

TAPHONOMY OR PAINT RECIPE:

In situ portable x-ray fluorescence analysis of two anthropomorphic motifs from the Woronora Plateau, New South Wales

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Abstract

Portable spectrographic techniques have desirable attributes for archaeological investigations because they can be applied in the field non-invasively and non-destructively. With the increasing ubiquity of portable spectrographic techniques in Australia it is timely that the complexities of field-based analyses are discussed. A review of portable x-ray fluorescence (PXRF), including the limitations of the technique, and discussion of the complex physical interactions encapsulated by the resulting elemental data, provide a firm basis for interpreting the analysis of a rock art panel on the Woronora Plateau, New South Wales. PXRF data supports the results of previous (laboratory-based) pigment characterisations, that a locally sourced, composite clay-based paint was used to produce rock art. Results highlight the requirement for specific knowledge and expertise, not only in relation to the technique, but also the rock art under investigation and, critically, its taphonomic context. Ultimately this case study demonstrates that portable spectrometry should be considered an addition to the existing repertoire of archaeometric techniques applicable to the study of rock art, rather than as a replacement for laboratory analyses.

Introduction

The application of portable x-ray fluorescence (PXRF) has a ca 35 year history in archaeometry, with a veritable explosion in its use for the investigations of archaeomaterials, such as ceramics and obsidian, in the last decade (Guilherme et al. 2008:444; Speakman et al. 2011:3483). The increasing ubiquity of portable spectrographic techniques has been largely driven by an increase in commercial availability, and the decrease in price of 'hand-held' instrumentation, combined with the growing importance of non-destructive methods in contemporary archaeology (Heginbotham et al. 2010:178; Joyce 2011:199). The most desirable attribute of portable spectrometry is that analyses are able to be conducted in the field (i.e. in situ), without destructive sampling or composition-altering sample preparation and therefore without adverse impact to the material culture being investigated. The trade-off is that there are limitations inherent in accuracy, precision and sensitivity of portable spectrographic techniques compared to laboratory-based instrumentation.

In respect of the serious ethical considerations associated with rock art research (Bednarik 1992; Clottes 1992; Watchman 1992a), the non-invasive nature of portable spectrometry represents unprecedented sampling freedom. Rapid acquisition of compositional information is possible, enabling the collection

of large (statistically robust) datasets (Williams-Thorpe 2008), thereby allowing the examination of archaeological patterns, contrasting the isolated cultural indices provided by previous opportunistic sampling/solely laboratory-based analyses of Australian rock art pigments (Cole and Watchman 1993, 1996; Huntley et al. 2011). Importantly, in situ analyses allow research questions to be addressed at an appropriate spatial resolution: the composition of pigments can be systematically studied across a motif, rock art panel, site, site complex or geographic region (bounded by an identified 'stylistic' art province).

The success of all archaeometric analyses rests with a critical evaluation of the physical properties (beneficial attributes and inherent limitations) of the selected technique(s) and their efficacy in relation to archaeological inquiry. For the analysis of archaeological pigments, techniques such as XRF are inherently limited because they identify the elemental composition only, not the structural (crystallographic or compound) nature of the sample (Lirtzis and Zacharias 2011:119). Elemental data is a powerful tool in pigment research, but only 'where well-defined questions have been posed, whose answer relies on the resolution of a given dichotomy' examinable by the technique employed (Aloupi et al. 2000:18). This fundamental principle underpins the case study presented herein.

With commercial PXRF instruments, field portability has come at the cost of power through the miniaturisation of x-ray tubes, which decreases detection limits and reduces the suite of elements that can be measured compared to laboratory-based energy dispersive XRF (Guilherme et al. 2008:444). There are many laboratory-based non-destructive techniques available for investigating the chemical composition of archaeomaterials that offer greater precision and are able to analyse a larger number of elements (Lirtzis and Zacharias 2011:110). There are also numerous high precision geochemical techniques with minimal sampling requirements that have been applied to the investigation of Australian ochres (Creagh et al. 2007; Green and Watling 2007; Popelka-Filcoff et al. 2012). The benefits of non-invasive, in situ rock art analyses must therefore be balanced against the resulting limitations of PXRF to define research questions of archaeological interest that can be examined.

The following section reviews the limitations and complexities encountered when applying PXRF to rock art. The intent is not to provide a comprehensive overview of the physics of PXRF for all rock art applications, rather a context for discussing the results of the case study presented. General issues associated with the field application of PXRF and the extremely specific nature of data obtained, which must be interpreted with reference to their unique taphonomic context, are highlighted.

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Complex Physical Interactions: Some Issues Associated with In Situ PXRF Analysis of Rock Art

The principle of XRF spectrometry is that primary x-rays from an x-ray tube or radioactive source are incident upon the surface of a sample and create inner shell (K, L and M) atom vacancies. These vacancies de-excite, producing secondary, fluorescent x-rays with measurable characteristic energies diagnostic of the elements present (Pollard et al. 2007:101). XRF analysis (including PXRF) is a bulk analytic technique where elemental characterisations are an average of the entire sample volume (Shackley 2011:10). PXRF estimates 'the bulk composition of the sample from what is essentially a surface measurement' (Potts 2008:10), especially in relation to light z elements (< iron). Figure 1 illustrates the surficial nature of light element PXRF analysis and the attenuation effects discussed below.

It is widely accepted that sample thickness affects the precision of elemental measurements from PXRF (Lirtzis and Zacharias 2011:127). Rock art pigments, like those from other archaeological contexts (wall frescos, illuminated manuscripts, pottery decoration, etc.), are often found to be what analysts term 'infinitely thin' in relation to XRF:

When the penetration depth of the incident radiation emitted by the exciting source, and the secondary x-ray emitted by the sample, is larger than (or of the same order of magnitude as) the sample thickness, then the sample is considered ... infinitely thin (Cesareo et al. 2008:209).

In other words, a sample is infinitely thin when incident x-rays completely penetrate, or pass through, the material being analysed.

The thickness of rock art pigments varies. Personal observation of articulated (i.e. still bonded to the shelter substrate) black and red rock art pigment from the Sydney Basin via scanning electron microscopy (SEM) show thickness is tens of microns (ca 7–50 µm), but varies in the order of tens of microns across millimetre lengths of discrete motifs. Published observations of *Gwion*¹ motifs from the Kimberley, Western Australia, where paints appear to be applied relatively consistently/thickly are generally ~25 µm (Watchman et al. 1997:Figure 3–20). My recent observations of articulated *Gwions* via SEM are that pigment thickness varies between ~25–275 µm, again over millimetre lengths of motif. Therefore, most, if not all, rock art will be infinitely thin, especially in relation to heavier z elements (> iron). Most importantly, pigment volume will vary within PXRF analytes.

Critical depth penetration is another essential consideration when selecting areas for analysis and interpreting PXRF data, especially in relation to archaeological materials, such as lithic artefacts and mineral pigments (ochre), that are susceptible to complex geological weathering processes resulting in compositional segregation at the sample surface (Cook et al. 1990; Potts 2008:10; Smith et al. 1998; Williams-Thorpe

¹ *Gwion* motifs have historically been referred to in academic literature as 'Bradshaw' figures. The nomenclature utilised here is derived from recent consultation with the traditional owners of the northwest Kimberley region and I thank the Wunambal Gaambera Aboriginal Corporation for their guidance.

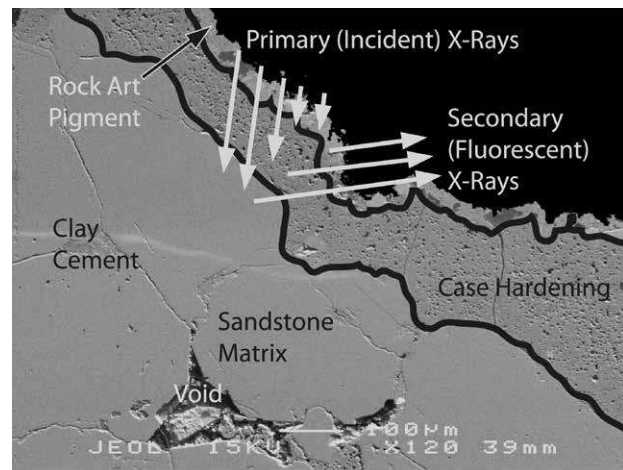


Figure 1 To scale schematic illustration of critical depth penetration with light element optimised PXRF. Compiled from SEM backscatter micrographs (Ford 2006) (image by Lucas Huntley).

2008:179). Previous empirical studies of light z element critical depth penetration in silicate rock (rhyolite—comparable to the sandstone shelter matrix in the case study) have demonstrated increasing x-ray attenuation with depth for PXRF (Potts et al. 1997). Critical depth penetration of elements such as potassium, calcium, titanium and iron have been shown to be ca 30 µm, 35 µm, 50 µm and 170 µm; however, the analyte volume is cone-shaped, meaning that *half* of the contribution of bulk chemical composition is derived from ca 5 µm, 5 µm, 7.5 µm and 50 µm, respectively (Potts et al. 1997:33, emphasis added).

It is well-established that air attenuates low energy x-rays, particularly affecting the measurement of light z elements (< titanium). For this reason laboratory-based energy dispersive XRF instruments often operate low energy analyses in a vacuum or change the chamber atmosphere, purging it with helium (Shackley 2011:30). During in situ analysis unprepared samples with uneven surface morphologies can introduce additional air gaps between the sample and PXRF instrument (Forster et al. 2011:393; Lirtzis and Zacharias 2011:132). In addition to attenuation, gaps between the instrument aperture and the surface of the analyte may introduce significant, and as yet unquantified, errors relating to angles of incidence and detection in respect to variation of fluorescence intensity (de Boer 1989; Jenkins 1999:39). These issues have led some analysts to conclude that fully 'quantitative results cannot be obtained directly from rock samples in the field which have irregular shaped surfaces' (Potts et al. 2005:769).

