



# Silcrete Geological Source Discrimination with LA-ICP-MS for Minimally Destructive Archaeological Stone Tool Provenience Studies

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## ABSTRACT

Silcrete is a soil duricrust that has been used as toolstone since at least the Middle Stone Age and is one of the earliest mineral resources to have been heat treated to improve material properties. In the last two decades, there have been substantial advances in the detection of heat treated silcrete artifacts, as well as promising developments in geochemical provenience research. Provenience, or sourcing, studies of stone artifacts typically rely on measuring concentrations of chemical elements in geological source samples from known locations and archaeological

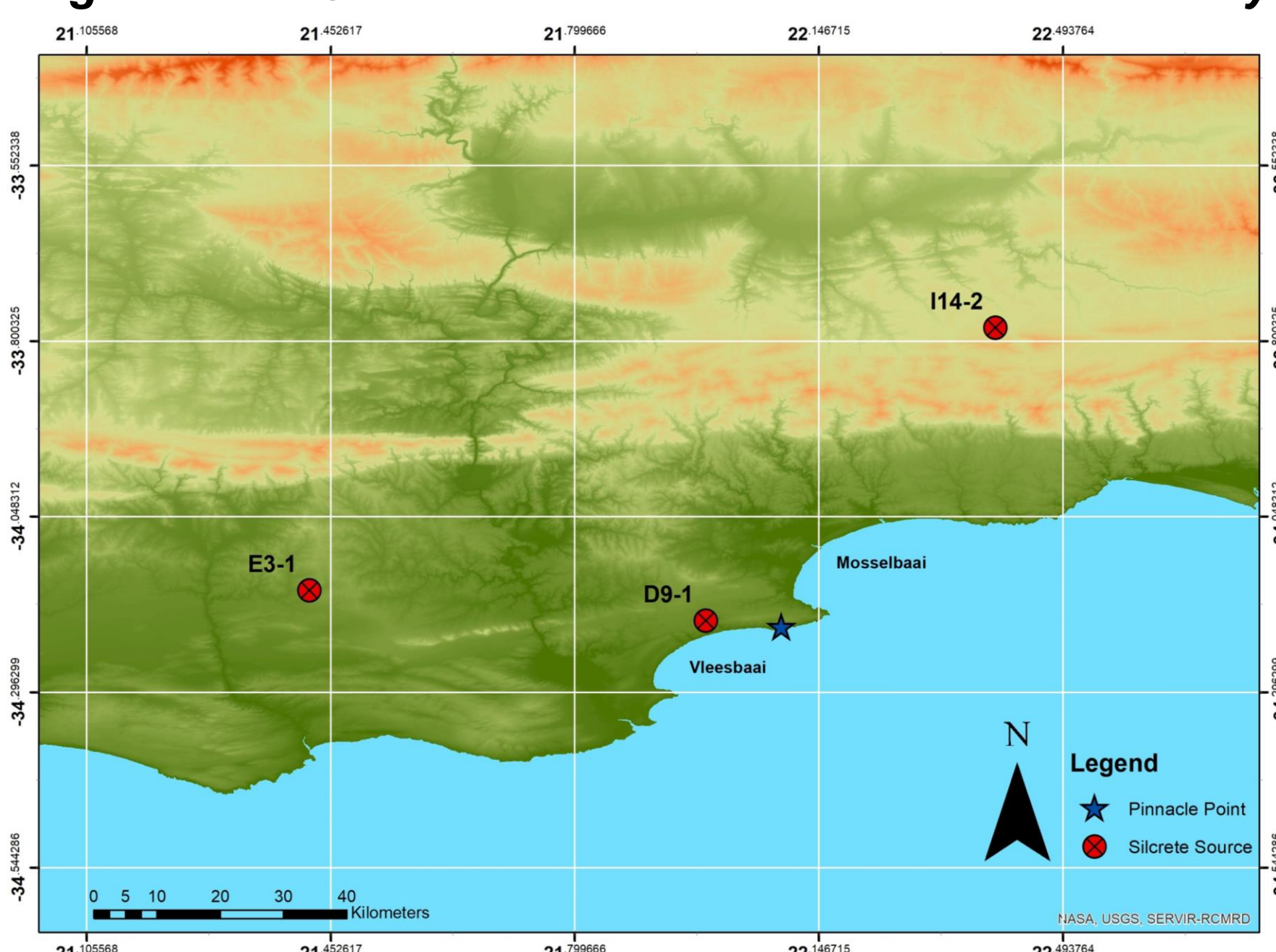
artifacts of unknown origin. Elemental concentrations are a form of “closed” compositional data in which an increase in one element requires an equivalent decrease in the concentrations of the other elements present. This can yield unique geochemical “fingerprints” that permit multivariate statistical discrimination among sources and predictive assignment of artifacts to a source.

