LASER-INDUCED TIME-RESOLVED LUMINESENCE AND LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR EVALUATION OF PHOSPHATES WITH HIGH DOLOMITE CONTENT

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FOR EVALUATION OF PHOSPHATES
WITH HIGH DOLOMITE CONTENT

FINAL REPORT

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PERSPECTIVE

Patrick Zhang, Research Director - Beneficiation & Mining

With the depletion of the higher-grade, easy-to-process Bone Valley deposits, the central Florida phosphate industry has moved into the lower-grade, more contaminated ore bodies from the Southern Extension. The phosphate deposits in the Southern Extension may be divided into two zones: an upper zone and a lower zone. The upper zone is readily upgradable using the current technology, but the lower zone is highly contaminated by dolomite. This makes it more critical to control the quality of the pebble product, particularly the MgO content. Current practices require either stockpiling of pebble product until quality control data from sampling become available, or making the shipping or discarding decision based on visual observations of rock as it is being produced. Obviously, this practice can result in the shipping of undesirable products to the chemical plant or the discarding of acceptable pebbles. A reliable instantaneous analytical method is the ultimate solution to this problem.

Laser Induced Breakdown Spectroscopy, LIBS, is a relatively new technology born shortly after the invention of the laser. In LIBS, a very energetic laser spark (plasma) is formed by focusing a laser to produce irradiance in the range from 1-10 MW/cm^2. Breakdown occurs because the electric field at the focus exceeds the dielectric strength of the surrounding environment. LIBS has been studied in a wide variety of materials including many gases, solids and liquids. This technique has been successful mainly in low-level trace element analysis of liquid samples. Recently, several bench-top LIBS have been developed and commercialized for dry solid samples.

This FIPR project is perhaps the first successful demonstration of the LIBS technology for on-line analysis of wet mineral samples. The optimal method for dolomite content analyses on a moving belt was found to be plasma-induced time-resolved luminescence based on characteristic lines of F/P in apatite at 604 nm with a relatively long decay time of 500 ns, and of Mg in dolomite at 518 nm with a shorter decay time of 200 ns. This method has been deemed novel, and FIPR has filed for patent protection on it.

The FIPR Board of Directors has approved further funding for developing a prototype, on-line LIBS analyzer for phosphate pebbles based on the method developed under the current project. We hope that, building on the success of analyzing pebbles, this technology could eventually be made suitable for on-line analysis of flotation streams.

ABSTRACT

A system and method were developed and demonstrated for online, essentially instantaneous analyses of ore compositions on a moving belt using laser-induced breakdown spectroscopy (LIBS). In this method, intensity ratios of emission lines characteristic of specific minerals or ions are calculated on areas of the moving belt, with elevated contents of identifying ions or species being detectable. The ratios are derived from ions present in the sample that differentiate a first substance from a second substance, thus allowing sorting of the samples.

