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Trace Element Fingerprinting of Australian Ocher Using Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) for the Provenance Establishment and Authentication of Indigenous Art*

ABSTRACT: The expansion of indigenous art and the interest it has generated both at a domestic and international level means large monetary transactions are taking place between art galleries or centers and purchasers. As such, an accurate and conclusive method for provenance determination of traditional indigenous artistic materials must be established that can, if necessary, be used to assist in authentication of artworks. Laser ablation inductively coupled plasma mass spectrometry was utilized for elemental differentiation and provenance establishment of ocher samples. This research was used to develop a robust scientific protocol which facilitates definitive and accurate determination of provenance of Australian ochers and the artworks created using them. Analysis of the results obtained through this study show that the trace metal distribution patterns alone appear to be sufficient evidence to establish provenance of specific ochers, although additional differentiation between ocher samples, using major element distribution patterns, was achieved through the utilization of X-ray analytical techniques.

KEYWORDS: forensic science, forensic chemistry, ocher, aboriginal art, art fraud, laser ablation–inductively coupled plasma–mass spectrometry, provenance establishment, trace elements, X-ray diffraction, X-ray fluorescence

Aboriginal paintings represent some of the worlds oldest art and their tradition, modified through generations of indigenous culture, is at present one of the most fascinating and popular modern investments in the art market. Increased awareness and appreciation of the quality and cultural significance of these artworks, in both the national and international marketplace, means that the price investors are willing to pay for genuine articles has increased substantially in recent years. Unfortunately, this growth in popularity correlates strongly with an equivalent growth in the "Black Market" for these works and in the production of fraudulent copies (1). This is both embarrassing for the artist and for the gallery that may purchase a fraud.

While modern artists favor bulk synthetic materials such as acrylic, oil, and watercolor media, which present their own unique problems for provenance determination, traditional artists, particularly during the last century, used a variety of more natural materials to create their artworks. These materials usually incorporate one or more varieties of ocher, a naturally occurring mixture of iron oxide and clay varying in color from white to dark brown and are often specifically and traditionally sourced with artists using materials from an area of particular cultural or ancestral significance to them (2–5). These materials are each mineralogically, texturally, and chemically unique with a diversity promoting the possibility for unambiguous determination of provenance (6).

Ochers consist primarily of the oxides and hydrated oxides of iron (hematite and goethite), silicon (quartz), aluminium (clay), and

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manganese (pyrolusite, psilomelane, and wad), with potassium, sodium, and lithium alumino-silicate inclusions. As ochers are a weathering product of various intrusive rocks, they will also contain the rare earth suite of elements. The distribution pattern of this suite of elements is often site specific to the region from which the ocher was obtained and this geological uniqueness can provide a further means for establishing provenance of the ochers.

The mineralogical composition and physical properties of ochers correspond to the physical-chemical conditions of weathering, sedimentation, and alteration processes taking place during their formation. These conditions give rise to different types of laterites, ferrolites, ochers and colored clays and soils, all of which may be used in the production of artworks and all of which are represented in early human art (7). Structurally and mineralogically, the characteristics of clay minerals and alumino-silicate minerals are directly related to their genesis and provenance and may be used as significant identification features when investigating historical painting techniques and materials.

Laser ablation ICP-MS is widely used as a powerful analytical technique for solid micro-sampling analyses in various scientific fields. It is a strictly destructive technique; however, damage can be isolated to a small area, $\sim 50 \ \mu m$ in diameter. This technique has not been previously utilized for the provenance establishment of ocher. As no reference methodology is available, it is important to first establish a robust and reproducible analytical protocol. The final sample preparation method must be able to achieve a complete breakdown of the ocher without the potential introduction of contamination or the loss of analytes. International research established that determination of provenance of mineralogical material, including ocher, is possible using various analytical techniques (8.9). Suitable techniques include neutron activation analysis and scanning electron microscopy (10,11) (fixed with energy dispersive spectroscopy [SEM-EDS] and wavelength dispersive spectroscopy [SEM-WDS]). Furthermore, particle-induced X-ray emission

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spectroscopy (12–14), powder X-ray diffraction (15–18), electron probe microanalysis (18), energy dispersive X-ray fluorescence (19,20), inductively coupled plasma mass spectrometry (ICP-MS) (21,22), and various spectroscopic methods (Raman, Fourier Transform-Infrared) (23–30) may also be employed for elemental characterization and provenance establishment purposes.

