Lasers project energy over a distance with minimal spatial spreading. Focusing a laser beam can bring high energy density and high electric fields to bear on small areas of solids or liquids. If the energy is absorbed, the condensed phase can rise in temperature so rapidly that a portion of the condensed phase is vaporized. The vapor can expand, emit light, condense into particulates, or react with surrounding gases. In many ways, laser ablation is like spark ablation, but without the high voltage pulse and current conduction that characterizes electrical discharges. If sparks and lasers function similarly, why bother with lasers? What behavior might one seek in a laser?

Perhaps the best example is the geochemical analysis system on the Mars Science Laboratory. By focusing a laser on a rock up to 20 m from the roving Laboratory, atomic emission can reveal the elemental make-up of the rock. Because Mars' atmosphere is cold, low-pressure CO\textsubscript{2}, preparation of working curves for this mission has required elucidation of the role of atmosphere around the sample on the slope and intercept of working curves, just as for sparks, arcs, and other plasma sampling and excitation are influenced by discharge gas.

Among the ways laser ablation behaves like spark or arc discharges are:

- Signal-to-background ratio and ion-to-atom ratio vary with time after the plasma is initiated. Early on, continuum is more intense, as is the level of ionization. Thus, signal-to-noise ratio is most easily maximized by time gating observation of emission.
- A focused laser beam samples a small region on the surface of a sample, not an average distribution from the sample. Shot-to-shot variations thus depend in some measure on sample heterogeneity. Additional sources of variation include laser beam shape and energy reproducibility, shot noise (from the Poisson distribution of thermally-emitted light), shot noise (from the Poisson distribution of number of atoms sampled), and flicker noise (from the variation in geometry of atom ejection trajectory vs. plasma position).
- Averaging over many laser firings asymptotically can improve the precision of measurement.
- The effect of melting and freezing of the sample surface can influence matrix effects. Low-boiling elements can be preferentially sampled early in a set of firings, and the remnant surface can be enriched in high-boiling elements. Solubility of minor components in the major elements of the matrix as a function of temperature significantly influences the evolution of the signal as laser firing continues.

A critical difference, however, is that the temporal waveforms available with lasers can be optimized on a scale not feasible with most if not all current-injection plasmas:

- Laser pulses lasting nanoseconds or longer tend to produce arc-like spectra, surface melting, and exhibit significant matrix effects. Debris rims of splattered and melted sample around the ablation crater are common.
- Laser pulses lasting picoseconds tend to sputter samples, as energy has little time to diffuse into the sample before ablation has occurred.
- Femtosecond laser pulses are most nearly ideal, in that they deposit energy highly localized in space and time. By the time thermal diffusion has carried energy away from the sampling point, most atoms that will eventually have been sampled are already propagating away from the surface, leaving a clean, debris-free edge to the sample crater.
- Laser wavelength has some influence on ablation behavior, but shorter pulses, in general, are more critical to clean sampling than is wavelength selection. Tighter focus is easier with UV light than IR light, and short pulses are also easier to obtain in the UV.
- Firing two pulses separated by less than 1 µs can significantly increase sampling by pre-ionizing the space above the specimen and starting heating of the sample spot before the second laser pulse commences removal of specimen material.
Figure 1 illustrates the effect of laser pulse width on specimen ablation. The first column shows, in cross-section, the form of the ablated crater. Scale varies with laser power, but is typically > 100 µm for nanosecond pulses, while being a few tens of microns for femtosecond pulses. In consequence of the changes in crater geometry, ejected sample plumes are more narrowly focused as shown in the second column. Melting is more likely for long pulses than short, so matrix effects are more pronounced for long pulses. This is shown schematically in the working curves, right column, where linearity, precision, and freedom from response changes due to thermal history are all better for ultrashort pulses. Unfortunately, femtosecond lasers are more expensive, bulkier, and less common than longer pulse lasers such as N₂, excimer, or Nd:YAG lasers.

![Figure 1: Laser Ablation Pulse Effects](image)