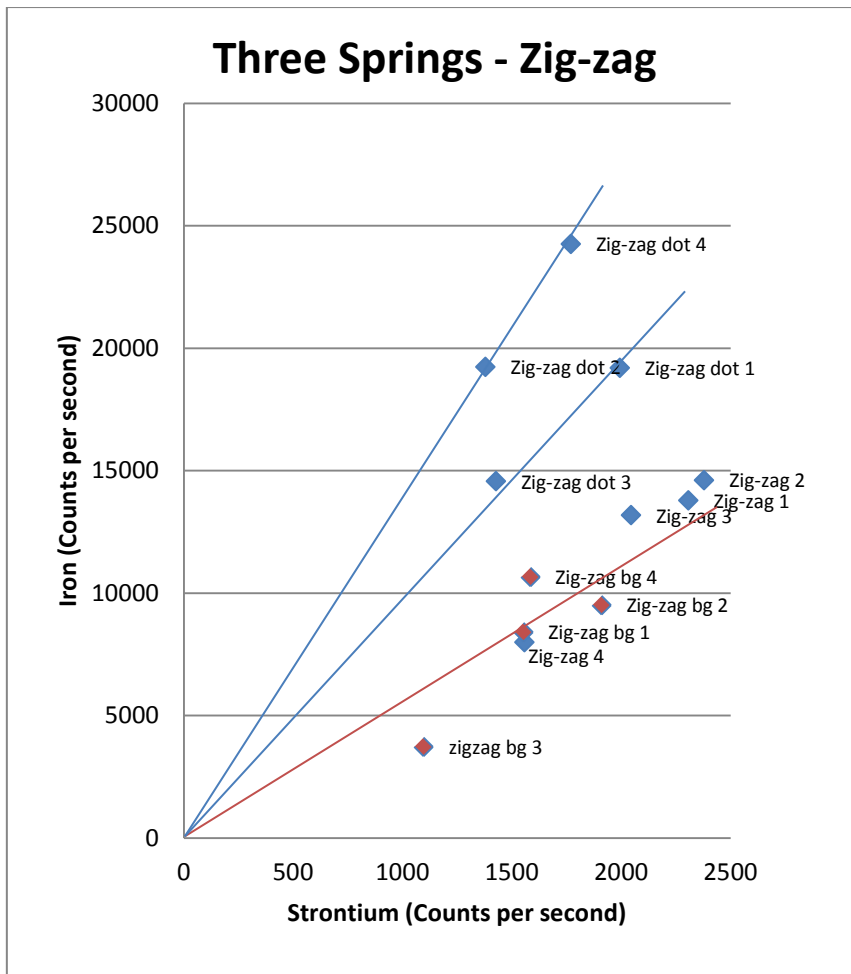
Figure 48. Scatter graph showing relative iron and strontium levels in readings from 'Zigzag' at Three Springs.

Three different chemical signatures can be seen in the zigzag at Three Springs.

The first of these is shared by the background readings and the pigment readings for zigzag 1-4. As these are readings from black pigment it is unsurprising that they do not contrast with the background, and again it seems likely that charcoal has been used.

The rest of the pigment readings are distinct from the background. These are readings from the red dots within the element. These dots appear to have been produced using two different pigments judging by the contrasting ratio of iron to strontium in zigzag 1 and 3 compared to zigzag 2 and 4. These pairs of dots are statistically different to both the background and black pigment, and to each other.

It is of course possible that these readings form one pigment group. However, the readings fit perfectly onto their respective ratio axes, and these axes are diverging suggesting different trends. Further readings would be needed to confirm whether or not these are actually different materials.

Bird
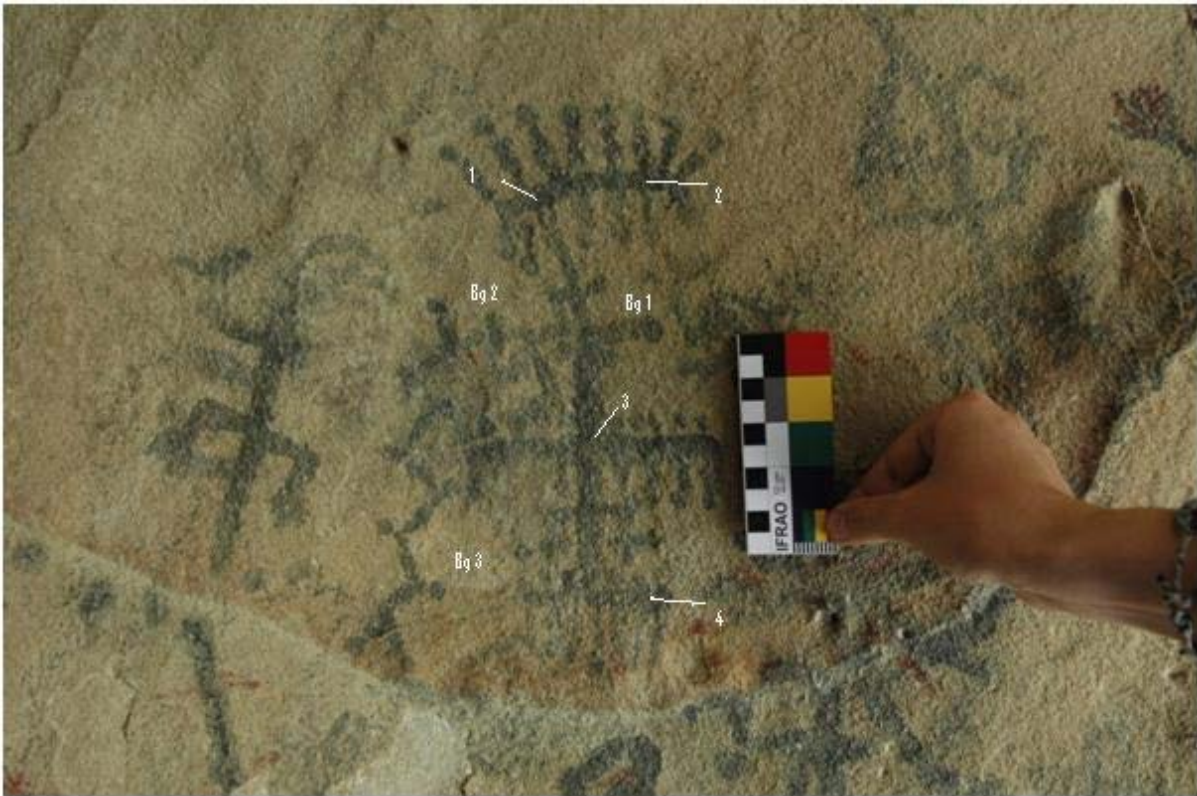
Figure 49. 'Bird' at Three Springs showing points from which readings were taken
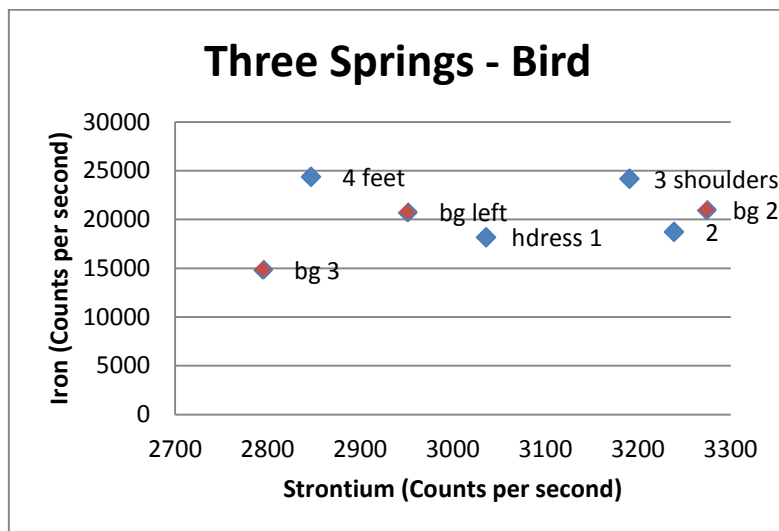
Figure 50. Scatter graph showing relative iron and strontium levels in readings from 'bird' at Three Springs

The pigments in the bird are not distinct from the background readings, as is supported by variance testing. The pigment material cannot therefore be identified in this element.

BRM
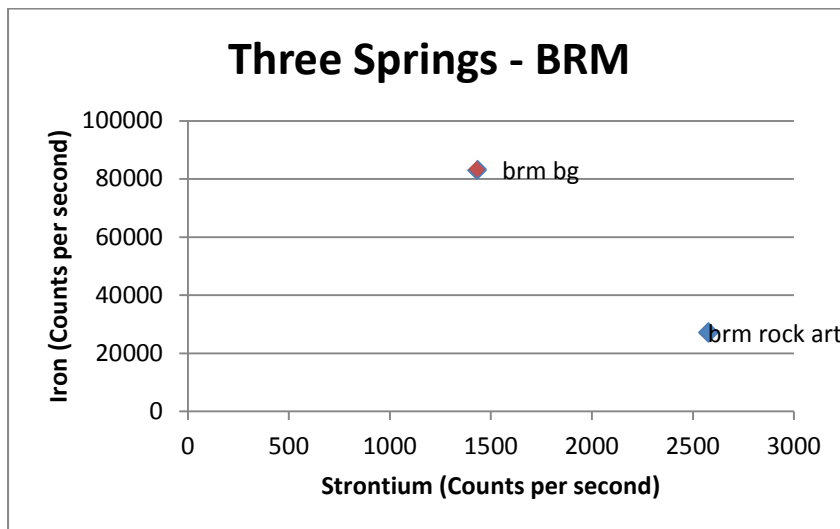
Three Springs - BRM

Figure 51. Scatter graph showing relative iron and strontium levels in readings from BRM at Three Springs

Readings were taken from rock art in the small cave underneath the BRM on site. In this element the pigments show lower iron levels than the background rock. However, there are not enough readings here to make a useful comparison.
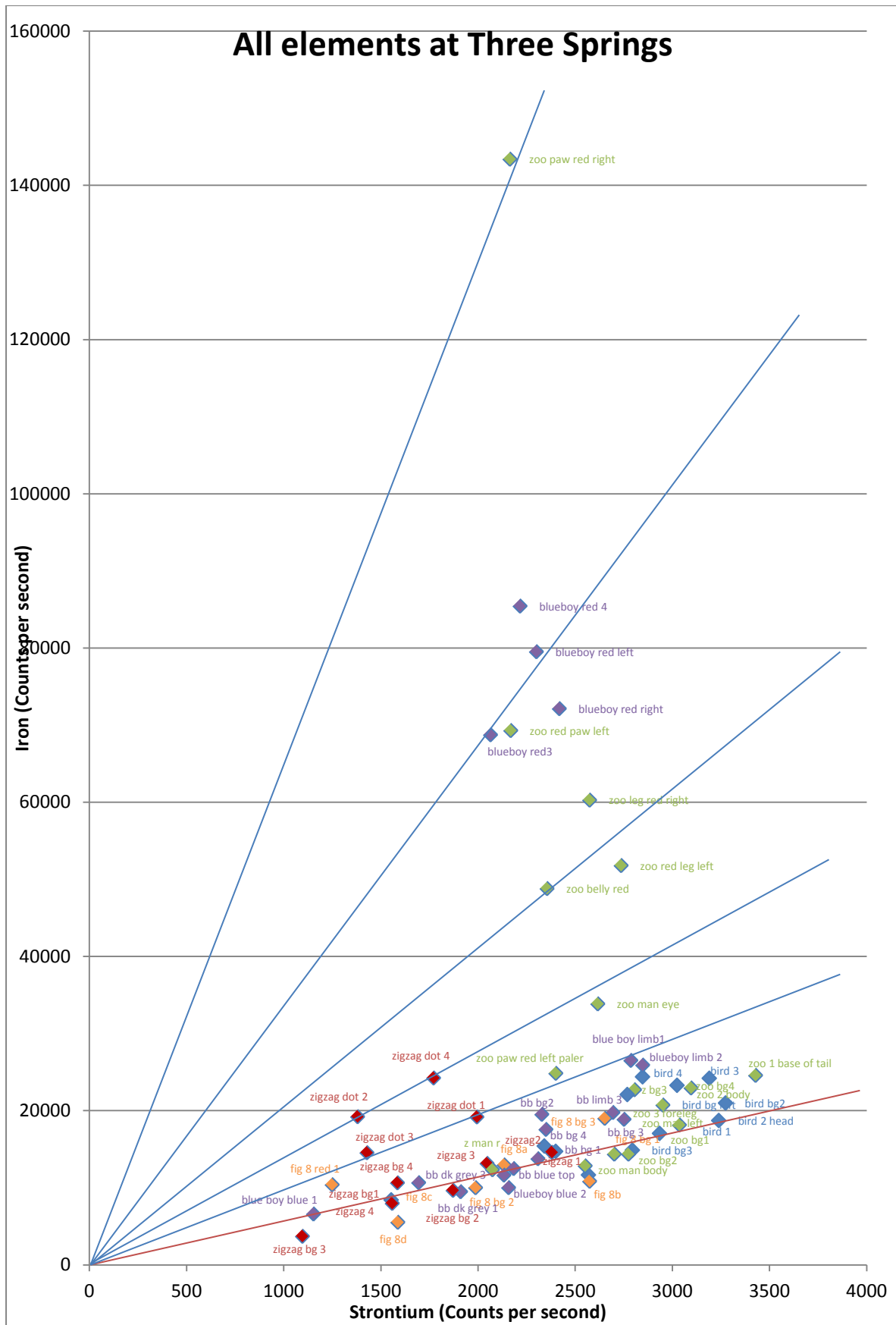
Figure 52. Scatter graph showing relative levels of iron and strontium in readings from all elements at Three Springs fig 8= ◆ zoomorph = ◆ bird = ◆ blueboy = ◆ zig-zag = ◆.

When comparing all of the elements from Three Springs it is clear once again that the background readings for each show similar proportions of iron to strontium to one another.

Although there is some overlap between the red pigments used in the zoomorph and blueboy, these still form significantly different groups of readings indicating that two different pigments were used here.

Most of the black pigments show the same proportions of iron to strontium as the background but the black pigment used in Blueboy's limbs contrasts with the background and the other black pigments in this panel, and this background material seems to be consistent across the panel. Most elements at Three Springs do not contain any manganese, and those with traces of manganese do not show levels which contrast at all with their background material, thus indicating the use of a carbon based black pigment (Nuevo *et al.* 2011:4).

The pigments in zigzag dot 2 and 4 show a much more subtle contrast with their background readings than the zoomorph and blueboy red pigments, but when examined separately the dots clearly contrasted with their background readings. Therefore these results indicate that different pigments were used in the dots, blueboy and the zoomorph, the contrast seen between two groups of readings within the dots indicate that two different pigments were also used to produce these. The zoomorph's right paw has an Fe/Sr ratio which contrasts with all the others, but this is a single reading which may be anomalous and which cannot be included in the variance analysis.

The results from the red pigments indicate that there are at least three, and probably four, different red pigments at Three Springs. The black pigments appear to be consistent across the site and the blue pigment seems to be optical blue. As the readings for the zigzag dots are very close relative to the other elements it is possible that these represent one pigment with a wide internal range, but there do appear to be two pigments there. Given the range of materials here it is safe to say that there were at least four red pigments painting events at Three Springs and eight painting events when black, grey, white and blue pigments are considered.

Pond

At this site there were two loci, Pond Boulder which includes Pond Alcove and Pond 'Window Box', with three panels between them. At each locus XRF readings were taken from each rock art element. Below are images showing where the readings for each element were taken and scatter graphs showing the relative readings of iron and strontium (Fe/Sr) for each.

Pond Alcove
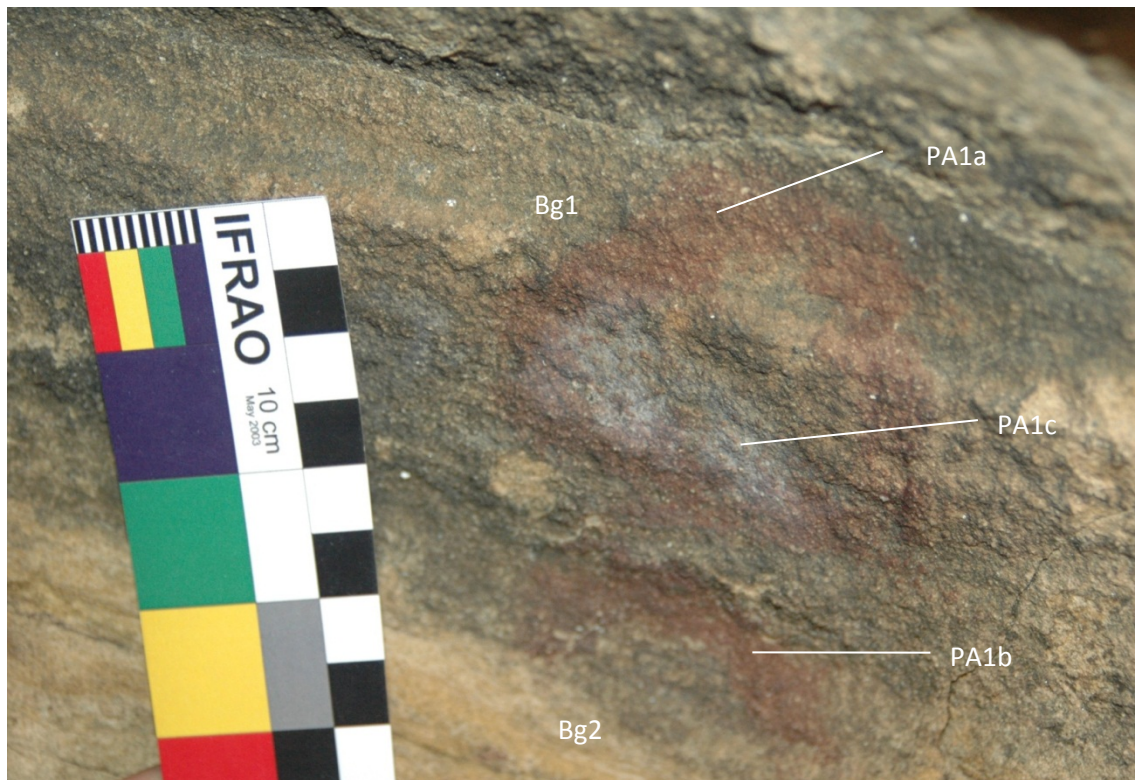
Figure 53. Pond Alcove showing points from which readings were taken
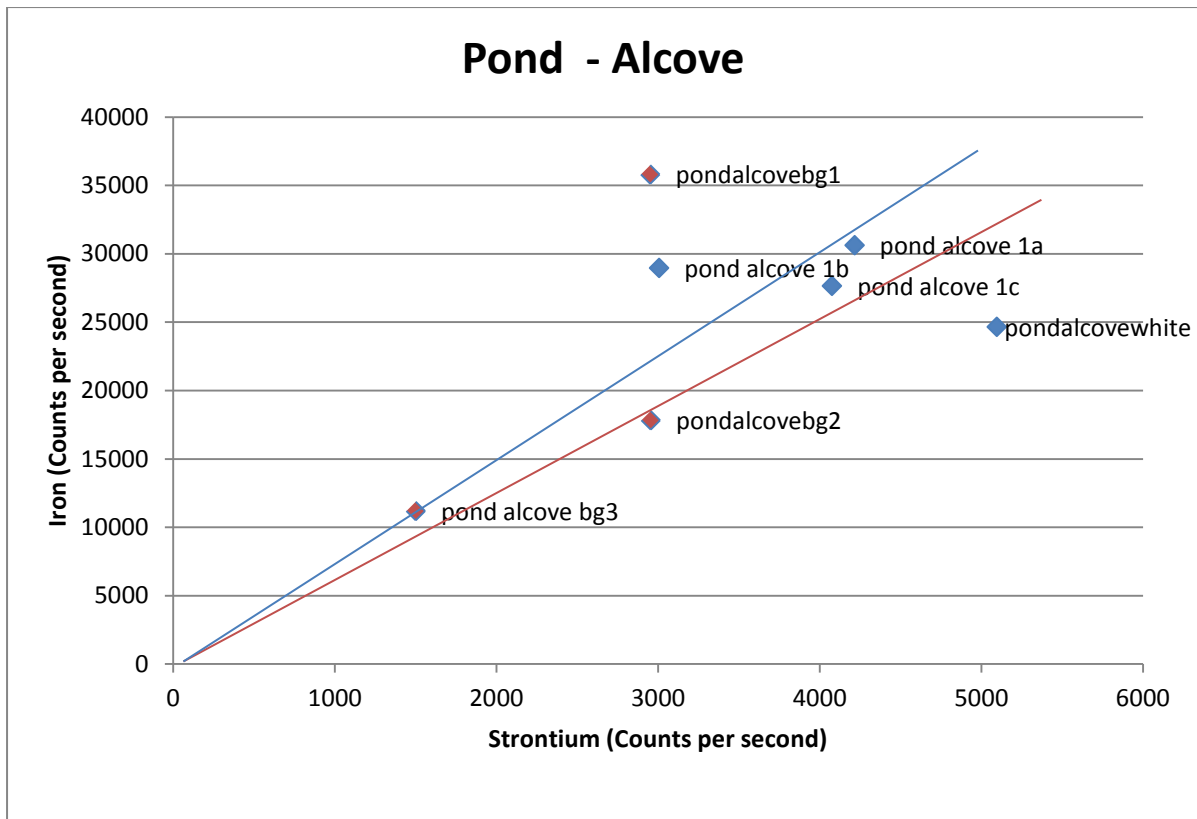
Figure 54. Scatter graph showing relative levels of iron and strontium in readings from Pond Alcove

Although an optimistic eye can attempt to pick out distinct groups of readings in this graph, the pigments here show too much similarity with the background rock to be able to draw any useful conclusions from. The possible white pigment does not contrast with the background rock in terms of iron content but it is unlikely that iron would have been used to make a white pigment. Its calcium levels are marginally higher than the rock to which it was applied, but not any higher than those in the red pigments. Therefore I cannot confidently state that white pigment was applied here.

Pond Boulder
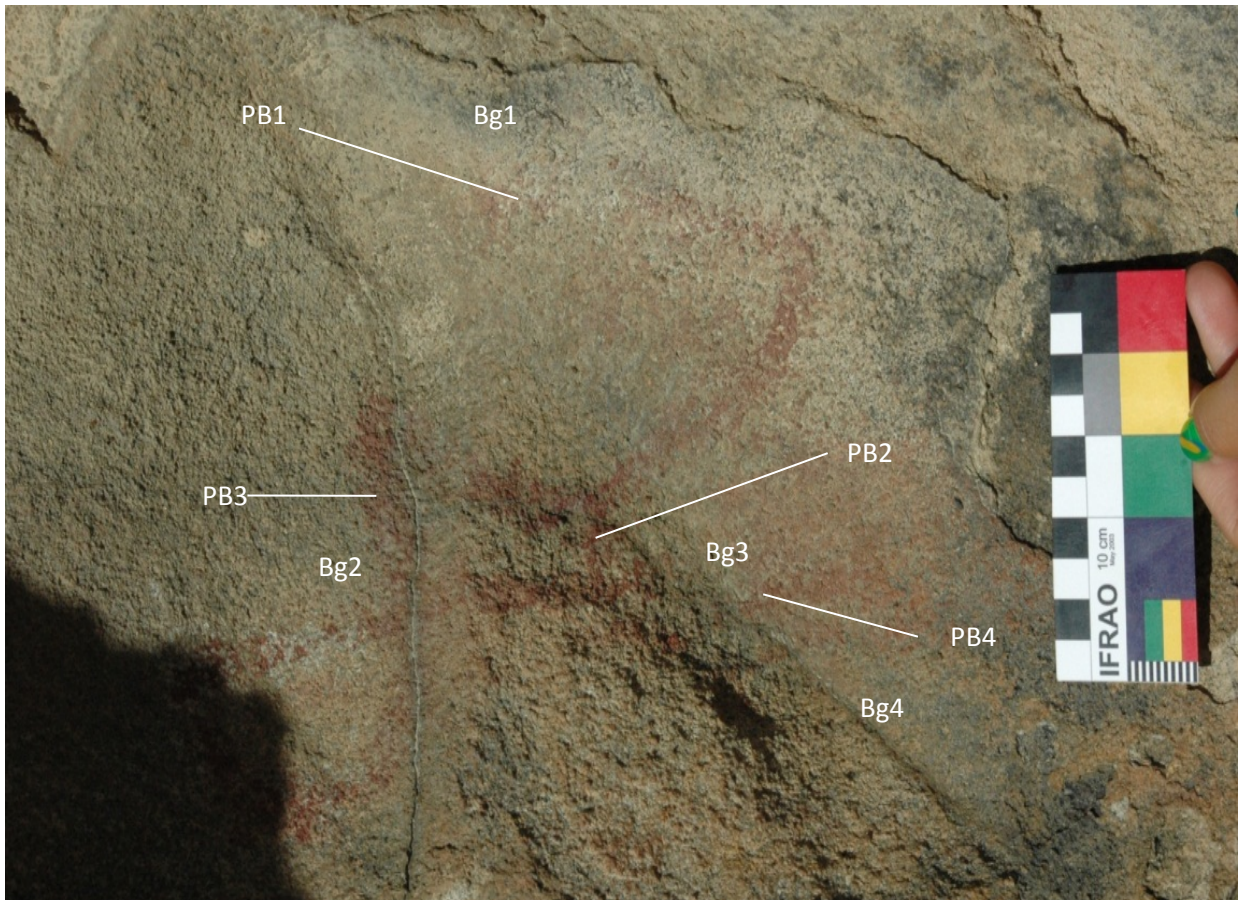
Figure 55. Pond Boulder showing points from which readings were taken
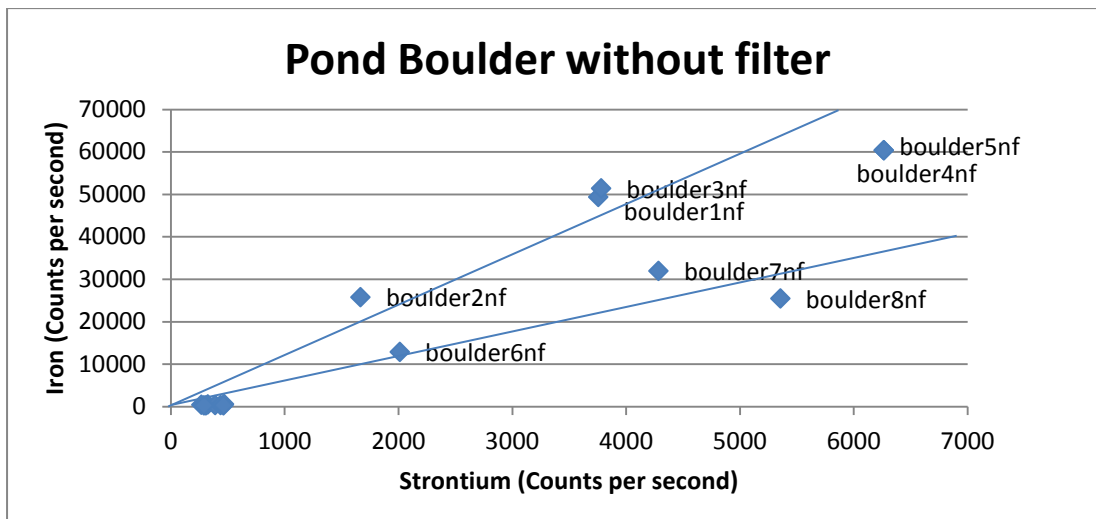
Figure 56. Pond Boulder - scatter graph showing relative levels of iron and strontium

In the results from Pond Boulder there appear to be two different groups of pigment readings. Unfortunately there are no background readings in the results but two distinct groups of readings

can be seen here. Boulder 1,2 and 3 seems to be different to readings 4-8. This may indicate that this element was not produced in one instance but that an original motif was added to at a later date.

'Window Box'

Figure 57. Overview of Pond 'Window Box'
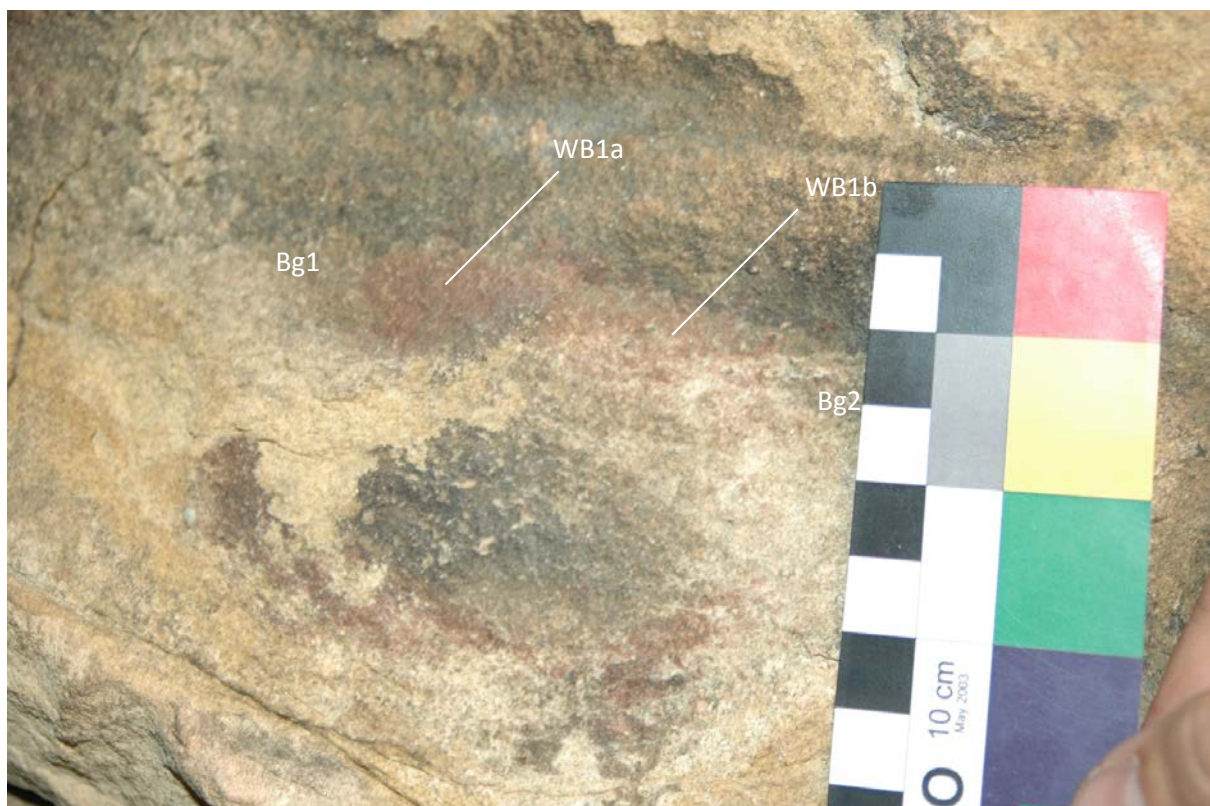
Figure 58. Pond 'Window-Box' element 1 showing points from which readings were taken
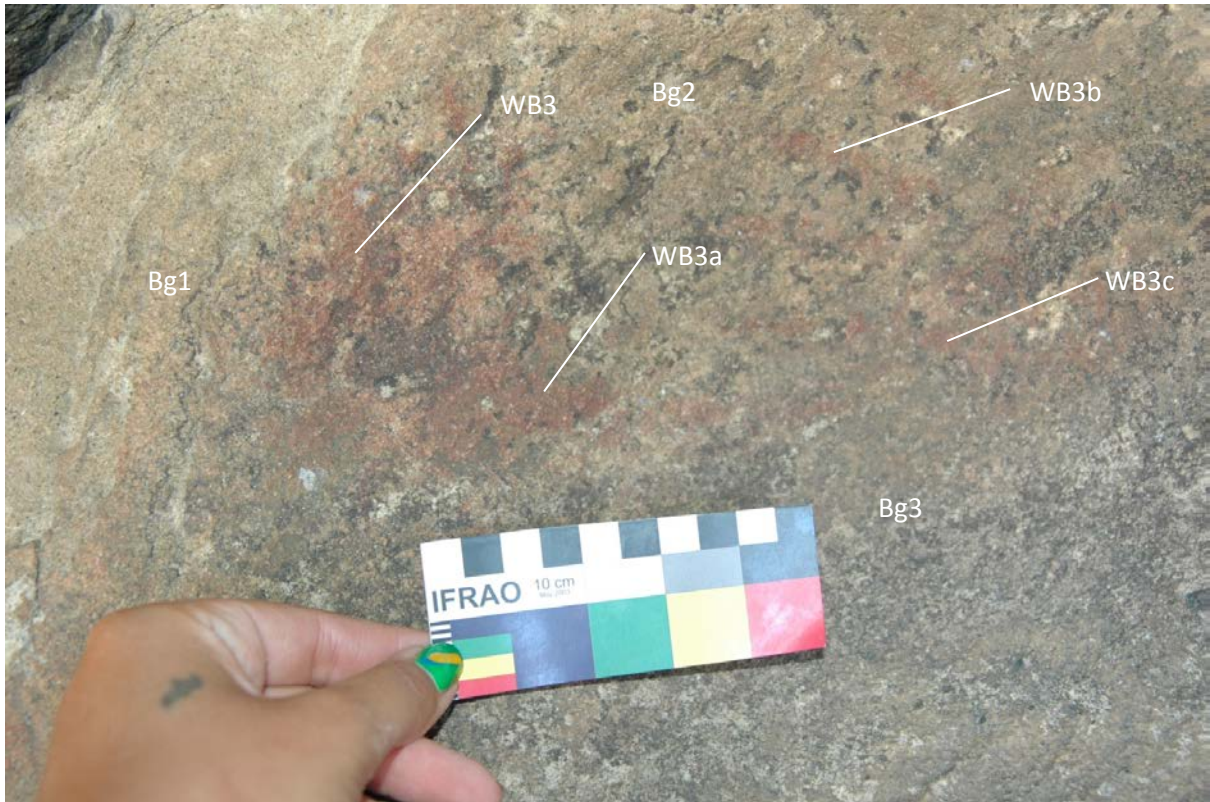
Figure 59. Pond 'Window Box' element 3 showing points from which readings were taken

Figure 60. Pond 'Window Box' element 4 showing points from which readings were taken

Figure 61. Pond 'Window Box' element 5 showing point of reading
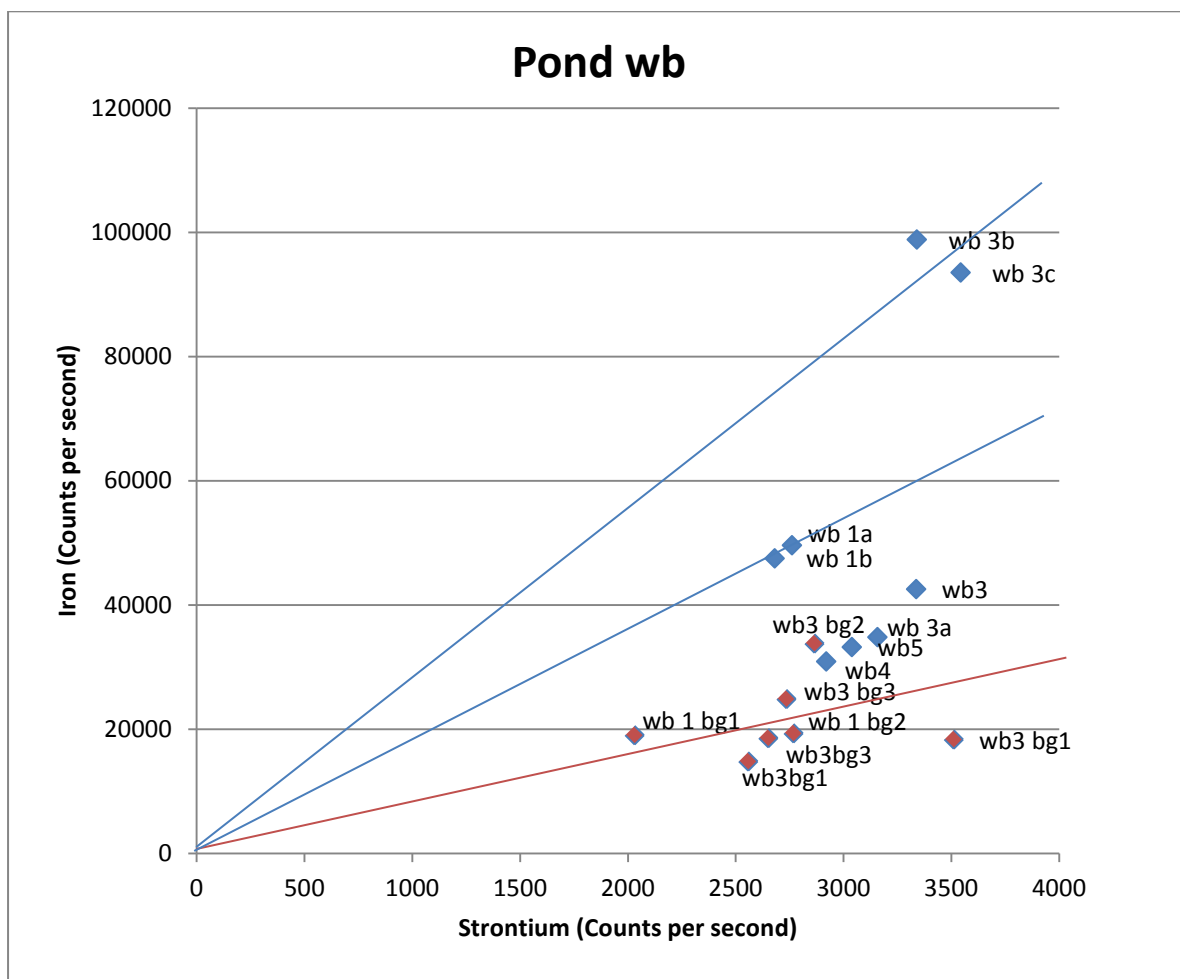
Figure 62. Pond 'Window Box' - scatter graph showing relative levels of iron and strontium

In the Pond 'Window Box' panel four elements were analysed, elements wb1, 3, 4 and 5. The background readings all show very similar composition, and this composition is also shared by readings from 4 and 5 as well as some of the readings from wb3. However two readings from wb1 contrast significantly with these, and two of the readings from wb3 are starkly different to all of the other readings from this panel. It seems likely therefore that at least two pigments were used here. It is possible also that two pigments were used in wb3 but it may be that some of the pigment in wb3 was simply too faint for its characteristic X-Rays to be detected.
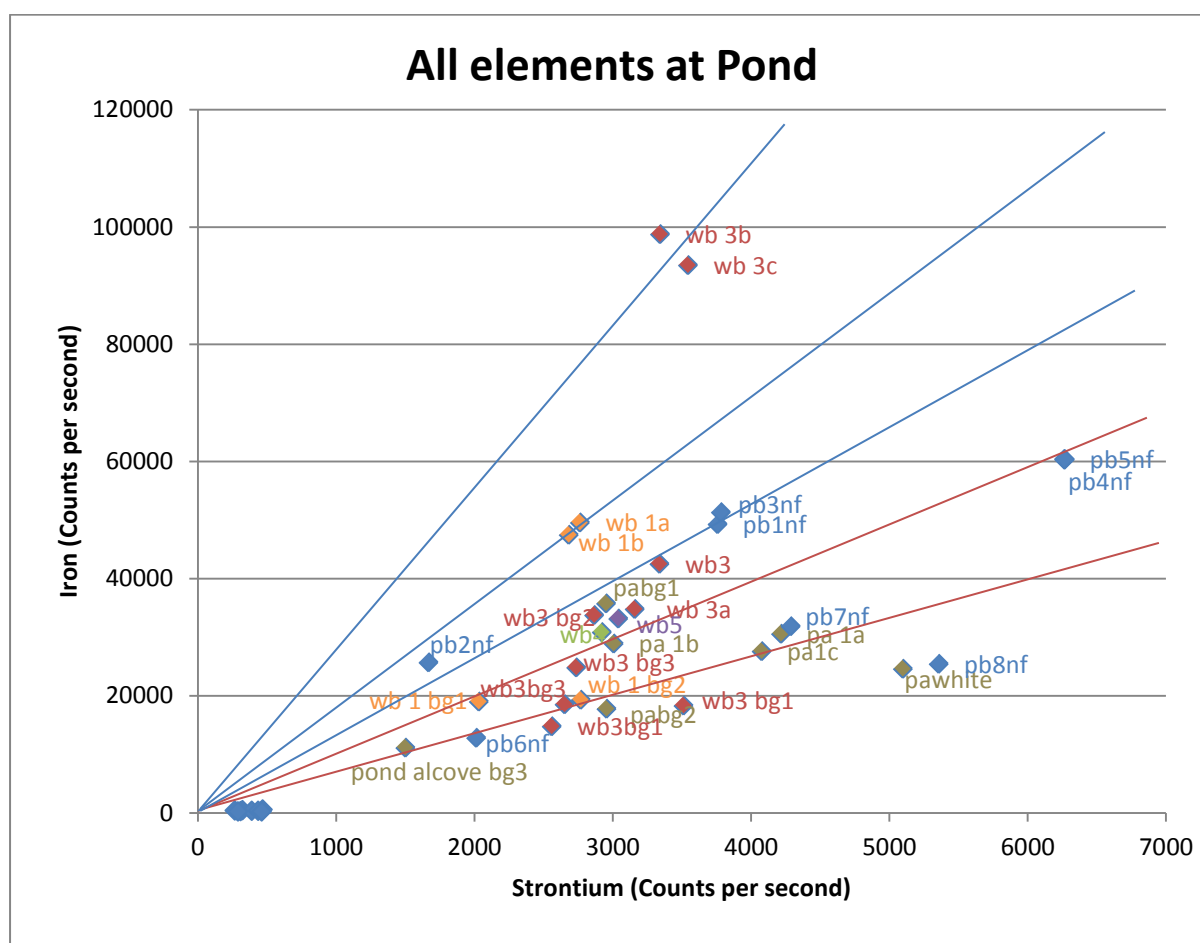
Figure 63. Scatter graph showing relative levels of iron and strontium in all elements at Pond window box 1=◆ pond boulder =◆ window box 4 =◆ pond alcove =◆ window box 3 =◆ window box 5 =◆

The elements at Pond Window Box appear to have been produced using different pigments to the rest of the elements at the Pond site and it appears that the Pond Boulder element contains two different pigments. Two of the wb3 readings are definitely different from the others, displaying substantially higher iron readings, and wb1 also appears to be in a group on its own.