Laser ablation-ICP-MS has the added advantages of requiring minimal sample preparation time, minute sample size, and low detection limits. This has a direct application for analysis of pigment directly on artwork, as LA produces extremely small sampling craters and consequently can be used without significantly damaging a painting. It is envisaged that LA-ICP-MS will be used to associate pigments on artworks to specific areas or schools of art and to specific artists thus assisting in determination of provenance artworks directly (31–33).

Research detailed in this paper was undertaken to develop a robust scientific method to facilitate determination of provenance of Australian ochers and the artworks created using them. Ocher of known provenance was analyzed using LA-ICP-MS and data processing achieved using a variety of statistical and chemometrical procedures including ternary plots, principle component analysis (PCA), chondrite normalization, and in-house search-match procedures. Results were compared and plotted to illustrate population separation and identification of samples based on their chemistry. These differences were identified, both between regions and within a single region, to ascribe provenance to artworks produced using the individual ochers.

Experimental

Sample Collection and Preparation

The ocher samples required for this study were donated by various communities from northern Western Australia, the Northern Territory (NT), and the Art Gallery of Western Australia (AGWA) (Fig. 1). Each ocher sample was powdered using both agate mortar and pestle grinding and ring-milling, using a tungsten carbide mill. Manual grinding, using an agate mortar and pestle, mimics the method by which indigenous artists prepare their paint materials, while ring-milling reduces the original mineral sample to a powder far more efficiently. In both cases, the sample was ground to pass through a 63-µm screen prior to further analysis. These two methods were then compared to determine whether the grinding method had any effect on the trace elemental distribution pattern of the ocher.

Each sample was designated a sample code: Warmun (W), NT, and AGWA. The Warmun samples were assigned numbers based on the grinding method they were subjected to. One ocher sample, Warmun 7 (W7) was used for testing the effect of different grinding methods on the elemental distribution pattern of the ocher. These samples were labeled RG1–RG18 for ring-milled ocher, while samples RG19–RG36 were powdered using an agate mortar and pestle.

Laser Ablation ICP-MS

In LA-ICP-MS protocols, a laser is used to volatilize (ablate) a solid sample prior to the introduction of the ablated material into the plasma. This method facilitates the direct introduction of solid material into the plasma and effectively eliminates time-consuming sample preparation procedures and the associated introduction of contamination. The precision of LA-ICP-MS is dependent on signal fluctuations as a result of pulse-to-pulse variations in the amount ablated and hence the amount of analyte reaching the plasma (34). An LSX 200 (CETAC; Omaha, NE) laser system coupled to a Plasma Quad III (Thermo-Elemental, Winsford, Cheshire UK) ICP mass spectrometer was used for all experiments.

Sample Analysis

Ocher Samples-Thirty-six samples of ocher, collected from across northern Western Australia and the NT, were mounted on



BlutacTM on Perspex disks and analyzed using LA-ICP-MS. Each subsample was analyzed for 54 elements using an ablation time of 90 sec, undertaking triplicate segmented line scan acquisition with an energy level of 55%, pulse rate of 10 Hz, and a spot size of 100 μ m. A National Institute of Standards and Technology 610 glass standard was used for standardization and setup purposes and to correct for in-run drift (35). Data were corrected for background using an instrumental gas blank.

Additives such as locally sourced water and Selleys Aquadhere[®] PVA glue, which are combined with powdered ocher to produce "paint" were also analyzed individually. Additionally, dried paint samples used by artists and containing various Warmun ochers were also analyzed. From these analyses, a trace element finger-print of the material being applied to the canvas was obtained; ensuring the elemental signature of the ochers alone was being identified and used for provenance establishment.