The structure (mineralogy, mixed grain size and density) of materials under investigation is one of the most well-documented factors affecting x-ray attenuation and self-element secondary fluorescence (Karydas 2005). Again, this is especially so for unprepared samples. Concisely put, in bulk analyses the 'matrix emission intensity of each element is a function not only of its concentration but also of the overall composition of the larger area under investigation' (Lirtzis and Zacharias 2011:119). The size of the 'area under investigation' (i.e. analyte volume) in PXRF is reduced compared to laboratory-based energy dispersive XRF, commensurate with the smaller x-ray tubes facilitating field portability. PXRF is therefore sensitive to mineralogy and grain size effects (Forster et al. 2011:394) and attenuation due to matrix density. Quantitative density measurement is required to

calculate coating thickness (Piorek 2008:62) and critical depth penetration (Potts et al. 1997:32). Density has been shown to be a significant attenuation factor in PXRF analysis of experimental aluminosilicate matrices (Forster et al. 2011), pigments (Mantler and Schreiner 2000) and lithics (Potts et al. 1997; Williams-Thorpe 2008).

Matrix density is of particular relevance in the case study presented here, as both the shelter substrate and clay-based rock art pigments are porous. Water absorbs x-rays more strongly than air and occurs in pigment rock art in two ways: as part of the crystalline structure of minerals (part of geological compounds), and in the pore spacing of rocks/clays. The latter has the greatest potential to impact field-based PXRF by reducing the spectral response of characteristic x-rays, leading to 'lower precision, poorer detection limits and lower accuracy' (Liangquan Ge and Lin 2005:28).

Orientation: Browns Road 29

The two bichrome anthropomorphic motifs analysed in this study are located in one of hundreds of known pigment rock art sites in the Sydney Catchment Authority's Metropolitan Special Area (MSA) on the southern Woronora Plateau (Dibden 2011:202; Ford 2006:7–8) (Figure 2). Browns Road 29 (BR29, AHIMS 52-2-1643) was recorded in 1991 as part of a systematic survey by the Illawarra Prehistory Group (Sefton 1991). Prior to this, the character and extent of rock art within the Cordeaux River catchment was unknown, except for a few isolated shelters (McCarthy 1961, 1967; Sim 1964), though various geographically discrete, impact assessment-based archaeological investigations in the Catchment during the late 1970s and early 1980s had noted the potential for shelters to contain art (e.g. Attenbrow and Happ 1983:6).

Rock art from the Woronora Plateau, including 31 sites from within the MSA (McDonald 1994:2008 as cited in Dibden 2011:71), has been incorporated into broad, regional-scale stylistic syntheses. Two major phases of pigment rock art have been defined in the Sydney Basin (McCarthy 1967, 1988; McDonald 2008). This broad sequence is again recognised in recent detailed analyses of the discreet MSA art assemblage by Dibden (2011) and both pigment phases are present at BR29. Dibden (2011:261) noted differences within the specific and nuanced formal signatures of complex locational, environmental and spatial patterning in the pigment art sequence not previously identified in broad-scale syntheses. Anthropomorphic motifs at BR29 are attributed to the most recent period of art production on the Woronora Plateau (Dibden 2011:339). This latter pigment art phase has an inferred chronology of somewhere between ca 4000 years ago and the colonial period in the broad Sydney Basin regional sequence proposed by McDonald (2008:249, 343); however, after evaluating several lines of evidence, Dibden plainly stated that 'in the absence of direct dates for the rock art, or of any associated archaeological deposit, establishing the timing of this sequence for the Upper Nepean, with any certainty is not possible' (2011:157).

BR29 is a clam-shaped rockshelter located in a cliff-line immediately below a major ridge running perpendicular to the Illawarra Escarpment. Bedding of the sandstone is relatively thin, resulting in multiple minor benches and a dramatically rugged landscape (Young and Young 1988:12). The site is approximately

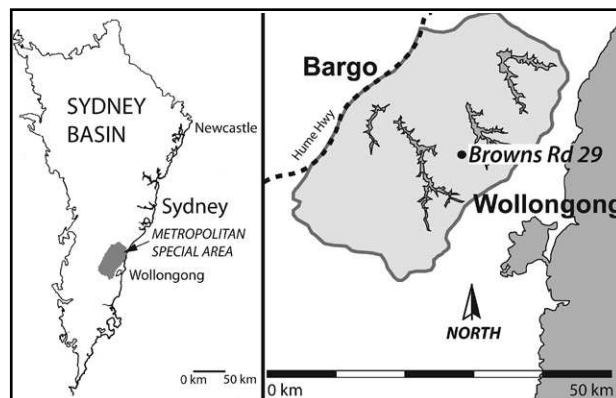


Figure 2 Location of BR29 (AHIMS 52-2-1643). The grey shading is the Metropolitan Special Area, with the Nepean, Avon, Cordeaux and Cataract Dams inset (left to right) (image by Lucas Huntley).

22.5 m wide at its mouth, with a northwest sloping ceiling ranging from approximately 3.5–0.7 m in height (Figure 3). The floor is mostly bedrock, with thin, step-like bedding cross-sections visible, as is detritus from the ceiling (exfoliated spall flakes and small block fall). A large joint in the bedding, located at the base of the ceiling, allows water to flow through the sandstone massif, while several smaller unconformities and eroded bedding planes are present across the ceiling within the rock art panels (Figure 4). BR29 contains 43 motifs, predominantly eels and anthropomorphs exemplified in the panel examined. Art at the site is notable for the relatively large size of the motifs and for the frequent use of colour (bichrome and polychrome, including yellow) (Dibden 2011:339).

The specific findings of previous pigment characterisation conducted on yellow pigment from the central anthropomorphic motif at BR29 (In Situ Loci 3, Figure 5), re-examined in this case study, are outlined in 'Research Aims' later. This previous pigment characterisation was undertaken as part of a pilot study designed to redress the imbalance presented by previous examinations of archaeological raw materials in the Sydney Basin, which had been predominantly lithic (Attenbrow 2002:122–123). The pilot demonstrated the viability of pigment characterisation and the potential of pigment provenancing studies within the complex, active geomorphic environment of the Hawkesbury Sandstone. Furthermore, a variety of information relating to pigment sources, application, chronology and taphonomy was gained. However, the results of this pilot study were by no means conclusive, being necessarily constrained by a sampling strategy that explicitly avoided adverse visual impact to the rock art (Ford 2006; Huntley et al. 2011).

Taphonomic Context of the BR29 Rock Art

Weathering of geological formations is complex, depending on many environmental factors and the material properties of the rock itself (Wells et al. 2008:1047). Mineral composition (particularly crystal structure) greatly influences the type and course of weathering, especially chemical (cavernous) processes (Twidale 1968:136–137). BR29 is a Hawkesbury Sandstone shelter, the dominant geology of the Woronora Plateau (Hazelton and Tile 1990; Twidale and Campbell 1993; Young and Young 1988:11). The geological strata of the MSA consists of the Illawarra coal measures (exposed in the Illawarra Escarpment/eastern boundary), a small remnant of Narrabeen Sandstone

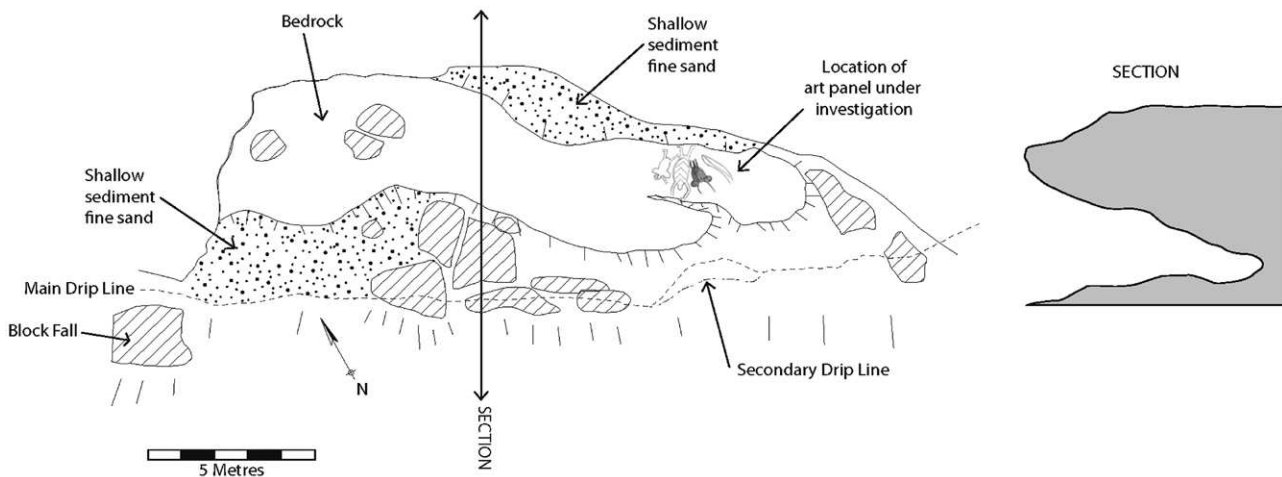


Figure 3 Plan and section drawing of BR29 (image by Lucas Huntley).

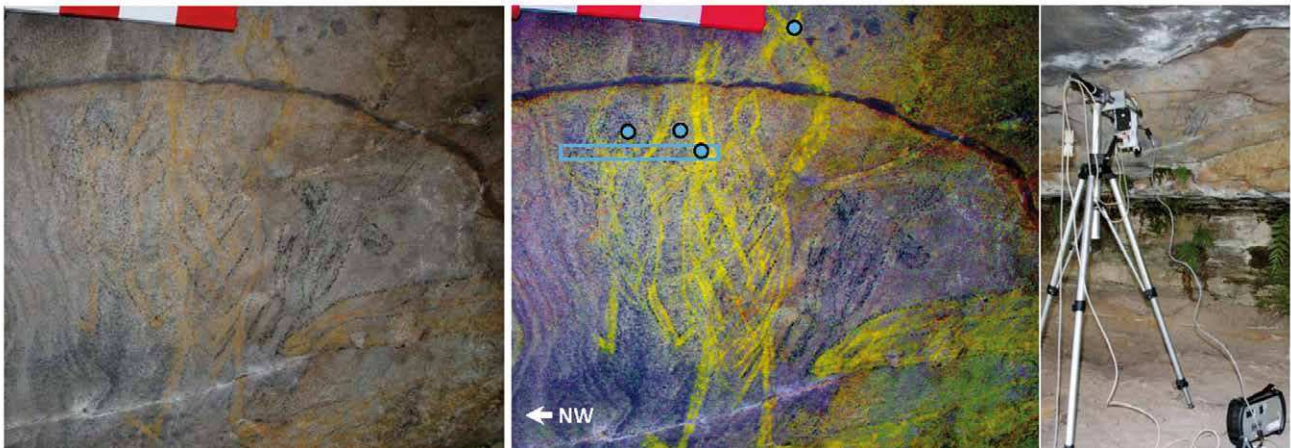


Figure 4 Overview of rock art panel showing the location of PXRF spectra (photograph by Jillian Huntley). Centre image enhanced with 12.5 scale YDS D-Stretched in Image J software. Scale bar is in 10 cm increments. Key: location of transect originally proposed for transect of PXRF analyses (□); location of PXRF spectra (●).

in the northeast corner, and Hawkesbury Sandstone (including minor shales) at the surface, capped by Wianammatta shale remnants in the central west and northeast (Ford 2006:Figure 4-24; Haworth 2003:43–45; Rose 1966). The Hawkesbury Formation is even-sized, medium-grained, quartzose sandstone, with thin, spatially constricted shale lenses (Hazelton and Tile 1990) composed almost entirely of quartz grains bonded by clay-rich cements often containing calcium (Twidale 1968; Vinnicombe 1980). Grain structure is typically 80–90% quartz, 5–10% feldspar (aluminosilicate crystals that often contain calcium) and 1–5% mica or kaolin (clay), with grain sizes ranging between 350–500 μm (Hunt et al. 1977:113; Wells et al. 2008:1048–1049). Iron-oxides (haematite, maghemite and goethite) are present throughout Hawkesbury Sandstone and concentrations from 5.7–20.4% are reported in the matrix cement (Hunt et al. 1977:114–115).

Recent literature is scant in relation to the geomorphology of Hawkesbury Sandstone and little quantitative research has been undertaken since the 1970s and 1980s in relation to either the processes causing, or the rates of, weathering in archaeological shelters. Shelters are formed by predominantly chemical processes, termed ‘cavernous weathering’ (Young 1987), which is prevalent in large sandstone outcrops along

cross-bedding plains, with extension of caverns back into joints (as at BR29) an important correlate (Johnson 1974:352; Lambert 1980:9).

Salt (sodium chloride) has been identified as a primary catalyst (and accelerant) for cavernous weathering in the Hawkesbury Sandstone (Lambert 1980; Young 1987; Young and Young 1992). Lambert (1980) undertook a quantitative study of the amount of salt contained within detrital sands found at the base of active cavernous weathering in three shelters. Prior to this work the prevailing view concerning salts was that they were only a primary catalyst in arid or coastal environments (Hughes 1978:3; Young and Young 1992:71). Lambert (1980:30), however, demonstrated that soluble salts (from 0.8–1.4%) were present in all detrital sands of the active cavernous erosion measured in the Hawkesbury Sandstone. Most surprisingly, the largest concentration of salt was found in the most inland shelter (some 50 km from the coastline). Of particular relevance to this case study is the fact that none of the cavernous weathering examined by Lambert displayed macroscopic salt encrustations (Lambert 1980:31). Lambert attributed the mechanism of salt weathering to crystallisation/hydration pressures; however, subsequent research indicated that salts in Hawkesbury Sandstone act to enhance the

dissolution of precipitous minerals, particularly quartz (Young 1987:964-965).

In Hawkesbury Sandstone the precipitation of secondary minerals and their deposition at, or near, the rock substrate surface results in a less permeable, structurally harder mineralised layer, known as case hardening (Young and Young 1992:74). Again, the presence of soluble salts has been noted as catalysing and accelerating case hardening, enhancing dissolution of precipitous minerals (Mol and Viles 2011:302), particularly iron, clay and calcite phases (Young and Young 1992:74). Mineralised or case hardened layers at the rock surface represent compositional segregation of the matrix, as discussed in the preceding section. Deposition of precipitates results in altered mineralogy and therefore different chemical composition at the rock surface. Case hardened surfaces are visible across the ceiling at BR29 in areas of fresh cavernous weathering or flake exfoliation. Observed case hardened surfaces across the rock art sites on the Woronora Plateau vary in thickness from 50 µm to 5 mm (see Ford 2006:Plate 18-36; Huntley et al. 2011:Figure 5-90).

Precipitous mineral deposition also forms coatings or mineral skins on rock substrate surfaces. Mineral accretions are the best described geological weathering products in rock art research, as their potential to contribute chronological information (numerical age determinations) has been well demonstrated in Australian contexts (e.g. Aubert 2012; Watchman et al. 1993, 1997, 2001, 2005). Silica rich accretions, commonly known as amorphous silica skins (hydrated amorphous silicon dioxide, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$) (Watchman 1996:ii), have been observed throughout rock art sites in the Hawkesbury Sandstone (Lovering 1952). Precipitous mineral deposition appears consistently across the ceiling at BR29. The accretion at BR29 (presumed to be amorphous silica) has formed small irregular, coral-form stalactite structures commonly in the order of ≤ 0.5 mm, but which can be up to 3 mm in height. These micro-stalactites occur in moderate, consistent density across the BR29 ceiling and their morphology and colour matches the description of common opal, coralloidal stalactites given by Lovering (1952:Figure 2-30) and Young and Young (1992:77-78). At BR29 the silica skin lies underneath the anthropomorphic motifs under investigation (Figure 5).

The chemical composition of silica skins is predominantly derived from weathered source rock. In Hawkesbury Sandstone this is generally the same rock on which they have formed (Watchman 1992b:62). The composition of the BR29 silica skin is presumably derived from the Hawkesbury Sandstone, though the mechanism of silica skin formation is somewhat less straightforward. Watchman's work in the 1990s concluded that typically in rock art sites throughout Australia 'silica skins are not formed from solutions that flow directly out of the rock immediately underlying the skin ... they are surficial precipitates, or accretions formed by deposition from water that flows across stable surfaces' (Watchman 1996:212, emphasis added). This appears not to be the case for the BR29 silica skin. Rather, the stalactite structures indicate that the origin of the accretion is slow percolation of ground-waters through the orthoquartzites (Hawkesbury Sandstones) (Clarke 1916; Lovering 1952:30; emphasis added). This mechanism of silica deposition has been noted in shelters which have roughly planar roofs due to their extension back along bedding planes, such as at BR29. The consistent presence and density of silica stalactites across



Figure 5 Detail of the rock art panel. The white ovoids indicate the location and approximate size of the PXRf instrument aperture. In Situ Loci 3 (i.e. Spectrum 3) is the location of previous pigment harvesting (photograph by Jillian Huntley).

the ceiling (rather than grouped stalactite structures along obvious seepage, fractures or joints) is further evidence that silica is precipitated through the sandstone massif (Young and Young 1992:77).

The microstructure of silica skins has implications for x-ray attenuation. Features of vitriform amorphous silica skins include air voids and spherical (quartz) grains ca 5 µm in diameter, dispersed through thin sheets or plates of deposited opal-CT (Watchman 1990a:29). Silica stalactites in the Sydney Basin sandstones observed under SEM show layered rings with small air voids between concentric, circular depositions of amorphous silica (Young and Young 1992:78). Internal air gaps, isolated large grains and the irregular surface micromorphology of the BR29 coral stalactites may contribute to x-ray attenuation, including variation in radiation path lengths, resulting in reduced fluorescent intensity during in situ PXRf analysis.

Finally, it is important to understand the properties of the rock art pigments themselves, as they have the potential to impact their own weathering (Odlyha et al. 1997 as cited in Sumner et al. 2009:241). Pigments act as a surface modifier, changing albedo, light transmissivity, thermal and moisture properties (Bullet and Prosser 1983 as cited in Sumner et al. 2009:242). The thin, dispersed nature of paints at BR29 is expected to significantly reduce the impact pigments have in relation to weathering. However, the physical properties of the paints, being porous and clay-based, indicate they could have an altered chemical composition due to the incorporation of precipitous minerals, particularly silicates and iron-oxides (Young and Young 1992:74). In addition, mineral pigments often undergo compositional segregation (particularly at their surface) through phase transitions due to heat or oxidisation (Cook et al. 1990; Smith et al. 1998).