The background readings from all the elements show similarity to readings from wb 3, 4 and 5, some of the readings from Pond Boulder, and all the readings from Pond Alcove. However, one set of readings from Pond Boulder does contrast with these, as do the groups identified in Pond Window Box. This indicates at least three pigments used here.

Variance analysis of all the results from this site indicates that there are two contrasting pigments at pond boulder and at least two at the pond window box. As the pigment at the alcove does not contrast with its background, it cannot be compared with the other pigments. Similarly the variation between the backgrounds of pond boulder and the window box makes it difficult to reliably compare the pigments of these panels. However, these results indicate at least two painting events in these panels and pigment can be seen in the alcove. From this it is fair to estimate up to five red pigments and potentially six painting events taking place at Pond when the possible white pigment is included.

Los Lobos

There are two separate caves at Los Lobos, the upper and lower caves. Here they are referred to Los Lobos and Los lobos lower. At each locus XRF readings were taken from each rock art element. Below are images showing where the readings for each element were taken and scatter graphs showing the relative readings of iron and strontium for each. These axes are shown in blue on each graph for the pigment readings and in red for the background.

Los Lobos 1
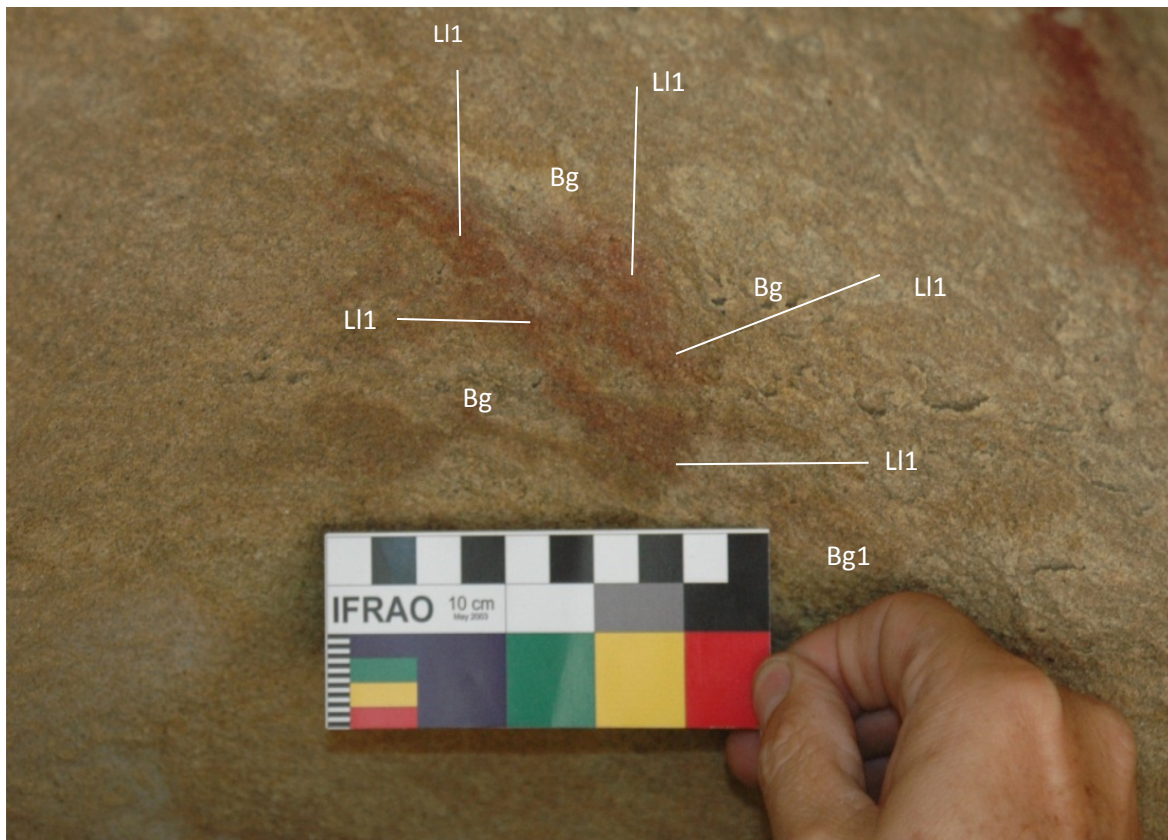
Figure 64. Element 1 at Los Lobos showing the points from which readings were taken
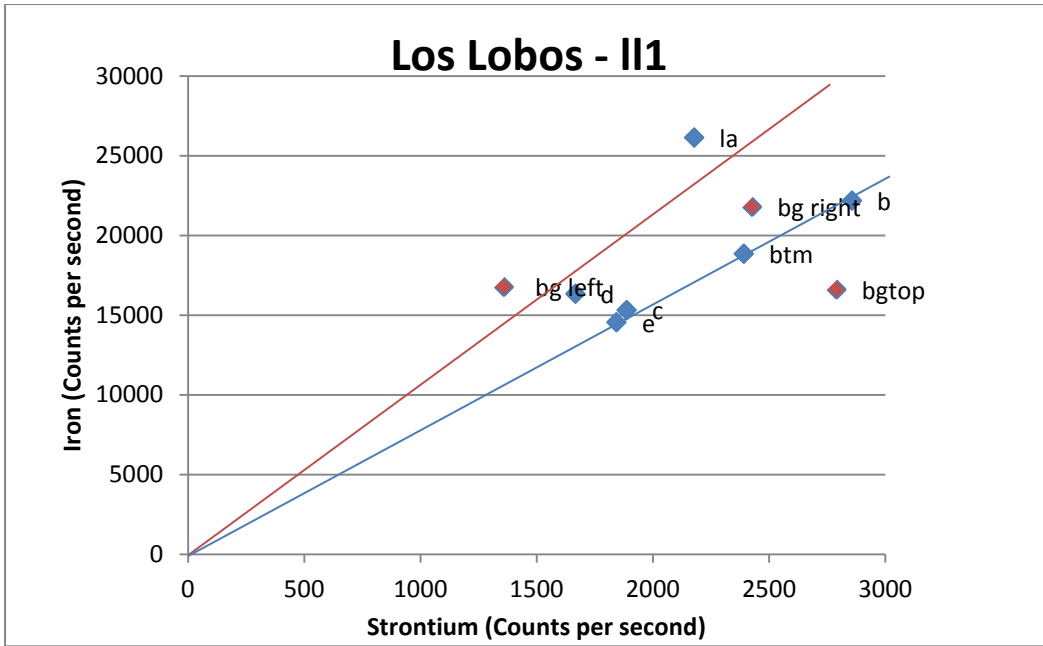
Figure 65. Scatter graph showing relative levels of iron and strontium in Los Lobos element

The pigment readings from this element are difficult to distinguish from the background, and statistical testing shows no significant difference between the two. It is not therefore possible to draw any conclusions from these results about the pigment used.

Los Lobos 2
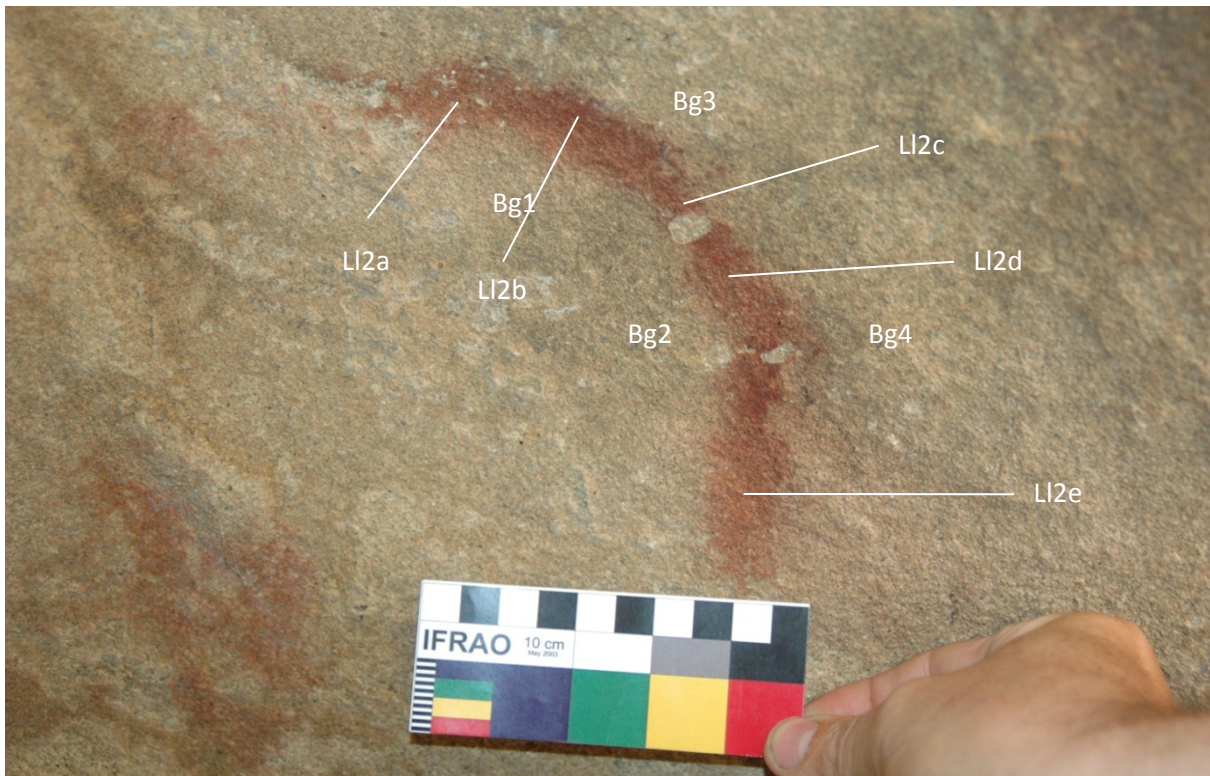
Figure 66. Element 2 at Los Lobos showing the points from which readings were taken
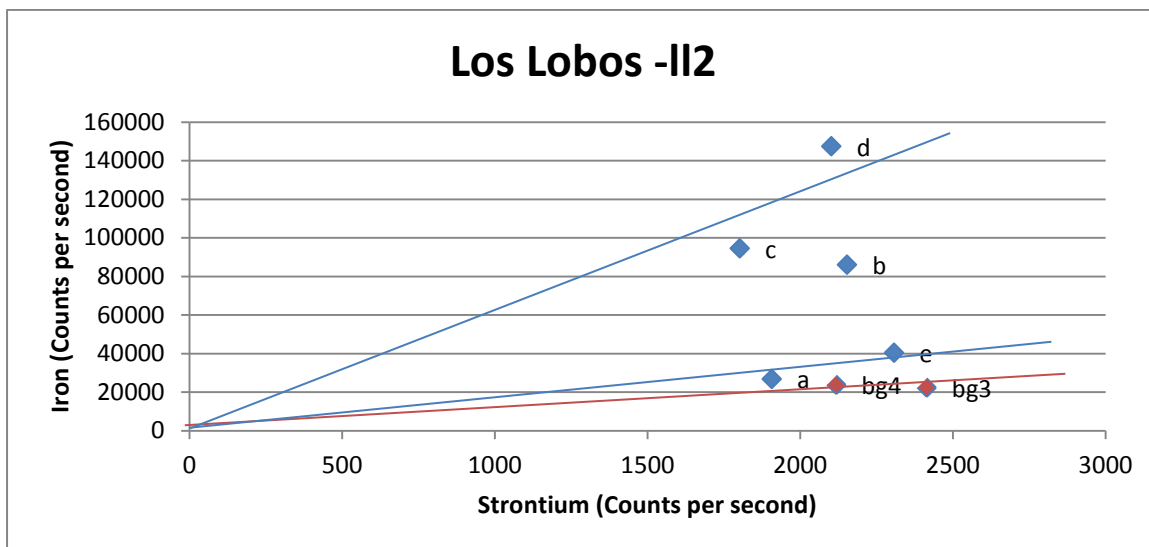
Figure 67. Scatter graph showing relative levels of iron and strontium in Los Lobos element 2

It is possible to see three groups of readings in this element. One group contains background readings and two groups of pigment readings. Out of the pigment readings b, c and d form one group and a and e are in the other. When examined using variance testing the group containing b, c and d is indeed significantly different to a and e, and to the background readings. However, readings a and e show a very strong statistical similarity to the background reading and so cannot be treated as a separate pigment group. It seems more likely that this pigment simply is not emitting a strong enough XRF signal to contrast with the rock to which it was applied. As such it is not possible to tell if this is a different pigment or not and must conclude that there is one distinct pigment in ll2.

Los Lobos 3

Figure 68. Element 3 at Los Lobos showing the points from which readings were taken
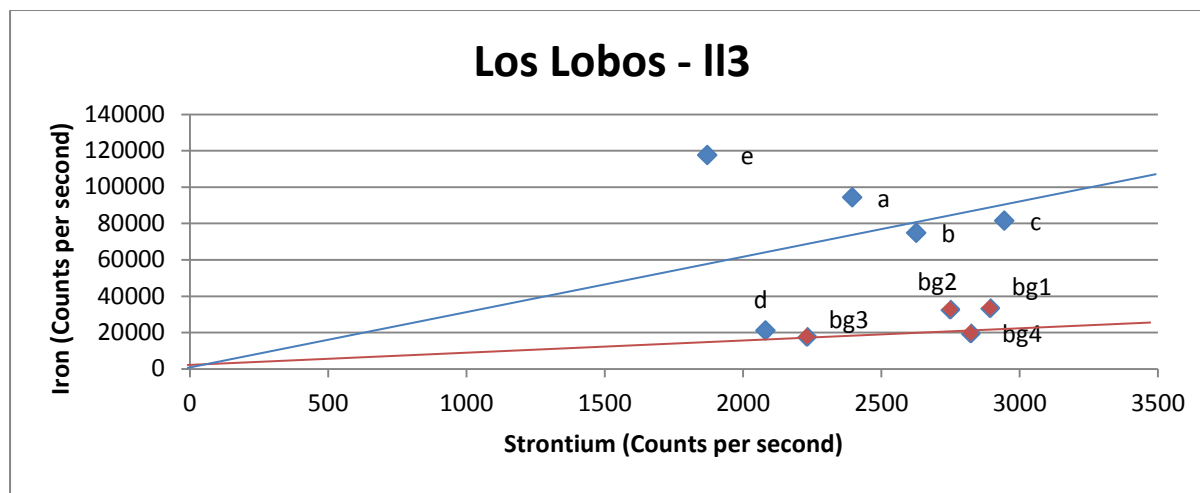
Figure 69. Scatter graph showing relative levels of iron and strontium in Los Lobos element 3

The readings for this element are quite varied relative to other elements, but they fit into a normal distribution and form a group which is significantly different to the background readings. Therefore it is likely that this element consists of one pigment.

Figure 70. Elements 4 and 5 at Los Lobos showing the points from which readings were taken
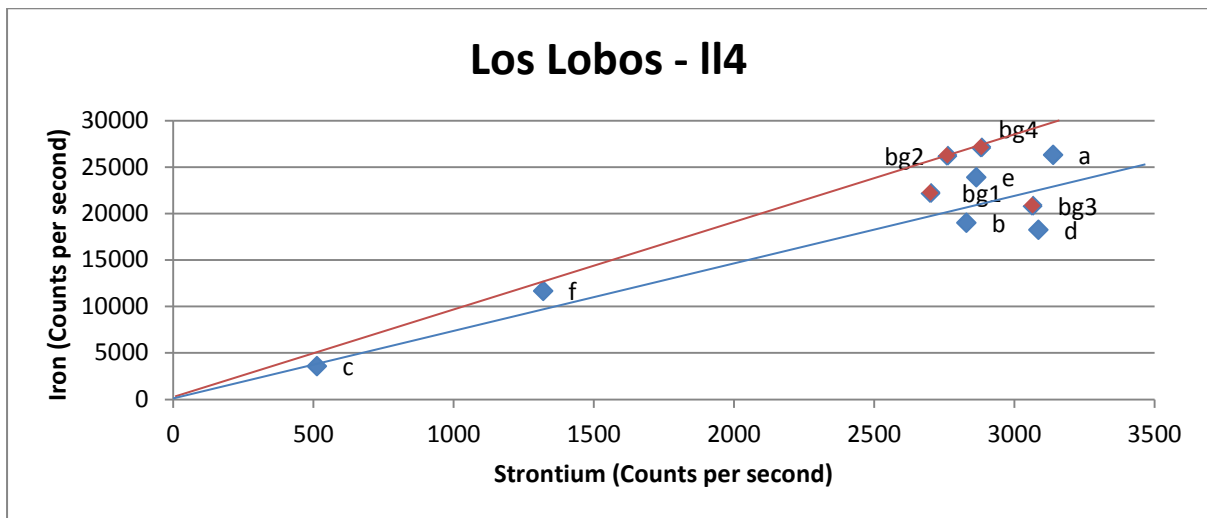
Figure 71. Scatter graph showing relative levels of iron and strontium in Los Lobos element 4

Element 4 at Los Lobos is a black linear element. Most of the results from this element form a discrete group which includes both pigment and background readings. Readings c and f are distant from this group but still have the same proportion of iron to strontium.

As carbon is too light for pXRF to detect it is logical that any carbon based black pigment would display the same proportions of these chemicals as the background rock. As this element does not display any manganese readings black pigment is likely to be made from charcoal (carbon).

Figure 72. Element 6 at Los Lobos showing the points from which readings were taken
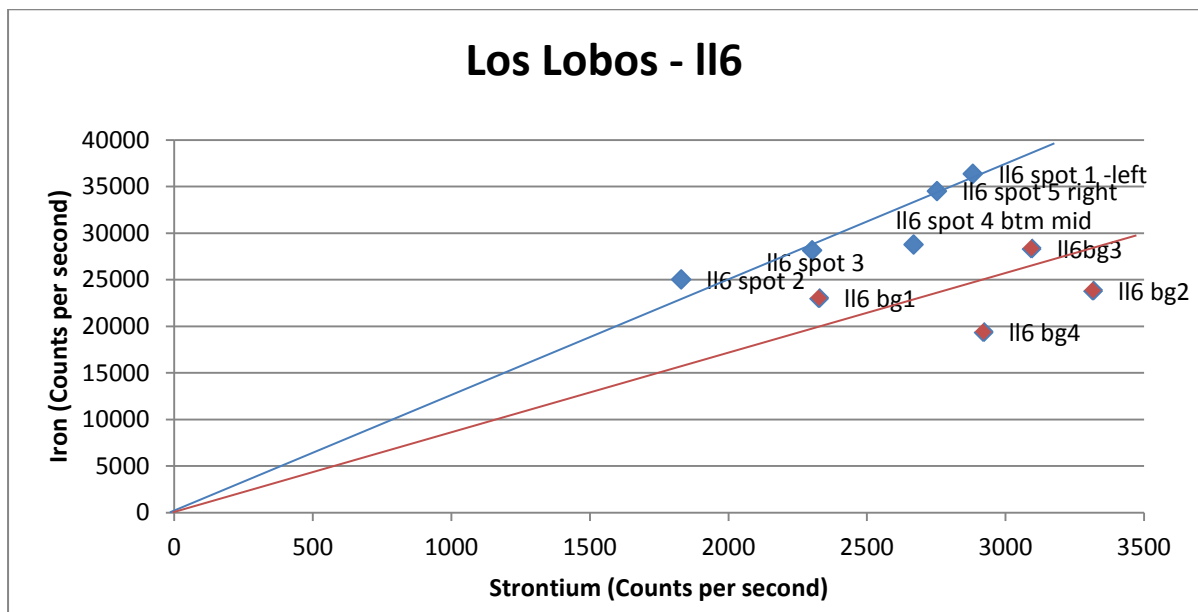
Figure 73. Scatter graph showing relative levels of iron and strontium in Los Lobos element 6

Element 6 is a collection of red dots. The results from these are all very similar to each other and distinctly different to the rock they were applied to. This indicates the use of the same pigment for all of these dots.
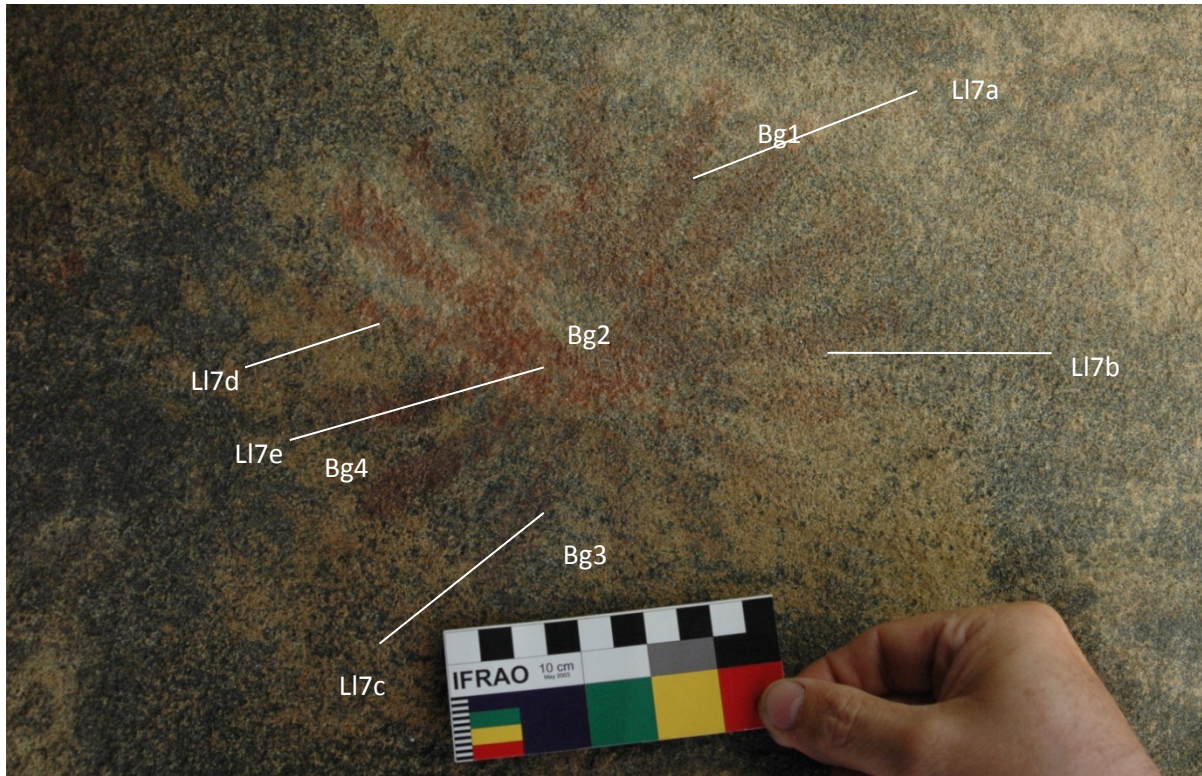
Figure 74. Element 7 (spokes from 12 o'clock – a=1, b=4, c=9, d=12, e=centre) at Los Lobos showing the points from which readings were taken
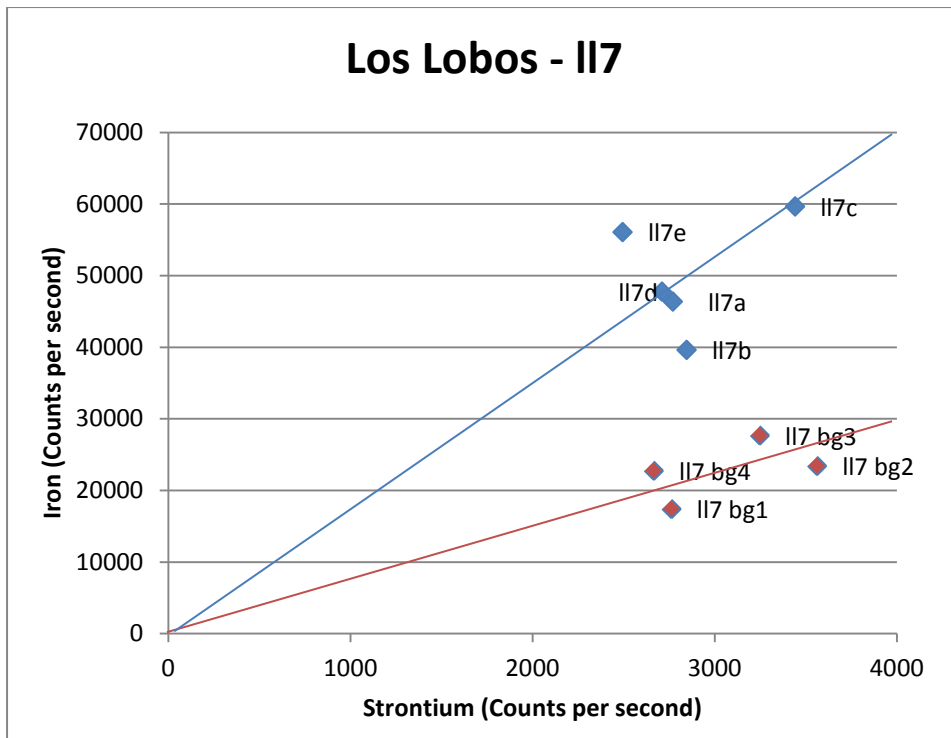
Figure 75. Scatter graph showing relative levels of iron and strontium in Los Lobos element 7

Element 7 is a radial 'sunburst' pattern. Readings were taken from each of the radial lines. Each of the pigment readings contrasts with the background and they form a distinct group around the blue axis. There is some internal variation in this pigment, as seen in element 3, but the group is distributed normally around its axis and is significantly different to the background readings.
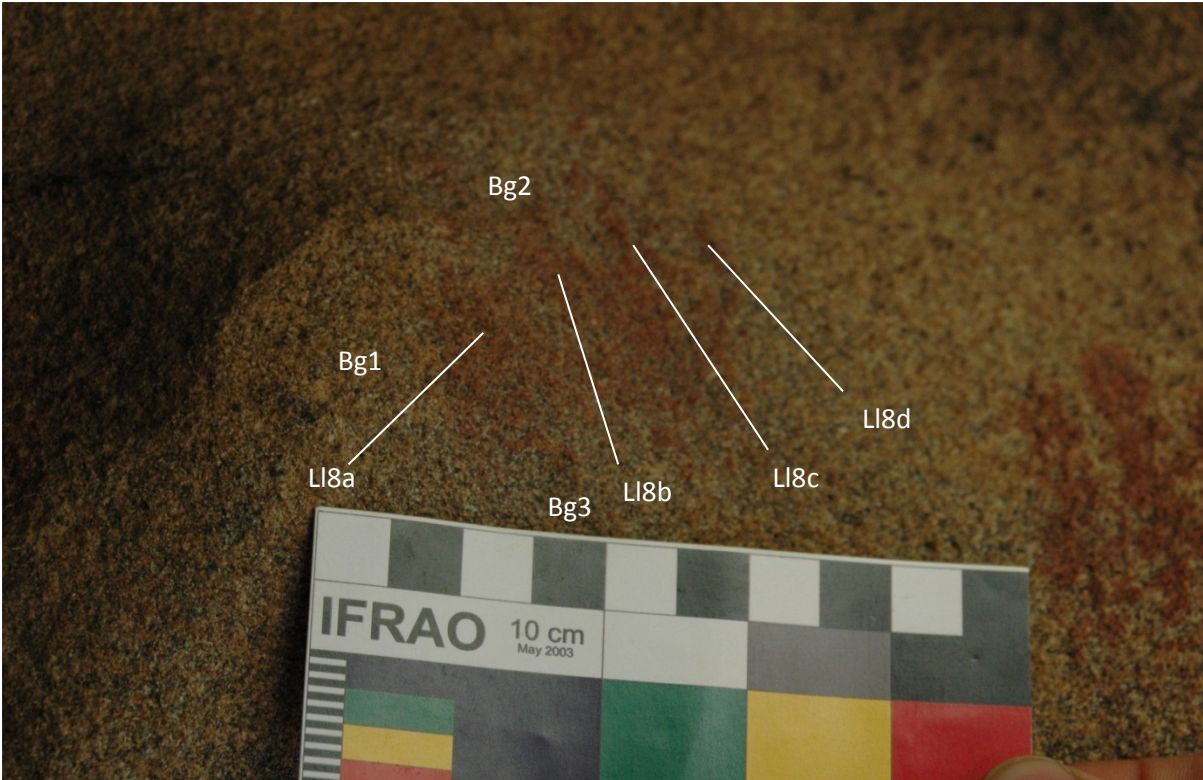
Figure 76. Element 8 ('finger marks' left to right) at Los Lobos showing the points from which readings were taken
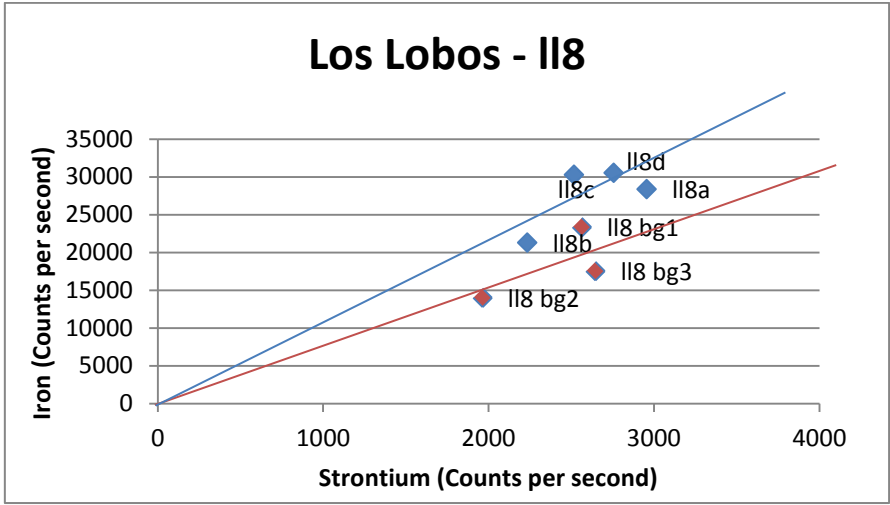
Figure 77. Scatter graph showing relative levels of iron and strontium in Los Lobos element 8

The pigment readings in element 8 are all consistent with each other and although it is a more subtle difference than is seen in some of the other elements, this group of pigment readings is significantly different to the readings from the bare rock.
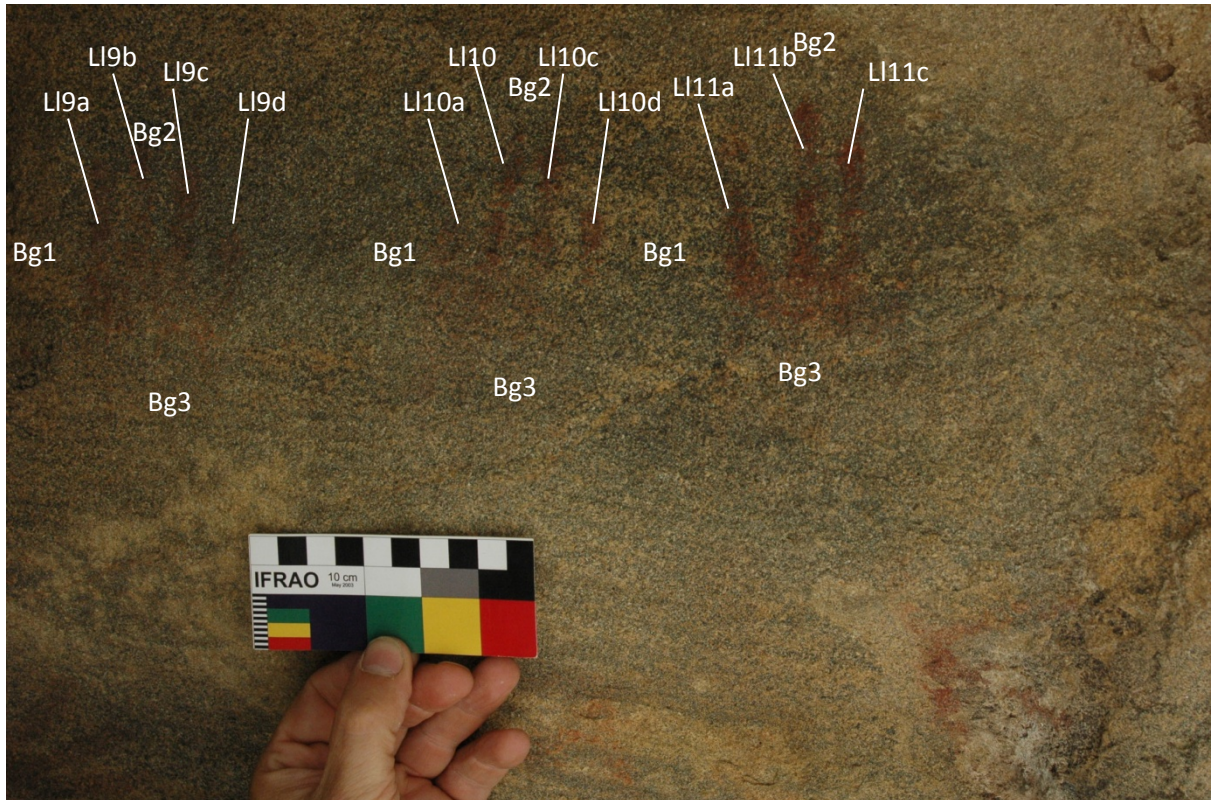
Figure 78.Los Lobos 9,10,11, 'Fingers' left to right showing points from which readings were taken

Elements 9,10 and 11 are red linear elements which have the appearance of finger strokes.
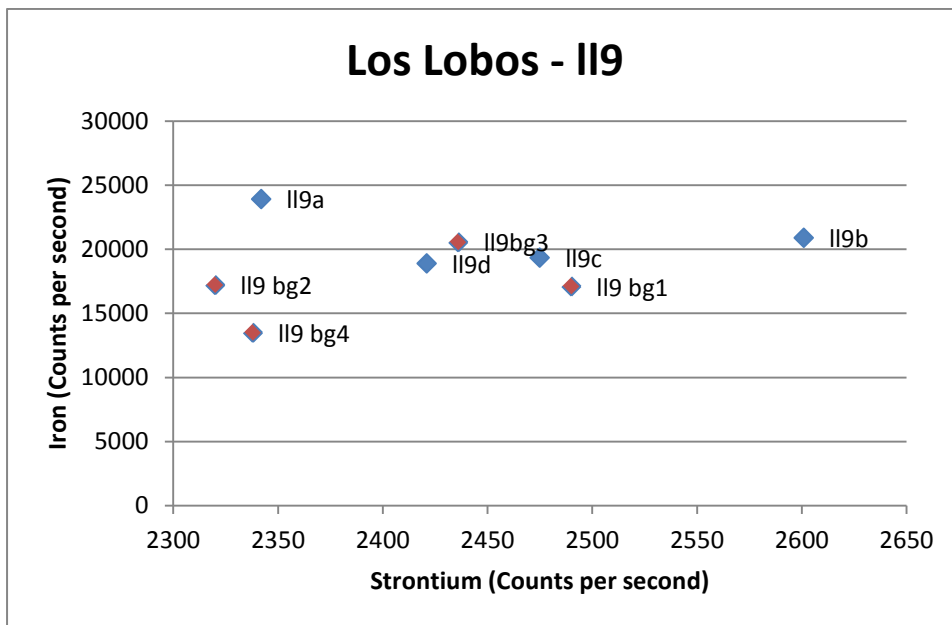
Figure 79. Scatter graph showing relative levels of iron and strontium in element 9 at Los Lobos Upper Cave