Artwork Samples—Twenty-six samples of ocher were obtained from eleven different artworks. Each pinhead-sized sample was mounted on BlutacTM on Perspex disks and analyzed using LA-ICP-MS. Each subsample was analyzed for 54 elements using an ablation time of 90 sec, undertaking duplicate segmented line scan acquisition with an energy level of 55%, pulse rate of 10 Hz, and a spot size of 100 μ m. The 26 ocher samples were procured from indigenous artworks, which were originally created on the Tiwi Islands off Australia's northern coastline. The ochers used in these artwork samples were compared directly with the ocher samples obtained from that region.

Results

Analysis of the data indicates that, with the exception of cobalt and tungsten, the ring mill grinding method employed to powder the ochers had no overall effect on their trace element composition. The relative increase in cobalt and tungsten concentrations in samples that have been ring-milled, as opposed to ground in a pestle and mortar, is illustrated in Fig. 2. This contamination is to be expected as incorporation of abraded material from the ring mill results in increased concentrations of these metals. However, the increased concentrations of these metals do not cause problems with the provenance establishment mathematical protocols and do not lead to false provenance identification, as tungsten and cobalt are not used for provenance establishment purposes. Elemental data for the PVA glue samples indicate that the majority of analytes are present at concentrations below 1 ppm. At these concentrations, the detection limits of the instrument are reached and thus the results are neither reproducible nor reliable. Although the data for trace metal concentrations in PVA glue were relatively imprecise, the concentrations were so low that it was possible to state that if glue was included in the analysis of ochers from paintings, it would not affect the element association profile of the pigment. Therefore incorrect determination of provenance of the ocher would not occur. Consequently, contamination of the inter-element association patterns of the ochers by incorporation of elements present in the PVA glue has no significant effect on either the trace element content of the ocher or on pattern recognition and interpretational protocols.

Replicate samples of local water were also analyzed to determine if they had the potential to contribute significant levels of contaminating trace metal to the trace metal content of artworks. The data were extremely reproducible. As with the PVA samples, the majority of elements were significantly below the instrumental detection limits and therefore will not significantly affect the inter-element ratios present in an ocher sample taken from an artwork. The exception to this is with respect to elements such as strontium and barium. However, these elements are not used for discrimination and provenance establishment as they are present at high levels in all ochers. Therefore, if an ocher sample from an artwork is analyzed and the data compared with the data for the original ocher, the inter-element association patterns for both will essentially be identical.

Reproducibility Studies

Laser ablation was conducted on all ocher samples. The LA-ICP-MS results obtained, indicated that it would easily be possible to provenance individual ocher sites using this technique. The application of LA-ICP-MS for the analysis of ocher samples is illustrated in Fig. 3. Here, trace element inter-element association patterns for Warmun ocher sample W4 have been plotted. Data obtained using LA-ICP-MS is less precise than data from traditional ICP-MS solution analysis because LA-ICP-MS is used for the analysis of small areas of a sample or small samples in their own right. Consequently, any variations in mineralogy within the sample would be more apparent in LA-ICP-MS data than within solution data, as the latter is used for analyzing a much larger



FIG. 2—Elemental distribution pattern of Warmun ocher sample 1 (W1) subjected to different grinding methods and analyzed using solution ICP-MS. Differences in tungsten and cobalt concentrations are noted.

Trace Elemental Composition of Warmun Ochre 4 (W4) Analysed by LA-ICP-MS



FIG. 3—Elemental distribution pattern of Warmun ocher 4 illustrating reproducibility of the LA-ICP-MS data.

sample where, because of the large mass of sample used, homogeneity does not become an issue. However, the reproducibility indicated by overlaying the trace elemental signatures for each replicate Warmun sample suggests that this technique has excellent application for the analysis and provenance establishment of ocher samples.

Search/Match Comparability Index

The search/match procedure was developed by Watling et al. (35) and centers around the concept of quickly identifying differences between samples using the raw count data for the isotopes instead of establishing difference between the absolute concentration of the elements. Samples that have a high statistical comparability using the search/match protocol are plotted against each other, providing a visual comparison of the concentrations or raw counts of the elements in the relevant ochers to confirm their relative comparability as determined by the search/match protocol.