Here, we present pilot research demonstrating the feasibility of using a powerful and minimally invasive technique, Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), to measure elemental concentrations in 30 silcrete samples from three geological sources in coastal South Africa (Figure 1) and discriminate among those sources. Solution ICP-MS and ICP-Optical Emission Spectroscopy have been used successfully for silcrete provenience studies but are destructive techniques that require laborious mechanical and chemical preparation of the digestion-resistant silcrete. For this pilot study, we sub-sampled each piece of silcrete for solution ICP-MS. Concentration data for a sub-set of the measured elements were used to discriminate among the three sources. The reserved undigested portion of each sample was embedded in epoxy, polished, and ablated with five replicate scan lines. Rather than measuring fully quantitative concentrations by LA-ICP-MS, which requires knowing the concentration of a major element for use as an internal standard, we acquired semi-quantitative data externally calibrated to silicate glass reference materials. Concentrations for trace elements were then ratioed to the measured silicon concentration in each sample, effectively normalizing the data without a true internal standard. Statistical analysis of the ratio data was able to recapitulate the source discrimination achieved with the solution ICP-MS data set.

## INTRODUCTION

Archaeological provenience studies are constrained by both the ethical obligation to use the least destructive techniques possible to preserve specimens for future analysis and by regulatory regimes that increasingly restrict how material culture objects may be studied. Portable X-Ray Fluorescence (pXRF) is a popular elemental analysis technique for archaeology because it can be non-destructive and permits bringing the instrument to the artifacts. pXRF is, however, limited to measuring sodium and heavier elements, and has lower sensitivity than ICP-MS. In this study, we sought to use LA-ICP-MS to achieve a balance between the minimally invasive advantage of XRF and the low detection limits and wider range of measurable elements made possible by ICP-MS. We demonstrate the main prerequisite to a provenience study, chemometric discrimination among geological sources, using a “Multi-Element Ratio Fingerprinting” approach derived from well-established geochemical provenience practices for obsidian and ochre.