The pigment readings from element 9 are scattered widely in this graph as are the background readings. The pigment is not distinguishable from the background and therefore cannot be characterised using these data.
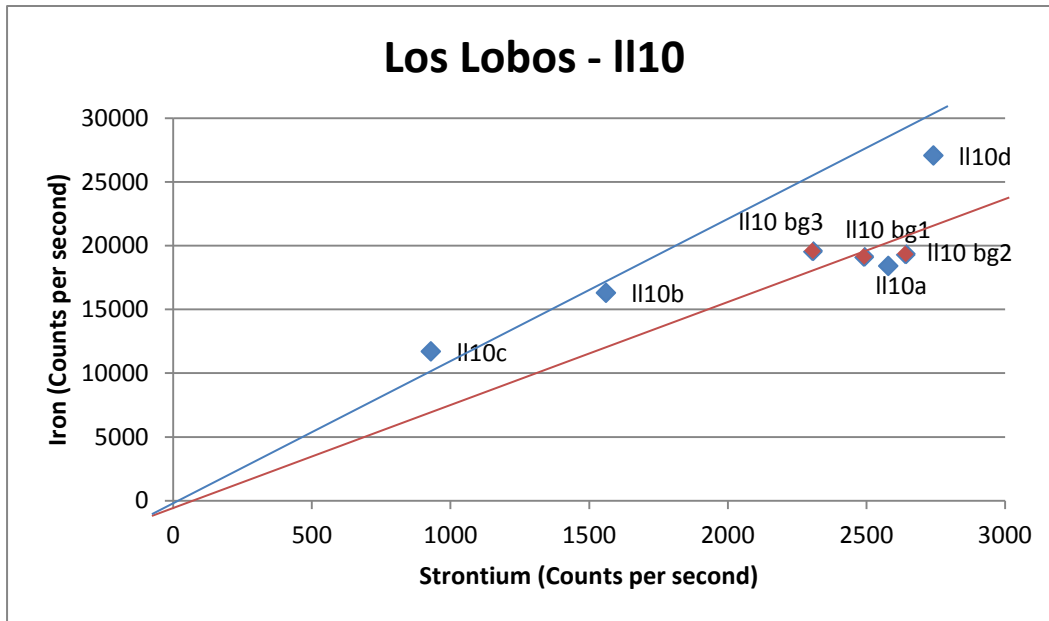
Figure 80. Scatter graph showing relative levels of iron and strontium in element 10 at Los Lobos Upper Cave

In element 10 one group of readings from the pigment can be seen and this follows the blue axis in the graph. One reading, 10a is mixed in with the background readings. This may represent variation within the pigment or be because there was an insufficient thickness of pigment to contrast with the rock.
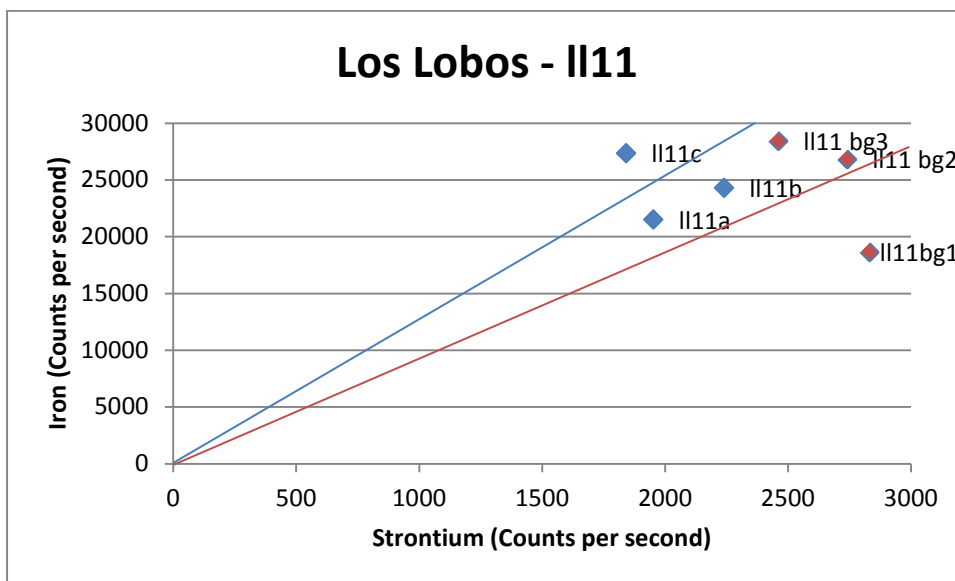
Figure 81. Scatter graph showing relative levels of iron and strontium in element 11 at Los Lobos Upper Cave

In element 11 there is some overlap between the background and pigment readings but one group of pigment readings can be seen which are subtly different to the background readings.
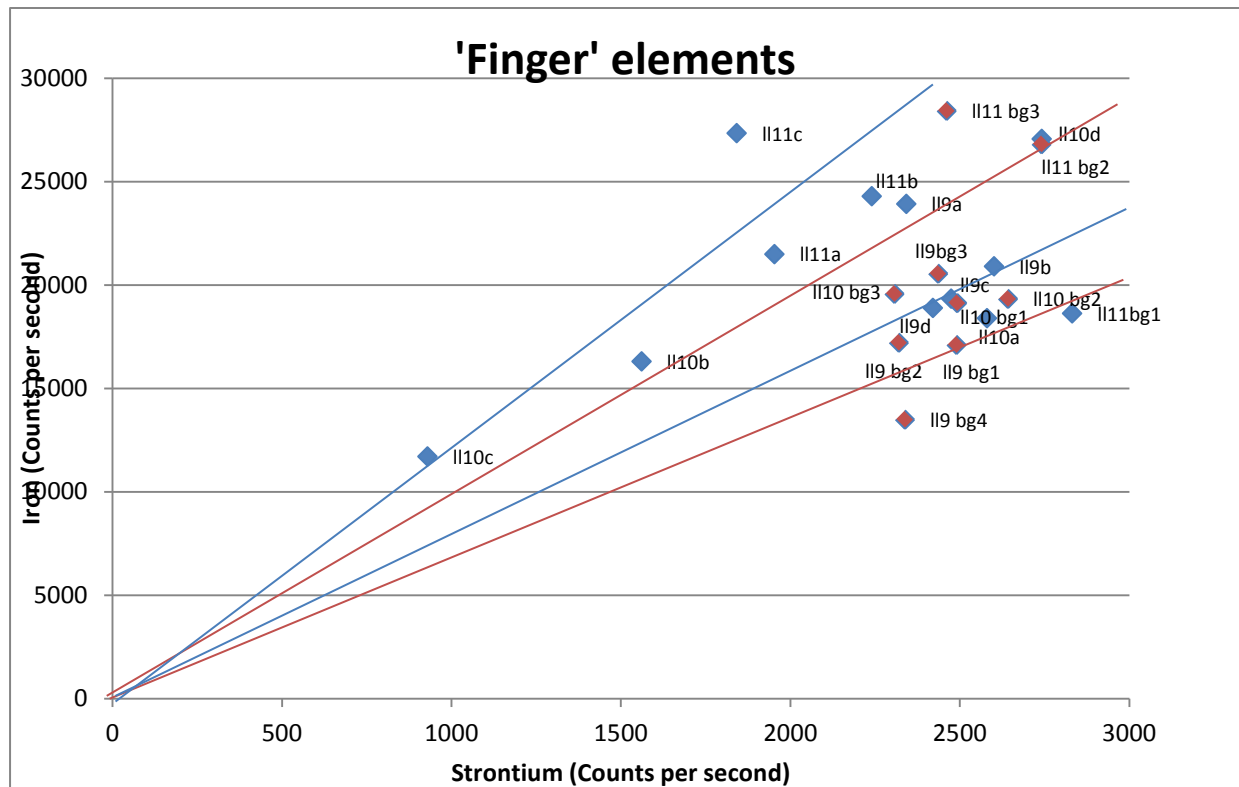
Figure 82. Scatter graph showing relative levels of iron and strontium in element 9,10 and 11 at Los Lobos Upper Cave

The scatter graph above shows the readings from elements 9, 10 and 11 which look like they were applied to the rock using finger strokes. Although there is some differentiation between the pigments and their respective background rocks, there is too much variation between the background readings of each element for a comparison to be made between the pigments used.

Los Lobos 12
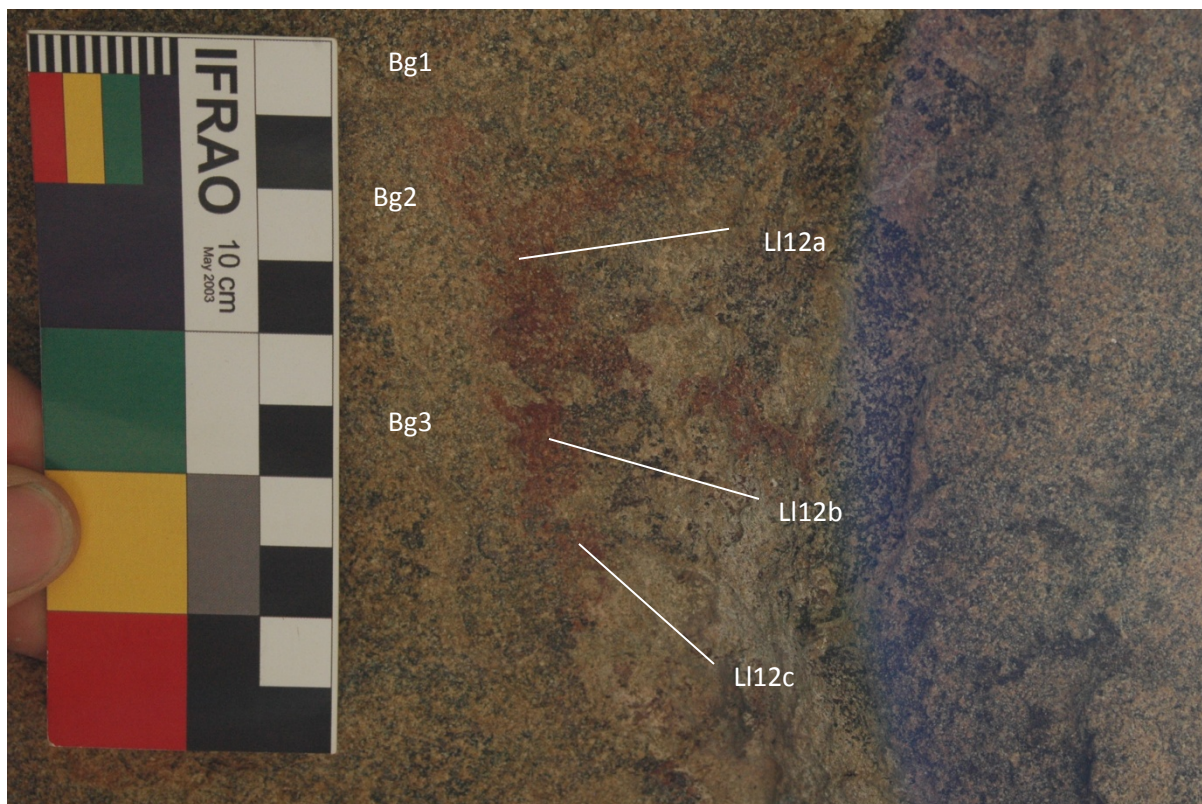
Figure 83. Element 12 at Los Lobos showing points from which readings were taken
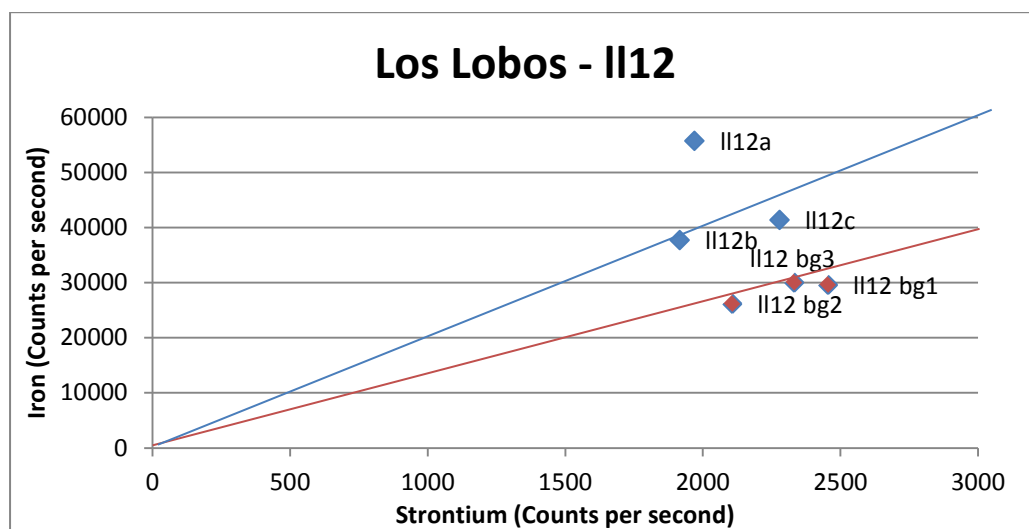
Figure 84. Scatter graph showing relative levels of iron and strontium in element 12 at Los Lobos Upper Cave

Element 12 shows a clear division between the pigment and background readings and the pigment readings themselves form one group indicating that one pigment was used here.

Los Lobos 13
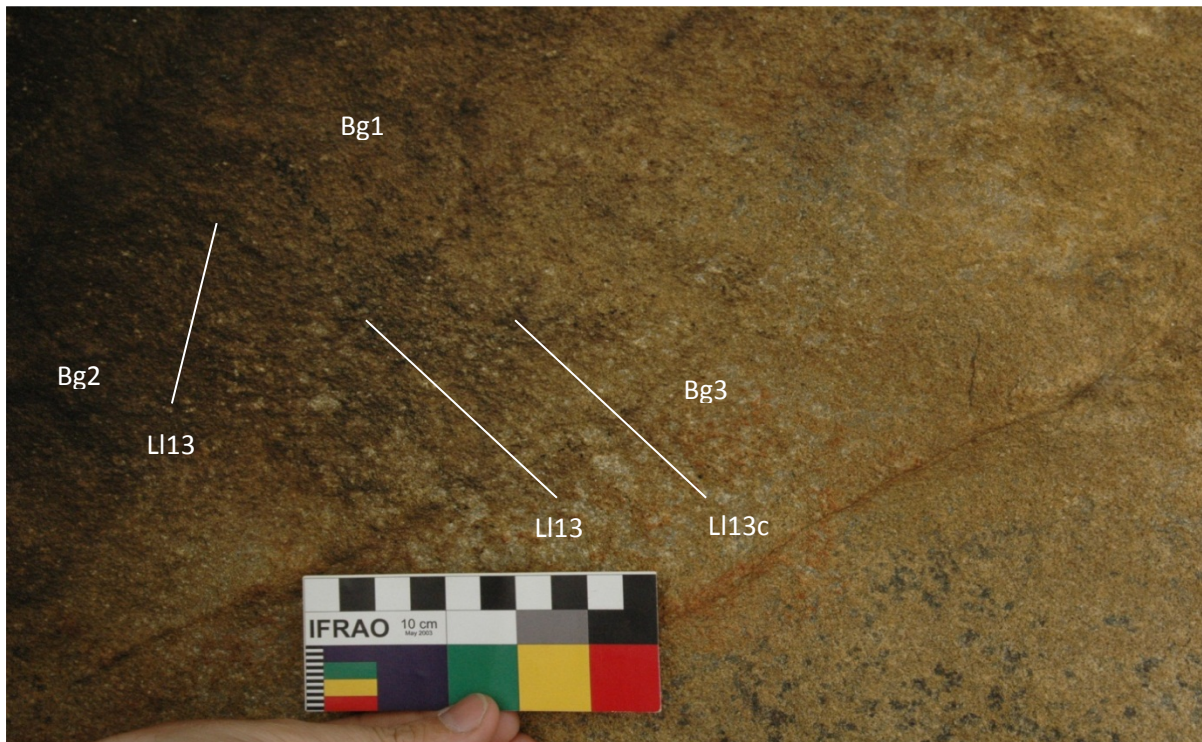
Figure 85.Los Lobos element 13 showing points from which readings were taken
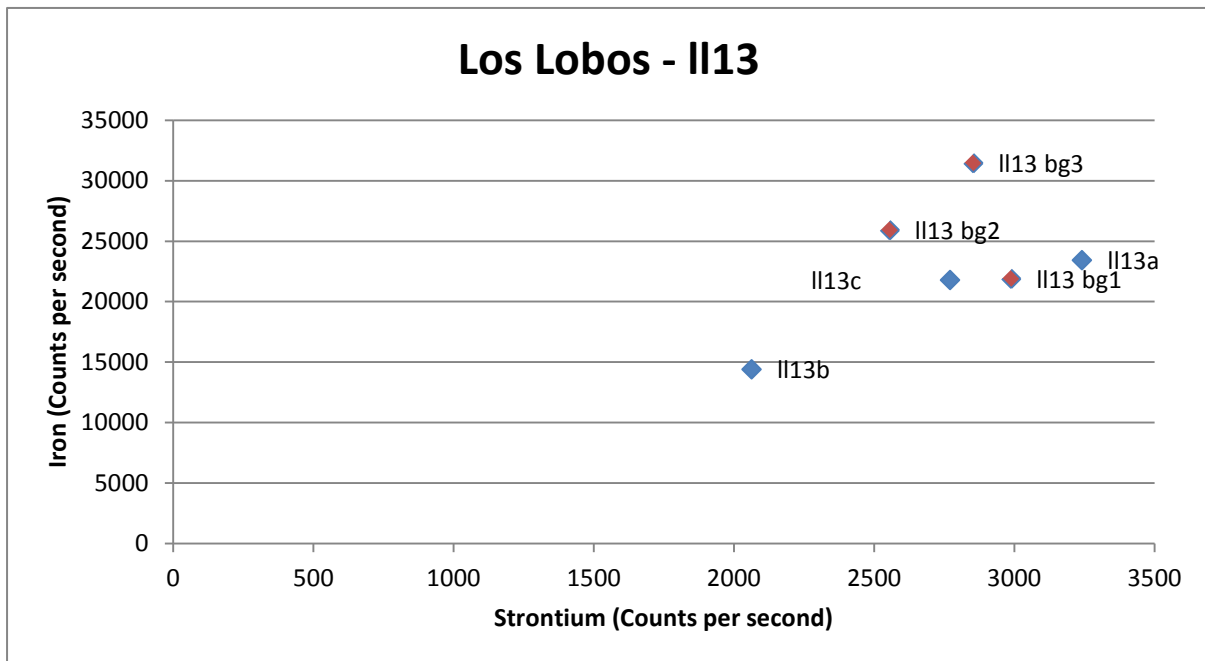
Figure 86. Scatter graph showing relative levels of iron and strontium in element 13 at Los Lobos Upper Cave

The pigments used in this element are very faint in appearance. This may explain the lack of contrast between the pigment and background readings that we see here.

Figure 87. Element 14 at Los Lobos showing points from which readings were taken
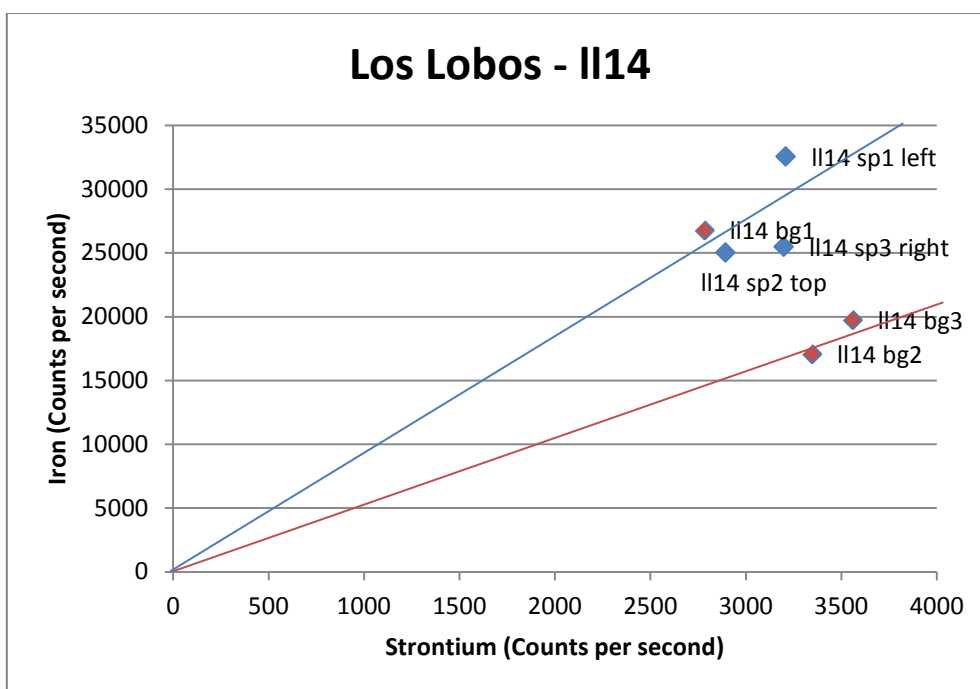
Figure 88. Scatter graph showing relative levels of iron and strontium in element 14 at Los Lobos Upper Cave

In this element one of the background readings is mixed in with the pigment readings. Otherwise however the background and pigments contrast with the background rock in terms of the proportions of iron and strontium, and form one pigment group.
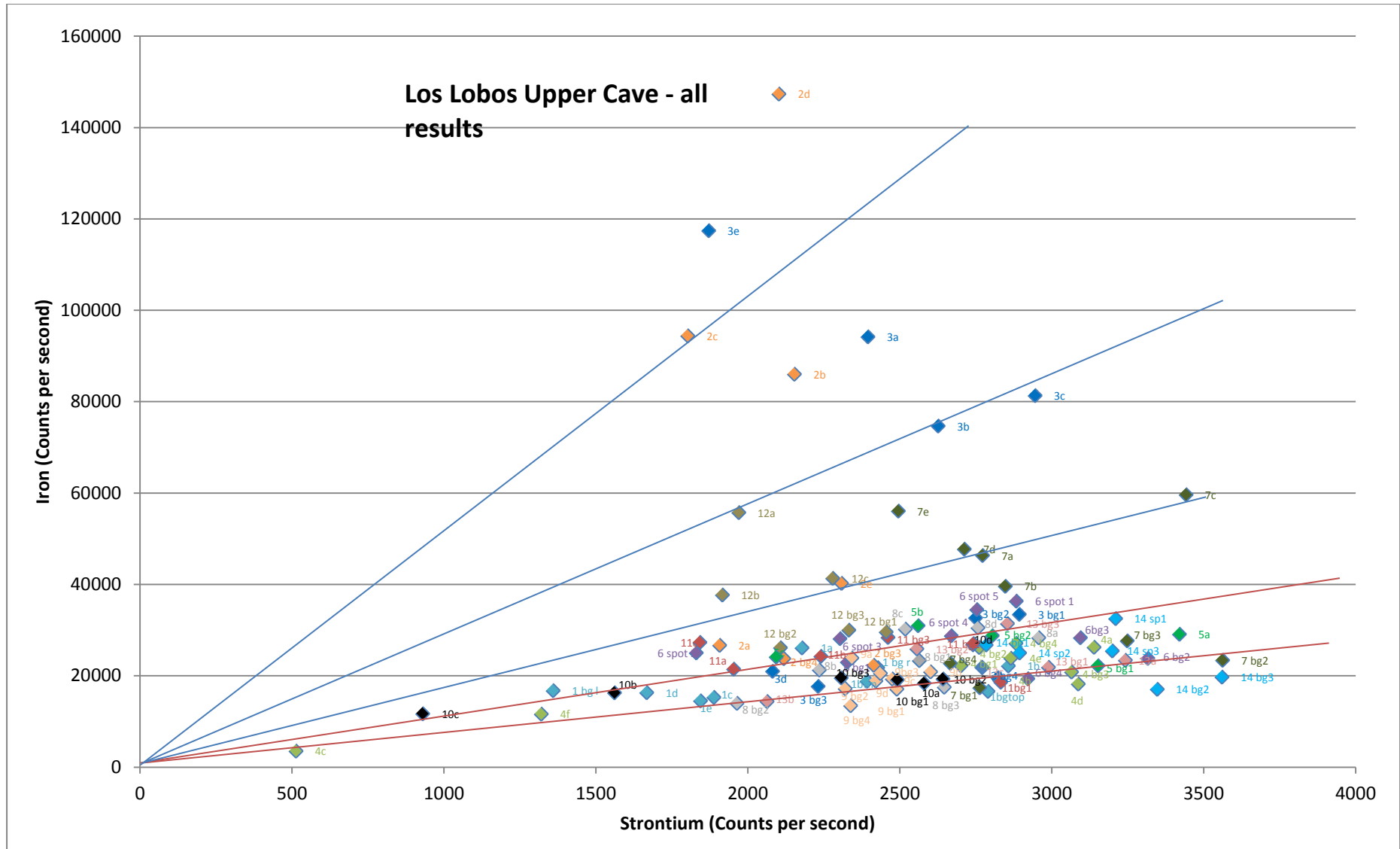
Figure 89. Upper cave, Los Lobos - all elements 1= 2= 3= 4= 5= 6= 7= 8= 9= 10= 11= 12= 13= 14=

At the upper cave site of Los Lobos most of the background readings follow one of the two red axes within the scatter graph above. They are joined within this group by some pigment readings from elements 4,5,6,8, 11,13 and 14, many of which were indistinguishable from or only subtly different to their background readings.

As already mentioned elements 3 and 7 displayed wider internal variation within their group of pigment readings than other elements. When compared with one another, however, 3 and 7 do not appear to have been produced using the same material as they follow different axes on the graph above, and therefore have different proportions of iron and strontium. Element 2 also contrasts with both of these.

When examined individually a number of pigments contrasted with their background rock but were only subtly different, such as elements 6,8,11 and 13. These are obscured in the graph above but may still constitute a different pigment group as they are clearly different to the rock to which they were applied, and to the other three pigments identified above.

Interestingly none of the results from Los Lobos upper cave indicate that more than one pigment was used in a single element, but it does seem that at least 4 red pigments were used here and therefore at least 5 painting events took place when black pigments are included.

Los Lobos Lower Cave

Four elements were examined in the lower cave at Los Lobos.
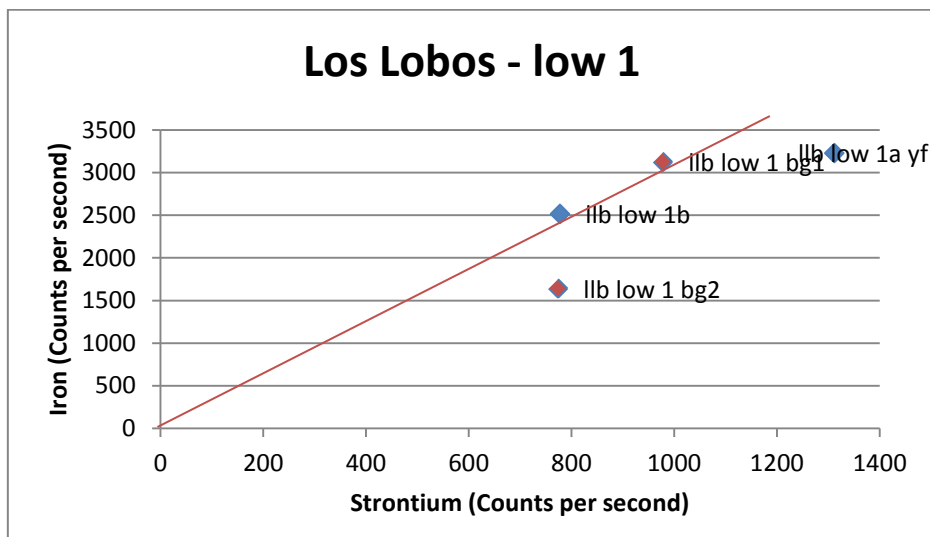
Figure 90. Scatter graph showing relative levels of iron and strontium in element 1 at Los Lobos Lower Cave

In element 1 at Los Lobos lower cave the background and pigment readings were unfortunately not distinguishable from one another so the pigments used could not be identified.

Low 2
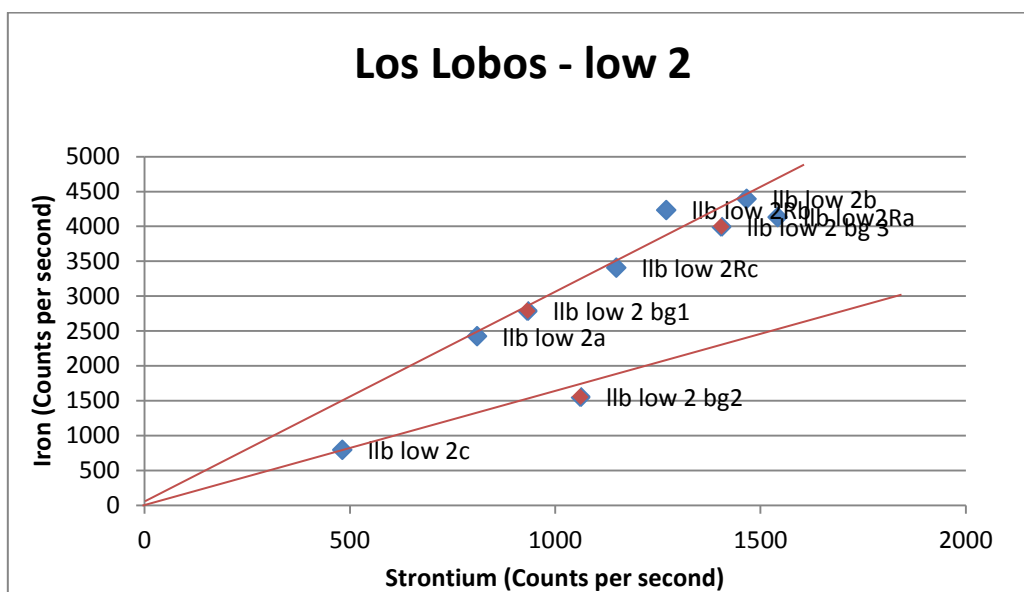
Figure 91. Scatter graph showing relative levels of iron and strontium in element 2 at Los Lobos Lower Cave

Element 2 has both red and black pigments. Here the readings from the red pigment are labelled 'R'. These red pigments are all very similar to each other but are not significantly different to those from the background rock. Therefore these readings may not accurately reflect the composition of the pigment used as the pigments themselves may be too faint to contrast with rock to which it was applied.
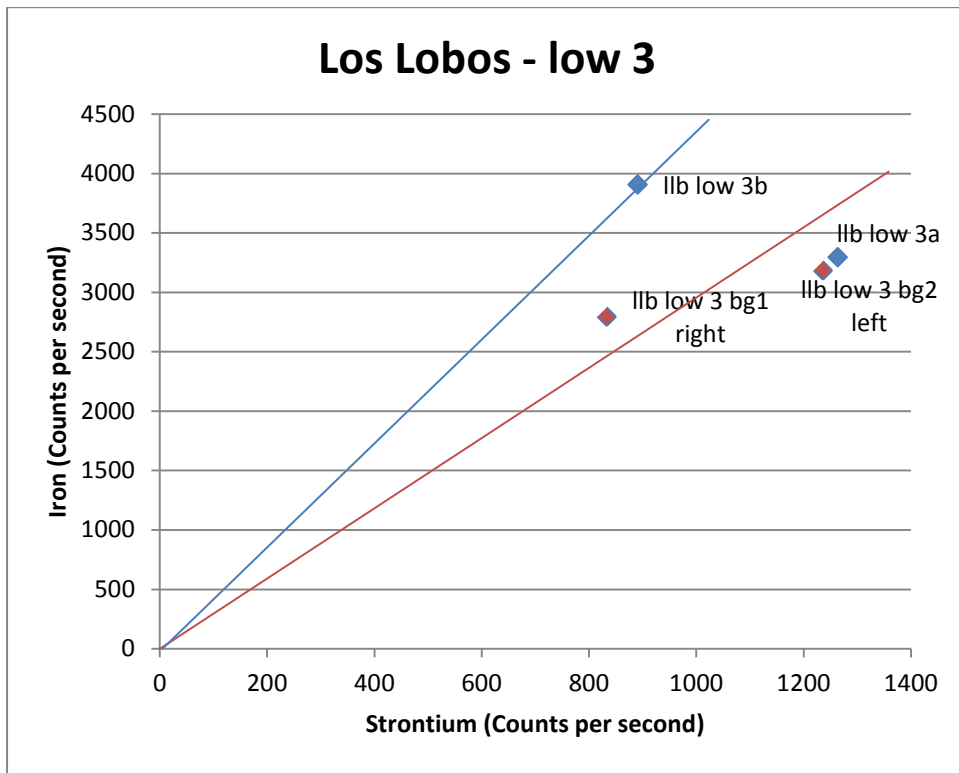
Figure 92. Scatter graph showing relative levels of iron and strontium in element 3 at Los Lobos Lower Cave

Similarly to the other elements from the lower cave at Los Lobos, in element 3 the pigment readings are not distinct from the background rock. It may be that the spread of these pigments on the rock was too sparse for their characteristic radiation to be detectable against that of the rock.
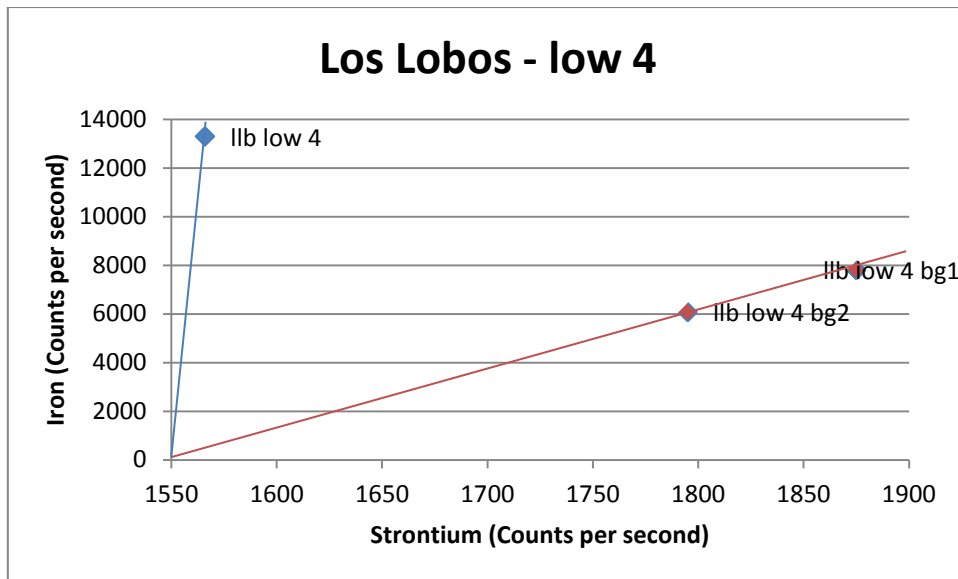
Figure 93. Scatter graph showing relative levels of iron and strontium in element 4 at Los Lobos Lower Cave

This element only has one pigment reading and this contrasts greatly with the background readings. However, this is a single reading which may not be representative of the pigment used. More readings would be needed to characterise this pigment.
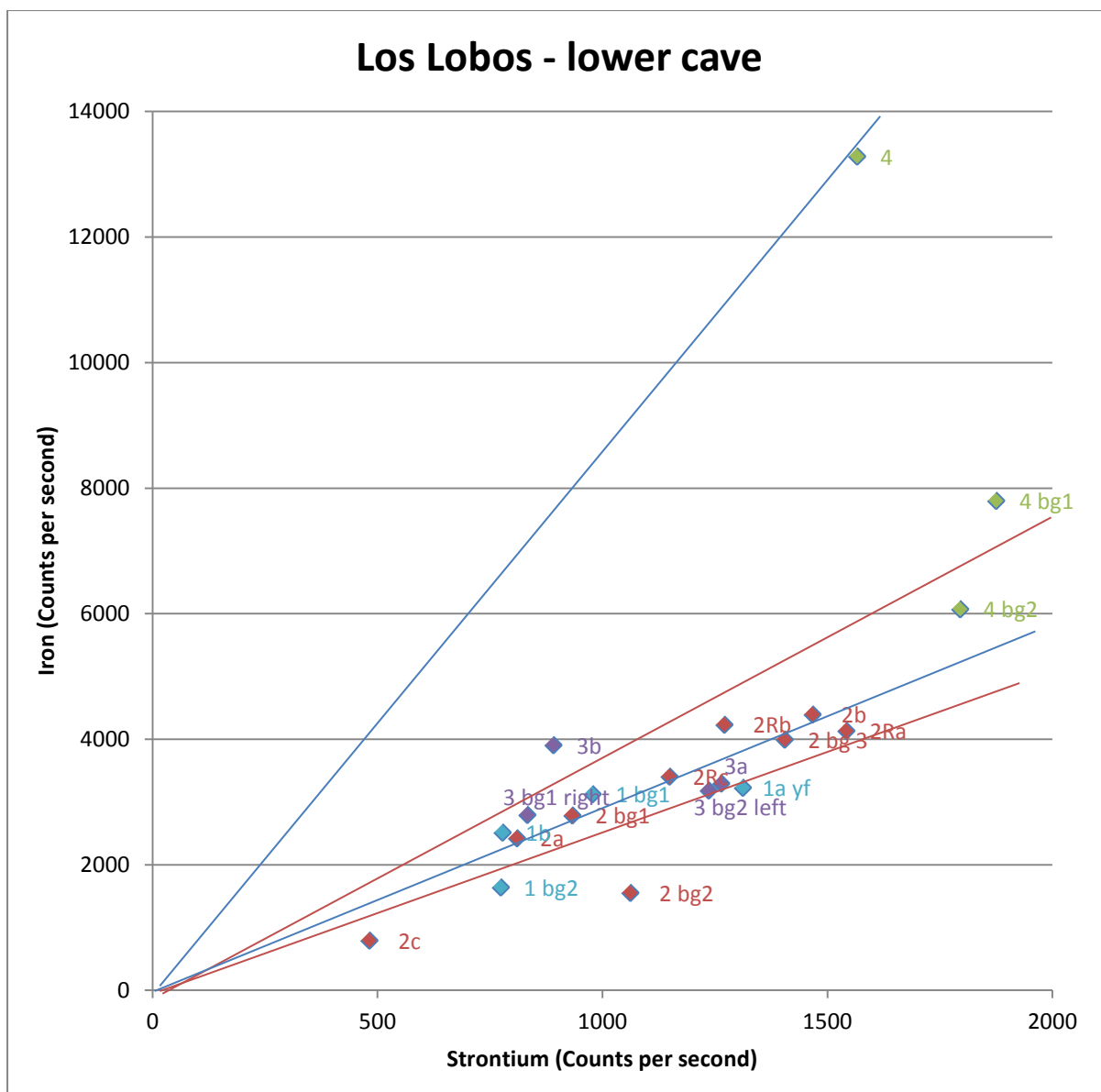
Figure 94. Scatter graph showing relative levels of iron and strontium in all elements at Los Lobos Lower Cave

When all of the elements in the lower cave are compared some variation in the background rock can be seen. In particular the rock used for element 4 appears to be different to the others although this difference is not great enough to be statistically significant.

