A COMPARISON OF INSTRUMENTAL TECHNIQUES AT DIFFERENTIATING
OUTCROPS OF EDWARDS PLATEAU CHERT AT THE LOCAL SCALE

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ABSTRACT

This study compares two widely accepted analytical techniques, Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) and Instrument Neutron Activation Analysis (INAA). These techniques are compared and contrasted to determine the composition of intra-formation Edwards Plateau chert. As a case study, three unique chert outcrops only several hundred meters apart (hyper-local (Speer 2014)) at the Gault Site (41BL323) in central Texas were tested with each of the techniques. The differences of each instrumental technique on Edwards Plateau chert is assessed using the geochemical data retrieved. The geochemical data were evaluated with multivariate statistics in order to determine which instrumental technique is most effective at distinguishing between these three unique Edwards Plateau chert outcrops. This study also seeks to determine if either of the instrumental techniques can effectively separate out geochemical differences of Edwards Plateau chert outcrops.

KEY WORDS

Chert sourcing, Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS), geochemistry, Edwards Plateau, Paleoindian, trace element studies

1. INTRODUCTION

The main research objective for this study is to determine if the methodology proposed here effectively characterizes intra-source variability so that chert artifacts can be matched to local sources using either Instrument Neutron Activation Analysis (INAA) or Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS). The three chert bearing Early Cretaceous Edwards Limestone outcrops under consideration are within several hundred meters

of the Gault Site (41BL323)(see figure 1). Each of these chert-bearing outcrops were identified, classified, and distinguished through elemental composition to document intra-formation variability.

Chert occurs in massive geologic settings; particularly those in Phanerozoic marine sediments, such as the Edwards Plateau of Texas and the Massif Central and La Voulte-sur-Rhone of central France (Kidder and Erwin 2001; Knauth 1994; Maliva, et al. 1989; Shackley 2008). Distinguishing between a primary and secondary source can be challenging. Chert is notorious for looking very similar among different geologic groups and additionally, has significant color and textural variability within a geologic group (Frederick and Ringstaff 1994).

Figure 1. Edwards Plateau Chert Outcrops analyzed with INAA and LA-ICP-MS at Gault Site (41BL323)

2. METHODS

2.1 Study Sample

In order to evaluate intra-source variability of distinct sources of Edwards chert, an analysis was conducted to study the geologic formations near the Gault archaeological site (referred to hereinafter as the “Gault source”). The location of the Gault Site with its well stratified deposits located near several primary Edwards chert outcroppings made it an excellent candidate for a test study. The Gault Site also allows a unique opportunity to better understand how prehistoric hunter-gatherer populations may have exploited these sources of Edwards chert.

First, analysis was conducted to determine if the geologic outcrops within several hundred meters of the Gault site were similar in geochemical composition to each other. LA-ICP-MS and INAA analysis were used to characterize 29 geologic samples. The Gault geologic source were analyzed by Speer at the Field Museum of Natural History with a LA-ICP-MS instrument in July 2012 with the procedures listed below. The INAA analysis was conducted at the University of Missouri Research Reactor by Matthew Boulanger in February of 2013. Only primary sources were sampled. The geologic samples are each representative of either a single nodule of chert, or a unique area sampled along a lens of exposed chert. Multiple samples were not taken of individual nodules. Three different outcrops of chert from undivided Edwards-Comanche Peak Limestones near the Gault Site were analyzed with 9-10 samples from each (29 geologic samples total). LA-ICP-MS and INAA were both used to create a geochemical profile for the Gault source. Principal factor analysis and discriminant analysis were used to evaluate the relationship between the Gault geological sources.