**Fig. 1: Three South African silcrete sources in this study**

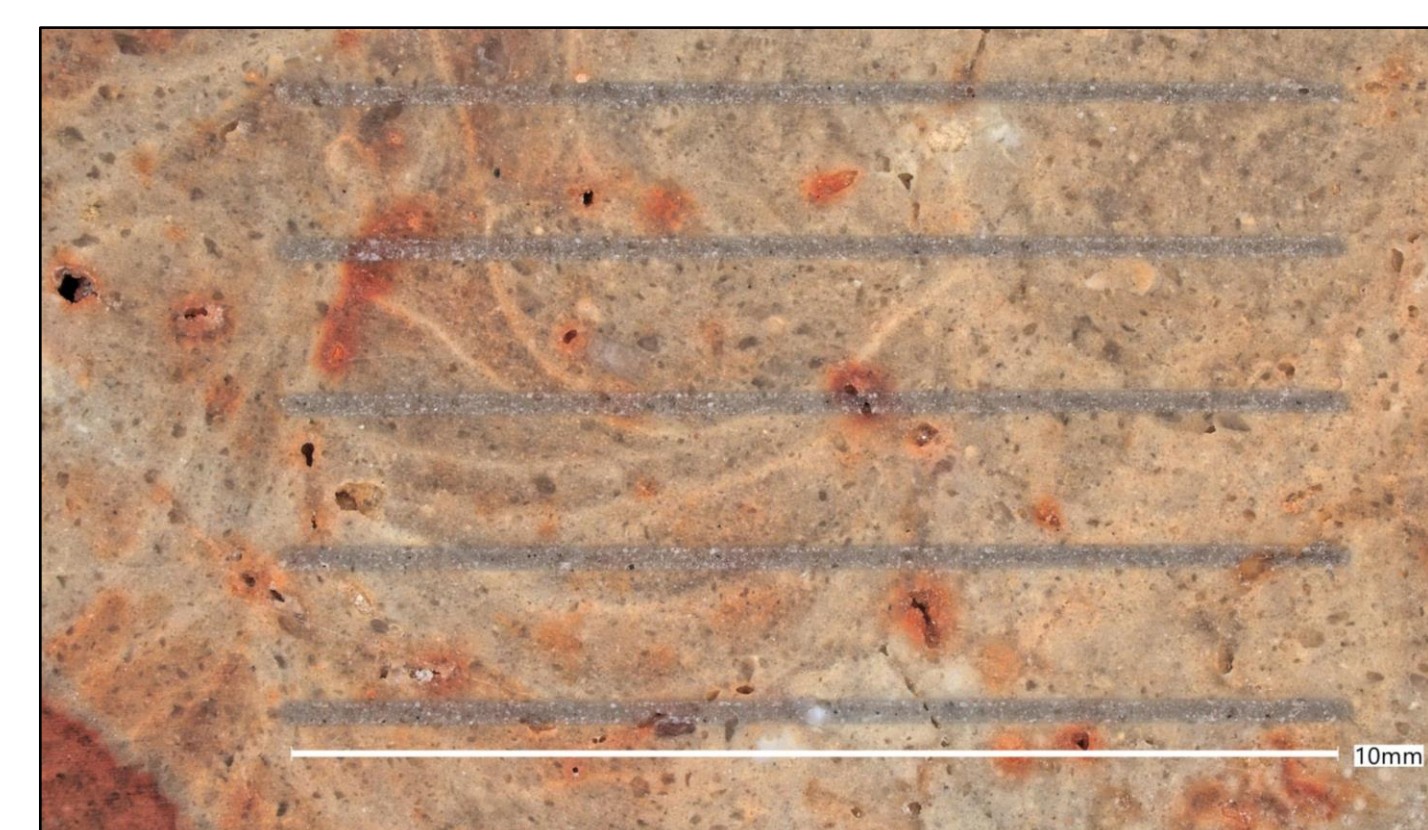


## EXPERIMENTAL & RESULTS

- 30 samples were embedded in epoxy and ground flat using 120 and 240 grit SiC abrasive pads.
- LA-ICP-MS was carried out using an Applied Spectra 266 nm Tandem LIBS/LA system coupled to a ThermoScientific iCAP TQ ICP-MS; each sample was analyzed with five replicate scan lines.

- Ablation Pattern: Scan line, 8-10 mm length
- Pre-ablation spot size: 200  $\mu$ m
- Pre-ablation scan speed: 0.25mm/sec
- Data collection spot size: 100  $\mu$ m
- Data collection scan speed: 0.05mm/sec
- Fluence for all: 0.6 mJ/cm<sup>2</sup>
- Repetition rate for all: 10 Hz
- Background Signal Window: 30 sec/ablation
- Carrier Gas and Flow Rate: 0.8 L/min He