The pigments themselves cannot be compared in any useful way as they did not contrast with their background rock enough to be characterised. This unfortunately also means that a comparison cannot be made between the upper and lower caves at this point. The presence of both black and red pigments at a different locus within the site however constitutes two extra painting events to be included at Los Lobos.

Santiago – Monolith

At this site there were two loci. These are the Monolith, and Lonely Boulder.

The 'Monolith' is a large rock formation standing next to a spring and a BRM at Santiago. Within this rock is a small shelter containing 14 rock art elements. Another 5 are on the outer faces of the rock. Lonely Boulder stands close to the river bed in the next field along from the Monolith.

As with the other sites, readings were taken from every element and the rock to which it was applied then for each element at this site the levels of Fe counts were plotted against the Sr counts in a scatter graph.
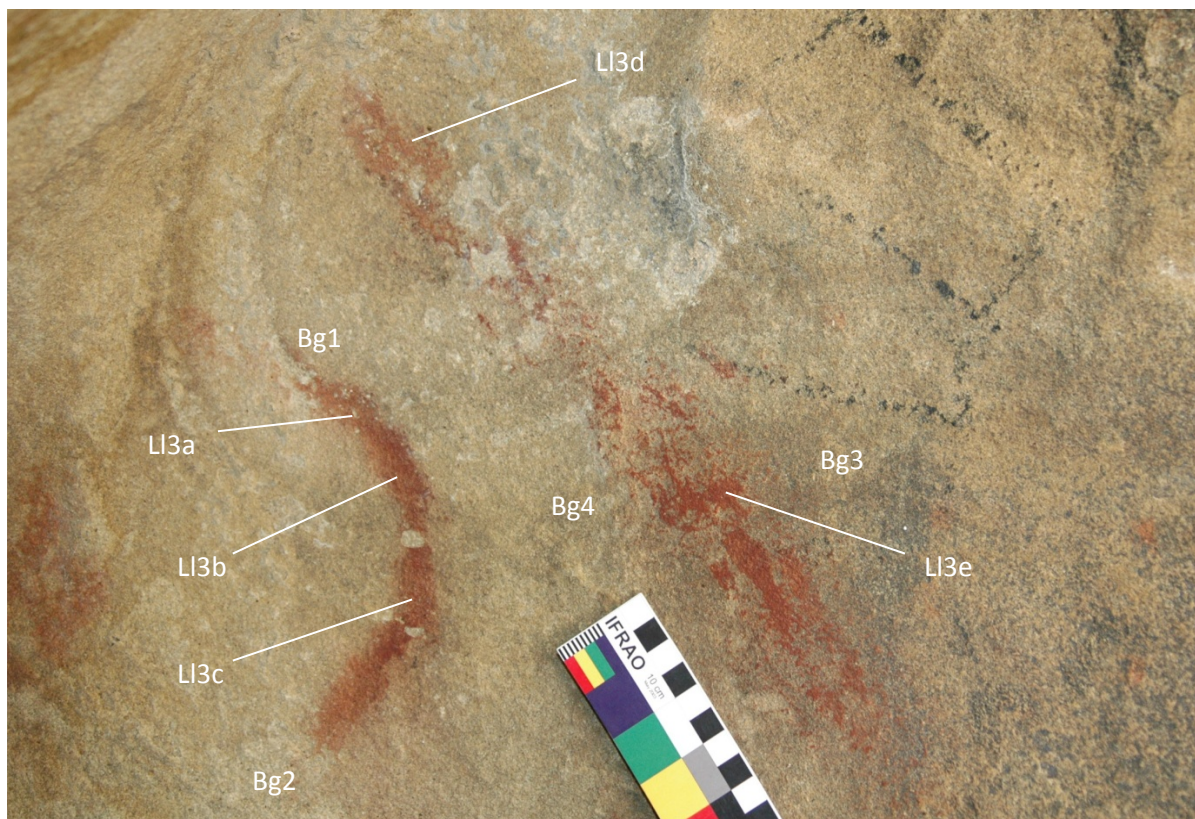
Ml1
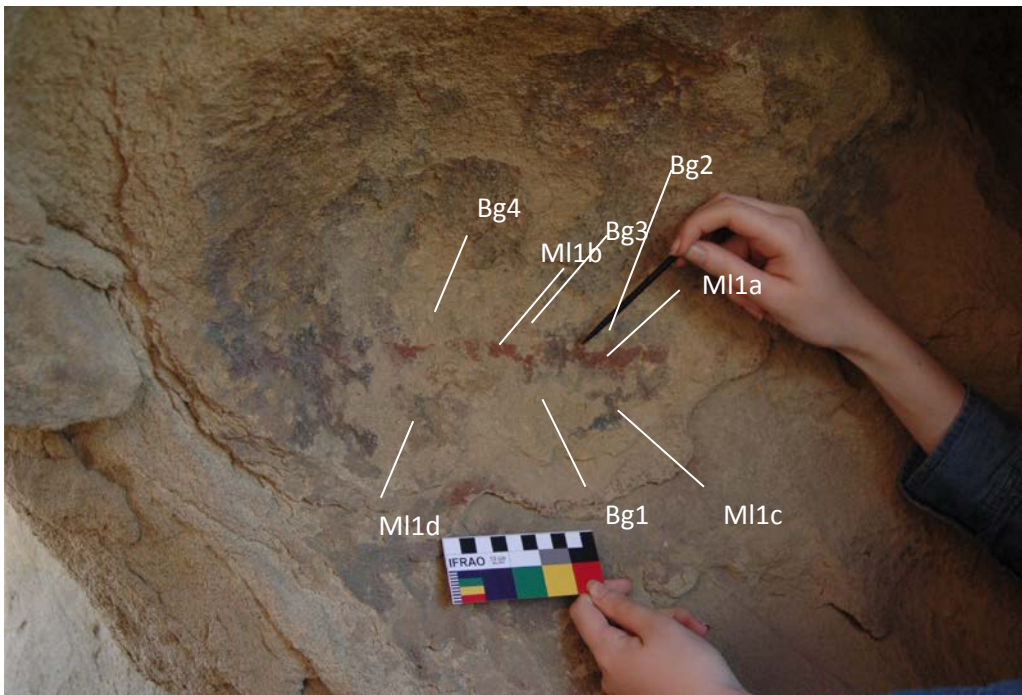
Figure 95. Element 1 at Santiago Monolith, showing the points from which readings were taken
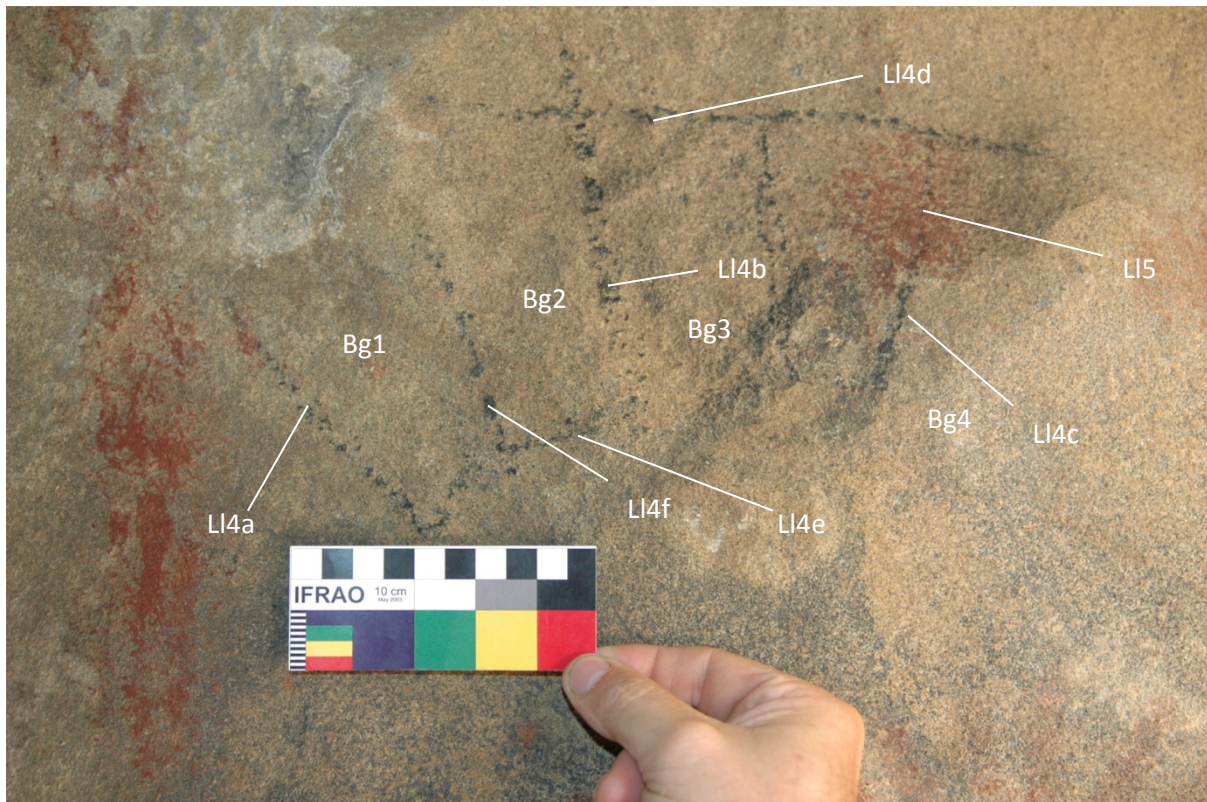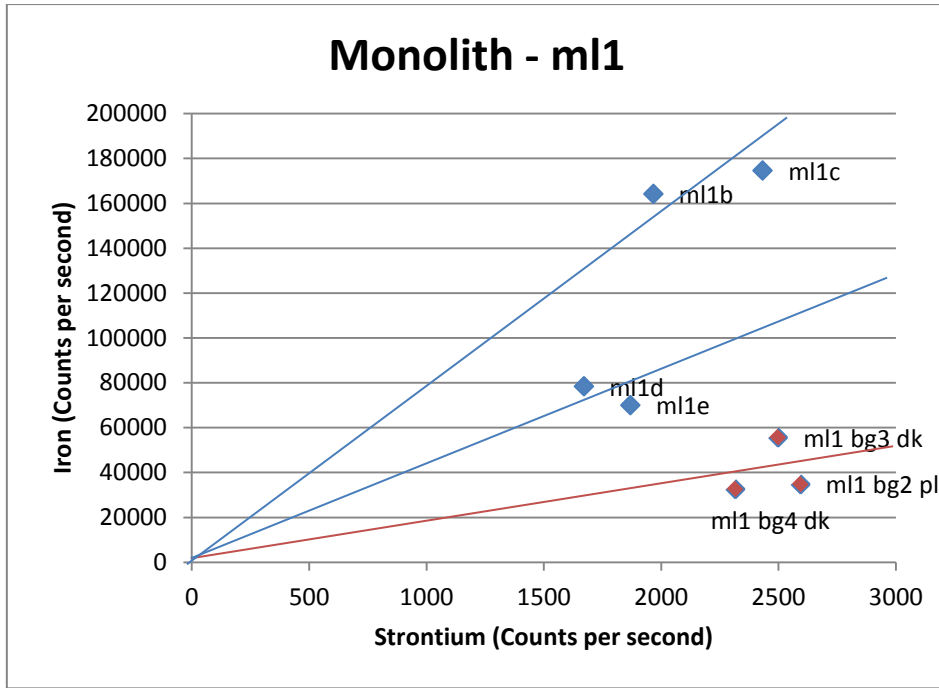
Figure 96. Scatter graph showing relative levels of iron and strontium in element 1 at Santiago Monolith

The background readings from this element form a distinct group which is separate from the pigment readings. The pigment readings seem to divide into two significantly different groups with ml b and c being different from ml d and e, indicating that two different pigments were used.
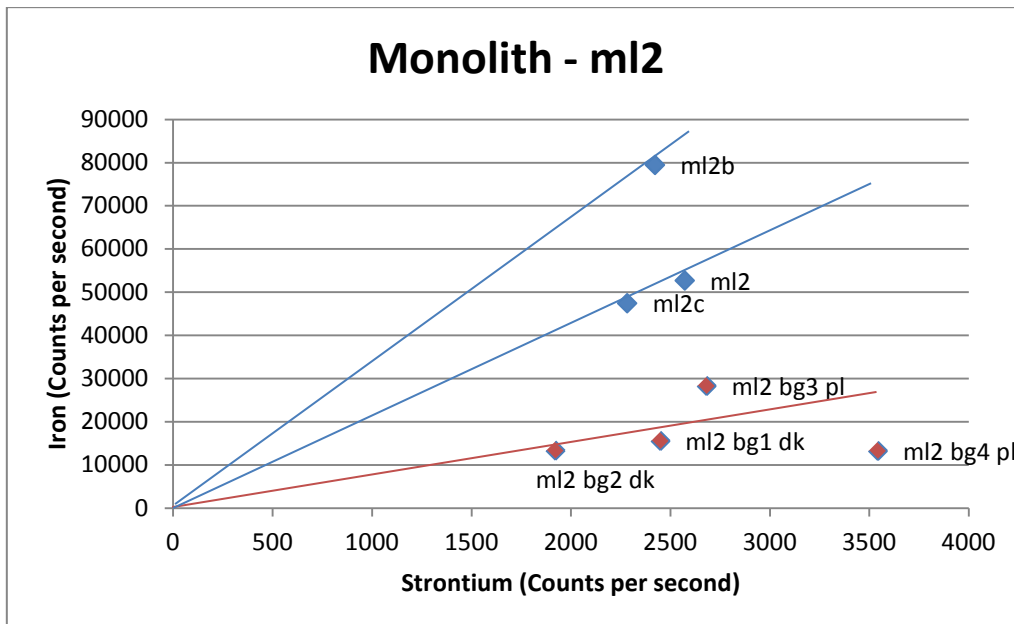
Figure 97. Scatter graph showing relative levels of iron and strontium in element 2 at Santiago Monolith

Here also the pigment readings are significantly different to the background readings and appear to form two separate groups, as 2b is different from 2 and 2c. Variance testing shows that the pigment readings are significantly different to the background.

Although it appears that ml2b is a different pigment material, it could not be subjected to statistical testing as it is a solitary reading and could be anomalous. It is also possible that reading 2b is from the same type of pigment as the other readings here and simply reflects internal variation in this material. Therefore only one pigment can be identified with confidence in this element.
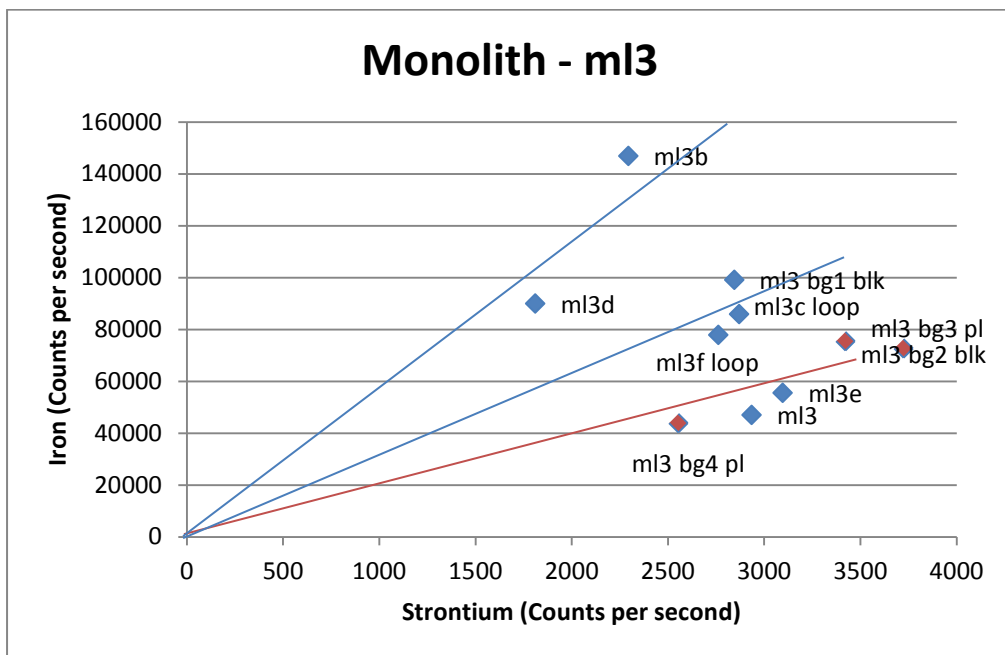
Figure 98. Scatter graph showing relative levels of iron and strontium in element 3 at Santiago Monolith

To the eye three possible groups appear in this scatter graph, two containing pigment readings and one with a mixture of pigment and background readings. When tested statistically however, only readings 3b and d were significantly different to the background rock and the ml3 loop readings display a relatively weak similarity to the background, ml3 and 3e.
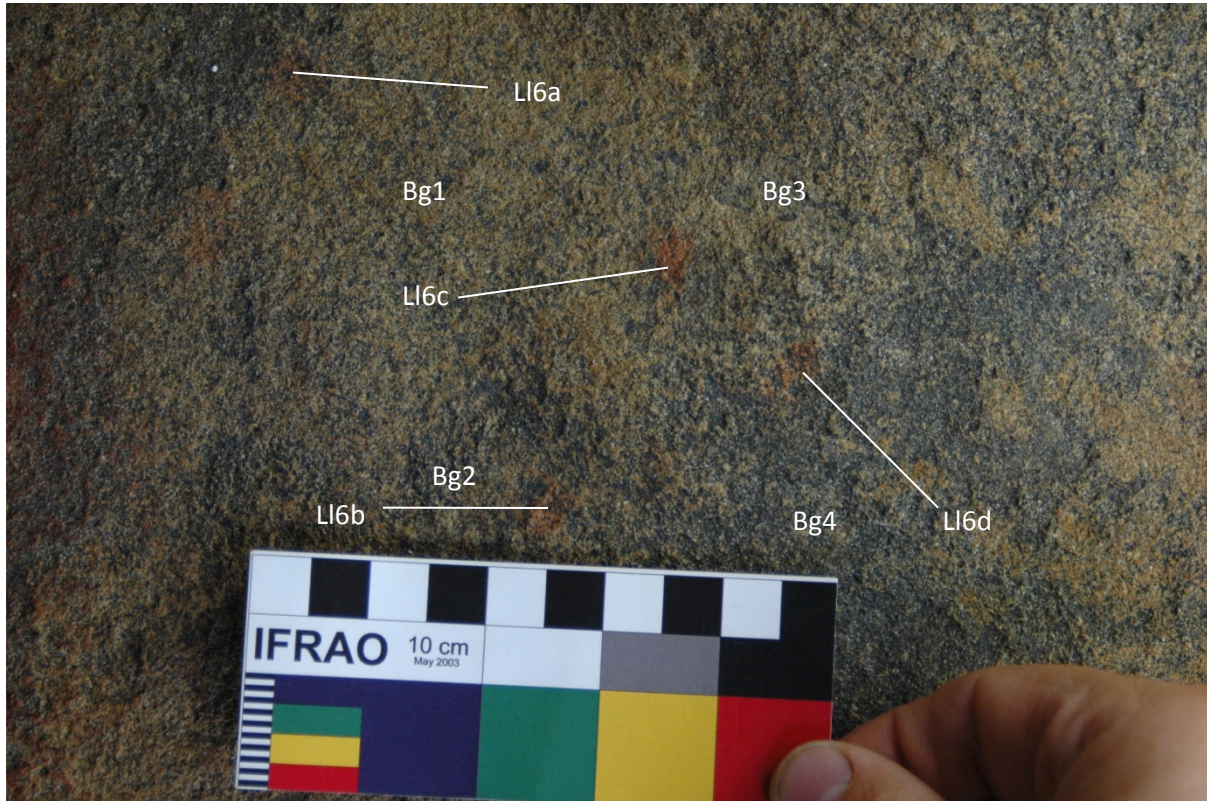
Ml5
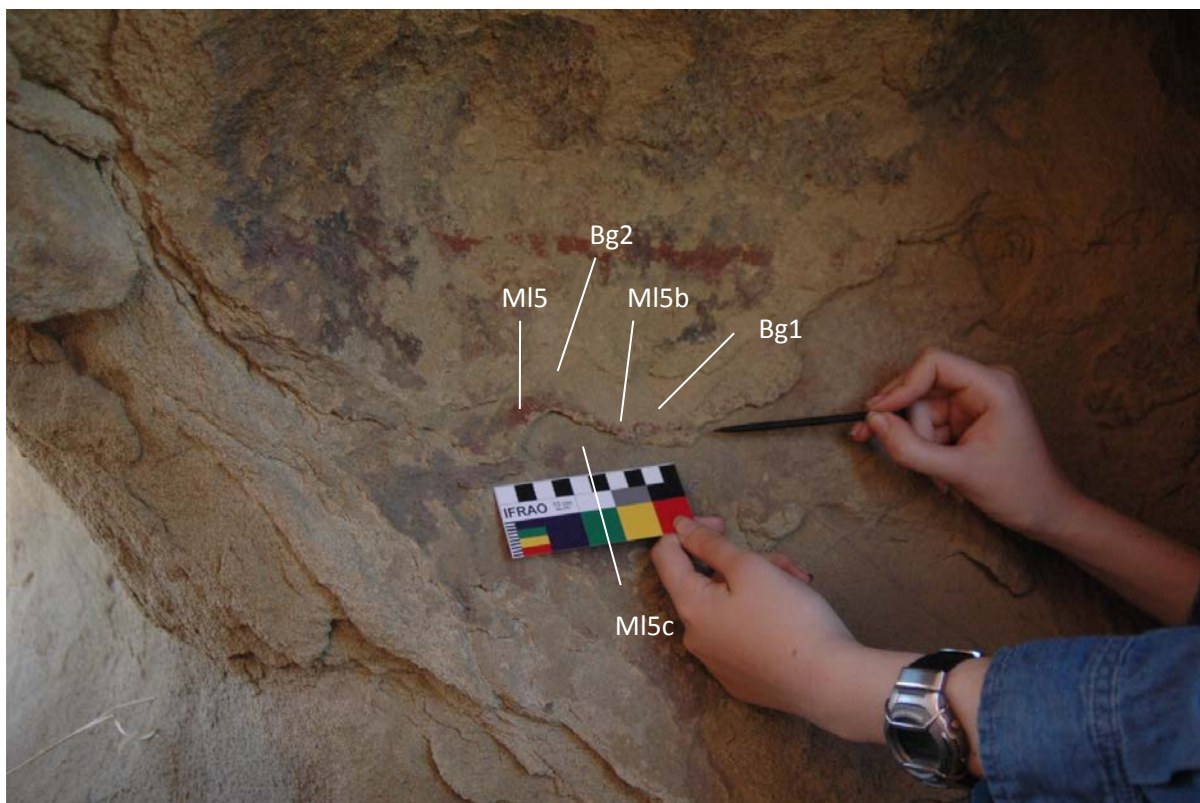
Figure 99. Element 5 at Santiago Monolith, showing the points from which readings were taken
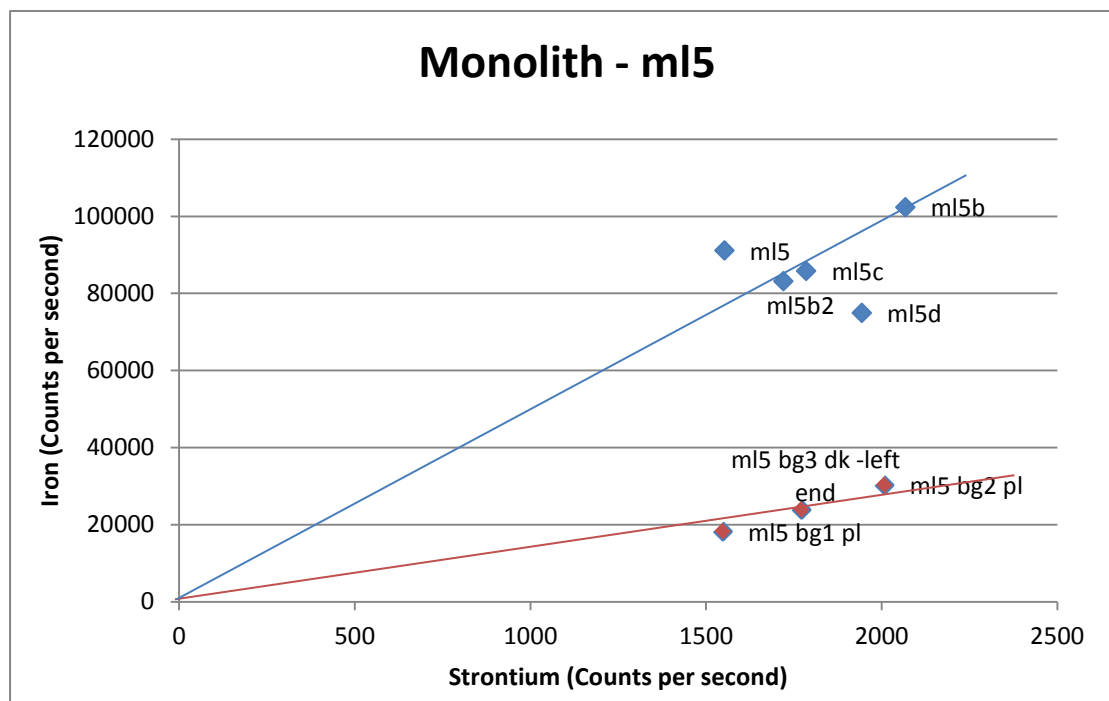
Figure 100. Scatter graph showing relative levels of iron and strontium in element 5 at Santiago Monolith

Element 5 is also distinct from its background with the pigment readings forming one clear group, which is statistically different to its background. This element shows a very clear contrast between its pigment and background readings as well as very consistent background readings. Its results indicate that only one pigment material was used here.

Ml6
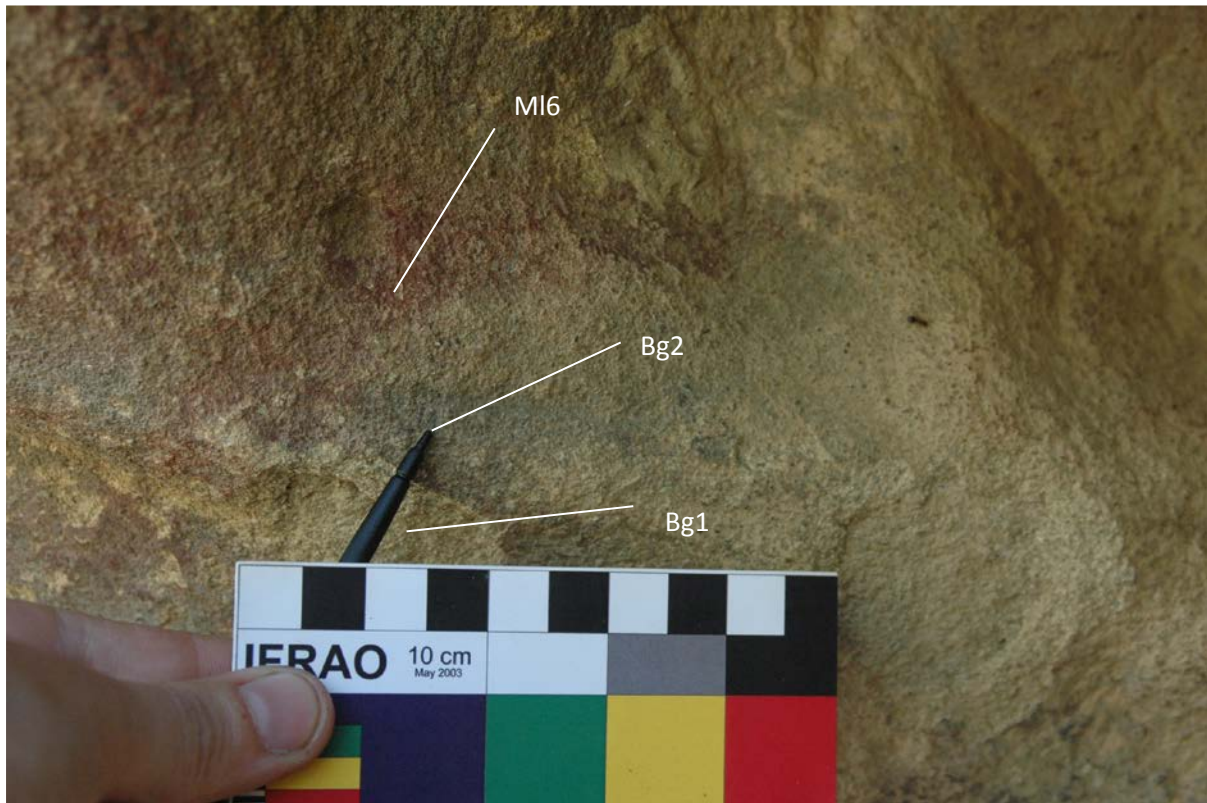
Figure 101. Element 6 at Santiago Monolith, showing the points from which readings were taken
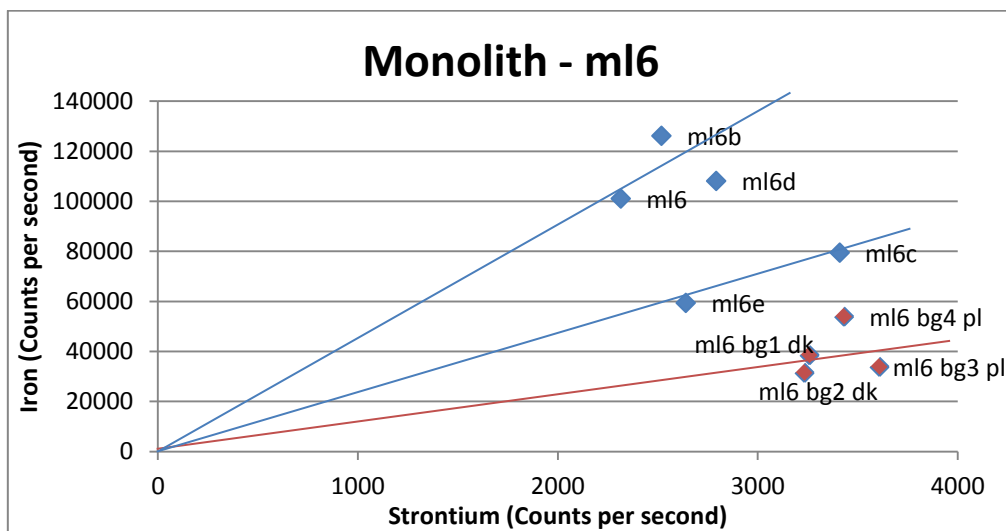
Figure 102. Scatter graph showing relative levels of iron and strontium in element 6 at Santiago Monolith

The pigment in this element forms two distinct groups of readings. One of these consists of ml6, 6b and 6d, the other 6c and 6e. These groups are statistically significantly different to one another and the background readings. This indicates the use of two pigments in this element.

Ml7
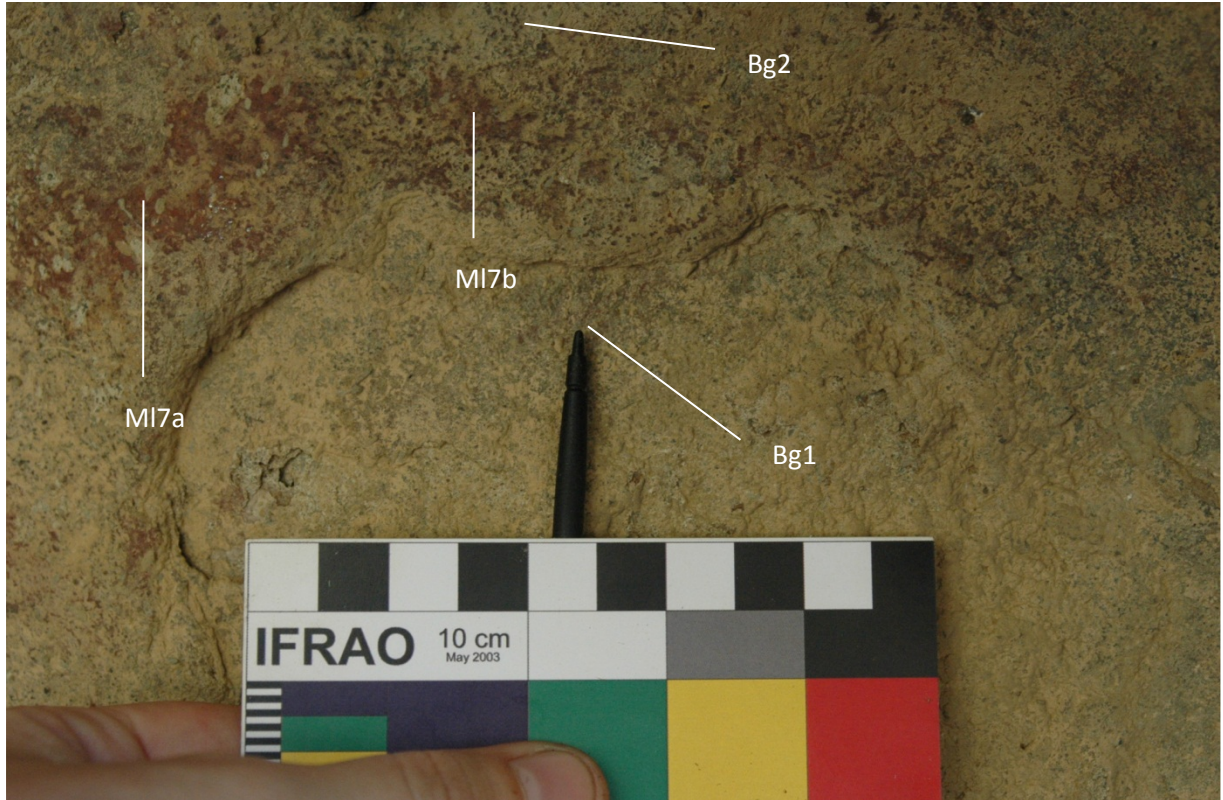
Figure 103. Element 7 at Santiago Monolith, showing the points from which readings were taken
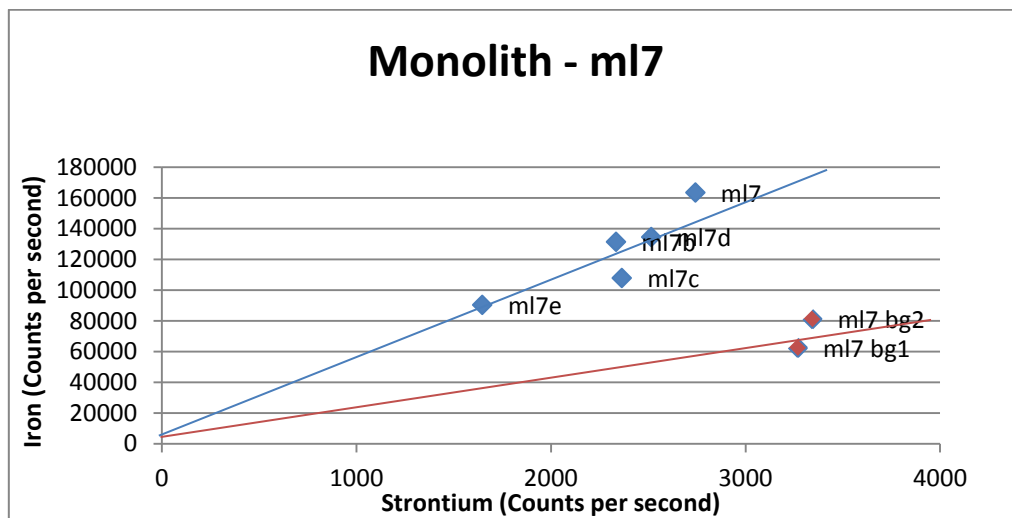
Figure 104. Scatter graph showing relative levels of iron and strontium in element 7 at Santiago Monolith

The pigment readings from this element form one group which is significantly different from the background readings, indicating that one pigment can be identified here.