2.2 Analytical Methods

INAA methods for chert and chert-like specimens have been described in sufficient detail elsewhere (Glascok 2004:98-100; Huckell, et al. 2011; Quigg, et al. 2011). For the LA-ICP-MS analysis the following methods were used. Geologic samples were analyzed with the New Wave UP213 Laser Ablation System. Analysis consisted of directing the beam of a laser (100 μm wide and operating at 10Hz) at 10 separate locations (single point) on each sample. In order to determine elements with concentrations in the range of parts-per-million (ppm) and below, the single point analysis mode with a laser beam diameter of 100 microns, operating at 70% of the laser energy (0.2 mJ) and a pulse frequency of 15 Hz was employed. A pre-ablation time of 20 seconds was set up in order to eliminate the transient part of the signal and ensure that surface contamination or corrosion did not affect the results of the analysis (Dussubieux, et al. 2009). The laser vaporizes a volume of material corresponding to a cylinder with a diameter of 100 microns. Ablated material from the sample is transported by a helium carrier gas to the ICP-MS (Varian 810 quadrupole ICP-MS unit). At the plasma torch section of the ICP-MS the sample encounters argon plasma between 8000°K to 10000°K and is ionized. The ionized samples are then introduced into the mass spectrometer section of the instrument where the ions are characterized by their mass/charge ratios to determine which element they represent and their overall relative quantity (Trejos, et al. 2003).

Each of the 10 single point locations were analyzed for 58 analytes and 9 individual readings with the first 3 readings discarded due to potential surface contamination. The remaining six samplings were then averaged for each sample. Each sample was therefore represented by the composition of 58 elements and an average calculated from 60 measurements (10 single points with 6 readings per point). For each chert sample, an average of 10

measurements corrected from the blank is considered for the calculation of concentrations. The blank is a reading taken with no material ablated or introduced into the ICP-MS. Silica is the most abundant component in chert, therefore, the ^{29}Si isotope was used for internal standardization (B. Gratuze 1999; B. Gratuze, M. Blet-Lemarquand, and J.N. Barrandon 2001).

Concentrations for major components, including silica, were calculated assuming that the sum of their concentrations in weight percent of oxide in chert is equal to 100% (adapted from Gratuze, 1999). Two different series of standard reference materials were used to determine the concentrations of major, minor and trace elements. The first series of external standards were NIST SRM 610 and 612. Both these standards are soda-lime-silica glass doped with trace elements in the range of 500ppm (SRM 610) and 50ppm (SRM 612). Certified values are available for a very limited number of elements. Concentrations from Pearce et al. (1997) were used for the other elements. The second series of standards used were Corning Glasses B and D (Brill 1999).

3. RESULTS

INAA was able to recover a total of 26 trace elements while LA-ICP-MS recovered 44; the two techniques had 23 trace elements in common (see Table 1 and 2 for other data). The element data retrieved from both INAA and LA-ICP-MS following normalization were analyzed using multivariate quantitative analysis in SAS JMP Pro 11. Prior to analysis, it was necessary to convert all data using a base-10 logarithm of each concentration to remove magnitude in differences between trace elements and provide nearly normal distribution. The data were analyzed using principal factor analysis with Varimax rotation method and Kaiser Normalization (Khattree and Naik 2008:158-168). The data were also analyzed using discriminant analysis with

Fisher's method (Johnson and Wichern 2007:590-594) for verification of geochemical patterns and to produce graphical results (Khattree and Naik 2008:242-255).

Following multivariate analysis the Pearson's product-moment correlation coefficient (r) was calculated for each element between INAA and LA-ICP-MS. This was performed to determine how closely the two instrumental techniques agree similar to that seen in other studies (Arnold, et al. 2007). The results of this correlation analysis are provided in Table 2. A complete discussion of how correlation coefficients are calculated can be found in Johnson and Wichern (2007:8) as well as how it is implemented in SAS Khattree and Naik (2008). The correlation coefficient is a value between -1 and 1. When the r value is equal to 0 then there is a complete lack of linear association between the elements being tested. "If $r < 0$ this suggests one value of the pair being tested is larger than its average while the other is smaller. If $r > 0$ this suggests one value of the pair to be large when the other value is large and also for both values to be small together"(Johnson and Wichern 2007:8).