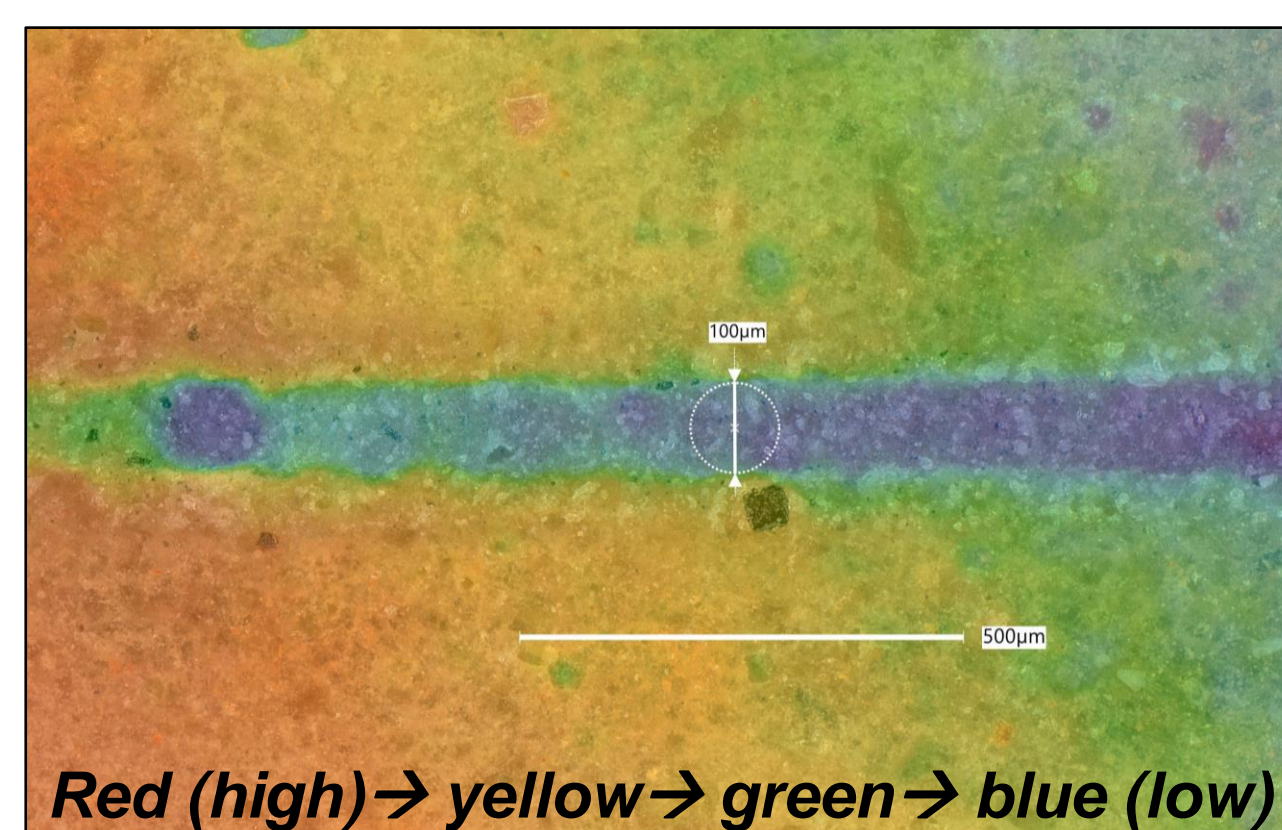
**Table 1: Parameters for Laser Unit**



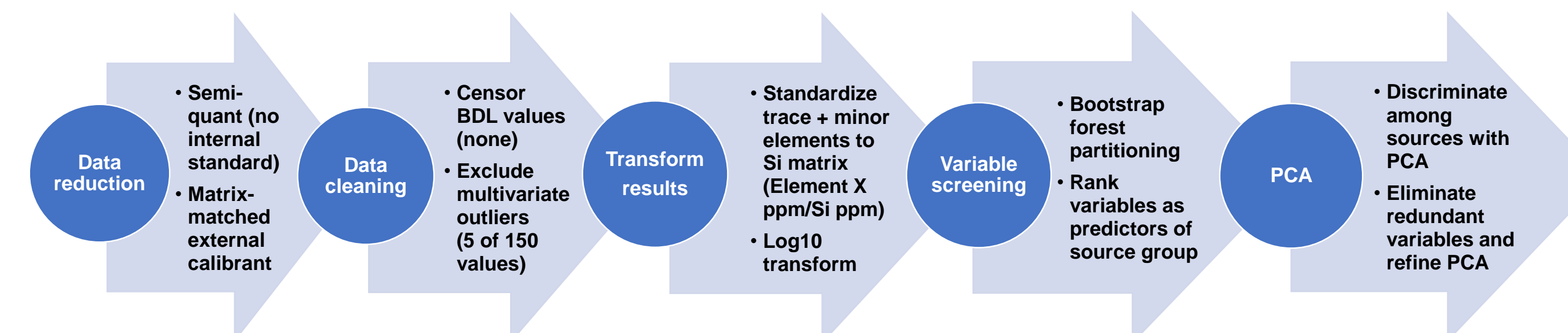
**Figure 2: 5 scan lines on sample D9.1.12B.18**