Ml8
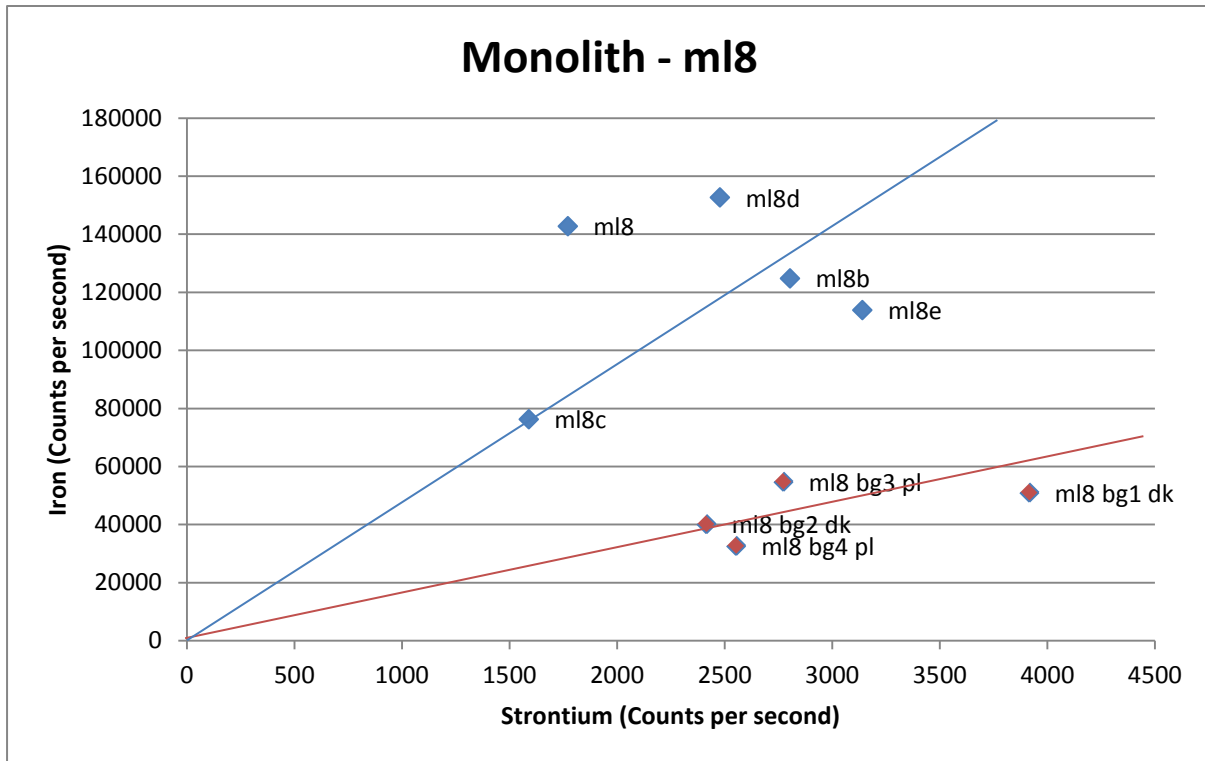
Figure 105. Scatter graph showing relative levels of iron and strontium in element 8 at Santiago Monolith

All the pigment readings are statistically distinct from the background readings and the pigment readings appear to form two possible separate groups, one consisting of ml8c, b and e, and the other of ml8 and d. However, it is more likely that the pigment readings here form one group with a range of readings, as might be expected from directly applied pigment. Raw ochre tends to have a certain amount of variation but this tends to be evened out when the material is ground up and homogenised. It is difficult to say with confidence therefore that more than one pigment was used. It may simply be that a different technique of application is apparent in this element.

Ml9
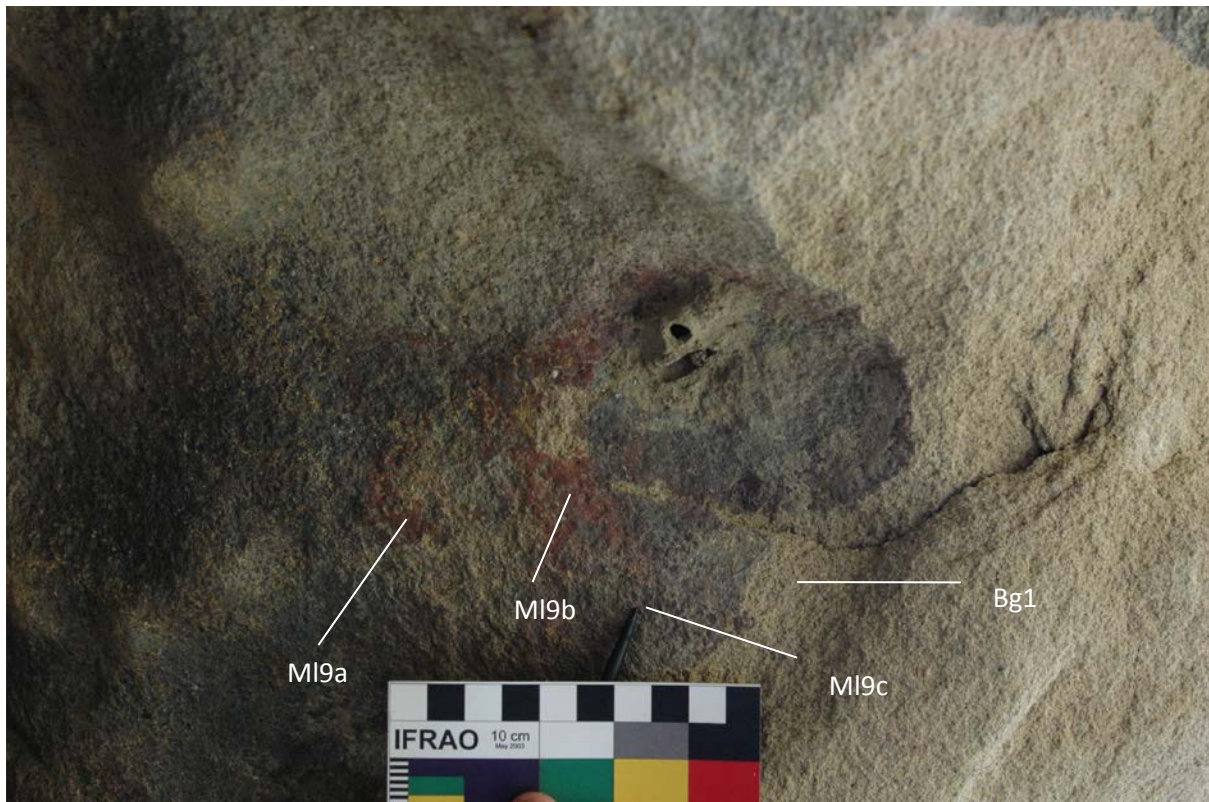
Figure 106. Element 9 at Santiago Monolith, showing the points from which readings were taken
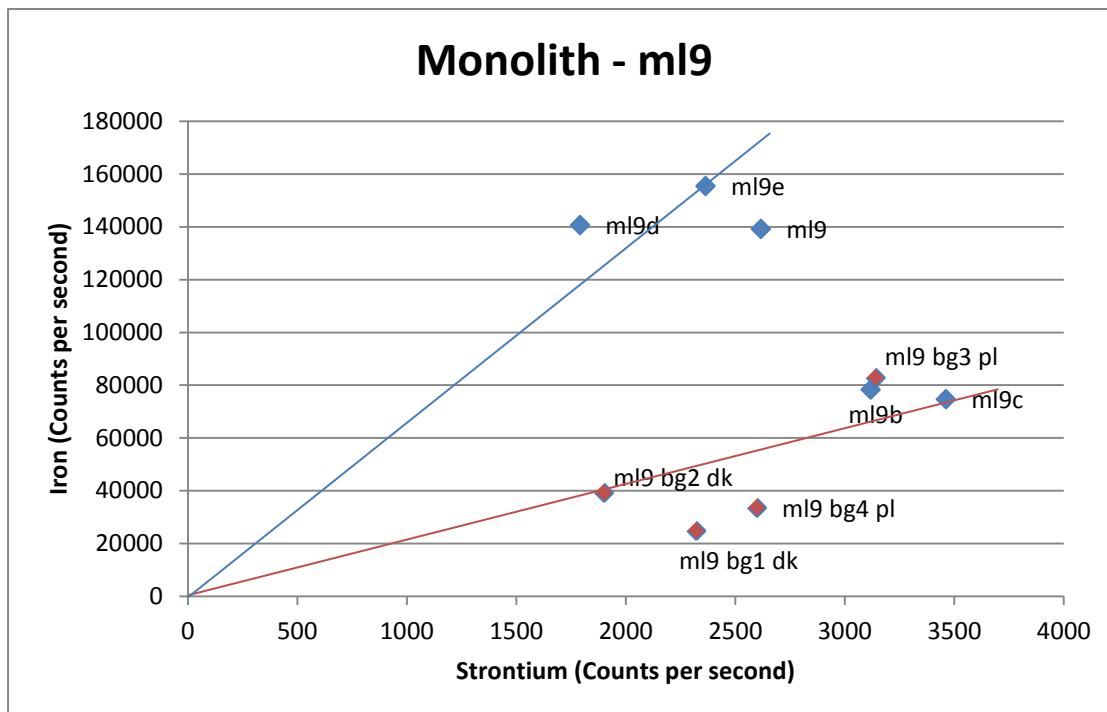
Figure 107. Scatter graph showing relative levels of iron and strontium in element 9 at Santiago Monolith

In element ml9 one significantly distinct group of readings can be identified (ml9, 9d and 9e). Readings 9b and 9c are different to these but are not significantly different to the background readings. This may be because these areas of pigment did not emit enough characteristic radiation to stand out from the background readings.
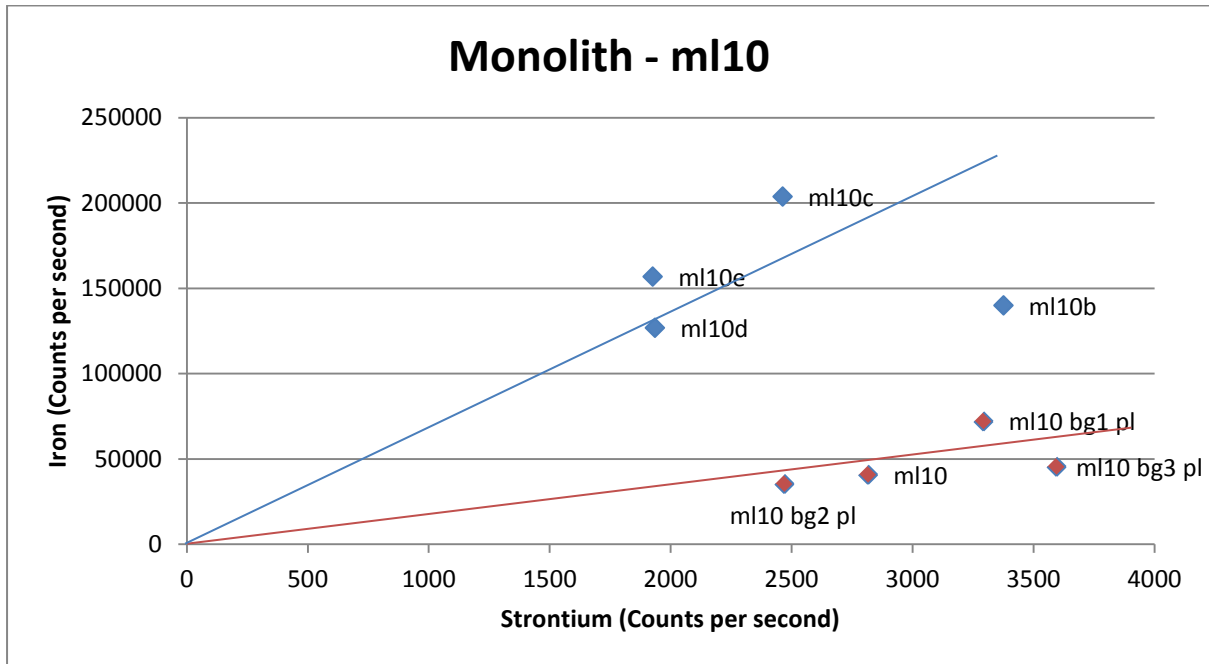
Ml10

Figure 108. Scatter graph showing relative levels of iron and strontium in element 10 at Santiago Monolith

Two groups of readings can be seen in ml10. One consists of pigment readings and the other of background results with one solitary pigment reading. Presumably this area of pigment was not able to produce a strong enough XRF signal to stand out from the background. The results indicate one definite group of pigment readings and may indicate a second pigment which includes reading 10b. This however is a lone reading and may be an anomaly. Once again the background readings here are very consistent with one another.

Ml11
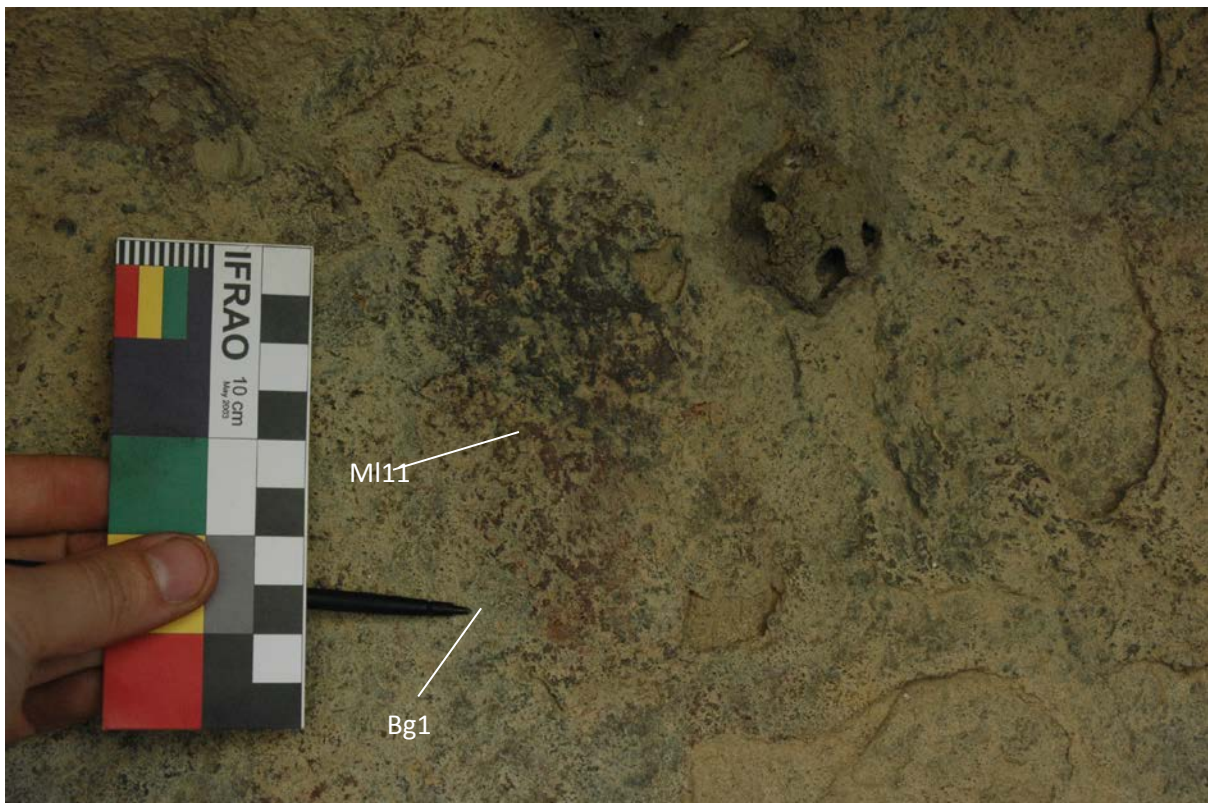
Fig 95. Element 11 at Santiago Monolith, showing the points from which readings were taken
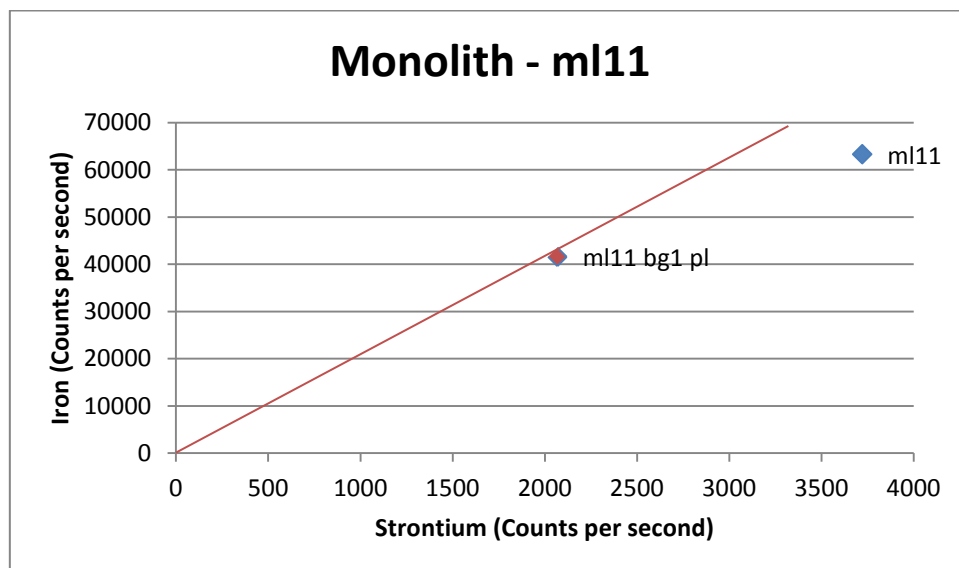
Figure 109. Scatter graph showing relative levels of iron and strontium in element 11 at Santiago Monolith

This element only has two readings, one from the pigment and one from the background. These do not contrast with one another and both are potentially anomalous as they are lone readings. As such no conclusions can be drawn from these results.

Ml12
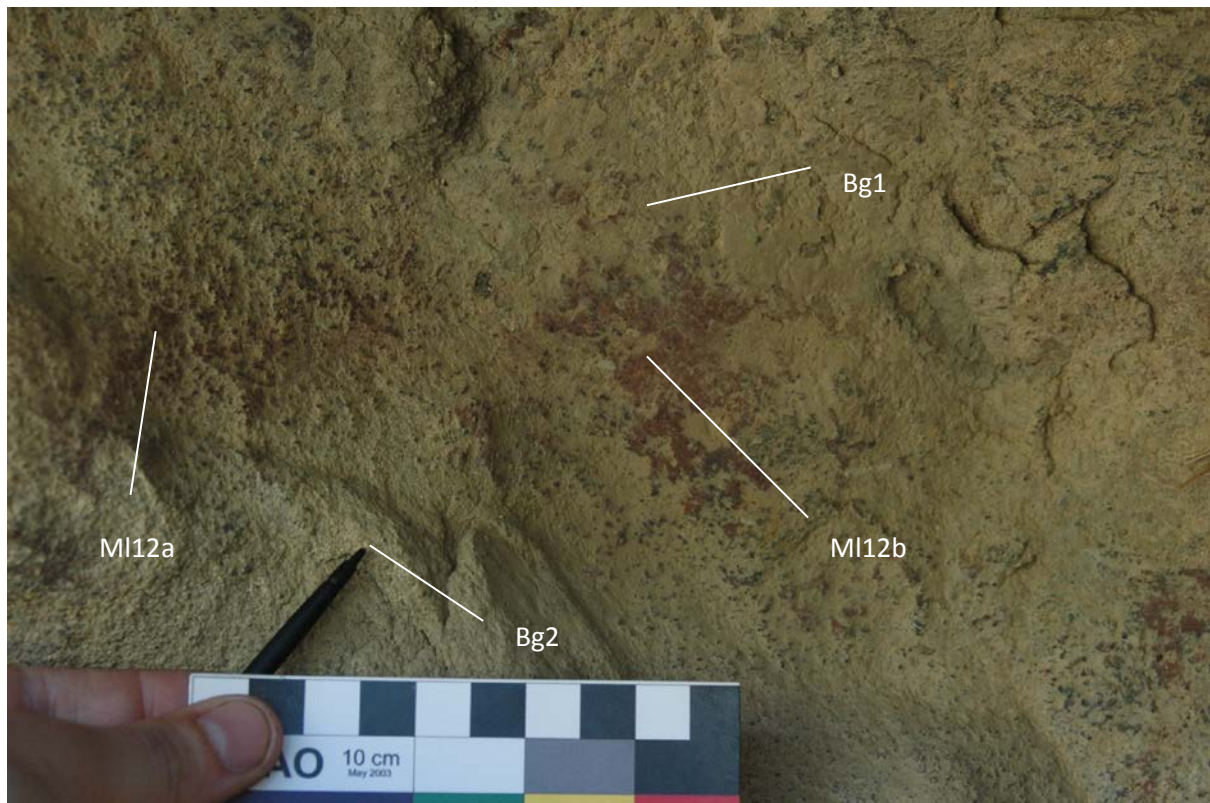
Figure 110. Element 12 at Santiago Monolith, showing the points from which readings were taken
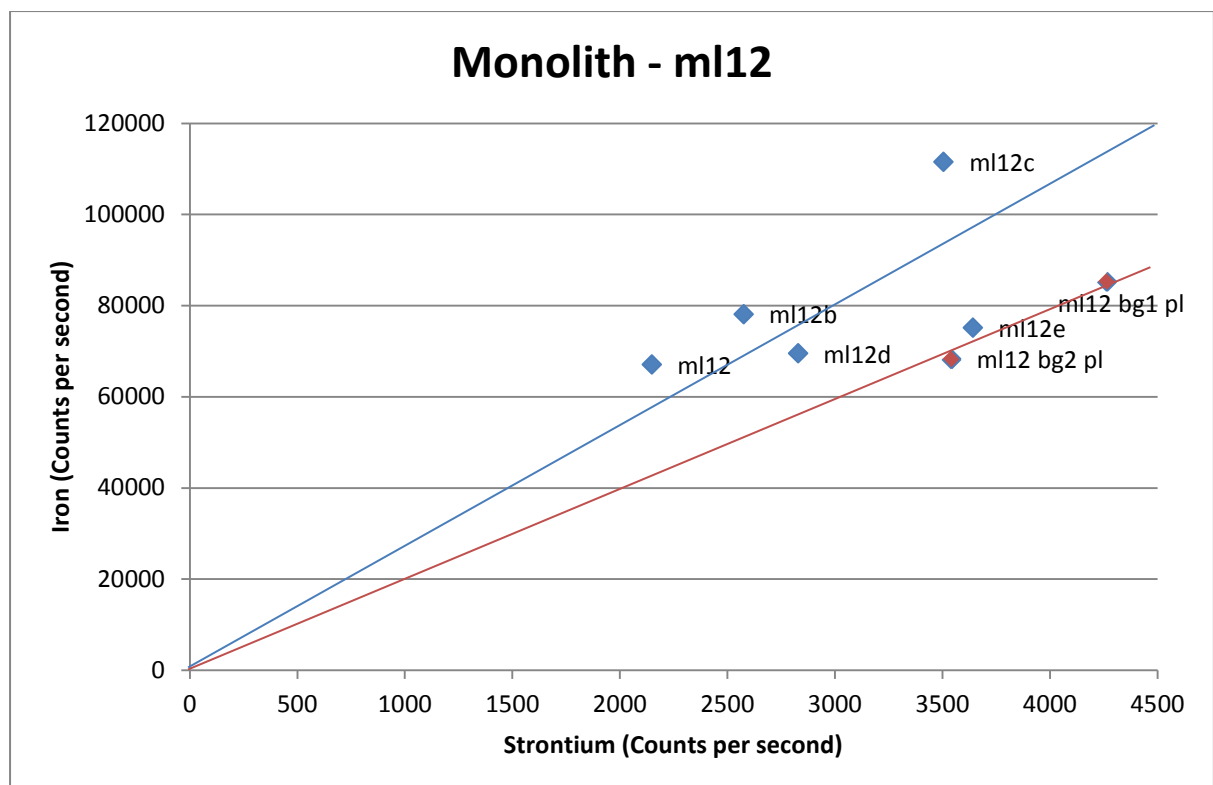
Figure 111. Scatter graph showing relative levels of iron and strontium in element 12 at Santiago Monolith

Although the pigment and background readings in element ml12 appear to overlap slightly, they contrast enough to display a statistically significant difference showing that one pigment material was used here.

Ml13
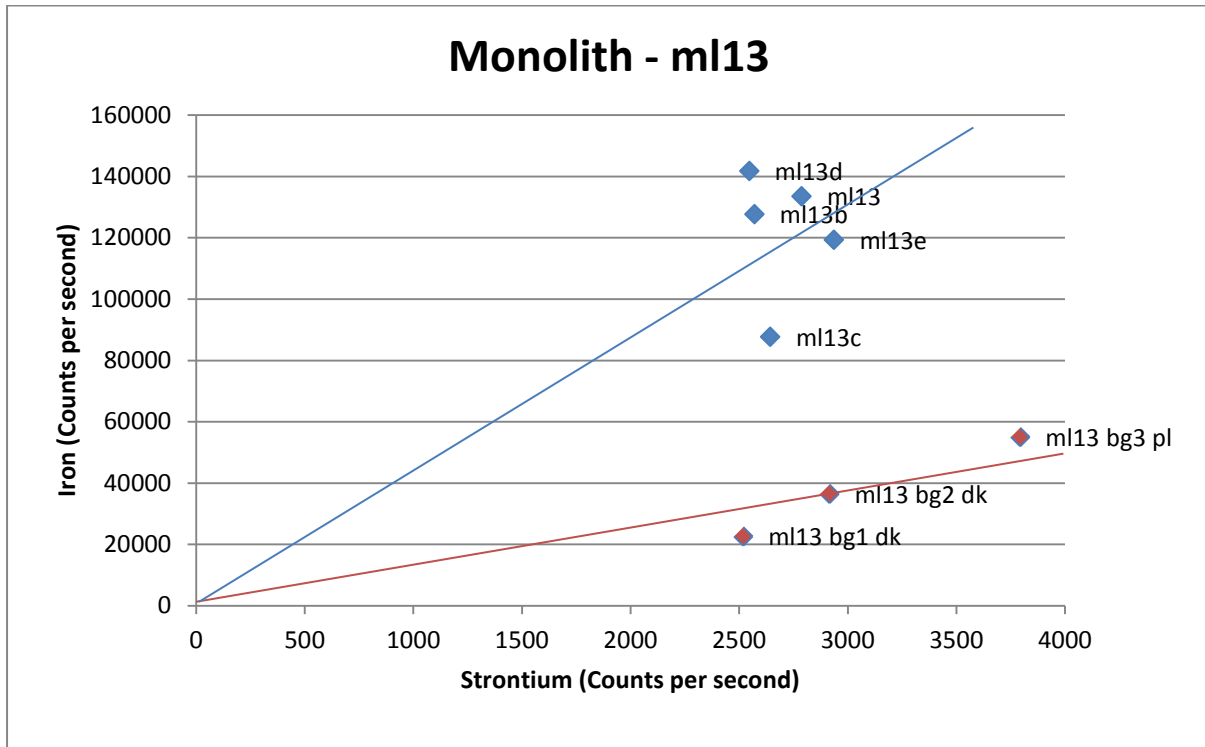
Figure 112. Scatter graph showing relative levels of iron and strontium in element 13 at Santiago Monolith

Ml13 similarly shows one pigment material which is significantly different to the background readings.

Ml14

Figure 113. Element 14 at Santiago Monolith
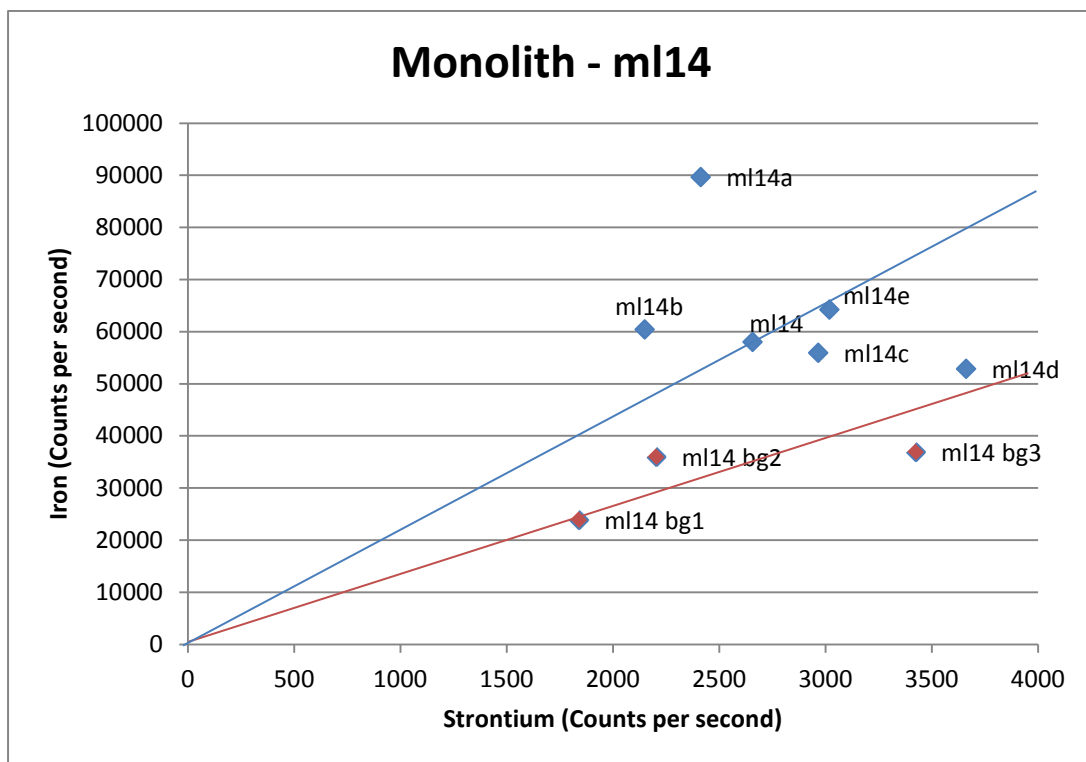
Figure 114. Scatter graph showing relative levels of iron and strontium in element 14 at Santiago Monolith

The pigment readings in element 14 are distinct from the background and form two possible pigment groups. Readings 14a and 14b form one group, 14,14e and 14c form the other. Reading 14d seems to be separate from the others. However, it may be that readings 14d, a and b demonstrate the range of readings within a single pigment, which has been seen in other elements at Santiago and Los Lobos. If all of these readings are treated as one group then this group still contrasts significantly with the background.

Ml15

Figure 115. Element 15 at Santiago Monolith
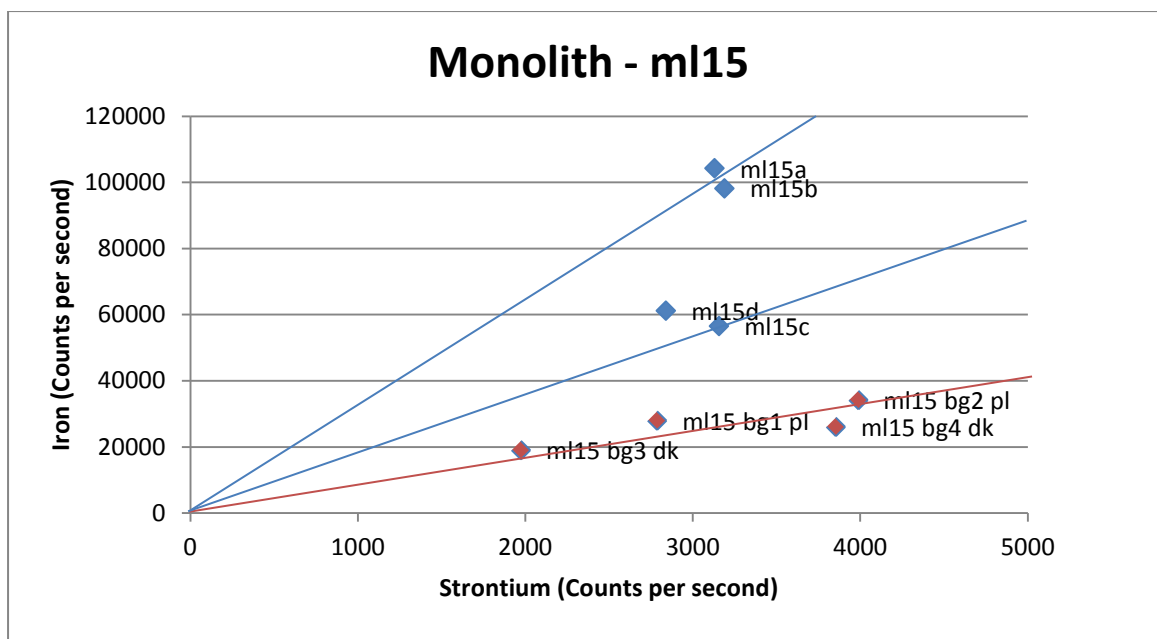
Figure 116. Scatter graph showing relative levels of iron and strontium in element 15 at Santiago Monolith

The background rock here varied between dark and pale areas. Readings were taken for both and are consistent with one another. The same variation and similar relative proportions of iron and strontium can be seen in both the dark and pale areas. The pigments form two discrete groups which are distinct from these background readings, indicating the use of more than one pigment to produce this element.

Ml16
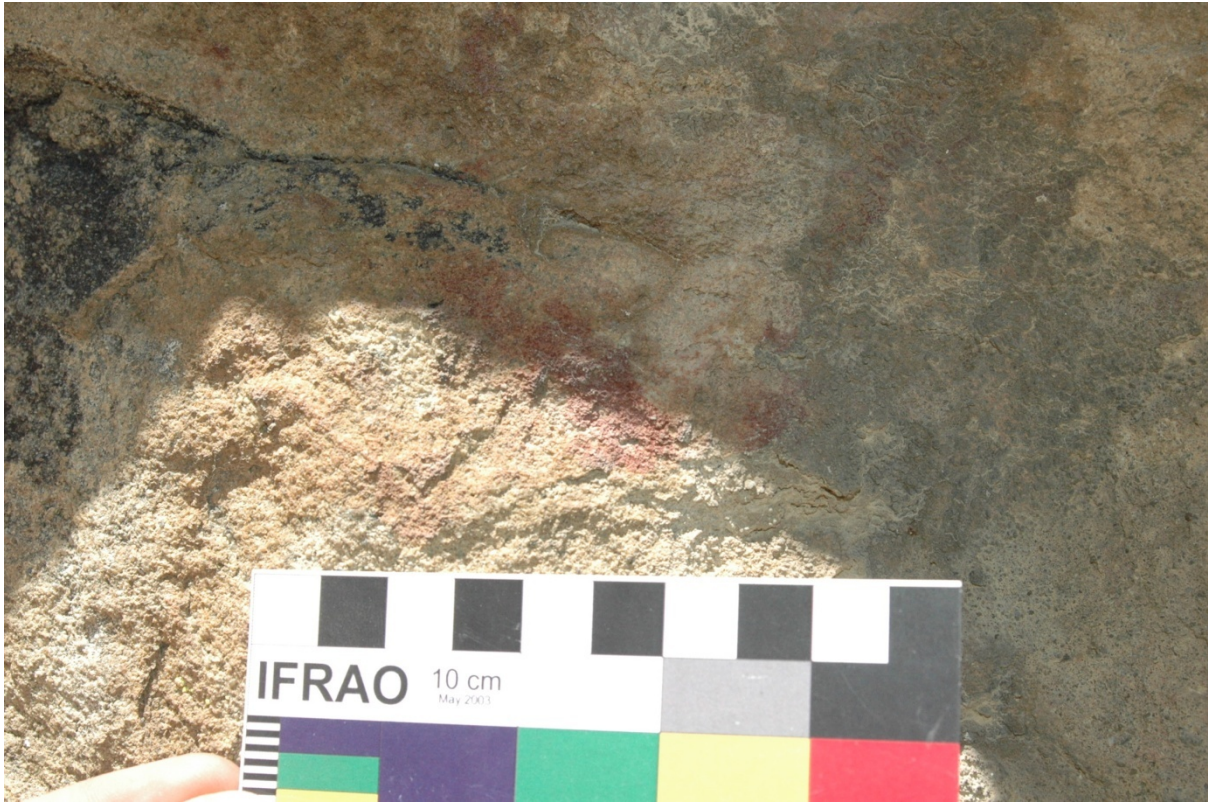
Figure 117. Element 16 at Santiago Monolith
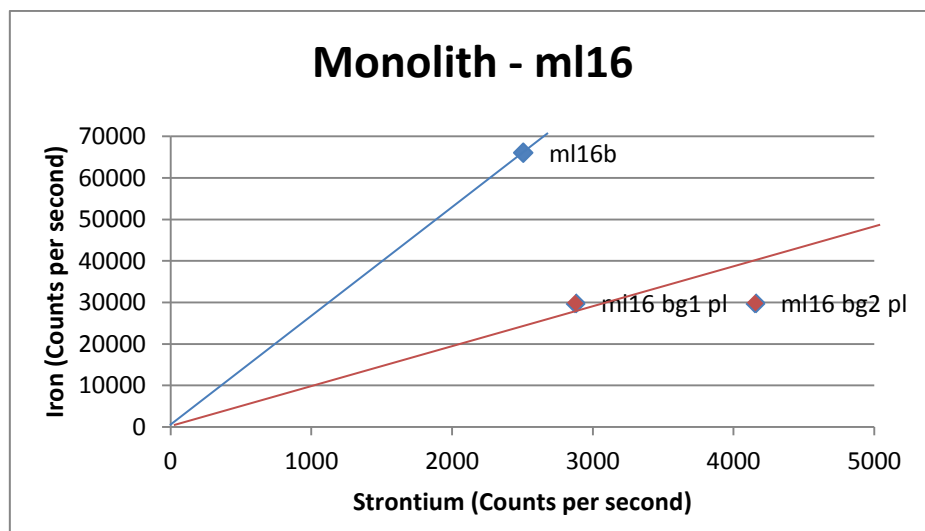
Figure 118. Scatter graph showing relative levels of iron and strontium in element 16 at Santiago Monolith

There is only one pigment reading from this element and it has a distinctly different reading to the background readings. However, as there is only one pigment reading this may be an anomaly and cannot be tested using the ANOVA test.