The physical properties of rock art paints that have the most potential to impact on in situ PXRf can be grouped as microstructural—specifically, grain size and porosity. The grain size of modern industrial pigments is ~1 µm, whereas rock art pigments generally contain a mixture of grains, ranging in size from very fine to very coarse. Monte Carlo simulations suggest that the error introduced by grain size heterogeneity in XRF analysis of pigment is low where average grains are < 5 µm (Mantler and Schreiner 2000:32). However, MSA rock art paints contain mixed grains, from very fine kaolin and mica clays a few

microns in diameter, to long, tubular-shaped feldspars typically tens of microns long and $\sim 5 \mu\text{m}$ wide, and a variety of quartz grains ranging from tens to hundreds of microns (Figure 1; also see Huntley et al. 2011:Figure 5-90). The porosity of these composite clay-based pigments, all of which have differential matrix density between constituents, such as iron-oxide, quartz, feldspar and clay grains, has the potential to attenuate x-ray signals.

The BR29 pigments appear typical of Sydney Basin rock art, with a dispersed and surficial morphology, i.e. pigment is preferentially located at the surface of the microtopography on the shelter substrate, rather than throughout adjacent dips and hollows (Figure 3). This dispersed morphology has been noted across the Sydney Basin and, in terms of application, is usually referred to as 'drawn' (though see Clegg 1988:20; Dibden 2011:158; Officer 1984:3). The dispersed nature of paints in motifs analysed for this study has contributed to a reduction in pigment volume within PXRF analytes. Even 'thick' rock art paint did not cover the entire surface area of the instrument aperture (Figure 3). Consequently, the geochemical properties of the underlying rock substrate were captured in the PXRF analyses, not only because of the infinitely thin pigments, but also because the rock art did not cover the entire analyte surface.

Research Aims Relating to the Application of In Situ PXRF at BR29

In situ PXRF analysis at BR29 was designed to test further the results of earlier pigment characterisations, which found that composite clay-based paints were used to produce rock art on the Woronora Plateau. Within the panel investigated a dichotomy was posed: are elements indicative of chemical (cavernous) weathering in the Hawkesbury Sandstone present throughout the rock art panel or only in the yellow pigment? If sulphur and chlorine (and to a lesser extent vanadium, manganese, iron, copper and zinc) were found to be present in consistent relative abundances throughout the panel, it was likely that they derived from cavernous weathering. Conversely, if these elements were present in only the yellow pigment, the interpretation of previous (laboratory) analyses—that yellow, sulphur rich, desiccated/chemically weathered Hawkesbury Sandstone was mixed into clay and then applied as paint to produce the central bichrome anthropomorphic motif—would be supported (Huntley et al. 2011:87, 91).

A subsidiary aim was to examine whether elements of interest previously observed via SEM-EDXA and PIXE/PIGE could be measured with PXRF and, if so, to compare their relative abundances. This would provide data relating to the resolution of in situ PXRF and could also produce useful information regarding the location and activity of geological weathering.

Methodology

PXRF has a practical sampling advantage, as strategies can be adjusted in an 'interactive' mode to accommodate the 'live' evaluation of results (Potts 2008:11). Originally, a spatial transect of PXRF spectra was proposed from the approximate location of previously harvested pigment (In Situ Loci 3, Figure 5), through the rock art panel northwest, selecting locations for spectral acquisition which contained yellow,

black and no pigment (Figure 4). It became apparent while evaluating the live spectra, however, that the best outcome would be achieved by selecting spectral acquisition locations that contained the most surviving rock art pigment, thereby maximising pigment volume within analytes. The sampling strategy was modified accordingly (Figures 4 and 5). Care was taken to ensure that spectral locations did not contain superimposed pigment (i.e. black and yellow). The number of analytes intended for this case study was higher in relation to both the number of in situ loci and of replicates per loci; however, failure of the titanium filter prevented this (see Forster et al. 2011 Table 3 for an indication of the number of replicate analytes required to achieve common error margins in alumina-silicate matrices).

Analyses were conducted using a Bruker Tracer III-V PXRF equipped with a rhodium tube, peltier-cooled Si-PIN detector and a 1024 channel analyser at a resolution of approximately 170eV FWHM at the manganese $K\alpha$ peak (5.9 keV at 1000 counts per second). Parameters for this case study were 12 keV, 20 μA , using a 0.0254 mm titanium filter in the x-ray path and a 300 second live-time count at 185 FWHM. This configuration optimized excitation of light elements (ca 1.3–9.5 KeV). The titanium filter reduced incident rhodium L line x-rays as the measurement of fluorescent chlorine and sulphur K line x-rays was desirable. A vacuum pump removed air from the instrument (between the x-ray tube and the beryllium window, and the beryllium window and the detector beam paths), minimising attenuation of incident x-rays.

PXRF spectra were processed using Bruker X-RayOps software to adjust tube operating voltage and current settings: S1PXRF for count rate, signal acquisition and live evaluation of data, and Spectra 7.1 for the calculation of Net Peak Areas (NPAs) (semi-quantitative measurement of element concentrations through standardless fundamental parameters; see Heginbotham et al. 2011 for a discussion of quantification methods in PXRF). Elements selected for fundamental parameter correction were based on previous SEM-EDXA, XRD and PIXE/PIGE data from Woronora Plateau rock art pigments (Ford 2006:A4-1; Huntley et al. 2011:87), as well as evaluation of 'raw' in situ PXRF spectra. Calculation of NPAs was undertaken using nine correction cycles for escape and background peaks from 0.6–10.5 KeV.

A spatial transect of PXRF spectra was obtained on an unweathered block of Hawkesbury Sandstone to act as a proxy for the internal shelter substrate (Figure 6). This transect acted as a control for elemental variance in the mineralogically heterogeneous matrix and as an aid in interpreting in situ data from the rock art panel. Spectral acquisition on the control block included areas of (presumably iron-oxide rich yellow, red and tan) natural staining and the edge of experimentally applied motifs (designed to mimic the dispersed pigment morphology of the rock art panel) (Figure 6).

Routine analysis of Ohio Red Clay, a standard reference material used in archaeometric investigations, was undertaken daily (Glascock 1992; Kuleff and Djingova 1998; MacDonald et al. 2008; Popelka-Filcoff et al. 2008:735). This internal standard measurement was designed to assess x-ray tube degradation and any variation in instrument performance over time. The inclusion of data from the internal standard was also used to help explore the effects of matrix mineralogy, porosity

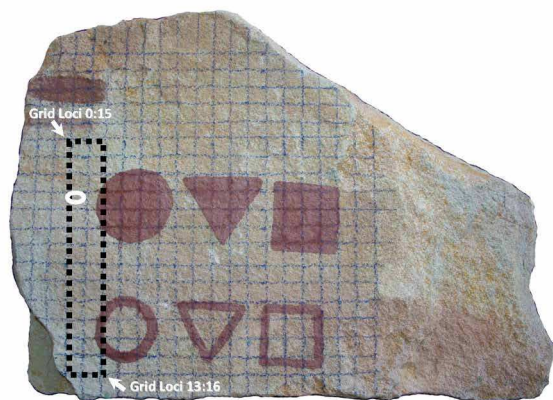


Figure 6 Hawkesbury Sandstone control block. Black dashed lines show the location reported spatial transects of PXRF analytes. The white ovoid shows the position and relative size of the PXRF aperture. Grid is 1.5 cm (photograph by Jillian Huntley).

and grain heterogeneity, as Ohio Red Clay is mineralogically homogeneous and very fine-grained (Forster 2011:391).

Multivariate analyses were used to compare trends in overall element characterisations with trends in discrete indicator element groups. Principal Components Analysis (PCA) (using a correlation matrix) and (Ward's) Hierarchical Clustering of NPA data was undertaken using JMP 9 software. Untreated NPA values were used for multivariate exploration, as no assumptions about normative distributions were made (Baxter and Jackson 2001). PCA and hierarchical clustering techniques were selected as they have an inverse relationship in terms of the premise of data processing (modelling vs explanatory approaches) (Baxter and Jackson 2001:131; Glascock et al. 2004). This was intended to explore variation (if present) in compositional groups defined by multivariate techniques with orthogonal vs agglomerative approaches.

Geochemical variability of data collected was explored by comparing trends within the relative abundance of indicator element groups (i.e. specific groups of elements indicative of cavernous weathering, clays and precipitous mineral deposition). NPA data classified as representative of different taphonomic and cultural phenomena (indicator elements) were treated by a logarithmic transformation to facilitate comparison of trends due to large variation in values (a function of differential critical depth penetration) (Baxter 2003:75; Glascock 1992; see also Table 2).

Results and Discussion

Trends in the relative abundance of elements (summarised in Table 1) were interpreted to address the aims of the case study presented. Direct comparisons of relative abundances are not useful, as NPA values reflect the discrepancy in bulk analyte volume. The multiplicity of attenuation effects relating to field sampling notwithstanding, there is a relationship between NPAs as a function of atomic weight and resulting critical depth penetration (Figure 1). NPA values measured in the spatial transect on the control block for silicon at <100, compared to iron in the thousands to tens of thousands, demonstrate the discrepancy (Table 2). Critical depth penetration with PXRF in this case study is estimated to be from ca ~10 µm and ~200 µm for silicon and iron, respectively (Potts et al. 1997:33). Silicon

therefore measures around 5% of the analyte volume of iron with PXRF, rather than reflecting the compositional concentration of silica in Hawkesbury Sandstone, which is 80–90% quartz (Wells et al. 2008:1048) with minor (variable) iron concentration in matrix cement measuring 5.7–20.4% (Hunt et al. 1977:114).

Trends in Overall Compositional Data

It is important to stress that the aims of this case study do not extend to archaeological provenance (or sourcing) studies in the conventional archaeometric sense (Dillian and White 2010; Speakman et al. 2011). Archaeometric use of the term provenance is established on the basis that there exist differences in chemical composition between different natural sources that exceed, in some recognisable way, the differences observed within a given source material (Weigand et al. 1977:24). Here I define characterisation studies in the broader framework of provenance as used by collection managers (Russell and Winkworth 2009), employing geochemical characterisation towards the notation of a biography of rock art as object (Gosden and Marshall 1999) and inferring past social context for the object from geochemical data. Studying the materials from which an artefact is composed (i.e. its geochemical composition), rather than the materials from which an artefact is made, greatly enlarges the research potential and scientific significance of the artefact and the archaeological/ethnographic site from which it is derived by enabling comparisons with other objects and sites (Russell and Winkworth 2009) regardless of the successful identification of source materials to their original geographic location.

