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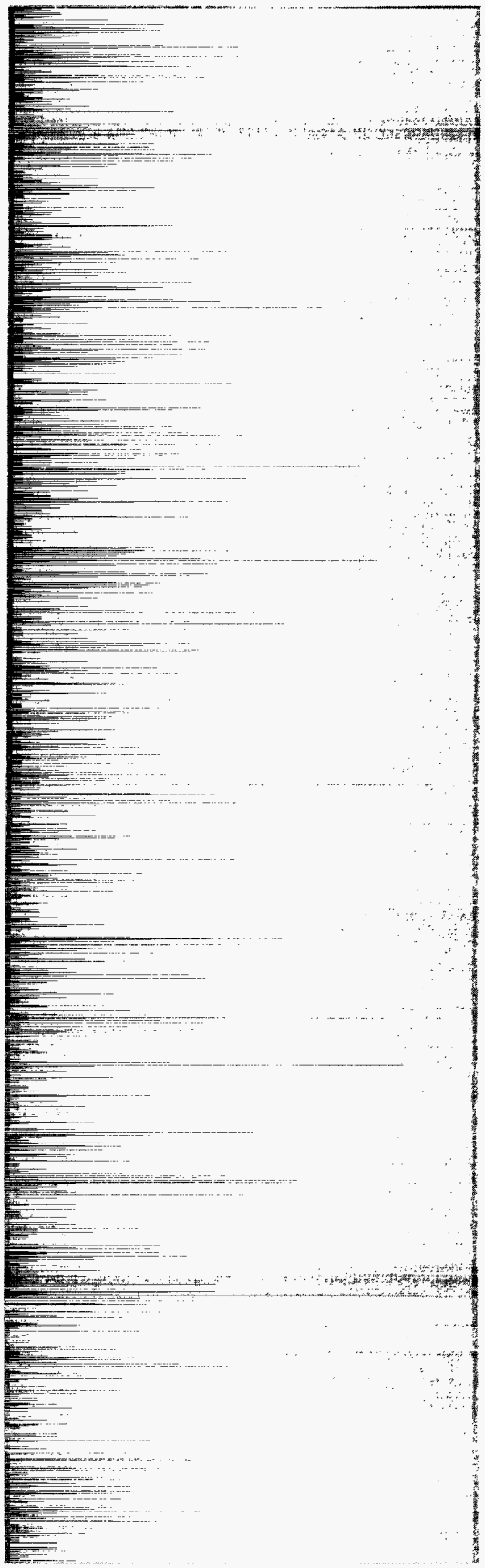

Field Deployment Test of Laser-Induced Breakdown Spectroscopy (LIBS) Technology at the Yucca Mountain Exploratory Studies Facility, Test Alcove #1, March 2-9, 1994: Milestone Report LA4047

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FIELD DEPLOYMENT TEST OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) TECHNOLOGY AT THE YUCCA MOUNTAIN EXPLORATORY STUDIES FACILITY, TEST ALCOVE #1, MARCH 2–9, 1994: MILESTONE REPORT LA4047

by

J. Blacic, D. Pettit, and D. Cremers

ABSTRACT

A field test in the Exploratory Studies Facility at Yucca Mountain, Nevada was performed to determine the feasibility of real-time elemental analysis of rock encountered in air core drilling using the technique of laser-induced breakdown spectroscopy (LIBS). Over the period March 2–9, 1994, hundreds of LIBS spectra were collected in real-time, reflecting the elemental composition of dust produced at the drill head of the second horizontal core hole in Test Alcove #1. The particle-laden, drill-coring effluent air stream served as the means to obtain a representative rock sample immediately surrounding the drill bit. LIBS spectra were taken with the spectral range centered at 250, 330, 410, and 500 nm so that representative, overlapping spectral coverage from 200 to 550 nm was obtained for the dust. Spectral lines for the major elements Si, Al, K, Na, and Fe and the minor elements Ca, Mg, Ti, and Mn were observed. Some simple engineering improvements to the cyclone separator were identified if this approach to dust analysis is pursued in the future.

OBJECTIVE

The main objective of this field test was to demonstrate, under realistic field conditions, the feasibility of real-time elemental analysis of rock using the technique of laser-induced breakdown spectroscopy (LIBS). LIBS is a form of atomic-emission analysis in which a small amount (micrograms) of material is vaporized into its atomic constituents and the atoms are electronically excited to emit light at wavelengths characteristic of the elements. LIBS is similar to standard, laboratory-based analytical methods such as flame or inductively coupled plasma (ICP) atomic emission, except that we use the very-high energy density in a laser pulse to both vaporize and excite the test material. The small solid-state lasers and charge-coupled device (CCD) detectors that are now commercially available make it possible to construct a field-portable instrument of this type that

could have a number of applications in the Yucca Mountain Project (YMP), as discussed below. The hydrochemistry horizontal core drilling in Test Alcove #1 of the Exploratory Studies Facility offered a target of opportunity to test a prototype LIBS instrument aimed at analyzing the cuttings dust associated with the drilling operations. Broader objectives of the test included familiarization with the chemistry of the rock units and morphology of the cuttings dust, familiarization with the operational aspects of coring and mining at the Exploratory Studies Facility, test of a dust-sampling approach, and examination of LIBS field-packaging and power issues.

