Correlation of wide spread ash flow tuffs can be very challenging and often requires expensive and time consuming geochemical analysis (such as radiometric dating). LIBS is a relatively new and efficient analytical technique that requires little to no sample preparation as well as very low running costs; handheld models can be used on location. LIBS uses laser ablation to create a short-lived plasma that releases photons of light as it cools. These photons can be captured and analyzed using chemometric techniques to discover hidden trends within the spectra. Thirty-seven samples from fourteen ash flow tuff units located within the MDVF (Mogollon-Datil volcanic field) were originally collected by Chapin et al. (2004) for Ar$^{40}$/Ar$^{39}$ dating and were donated for this study by William C. McIntosh. All samples were crushed to expose the sanidine phenocrysts; sanidines were separated using heavy liquids (lithium metatungstate) and mounted in epoxy for LIBS analysis. A multivariate chemometric technique called PLSR (partial least-squares regression) was used on the LIBS spectra to create an algorithm that is a series of binary models that each distinguish between one tuff and all the other tuffs. Three separate algorithms were created; the 4-sample model (all tuffs with 4 or more samples from different locations), the 3-sample model (3 or more samples per tuff), and the all-sample model, which yielded success rates of 100%, 79.2%, and 69.4%, respectively. Fourteen of the samples were also analyzed using electron microprobe to support the validity of the LIBS spectra. The concentrations of K$_2$O, Na$_2$O, and CaO from the microprobe data were used to create a ternary diagram that is comparable to a ternary diagram constructed with intensities of K, Na, and Ca peaks from LIBS spectra. Ba and Sr concentrations from the electron microprobe that were above detection limits were also compared with Ba and Sr spectra peaks. Both the microprobe concentrations and the LIBS spectra yielded similar results. The results of the algorithms suggest that the success rate of each algorithm is dependent on the amount of samples that were analyzed. The results further suggest that with enough samples a successful algorithm can be created which can be used as a tool for correlation of ash flow tuffs.

References: