DOI: 10.1007/s10967-006-6836-x *Journal of Radioanalytical and Nuclear Chemistry, Vol. 272, No.1 (2007) 17–27*

Trace element characterization of ochre from geological sources

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(Received April 19, 2006)

As evident from archaeological excavation, ochre was widely used for ceremonial, mortuary, and other purposes around the world. However, the ancient meaning and procurement practices of ochre are not well understood. This study examines the variation in the major, minor and trace element patterns of ochre from iron oxide sources in southeastern Missouri to better understand the differences that may occur within and between sources. Samples were analyzed by instrumental neutron activation analysis (INAA), X-ray fluorescence spectroscopy (XRF), and the data were interpreted by Pearson's linear correlation and multivariate analysis. The data indicate geochemical trends in ochre that satisfy the provenance postulate.

Introduction

Ochre and other iron oxide pigments were important and highly prized materials in many ancient cultures. They were used for both ceremonial and mortuary purposes and played an important role for cultural expression. Pigments made from ochre are often discovered as long-lasting colorful remains in archaeological contexts, from rock art to ochre-dusted bones in burials, to ancient paint artist palettes or decorated pottery.[1,2] These striking minerals are found in the famous rock art paintings such as the prehistoric cave art at Lascaux, France,[3,4] to modern paintings and frescoes.[3,5] In addition, iron oxide pigments can be found decorating clothing hides,[6] as pigments in ceramic slips and glazes,[7,8] and they are found frequently dusted over bones in burials in many parts of the world (including the Paviland ochres found in Great Britain).[9] A general ethnographic overview of decorative, medicinal and ceremonial uses of ochre in North America has been compiled in ELLIS et al.[10]

While some of the cultural implications of ochre are known based on the use of raw minerals and artifacts found in archaeological sites, very little is known about the procurement and processing of ochre by ancient peoples. It is possible that ancient people sought particular sources of ochre for specific characteristics, and that ochre was traded along ancient exchange routes. In addition, people may have processed the iron-based pigment to obtain a particular particle size, or added binders as part of the pigment processing.[4] Given their prominence and prevalence in archaeological sites, it is necessary to understand the chemistry of ochre before engaging in studies of artifact sourcing and ancient technology.

The definition of ochre is vague, as ochre can vary in mineralogical content from a pure iron oxide to a diluted mixture of iron oxide and other minerals. Ochre is typically composed of two common forms of iron oxide (Fe_2O_3 and FeO), mixed with clays, silicates, and other minerals and they range in color from deep purple to light yellow, but the most common color is a blood red.[11] Red ochre is made up of the mineral hematite and is 70 weight percent Fe. Yellow ochre (goethite or limonite) has the general chemical formula $FeO(OH)_x$ where the iron content can vary by hydroxide content but is nominally 63 weight percent Fe.[12] ROBERTSON[11] defines ochre as "ferruginous oxides and hydroxides, generally manganese-poor, which are spatially and genetically associated with sulphide orebodies". Ochre is found in a variety of geological contexts including "sedimentary, igneous, metamorphic rocks, and weathered products, soils and unlithified sediments derived from any of these rock types".[10] Because ochre and other minerals associated with hematite and goethite are so ubiquitous in archaeological contexts and occur in many types of formations, understanding the geochemistry of the sources is vital for understanding the archaeological record.

For other artifact types such as ceramics and obsidian, elemental analysis has been used to understand the fundamental geochemistry of the raw materials as well as the finished artifact.[13,14] Elemental analysis, especially trace elemental analysis, leads to the establishment of chemical patterns or "fingerprints" that are characteristic of a particular source. Analysis of both sources and artifacts can be used to locate ancient sources, understand ancient technologies and map ancient trade routes.[13–16]

Multivariate statistical treatment of elemental data allows an understanding of the variance within the sample set and calculates probabilities for sample

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grouping. Displaying the samples in principal component (PC) space helps to identify patterns or groups within the data. WEIGAND et al.[17] described the concept of the provenance postulate, where, the inter-source variation must be greater than the intra-source variation to be able to link artifacts to sources. If the elemental signatures of the artifact source groups follow the provenance postulate, then elemental analysis may be used to "source" the artifacts if all possible sources are known. The objective of this work was to investigate whether the provenance postulate can be applied to the elemental signature of ochre from selected sources.

Studies connecting ochre and their sources are few in number as compared to provenance studies of other materials such as ceramic and obsidian. A review of the literature shows several studies of ochre by various spectroscopic methods including Raman spectroscopy and other elemental analysis methods such as particle induced X-ray emission (PIXE) and scanning electron microscopy energy dispersive spectrometry (SEM-EDS). These studies include investigation of the technology of painters at Lascaux using PIXE by MENU et al.,[3] SEM-EDX, PIXE and TEM analysis of pigments and technology of Paleolithic painters by CHALMIN et al.,[4] Raman examination of rock art in Quercy, by SMITH et al.,[18] Raman analysis of ancient Egyptian pigments, by DAVID et al.,[20] Raman and PIXE analysis of Eritrean rock art by ZOPPI et al.,[20] and sourcing of the Paviland ochres by XRF and petrography by YOUNG et al.[9] WEINSTEIN-ILANI and co-authors[21] describe the possible sourcing of ochre from the El-Wad cave in Israel by SEM-EDS. EDWARDS gives a summary of Raman investigations of pigments up until 2005[23] and a general summary of the physical and chemical methods that have been used to analyze pigments was compiled by ROWE.[23]

Several authors have examined Australian ochre, both in ancient and modern contexts. Mineral magnetic analysis of ochre was used by MOONEY et al.[24] to characterize ochre from known sites. SMITH et al.[25] used oxygen-isotope ratios in quartz to determine the provenance of Australian ochre, and JERCHER and co-authors[26] used Rietveld XRD and XRF to determine the mineralogy and elemental composition of modern Aboriginal ochre. GOODALL et al.[27] found subgroups within a data set of ochre obtained from Fern Cave, using photoacoustic spectroscopy (FTIR-PAS), PIXE and proton-induced gamma-ray emission spectroscopy (PIGE).