Ml17

Figure 119. Element 17 at Santiago Monolith
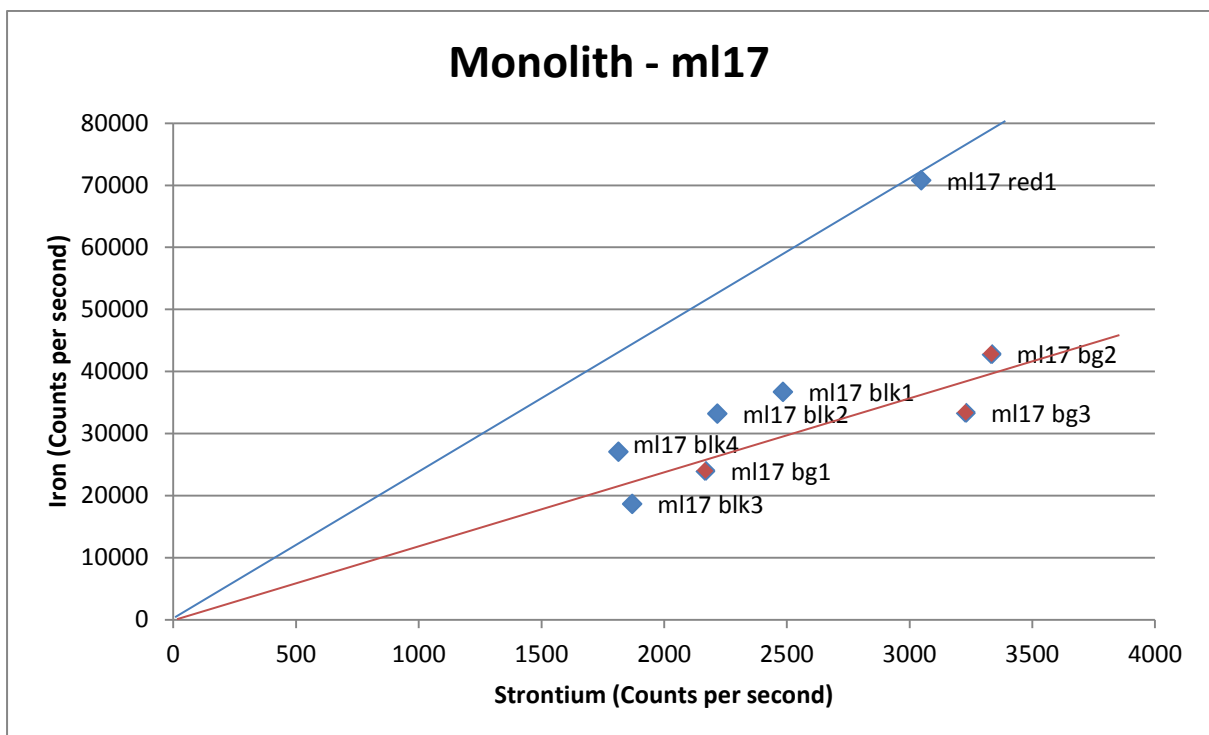
Figure 120. Scatter graph showing relative levels of iron and strontium in element 17 at Santiago Monolith

Element ml17 contains black and red areas. The black areas contain less Fe than the red pigment but the same levels to the background readings. There is only one red reading which means that it was not possible to check if it is statistically different to the other readings. It does however appear to be separate. As with other single readings this may be anomalous and therefore cannot be relied upon.

Ml18
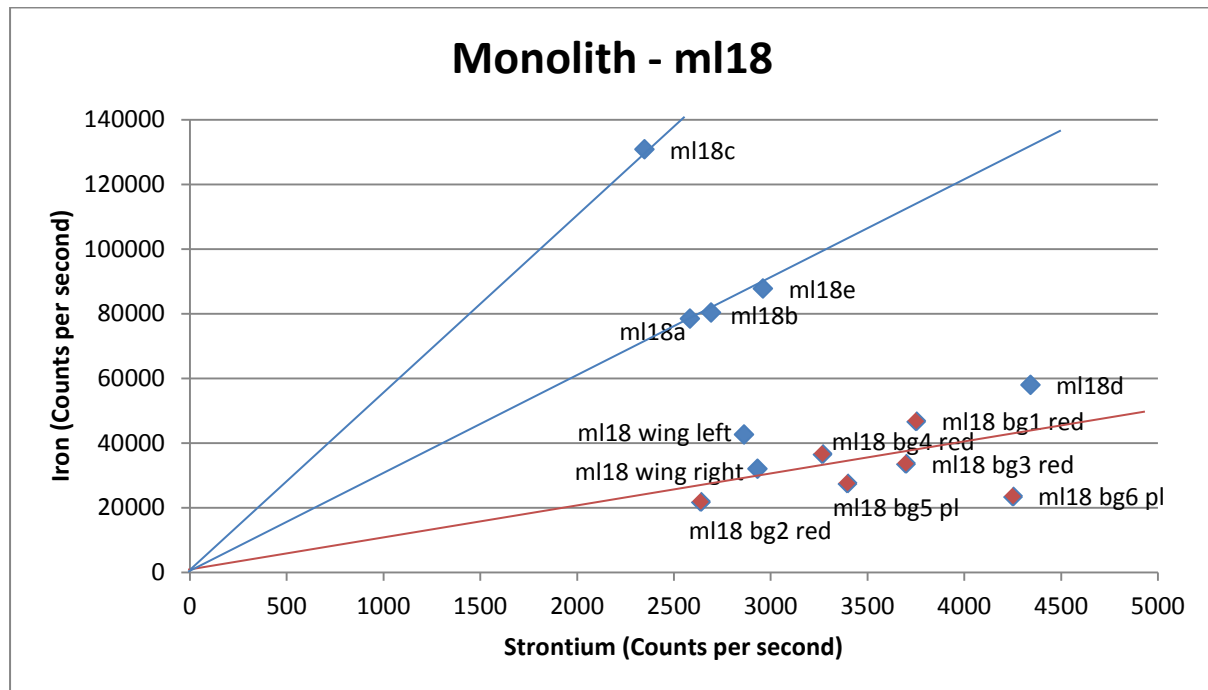
Figure 121. Scatter graph showing relative levels of iron and strontium in element 18 at Santiago Monolith

In element 18 there appear to be three separate groups of readings. The first of these contains the majority of readings and includes both background and pigment readings. Some of the background readings are from red-tinged stone which could have been too faint pigment rather than natural stone colouring. However, the readings are all too similar for any statistically significantly different pigments to be identified. The second group consists of ml18a, b and e which have very consistent readings with one another.

The third possible group is in fact a single reading, ml18c. This may represent a different pigment but further readings would be needed to verify this. It is also possible that readings c and d are both outlying readings from the same pigment as a, b and e, and that this pigment is quite internally varied.
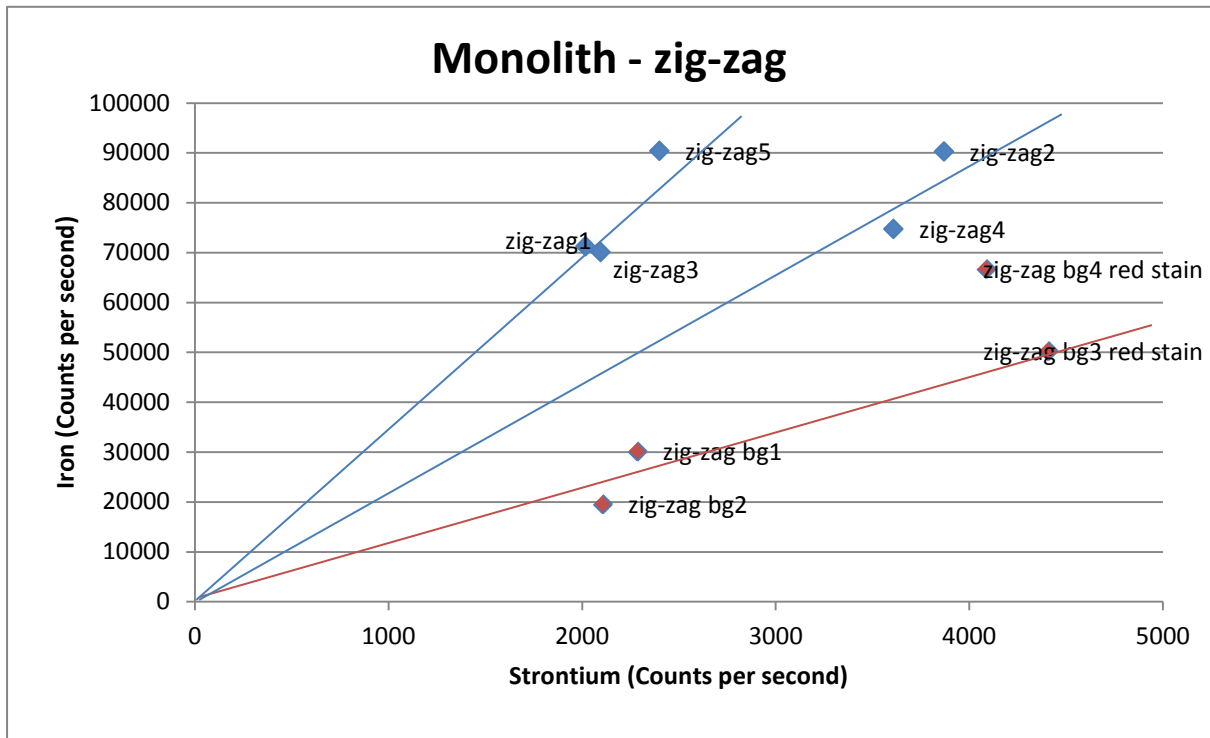
Figure 122. Scatter graph showing relative levels of iron and strontium in the zigzag at Santiago Monolith

The background readings from the zigzag contain readings from a 'red stain' which may or may not have been pigment. The results from this stain, however, do not contrast with the other background readings. Within the zigzag itself there are two groups; 1,3 and 5, and 2 and 4.

Variance testing shows that these groups are significantly different to each other as well as the background rock to which they were applied, indicating the use of 2 pigments in the zigzag.
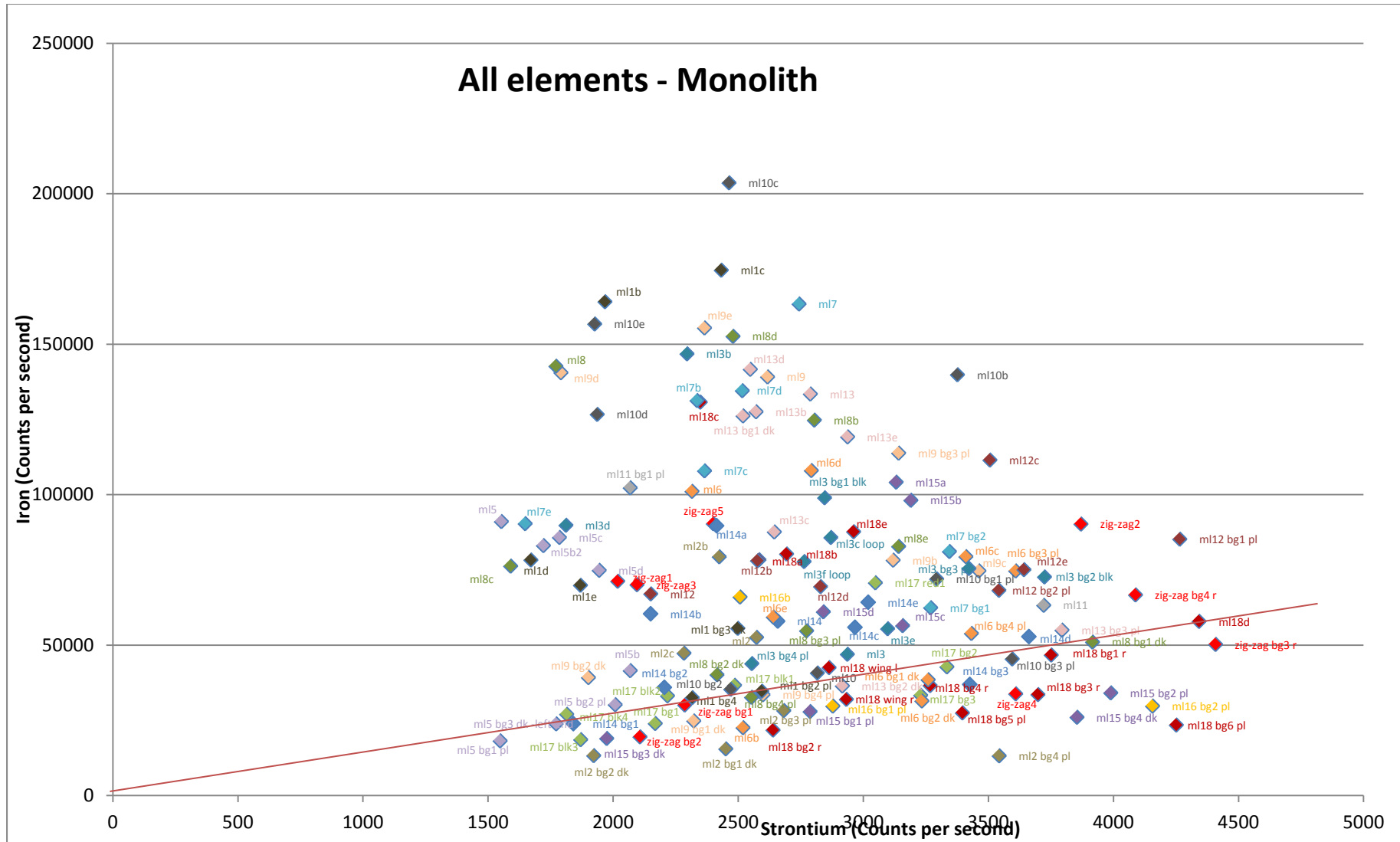
Figure 123. All elements at Santiago Monolith ml1=◆ ml2=◆ ml3=◆ ml5=◆ ml6=◆ ml7=◆ ml8=◆ ml9=◆ ml10=◆ ml11=◆ ml12=◆ ml13=◆ ml14=◆ ml15 =◆ ml16=◆ ml17=◆ ml18=◆

zig-zag =◆

The chart above shows the levels of strontium and iron readings for all the rock art elements on the Monolith. Most of the background readings show similar iron levels to one another although those for Ml11, 13 and 19 are noticeably higher than those for the other elements.

The rest of the readings are rather crowded, with no groups of readings standing out as being distinct, however some clear differences between and within rock art elements can be seen. It does not help that there are so many elements represented here as there is a certain amount of overlap between these elements. The pigment readings are distinct from their own background readings, but it is possible that variation in this background rock may explain some of the variation seen in the pigments.

Once again an optimistic eye can identify broad groups in this array which can be weakly supported by statistical analysis. This analysis however simply identifies that there is variation between pigments, but does not identify groups of readings that can confidently be identified as sharing a common pigment material. It seems that although distinct groups of pigment readings can be identified in most of the elements at Santiago, there is a wide array of readings within the two panels here. It is therefore very difficult to identify an exact number of pigment materials or painting events. I would argue though that there was clearly more than one and it seems likely that the variation in pigments indicates a wide range of materials and multiple painting events here.

A number of elements at Santiago show a relatively wide range of readings within one pigment. This may have contributed to the extent of apparent overlap between readings. It may also indicate that some of these elements were produced using directly applied raw ochre. The spectra gained from raw ochre samples display similar variation in readings, and it is logical that this variation would be reduced when ochre is ground into powder and therefore homogenised.

This wide range of readings could be explained by natural variation in ochre of the sort seen in a number of the elements here. However in each of these elements this internal variation still fits into a normal distribution and was not as broad as the variation in these panels as a whole. It therefore appears that although they were internally varied, different pigment materials can still be identified here. Some elements also contained two discrete pigment groups.

Based on this I would suggest that the variation in readings at Santiago reflects a number of different pigments in use rather than natural variation in readings. This may indicate that the panel was

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revisited and that different elements were created or added to at different times or by different people. Given the multiple pigments within some elements and the clear variation between some groups of readings I would argue that there are at least three red pigments in the rock art at Santiago but most likely more, and that when the black pigment is included these results show a total of at least four painting events.

Black readings such as Ml17blk are very similar to or slightly lower than the background readings. This makes sense if the black pigment used is carbon based, because the material would reduce the XRF signal which reaches the detector. It would not however show up as a different chemical signature as the portable XRF cannot detect organic chemical elements.

When the readings from Lonely Boulder were examined they unfortunately did not contain any strontium which means that this form of analysis was not possible.

Conclusion

In conclusion, this chapter has analyzed 5 sites, with a total of 411 readings from 13 total panels with 57 individual elements. On average, I took 82 readings per site, with an average of 7 readings per individual element, although some more complex elements at Three Springs had up to 17 readings. Of these readings, an average of 5 were from pigments and 4 were background rock readings. The numbers of readings for each site are shown in the table below.

Site	No. Panels	No. Readings	No. Elements	Average readings per element
Pinwheel	2	59	9	**6.5**
Three Springs	3	63	6	**10.5**
Pond	3	29	5	**5.8**
Los Lobos	3	119	18	**6.6**
Santiago	2	141	19	**7.4**
Total	**13**	**411**	**57**	**7.2**

Table 1. Table showing the number of readings taken at each site

This analysis has provided a large and robust data base. As I have already briefly mentioned in this chapter, these results allow estimation of minimum numbers of painting events and give clear indications of processing technologies utilised in producing the rock art. The information gleaned from these results allows for the research aims and questions to be thoroughly addressed in the next chapter

CHAPTER 4 – DISCUSSION: ADDRESSING THE AIMS AND QUESTIONS

The following chapter provides a summary of the results gathered and a discussion of the interpretation and significance of these results. In particular this chapter looks at the aims and research questions outlined in the introduction, by discussing the extent to which XRF can be used to characterise rock art pigments and the information gained about Chumash rock art in the Windwolves Preserve by applying the technique. In addition to this I discuss limitations to the use of pXRF in rock art examination and the opportunities for further analysis which have been opened up by pXRF analysis.

Summary of results

The XRF results from these sites indicate the presence of a variety of constituent elements in the pigments used, particularly in the red rock art elements. Prior to the application of portable XRF technology it was not possible to identify different phases of rock art production unless physical overlay of pigments is visible. When an element or panel is monochrome such overlay is difficult to identify. By examining the chemical composition of pigments it is possible to identify different pigments which appear the same when examined visually. This means that sites which may appear to have been produced in one event can actually be shown to have multiple painting events. Table 2 shows the minimum number of painting events identified at each site. These numbers potentially represent the number of occasions on which the sites were visited or the number of people who were contributing to the rock art. When combined with physical overlay of elements, and the different coloured pigments present, it should be possible to estimate a minimum number of painting events as shown in table 2.

Site	Pinwheel	Three Springs	Pond	Los Lobos	Santiago - Monolith
No. red pigments	3	3	5	4	3+
Total minimum no. painting events (MPE)	3	8	6	7	4

Table 2. Table showing the number of painting events at each site

The XRF results from each of these sites indicate the presence of more than one pigment material in use in red rock art elements. If the application of each of these different pigments is treated as a different painting event then this gives us a possible total minimum of 28 painting events between the sites and more than one at each site.

The rock art panels at Santiago, located directly overlooking BRMs, contain 18 rock art elements. The majority of these elements contain at least two if not three chemically different pigments, however when all of the readings are compared with one another we see a varied spread of readings. This could be for a number of reasons.

Firstly, it is possible that these varied readings represent natural variation in ochre. However, if this were the case I would expect a wide spread of readings within each element. As each element shows one or more discrete groups of readings, it is most likely that these readings reflect the use of different pigments rather than simply representing a spread of readings from a particularly varied material. This indicates, therefore, that the elements at Santiago were retouched, and added to using a variety of different pigments.

The rock art on two of the panels (Alcove and Window Box) at Pond is similarly very close to BRMs. Pond Boulder is further away from the BRMs. Two pigments were identified in the rock art element at Pond Boulder. Two possible pigments were identified within element 3 in the Window Box at Pond, and element 1 is clearly different to the other elements. However, at this site many of the rock art elements failed to contrast sufficiently with the rock on which they were painted. This means it was not possible to see if any other different pigments were used.

Of all the sites in this study Pinwheel cave is furthest from its BRM complex. Inside Pinwheel cave are six elements, most of which are not chemically distinct from the rock on which they were painted. In addition to this the rock itself is very varied chemically in most of the cave, making it very difficult to accurately separate chemical elements present within the pigment from those present in the rock.

Element 1, the Pinwheel motif, contains up to three different pigment materials (see fig 124). Two of these may be from the same source material as suggested by the trace element analysis, but have been processed differently. These contain distinctive trace elements

which may indicate a different source material. One of the pigments used in Pinwheel 1 also shows the same chemical composition as that used in the second locus at the site.
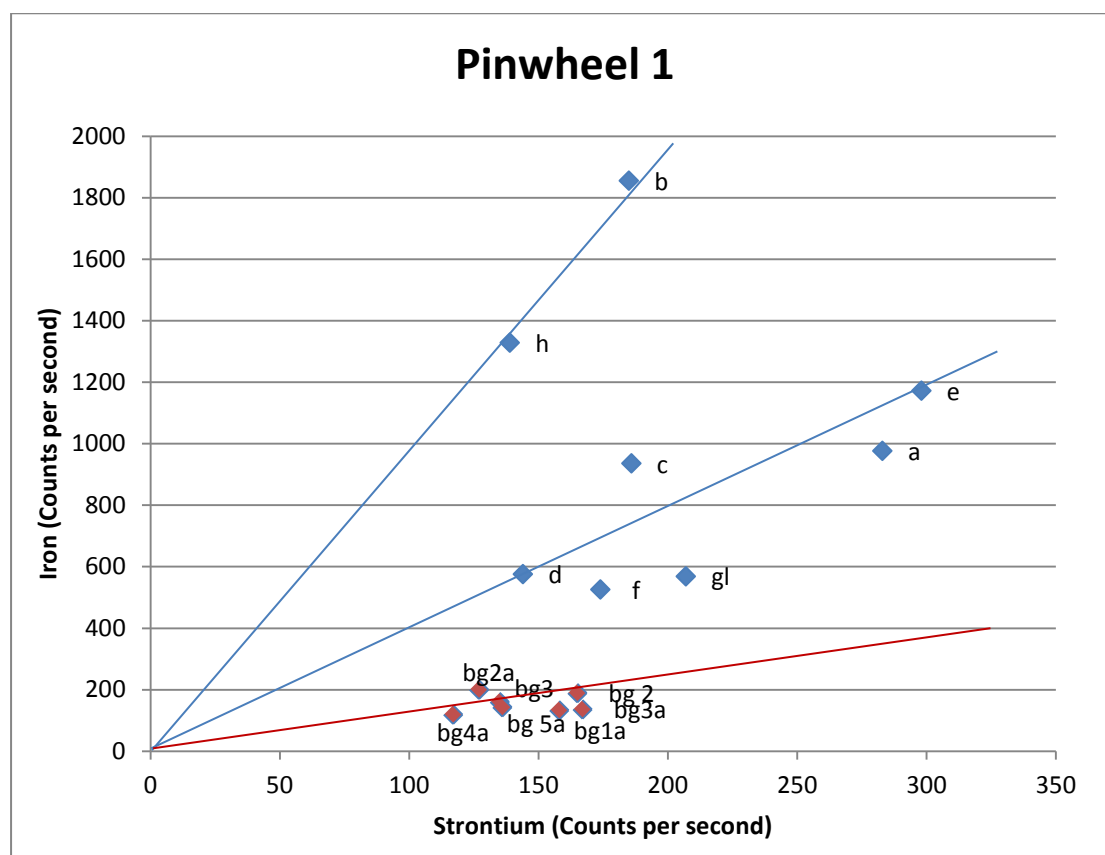
Pinwheel 1

Figure 124. Iron to strontium levels at Pinwheel 1

The rock art at Los Lobos appears at two loci and is also very close to BRMs. Although some elements are not chemically distinguishable from the rock on which they were painted, many of them did display distinct chemical signatures. At the upper cave locus a number of elements seemed to contain two or three separate pigment materials, and some of these elements also had pigments in common with one another. This may suggest that particular elements were revisited and retouched at the same time as each other.

At Three Springs the rock art is polychrome and the panel is complex. An absolute minimum of three red pigments can be identified and there is possible retouching in the zigzag element. The black pigments at Three Springs are most likely carbon based (Nuevo *et al.* 2011:4) and very interestingly, the blue pigments here appear to consist of optical blue (Scott *et al.* 2002:190), rather than involving copper or cobalt which can be used to form blue pigments (Scott *et al.* 2002:190; Reeves *et al* 2009).

Interpretation

The question now is of the significance of these multiple pigments and painting events. In order to discuss the significance of these results I will refer back to the research aims and questions posed in the introduction:

Primary aim: Establishing a methodology

- Can XRF be used to effectively characterise the chemical composition of *in situ* rock art pigments?
- Can these pigments be differentiated from one another using this method?
- Can this method be used to infer pigment preparation techniques?
- Can XRF data be used to establish a chronology for rock art?

Can XRF be used to effectively characterise pigments?

Yes. The use of portable XRF at the sites described above effectively provided information about the chemical composition of pigments in the *in situ* rock at each of the sites. The red pigments are iron based and pXRF was able to differentiate between pigments, by identifying materials with different proportions of iron relative to strontium. As well as this, XRF allowed the identification of trace elements in these iron based pigments which may indicate different ochre source material in the pigments at Pinwheel, for example. This method examines ratios of elements rather than comparing numbers of counts for each chemical element. This is because it is a qualitative analysis, and it accounts for the nature of the material on which the rock art was produced.

The numbers of counts registered by the portable XRF is affected by the density of samples and the roughness of surfaces. A rough surface contains more air pockets and stops the detector from getting close to the pigment being measured. As a result there is some variation in the number of counts for each element within rock art elements and panels, and so a comparison between the proportions of iron and strontium has been used.

This approach has very quickly and effectively identified differences in red pigments and has also been useful in examining black, grey and blue pigments. Black pigments are likely to consist of carbon or manganese (Nuevo *et al.* 2011:4) and so by checking for manganese I have been able to infer the composition of black and grey pigments. Similarly, by checking for metals such as cobalt or copper it has been possible to determine whether blue pigments were a result of a metal oxide or optical blue (Scott *et al.* 2002:190), which displays readings with a distinct absence of such materials.

Can these pigments be differentiated from one another using this method?

Yes. As described above, this method has proved to be very effective in differentiating between different red pigments by looking at iron ratios, as well as identifying the materials used in many of the black, blue, white and grey pigments were also identified. In addition to the examination of iron to strontium ratios, the identification of traces elements can also be used to differentiate between ochre materials. For example the differing levels of arsenic in the pigment at Pinwheel (see fig 125) can be used to separate different pigments within one element.
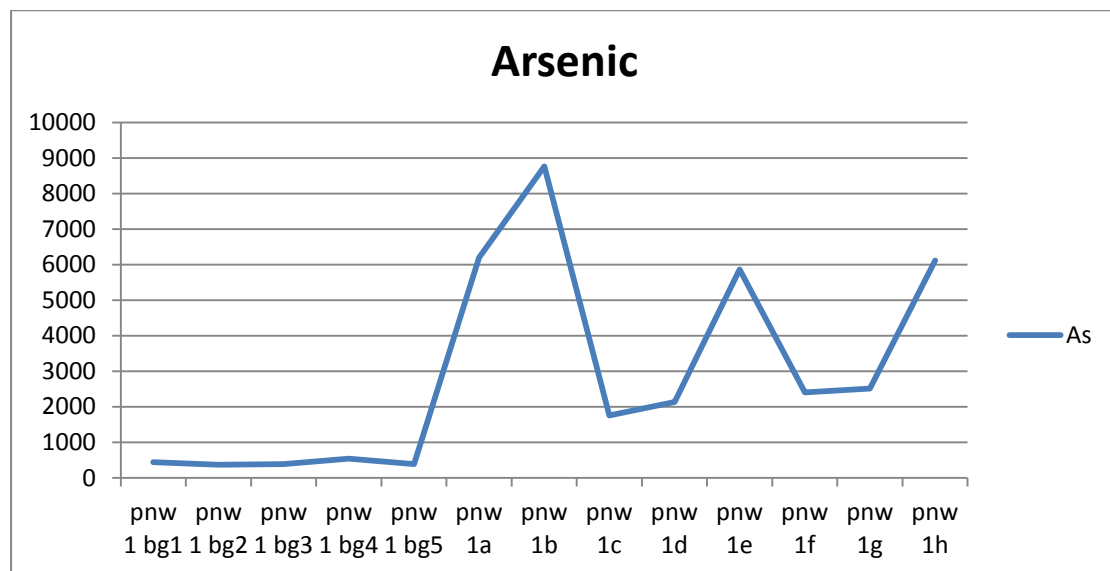
Figure 125. Relative arsenic levels (counts per second) in Pinwheel 1

Readings a,b,e and h displayed similar levels of arsenic but appear in different groups on the chart (see below). This may be explained by the use of the same source ochre material but different binders.
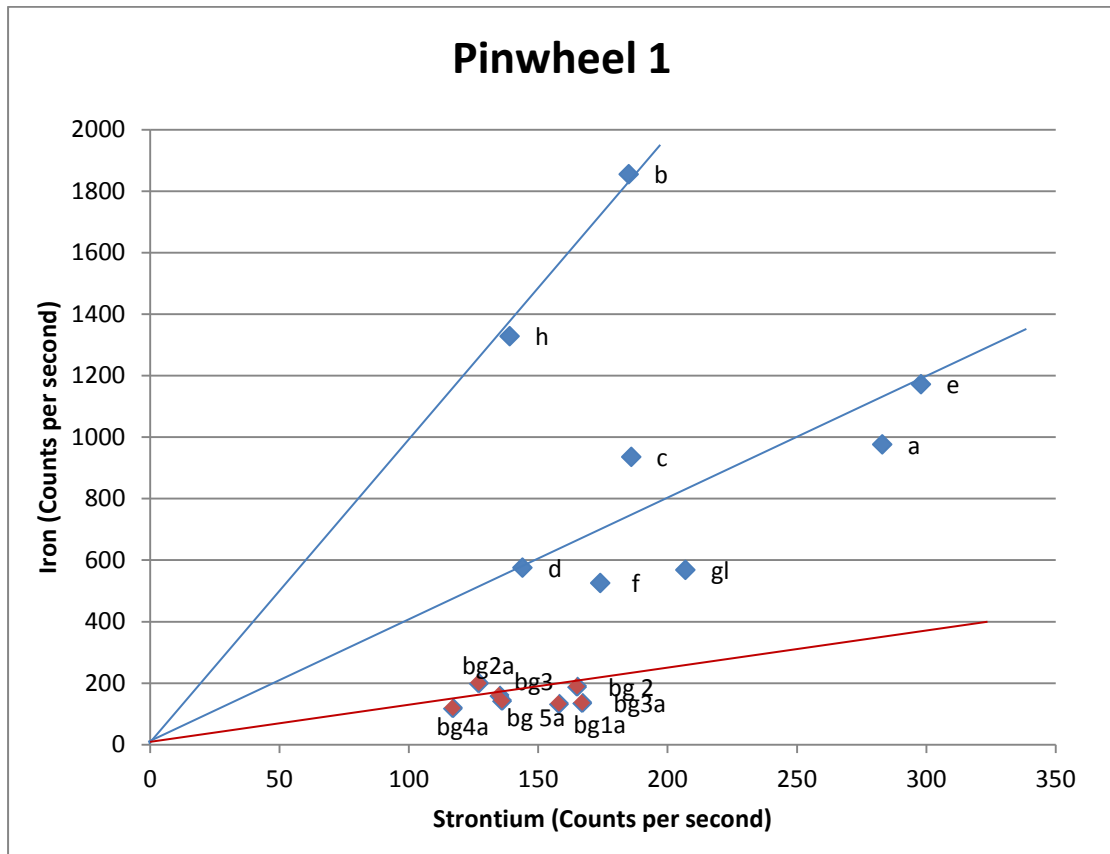
Figure 126. Iron to strontium levels in Pinwheel 1

In fig 126 readings a and e are also separated along the axis from the rest of their group and present higher readings of both iron and strontium. The proportions of these remain the same however. It is possible that the appearance of clusters of readings on a single axis is therefore significant; it may also be that one pigment has overlain another at this point and so the arsenic reading from one pigment appears in the spectrum for the other. These possibilities definitely deserve further investigation.

One great advantage to this method is that this method very quickly and non-destructively differentiates between materials with only subtle differences, and so is very valuable. As well as differentiating between pigments this method has allowed the identification of common pigments which are shared by elements within a site or panel as shown in the table below.

It was not however possible to confidently discuss shared or contrasting materials between sites. This is because the background materials at each site are different to one another (see

fig 127) and these may contribute to the final readings for each element. It would be necessary to extract the pigment readings from the overall reading in order to compare its composition accurately with a pigment from a different site. For this reason I would not yet be able to accurately establish sources for the ochres used.
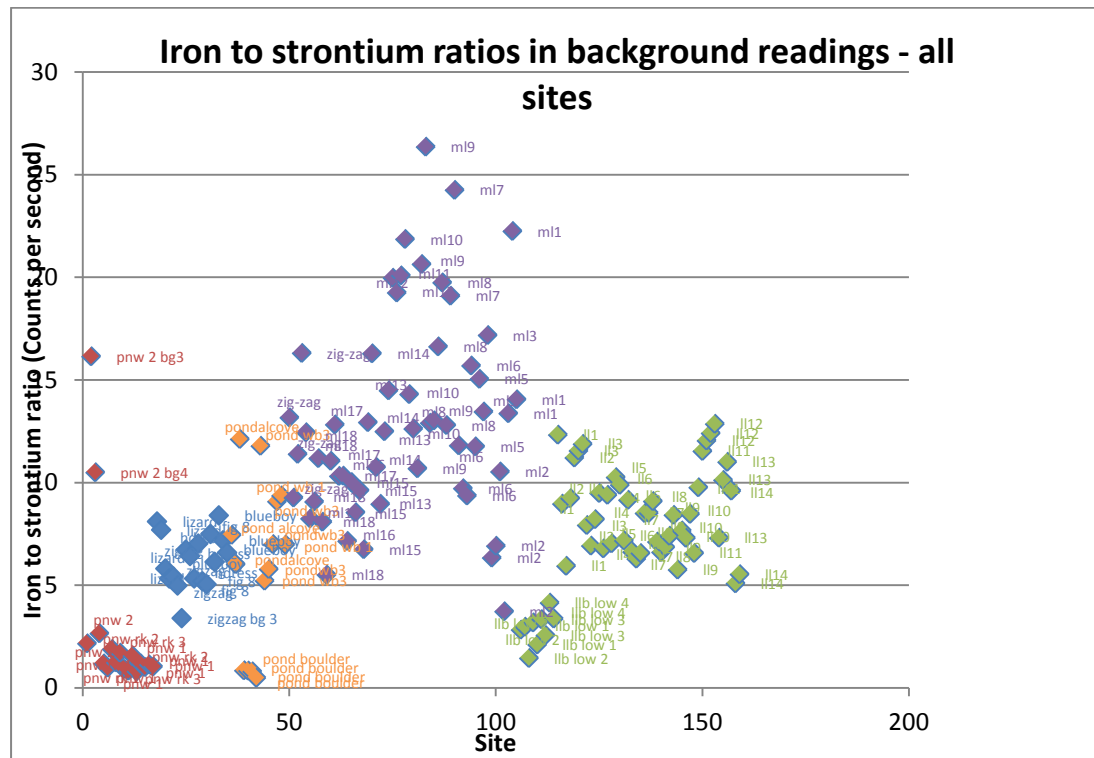
Figure 127. Iron to strontium ratios in background readings from all sites in the study

Can this method be used to infer pigment preparation techniques?

It can but to a limited degree. As well as the discussion on social significance of rock art, these readings also give indications about technology used to produce this rock art. They do also open up a lot of further questions about the materials and processing techniques which were used to produce rock art, and the potential for further investigation of this rock art by pXRF and by complementing this using other analytical techniques.

