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**Toward Real-Time Geochemical Analysis in the Field: Provenance
Determination and Correlation Studies of Carbonates Using Handheld
LIBS**

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Discrimination of rock units and their correlation is central for many geologic studies. Optical spectroscopy, a technique in which light is acquired at hundreds of wavelengths simultaneously and spectral analysis is subsequently performed for each discrete pixel, is a powerful non-destructive analytical tool that can be applied to this requirement across a range of spatial scales that range from nanometers on a mineral surface to hundreds of kilometers across the Earth's surface. Laser-induced breakdown spectroscopy (LIBS) is a straightforward and versatile spectroscopic technique based upon analysis of the spectral emission from laser-induced plasmas. LIBS provides *in-situ*, simultaneous, multi-element analysis in real time and is largely free of the need for sample preparation, thus making it an attractive analytical tool for use outside of the conventional laboratory setting. LIBS is especially sensitive to the light elements (H, Li, Be, B, C, N, and O) that are difficult to determine by many other analytical techniques. The field of LIBS has been rapidly maturing as a consequence of interest in laser spectroscopy for a broad spectrum of applications and the recent development of commercial LIBS analytical systems for laboratory and field use.

The objective of this study was to ascertain if LIBS is capable of detecting elemental differences between various types of carbonates and then accurately discriminating carbonates of different provenance. This study was divided into three parts: (i) analysis of pure metal carbonates minerals to demonstrate the ability of LIBS as a technique for geochemical discrimination; (ii) a study to determine if carbonates could be differentiated on the basis of their LIBS broadband spectra; and (iii) a provenance study of carbonates from different locations worldwide using two commercial LIBS instruments—a Z500

handheld instrument (SciAps, Inc.) and a RT100-HP laboratory system (Applied Spectra, Inc.). Broadband LIBS spectra were collected for a total of 165 samples consisting of metal carbonates, carbonate muds, seashells, chalks and marls, limestones/dolomites, and marbles, to create a spectral source library. The library data was processed using multivariate statistical pattern recognition methods such as Principal Component Analysis (PCA) and Least Squares Discriminant Analysis (PLS-DA) after using various preprocessing techniques to optimize the LIBS classification results. Different aspects of the classifier setup considered in this study include the training/testing routine, the number of latent variables used in the regression model, and whether PLS-DA operating on the entire broadband LIBS spectrum is superior to that using only a selected subset of LIBS emission lines.

The metal carbonates were discriminated with 100% success. The other carbonate types could be effectively discriminated by geographic locality with high rates of sample-level classification using the handheld LIBS instrument. For example, carbonate muds from three Caribbean and two Pacific areas were well discriminated, implying chemically distinct environments of deposition. Limestones from different regions were also well discriminated, as were different limestone and dolomite formations within specific areas. Performance was better using the laboratory LIBS system, but only marginally so. These results point to the robustness of the LIBS technique for geochemical fingerprinting and suggests that LIBS analysis combined with the appropriate statistical signal processing has the potential to be a useful tool for determining the provenance of carbonate materials and for stratigraphic correlation at a high level of accuracy.

