



# Developments in Instrumental Multi-Elemental Analysis for Ochre Geochemistry

Rachel S. Popelka-Filcoff<sup>1,2,3</sup> Michael D. Glascock<sup>2</sup> and J. David Robertson<sup>1,2</sup>

<sup>1</sup>University of Missouri-Columbia, Department of Chemistry, <sup>2</sup>University of Missouri Research Reactor (MURR), <sup>3</sup>National Institute of Standards and Technology

## Abstract

Iron oxides, ochre and associated minerals were widely used during ancient times. However, geochemical data and archaeological provenance information for ochre are not well documented. This study presents data from instrumental neutron activation analysis (INAA) that indicate geochemical trends in ochre. Ochre was sampled thoroughly from geological sources in order to understand the elemental variation and associations in ochre. This poster examines a compositional ochre database from Arizona and results from multivariate statistical analysis and other data analysis. Conclusions about trends in ochre geochemistry, statistical methods for ochre and ochre composition for archaeological materials are presented.

## Archaeological Ochre



Figure 1: An example of iron oxide/ ochre artifacts: Hematite plummets from eastern Missouri. Photo: Patti Wright

Ochre and other iron oxides play a significant role for cultural expression. Artifacts made from iron oxides include:

- rock art pigments
- ochre-dusted bones in burials
- specular hematite artifacts

Ochre is a long-lasting colorful material that is generally impervious to weathering and extreme conditions, making it a universal material in the archaeological record.

However, less is known about ochre procurement, processing and cultural significance. Some recent studies have investigated the trace element chemistry of iron oxides by INAA (instrumental neutron activation analysis). These studies identified elements important in characterizing ochre. Still, little is understood about the trace element geochemistry of ochre and its relationship to archaeological materials.

## Project Goals

- Determine elements important in ochre analysis
- Determine if trace element indicators specify ochre types
- Create an elemental ochre database
- Identify geochemical associations of elements in ochre

## Ochre Mineralogy

Intense red and yellow pigments and artifacts are often identified on archaeological sites as "ochre". However, the definition of ochre is broad and often encompasses many types of common iron oxides. Ochre can vary in mineralogical content from a pure iron oxide to a diluted mixture of iron oxide and clays, silicates, and other minerals. In identified iron oxide source areas, a mixture of minerals and oxidation states of iron oxides are found concurrently. In general, red ochre is made up of the mineral hematite (Fe<sub>2</sub>O<sub>3</sub>) and is 70 weight percent Fe. Yellow ochre (goethite or limonite) has the general chemical formula FeO(OH), where the iron content can vary by hydroxide content but is nominally 63 weight percent Fe.



Figure 2: An abandoned iron mine with both hematite and goethite deposits.

## Analytical Methods



Figure 3: MURR reactor pool

The ochre samples from Arizona used in this study were characterized by INAA. The raw ochre sample was prepared using standard methods at the Archaeometry Lab at MURR. Standards used in this project were Ohio Red Clay, NIST 2689 (Coal Fly Ash) and NIST 690 (Iron Ore Canada). Samples and standards were analyzed at the University of Missouri Research Reactor (MURR).



Figure 4: Nuclear interactions in INAA. Diagram: Michael D. Glascock.

## Statistical Treatment of the Data

### • Ratio of [element] to [Fe] in sample

The elemental data presented for all data sets are calculated as a ratio to iron (Fe) in the individual sample. This operation helps correct for varying amounts of Fe in each ochre that can influence the concentration of trace elements. In a later section, ratios to Al and Ca are also discussed.

### • Log<sub>10</sub> of data

A log<sub>10</sub> transfer was applied to all elemental data. This is standard statistical practice in order to compensate for the differences in elemental concentrations in the data set which can be across several orders of magnitude from ppm to percent, depending on the element.

• **Pearson's Linear Correlation Test (two-tailed)** A Pearson's linear correlation test was performed to identify elements positively and negatively correlated with Fe. Those negatively correlated were eliminated from the analysis.