A comparability index value, as a percentage fit of the search sample to samples in the database, is then assigned to the relative comparison of each sample in the database. The percentile figure is not absolute and is based only on an assumption that the best comparability must be 100% (this is the comparability of the search reference sample to its original entry in the database) and 0% for the worse comparability of a sample to the reference. While the comparability indices are not absolute, as a screening technique this method works extremely well. The percentile fits are plotted for each sample with the data plot indicating convex breaks in slope, which represent the start of new subpopulations in the database. Raw count data of the highest comparable samples are then subjected to additional inspection using visual comparison of the spectral patterns. The samples showing a high degree of comparability are then subjected to more conventional statistical examination to confirm the interpretation.

Given that all ocher samples analyzed so far can be discriminated from each other, there is significant potential for the development of a useable search/match database. For this to be useable, it must be possible to analyze an unknown sample of ocher and compare it to a series of reference samples to determine the provenance of that sample, if a database of equivalent sample material already exists, or that real similarities and differences exist between samples. A search/match protocol (32) was programmed in Microsoft Excel to allow cross comparison of ocher samples collected from various sites within Australia. Percentile comparability results obtained using the search/match protocol are detailed in Table 1. The database of Australian ochers was searched using the elemental data obtained for sample RG1, a ring-milled sample of Warmun ocher 1 (W1). This ocher sample, like all others, had been both ring-milled and mortar ground and both sets of data are present in the database. As expected, the best fit for each replicate of W1 was either with RG1, RG2, and RG3 (ring-milled triplicate samples of W1) or with RG19, RG20, and RG21 (mortar and pestle ground samples triplicates of W1). As all W1 ocher samples were found to have a high percentile comparability, we can conclude that the grinding method does not affect the elemental distribution pattern of an ocher. As such, samples sourced form the same area, despite differences in powdering preparation, will give a closely matched elemental distribution pattern.

The comparability test also determined that samples RG13, RG14, and RG15 were from the same population as the previous six. These samples were triplicate ring-milled samples of Warmun ocher 8 (W8). Inter-elemental association patterns of these three ochers were plotted with reference to the three best fits to the test sample (RG1, RG2, and RG3) and differences between the two datasets were identified. This confirmed that, although closely related, it was possible to distinguish between samples from the two separate regions. A break is observed at sample RG21 in the data (Fig. 4). This correlates to a change in the population from sample RG14 onwards. Sample RG20 is situated at the break in slope and can therefore potentially belong to both populations. However, comparison of the spectral plot data (Fig. 5) confirms that sample RG20 belongs to the previous sample series and not to samples associated with RG14.

TABLE 1—Closest 10 matches for search/match macro of ocher sample W1.

Sample	Percentage match (%)
RG1	100.00
RG2	99.33
RG3	98.61
RG19	98.10
RG21	97.95
RG20	96.83
RG14	95.23
RG15	95.13
RG13	94.76



FIG. 4—Comparability plot (a) obtained by testing sample RG1 using a search/match protocol, (b) comparability plot of the first 10 samples, and (c) the percentages obtained from this analysis.

However, these plots and the search/match protocol they represent may not be considered a statistically adequate means of verifying sample co-provenance. Accordingly, all samples that are within populations bounded by slope breaks must be examined to verify the coincidence of elemental profiles before comparability data can be acknowledged as accurate. Further statistical analysis, such as PCA may also be used to corroborate the comparability data. Therefore, while the potential to use the search/match protocol described, as a prescreening technique to search a database, is perfectly valid, further corroboration of conclusions may also be undertaken using a more conventional statistical approach such as a PCA.

Ternary Diagrams

Ternary plots represent the direct comparison of the relationship between three components in a system. The ternary plots allow diagrammatic distinction of sample regions based on a three-element combination. Watling has previously established the mechanism by which ternary plots can be utilized for data population separation (32). Although the Warmun and AGWA samples were tightly grouped, this plot allowed the two regions to be separated based on an apparent trend between the association of rubidium and cesium with respect to palladium. This trend may be the result of a fundamental association of these two elements in the geological process.