FIELD APPARATUS

The particle-laden, drill-coring effluent air stream served as the means to obtain a representative rock sample immediately surrounding the drill bit. A miniature cyclone separator 5 cm in diameter and 30 cm in length powered by a small vacuum cleaner processed a portion of the drill-coring effluent air stream. Input to the LIBS cyclone separator was from a tap into the dust line just before it entered the Torit bag filter (Fig. 1). In an earlier visit to the site, we determined that the pressure (partial vacuum) in the filter line at this point was greater than that produced by our small vacuum cleaner, so we could extract a significant quantity of dust. The cyclone separator was designed to give a 50% mass-fraction removal for particles in the 1- to 5-μm-diameter size range. The remainder of the particles were caught in the vacuum cleaner filter, which had a size cutoff of 0.2 μm.

A pulsed Nd-YAG laser producing 20 mJ/pulse (8 ns duration) of 1.06 μm light was used as the excitation source by focusing the 3-mm-diameter exit beam into a spot less than a millimeter in diameter with a 45-mm-focal-length lens. The depth over which the beam remained tightly focused was about a centimeter. The focal point was centered inside a chamber 5 cm in diameter where the dust from the cyclone fell through the laser-focal-point region and into a 250-cm^3 collection jar. Laser power was insufficient to form an air plasma when no dust particles were present. When sufficient particles were present, a plasma formed—enveloping the dust and the surrounding air—and provided a means to thermally excite atomic emission at temperatures above ~15 000 K. The entire laser beam was fully contained, giving Class I eye-safe operation for those working in the area. A 3.2-cm-diameter window with a filter of optical density 15 for the 1.06 μm laser light provided eye-safe visualization of the dust flow and plasma formation. The cyclone, laser head, and sample chamber were mounted together in a compact unit (Fig. 1).

An ultraviolet-grade fiber-optic bundle of 1.25 mm diameter on the gathering end and line shaped on the opposite end directed the plasma emissions to the 25-μm-wide spectrometer slit. The spectrometer was a Jarrell Ash f3.8, 15.6-cm-focal-length unit with a 1200-line/mm grating, giving a spectral range of 105 nm and a resolution of 0.4 nm. The spectrograph was calibrated each day

using Hg, Al, Fe, Pb, and Sn standards. Spectra were taken with the spectral range centered at 250, 330, 410, and 500 nm so that representative, overlapping spectral coverage from 200 to 550 nm was obtained for the dust. We found the spectra centered at 410 nm to be particularly useful, hence that is where most of the data were taken. A Photometrics model CH 250 1024 × 1024 CCD array (thinned, back-illuminated and metachrome-coated) recorded the spectra. Kestral software was used to acquire and display the spectra with a Macintosh IISI computer. All the sensitive equipment was built into two water/dust proof shipping containers, with filtered muffin fans providing the necessary ventilation (Figs. 1 and 2).

Fig. 1. LIBS test setup adjacent to core-drilling operations in Test Alcove #1. The 4-inch dust line is tapped at the left just before entering the large bag filter (Torit). The laser-cyclone assembly is the black unit positioned at the left side of the wooden table in front of the blue-painted bag filter unit. The cyclone is the vertical cylinder/cone unit with the blue label, and the cylindrical laser head is to the left with the red/white laser warning sign on it. The centered spark chamber with yellow/green-colored eye-safe filter-window can be seen with the sample collection bottle below. The vacuum cleaner is the black box directly behind the cyclone, and the fiber-optic cable enters the white spectrometer box to the right on the table.

Fig. 2. View of the LIBS system with the core-drilling rig in the background. The spectrograph and CCD camera are contained in the white, oblong box on the large wooden table to the right, and the computer, CCD controller, pulse generator, and power supply are contained in the square-shaped white box on the small table to the left. The flat-panel display, dust/water-protected keyboard and track ball shown on the larger table were used to control the system.

RESULTS

During the drilling operation the laser was pulsed once every 7 s, and a spectrum was taken and stored to disk. At a drilling rate of 3.5 ft/hr, every 30th spectrum represents a 0.1-ft advance in the hole. Because of axial dispersion of dust traveling in the lines and dust clinging to the hose walls and periodically breaking loose, we estimated that ±0.2 ft is the minimum resolution of down-hole distance. The spectra were viewed in real time as they were taken, and the emission lines from the major elements were manually identified. Real-time computer analysis of the emission lines for elemental composition has not been implemented as of this writing.