In contrast to the work in Australia, there have been few studies on the characterization of ochre from sources in North America. ERLANDSON et al.[28] described the use of PIXE analysis on samples from eight ochre sources in western North America (California, Oregon, Alaska and Wyoming) and demonstrated that the elemental signature from these measurements satisfied the provenance postulate. Although the conclusions are based on only one or two samples per source, this work does suggest that these sources can be differentiated from one another based on their major, minor, and trace-element content. MRZLACK[2] recently published a master's thesis using PIXE to characterize several ochre artifacts from a cave in Alaska. She concluded that ochre from the site came from the same source, which may be related to sources in Oregon.

An independent study by ELLIS et al.[10] reports on the NAA and inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of ochre artifacts from Texas. They describe several pilot studies that elucidated information on the intra- and inter-source variability in the data set. The authors analyzed worked nodules found in four Texas archaeological sites by ICP-OES (inductively coupled plasma optical emission spectrometry) and INAA. Within the study, they investigated intra-sample variation and found that some elements were affected by weathering of the sample. In addition, the authors concluded that INAA is an optimal technique for studying the trace elemental composition of ochre and also understanding variation within ochre.

Unlike other artifact types, there is very little in the literature on ancient ochre sources in the United States. There are only a few documented known ancient ochre sources in the United States most notably Sunrise Mine in Wyoming.[29,30] In the ERLANDSON study,[28] ochre samples were selected from known or suspected ancient source locations. Two of the source locations were from known archaeological sources (Sunrise Mine, Wyoming, and Red Rock Quarry, California). In these cases, the samples came from locations where archaeologists believe ancient people may have procured the raw ochre to process for cultural use.[28]

While the aforementioned studies suggest that it may be possible to source ochre through elemental analysis, these investigations involved a very limited number of samples and it is apparent that there is a clear need for a systematic study of the variation in elemental content and geochemistry of ochre from a large sample set. This study investigates the systematic sampling and elemental analysis of ochre to determine the "Fe oxide element signature" of a given ochre source, to determine whether this signature can be clearly distinguished from sources by region. Prior studies of ochre characterized only one or two samples from sources in North America and thorough and comprehensive studies are necessary to examine the inter- and intra-site variation within a potential ochre source.

The objective of this study was to identify the inherent variation of the major, minor, and trace-element signature of ochre materials. A subsequent multivariate analysis demonstrates whether or not ochre materials satisfy the provenance postulate and how these ochre sources can be distinguished. This work is also the initial step in the development of an elemental database for ochre materials. The database can be further augmented, to provide a more detailed and accurate picture of ochre variability. Ultimately, the main objective of chemical characterization of ochre is the development of a database for sourcing ochre artifacts similar to those established for ceramics, obsidian and other archaeological material created by GLASCOCK et al.[13]

Experimental

Samples were selected for this study with a number of objectives in mind. While it is not known if any of these iron oxide sources were used in ancient times as a source of ochre, it is not inconceivable that these sites were used as ochre sources by ancient peoples in that they are easily accessible and they provide materials with distinctive color and large distribution of Fe-bearing minerals as compared to other minerals in the Missouri landscape. POPELKA-FILCOFF and DESCANTES[31] systematically collected the Missouri samples from abandoned iron mines in southeastern Missouri on Mark Twain National Forest property and private property in 2004.

Southeastern Missouri hosts both igneous and sedimentary iron ore formations. All of the areas sampled in this study came from sedimentary formations.[32] The igneous formations are significantly older than the sedimentary formations in geological time, and are generally more profitable commercially (for example the mining locations of Pilot Knob, and Iron Mountain).[33] The smaller sedimentary formations were also exploited commercially for iron ore from the mid 19th through early 20th centuries, but were often quickly exhausted. Unlike igneous formations, the sedimentary mines are susceptible to weathering and other environmental digenetic changes.

The sources were selected based on archaeological surveys of historical mine sites (Table 1). Once on site, samples were systematically collected from the rims and sides of the mine pits to avoid possible disturbances deep within the mine pit. Up to 20 samples were collected per source, and each sub-location sampling included at least five samples. This sampling method allows an evaluation of the provenance postulate.[13,17] The source locations and their characteristics are described in Table 1 and shown in Fig. 1.

The ochre samples were analyzed by INAA and XRF in order to provide a more comprehensive characterization of the material. The ochre material was first processed by drying the sample at 100 °C in an oven overnight to remove moisture. Solid ochre was not pulverized prior to drying. Powdered ochre samples were dried in porcelain crucibles. It was clear upon processing the ochre in the laboratory that some samples thought to be ochre in the field were actually large pieces of other minerals such as quartz covered in a thin layer of Fe oxide. These non-ochre samples were difficult to process, and were not a good representation of the ochre present at the source. Therefore, some of these non-ochre samples were eliminated from the analysis, and some of the sub-sources did not have five complete samples per sub-source. This situation occurred with samples that were in more of a "chunk" form and does not apply to the "soil-like" ochre examples.