The lack of separation of Warmun samples from those supplied by AGWA, using this plot, does not mean that these two sets of samples are co-provenanced. By applying a different set of analytes, it is still possible to separate samples from the different areas into specific populations and thus confirm the use of the ternary plot system for generic area discrimination for ocher samples. Using the ternary plot system, based on the number of elements determined (54) in this study, it is possible to have 24,804 different combinations of three elements. Using these, populations that are not related will move relative to each other in the body of the diagram. Populations that are related to each other will remain co-positioned in the body of the plot.

However, for certain element combinations, there will be occasions where two populations plot on top of each other even though they are from different areas. This is the case for the Warmun and AGWA samples in Fig. 6. The separation of the three distinct study areas is confirmed diagrammatically in Fig. 7. Therefore, by combining data from Figs. 6 and 7, it is possible to generically separate all three-study areas. A distinct trend between the association of rubidium and cesium with respect to palladium (Fig. 7) was also observed. By using a variety of combinations of three elements, it is possible to use ternary association diagrams to generically separate samples from the three study areas.

As determination of provenance the ocher samples was proven possible, further statistical analysis was required to ensure the



FIG. 5—Comparison of the spectral plots for two populations to illustrate differences between populations.



Ternary plot illustrating population separation

FIG. 6—Ternary plot illustrating population separation using a ⁹⁰Zr, ¹⁰⁸Pd, and ¹¹¹Cd combination. Obvious grouping is still present with both the Warmun and Art Gallery ochers.



FIG. 7—Ternary plot illustrating population separation using a 65 Rb, 108 Pd, and 133 Cs element combination.

robustness of the data. PCA offers the potential for an unambiguous visual distinction between samples. Elemental data are taken and linearly combined to produce independent (orthogonal) vectors, which can be plotted in two-dimensional (2D) diagrams, making the process more efficient.

While ternary plots are capable of being used to discriminate between ocher samples, PCA diagrams provide a more statistically sound approach in establishing that discrimination can be achieved. If after all reasonable manipulations of data populations remain together, the logical conclusion is that they were originally part of the same population and samples are therefore co-provenanced. This overcomes both data dependency and ill conditioning of the data. PCAs were conducted on the LA-ICP-MS data obtained from analysis of various ocher samples, using selected elements expected to show the greatest variation between samples. A PCA can either be used for correlation or covariance output. Correlation mode is used, meaning the data are both mean centered and root mean sum of squares scaled, resulting in all the data having a mean of 0. This essentially weights all system components equally. With covariance analysis, the data are only mean centered. To avoid particular elements affecting the data more than others, the PCAs were conducted using correlation mode.

Distinguishing Between Subpopulations in the Same Region

The entire LA-ICP-MS dataset for the Warmun ochers was analyzed using PCA. The correlation between certain elements was strong. These elements include ⁴⁵Sc, ⁸²Se, ⁸⁵Rb, ¹⁰⁸Pd, ¹⁷⁸Hf, ²³²Th, and ²³⁸U and they are distinctive discriminators for this area. The data for these elements were then used to conduct further PCA on specific ring-milled samples of Warmun ochers, which originated from three different regions in the area. The data plot indicated that the three groups could be unambiguously separated and that it was possible to subdivide larger areas using this technology. Plotting the PCA results (Fig. 8), confirmed a clear separation of the Warmun ocher samples into the three regions of Fitzroy Crossing (samples RG7, RG8, and RG9 from W4), Warmun (samples RG10, RG11, and RG12 from W7), and Springvale Station (samples RG16, RG17, and RG18 from W9) could be achieved.

Classification of Unknowns Using PCA

The data for the Warmun ocher 9 (W9) was used to test the robustness of sample provenance classification methods. The material had been ground using a mortar and pestle (sample RG35) and results were used as an unknown to determine whether it would be possible to relate this sample back to its area of origin and associate it with samples RG16, RG17, and RG18 which came from the same region.

The PCA discriminate plot (Fig. 8) illustrates that sample RG35 was correctly classified as being closely related to, or from the same region as, samples RG16, RG17, and RG18. Therefore, LA-ICP-MS and the appropriate statistical methods, make it possible for ocher samples to be provenanced. Furthermore, samples collected from only 300 km apart can be distinguished from one





FIG. 8—PCA discriminate plots of the data, using the elements boron, scandium, selenium, rubidium, palladium, hafnium, thorium, and uranium, illustrating separation of the Warmun ocher 9 samples into three populations. An unknown (RG 35) sample, a replicate of previously entered data, being classified as a particular population.