We found that the dust flow rate varied considerably during the drilling operation, depending on the extent of rock fracture that was encountered by the drill. When drilling through unfractured rock, the dust flow rate was such that we obtained spectra with nearly every laser pulse. The particle recovery was sufficient to require changing of our collection jar every few minutes, and at times we became overwhelmed with the volume of dust. The rock-flour dust was very fine (peak in grain-size distribution ~3 μm, Fig. 3) and tended to clump and build up in the cyclone neck and at times would even clog the sample chamber, preventing sparking. At these high dust flow rates, the system required periodic cleaning. We concluded that for future operation, a simple motor-driven screw in the cyclone neck will help prevent this buildup. When the drill core encountered highly fractured rock, most of the dust was blown out into the formation and lost. During this lost circulation phase, collection of spectra was erratic, with one spectrum being collected every 15 to 25 laser pulses. The collection jar would take an hour or more to fill during lost circulation which was common during the drilling of this particular hole.

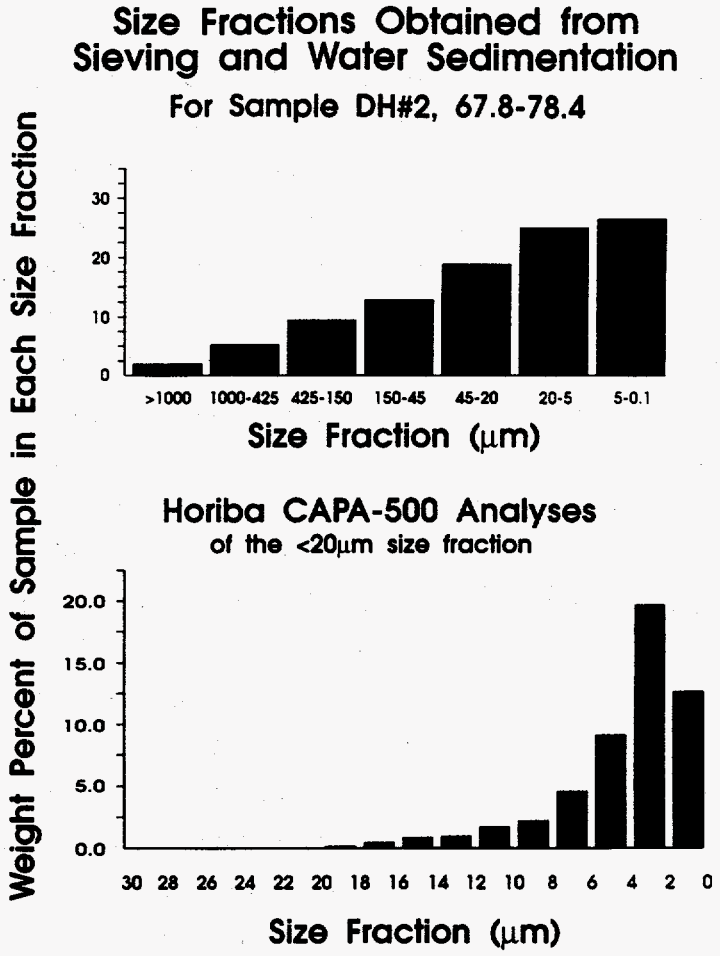

Fig. 3. Grain-size distribution of cuttings dust collected from the drilling interval 67.8–78.4 ft.

SPECTRA

Figures 4–7 show representative spectra, arranged in ascending wavelength, collected at different depths along the drill hole. In all of the spectra, we have made assignments of elements to specific peaks in cases for which such assignments were relatively unambiguous. However, in many cases we observed composite peaks in which a number of closely adjacent lines blend into a single, broad, complex peak that can be difficult to interpret. One important conclusion of our experiment is that a system with 2–3 times greater spectral resolution than the system we fielded, with at least three spectral bands across the ultraviolet and blue-green regions of the spectrum, will be needed in order to adequately analyze rock materials of this chemical complexity. For example, the region centered around 280 nm (Fig. 4) is optimal for characterizing Mg and Si; the band around 335 nm (Fig. 5) is optimum for Ti and K; and the band centered at 395 nm (Fig. 6) is optimum for Ca and Al. Spectrographs with software-controlled grating turrets and other optical designs are available commercially in physical sizes that would fit within the package we fielded, but these were beyond the resources available to us for this feasibility experiment. Future designs should take advantage of these capabilities.