Table 1. Details and characteristics of ochre samples and sources

Site	Source name	Location	Missouri county	Number of samples analyzed
A	Meramac Spring Park	I	Phelps	4
		II		5
		III		3
		IV		5
		V		4
B	Private Property	I	Wayne	5
	(near site 511 (USFS)	II		5
		III		5
		IV		0
C	Site 741(USFS)	I	Wayne	5
	Bald Eagle Mine	II		5
		III		0
		IV		0
D	Site 810 (USFS)	I	Wayne	3
E	Road Cut, Big Spring	I	Carter	5
		II		5
		III		5
		IV		5

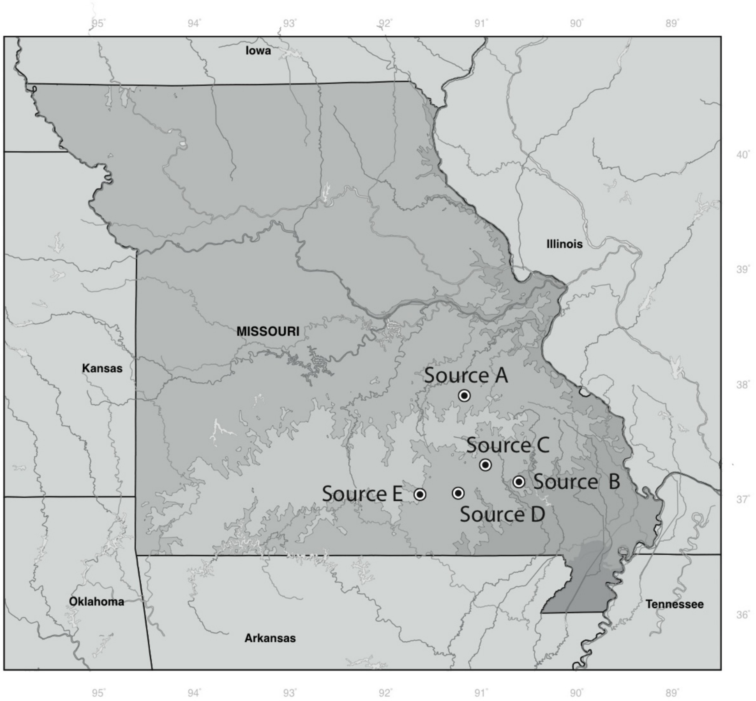

Fig. 1. Map of ochre sampling locations around southeastern Missouri

After drying, the raw ochre sample was crushed with a rock hammer into smaller pieces (<0.25 inch particle size). An alumina vessel and ball were used in a mixer mill to crush these pieces into a fine powder for analysis. Following a 15-minute powdering cycle, the alumina vessel was subjected to two five-minute cycles of grinding high-purity quartz glass to clean the alumina vessel and ball between ochre samples. After the quartz cleaning cycles, the alumina vessel and ball were rinsed with de-ionized water to minimize any potential cross-contamination of samples. The cleaning cycle of two quartz-grinding steps was experimentally determined to reduce the possibility of cross-contamination. This was evaluated by analyzing the quartz by XRF, and by comparing the results of incremental quartz cleaning steps by the Student's *t*-test. The resulting powdered ochre sample was used for both INAA and XRF analysis. These powders were again dried at 100 °C overnight before preparation for either INAA or XRF.

The INAA analysis followed standard geochemical procedures developed by GLASCOCK.[13] For the short counts, about 60 mg of sample was irradiated in 1.2 ml high-density polyethylene vials, using the MURR pneumatic tube system for five seconds at a thermal flux of approximately $8.0 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot s^{-1}$. After a decay of 25 minutes, the samples were counted for 720 seconds on a 25% relative efficiency high resolution HPGe detector. For the mid-count and long-count measurements, about 60 mg of sample was sealed in high purity quartz vials and irradiated for 24 hours at a thermal neutron flux of approximately $5.2 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot s^{-1}$. After a decay period of seven days, the "mid" count data was acquired for 2,000 seconds. After decay of an additional three weeks, the "long" count data were acquired for 10,000 seconds on automated sample changers. The comparator standards used in the INAA measurements were NIST SRM 1633a (Fly Ash) and SRM 688 (Basalt), and the quality control standards were NIST SRM 278 (Obsidian Rock) and Ohio Red Clay.[13]

The samples were prepared for XRF analysis by mixing approximately 3 g of finely ground sample with approximately 0.7 g of X-ray Mix (Chemplex) in a virgin polycarbonate vial for 15 minutes on a mixer mill. The resulting mixture was then pressed into a 32-mm diameter pellet. The XRF measurements were made on an X-LAB 2000, manufactured by Spectro, using a combination of three excitation targets with a Pd anode; molybdenum for Cr–Y and Hf–Th (35 kV, 4.4 mA), aluminum oxide for Zr–Nd (52 kV, 5.7 mA), and highly-oriented pyrolytic graphite for Na–V (15 kV, 13 mA). The concentrations were determined using a combination of the Compton and fundamental parameters models. The XRF method was calibrated with over 70 pressed pellets of standard reference materials. Pressed pellets of NIST SRM 2689 Coal Fly Ash and NIST SRM 690 Iron Ore and Ohio Red Clay were used as quality control samples for the XRF analysis (Table 2). SRM 690 has a very high Fe concentration, and is low in other elements. In fact, very few other elements besides Fe are certified by NIST for this standard. Therefore, SRM 690 is used to validate the Fe values in high Fe samples (>50% Fe), as calibration of the XRF is not adjusted for very high concentrations of Fe. Since Ohio Red Clay and SRM 2689 are low Fe, they were used to confirm all other elements in the analysis as well as samples with lower iron values. Table 3 lists the results of the XRF analysis of the standard reference materials.