Distinguishing Ochers within a Population

The LA-ICP-MS data for ocher samples W1, W3, and W4, both powdered using a ring-mill and mortar and pestle, were analyzed by using PCA. These samples all originated from Fitzroy Crossing, in northern Western Australia.

The PCA was used to determine the possibility of provenancing ocher within an area (Fig. 9). The variation of elemental composition within ochers from a single region provides evidence that provenancing can be achieved and the area of sample origin narrowed down further, to within 2500 km².

Chondrite Normalization

The primeval crust of the earth had a recognized rare earth element distribution pattern, which can now be seen only in stony meteorites or chondrites. This pattern is altered by geological processes, metamorphic events, and recrystallization partitioning. This existing ratio can be normalized to the original crustal relationship to give a chondrite normalized pattern which, when compared between areas, can assist in identification of provenance and give an indication of the geological history of the region.



FIG. 9—PCA discriminate plot depicting separate populations within a single region. This allows area of provenance to be reduced to a specific site.

Large geographical areas, such as Warmun in northern Western Australia, make it possible to find chondrite normalized rare earth patterns representing a number of different geological environments. When plotted, the chondrite normalized data for Warmun samples W1 and W9 exhibits completely different patterns. (Figs. 10 and 11). This kind of geological information makes it possible to develop refined and site-specific identification profiles that can be used with chemical data to accurately locate specific collection sites within a general area. The utilization of chondrite normalization, as well as comparability tests proved useful for differentiating both between samples and between regions, based on raw data alone. Determination of provenance of these ochers is therefore possible.

A mock fraud investigation was carried out to test the validity of the study procedures for provenancing fraudulent artwork. A sample of Tiwi Island artwork was analyzed together with ochers from various regions across northern Australia. The Tiwi islands comprise Bathurst Island and Melville Island off the northern coast of Australia. It follows that the materials used on these artworks are of the same origin and thus may be linked through their inter-elemental ratios determined using this technique. Each ocher sample was analyzed in duplicate and extremely good reproducibility was achieved (Fig. 12). As the reproducibility of the technique had been previously established, duplicate scans on each sample were sufficient to obtain representative trace element distribution patterns. As with the other data samples, a search/match protocol was used to determine how comparable the ochers from the Tiwi region were with the artwork sample. From these analyses, the elemental distribution patterns of both the Tiwi Island ocher samples and samples from the artworks were found to match. This proves that they originated from the same source and confirms the application of LA-ICP-MS for establishing provenance of artworks through ocher analysis.

Conclusions

Ochers sourced from different regions in Australia have unique and distinguishable trace metal signatures. A high level of data reproducibility, identified in determining these trace metal compositions using LA-ICP-MS confirms this technique as an excellent analytical tool for this purpose. Furthermore, this analytical reproducibility is proof that only a single sample of ocher from a specific site is required to obtain accurate and representative trace elemental concentrations for ochers from that site. As such, it follows that a single fragment of ocher sampled from an original artwork is sufficiently homogenous for data obtained from its analysis



FIG. 10—A graphical plot of chondrite normalized data plotted for sample Warmun 1 (W1) powdered using an tungsten-carbide ring-mill. The same pattern appeared for the Warmun 1 ocher that was powdered using a mortar and pestle.



FIG. 11—A graphical plot of chondrite normalized data plotted for sample Warmun 9 (W9) powdered using an agate mortar and pestle.



FIG. 12—A log plot for the duplicate samples of ocher taken from artworks, analyzed by LA-ICP-MS.

to be used legitimately to establish geographical origin. The artwork samples could be related back to ocher samples of the same mineralogy and geological origin.

A database of ochers has also been initiated. Although more samples from more regions around Australia are required before it can be put to practical use, ultimately it is hoped that by using this database, ochers may be related back to a particular geographical origin within Australia and artworks can be unambiguously associated with a particular artist. As the conclusions drawn from this research are limited to the samples investigated, studies are required to investigate and confirm the nature of the organic constituents of the ocher paints, pigments, fixatives, and artist specific additives to ensure accurate and comprehensive provenance determination of artworks. Isotopic analysis, via high-resolution MS, requires investigation as it may have potential for provenancing ocher.