Figure 7 illustrates another aspect of the data that can be a problem at times of low dust production, such as the long periods of lost circulation that were encountered on this drill hole. Apparently when only a few small dust grains are present in the chamber, sparking may occur in which the plasma is dominated by the air constituents rather than rock constituents. In these cases the spectra are dominated by strong nitrogen lines near 400 nm and 500 nm. This was not a problem during the times when moderate to large amounts of dust were being produced. Figure 7 also illustrates a minor problem in which we occasionally observed Hg lines from the fluorescent lighting in the tunnel. This is easily eliminated by covering or shading the window into the spark chamber.

Additional analysis of the data can bring out details of compositional variation with depth along the hole. An indication of the potential of such analysis is shown in the following two figures. In Fig. 8 we show some detail using spectra from the 25-ft level which represent compositions approximately 0.1 ft apart at this depth. The spectra have been base-line-corrected and normalized to the strong aluminum emission at 396 nm (compare with Fig. 6). Variations in silicon, calcium, manganese, and titanium content can be seen over this restricted depth interval, based on variations of specific peak heights relative to aluminum; with suitable calibrations these relative-intensity variations can be quantitatively converted to composition information. In addition multidimensional plotting of key-element ratios can give estimates of mineralogic variations. On a broader scale Fig. 9 shows variations in one element, titanium, over most of the depth of the hole. This indicates the potential for stratigraphic correlations between holes based on key-element signatures.

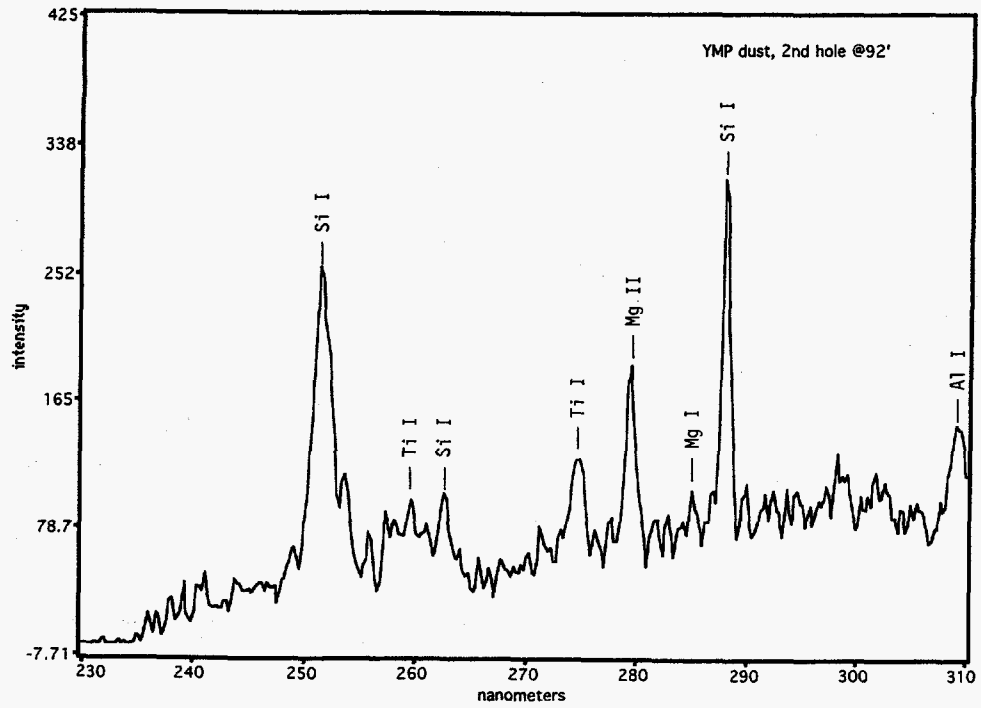

Fig. 4. LIBS spectrum over the wavelength range 230–310 nm taken at approximately 92 ft within the drill hole. Prominent peaks are identified by element; "I" indicates neutral atomic species, and "II" indicates once-ionized species.