For the most part, values produced by XRF were within 2σ of the NIST or certified values, on at least three replicate analyses. In most cases, the relative standard deviation (RSD) is under 5%, demonstrating good precision for the technique.

Splits of the same ochre material were analyzed by both INAA and XRF as the two techniques compliment each other in the elements that can be quantified in ochre samples. Table 3 lists those elements analyzed by both INAA and XRF.

Table 2. XRF results (mean±s.d.) for NIST standards SRM 690 Iron Ore, SRM 2689 Fly Ash and Ohio Red Clay

Element	NIST 690		NIST 2689		Ohio Red Clay	
	XRF (*n*=5)	Certified value	XRF (*n*=3)	Certified value	XRF (*n*=4)	Certified value*
Al, %			12.18 ± 0.03	12.94 ± 0.21	10.86 ± 0.03	8.89 ± 0.15
Si, %			22.866 ± 0.04	24.06 ± 0.08	28.865 ± 0.042	
P, %			0.156 ± 0.002	0.1 ± 0.01	0.039	
K, %			2.656 ± 0.014	2.2 ± 0.03	4.133 ± 0.016	3.31 ± 0.03
Ca, %			2.285 ± 0.01	2.18 ± 0.06	0.135 ± 0.004	0.38 ± 0.04
Ti, %			0.908 ± 0.004	0.75 ± 0.01	0.722 ± 0.003	0.57 ± 0.02
V, μg/g			377 ± 16		258.5 ± 12.5	198 ± 3
Cr, μg/g			217.333 ± 14	[170]	93.725 ± 9.225	89.2 ± 1.8
Mn, %			0.029 ± 0.001	[0.0300]	0.027 ± 0.001	0.025
Fe, %	65.086 ± 0.096	66.85	8.573 ± 0.017	9.32 ± 0.06	5.138 ± 0.011	5.19 ± 0.08
Cu, μg/g			138.4 ± 4		19.3 ± 1.7	
Zn, μg/g			238.6 ± 4.5	[240]	94.6 ± 2.5	97 ± 6
As, μg/g			141.8 ± 3.1	[200]	13.95 ± 1.08	13 ± 4
Rb, μg/g			148.1 ± 1.5		178.925 ± 1.325	176 ± 3
Y, μg/g			79.233 ± 1.266		41.15 ± 0.95	
Zr, μg/g			290.1 ± 6.033		269.18 ± 4.25	166 ± 10
Ba, μg/g			832.133 ± 4.433	[800]	653.5 ± 3.7	614 ± 26
Pb, μg/g			76 ± 2.4	[52]	16.1 ± 1.2	

Values in brackets indicate are recommended but not certified by NIST.

* M. D. GLASCOCK, Characterization of archaeological ceramics at MURR by neutron activation analysis and multivariate statistics, in: Chemical Characterization of Ceramic Pastes in Archaeology, H. NEFF (Ed.), Prehistory Press, Madison, WI, 1992, p. 11.

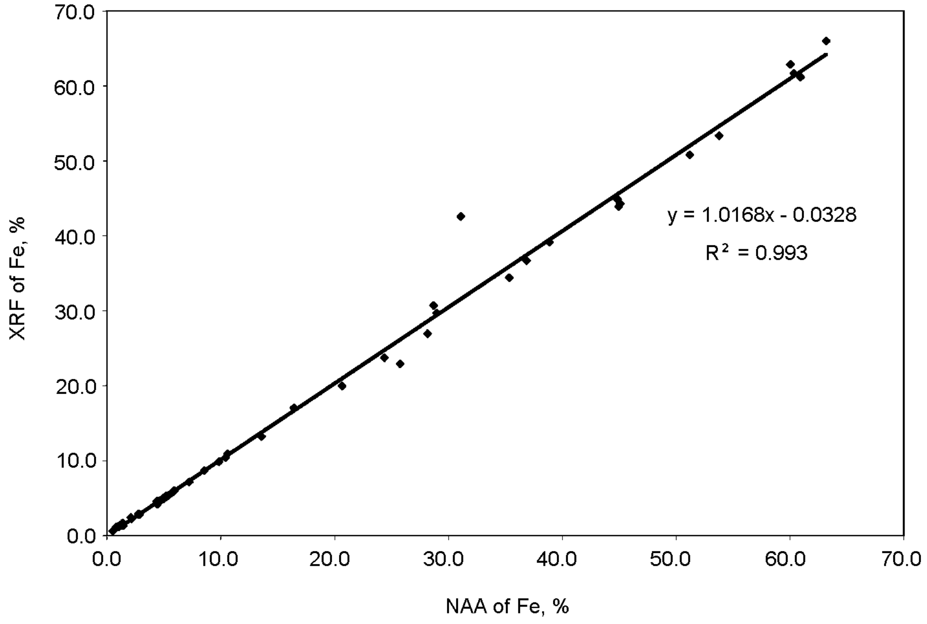

Fig. 2. Correlation between INAA and XRF in the measurement of Fe

Table 3. Elements routinely measured by INAA and XRF in ochre samples

INAA	Al, As, Ce, Co, Cr, Dy, Eu, Fe, Hf, K, La, Lu, Mn, Na, Nd, Sb, Sc, Sm, Th, Ti, U, V, Yb, Zn
XRF	Al, As, Ba, Cr, Cu, Fe, K, P, Pb, Rb, Si, Y, Zn, Zr