### • Principal Component Analysis

A statistical comparison of the INAA data was performed using principal components analysis (PCA) using the GAUSS software developed by Glascock (1992), Neff (1994) and Grimm (2004).

	Iron	Aluminum	Calcium
Elements Positively Correlated	As, Ce, Co, Cr, Dy, Eu, Mn, Nd, Sb, Sc, Sm, U, V, Yb, Zn	As, Ce, Cs, Dy, Eu, Fe, Hf, K, La, Lu, Mn, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, V	Ba
Elements Negatively Correlated	Al, Ba, Ca, Na, Ti	Al, Ba, Ca, Co, Cr, Ti, Yb, Zn, Zr	Al, As, Ce, Co, Cr, Cs, Dy, Eu, Fe, Hf, K, La, Lu, Mn, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, Ti, U, V, Yb, Zn, Zr

Table 1: Elements positively and negatively correlated (Pearson) with Fe, Al, and Ca in ochre from Arizona.

## Geochemical Relationships of Trace Elements in Ochre Iron, Aluminum and Calcium Ratios

A data analysis was performed with ratios of all analyzed elements to Fe, Al and Ca. It was found that only Ba was correlated with Ca by the Pearson's test therefore these data were not used further.

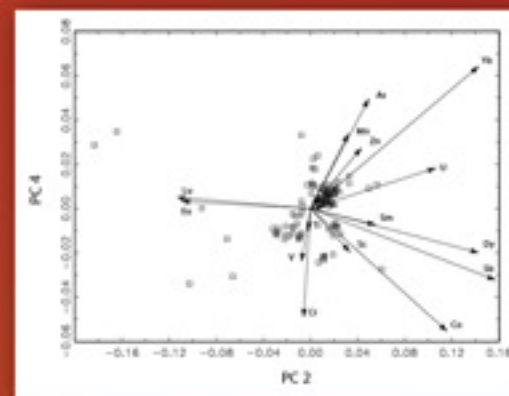


Figure 5: PC4 vs PC2 for ochre data from Arizona identifying elements from Fe-ratio data

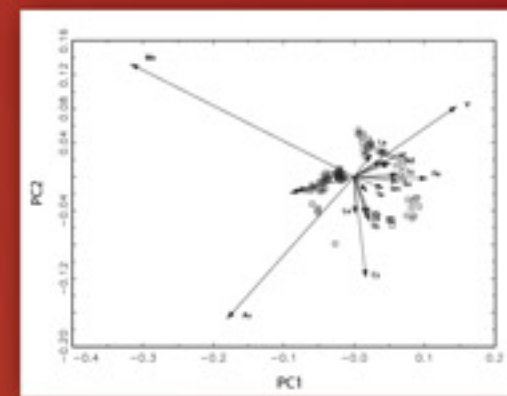


Figure 6: PC2 vs PC1 for same Arizona data but as a ratio to Al

Figures 5 and 6 are the same data, with Figure 5 as ratio to Fe and Figure 6 as a ratio to Al. These results imply that ratios to Al represent variation in the external mineral composition of the ochre, and ratios to Fe are more effective at determining trace elements important in ochre analysis. This is important for archaeological ochre where the major composition of the material can be highly variable.

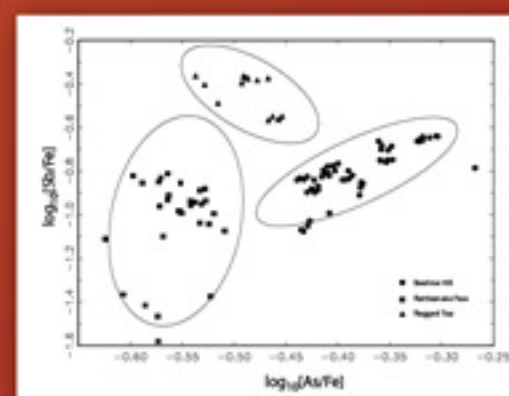


Figure 7: Three geological sources are clearly distinguished by ratio of Sb and As to Fe.