It appears that the XRF spectra may provide a clue as to which ochres were directly applied and which were processed. Raw ochre samples were excavated from each of the sites in this project and they display a wide range of readings (see appendix 2). A similar range of readings appears in some of the *in situ* rock art, particularly at Los Lobos and Santiago as shown below.
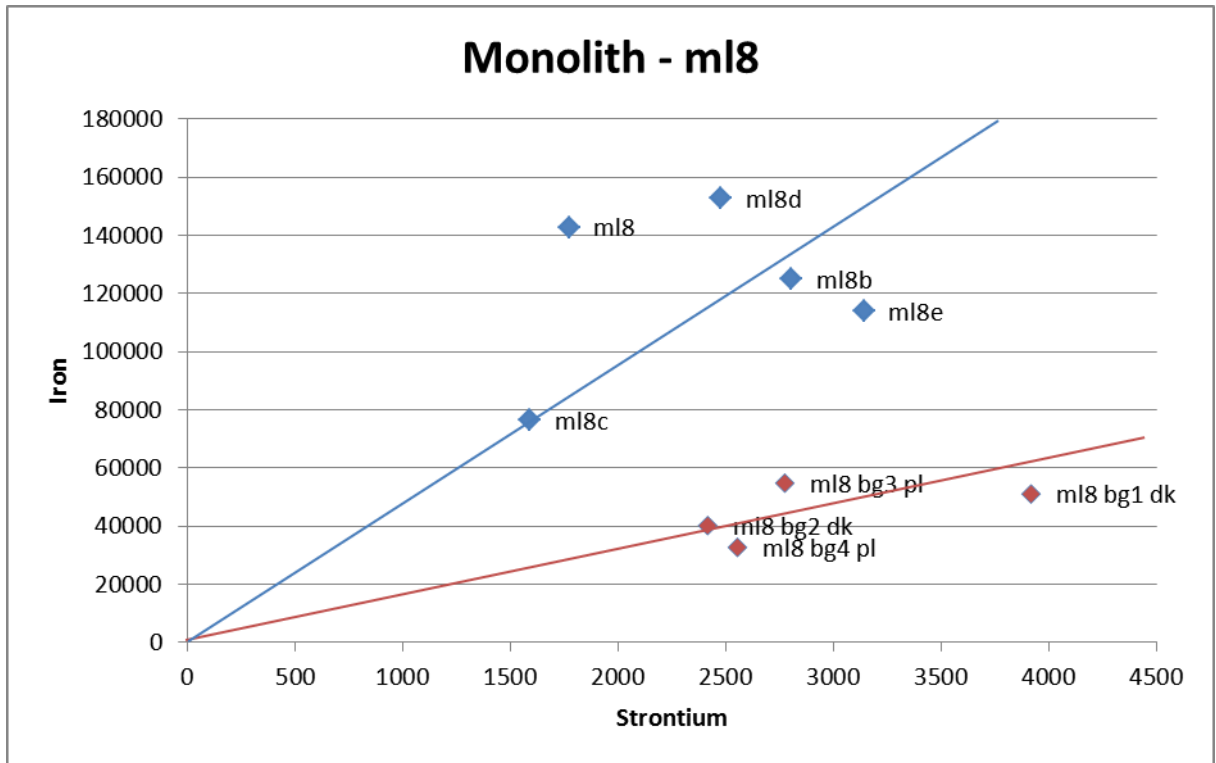
Figure 128. Relative iron and strontium levels (counts per second) in Santiago Monolith 8

Other rock art elements, such as Three springs 'Blueboy', some elements at Santiago and Los Lobos readings (5,6 and 7 - see fig 128) display a much narrower range of readings around the same mean, indicating that they may have been homogenised by processing.
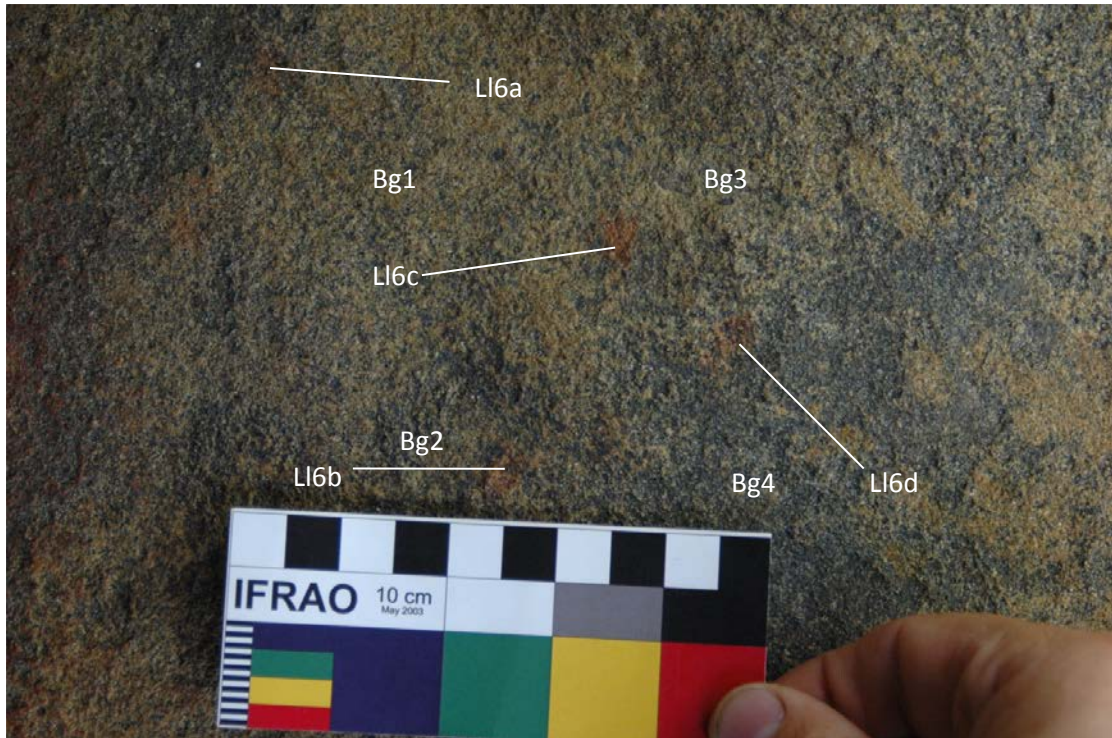
Figure 129. Los Lobos element 6
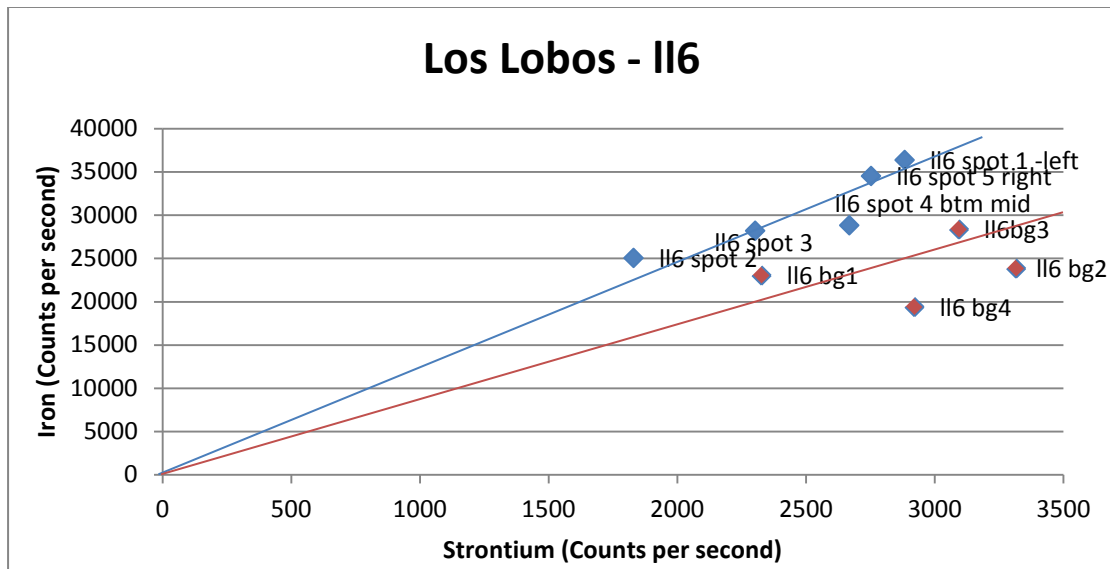
Figure 130. Relative iron and strontium levels in Los Lobos 6
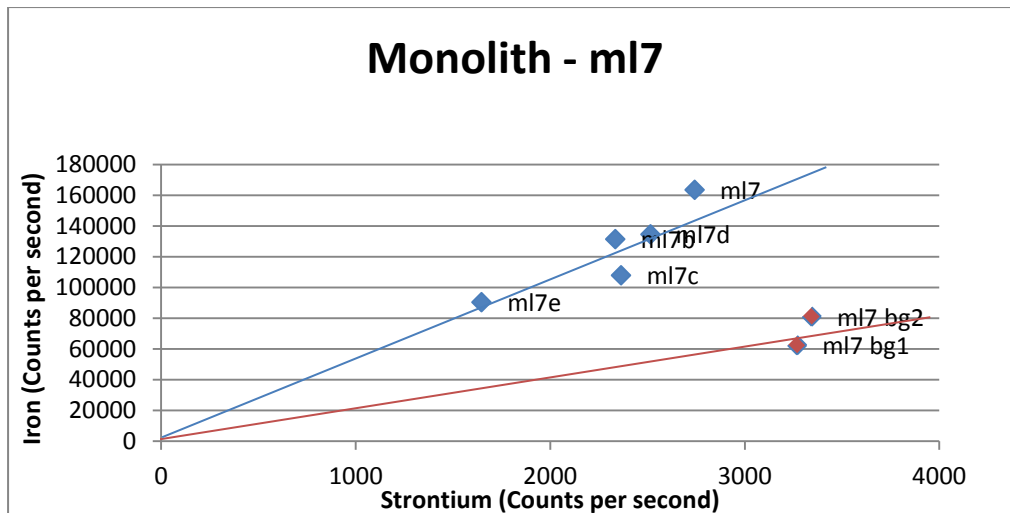
Figure 131. Relative iron and strontium levels in Santiago Monolith 7

The appearance of pigments with greater natural variation within a site could show that they were directly applied ochre pigments rather than materials which had been ground and mixed, and therefore homogenised. In this case this would indicate different technologies applied to rock art production, and raises the question of whether there were different types of rock art in which these different methods were employed, or whether this represents a change in technology over time.

The appearance of different chemical signatures in the pigments used could result from a number of factors. I have particularly been examining different relative proportions of iron within pigment materials. These differing levels of iron indicate that different resultant pigments were used within and between sites, however these changing levels could be the result of different raw materials, different preparation techniques, different binders (Scott and Hyder 1993:157-158) or of chemical changes caused by subsequent weathering (Moussa *et al.* 2009:302). Binders could include blood or cucumber extract (Scott and Hyder 1993:157-158). The addition of blood would change the iron level present in the pigment. The challenge in identifying blood binders would be in determining whether an increase in iron has resulted from the binder or the raw material itself.

In this area of California iron occurs naturally in the rock, as demonstrated in the spectra gathered in the Windwolves Preserve. It also occurs in ochre, and in blood, which is known to have been used as a binder for pigments (Scott and Hyder 1993:157-158). By taking background readings and comparing these with the pigments we can ensure that increased

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iron levels seen in pigment readings are not simply the result of natural variation in the rock to which it was applied.

Similarly iron levels may fluctuate naturally within the ochre used to produce pigments causing the appearance of different materials. The range of readings from Santiago could be explained, to an extent, by natural variation. However, if this were the case here I would expect to see a scattering of readings rather than the discrete groups that can be seen at this site. This view is based on the readings obtained from excavated ochre samples as seen in Appendix 2. Some variation is seen within each sample but the readings still cluster around a mean reading for that sample.

Usefully, initial XRF analysis has allowed a conclusion that the blue colour seen at Three Springs was produced using optical blue rather than copper. The ability to determine which of these ingredients produce this colour by examining XRF data would allow us to glean very useful information about the technology used to produce rock art. It could also potentially allow us to determine the source of raw materials used to produce pigments. In order to examine the exact constituents of each pigment type and to establish both binders and potential source materials it would be necessary to separate background and pigment readings from one another.

At Three Springs zoomorphic figures can be seen in the rock art. Some of these (Blueboy) are finely painted and contrast with much of the broad-lined linear and curvilinear elements. The pXRF results indicate that these were produced using different pigments.

Can XRF data be used to establish a chronology for rock art?

It can assist in the creation of relative chronologies. It is possible for chronologies to be established in rock art sites by examining the physical overlay of pigments. By using XRF in conjunction with this visual analysis pigments which share a chemical composition can be identified across a panel. This can then allow the construction of a more detailed chronology which includes elements which are not themselves physically overlaid, but appear to have been produced using the same pigment, and therefore potentially at the same time, as other elements which are part of a visually established chronology.

For example at Pinwheel two pigment materials can be seen in element 1, the Pinwheel motif. Pigment 1a appears to have been applied first, but then to have had pigment 1b added to it. Pigment 1b however is consistent with the material used in the Pinwheel rock elements on the panel next to the cave and so it can be inferred that these were produced when the original pinwheel motif was revisited and added to.

Also, at Three Springs the zoomorph is less finely painted than 'Blueboy', but still contrasts chemically with both 'Blueboy' and the curvilinear elements. Different forms of rock art elements have been considered previously to have been produced at different times on other sites (Hyder and Oliver 1986) and this is supported by the chemical differences. Coupled with physical overlays of pigments which are visible these chemical spectra can be used to establish a more comprehensive chronology of the panels.

Secondary aim – pXRF applied to regional questions

- Were the same pigments used on a number of sites and were different pigments used within rock art elements, panels or sites?
- Based on this information, how many painting events occurred at each site?
- What is the significance of these results in terms of technology and chronology?
- Was rock art exclusive in nature, and how much can we tell about who was producing it?

Were the same pigments used on a number of sites and were different pigments used within rock art elements, panels or sites?

The results indicate a number of different pigment materials in use and therefore suggest multiple painting events at each site. The analysis of XRF allows differentiation between pigments to the point that a minimum number of painting events can be estimated.

The variation in resultant pigments indicates that rock art panels may have been repeatedly revisited at different times, and potentially by different people. This indicates that the rock art was not produced on one occasion. It is of course possible that an individual returned to

retouch their own work but this indicates that it was important for the rock art to remain visible over time. Similarly it is possible that someone else added to the rock art. The use of different pigment material may indicate this as it is likely that an artist would stick to their own recipe or preparation technique.

Common materials can be seen in different rock art elements within sites. The elements which share pigment material are shown in groups in the table below.

Site	Pigment 1	Pigment 2	Pigment 3
Pinwheel	Pnw 1b, pnw 1h	Pnw 1c, pnw 1d, pnw 1f, pnw 1g, pnw rock elements	Pnw 1a, pnw 1e
Three Springs	Zoomorph *	Blueboy *	Zig-zag*, fig 8*
Pond	Wb 3b and c	Wb 1	Wb 3 and 3a, wb 4 and 5, Pond boulder
Los Lobos	Ll3, Ll2b,c and d	Ll12, Ll7, Ll4, Ll10, Ll2a and c	
Santiago			

Table 3. Table showing elements with shared pigment composition *(multiple readings)

Comparison between pigment materials within each site is relatively straightforward, as long as the background material is consistent across the site. The issues of fluctuating background rock are discussed more in the following sections, and are very clear in most of the elements in Pinwheel Cave, and in Los Lobos element 9. Here great variation in the background readings correlates with chaotic pigment readings which did not contrast with their respective background rock. Similarly a number of rock art elements at all the sites had readings which were indistinguishable from their background readings and so unfortunately in these cases I was unable to identify to characterise the pigments present using this method.

The effect of background readings is also a complication when trying to compare the pigments used between sites in this study. Although parallels can be drawn between some of these pigments, not all of the background readings are consistent, for example clear differences can be seen between the background readings of Pinwheel and Three Springs even though some similarities can be seen. It would be necessary to establish the effect of the background readings on the pXRF results before a reliable comparison between sites is possible.

Based on this information, how many painting events occurred at each site?

As shown in the table at the start of this chapter at least 18 painting events are clear between these sites, and between three and five within each site.

Site	Pinwheel	Three Springs	Pond	Los Lobos	Santiago - Monolith
No. red pigments	3	3	5	4	3+
Total minimum no. painting events (MPE)	3	8	6	7	4

Table 4. Table showing the number of red pigments and total minimum painting events (MPE)

What is the significance of these results in terms of technology and chronology?

As discussed earlier these results give indications about both technology and chronology at the selected sites. Firstly the readings identify the chemical composition of each pigment. The red pigments were produced using iron based ochres such as haematite; black pigments were carbon based as indicated by the lack of manganese in the readings; and white pigments were most likely calcium based but calcium levels were difficult to discern against the fluctuating calcium levels in the rock. Grey and blue pigments (seen at Three Springs) presented the same chemical components as the black readings indicating that they were also carbon based. The lack of copper or cobalt in the blue readings indicates the use of optical blue for these which would also contain calcium which is unfortunately difficult to pick out.

Amongst the red pigments there is variation both in the proportions of iron to strontium and in the range of readings seen in individual pigments. The variation in iron to strontium ratios indicates the use of more than one iron based pigment. The changes in composition could be due to either different source materials or different preparation techniques. For example the addition of blood as a binder would result in a high iron reading when compared to non-blood binders or ochre which was not mixed with a binder. The use of different source materials can be verified by variation in trace elements, and indeed at Pinwheel two different pigments which were identified displayed different levels of arsenic.

Variation in the range of readings within particular pigments may indicate the extent to which materials have been processed. An ochre which has been ground into a powder before application to a surface is likely to display much less internal variation than one which is applied in its raw form. This is because the grinding process is likely to homogenise the material. Directly applied pigment will show the same variation identified in raw pigment samples derived from excavation as shown in fig 132.
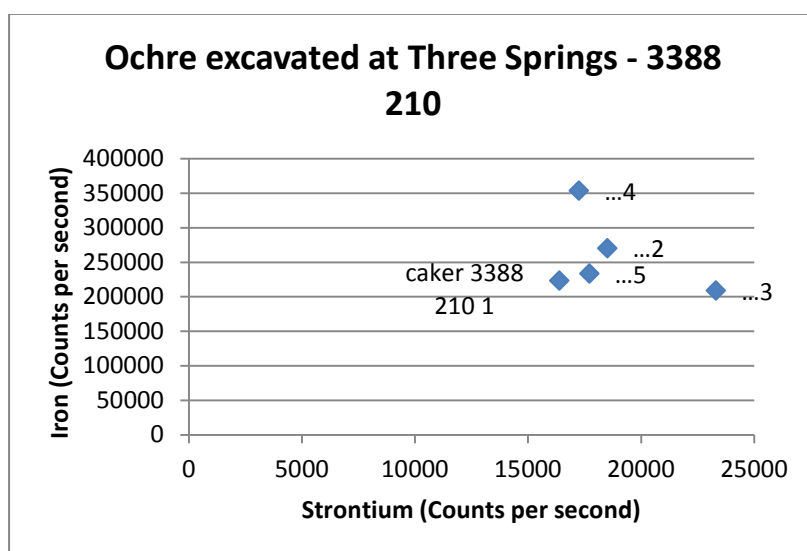
Figure 132. Relative iron and strontium levels in raw ochre sample

Further examples of such raw ochre readings can be seen in appendix 2. The table below shows which rock art elements from each site appear to be either directly applied or processed.

Site	Directly applied pigments	Processed pigments
Pinwheel		All pigments
Three Springs	Zoomorph*	Blueboy*, Zig-zag*
Pond	Pond boulder*	Wb 3, wb 1
Los Lobos	Ll2, Ll3	Ll7, Ll12
Santiago	Ml3, ml8, ml4	Ml1, ml2, ml5, ml6, ml7, ml9, ml10, ml12, ml15, zig-zag

Table 5.Table showing directly applied and processed pigments. * multiple readings

In terms of chronology, the identification of differing pigment materials within and between rock art elements shows phases of production within these elements and within rock art panels. The table below shows the elements which share chemical composition. This shared material may link these elements to one another chronologically.

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Site	Pigment 1	Pigment 2	Pigment 3
Pinwheel	Pnw 1b, pnw 1h	Pnw 1c, pnw 1d, pnw 1f, pnw 1g, pnw rock elements	Pnw 1a, pnw 1e
Three Springs	Zoomorph	Blueboy	Zig-zag, fig 8
Pond	Wb 3b and c	Wb 1	Wb 3 and 3a, wb 4 and 5, Pond boulder
Los Lobos	Ll3, Ll2b,c and d	Ll12, Ll7, Ll4, Ll10, Ll2a and c	
Santiago			

Table 6.Table showing elements with shared pigment composition

Some areas of pigments overlay one another, such as those in element 1 at Pinwheel (see fig 133) thereby demonstrating the order in which they were applied. The identification of common materials between elements can also be used to tie separate elements into existing chronologies based on the overlay of pigments. This can also be seen at Pinwheel as one of the phases of pigment in element 1 has the same iron to strontium level as the elements on the rocks next to the main cave site. It can therefore be inferred that these were produced at the same time and during the same phase relative to the rest of element 1. Unfortunately it is difficult to identify visually which pigment was applied first. Although pXRF can be used to identify different pigments which represent different phases, I am not currently able to use the data to speculate about the order of sequence of painting events.

Figure 133. Pinwheel element 1

Was rock art exclusive in nature and how much can we tell about who was producing it?

Sites showing many different pigments, it seems, are most likely to have been revisited and reused by a number of people. There is also the question of how often these sites were revisited without retouching, or without leaving any other physical evidence behind, and the extent to which this reflects great cultural significance and community involvement in rock art.

The involvement of multiple individuals in rock art production immediately presents a challenge to the idea that rock art was very exclusive or restricted (Whitley 1987:179). If rock art is being revisited and changed over time this suggests that it holds an actively involved position in society, that it is important and develops with the community. If a rock art element is retouched at a later date, potentially by a different person, then it does not simply reflect the experience of one privileged individual at one particular time as has been suggested (Whitley 1987:179).

It is also interesting that the site of Santiago shows the greatest variation of pigment materials between elements, and relatively wide variation within some pigments. As the rock art at Santiago was directly adjacent to the BRM here, this may indicate that many of the people working at the site were contributing to the rock art over time.

In particular, it is known that BRM sites were female workspaces (Robinson 2010:802). It is therefore reasonable to suggest that the rock art next the BRMs was being produced by the women working there. As Robinson (2010) points out the majority of members of the community would have been in the area of these BRMs and therefore would have been close to the rock art while acorns were being processed (Robinson 2010:804). It is possible therefore that these other members of the community were also involved in the production of rock art at such sites. The idea that a number of people were contributing to these panels is supported by the variation in pigment readings found at Santiago for example. This would indicate that rock art production by women was not restricted to puberty rites as Keyser and Whitley (2006) suggest (Kesyer and Whitley 2006:5). It is likely that far from being a

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restricted ritual phenomenon rock art was actually an integral part of life in which many people, including women, were actively involved.

Limitations of portable XRF approach

There are a number of limitations within this technique. The many elements which were not chemically detectable are examples of a recurring issue in this type of analysis. Certain elements such as carbon, oxygen and nitrogen cannot be detected using portable XRF which has limited the ability to positively identify some black pigments, or to examine organic components of pigments. Portable XRF is also unable to examine the particular chemical compounds used to create pigments.

There are known to be issues with empirical calibration in portable XRF devices, particularly when attempting to compare quantitative results between different instruments (Shackley 2011:13). Shackley highlights the need to ensure careful calibration of devices when performing quantitative analysis and comparing quantitative data sets from different instruments and different sites as often instruments which are described as calibrated have not been empirically calibrated (Shackley 2011:13).

In this study a qualitative comparative analysis was performed, and comparisons are only being drawn between elements being examined using the same instrument and the same settings. As such these results should be internally reliable. It is helpful to know however that caution needs to be observed if quantitative analysis is to be undertaken. Such quantitative analysis would be very useful for comparisons between sites and sourcing of ochre materials, as well as the determination of the effects of background rock and binder compositions.

There is also great variation in the incidence of calcium in the rock to which pigment was applied, and so in order to identify calcium compounds which were used as pigments it is necessary to use a technique such as X-Ray diffraction which is able to identify specific compounds.

It would also be very beneficial to be able to examine the particular compounds used, as well as the proportions of chemical elements within all of the pigments. There may be more

information to be gleaned from the elements which could not be detected using this method. It may therefore be useful to investigate other methods of gaining chemical spectra to look at the make-up of pigments. In particular a method such as Raman spectrometry or XRD could identify contrasting compounds within pigments which cannot be spotted by the elemental analysis performed using portable XRF. These techniques would also be helpful in the identification of organic materials within the pigments. As portable XRD and Raman spectrometers are now becoming available it will be possible to use these techniques on *in situ* pigments.

It is also difficult to tell exactly how the chemical composition of the rock onto which pigment was applied will affect the resulting spectrum, or how pigment preparation techniques might affect these results. For example, the use of different binders will change the final composition of the pigment as would the use of ochre from a different source, but as yet it is unclear how to separate the two when examining XRF data.

This technique can clearly be used to identify some of the different techniques used to produce rock art and to process pigments but at this point it is difficult to distinguish the effect of different binders from different source materials, unless clear trace elements can be seen.

This method is affected by environmental variables, namely the background rock to which pigments were applied. It is important to control these variables as much as possible and therefore to be careful about making comparisons between rock art pigments on different surfaces as the effect of these surface materials is not yet known with any certainty. In future a greater sample of readings from both pigment and background surfaces would allow greater clarity and definition in the results.

As a result of the environmental variables there are a number of difficulties when comparing the readings between all of these sites. It is possible to plot the iron to strontium ratios of all the readings and compare them to identify similar and contrasting pigments, as has been done in this study. However, when the background readings are examined it is clear that the rock surfaces to which each pigment was applied vary between sites. This variation could be responsible for some of the variation that we see between sites, and could also distort readings so that they appear to be more similar than they are. Useful comparisons can be

made between elements within a site as long as the background rock is consistent as this removes the rock as a variable.

At Pinwheel many elements could not be compared because of the background variation. In order to make a valid comparison between elements painted onto different rock surfaces, it would be necessary to determine precisely how the rock surface affects the resultant readings. This will also be necessary for source material comparison as it would be necessary to find a way to separate the pigment readings from those of the background rock.

It is also difficult to determine the full influence of the chemical composition of the bare rock and of the thickness of applied pigments. The resultant readings may not simply be an accumulation of readings from the pigment and the bare rock, and as such a straightforward subtraction of the rock reading from the pigment reading may not provide accurate total readings for the pigment. For example, in many of the rock art elements here a simple subtraction would result in the appearance of no strontium, or even negative strontium readings in the pigment. As strontium occurs naturally in ochre samples from these sites its absence seems unlikely. Therefore it is important to establish exactly how the background and pigment readings interact before an accurate pigment spectrum can be produced from which reliable comparisons can be made between raw materials and applied pigments.

It is important to identify the effect of heating ochre on the resulting spectra, as it has been shown that heating goethite can produce artificial haematite which looks the same as natural haematite (Gialanella *et al.* 2011:8). It is also likely that directly applied ochre will be less internally consistent than processed ochre which has been ground and homogenised. It would therefore be advantageous to experiment with different ochres, process and apply each using various methods and then examine the resultant spectra.

 All of these factors however need to be tested experimentally in order to establish their influence on the end readings in order to gain the most useful information from these readings. It may also be helpful to look at these pigments with Raman or XRD. Using these methods it would be possible to determine the different compounds contained within each pigment material as well as their constituent chemical elements. These methods may also provide information about the organic elements involved for which examination by portable XRF is limited.

These techniques could enhance the knowledge gain by pXRF analysis by allowing differentiation between materials which look very similar when examined using XRF, and confirming pigments already identified by XRF analysis. In order to do this X-Ray diffraction would enable analysis of the structure of chemical compounds (Pollard *et al.* 2007:113), and Raman spectroscopy can be used to look at organic materials in black pigments and binders for all colours of pigment (Pollard *et al.* 2007:84).

Conclusion

The results of this study have demonstrated the great potential of pXRF to contribute to rock art research by differentiating between different pigments and allowing the identification of phases of production as well as potentially indicating preparation and application techniques. They have also opened up many more directions to follow in rock art analysis which are described in the following chapter. These results have clearly contributed to current debate surrounding rock by indicating reuse and revisiting of sites, and providing information which relates to the pigment material and processing techniques used to produce rock art in the Windwolves Preserve.

CHAPTER 5 – CONCLUSION: SALIENT FINDINGS AND FUTURE DIRECTIONS

The results of the pXRF analysis performed in the Windwolves Preserve show that there is great potential for the application of portable XRF technology in rock art research, and this results make a valuable contribution to existing debates surrounding California rock art (Blackburn 1977; Hyder 1989; Hyder and Oliver 1986; Insoll 2012; Lee and Hyder 1991; McCall 2007; Quinlan 2000; Robinson 2010b; Whitley 1987). The technique is not without its limitations and complications from external factors, but these can easily be resolved, as is discussed in the following chapter.

Discussion of these results has also led to a number of further questions regarding the effect of certain environmental and technological factors on the chemical composition of rock art which survives today, questions which can also be addressed by further pXRF work and broadening our knowledge of pigment composition through the use of other analytical techniques and experimental work. I discuss such future directions further in this chapter.

Complex issues and difficulties in pXRF analysis

There are some limitations to this method of analysis and the use of pXRF. These include the inability for portable XRF to identify organic elements or to identify chemical compounds. It has, however, been very effective in characterising the main elements with pigments as well as inorganic trace elements, and in differentiating between pigment materials. Another limitation is the small sample size for some of the pigment materials, as this impedes statistical analysis. This issue is also easily overcome by revisiting sites to gain addition XRF readings for areas which are lacking readings.

Environmental factors also have a great influence over the resultant spectra gained from pXRF analysis. These include the erosion of certain pigments which has rendered some pigments indistinguishable from the rock to which they were applied, as well as great variation in some of the background rock. This approach is clearly limited by the lack of a precise understanding of how the chemical compositions of the background rock and pigments may or may not combine to form the final readings which are gathered by the pXRF device, or how the processing of raw ochre and the addition of binders affects these results.

The contribution of pXRF to rock art analysis

To summarise, it is clear that pXRF is valuable in characterising the elemental composition of rock art pigments and that pXRF data can be used to differentiate between materials and to infer different sources for materials. It has been possible to infer some of the techniques used in pigment application such as the difference between direct application and processed pigments, and it possible that some of the pigments with high iron content were produced using a blood binder.

Using this information it has been possible to estimate the number of painting events at each site, and to show a minimum of 18 painting events between the five sites and between three and five different pigments and painting events at each site. This approach has been able to differentiate between pigments that look identical to the naked eye and therefore have never previously been identifiable.

Some rock art elements at each site display two or more pigments indicating that they have been revisited and either retouched or added to at a different time or by another hand. This therefore contributes greatly to discussion of the extent to which sites were revisited, reused and involved in the lives of Chumash people.

This information is of great importance when discussing the exclusivity of Chumash rock art and the circumstances surrounding its production. For example rock art produced for a particular rite or as a result of an individual vision quest (Keyser and Whitley 2006:5; Whitley 1992) would be produced at a particular moment rather than developing over time.

These results show that rock art production is a complex process which does not necessarily have one single explanation. It is clear to me that these examples of rock art were not produced in single events, nor does it seem that they were exclusive to one individual. The results indicate that rock art was revisited, reused and preserved, as if it held cultural importance to a number of people over time.

In addition to this, if some visitors have added pigment to rock art elements it is possible that other people visited to observe or share this rock art without leaving a mark and so by examining the number of times rock art has been added to we are only considering the minimum number of visitors to the site.

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Some of the rock art showed greater variation (eg. Los Lobos and Santiago) than others (Pinwheel), indicating that these may be different phenomena and that some rock art panels were more public than others. The variation seen at Santiago and Los Lobos certainly suggests that a larger number of people were involved in rock art than at Pinwheel.

The great variation at Santiago and Los Lobos indicates that far more people may have been involved in rock art production here than would be expected if rock art was an exclusive or restricted phenomenon (Whitley 1987:179). In addition to this, all these sites are associated with bedrock mortar stations (Robinson 2010:804) which are female workspaces (Robinson, 2010:802) and the rock art with the most variation is very close to those BRMs. This proximity suggests strongly that women are likely to have had a much greater role in rock art production than has often been acknowledged, a role extending beyond rock art involved in puberty rites which is described by Whitley (Keyser and Whitley 2006:5).

Future directions in rock art analysis

There is great potential for more work to be done in this area. Portable XRF has shown itself to be a very useful tool in the examination of *in situ* rock art, and the method I have employed has allowed a swift analysis of many rock art elements. This analysis has revealed a greater number of painting events that might have been expected which presents a challenge to the ideas that rock art was restricted and Shamanistic in nature (Keyser and Whitley 2006:5; Whitley 1998) or produced in a single event (Whitley 1987:179).

In addition to this pXRF has provided data which indicates the use of particular preparation and application techniques, such as grinding, mixing with binders and direct application. The analysis performed here has also raised a number of questions relating to the specific effects of particular factors on the end results. Such questions can be addressed both by performing further pXRF and employing other analytical techniques such as XRay diffraction or Raman spectroscopy (Olivares *et al.* 2012) which would enhance the depth of knowledge gained from pXRF work.

Further to this, experimental reconstruction of methods of rock art production and intentional manipulation of particular factors such as the selection of ochre material,

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processing of ochre and the addition of binders would allow analysis of the individual effects of these factors and greatly enhance our understanding of the spectra produced by pXRF analysis.

To conclude, pXRF analysis has provided a great amount of valuable information regarding the production of Chumash rock art and provided a valuable and original contribution to core debates in Chumash rock art research including the social role, production circumstances and technology involved in the production of rock art. This work has demonstrated the potential of pXRF to contribute to research both in Chumash rock art and the many rock art panels that are being examined around the world, and has also opened up further questions and revealed the potential for many more exciting directions in rock art study.

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APPENDIX 1. ANOVA VALUES FOR ELEMENTS AT ALL SITES.

Values show probability of elements being the same. 0.01 = 1% 0.99 = 99%.

Pond

0	Pond alc bg	pb 1 and 2	pb 3 and 4	pb bg	Pond wb bg	Pond wb group 1	Pond wb g2	Pond wb group 3
Pond alc bg	0	0.0059	0.0034	0.0023	0.9999	0.6513	0.00044	0.00016
pb 1 and 2	-	0	1	0.9997	0.01368	0.0003	0.00016	0.00016
pb 3 and 4	-	-	0	1	0.00784	0.00024	0.00016	0.00016
pb bg	-	-	-	0	0.00524	0.00022	0.00016	0.00016
Pond wb bg	-	-	-	-	0	0.4136	0.00028	0.00016
Pond wb group 1	-	-	-	-	-	0	0.01186	0.00016
Pond wb g2	-	-	-	-	-	-	0	0.00026
Pond wb group 3	-	-	-	-	-	-	-	0

Three Springs

0	Blueboy blue	Blueboy grey	Blueboy limbs	Blueboy red	Blueboy bg	Fig 8 black	Fig 8 bg	Zoo body black	Zoo body red
Blueboy blue	0	1	0.9985	0.00018	1	0.9998	1	1	0.000178
Blueboy grey	-	0	0.9586	0.00018	1	1	1	1	0.000178
Blueboy limbs	-	-	0	0.00018	1	0.7005	0.9848	1	0.000178
Blueboy red	-	-	-	0	0.000178	0.000178	0.000178	0.000178	0.000244
Blueboy bg	-	-	-	-	0	0.9916	1	1	0.000178
Fig 8 black	-	-	-	-	-	0	1	0.9883	0.000178
Fig 8 bg	-	-	-	-	-	-	0	1	0.000178
Zoo body black	-	-	-	-	-	-	-	0	0.000178
Zoo body red	-	-	-	-	-	-	-	-	0

0	Zoo man black	Zoo man red plus left paw	Zoo bg	Zig-zag dots 1 and 3	Zig-zag dots 2 and 4	Zig-zag bl	Zig-zag bg	Bird	Bird bg
Blueboy blue	1	0.2437	1	0.8482	0.01226	1	1	1	1
Blueboy grey	1	0.0909	1	0.5609	0.003265	1	1	1	1
Blueboy limbs	0.9945	0.9342	0.9998	1	0.2348	0.9856	0.872	1	0.9965
Blueboy red	0.000178	0.000178	0.000178	0.000178	0.000178	0.000178	0.00018	0.00002	0.00018
Blueboy bg	1	0.4568	1	0.9689	0.03397	1	0.9995	1	1
Fig 8 black	1	0.02096	0.9983	0.2225	0.000678	1	1	0.99944	0.9999
Fig 8 bg	1	0.135	1	0.6795	0.005405	1	1	1	1
Zoo body black	1	0.4889	1	0.9763	0.03851	1	0.99992	1	1
Zoo body red	0.000178	0.000179	0.000178	0.000178	0.000305	0.000178	0.00018	0.00002	0.00018
Zoo man black	0	0.1825	1	0.769	0.008113	1	1	1	1
Zoo man	-	0	0.3383	0.9999	0.9982	0.1375	0.04707	0.4222	0.2042

III

red plus left paw									
Zoo bg	-	-	0	0.9222	0.02032	1	1	1	1
Zig-zag dots 1 and 3	-	-	-	0	0.7185	0.6851	0.3839	0.9589	0.8009
Zig-zag dots 2 and 4	-	-	-	-	0	0.005538	0.00152	0.02295	0.00949
Zig-zag bl	-	-	-	-	-	0	1	1	1
Zig-zag bg	-	-	-	-	-	-	0	0.9997	1
Bird	-	-	-	-	-	-	-	0	1
Bird bg	-	-	-	-	-	-	-	-	0

Los Lobos

0	llb low2 bg	llb low2	llb low2R	llb low1 bg	llb low1	llb low3 bg	llb low3	ll1 bg	ll1 – a
llb low2 bg	0	1	1	1	1	1	1	0.9576	0.9924
llb low2	-	0	1	1	1	1	1	0.9655	0.9944

IIb low2R	-	-	0	1	1	1	1	0.9863	0.9985
IIb low1 bg	-	-	-	0	1	1	1	0.9722	0.9959
IIb low1	-	-	-	-	0	1	1	0.9811	0.9977
IIb low3 bg	-	-	-	-	-	0	1	0.9855	0.9984
IIb low3	-	-	-	-	-	-	0	0.9963	0.9998
Il1 bg	-	-	-	-	-	-	-	0	1
Il1 - a	-	-	-	-	-	-	-	-	0

0	**Il2 bg**	**Il2a,e**	**Il2b,c,d**	**Il3 bg**	**Il3 -e**	**Il4 bg**	**Il4**	**Il5 bg**	**Il5**
IIb low2 bg	0.7993	0.01506	0.000157	0.9079	0.000157	0.9877	0.9993	0.98177	0.6937
IIb low2	0.8216	0.01702	0.000157	0.9218	0.000157	0.9906	0.9996	0.98858	0.7204
IIb low2 R	0.8953	0.02724	0.000157	0.9624	0.000157	0.9973	0.9999	0.99554	0.8157
IIb low1 bg	0.8423	0.0192	0.000157	0.934	0.000157	0.993	0.9997	0.98911	0.746
IIb low1	0.87737	0.02341	0.000157	0.9514	0.000157	0.9958	0.9999	0.99332	0.7865

IIb low3 bg	0.8916	0.02652	0.000157	0.9606	0.000157	0.997	0.9999	0.9951	0.8106
IIb low3	0.951	0.04528	0.000157	0.9867	0.000157	0.9995	1	0.9991	0.8989
II1 bg	1	0.9599	0.000157	1	0.000248	1	1	1	1
II1 - a	1	0.8673	0.000157	1	0.000185	1	1	1	1
II2 bg	0	0.9974	0.000157	1	0.000619	1	1	1	1
II2a,e	-	0	0.000157	0.9852	0.1818	0.8969	0.7112	0.9195	0.9995
II2b,c,d	-	-	0	0.000157	0.000157	0.000157	0.00016	0.0002	0.00016
II3 bg	-	-	-	0	0.000342	1	1	1	1
II3 -e	-	-	-	-	0	0.000194	0.00017	0.0002	0.00104
II4 bg	-	-	-	-	-	0	1	1	1
II4	-	-	-	-	-	-	0	1	1
II5 bg	-	-	-	-	-	-	-	0	1
II5	-	-	-	-	-	-	-	-	0

0	II6 bg	II6 spots	II7 bg	II7	II8 bg	II8	II9 bg	II9
IIb low2 bg	0.9936	0.3022	0.9994	0.001771	0.999	0.7323	0.9999	0.9883
IIb low2	0.9953	0.3254	0.9996	0.002023	0.9993	0.7577	0.9999	0.9911
IIb	0.9988	0.4245	0.9999	0.00339	0.9999	0.8461	1	0.9974

low2R				8				
IIb low1 bg	0.9966	0.3492	0.9997	0.0023	0.9996	0.7818	0.9999	0.9934
IIb low1	0.9981	0.3908	0.9999	0.002854	0.9998	0.8195	1	0.996
IIb low3 bg	0.9987	0.4184	0.9999	0.003299	0.9999	0.8416	1	0.9972
IIb low3	0.9998	0.5482	1	0.00606	1	0.9199	1	0.9995
II1 bg	1	1	1	0.6379	1	1	1	1
II1 - a	1	1	1	0.4383	1	1	1	1
II2 bg	1	1	1	0.8776	1	1	1	1
II2a,e	0.8568	1	0.705	1	0.7368	0.999	0.6172	0.8938
II2b,c, d	0.000157	0.000157	0.000157	0.000157	0.000157	0.000157	0.000157	0.000157
II3 bg	1	1	1	0.754	1	1	1	1
II3 -e	0.000182	0.006872	0.000165	0.5763	0.000167	0.000855	0.000161	0.000193
II4 bg	1	1	1	0.4864	1	1	1	1
II4	1	0.9997	1	0.2715	1	1	1	1
II5 bg	1	1	1	0.5302	1	1	1	1
II5	1	1	1	0.9377	1	1	1	1
II6 bg	0	1	1	0.4231	1	1	1	1
II6 spots	-	0	0.9997	0.9988	0.9998	1	0.9988	1
0	II6 bg	II6 spots	II7 bg	II7	II8 bg	II8	II9 bg	II9
II7 bg	-	-	0	0.2667	1	1	1	1
II7	-	-	-	0	0.2927	0.9198	0.2058	0.4809
II8 bg	-	-	-	-	0	1	1	1
II8	-	-	-	-	-	0	1	1