Results

Figure 2 demonstrates the good agreement between INAA and XRF for measurements of iron. Other elements that also had a one-to-one correlation measured both by INAA and XRF include: Al, As, Ba, Cr, K, Rb, and Zn. There was not agreement on the values for Cr between INAA and XRF. This is probably due to fast neutron reaction interferences on the high Fe in the sample in the case of INAA, which was not corrected.

Since ochre is made up of iron minerals admixed with clays, aluminosilicates and other minerals, the Fe concentration across the Missouri data set of ochre ranged anywhere from 0.5 to 70 wt.%, depending on local geochemistry and choice of field sample. In the case of low iron, the elements composing the clays and minerals such as K, Si, and Al made up the difference in the sum total of the sample. Because the wide range in iron concentration can readily influence the conclusions drawn on the major, minor and trace element concentrations, all elemental analysis results were examined as a ratio between the element and Fe in the sample, to effectively treat the variation in Fe concentration as a dilution factor by other components in the sample. In order to include the major, minor, and trace elements in the comparison, and to also take into account the non-normal distributions of the individual elements, the analysis was performed on log-10 transformed concentration ratio values.[15]

A two-tailed Pearson's correlation test was applied to the data relative to Fe concentration to ascertain which elements were significantly positively or negatively correlated with Fe. It is assumed that the elements associated with Fe are related to the Fe oxide signature that is related to the origin of the Fe oxide, whereas the elements not associated with, or negatively correlated with, Fe are instead related to elements that replace Fe, which are essentially diluents to the ochre.

The results of the Pearson's correlation identified those elements significantly negatively correlated with Fe. Significant values were evaluated in both the 95% and 90% confidence interval. Elements identified as being significantly negatively correlated (and therefore diluents) by INAA include Al and Na, and those identified by XRF include Al, Ba, Si, and Zr. Geochemically, this group of elements comprises major components of other minerals that will be present with Fe oxides and, therefore, be possible diluents to the samples. Elements significantly positively correlated and therefore associated with Fe by INAA include: As, Co, Cr, Sb, U, V, and Zn, and for XRF: As, Cu, P, Pb, and Zn. The following elements were used in the statistical analysis: As, Ba, Cu, Ce, Co, Cr, Dy, Eu, P, Hf, La, Lu, Mn, Nd, P, Pb, Rb, Sb, Sc, Sm, Tb, Th, Ti, U, V, Y, Zn, and Zr.

A statistical comparison of the XRF and INAA data was performed using principal components analysis (PCA) using the GAUSS software developed by GLASCOCK and NEFF with additions by William GRIMM, 2004.[13,14]

Figure 3 shows the PCA analysis of Missouri ochre by INAA. Principal components 4 and 2 were used in this analysis as the plot of these two components displays the elements that drive the variance most clearly. Despite the operation to normalize Fe content by use of a ratio, and even the elimination of Fe from the calculations, principal component (PC) 1 (79% of the variance) seems to be most influenced by Fe concentration. Therefore, the first principal component was not used for understanding the elements related to the ochre signature independent of Fe concentration. Principal components 1 through 5 describe 94% of the total variance for the data set. While the other principal components are not presented here, they did demonstrate similar trends to those observed for PC 4 and 2. Elements with the longest vectors were aggregated from the plots of combinations of PC 1 through 5. These elements were then used in the elemental bivariate plots described below.

Trends in the PC plot (Fig. 3) indicate some general grouping of the individual samples associated with their source sampling. In addition, vectors from elements from the same group in the periodic table often point in the same direction in the PC plot. A clear example of this is the vectors representing Hf and Zr.

Element ratios with the longest vectors in PC space, and thus greatest variance in the data set include: Cu, Eu, As, P, V, and Sb. These element ratios were plotted in several combinations in bivariate plots to investigate which pairs of element ratios were able to separate subgroups of the southeastern Missouri ochre samples. To satisfy the provenance postulate, inter-source variation must be larger than intra-source variation. In this case, the sources are the individual locations of sampling (Sources A, B, C, D and E).

Figure 4 is a bivariate plot of $\log_{10}$(Sb/Fe) vs. $\log_{10}$(Eu/Fe). This plot demonstrates some of the clearest distinctions between sampling sources and is representative of other similar bivariate plots. Ellipses on the plot are 90% confidence intervals. While there is some overlap of groups, many groups form a distinct cluster.

As in Fig. 4, a bivariate plot of $\log_{10}$(P/Fe) vs. $\log_{10}$(Cu/Fe) again demonstrates clear grouping of the sources (Fig. 5). The elements in this plot are those analyzed by XRF and not routinely analyzed by INAA. These elements also display variance and grouping of the ochre, but in a different arrangement than that of Fig. 4. As seen in Fig. 3, elements in the same group in the periodic table also show similar trends in the composition of ochre. Figure 6 is a plot of $\log_{10}$(Sm/Fe) vs $\log_{10}$(Eu/Fe) demonstrating a linear relationship between elements from the same group of the periodic table, in this case, the rare earth elements.