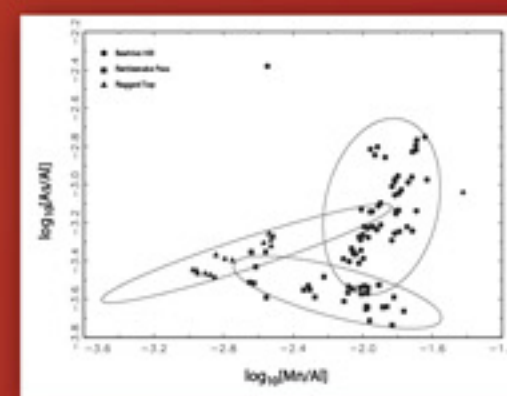


Figure 8: Plot of log<sub>10</sub>[As/Al] vs log<sub>10</sub>[Mn/Al] using the same Arizona data set.

As above, these bivariate plots are constructed using the same data set with differing ratios (Fe and Al). The Fe-ratio plot demonstrates clear differentiation between sources based on trace elemental composition, while the Al-ratio represents major components of the ochre, suggesting similarities in major oxide composition between sources.

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## Rare Earth Elements

Rare earth elements (REE) are demonstrated to be important in distinguishing ochre. A further investigation was performed to understand patterns and trends in REE.

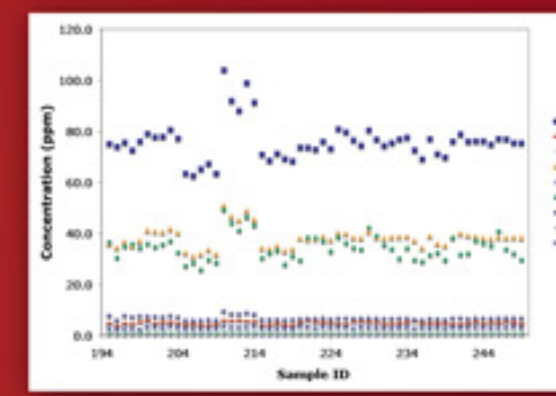


Figure 9: Plot of concentration for ochre samples from Beehive Hill, Arizona demonstrating trends in REE concentration.

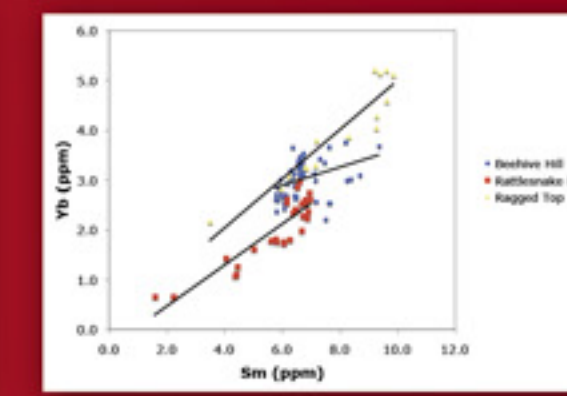


Figure 10: Plot of Yb vs Sm for Arizona data set showing the linear relationships of heavy vs light REE elements.

The first examination was on the concentrations of REE in the iron oxides (without any ratio operations). In general, concentrations of Ce, La and Nd were higher than other REEs. Heavy REEs are considered high field strength elements, which do not generally have high affinity for sites in minerals, and Ce is generally found at higher concentrations as compared to other REEs.

Figure 10 displays the ratio between Yb (heavy REE) and Ce (light REE) in the data set. The data demonstrate that relationships between light and heavy REE can distinguish between the ochre sources for both differences in concentration and linear slope. These relationships are possibly related to differences in REE substitution in iron oxides, which may reflect the original source of ochre.

## Conclusions

By using ratios and statistics, the elements important in distinguishing ochre sources were found independently of other mineral composition. Ratios to Fe appear to be the best method for identifying elements for characterization of ochre. Trends in rare earth elements (REE) also can be used to distinguish ochre sources. This study emphasizes the importance of understanding the geochemistry of iron oxides for studying archaeological ochre and builds on the foundation of an elemental database for current and future ochre elemental analysis studies. These geochemical correlations can be used in future archaeological ochre analysis and sourcing studies.

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