Table 1 – Characteristics of Instrumental Techniques

Instrumental Technique	Cost per Sample (in U.S. Dollars)	Number of Elements Able to Test	Resolution	Time to Analyze 20 samples	Destructive?	Sample Preparation
Instrument Neutron Activation Analysis (INAA)	\$125	25-30	PPM-PPB	Several Days to Weeks	Minimal (requires >5 mg)	Some (creates radioactive waste)
Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS)	\$20	All elements with Atomic Masses between 7-250	PPM-PPT	8 hrs	No	None

Table 2 – Pearson's Product-Moment Correlation Coefficient between INAA and LA-ICP-MS

Element	Correlation Coefficient
Sc	0.3636
Ti	-0.0463
V	-0.0170
Cr	0.0697
Co	0.8050
Zn	0.5232
Rb	0.3095
Sr	0.4949
Zr	-0.3304
Sb	0.3698
Cs	-0.0183
Ba	0.4351
La	-0.2139
Ce	0.2777
Ta	0.2063
U	0.4576
Nd	-0.2411
Sm	0.1755
Eu	-0.1069
Tb	-0.1281
Yb	0.2943
Hf	0.2231
Th	-0.4199

3.1 Local Variability

The analysis of these geologic samples demonstrated that each of the primary sources of chert is somewhat different in chemical composition and some intra-source variation can be distinguished. However, all of the geologic samples analyzed from each area do not indicate significant variation beyond the 95% confidence level among their group and outside of their group there is some geochemical similarity (see figures 2 and 3).

The intra-source analyses of the samples demonstrated the three local Gault sources of chert are highly similar in geochemical composition. These three local sources are all similar at the 95% confidence interval (see figures 4 and 5). Each outcrop sampled also appears to show separation into their own unique groupings, even though each sample was taken from separate nodules or different points on a chert lens.

Figure 2. LA-ICP-MS principal factor analysis of geologic samples

Figure 3. INAA principal factor analysis of geologic samples

Figure 4. LA-ICP-MS 95% confidence intervals of principal factors

Figure 5. INAA 95% confidence intervals of principal factors

4. DISCUSSION

It is well known that INAA is much more precise than ICP-MS (James, et al. 2005). This research analyzes geologic samples from an important, well stratified prehistoric site that can help develop an understanding of issues of mobility, quarry behavior, organization of technology, and patterns of discard. The comparison of the two techniques may help refine differences at the hyper-local scale and perhaps establish when and whether particular sources were geologically available to different prehistoric cultures.

The Edwards Plateau chert sources discussed here are of particular importance because many of the artifacts found at the Gault Site appear macroscopically to be derived from chert sources within 30 km of the Gault Site. Macroscopically similar chert can occur across the Edwards Plateau and inferences about the origin of the raw material used for tool manufacture can be inaccurate when based on outward characteristics (Speer 2013).

An interesting anomaly occurred as the samples were all identical in the testing. INAA captured major elemental readings of titanium in the hundreds ppm while LA-ICP-MS remained as a trace element. This study shows above all else the need to test more samples and use multiple techniques to establish accurate geochemical profiles for chert outcrops.

Lastly, by looking closely at Table 2 there is clearly a lack of correlation between the results determined between LA-ICP-MS and INAA. The most likely explanation for this is that LA-ICP-MS was carried out in this instance as a spot technique on a flake surface. Every ablation was carefully selected to avoid any inclusion of dolomite, quartz fragments, or other inclusions. Counter to this, INAA is a bulk processing technique that analyzes every composed of the crushed piece. Of all the correlation coefficients only Co, Zn, and Sr appear to agree, with

coefficients at or above 0.50. Both techniques tend to agree with each other when principal factor analysis is implemented showing some clustering of the samples but each have significant outliers.

5. CONCLUSIONS

It is clear that both techniques fail to provide the resolution needed to achieve a clear separation of the three outcrops. Each technique also does not appear to correlate with the other except for 3 trace elements. This needs to be further investigated as to whether some of these elements are migratory through the chert matrix or have other, significant diagenetic properties. Future studies will try to apply canonical discriminant analysis by using a much larger sample size. Additionally, newer instrumental techniques may be applied that can reach the precision of INAA and capture the number of elements that LA-ICP-MS can. The goal of course is to find a technique that can accomplish this without destroying the sample and unfortunately, INAA requires destructive sampling.

It is hoped that this research can advance understanding of the concept of local versus non-local chert toolstone resources for central Texas hunter-gatherers from all time periods; as well as determine what types of mobility were practiced in light of high quality resources. The objectives completed here are important in creation of new avenues of approach to provenance issues and reconsideration of current methods for others.

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