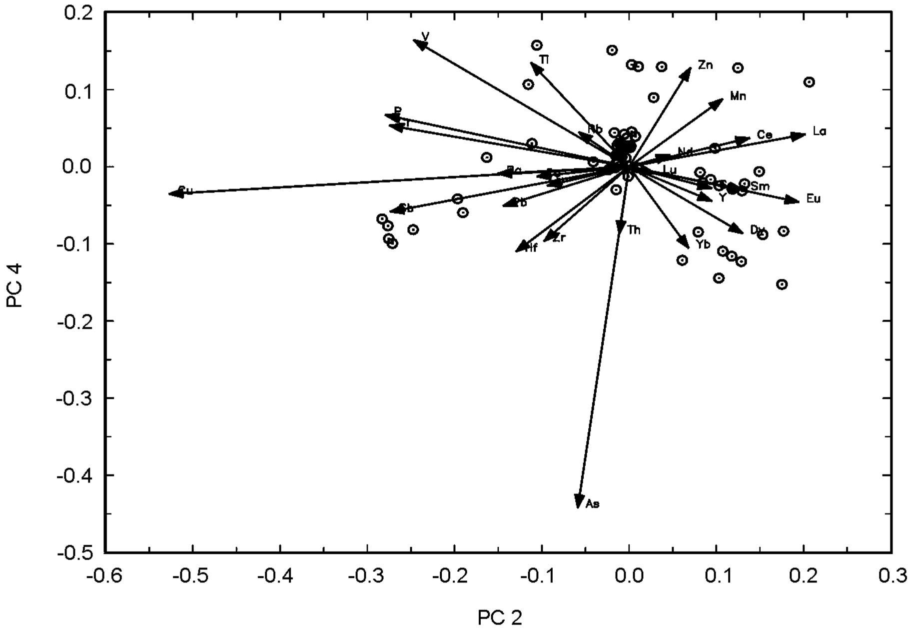

Fig. 3. Principal component 4 vs. Principal component 2 for the concatenated $\log_{10}$ elemental data of INAA and XRF. Elements are presented as a ratio to Fe

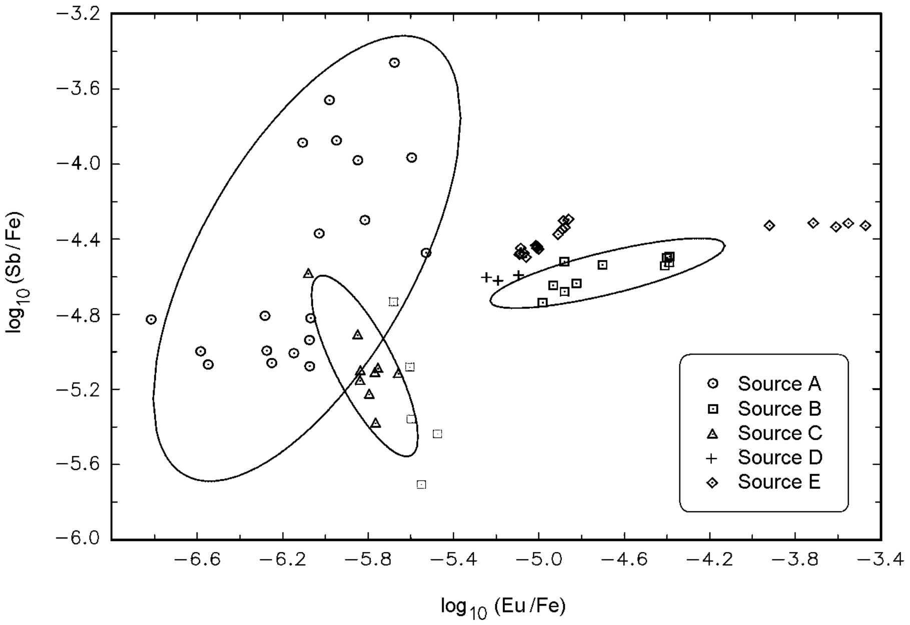

Fig. 4. Bivariate Plot of $\log_{10}$[Sb/Fe] vs. $\log_{10}$[Eu/Fe], with individual sources identified. Confidence ellipses are 90%