Il9 bg	-	-	-	-	-	-	0	1
Il9	-	-	-	-	-	-	-	0

0	Il10bg	Il10	Il11 bg	Il11	Il12 bg	Il12	Il13 bg	Il13
Ilb low2 bg	0.998	0.8429	0.9397	0.3313	0.2866	0.000159	0.9192	0.9996
Ilb low2	0.9986	0.8624	0.95	0.3556	0.3091	0.00016	0.9319	0.9998
Ilb low2R	0.9997	0.9243	0.9784	0.4588	0.4059	0.000163	0.9684	1
Ilb low1 bg	0.9991	0.8802	0.9589	0.3805	0.3322	0.00016	0.943	0.9998
Ilb low1	0.9995	0.9066	0.971	0.4238	0.3728	0.000162	0.9586	0.9999
Ilb low3 bg	0.9997	0.9213	0.9772	0.4523	0.3999	0.000163	0.9668	1
Ilb low3	1	0.9676	0.9934	0.584	0.5282	0.00017	0.9893	1
Il1 bg	1	1	1	1	1	0.02168	1	1
Il1 - a	1	1	1	1	1	0.009064	1	1
Il2 bg	1	1	1	1	1	0.06786	1	1
Il2a,e	0.781	0.9948	0.973	1	1	0.9779	0.9818	0.6739
0	Il10bg	Il10	Il11 bg	Il11	Il12 bg	Il12	Il13 bg	Il13
Il2b,c,d	0.000157	0.000157	0.000157	0.000157	0.000157	0.000157	0.000157	0.000157
Il3 bg	1	1	1	1	1	0.036	1	1

II3 -e	0.00017	0.000496	0.00028	0.005853	0.007516	1	0.000319	0.000163
II4 bg	1	1	1	1	1	0.01129	1	1
II4	1	1	1	0.9998	0.9996	0.003743	1	1
II5 bg	1	1	1	1	1	0.01368	1	1
II5	1	1	1	1	1	0.1044	1	1
II6 bg	1	1	1	1	1	0.008438	1	1
II6 spots	0.9999	1	1	1	1	0.3579	1	0.9995
II7 bg	1	1	1	0.9998	0.9995	0.003633	1	1
II7	0.3338	0.8392	0.6888	0.9981	0.9991	1	0.7334	0.2435
II8 bg	1	1	1	0.9999	0.9997	0.004251	1	1
II8	1	1	1	1	1	0.09016	1	1
II9 bg	1	1	1	0.9992	0.9984	0.002384	1	1
II9	1	1	1	1	1	0.01101	1	1
II10bg	0	1	1	1	0.9999	0.005379	1	1

	0	**II14 bg**	**II14 sp**
IIb low2 bg		1	0.9693
IIb low2		1	0.9755
IIb low2R		1	0.991
IIb low1 bg		1	0.9806
IIb low1		1	0.9873

llb low3 bg	1	0.9904
llb low3	1	0.9978
ll1 bg	1	1
ll1 - a	1	1
ll2 bg	1	1
ll2a,e	0.5246	0.9457
ll2b,c,d	0.000157	0.000157
ll3 bg	1	1
ll3 -e	0.000159	0.000227
ll4 bg	1	1
ll4	1	1
ll5 bg	1	1
ll5	1	1
ll6 bg	1	1
ll6 spots	0.9961	1
ll7 bg	1	1
ll7	0.1546	0.5939
ll8 bg	1	1
ll8	1	1
ll9 bg	1	1
ll9	1	1
ll10bg	1	1

Santiago Monolith

0	Zig zag 1,3, 5	Zig zag 2 and4	Zig zag bg	ml18 Wings and d	ml18 a,b,e	ml18 bg	ml17 bg	Ml17 blk	ml15 bg

Zig zag 1,3,5	0	0.4731	0.00075	0.00111	1	0.000168	0.000346	0.001832	0.000163
Zig zag 2 and4	-	0	0.9778	0.9899	0.9988	0.5735	0.9109	0.9969	0.5098
Zig zag bg	-	-	0	1	0.05793	1	1	1	1
ml18 Wings and d	-	-	-	0	0.08029	1	1	1	1
ml18 a,b,e	-	-	-	-	0	0.004182	0.02587	0.118	0.003118
ml18 bg	-	-	-	-	-	0	1	1	1
ml17 bg	-	-	-	-	-	-	0	1	1
Ml17 blk	-	-	-	-	-	-	-	0	1
ml15 bg	-	-	-	-	-	-	-	-	0

0	ml15a,b	ml15c,d	ml14 bg	ml14a,b	ml14,c,e	ml13	ml13 bg	ml12 excl e	ml12 bg
Zig zag 1,3,5	1	0.1593	0.001409	1	0.2609	0.9599	0.0005	1	0.1519
Zig zag 2 and4	0.9532	1	0.9941	0.912	1	0.000543	0.9533	0.9997	1

0	ml15a, b	ml15c ,d	ml14 bg	ml14a, b	ml14,c ,e	ml13	ml13 bg	ml12 excl e	ml12 bg
Zig zag bg	0.01246	0.9999	1	0.007947	0.9983	0.000151	1	0.0791	0.9999
ml18 Wings and d	0.01821	1	1	0.01175	0.9995	0.000151	1	0.1081	1
ml18 a,b,e	1	0.9402	0.09724	1	0.9827	0.1915	0.03943	1	0.9343
ml18 bg	0.000756	0.9102	1	0.000497	0.8022	0.000151	1	0.0062	0.9176
ml17 bg	0.004991	0.9972	1	0.003127	0.9846	0.000151	1	0.0364	0.9977
Ml17 blk	0.02882	1	1	0.01887	0.9999	0.000151	1	0.1556	1
ml15 bg	0.000577	0.8745	1	0.000394	0.7485	0.000151	1	0.0046	0.8835
ml15a, b	0	0.677	0.02285	1	0.8213	0.4948	0.00804	1	0.6626
ml15c, d	-	0	1	0.5769	1	0.000188	0.9993	0.9665	1
ml14 bg	-	-	0	0.01485	0.9998	0.000151	1	0.1296	1
ml14a, b	-	-	-	0	0.7369	0.596	0.00505	1	0.5619
ml14,c ,e	-	-	-	-	0	0.000249	0.9944	0.9921	1
ml13	-	-	-	-	-	0	0.00015	0.1472	0.00018
ml13 bg	-	-	-	-	-	-	0	0.0547	0.9994
ml12 excl e	-	-	-	-	-	-	-	0	0.9626

ml12 bg	-	-	-	-	-	-	-	-	0

0	ml10 and bg	ml10 c,d,e	ml9 bg	ml9b,c	ml9,c,d	ml8 bg	ml8,d	ml8b,c,e
Zig zag 1,3,5	0.01089	0.000151	0.04303	0.707	0.000152	0.008817	0.000151	0.9997
Zig zag 2 and4	1	0.000151	1	1	0.000151	1	0.000151	0.003932
0	ml10 and bg	ml10 c,d,e	ml9 bg	ml9b,c	ml9,c,d	ml8 bg	ml8,d	ml8b,c,e
Zig zag bg	1	0.000151	1	0.8924	0.000151	1	0.000151	0.000152
ml18 Wings and d	1	0.000151	1	0.935	0.000151	1	0.000151	0.000152
ml18 a,b,e	0.3671	0.000151	0.685	1	0.000151	0.3265	0.000151	0.56
ml18 bg	1	0.000151	0.9953	0.3473	0.000151	1	0.000151	0.000151
ml17 bg	1	0.000151	1	0.7424	0.000151	1	0.000151	0.000151
Ml17 blk	1	0.000151	1	0.9695	0.000151	1	0.000151	0.000152
ml15 bg	0.9999	0.000151	0.9908	0.2951	0.000151	1	0.000151	0.000151
ml15a,b	0.124	0.000151	0.3274	0.9939	0.000151	0.1054	0.000151	0.8826
ml15c,d	1	0.000151	1	1	0.000151	1	0.000151	0.000613
ml14 bg	1	0.000151	1	0.9543	0.000151	1	0.000151	0.000152
ml14a,	0.08718	0.000151	0.2497	0.9838	0.000151	0.07338	0.000151	0.9335

b		1			1		1	
ml14,c,e	1	0.000151	1	1	0.000151	1	0.000151	0.001259
ml13	0.000152	0.000151	0.000155	0.001546	0.005851	0.000152	0.000186	1
ml13 bg	1	0.000151	1	0.8277	0.000151	1	0.000151	0.000151
ml12 excl e	0.4442	0.000151	0.7616	1	0.000151	0.3996	0.000151	0.4768
ml12 bg	1	0.000151	1	1	0.000151	1	0.000151	0.000573
ml10 and bg	0	0.000151	1	0.9996	0.000151	1	0.000151	0.000159
ml10 c,d,e	-	0	0.000151	0.000151	0.9003	0.000151	1	0.000151
ml9 bg	-	-	0	1	0.000151	1	0.000151	0.000208
ml9b,c	-	-	-	0	0.000151	0.9992	0.000151	0.01156
ml9,c,d	-	-	-	-	0	0.000151	1	0.000778
ml8 bg	-	-	-	-	-	0	0.000151	0.000157
ml8,d	-	-	-	-	-	-	0	0.000154
ml8b,c,e	-	-	-	-	-	-	-	0

0	ml7 bg	ml7	ml6 bg	ml6,b,d	ml6c,e	ml5 bg	ml5	ml3 bg
Zig zag 1,3,5	0.418	0.02663	0.000401	0.994	0.6302	0.001522	0.5335	0.149
Zig zag 2 and4	1	0.000151	0.9313	0.001391	1	0.9951	0.000165	1

Zig zag bg	0.9865	0.000151	1	0.000151	0.9315	1	0.000151	0.9999
ml18 Wings and d	0.9944	0.000151	1	0.000151	0.9619	1	0.000151	1
ml18 a,b,e	0.9975	0.000354	0.03102	0.3476	0.9999	0.1032	0.02308	0.9318
ml18 bg	0.6308	0.000151	1	0.000151	0.4186	1	0.000151	0.9204
ml17 bg	0.9367	0.000151	1	0.000151	0.8092	1	0.000151	0.9979
Ml17 blk	0.9985	0.000151	1	0.000151	0.9842	1	0.000151	1
ml15 bg	0.5672	0.000151	1	0.000151	0.361	1	0.000151	0.8871
ml15a, b	0.932	0.001678	0.006131	0.7077	0.9867	0.02452	0.09807	0.6568
ml15c, d	1	0.000151	0.9984	0.000282	1	1	0.000152	1
ml14 bg	0.9969	0.000151	1	0.000151	0.9747	1	0.000151	1
ml14a, b	0.8804	0.002686	0.003835	0.7964	0.9689	0.01597	0.1384	0.5559
ml14,c, e	1	0.000151	0.9898	0.000484	1	0.9998	0.000154	1
ml13	0.000437	0.995	0.000151	1	0.00107	0.000151	1	0.000184
ml13 bg	0.9692	0.000151	1	0.000151	0.8811	1	0.000151	0.9995
ml12 excl e	0.9992	0.000277	0.04343	0.2799	1	0.137	0.01618	0.9609
ml12 bg	1	0.000151	0.9987	0.000272	1	1	0.000152	1

ml10 and bg	1	0.000151	1	0.000153	0.9999	1	0.000151	1
ml10 c,d,e	0.000151	0.001015	0.000151	0.000151	0.000151	0.000151	0.000154	0.000151
ml9 bg	1	0.000151	1	0.000166	1	1	0.000151	1

0	ml7 bg	ml7	ml6 bg	ml6,b,d	ml6c,e	ml5 bg	ml5	ml3 bg
ml9b,c	1	0.000151	0.7806	0.00419	1	0.9594	0.000207	1
ml9,c,d	0.000151	0.7563	0.000151	0.002152	0.000151	0.000151	0.06611	0.000151
ml8 bg	1	0.000151	1	0.000153	0.9998	1	0.000151	1
ml8,d	0.000151	0.06898	0.000151	0.000161	0.000151	0.000151	0.00107	0.000151
ml8b,c,e	0.003017	0.8646	0.000151	1	0.008122	0.000152	1	0.000559
ml7 bg	0	0.000151	0.9526	0.001073	1	0.9975	0.000161	1
ml7	-	0	0.000151	0.9646	0.000151	0.000151	1	0.000151
ml6 bg	-	-	0	0.000151	0.8421	1	0.000151	0.9988
ml6,b,d	-	-	-	0	0.002904	0.000151	1	0.000267
ml6c,e	-	-	-	-	0	0.9779	0.000186	1
ml5 bg	-	-	-	-	-	0	0.000151	1
ml5	-	-	-	-	-	-	0	0.000152
ml3 bg	-	-	-	-	-	-	-	0

0	ml3 loops and bg blk	ml3,e	ml3b,d	ml2 bg	ml2	ml1 bg	ml1b,c	ml1d,e
Zig zag 1,3,5	1	0.02593	0.002782	0.000153	0.8883	0.01935	0.000151	1
Zig zag 2 and4	0.9903	1	0.000151	0.2272	1	1	0.000151	0.007436
Zig zag bg	0.02813	1	0.000151	1	0.7136	1	0.000151	0.000152
ml18 Wings and d	0.04015	1	0.000151	1	0.7907	1	0.000151	0.000152
ml18 a,b,e	1	0.5614	0.000161	0.000691	1	0.492	0.000151	0.6966
ml18 bg	0.001799	0.999	0.000151	1	0.1809	0.9996	0.000151	0.000151
ml17 bg	0.01188	1	0.000151	1	0.5143	1	0.000151	0.000151
0	ml3 loops and bg blk	ml3,e	ml3b,d	ml2 bg	ml2	ml1 bg	ml1b,c	ml1d,e
Ml17 blk	0.06139	1	0.000151	1	0.8705	1	0.000151	0.000153
ml15 bg	0.001335	0.9977	0.000151	1	0.1479	0.9991	0.000151	0.000151
ml15a, b	1	0.2334	0.000245	0.000216	0.9997	0.1898	0.000151	0.9477
ml15c, d	0.8406	1	0.000151	0.589	1	1	0.000151	0.001116
ml14 bg	0.04958	1	0.000151	1	0.8323	1	0.000151	0.000152
ml14a,	1	0.1722	0.00032	0.00018	0.9988	0.1377	0.000151	0.9751

b				7			1	
ml14,c, e	0.9335	1	0.000151	0.4261	1	1	0.000151	0.002397
ml13	0.3195	0.000153	0.8161	0.000151	0.004556	0.000152	0.000151	1
ml13 bg	0.0186	1	0.000151	1	0.618	1	0.000151	0.000152
ml12 excl e	1	0.6449	0.000157	0.000995	1	0.5755	0.000151	0.615
ml12 bg	0.8298	1	0.000151	0.604	1	1	0.000151	0.001044
ml10 and bg	0.2263	1	0.000151	0.9904	0.9922	1	0.000151	0.00017
ml10 c,d,e	0.000151	0.000151	0.01044	0.000151	0.000151	0.000151	1	0.000151
ml9 bg	0.5043	1	0.000151	0.8945	0.9999	1	0.000151	0.00028
ml9b,c	0.9995	1	0.000151	0.1066	1	1	0.000151	0.02102
ml9,c,d	0.000151	0.000151	0.9894	0.000151	0.000151	0.000151	0.7573	0.000443
ml8 bg	0.1966	1	0.000151	0.9941	0.9877	1	0.000151	0.000165
ml8,d	0.000151	0.000151	0.3396	0.000151	0.000151	0.000151	1	0.000152
ml8b,c, e	0.7369	0.000178	0.4017	0.000151	0.03122	0.000169	0.000151	1
ml7 bg	0.9835	1	0.000151	0.2671	1	1	0.000151	0.005737
ml7	0.000709	0.000151	1	0.000151	0.000152	0.000151	0.000442	0.7583
ml6 bg	0.01441	1	0.000151	1	0.5585	1	0.000151	0.000151
ml6,b,	0.5187	0.000151	0.6209	0.000151	0.01212	0.000151	0.000151	1

	0	ml3 loops and bg blk	ml3,e	ml3b,d	ml2 bg	ml2	ml1 bg	ml1b,c	ml1d,e
d		8		1		6	1		
ml6c,e	0.9984	1	0.000151	0.1394	1	1	0.000151	0.01497	
ml5 bg	0.05291	1	0.000151	1	0.8444	1	0.000151	0.000153	
0	ml3 loops and bg blk	ml3,e	ml3b,d	ml2 bg	ml2	ml1 bg	ml1b,c	ml1d,e	
ml5	0.04824	0.000151	0.9978	0.000151	0.000368	0.000151	0.000152	1	
ml3 bg	0.8253	1	0.000151	0.6099	1	1	0.000151	0.001017	
ml3 loops and bg blk	0	0.3852	0.000181	0.000347	1	0.3249	0.000151	0.8484	
ml3,e	-	0	0.000151	0.9501	0.9994	1	0.000151	0.000213	
ml3b,d	-	-	0	0.000151	0.000151	0.000151	0.004196	0.2845	
ml2 bg	-	-	-	0	0.04489	0.9698	0.000151	0.000151	
ml2	-	-	-	-	0	0.9983	0.000151	0.05406	
ml1 bg	-	-	-	-	-	0	0.000151	0.000192	
ml1b,c	-	-	-	-	-	-	0	0.000151	
ml1d,e	-	-	-	-	-	-	-	0	

Pinwheel

	Pinwheel 1a	Pinwheel 1b	pnw1 bg	pnw rk1	pnw rk1 bg	pnw rk 2	pnw rk2 bg	pnw3 bg
Pinwheel 1a		0.000253	0.4922	1	0.4228	1	0.7242	0.6375
Pinwheel 1b	-		0.000146	0.000163	0.000146	0.000172	0.000146	0.000146
pnw1 bg	-	-		0.8771	1	0.7966	1	1
pnw rk1	-	-	-		0.8256	1	0.9753	0.9498
pnw rk1 bg	-	-	-	-		0.7326	1	1
pnw rk 2	-	-	-	-	-		0.9425	0.8994
	Pinwheel 1a	Pinwheel 1b	pnw1 bg	pnw rk1	pnw rk1 bg	pnw rk 2	pnw rk2 bg	pnw3 bg
pnw rk2 bg	-	-	-	-	-	-		1
pnw3 bg	-	-	-	-	-	-	-	

	pnw3	pnw 4bg	pnw4	pnw5 bg	pnw5	pnw6 bg	pnw6
Pinwheel 1a	0.7654	0.4799	0.9565	0.5254	0.6344	0.1809	0.2355
Pinwheel 1b	0.000146	0.000146	0.007201	0.000146	0.000146	0.000146	0.000146
pnw1 bg	1	1	0.02362	1	1	1	1
pnw rk1	0.9837	0.8689	0.6568	0.8976	0.9487	0.5161	0.6087
pnw rk1 bg	1	1	0.01796	1	1	1	1

pnw rk 2	0.9586	0.786	0.7597	0.8237	0.8976	0.4119	0.5001
pnw rk2 bg	1	1	0.05528	1	1	0.9994	0.9999
pnw3 bg	1	1	0.04026	1	1	0.9999	1
pnw3		1	0.06469	1	1	0.9987	0.9997
pnw 4bg	-		0.02254	1	1	1	1
pnw4	-	-		0.02677	0.03981	0.005034	0.00723
pnw5 bg	-	-	-		1	1	1
pnw5	-	-	-	-		0.9999	1
pnw6 bg	-	-	-	-	-		1
pnw6	-	-	-	-	-	-	

APPENDIX 2 – EXCAVATED PIGMENT SAMPLES (OCHRE)

A number of pieces of ochre have been recovered from excavated sites in the Wind Wolves Preserve. These were analysed using a portable XRF device, just as the *in situ* pigments have been analysed and their results (in counts per second) are shown in the charts below. The readings from most of these samples formed very close groups suggesting a small degree of internal variation (fig 12a), but many showed outlying readings with a larger range around their core. These outlying readings are consistent with a normal distribution but could make a material look very varied when its core readings are in fact consistent (fig 12b). It would also be possible to confuse these outlying readings with readings from a separate pigment material.
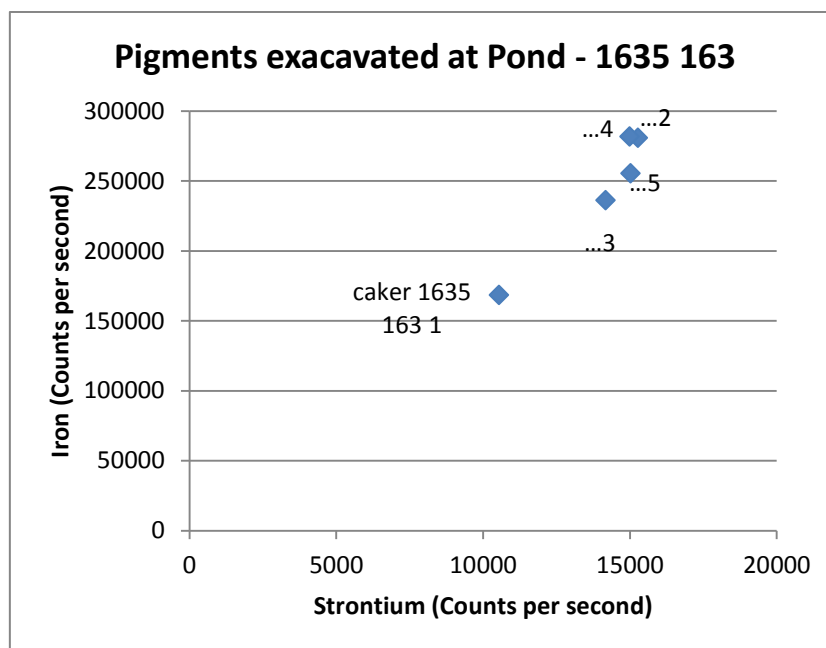
This is important to consider when looking at pigments *in situ*, and when trying to determine how many different pigment materials are identifiable. In order to state that a group of *in situ* readings belong to one material, it must be considered that readings from the same pigment could appear to vary around their mean.
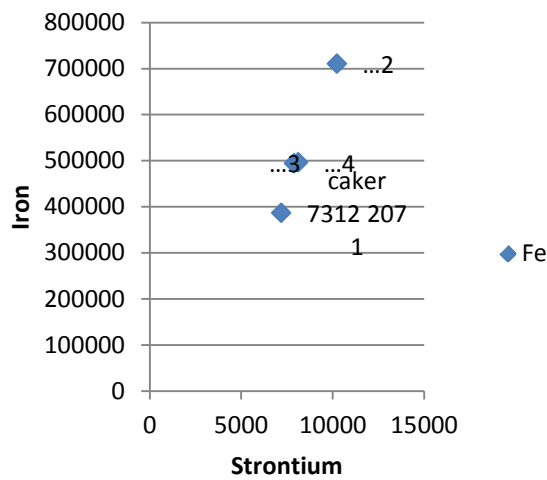
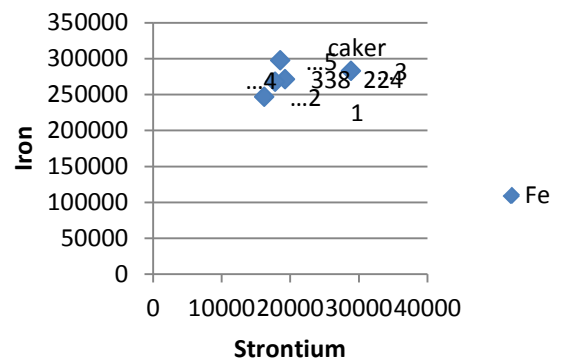**Ochre excavated at Three Springs - 3388 210**
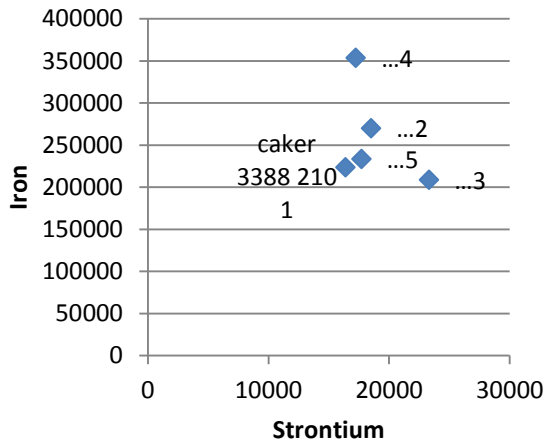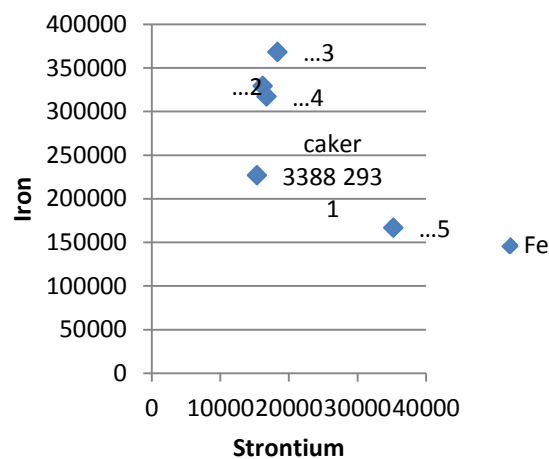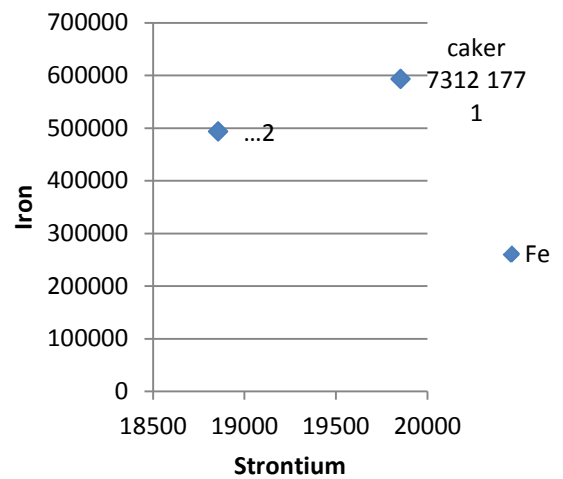
Ochre excavated at Three Springs - 3388 210
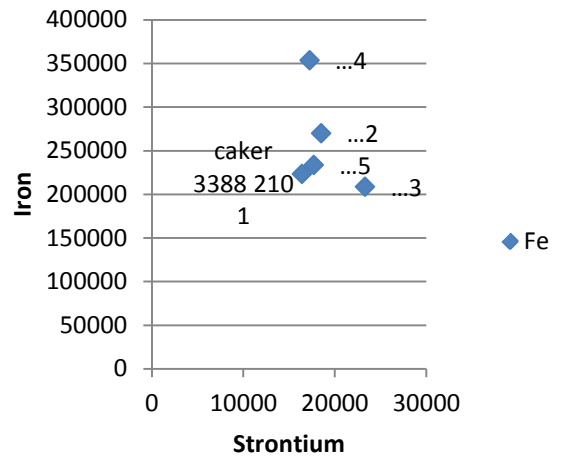
Pigments - 7312 207

Ochre excavated at Three Springs - 3388 224

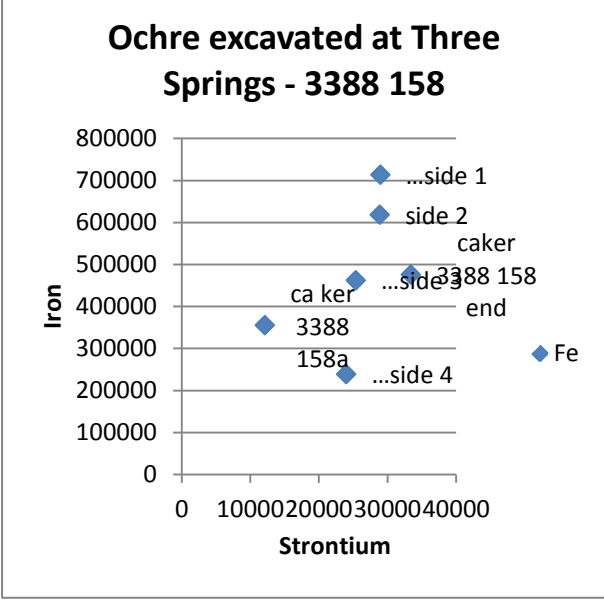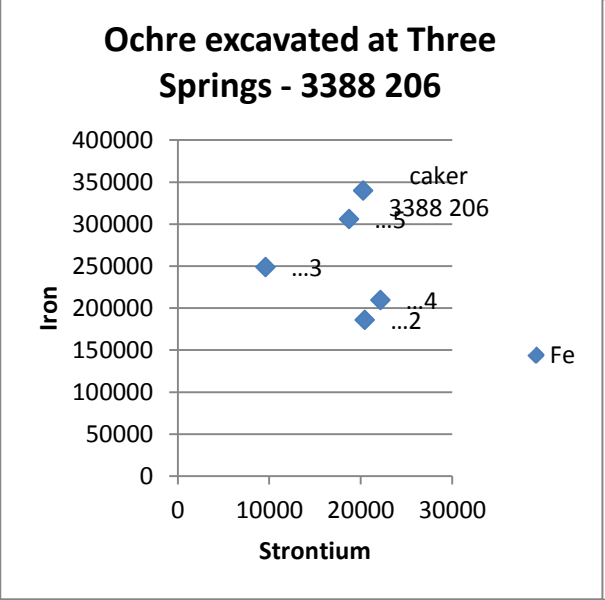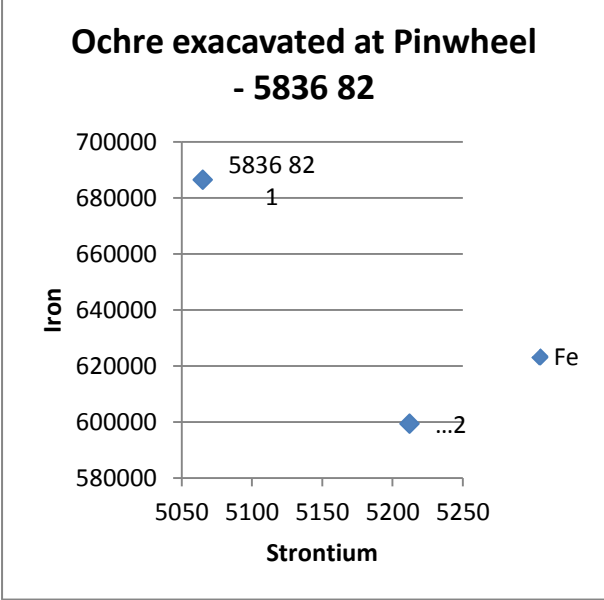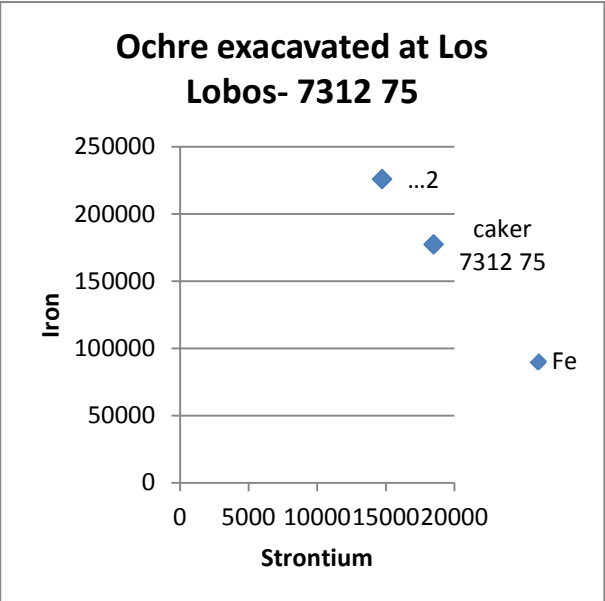**Ochre excavated at Three Springs- 3388 293**

Pigments - 7312 177

II

Ochre exacavated at Los Lobos - 7312 122

Ochre exacavated at Los Lobos- 7312 75

Ochre exacavated at Pinwheel - 5836 82

Ochre excavated at Three Springs - 3388 206

Ochre excavated at Three Springs - 3388 158

Ochre exacavated at Pinwheel - 5836 17

III

Ochre excavated at Three Springs - 3388 107

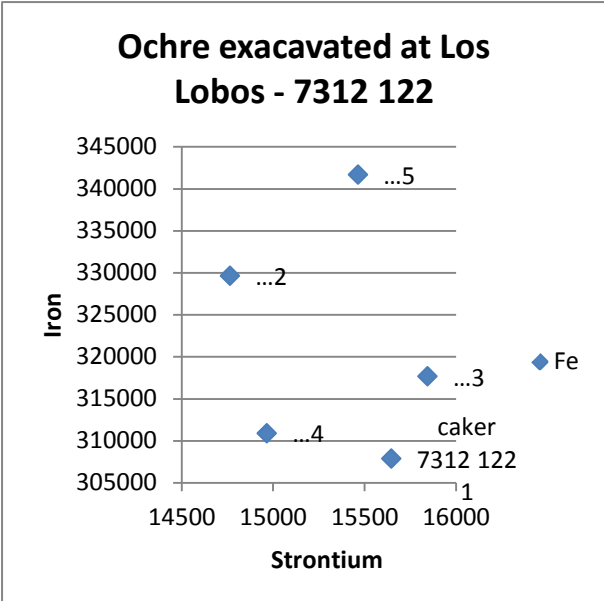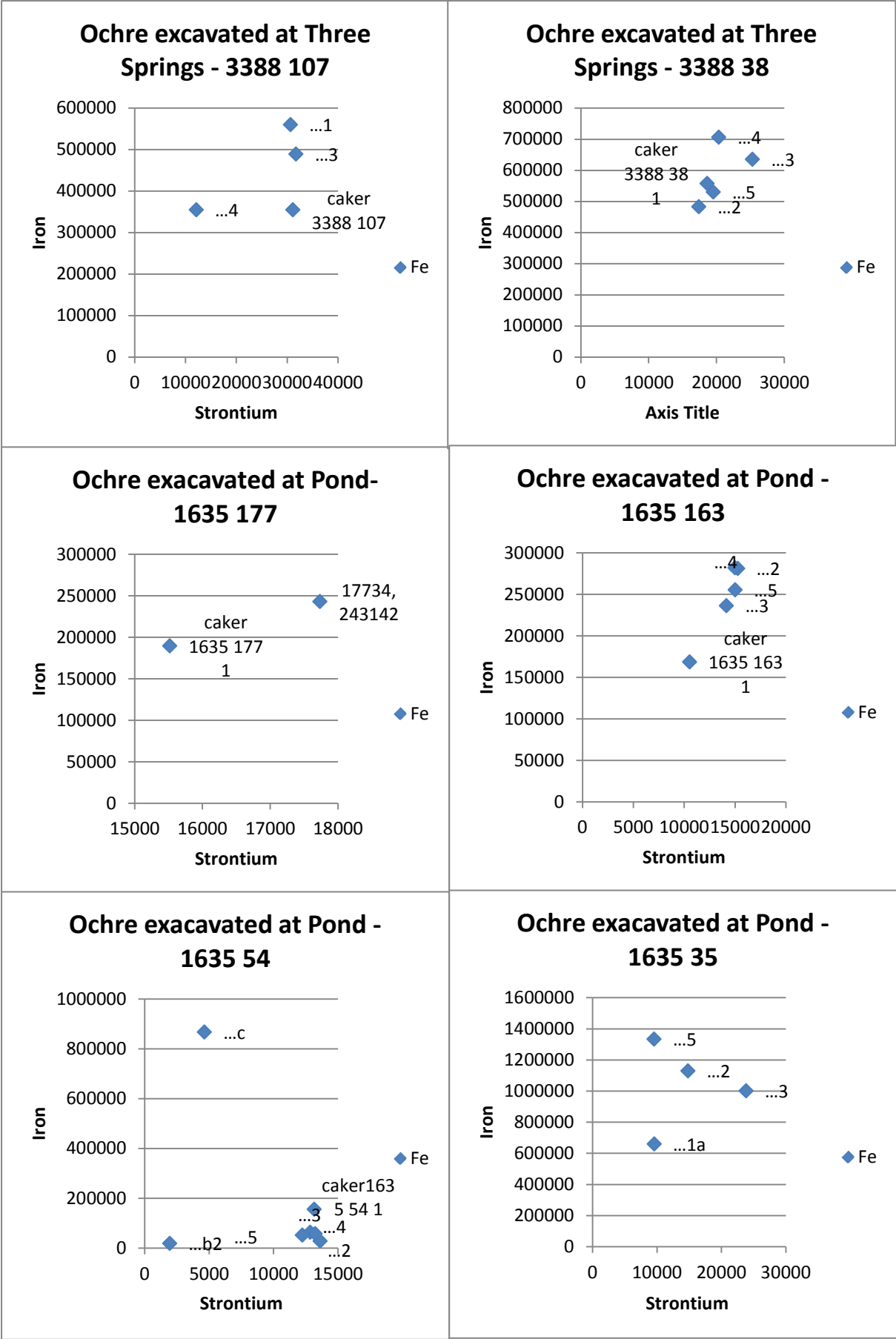**Ochre excavated at Three Springs - 3388 38**
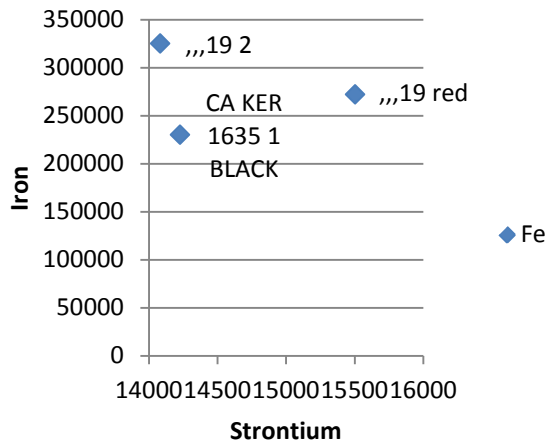
Ochre exacavated at Pond- 1635 177

Ochre exacavated at Pond - 1635 163

Ochre exacavated at Pond - 1635 54

Ochre exacavated at Pond - 1635 35

IV

Ochre exacavated at Pond - 1635 19

Iron vs Strontium scatter plot with points labeled: ,,,19 2; CA KER 1635 1 BLACK; ,,,19 red; Fe

Ochre exacavated at Pond - 1635 10

Iron vs Strontium scatter plot with points labeled: ,,, 102a; ,,, 10 2; ,,, 10 4; ,,, 10 3; ,,, 10 5; Fe