Given the protocol for establishing provenance of ocher samples and in turn artwork samples has been established, the potential to establish a comprehensive reference database exists. This database, centered on the ochers' specific trace elemental distribution pattern, would facilitate retrospective searching and provenance establishment of existing artworks. The specific "fingerprint" of the ocher would be stored electronically and compared with similar "fingerprints" from spatially associated equivalents to establish regional "fingerprints."

In this way, it is possible to identify regional variations in natural pigments and relate these back generically to regional art centers. This database could then be used to determine if the ocher on a particular artwork came from the area used by that artist. A specific fingerprint could then be used as evidence of the ocher's identity and origin and its potential association with a regional school of art and

artist. Once established, the identity of the ocher may assist the legal process by providing supporting evidence in fraud investigation.

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References

- 1. Vanstone A. Art crime, justice and customs ministry. Canberra, ACT: Australian Institute for Criminology, 1999.
- 2. Morphy H. Aboriginal art. London: Phaidon Press, 1998.
- Kleinert S, Neale M. The Oxford companion to aboriginal art and culture. London: Oxford University Press, 2000.
- 4. Caruana W. Aboriginal art. London: Thames and Hudson, 1993.
- Michaels E. Bad aboriginal art: tradition, media and technological horizons. New South Wales: Allen and Unwin, 1994.
- Ridges M, Davidson I, Tucker D. The organic environment of paintings on rock. In: Ward GK, Tuniz C, editors. Advances in Dating Australian rock-markings. Melbourne: Australian Rock Art Research Association, 2000;61.

- Hradil D, Grygar T, Hradilova J, Bezdicka P. Clay and iron oxide pigments in the history of painting. Appl Clay Sci 2003;22(5): 223–36.
- Zackheim O, Illani S, Weinstein E. Provenance of ochre from the Natufian assemblages of el-Wad, Eynan and Hayonim. Proceedings of the Annual Meeting of the Israel Geological Society; 1999 March 8–10; Dead Sea, Israel. Jerusalem: Israel Geological Society, 1999;97.
- Weinstein EM, Ilani S. Provenance of ochre in the Natufian layers of el-Wad Cave, Mount Carmel, Israel. J Archaeol Sci 1994;21(4):461.
- Popelka RS, Robertson JD, Glascock MD, Descantes C, Shergur J. New directions in archaeometry utilizing neutron actitivation analysis (NA). Proceedings of the 228th American Chemical Society National Meeting; 2004 Aug 22–26; Philadelphia, PA. Washington, DC: American Chemical Society, 2004.
- Ajo D, Casellato U, Fiorin E, Vigato PA. Ciro Ferri's frescoes: a study of painting materials and technique by SEM-EDS microscopy, X-ray diffraction, micro-FT-IR and photoluminescence spectroscopy. J Cult Herit 2004;5:333–48.
- 12. David B, Clayton E, Watchman A. Initial results of PIXE analysis on Northern Australian ochres. Aust Archaeol 1993;36:50–7.
- 13. Menu M, Walter P. Prehistoric cave painting PIXE analysis for the identification of paint 'pots'. Nucl Instrum Meth B 1992;64:547–52.
- 14. Olsson J, Calligaro T, Colinart S, Dran JC, Lovestam N, Moignard B, et al. Micro-PIXE analysis of an ancient Egyptian papyrus: identification of pigments used for the "Book of the Dead". Nucl Instrum Meth B 2001;181:707–14.
- Na N, Ouyang Q, Ma H, Ouyang J, Yanping L. Non-destructive and in situ identification of rice paper, seals and pigments by FT-IR and XRD spectroscopy. Talanta 2004;64:1000–8.
- Pomies MP, Morin G, Vingnaud C. XRD study of the goethite-heamatite transformation: application to the identification of heated prehistoric pigments. Eur J Inorg Chem 1998;35(1):9–25.
- Wilen JE. Mineralogical analysis of red ochre samples from four sites in Knight's Valley, California; XRD and its potential for preliminary identification and sourcing of hematitic deposits. Geol Soc Am Bull 2000;32(7):275.
- Klepka M, Lawnicak-Jablonska K, Jablonski M, Wolska A, Minikayev R, Paszkowicz W, et al. Combined XRD, EPMA and X-ray absorption study of mineral ilmenite used in pigments production. J Alloy Compd 2005;401:281–8.
- Szokefalvi-Nagy Z, Demeter I, Kocsonya A, Kovacs I. Non-destructive XRF analysis of paintings. Nucl Instrum Meth B 2004;226:53–9.
- Caneva C, Ferritti M. XRF spectrometers for non-destructive investigations in art and archaeology: the cost of portability. Proceedings of the 15th World Conference on Non-destructive Testing; 2000 October 15–21; Rome. Hamilton, Canada: International Committee for Nondestructive Testing, 2000.
- 21. Gratuze B. Obsidian characterisation by laser ablation ICP-MS and its application to prehistoric trade in the mediterranean and the near east: sources and distribution of obsidian within the Aegean and Anatolia. J Archaeol Sci 1999;26:869–81.
- 22. Hill SJ. Inductively coupled mass spectrometry and its applications. Sheffield: Sheffield Academic Press, 1999.

