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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.

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 Fig. 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).

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–

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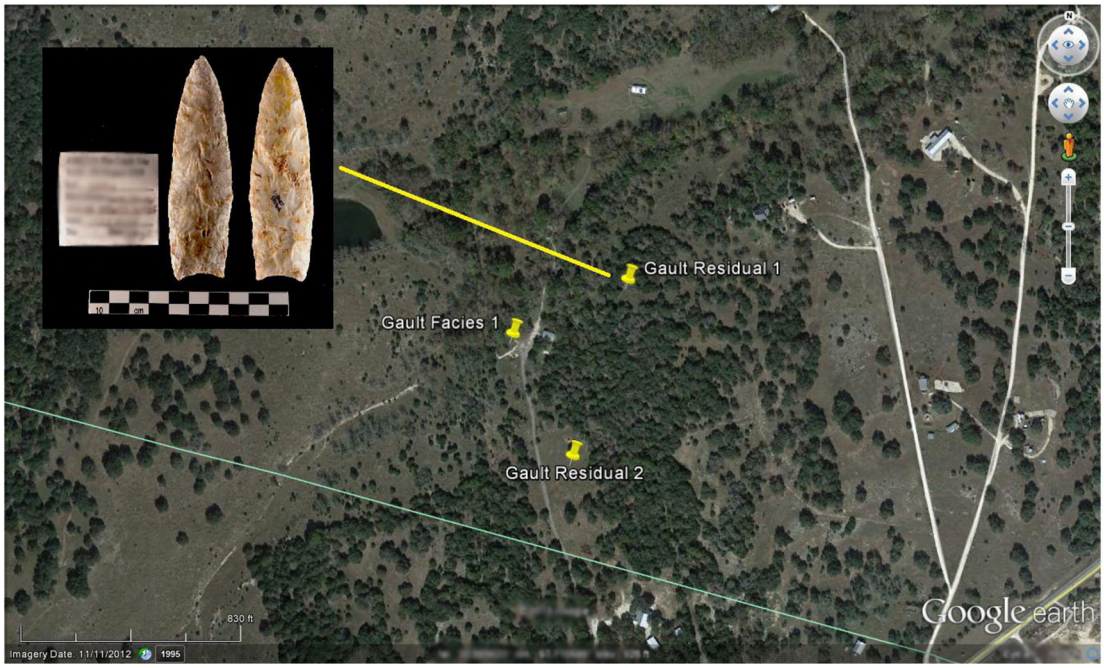

Fig. 1. Edwards Plateau chert outcrops analyzed with INAA and LA-ICP-MS at Gault Site (41BL323).

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 (Glascock, 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 10 Hz) 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 μm, 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 s 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 μm. 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 10,000 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 29Si isotope was used for internal standardization (Gratuze, 1999; Gratuze et al., 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 500 ppm (SRM 610) and 50 ppm (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 Tables 1 and 2 for other data). The element data retrieved from

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 and 250	PPM-PPT	8 h	No	None