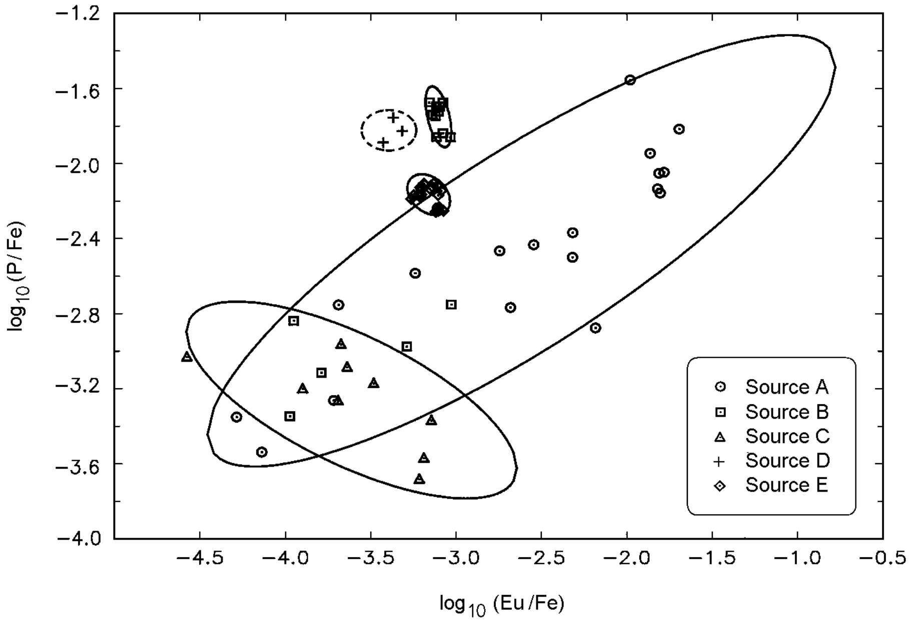

Fig. 5. Bivariate plot of log$_{10}$[P/Fe] vs. log$_{10}$[Cu/Fe] with individual sources identified. Confidence ellipses are 90%

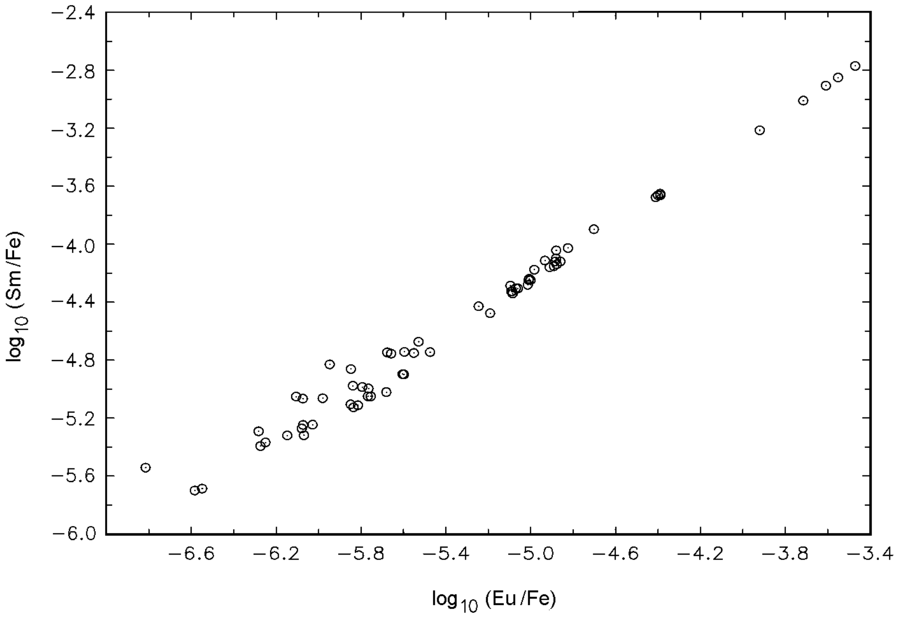

Fig. 6. Bivariate plot of log$_{10}$[Sm/Fe] vs. log$_{10}$[Eu/Fe] indicating linear trends in these elements in ochre

Discussion

In the majority of bivariate plots, samples from source A were widely distributed. Ideally, samples taken from locations only meters apart should have similar geochemical signature. In the case of source A, however, the location is now a privately owned park, which in the past (late 19th and early 20th centuries) was heavily mined for iron ore. At the actual sampling locations, there were piles of Fe-oxide and other minerals throughout. It is conceivable that despite sampling in a close geographic location, the entire site is heavily disturbed with tons of material moved throughout the decades of mining. Therefore, the sampling may not be representative of a particular location. Sources B, C, and D are also similar to source A in terms of geography, history and disturbance. These sources are located on National Forest and private land and identified by Mark Twain National Forest Service archaeologists as being sites where historical iron ore mining was performed.[32] Several of these sources were old mine pits filled with modern trash. Although sampling was done on the "rims" of the sources, disturbance was evident throughout. In the case of source B, three distinct sub-locations were sampled including a field, a creek bed, and a site with obvious remnants of mining activity, several hundreds of meters apart.

In contrast, samples from sources B, C, and D on the bivariate plots (Figs 4 and 5), group together in tighter clusters than source A, although there is still some spread within the clusters. However, within sources B and C, sub-source differences can be seen. For example, one sub-source location is distinct but still included within the source B ellipse. One group of B samples is more closely associated with source A than B. Source D is only defined by three samples due to problems with the field sampling as described earlier. A suggested region on the bivariate plots is indicated, but at least four samples are needed to calculate a probability ellipse. Source C samples are closely related to each other but no obvious sub-groups are observed. Samples from source C appear to be possibly associated with source A in the bivariate plots, but can be seen to be a distinct group from source A.

Source E has a slightly different history and yields very different results from sources A through D. All 20 samples for source E were taken from a road cut from sub-locations a meter or so apart. The material in the road cut exhibited a very strong red-orange color in contrast to the surrounding soils. These samples were more "soil-like" rather than the other samples from sources A–D, which tended to be rocks or nodules of Fe mineral material. This can clearly be seen in the elemental data, where samples from Source E are 5% Fe in contrast to other sources, where the samples are anywhere from 10 to 55% Fe. In a given bivariate plot, samples from source E generally cluster very closely together. One E subgroup is distinctly separate, yet associated with the other samples from source E. Throughout the permutations of elemental bivariate plots, it was seen that this small group of samples were consistently higher in all of the rare earth elements, which can be clearly seen on the $\log_{10}$(Sb/Fe) vs. $\log_{10}$(Eu/Fe) plot (Fig. 4). Source E is an excellent example of a less disturbed source location that yields a more easily defined chemical signature as well as a tighter group in the PC and bivariate plots.