Though many archaeometric studies of ochre have been conducted in Australia, no technique or approach (i.e. combination of techniques) has satisfactorily resolved archaeometric provenancing of pigment beyond the resolution of indices and trends to broad geographical regions and/or non-geographically described mineralogical sources (Creagh et al. 2007; David et al. 1993; Goodall and David 2001; Goodall et al. 2009; Green and Watling 2007; Popelka-Filcoff et al. 2012; Smith and Fankhauser 2009; Smith and Pell 1997; Smith et al. 1998, 2002). Even the latest generation of very high precision geochemical techniques can only evaluate *trends* observed in compositional groups of ethnographically known Australian ochre sources (Popelka-Filcoff et al. 2012, emphasis added). Trends in the chemical composition of pigment(s) provide important archaeological indications regarding procurement and use, regardless of unequivocal geochemical 'fingerprinting'.

In the BR29 pigment measured for this study there is a strong overall trend to low relative abundances for in situ analytes compared to the control block and internal standard. This demonstrates that the attenuation effects outlined above (surface morphology, heterogeneous mineralogy and grain size, matrix density, compositional segregation at the shelter surface and the silica skin at BR29) are having a marked impact, lowering fluorescent yields. Notable exceptions to the overall low relative abundance trend in situ are aluminium (which is consistent throughout all analytes), silicon, sulphur, chlorine, vanadium and manganese, which all trend higher in situ, and chromium, which was either at or below the limit of detection for all analytes, except two of the three experimental (red) motifs on the control block (Figure 6).

> Element v Spectra Location	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Cu	Zn
Control Block No Pigment (25 loci, 1 spectrum each)	Moderate	Moderate	Low*	Very High to Very Low	High	Moderate to High [^]	High to Moderate	Moderate	Negligible	Low	Moderate	Moderate	Low≈	Moderate [°]
Control Block Applied Pigment (3 loci, 1 spectrum each)	Moderate	Moderate	Low*	Very High to Very Low	High	Moderate to High [^]	High to Moderate	Moderate	Low◀	Low to Moderate	Very High	High	Low≈	Moderate [°]
In Situ Loci 1 – Black Pigment (2 spectra)	Moderate	High ◇	High	Moderate to High	Moderate to High	Low to Negligible	Low	Moderate to High	Negligible	Moderate	Low	Negligible	Low	Moderate
In Situ Loci 2 – No Pigment (2 spectra)	Moderate	High	Moderate	Moderate to High	Moderate†	Negligible	Low	Moderate to High	Negligible	Moderate	Low	Low to Negligible	Low	Moderate
In Situ Loci 3 – Yellow Pigment (1 spectrum)	Moderate	High ◇	Moderate	Moderate to Low	Moderate	Negligible	Low	Moderate to High	Negligible	Moderate	Moderate	Moderate	Low	Moderate
In Situ Loci 4 – Yellow Pigment (2 spectra)	Moderate	High ◇	High	Moderate to Low	Moderate to High	Negligible	Low	Moderate to High	Negligible	Moderate	Moderate	Moderate	Low	Moderate
Ohio Red Clay Powder (2 spectra)	High	Moderate to High	Low to Negligible	Low to Moderate	High	Moderate	Low	Moderate to High	Negligible	Moderate	High	Moderate	Low	Moderate
Ohio Red Clay Fired Solid (1 spectrum)	High	Moderate to High	Low to Negligible	Low to Moderate	High	Moderate	Low	Moderate to High	Negligible	Moderate	High	Moderate	Low	Moderate

Table 1 Summary of trends in (NPA) PXRF data.

◇ Si – Overall High relative abundance, lower than loci with no pigment.

*S – Generally Low through Moderate and High relative abundances were observed at some isolated grid loci that have natural yellow colouration (Figures 6 and 9).

†K – While the relative abundance in this In Situ Loci with no pigment remains Moderate overall, it trends down (measuring around half) compared to the K measured in the loci containing rock art.

[^]Ca – The general trend is Moderate to High, however various relative abundance from Low to Negligible through to High were observed.

◀Cr – High relative abundances were observed in two of the three control block loci containing experimentally applied pigment. Both loci with high Cr were spectra from the same discrete circle motif (Figure 6).

≈Cu – The overall trend in the control block was Low. Some variation including isolated Moderate to High measurements was recorded but no discernible pattern (other than mineralogical heterogeneity) was observed.

[°]Zn – There were isolated High relative abundances in the control block, though, as for Cu, there was no discernible patterning (other than mineralogical heterogeneity).

> Element v Spectrum Name	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Cu	Zn
Grid Loci 0:15	52	325	36	575	2720	661	6938	275	1	22	9791	88	410	954
Grid Loci 0:16	58	284	14	732	2719	231	5407	304	29	16	6846	68	585	1108
Grid Loci 1:15	65	358	54	3	3267	755	5279	400	1	15	15855	93	51	80
Grid Loci 1:16	36	282	1	722	2193	192	5304	269	1	10	7497	102	607	1294
Grid Loci 2:15	56	417	37	1	3668	427	5653	395	23	43	19319	199	6	65
Grid Loci 2:16	59	298	9	8	2968	71	5390	271	1	18	10869	119	29	82
Grid Loci 3:15	55	175	23	25	940	362	2668	588	178	57	142828	1212	19	57
Grid Loci 3:16	42	331	7	612	2278	136	5167	316	1	30	13482	130	580	1177
Grid Loci 4:15	69	193	11	1	955	312	2141	529	94	75	131036	1151	48	82
Grid Loci 4:16	60	463	2	89	2559	164	4389	396	1	30	8669	-1	154	261
Grid Loci 5:15	64	435	100	15	2979	801	5808	247	19	9	7907	104	121	81
Grid Loci 5:16	86	389	36	415	2497	99	6568	301	1	39	10329	109	353	663
Grid Loci 6:15	99	882	39	52	5330	139	8166	582	1	26	13873	0	35	78
Grid Loci 6:16	47	373	73	11	2836	341	4464	380	8	39	11344	16	18	65
Grid Loci 7:15	53	394	23	8	2709	281	7816	322	8	22	20429	190	6	76
Grid Loci 8:16	73	400	12	1	3124	171	10913	380	1	22	10426	84	39	129
Grid Loci 8:15	57	292	122	7	2819	1002	11514	453	12	30	26565	212	64	90
Grid Loci 8:16	74	346	11	43	2765	71	11283	460	1	38	11679	147	119	161
Grid Loci 9:15	60	365	74	1	2800	839	9657	341	13	15	13388	143	27	61
Grid Loci 9:16	65	438	8	8	2860	0	10086	429	1	35	8832	43	55	193
Grid Loci 10:15	58	307	108	1	2151	685	6484	438	1	53	76688	725	12	119
Grid Loci 10:16	66	451	16	27	2946	205	8020	408	2	13	7870	60	87	41
Grid Loci 11:15	46	458	79	7	2440	718	5011	307	1	13	6392	59	65	124
Grid Loci 11:16	50	438	5	1	3070	148	7400	317	5	43	5519	24	29	126
Grid Loci 12:15	58	365	61	1	3411	447	6197	369	22	16	5974	94	44	82
Grid Loci 12:16	68	451	33	20	3453	306	12467	460	1	20	5896	52	39	123
Grid Loci 13:15	59	512	3	8	2577	0	7503	423	16	27	5425	97	40	172
Grid Loci 13:16	47	512	5	28	2467	99	3345	228	1	22	2657	1	17	90
<i>In Situ</i> Loci 1 – Black	82	1165	202	254	534	9	1456	665	0	153	1460	1	42	151
<i>In Situ</i> Loci 2 – No Pigment (Replicate 1)	67	1184	49	121	235	28	1348	751	0	77	1096	1	57	107
<i>In Situ</i> Loci 2 – No Pigment (Replicate 2)	58	1533	66	164	286	7	1580	787	0	80	1142	13	60	95

> Element v Spectrum Name	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Cu	Zn
<i>In Situ</i> Loci 3 – Yellow	69	980	52	48	451	-4	1368	614	0	87	9165	72	28	85
<i>In Situ</i> Loci 4 – Yellow (Replicate 1)	74	1002	106	44	357	11	1282	600	-1	62	2684	37	82	108
<i>In Situ</i> Loci 4 – Yellow (Replicate 2)	74	944	84	61	614	13	1382	639	0	89	6357	69	57	39
Ohio Red Clay (Standard) April 2011	70	418	8	29	3042	163	1596	430	28	113	37071	465	71	64
Ohio Red Clay (Standard/Powder) December-1 2011	104	838	6	39	5641	246	2828	787	1	150	53387	509	76	98
Ohio Red Clay (Standard/Powder) December-2 2011	131	951	6	82	5732	187	2620	765	1	172	52385	565	76	152

Table 2 Net Peak Area (NPA) values calculated with standardless fundamental parameters. Data from the K electron shell. Minimum detection limits have not been corrected. Values given in **bold italics** are analyte locations on the control block containing applied pigment (refer to Figure 6).