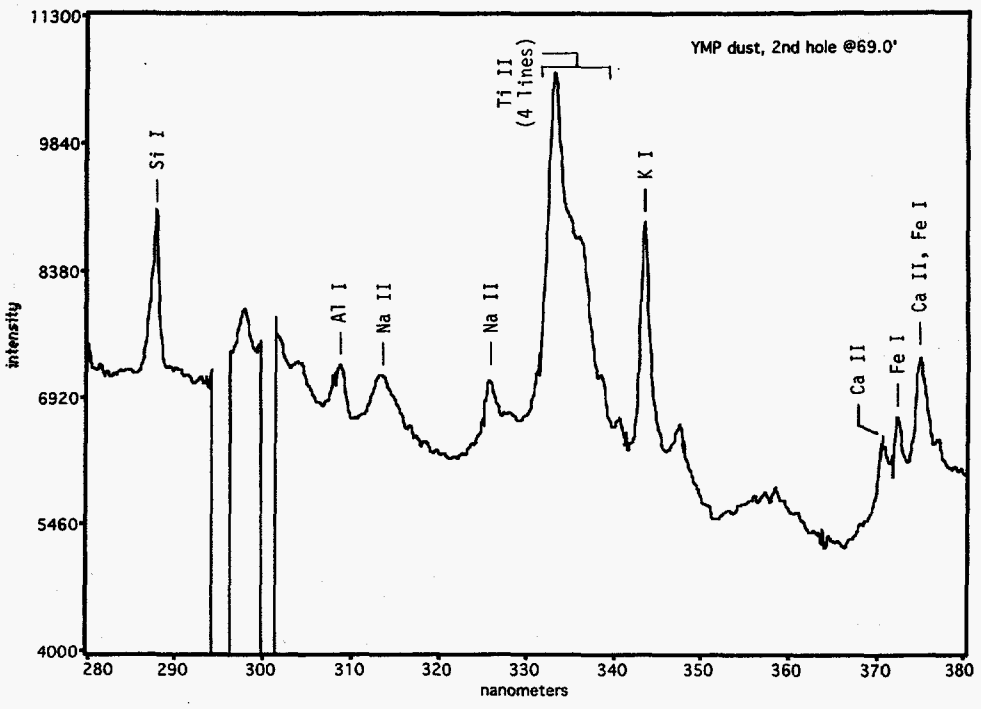

Fig. 5. LIBS spectrum over the wavelength range 280–380 nm taken at approximately 69 ft within the drill hole. The two holes in the spectrum near 295 nm and 300 nm resulted from two bad lines of pixels in the CCD chip of the detector. Peak notation is the same as in Fig. 4.

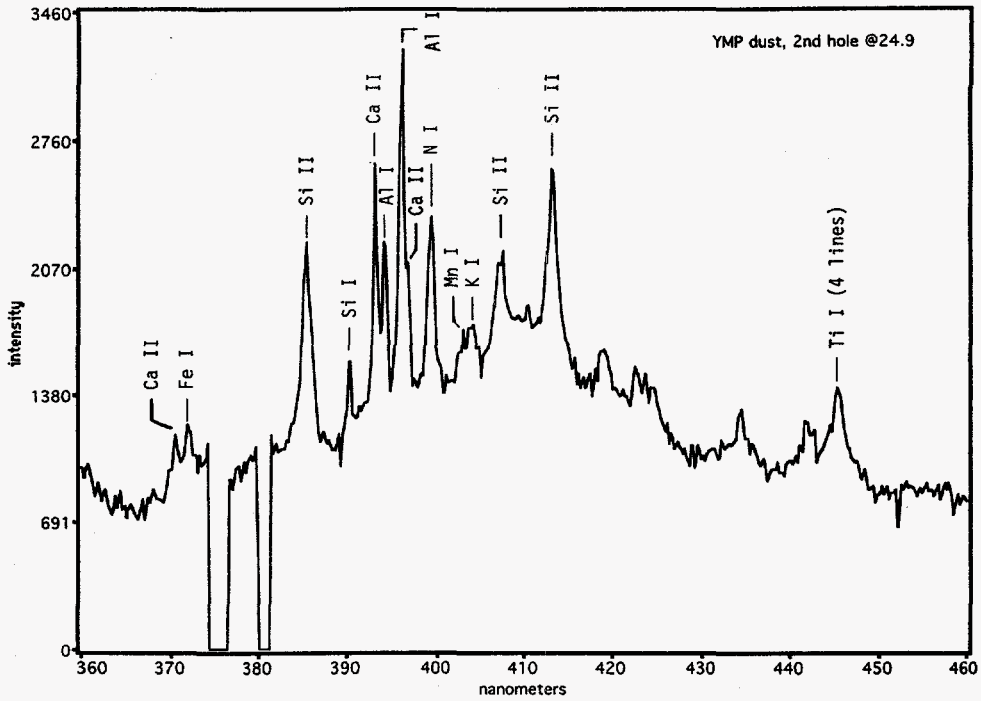

Fig. 6. LIBS spectrum over the wavelength range 360–460 nm taken at approximately 24.9 ft within the drill hole. Most of the data were acquired in this wavelength band, and although there is some variation in spectral features and relative peak intensities, all of the spectra are similar. Peak notation is the same as in Fig. 4.

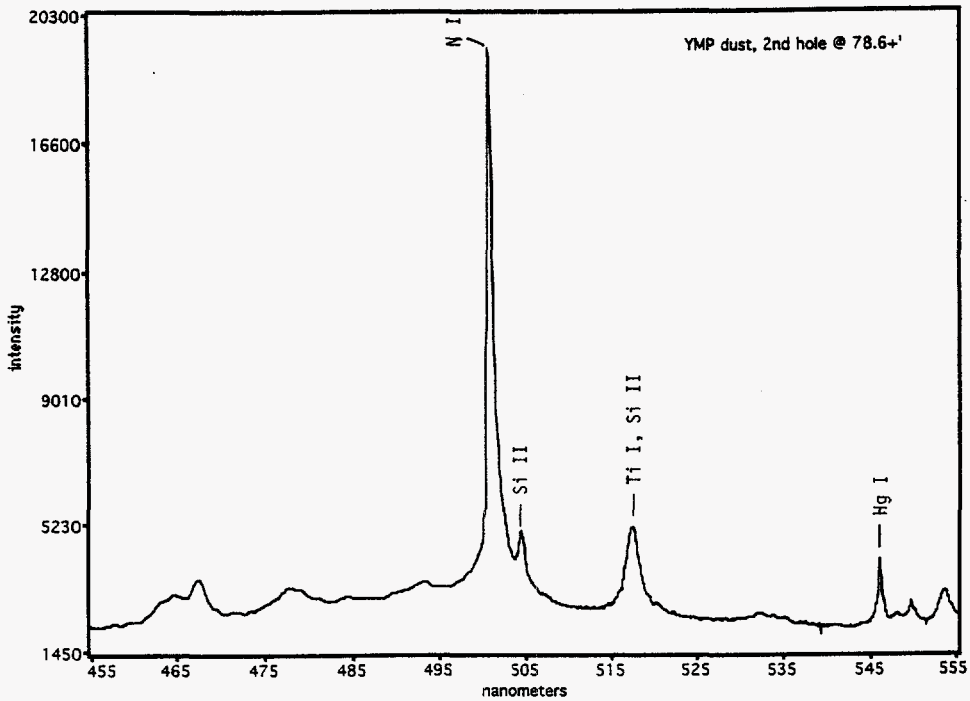

Fig. 7. LIBS spectrum over the wavelength range 455–555 nm taken at approximately 78.6 ft within the drill hole. The intensity of the nitrogen peak at ~500 nm (also at ~400 nm, not shown) is typical of spectra taken during periods of lost circulation when very little dust was reaching the instrument. Peak notation is the same as in Fig. 4.

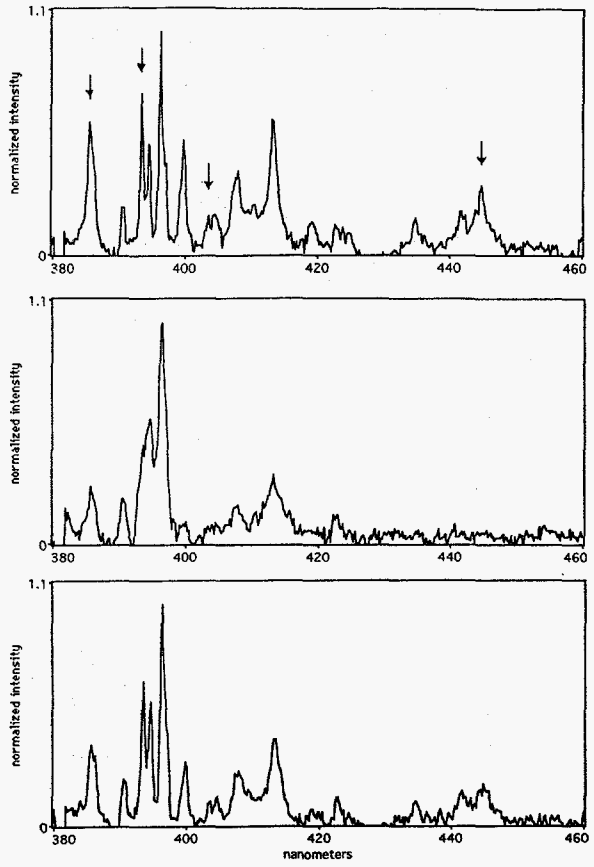

Fig. 8. Processed spectra from the 25-ft level. Each of the three spectra represent data equivalent to about 0.1 ft differences in depth along the hole at this level. In each spectrum the base line has been flattened to remove the broad, white-light pedestal on which the emission lines are superimposed. In addition the spectra have been normalized to the Al emission line at 396 nm in order to bring out variations of other elements relative to Al. Four lines are highlighted by arrows in the top panel, indicating emissions for Si, Ca, Mn, and Ti, respectively, from left to right (compare to Figure 6).

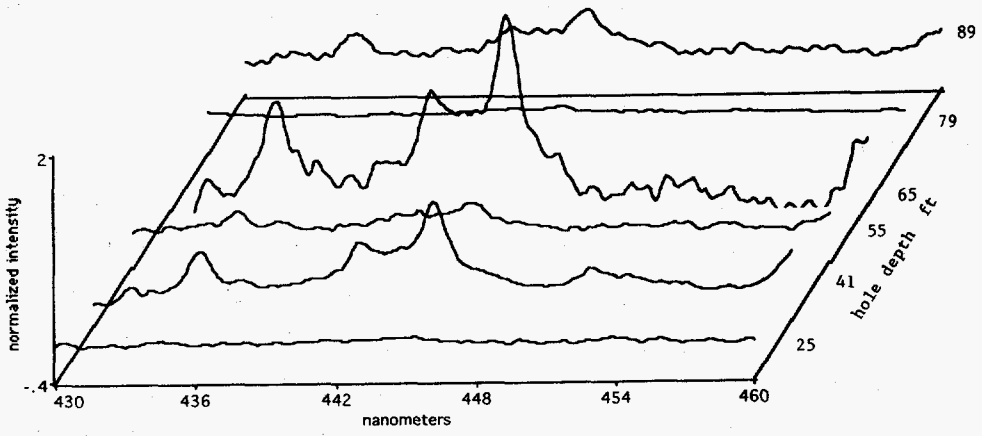

Fig. 9. Portions of selected spectra from different depths along the hole to illustrate variations in titanium content based on emissions at 442 and 445 nm. The spectra have been base-line corrected and normalized to Al, as described for Fig. 8. The approximate hole depth for each spectrum is indicated along the right margin of the plot.

After the field test, we performed laboratory ICP atomic emission and x-ray fluorescence (XRF) analyses on a sample of the drill-hole dust. The average results of this analysis are shown in Table I.

Table I
Average Composition of Drill-Hole Dust

Major and minor constituents (%)		Trace elements (ppm)			
SiO_2	74.9	P	60	V	10
Al_2O_3	12.3	B	10	Cu	105
K_2O	4.5	Ba	65	Zr	200
Na_2O	3.8	Li	33	Cl	205
Fe_2O_3	1.2	Pb	17	F	340
CaO	0.2	Cr	21		
MgO	0.1	Ni	120		
TiO_2	0.1	Sr	67		
MnO	0.1	Rb	178		
Trace metals	~0.1	Zn	115		
TOTAL	97.3				

Summarizing the results, we observed spectral lines for the major elements Si, Al, K, Na, and Fe and the minor elements Ca, Mg, Ti, and Mn. Other minor and trace elements may be extractable from the many small peaks as yet unidentified in the spectra; we are continuing analysis of the data with the aid of some higher-resolution spectra taken in the laboratory using the dust samples we collected during the field experiment. We have identified the optimum spectral bands and the required level of resolution needed for future work.

CONCLUSIONS

Over the period March 2–9, 1994, hundreds of LIBS spectra were collected in real time, reflecting the elemental composition of dust produced at the drill head of the second horizontal core hole in Test Alcove #1. We consider this fundamental aspect of the test a complete success.

All major and minor elements were identifiable in the spectra, although additional spectral resolution would improve the analysis and bring out additional elements. We believe this is achievable within the mass/power envelope we fielded in this feasibility experiment.

The dust-sampling system worked nominally (sometimes too well), but the fineness of the cuttings and the associated dust clogging in our system were a surprise and gave us some problems, as did the extensive and unanticipated loss of circulation over which we had no control. Some

simple engineering improvements to the cyclone separator are in order if we pursue the dust analysis in the future.

POTENTIAL APPLICATIONS OF LIBS AT YUCCA MOUNTAIN

Further development of a real-time LIBS dust elemental analyzer for field use will depend on specific requirements within the YMP. We have demonstrated the basic feasibility of LIBS dust analysis, and we have determined the hardware improvements and operational procedures that, along with software development, will be needed to design a practical field system. The dust analysis is probably the hardest problem for the LIBS approach in that the sample is relatively difficult to control. A more optimum use of LIBS is on solid surfaces where multiple sparks on a single point can enhance signal-to-noise ratio and one has more control over the sample. Several applications of LIBS to elemental analysis of static solid surfaces that we believe would be of interest in the YMP suggest themselves:

(1) Core analysis. We noted during our field test that the rate of advance of the drill hole was not dependent on the drilling rate but on the rate at which the core could be logged; the drillers were often idle, waiting for the logging team to catch up on core that had already been produced. This suggests that instead of or in addition to the real-time manual core analysis, LIBS could be used to characterize the core as part of the normal logging procedures. An individual point analysis with LIBS takes less than 10 seconds, so it would be easy to spark along the length of the core with a relatively high density of analysis points in a matter of a few minutes. This would not interfere with normal lithologic descriptions or video-taping procedures and could in fact be incorporated into the imaging of the core as a way of documenting the analysis points.

(2) Fracture-filling analysis. An important aspect of the licensing and performance of a repository at Yucca Mountain will be the characterization, quantification, and documentation of the radionuclide sorptive capacity of the host rock. A key element of this process will be the characterization of the fracture-mineral fillings, particularly the manganese minerals that occur heterogeneously throughout the Yucca Mountain block. Up to this time such characterization has been done by time-consuming optical and scanning electron microscopy of a small number of samples returned to the laboratory. It is not clear to us how complete fracture-filling characterization could be done with such methods within reasonable man-power limits and within the limited exposure time of the tunnel walls. Potentially thousands of analyses may be needed to fully characterize the distribution of sorbing minerals in the rock mass and along fracture surfaces in the vicinity of the repository. This means that extensive sampling or in situ measurements will have to be performed along the walls of much of the tunnel produced before wire and shotcrete support is put in place (probably a few days after exposure, thereafter severely limiting access). We believe

LIBS may be an optimum, perhaps unique, solution to this problem because of its capability for fine spatial resolution (point analysis) and rapid, near-real-time character.

We envision a portable unit with an analysis head that contains an optical-fiber-conveyed laser source, optical-fiber-conveyed spark signal, optical-aiming magnifier and reticule to fix the analysis point, and a photographic or video-imaging element to document each analysis point. The head would be placed on the surface of a tunnel wall or core sample with a soft, conforming seal to safely enclose the laser beam. Such a device might be used as part of the tunnel-wall characterization activities planned to be used at the gantry access of the tunnel boring machine (TBM). Point analyses along lines on the tunnel wall, obtained as the TBM advances, would, along with similar analyses of available core samples, allow construction of a fracture-filling data base. From such a data base a statistical estimate of, for example, the amount of sorptive manganese mineral fracture fillings within the repository block could be constructed. It is difficult for us to conceive of any other way in which such an important data estimate could be achieved in a credible way within reasonable man-power limits.

(3) Bore-Hole Logging.

The laser and detector components of a LIBS for sparking on solid surfaces at close range are sufficiently small and low-powered that a bore-hole logging tool based on LIBS could be developed. Such a tool would complement the data produced by gamma logs and other geochemistry logging methods. Each logging method has optimum sensitivity for particular elements, and the lists of elements only partially overlap. Hence, a LIBS tool could provide information not available from other methods as well as a check on overlapping elements. Issues that would have to be examined include use of a high-pulse-rate laser (e.g., ~10 Hz) and high-speed digital-data transmission uphole. The latter is probably adaptable from existing tools, and high-pulse-rate lasers are available that use active cooling.

RECOMMENDATIONS

Based on the results of our feasibility field experiment, we recommend that the program consider the following actions:

(1) This report should be distributed to potential users of data that could be produced from drill-cuttings dust by the LIBS method. Questions that should be asked of these users: Is there a need for continuous, real-time elemental analysis during the drilling? What elements in the rock are of interest, and how will the data be used? Roy Long of the Site Investigations Branch has expressed interest in the possibility of using LIBS in conjunction with surface-drilling operations at Yucca Mountain. Our understanding of the surface-drilling operations suggests that a different approach to that used in the Test Alcove drilling would be needed. Perhaps a feasibility experiment on a surface-drilling operation is in order. This possibility should be explored.

(2) We recommend support for a laboratory investigation of the spectral characteristics of manganese minerals by the LIBS method. Because some of the manganese minerals that occur at Yucca Mountain contain significant quantities of diagnostic elements such as Pb, Ba, K, Li and Sr, it may be possible to determine relative proportions of mixtures of these minerals on fracture surfaces in a rapid manner by LIBS. This possibility should be investigated. If the approach we suggested above for characterization of the fracture-filling minerals expected to be encountered by the TBM is to be implemented, the laboratory work should begin as soon as possible, so that a timely field capability can be developed.

(3) A study of the potential need for and relative merits of a bore-hole geochemistry tool based on the LIBS methods should be undertaken. If such a need is determined, we recommend a feasibility study to investigate engineering issues associated with development of a LIBS bore-hole logging tool.

ACKNOWLEDGMENTS

We received outstanding operational support from Joel Spoeneman and Alan Mitchell during the field test. The miners and drillers were very tolerant of our activities and sensitive to our needs. We would like to express our thanks to all of the people at the drill site; their help made our job easier and significantly contributed to the success of our operations.

At Los Alamos, Monty Ferris contributed many helpful suggestions during the design and construction of the LIBS equipment. Leeanne Foster aided interpretation of the data by obtaining high-resolution spectra of samples of the cuttings dust, and Steve Chipera analyzed the grain-size distribution of the cuttings. Dale Counce performed the ICP analysis, and Emily Kluk performed the XRF analysis.