Source A appears to be chemically distinct from Source E and B. This distinction indicates that inter-source variation is seen in this data set and that sources geographically diverse can also be discriminated in elemental plots. Variation in these sources, inter-source or intra-source, can be attributed to local geochemistry of the iron-bearing materials. The mining disturbance may cloud results of the sampling, but ideally, the chemical "signature" of the five broad sources can be identified in elemental patterns.

In general, the variation in ochre seems to occur in the transition metals and rare earth elements. Other major components such as K and Si reflect the inverse relationship between these elements and Fe. As Fe concentration decreases, these elements tend to increase as they are the major elements in the composition of the other rock or earthy materials in ochre. Those elements identified as being significantly positively correlated by the Pearson's correlation include transition metals as well as elements from Group 4 and 5 of the periodic table. In general, the rare earth elements are positively correlated with Fe, however the correlation is small and not statistically significant. It is logical that transition metals and rare earth elements vary in ochre materials and are related to the Fe oxide signature, as many are closely related to Fe chemically and in oxidation/reduction trends.

Figure 6 demonstrates that elements in the same periodic group exhibit similar trends in ochre. While $\log_{10}$(Sm/Fe) vs $\log_{10}$(Eu/Fe) is shown in this paper, other pairs of elements also demonstrate similar trends. Understanding these trends, among others will help elucidate trace element behavior within Fe minerals overall.

Conclusions

This study provides insight into sampling methodology and ways to characterize multiple locations within an ochre source. The elements identified in this study may not be universal for other source locations, but provide the beginnings for an analytical database for ochre.

By analyzing iron minerals from systematically selected Fe-bearing mineral sources in southeastern Missouri, it can be seen that a Fe-oxide signature exists for the areas sampled, and that ochre materials can feasibly be sourced. Despite significant site disturbances and environmental changes, it was found that source location of the ochre materials could be distinguished by elemental analysis. Disturbance in the sources from "modern" mining needs to be taken into account for this project as well as any other studies concerning provenance of iron-bearing pigments. In an ideal situation, samples would be taken from sources known to be used by ancient people that had not been disturbed by modern practices. For an understanding of the archaeological context, the history or ethnohistory of a source is necessary for understanding the source use and changes over time.

This study also illustrates the importance of meticulous sampling and choice of sources. Although ochre sources do have signature chemistry, one sample is unlikely to be representative of the entire source. Multiple samples from each location in addition to multiple sampling locations are necessary to comprehensively characterize an ochre source. Although the sources of ochre may be hard to distinguish due to some internal variation, it is possible to geochemically characterize regions. The broad definition of ochre encompasses many types of iron minerals in several geological contexts. As a result of this diversity, iron concentrations can vary dramatically. To account for this variability, ratios of analyzed elements to Fe to minimize variation due to Fe concentration. A combination of INAA and XRF provides characterization of the important elements used in understanding sourcing of ochre. These elements broadly belong to the transition metals and rare earth elements, implying a connection of these elements to variance of Fe minerals.

This study demonstrates the value of using a combination of the Pearson's two-tailed correlation test and multivariate statistics (PCA analysis), for characterizing ochre. The Pearson's analysis identified elements associated with surrounding minerals (negatively correlated with Fe) and elements associated with the Fe oxide signature (positively correlated with Fe). Multivariate statistics of elements with a positive correlation with Fe were used to describe the variance in the elements within the data set. The results of this study demonstrate that ochre satisfies the provenance postulate in that inter-source variance is greater than intra-source variance. Their "chemical fingerprint" can distinctly identify samples from meticulously sampled, tightly grouped locations.

The five sources in southeastern Missouri provide a foundation for future ochre analytical studies. Similar studies that characterize ochre sources as well as artifacts need to be completed to fully understand ochre geochemistry and provenance. At the current time, projects are underway to analyze ochre from known locations in Arizona and Australia. Once a core group of elements are found that can discriminate ochre universally, analytical methods can be optimized for analysis of these elements. Examples of this include optimization of the INAA and XRF methodology for elements important in the provenance of ochre. In addition, as more ochre samples are added to the database and new patterns are found, sources of the ochre can be more readily determined. As XRF is adaptable to field portable instrumentation, discriminatory elements determined by XRF can be used in future studies with field-portable XRF instruments, which are rapidly becoming more accessible and less expensive. An in-the-field elemental analysis instrument could be used to analyze ochre pigments quickly and non-destructively. This project lays a framework for further study of archaeological ochre characterization and study, ultimately leading to the possibility of analysis of pigments in a variety of artifacts.

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The authors would like to acknowledge the following people for their assistance in this research: Archaeometry Laboratory Staff, Dr. Carol DIAZ-GRANADOS, Dr. James WETTSTAED, Dr. Cheryl SEEGER, Dr. Gretchen MOORE, Dr. Cynthia PRICE, Dr. Kolleen BEAN, Danny MARSHALL, William GRIMM, and Dr. Kevin SHELTON. Funding was provided by the National Science Foundation Graduate Research Fellowship and the National Science Foundation Grant BCS-0504015.

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