ELEMENTAL ABUNDANCE MEASUREMENT USING MICRO-LIBS FOR SPACE EXPLORATION.

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Introduction: As LIBS has been applied to a wider and more useful range of samples, it has been realized that signals generated with the laser plasma are highly dependent upon the matrix from which they have been ablated. In this case, analytical results dependence on physical properties of the sample. This at times leads to the paradoxical situation where precisely matrix matched calibration standards are required to analyze an unknown sample. While several strategies for solving the calibration problems of LIBS have been proposed, none so far is generally applicable to geological samples, especially to extraterrestrial analysis, in which foreknowledge of the sample composition is particularly challenging.

Micro-LIBS: Standoff LIBS has been developed for space applications [1,2], and is part of the 2009 Mars Science Laboratory (MSL) payload. Micro-LIBS is Laser Induced Breakdown Spectroscopy (LIBS) applied for interrogation of surfaces at <50 μm interrogation diameter and with <1 mJ of laser pulse energy. A μLIBS instrument could be used to produce elemental abundance maps of mineralogical surfaces near to or at the grain size of the sample.

Analysis Appraoch: We are devoping a data analysis technique which uses multiple emission lines per element. By using the extra degrees of freedom associated with observations on the multiple emission lines per element and developing the physical constitutive relationships between these emission lines, an observation of the time-integrated thermal profile (spatial and temporal) of the high temperature gas that drives emission can be solved in conjunction with the relative elemental abundances. In mathematical form, the ionized gas/plasma state matrix (temporal and spatial), P, describing the thermal evolution of the ionized gas from which emission is occurring is solved simultaneously with the relative elemental abundances in the gas, C^m, using known elemental partition functions, Z^m, for the elements, m, and the vector of observed elemental lines of emission, $F_{obs}{}^m$. As shown in [3] these relationships should collectively minimize the following least squares function:

$$\chi^2 \equiv \sum_m \left(\sum_j \left(C^m \left[\{1 \quad . \quad . \quad 1\}_L \; \left[\left[\tilde{P} \right]_{LKQ} \left\{ \xi(E_j) \right\}_Q \right] \left\{ Z^{-1} \right\}_K^m \right] - \left\{ F_{obs\,j} \right\}^m \right)^2 \right)$$

Optimization of the ionized gas observational spatial (index L) and temporal grid (index K) for solving this
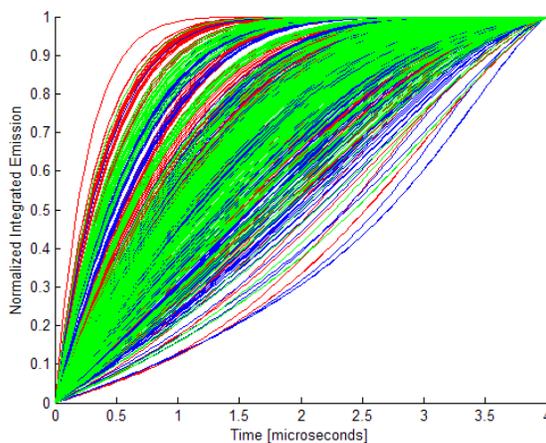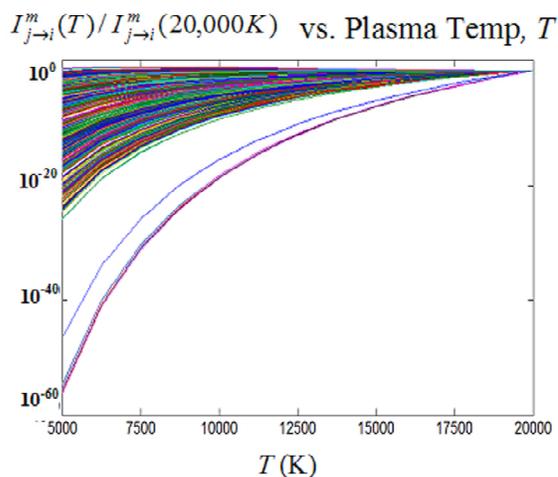