- RF Power: 1250 Watts
- Auxiliary Gas: 1.2 L/min Ar
- Dwell time per mass: 0.1 seconds
- Mode: Kinetic Energy Discrimination
- Masses measured: Li7, Na23, Mg24, Al27, Si29, K39, Ca44, Sc45, Ti48, Mn55, Fe56, Fe57, Cu63, Cu65, As75, Sr88, Mo95, Mo98, La139, Ce140, Tl205, Pb207, Pb208, and Th232

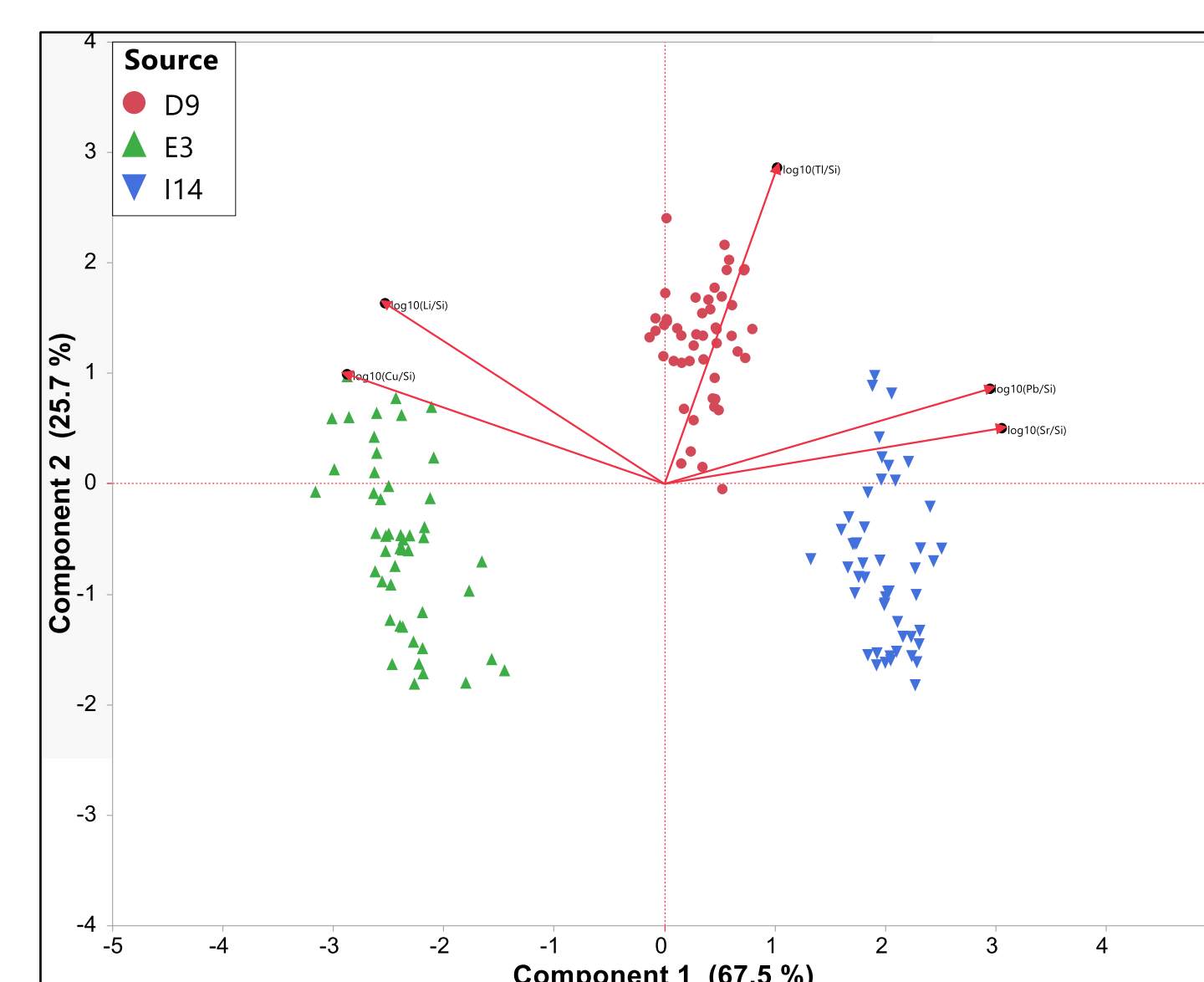
**Table 2: Parameters for ICP-MS**



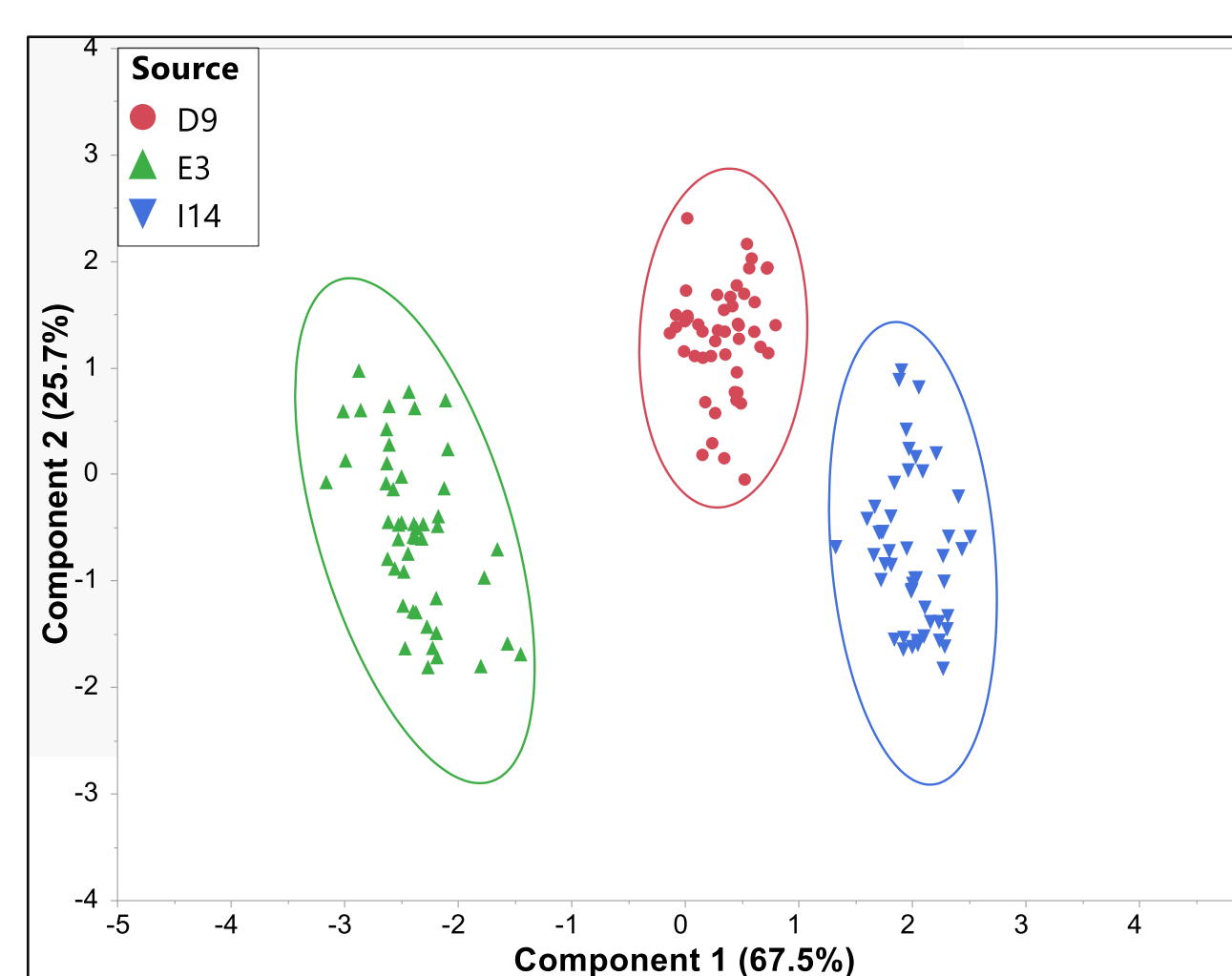
**Figure 3: Depth heat map of a scan line**



**Figure 4: LA-ICP-MS data processing workflow for Multi-Element Ratio Fingerprinting (MERF)**



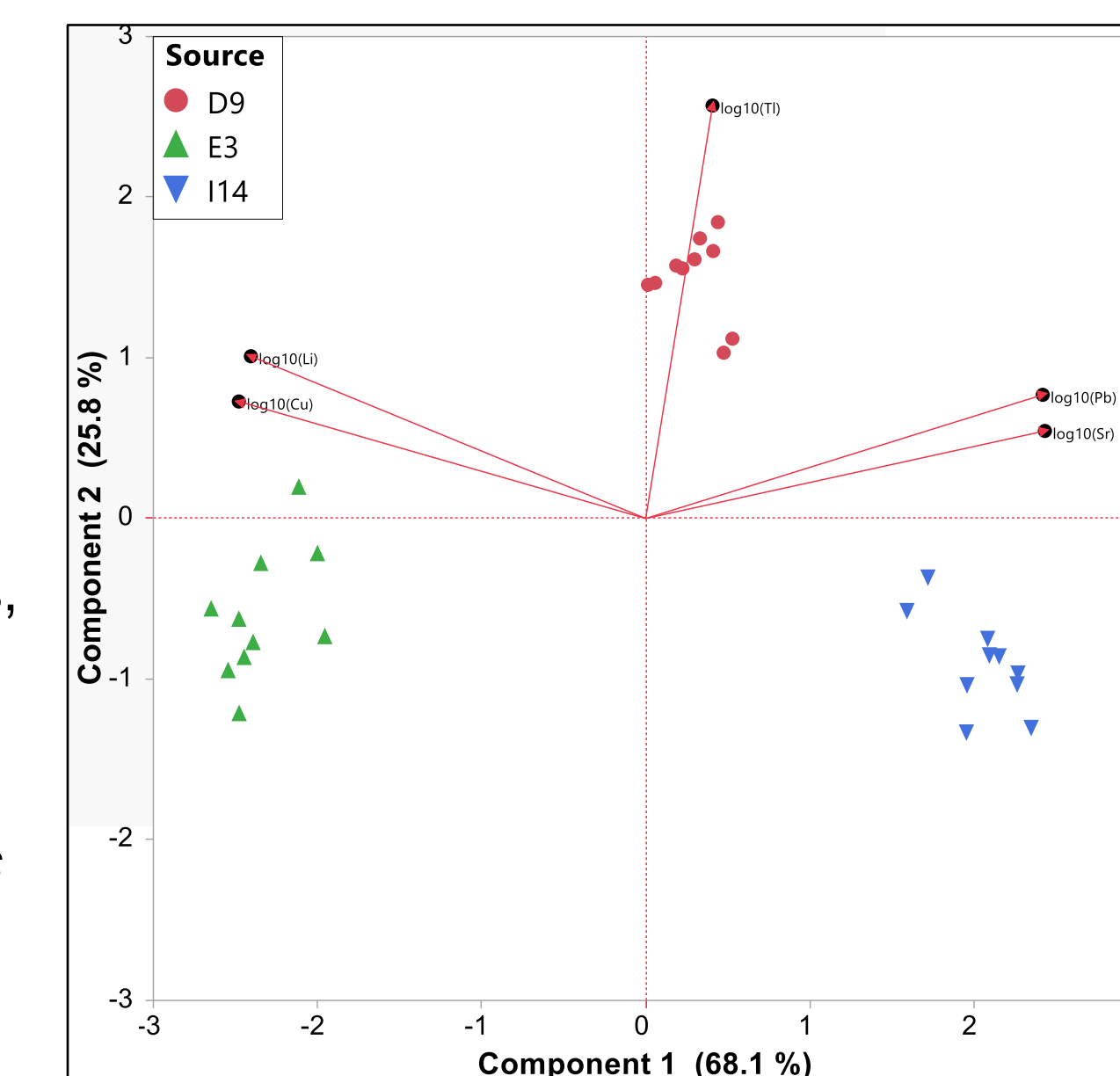
**Figure 5: PCA biplot by silcrete source group**



**Figure 6: 99% density ellipses applied to the Fig. 5 biplot showing discrimination among the three source groups**

## DISCUSSION

The Principal Components Analysis (PCA) biplots in Figures 5 and 6 illustrate successful discrimination among the three silcrete geological sources using five elemental ratio variables. Semi-quantitative concentrations of Li, Cu, Sr, Tl, and Pb were standardized to the associated Si concentration and then log10 transformed (Figure 4). Standardizing to Si mitigates the impact of differences in ablation and ionization efficiency between replicates and samples, serving the same purpose as an internal standard element in fully quantitative data. The log10 transformation helps to ensure that large differences in magnitude among the variables (e.g., % weight vs sub-ppm) do not bias the PCA results. The PCA depicted in Figures 5 and 6 used the individual replicate ablation results from each sample to account for the intra-specimen variability that can be detected by a solid-state, microanalytical approach to elemental characterization.



**Figure 7: PCA biplot of solution ICP-MS results using the same elements as the LA-ICP-MS PCA in Figures 5 and 6**

Figure 7 depicts a PCA biplot using solution ICP-MS results for the same 30 silcrete samples that were analyzed by LA-ICP-MS, using the same five elements as Figures 5 and 6. The major differences are as follows: 1) solution ICP-MS was carried out on three replicate digestions of each specimen and the results were averaged for the PCA because the goal of solution ICP-MS is bulk characterization, and 2) the PCA in Figure 7 uses log10 transformed concentrations that have not been standardized to Si concentration. Standardization to a matrix element is not necessary because internal standard elements were spiked into the replicate dilute aliquots prior to analysis. Figure 7 illustrates that LA-ICP-MS and solution ICP-MS yield functionally identical source discrimination results, facilitating archaeological silcrete artifact provenience studies despite the digestion-resistant and heterogeneous nature of this material.

## CONCLUSIONS

### Multi-Element Ratio Fingerprinting with LA-ICP-MS

#### Advantages

- LA-ICP-MS is more powerful than XRF while still minimally invasive
- No physical homogenization, digestion, or hazardous waste (fast, clean, and green relative to solution ICP-MS or OES)
- Easy replicate analyses to assess intra-specimen variability, increase sample size, and improve statistical power
- Semi-quant data can be made fully quantitative later by measuring an internal standard element with a second technique

#### Disadvantages

- Not non-destructive and field-portable like pXRF, which is widely used in archaeology
- LA-ICP-MS works best when measuring a limited number of elements, especially if trying to minimize size of the ablated area
- Pseudo-bulk analysis with replicate ablations only approximates bulk analysis of a digested sample by solution ICP-MS

In conclusion, this study demonstrates that MERF LA-ICP-MS is a viable approach to geochemical discrimination of silcrete sources for archaeological provenience studies. Microanalytical mass spectrometry offers substantial advantages relative to XRF and solution ICP-MS for heritage science applications that require balancing sensitivity and breadth of measurable analytes with the obligation to preserve specimens for future study, public education, and return to stakeholders.