- 23. Bikiaris D, Sister Danilia, Sotiropoulou S, Katsimbiri O, Pavlidou E, Moutsatsou AP, et al. Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies: application on wall paintings at Meteora and Mount Athos, Greece. Spectrochim Acta A 1999;56:3–18.
- Burgio L, Clark RJH, Sheldon L, Smith GD. Pigment identification by spectroscopic means: evidence consistent with the attribution of the painting Young Woman Seated at a Virginal to Vermeer. Anal Chem 2005;77:1261–7.
- Burgio L, Clark RJH, Theodoraki K. Raman microscopy of Greek icons; identification of unusual pigments. Spectrochim Acta A 2003;59:2371– 89.
- Civici N, Demko O, Clark RJH. Identification of pigments used on late 17th century Albanian icons by total reflection X-ray fluorescence and Raman microscopy. J Cult Herit 2005;6:157–64.
- Clark RJH. Pigment identification by spectroscopic means: an arts/ science interface. C R Chimie 2002;5:7–20.
- Clark RJH, Lucia Curri M. The identification by Raman microscopy and x-ray diffraction of iron-oxide pigments and of the red pigments found on Italian pottery fragments. J Mol Struct 1998;440:105–11.
- Mortimore JL, Marshall LR, Almond MJ, Hollins P, Matthews W. Analysis of red and yellow ochre samples from Clearwell Caves and Catalhoyuk by vibrational spectroscopy and other techniques. Spectrochim Acta A 2003;60:1179–88.
- Edwards HGM, Newton EM, Russ J. Raman spectroscopic analysis of pigments and substrata in prehistoric rock art. J Mol Struct 2003;551:245–56.
- Smith KM, Horton K, Watling RJ, Scoullar N. Detecting art forgeries using LA-ICP-MS incorporating the *in situ* application of laser-based collection technology. Talanta 2005;67:402–13.
- 32. Watling RJ, Taylor JJ, Shell CA, Chapman RJ, Warner RB, Cahill M, et al. The application of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for establishing the provenance of gold ores and artefacts. In: Young SMM, Pollard AM, Budd P, Ixer RA, editors. BAR S792 metals in antiquity, vol. 6. Oxford: Hadrian Books Ltd, 1999;53.
- Horton K. Provenance establishment of pallet paints with respect to the identification of forged art (Dissertation). Perth, WA: Curtin University of Technology, 2003.
- 34. van de Weijer P, Baeten W, Bekkers M, Vullings P. Fast semi quantitative survey analysis of solids by laser ablation inductively coupled plasma mass spectrometry. J Anal Atom Spectrom 1992;7:599–603.
- Watling RJ, Lynch BF, Herring D. Use of laser ablation inductively coupled plasma mass spectrometry for fingerprinting scene of crime evidence. J Anal Atom Spectrom 1997;12:195–203.

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