Figure 1: Left: Normalized emission intensity (relative to emission at 20,000K) vs. ionized gas temperature of 78 of the strongest emission lines (singly and doubly ionized) for Al, Ba, C, Ca, Cl, Cr, Fe, H, Hg, K, Li, Mg, Mn, N, Na, Ni, O, P, S, Si, Ti illustrates that plasma emission is a very strong function of ionized gas temperature. Right: **:** Normalized plasma elemental time-integrated spectral emission as a function of differing thermal decay profiles illustrating the strong relative variation in collected emission depending on the structure of the thermal decay profile. A) Three different assumed 1 node thermal decay profiles and B) the associated response in time-integrated collected emission vs. time for the same 78 elemental emission lines described on Left.

equation will ultimately depend on the laser beam geometry, laser pulse profile, surface chemistry and instrument emission collection radiometry. Optimization of the numerical space-time grid is necessary for different sample types and beam configurations in order to incorporate improved knowledge of thermal emission profiles into μLIBS analysis.

Atomic emission intensity from an ionized gas is highly correlated to ionized gas temperature. Fig. 1, left side, illustrates the normalized emission (normalized to atomic emission at 20,000K) for 21 key elements [3]. However, spectrometers measure time-integrated emission, not emission intensity, and as a μLIBS plasma rapidly cools while it radiates and expands, the associated atomic emission intensity varies significantly, highly dependent on the plasma's thermal decay profile. Fig. 1, right side, illustrates the simulated results of time-integrated emission vs. time from the same elements as a function of assumed 1D thermal emission decay profiles. In many cases the shape of the thermal decay profile allows cooler plasmas (green) to produce more intense time-integrated emission. Understanding the nature and thermal decay profile of LIBS emission plasmas is critical to being able to accurately interpret concentration of ionized elements which produce LIBS emission.

Mars Atmospheric Interactions: A potential complicating factor for μLIBS trace elemental analysis of the biogenic element, carbon, is the photo-fragmentation of elements from an atmosphere such as Mars atmospheric CO_2 into C^+ that can occur at high laser beam intensities. This issue has been identified in previous LIBS studies [4,5], however, these cases were for long standoff distances where high beam intensities maintained over relatively long distances can photo-dissociate significant quantities of CO_2 whose subsequent emission can provide an artificial noise source relative to the true measurement. In case [5], the number density of CO_2 was ~104 times greater than Mars atmosphere given the high pressures of interest (~10MPa vs. Mars ~1kPa).

Fig. 2 illustrates the resultant analysis of percent ionization of CO_2^+ in the micro-LIBS beam for an F/#4 optical beam (common in-situ instrument configuration) as a function of distance from the ablation surface and laser intensity in a Mars atmosphere with a 532nm beam. Integrating all of the photo-ionized C^+ over the beam volume as a source of equivalent emitters, a comparable-size pure solid carbon sphere at the beam waist would be 290nm and 1240nm in diameter for the 1GW/cm^2 and 10GW/cm^2 532nm excitation beams, respectively. Given the repeatable nature of photo-ionization of the atmosphere between measurements,
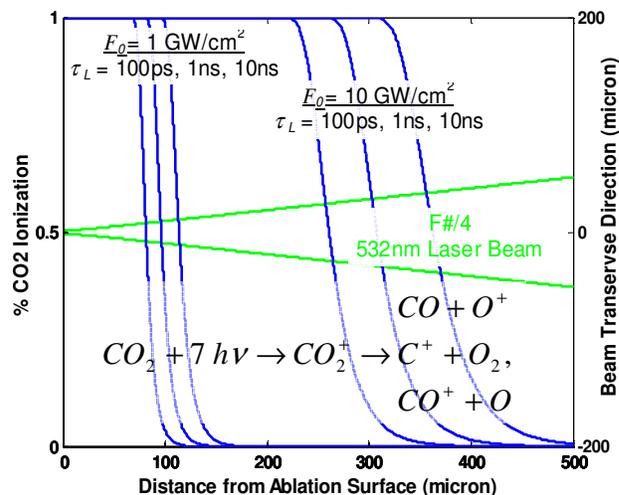
Figure 2: 532nm photo-ionization of Mars CO_2 with F#/4 focused laser at peak magnification for different intensities, F_o, and laser pulse durations, τ_L.

this "noise" source should be removable through in-situ calibration measurements

Summary: Elemental abundance measurements are of particular value for space science exploration because together with information on the spatial arrangements of these elements, inferences can be made regarding the processes which led to the observed deposition patterns. These patterns are indicative of past climate and may expose the presence of extinct life or possible habitats of extant life. Micro-LIBS is a potential powerful instrument for these measurements.

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