Multivariate analysis (PCA and cluster) of analytes provides clear evidence for the multiple attenuation effects described for field-based PXRF through the separate grouping of the in situ and other analytes, illustrating the effect of pigment volume within the bulk PXRF analytes, and highlighting the structural (mineralogical and/or grain size) heterogeneity of the Hawkesbury Sandstone shelter matrix. Figures 7 and 8 graphically represent the separate grouping of in situ analytes from the control block and standard. The separate clustering and projections in multivariate space of the three internal standard analytes illustrate the effects of signal attenuation via matrix density. PXRF data from the same standard in two different density states group separately, despite having exactly the same chemistry. The two standard spectra that group together are from the powdered Ohio Red Clay, with the third, separate standard spectrum collected on a solid matrix of the same standard reference material (spectra 36 and 37, and 35 respectively in Figure 7). Separation in both multivariate analyses (cluster and PCA) of the partial experimental motif analytes from the control block (Figure 6) demonstrates the important contribution of pigment volume within PXRF spectra (spectra 21 and 7, and 9 in Figure 7). The separate groupings of Hawkesbury Sandstone without applied pigment in both multivariate analyses, graphically represented by the grey squares in Figure 7, show the mineralogical heterogeneity of the internal shelter matrix for which the control block is a proxy. The clustering of both yellow and black pigment analytes (Figure 7) is consistent with the interpretation of previous archaeometric research: that a composite (clay-based) recipe was used to create various colours of rock art paint on the south Woronora Plateau. This interpretation is further supported by the trends present in groups of indicator elements.

Trends in Indicator Elements

In order to untangle the complex taphonomy of the BR29 rock art panel, groups of elements indicative of various natural and cultural processes were identified and resulting trends in their NPA data examined. Within defined indicator element groups, an overlap exists between the products of geological weathering and the geochemical signatures of rock art production. This is intuitively obvious because rock art pigments are natural minerals (often termed ochres), that are themselves products of geological weathering (Rowe 2001:200; Watchman 1990b). The overlap of geochemical indicators, where specific elements and groups of elements are present in geological weathering and rock art pigments, highlights the need for detailed knowledge of site specific taphonomy for the successful interpretation of PXRF analysis.

One of the primary catalysts for, and geochemical signatures of, cavernous weathering is salt (Lambert 1980; Young 1987; Young and Young 1992). Previous analytic work describing soluble salts in the detrital sands of cavernous weathering alcoves determined sodium, magnesium, sulphur, chlorine, potassium and calcium to be chemical components (Lambert 1980:30). Sodium and magnesium are below the detection limits of the PXRF instrument used in this study. Of the remaining elements, chlorine was the major chemical component identified in detrital sands, making up

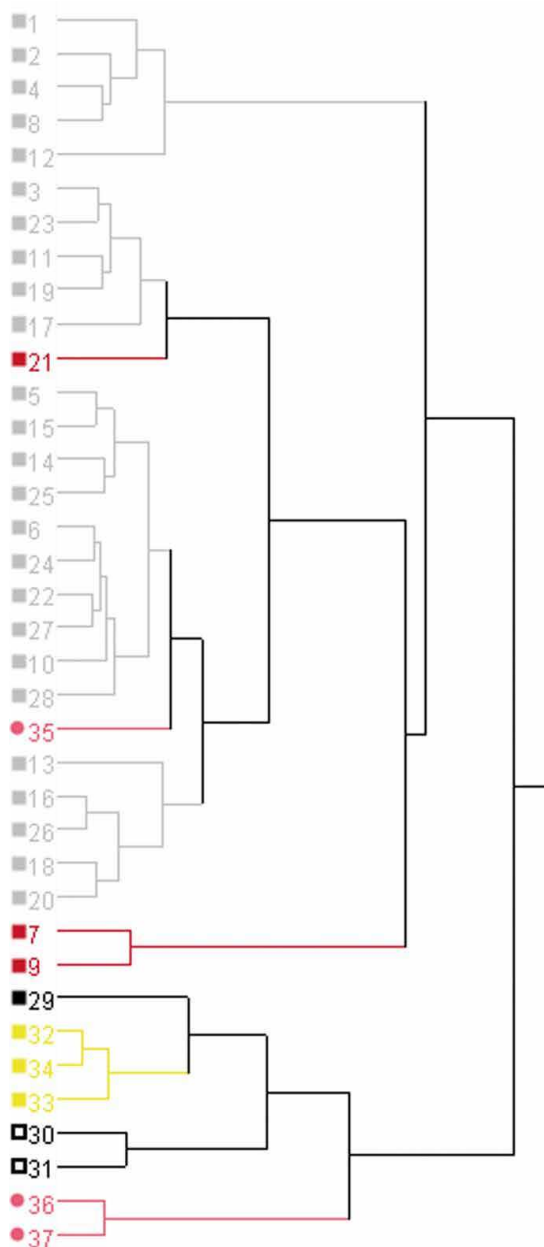


Figure 7 Dendrogram scaled by distance. Key: BR29 analytes (black, open and yellow squares); Ohio Red Clay standard (bright red circles); and control block (no pigment, grey squares/partial red experimental motifs, dark red squares).

~60% of the overall ion composition (Lambert 1980:30). Sulphur, potassium and calcium were minor components of the detrital sands, measuring ~3%, ~1.3% and ~5% ion composition, respectively (Lambert 1980:30). Within the panel at BR29, chlorine, sulphur, potassium and calcium are thus identified as elements indicative of salts and therefore chemical (cavernous) weathering. Measurement of these indicator elements was essential for addressing the primary aim of PXRF analysis at BR29: was detrital (chemically weathered) Hawkesbury Sandstone used as the colour-producing constituent in yellow paint? In addition, PXRF provided a means of examining the presence and relative abundance of cavernous weathering elements not necessarily macroscopically visible (Lambert 1980:31). The results are presented in Figure 9.

Potassium and calcium trend lower at BR29 compared to the control block and standard, whereas sulphur and chlorine trend higher (Figure 9). Sulphur and chlorine are present, and in greater relative abundance, on the art panel than within the sandstone matrix (for which the control block is a proxy). Chlorine, sulphur, potassium and calcium are light elements, with a critical depth penetration of less than or equal to ~30 μm (Potts et al. 1997:33), excluding the (unquantified) impact of attenuation effects. As the lightest elements of the cavernous weathering indicator group, sulphur and chlorine measurements are the most surficial. The results illustrated in Figure 9 therefore indicate that sulphur and chlorine are present at the surface of the panel, throughout rock art pigments and in the shelter substrate. This assertion is supported by the presence and reasonably consistent relative abundance of sulphur and chlorine throughout the panel, including black and yellow pigment analytes and the analyte with no pigment (inset, Figure 9).

The patterning in chlorine and sulphur relative abundances at BR29 is of interest, not only as an indication of a potential catalyst for cavernous weathering, but also as potential constituents of rock art paint. Relative abundance of chlorine and sulphur is reasonably consistent throughout the in situ analytes, though on closer inspection sulphur measured equivalent to chlorine or in a higher relative abundance in spectra from yellow rock art paint. Chlorine is a major chemical component of cavernous weathering (Lambert 1980), while sulphur has been identified as a major chemical component of the yellow rock art paint from the sample located in the present In Situ Loci 3 (Huntley et al. 2011). The similar or higher measurement of sulphur in yellow pigment is consistent with the findings of previous research and indicates that sulphur is both present as an indicator of chemical weathering on the art panel *and* as a constituent in the yellow rock art pigment.

The dispersed and surficial nature of the pigments at BR29 (Figure 5), in addition to the infinitely thin nature of pigment, incorporates the shelter substrate into the bulk analyses. To this end, calcium can be used as a proxy for the contribution of the sandstone shelter substrate in the PXRF spectra. Calcium is a known constituent of the clay-rich cements and feldspars in Hawkesbury Sandstone (Hunt et al. 1977; Twidale 1968; Vinnicombe 1980; Wells et al. 2008). However, calcium was not observed in the previous analysis of rock art pigment on the southern Woronora Plateau (Ford 2006:Appendix 6; Huntley et al. 2011:87). Patterning in Figure 9 suggests that the pigment volume of In Situ Loci 3 (yellow pigment) is the largest measured, as no calcium was observed. This is consistent with this loci being identified previously as the thickest extant pigment application within the panel (see Huntley et al. 2011:88).

All of the matrices analysed are clay rich aluminosilicates with high relative abundances of potassium. While consistent with the overall trend to lower yields in field-based analysis, moderate (rather than low) relative abundance of potassium was measured in situ at BR29 (Figure 10). Potassium is a moderate chemical component of clay. Potassium was identified as a minor chemical component of cavernous weathered detrital sands, however the small fraction (approximately 1.3 weight percent of ions in 50 g of dissolved sand measured [Lambert 1980:30]) is considered below the detection limits of in situ PXRF. Potassium measured in pigment analytes at BR29 is considered to have derived in

small part from the sandstone matrix substrate of the shelter (including the case hardened surface and silica skin) and predominantly from the clay-based rock art paint. The low relative abundance of potassium in Loci 2 (no pigment), compared to the analytes from rock art pigment locations, supports this and is consistent with previous research that concluded clay was a common constituent of rock art paints on the Woronora Plateau (Ford 2006; Huntley et al. 2011).

Consistent relative abundances of aluminium throughout analytes reflects the consistency of the (aluminosilicate) matrices analysed and the mobility of aluminium as a precipitate, making it consistently present within the BR29 case hardened shelter substrate and the silica skin. Conversely, titanium measured a lower relative abundance in situ, consistent with the overall trend. The contribution of the titanium filter in the light element methodology PXRF is assumed to be constant due to the consistency of aluminosilicate matrices. The trend to a lower relative abundance of titanium at BR29 (as described for potassium) is considered to derive primarily from the contribution of clay within compound rock art pigments. Similarly, the very subtle trend in aluminium to lower relative abundance between In Situ Loci 2 and the analytes that contain rock art pigment may represent a greater contribution of aluminium in the clay-based pigments. Given it is the lightest element measured, the very surficial nature of the analysis means that the expression of the trend in aluminium would not be as pronounced as in titanium or potassium (Figure 10).

The strong trend in silicon to markedly higher relative abundance in situ is comparable to the trend discussed for sulphur and chlorine. Just as chlorine and sulphur are indicative of taphonomic processes (cavernous weathering), the trend to high relative abundance of silicon is interpreted as predominantly the chemical signature of the (amorphous) silica skin located across the BR29 ceiling. Previous laboratory analyses identified silicon as a major chemical component of yellow rock at BR29 (Huntley et al. 2011:87). The silicon trend at BR29 is a minor of the trend discussed for potassium (Figure 10). While silicon is a major chemical component of clay, the higher relative abundance of silicon measured for In Situ Loci 2 (no pigment) suggests that there is higher silicon on the shelter substrate (the silica skin). The marked trend to high silicon abundance in situ is complementary evidence for the dispersed and surficial nature of the pigments, and contrasts with the overall trend to lower x-ray yields.

The final indicator element group represents the chemical signatures of precipitous minerals that result in case hardening and accretions (Figure 11). The scant quantitative data available suggest that, as a result of mineral precipitation in sandstones, the exterior of quartz grains becomes coated in kaolinite and/or calcite (Young and Young 1992:74), resulting in clay- and calcium-rich chemical signatures, inconsistent with the calcium pattern observed by PXRF. In my observations of mineralogical segregation/case hardening in Hawkesbury Sandstone via SEM, the coating is preferential to the immediate surface

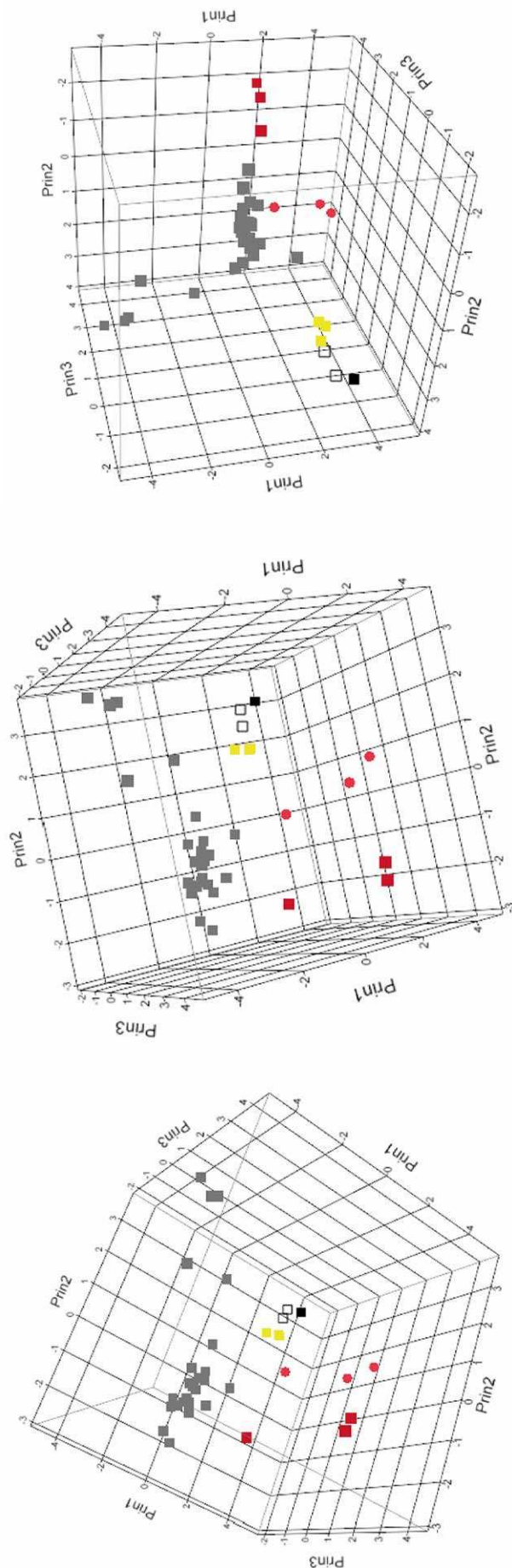


Figure 8 Projections of the same 3D scatter plot – first 3 components of PCA (untreated NPAs). Eigenvalues 4.23, 2.75 and 2.22, respectively. Key = as for Figure 7.

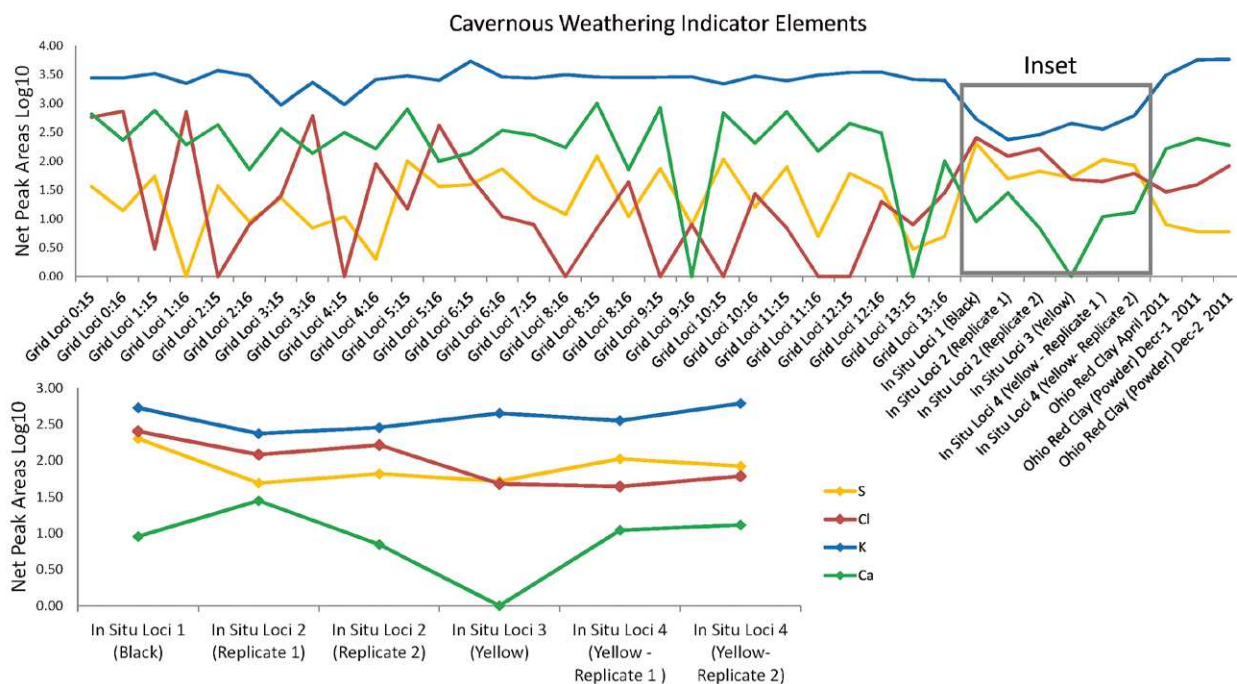


Figure 9 Cavernous weathering indicator elements. NPA PXRF data treated with logarithmic transformation (Base 10).

of the substrate (Figure 1) and contains many other precipitate elements that occur in both the case hardening of the sandstone and in the silica skin which lies on top of it (Figure 11).

Johnson (1974) suggested that precipitation of iron minerals is the primary mechanism for case hardening in Hawkesbury Sandstone. While the overall iron trend at BR29 is again to low relative abundance, there is an obvious trend to higher relative abundance for iron in yellow paint (Figure 11). Trace element concentrations of iron were measured in yellow paint from BR29 by PIXE/PIGE (Ford 2006:A4-1), however iron was not identified as a chemical component of yellow paint via SEM-EDXA, nor were iron-oxide minerals identified through XRD (Huntley et al. 2011:87, 89–90). Iron measured by PXRF is interpreted as being both a chemical component of in situ mineralogical segregation, present (albeit in expectedly minor concentrations) within the silica skin and case hardened surface at BR29, and a constituent of the yellow rock art paint.

Trace element proportions of precipitate elements—manganese, vanadium, chromium, cobalt, copper and zinc—were observed by PIXE/PIGE in yellow pigment at BR29 (Ford 2006:A4-1; Huntley et al. 2011:87). Manganese was also observed as a minor chemical component of black stencil pigment within the MSA (Huntley et al. 2011:87). Overall, in situ manganese, vanadium and cobalt trends observed with PXRF are similar to, though more subtle than, the trend discussed for iron (higher in yellow at BR29 and in the internal standard; see Table 1). The lower relative abundance of manganese and copper for the In Situ Loci 3 analyte, argued to have the largest pigment concentration by volume at BR29, is interpreted as additional attenuation from the high iron content of this particular spectrum.

Copper and zinc have consistently low and moderate respective relative abundances throughout all analytes (Table

1). No discernible pattern was observed, except that these elements do not follow the overall trend to lower relative abundance in situ (Figure 11). As the heaviest of the elements measured by PXRF, copper and zinc have the largest analyte volume (resulting from the deepest critical depth penetration). Variation in copper and zinc relative abundance is therefore less attributable to field-based attenuation effects and more reflective of the heterogeneous mineralogy and mixed grain size of the Hawkesbury Sandstone matrix. The consistency of copper and zinc at BR29 is therefore indicative of the fine-grained, homogenous micromorphology of the case hardened shelter surface (Figure 1), as evidenced by the contrasting fluctuations in copper and zinc measurements in the internal sandstone matrix for which the control block transect is a proxy.

'Visibility' of Indicator Elements with PXRF

A subsidiary aim of this research was to explore, via PXRF, the 'visibility' of elements previously identified by SEM-EDX and PIXE/PIGE. Albeit with different precision, elements of interest (aluminium, silicon, sulphur, chlorine, potassium, calcium, titanium, vanadium, manganese, iron, cobalt, copper and zinc) were measured at qualitative and semi-quantitative resolution by PXRF. The smaller suite of elements observed by PXRF compared to SEM-EDAX and PIXE/PIGE (Ford 2006:Appendix 6; Huntley et al. 2011:87) is due to the detection limits of the technique. Interpretations of PXRF data have therefore been mindful of the very different physical context from which comparative SEM-EDXA and PIXE/PIGE data derive. SEM-EDXA and PIXE/PIGE are surface measurements with small spot sizes and with an analyte surface area of microns, compared to XRF which is a bulk analytic technique with an analyte surface area of millimetres. In addition, bulk measurements with PXRF derive from differential analyte

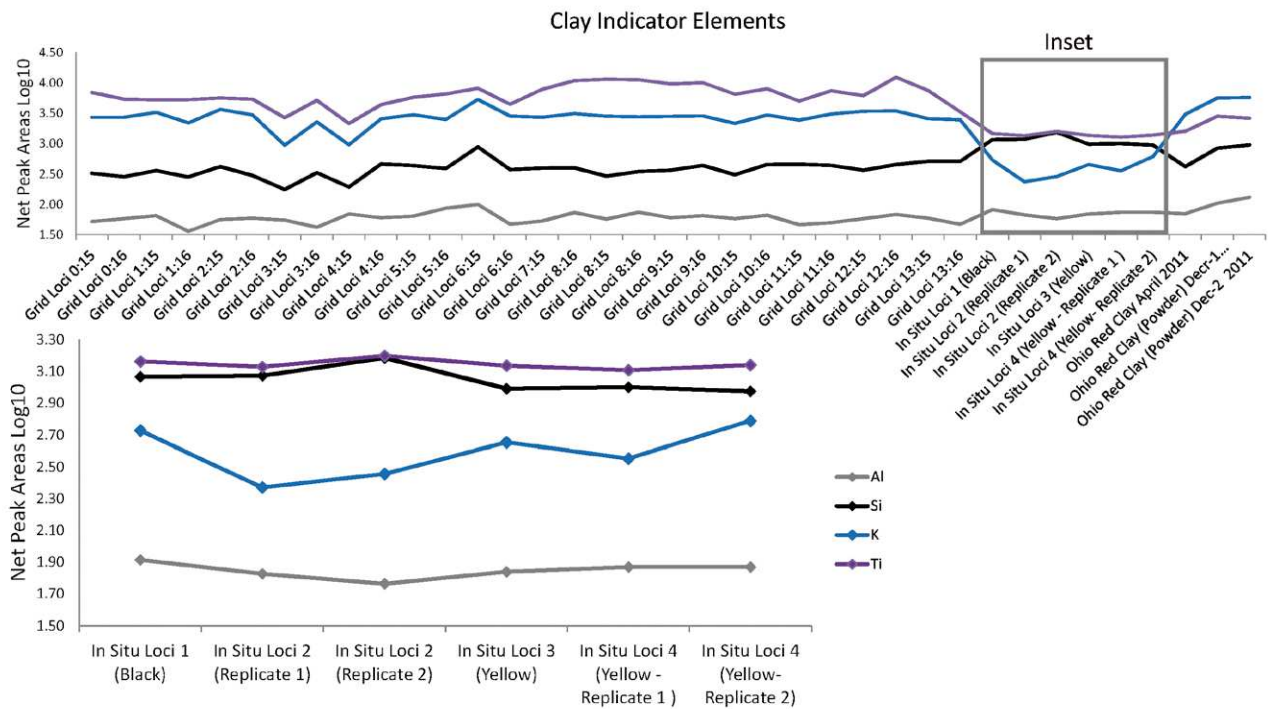


Figure 10 Clay indicator elements. NPA PXRF data treated with logarithmic transformation (Base 10).

volumes across elements by atomic weight; meaning that untreated semi-quantitative data is not directly comparable to SEM-EDXA and PIXE/PIGE results. The types and resolution of geochemical data gained by techniques such as SEM-EDXA, PIXE/PIGE and PXRF mean that the best results will continue to be achieved by analysts with an understanding, not only of the strengths and limitations of different analytic techniques, but also of the types and resolution of data that can best answer particular archaeological research questions.

Archaeological Implications of Geochemical Data from PXRF Analysis at BR29

The trends observed in defined indicator element groups are complemented by the patterns in overall chemical composition. Despite a multiplicity of attenuation effects relating to field based PXRF markedly reducing x-ray yields, data trends have been successfully used to address the research questions posed. Higher relative abundances of clay indicator elements present in in situ yellow and black pigment analytes support the findings of previous research that composite, clay-based paint was used to create the rock art. Exposure of the clay bearing Illawarra coal measures on the eastern boundary and Wianammatta shale remnants in the central west and northeast of the MSA (Haworth 2003:43–45) suggest a local provenance for these paint constituents. Similarly, the trends in indicator elements for cavernous weathering show that, while salts are present throughout the BR29 panel, sulphur is more abundant in yellow paint, supporting previous inferences that sulphur is the yellow colour-producing component within the clay-based paint. Again, locally available yellow detrital sands within the Hawkesbury Sandstone are suggested as the possible source of the colouring agent (Huntley et al. 2011).

Summary

Archaeologists have a responsibility to understand any technique (scientific or otherwise), that may extract information from the material remains of past cultures (Lougoute 1982). This case study contributes to understandings of the archaeological and conservation science potential of ‘novel’ PXRF for rock art applications, while highlighting the complexities of such investigations. Archaeometric researchers should remain mindful of taking a problem and reducing it to manageable portions, applying physical science methods, such as chemical analysis, to a topic reduced to the point that it can be resolved (Plog 1982). The dichotomy posed in this case study (are sulphur and chlorine attributable to cultural phenomena [rock art paint] or are they evidence of taphonomic processes [chemical cavernous weathering]?) was ultimately proven a false separation. PXRF data demonstrates that the chemical composition of rock art pigments represents a complex record of both cultural and environmental processes. Results illustrate the potential power of portable spectrographic techniques for rock art research if applied prudently by an analyst, or analysts, with the requisite knowledge of the archaeometric technique, the specific taphonomic context of the material(s) being analysed, and sufficient knowledge to interpret the archaeological significance of the data generated (Potts 2008:10).

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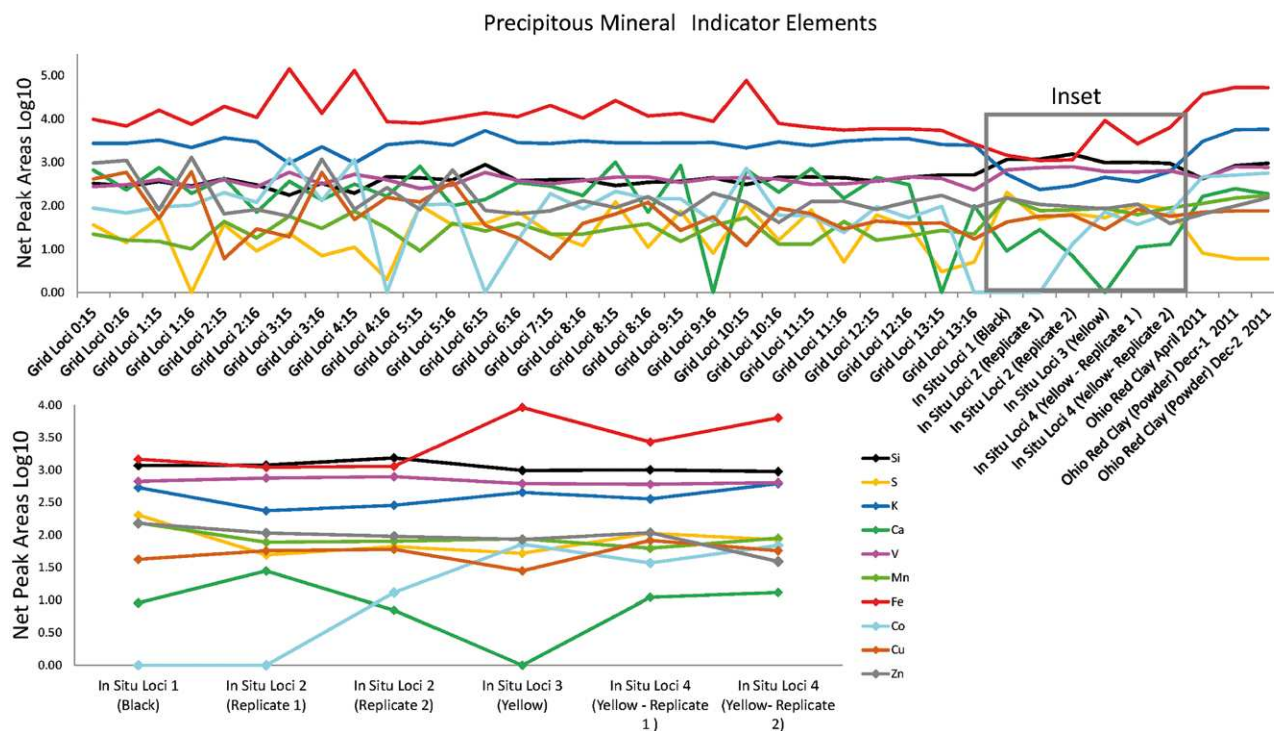


Figure 11 Precipitous mineral indicator elements. NPA PXRF data have been treated with logarithmic transformation (Base 10).

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