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INTRODUCTION

Dolomite separation is becoming a pressing problem as the central Florida phosphate industry moves to the south, where the deposits are lower grade and have high magnesium content. Bypassing these high-dolomite deposits would waste about 50% of the phosphate. The most common problem with the available flotation processes is the significant loss of fine phosphate when the ground high-dolomite pebbles go through the desliming process, which separates the particles by size. Thus it is important to develop an economically viable method for real-time evaluation of dolomite contents in phosphate rocks in order to remove dolomite prior to deep beneficiation.
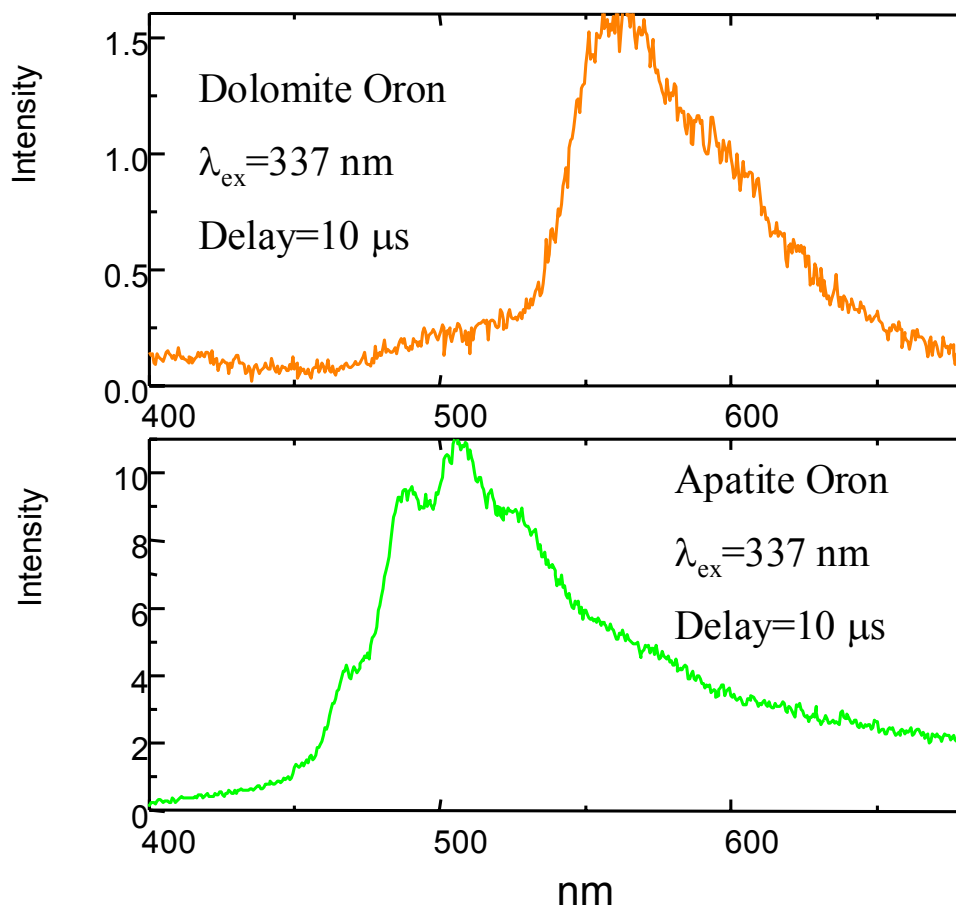
LASER-INDUCED TIME-RESOLVED LUMINESCENCE SPECTROSCOPY

INSTASPEC EQUIPMENT

Two years ago, laser-induced time-resolved luminescence was proposed as a tool for the task of dolomite separation from phosphate deposits. The idea was based on scientific research, which proved that natural apatite contains several characteristic luminescence centers, which enables it to be differentiated from dolomite. The mostly widespread characteristic luminescence center in apatite is uranyl $(UO_2)^{2+}$, with typical vibrational green band luminescence under nitrogen laser excitation (Figure 1). Nevertheless, it appears that such luminescence is absent in phosphate rock samples from Florida. Figure 2 demonstrates typical laser-induced luminescence spectra of apatite and dolomite from Florida. It is clearly seen that the steady-state luminescence spectra are practically the same. After a relatively long delay time of more than 5 μs, the luminescence of organic matter with very short decay time is several orders of magnitude lower and luminescence of apatite and dolomite becomes different. The broad band of dolomite is evidently connected only with remnants of organic matter emission with a long decay time, while in apatite it may be ascribed to Mn^{2+} luminescence with strongly forbidden d-d transitions and correspondingly a very long decay time.

According to accumulated experience, broadband luminescence features are not the best ones for the evaluation task. This is especially true when we are dealing with poorly identified organic matter luminescence, which may change very suddenly. For this reason we prolonged our effort to find a feature by which we could more confidently make differentiations.

In order to find potential luminescence centers, an ICP-MS analysis of Florida phosphates was accomplished. The best known ones in apatite are the rare-earth elements (REE). It is seen that these are present in Florida apatite in quantities which are quite sufficient for laser-induced luminescence analyses (Figure 3). The highest concentration and quantum efficiency has Ce^{3+}, but unfortunately its luminescence is in the UV-violet part of the spectrum and has a very short decay time, comparable with that of organic matter. Thus its luminescence will not be seen under a strong background. Of the other REE, theoretically Dy^{3+} is the best candidate because of its favorable combination of concentration, quantum efficiency, and spectral and temporal characteristics. According to the Dy^{3+} excitation spectrum, the third harmonic of the Nd-YAG laser at 355 nm was the most suitable amongst the lasers at our disposal. As we expected, narrow lines of Dy^{3+} with a long decay time of 500-600 μs do appear under 355 nm excitation in apatites, while they have never been detected in dolomite (Figure 3). The reason for this is that dolomite is a very bad matrix for the formation of luminescence centers, even if it has suitable concentrations of corresponding impurities. Besides, the isomorphous substitution of Ca^{2+} in apatite for trivalent REE occurs much more easily than is the case for Mg^{2+} in dolomite.

Figure 1. Time-Resolved Luminescence Spectra of Negev Apatite and Dolomite at 337 nm Excitation.
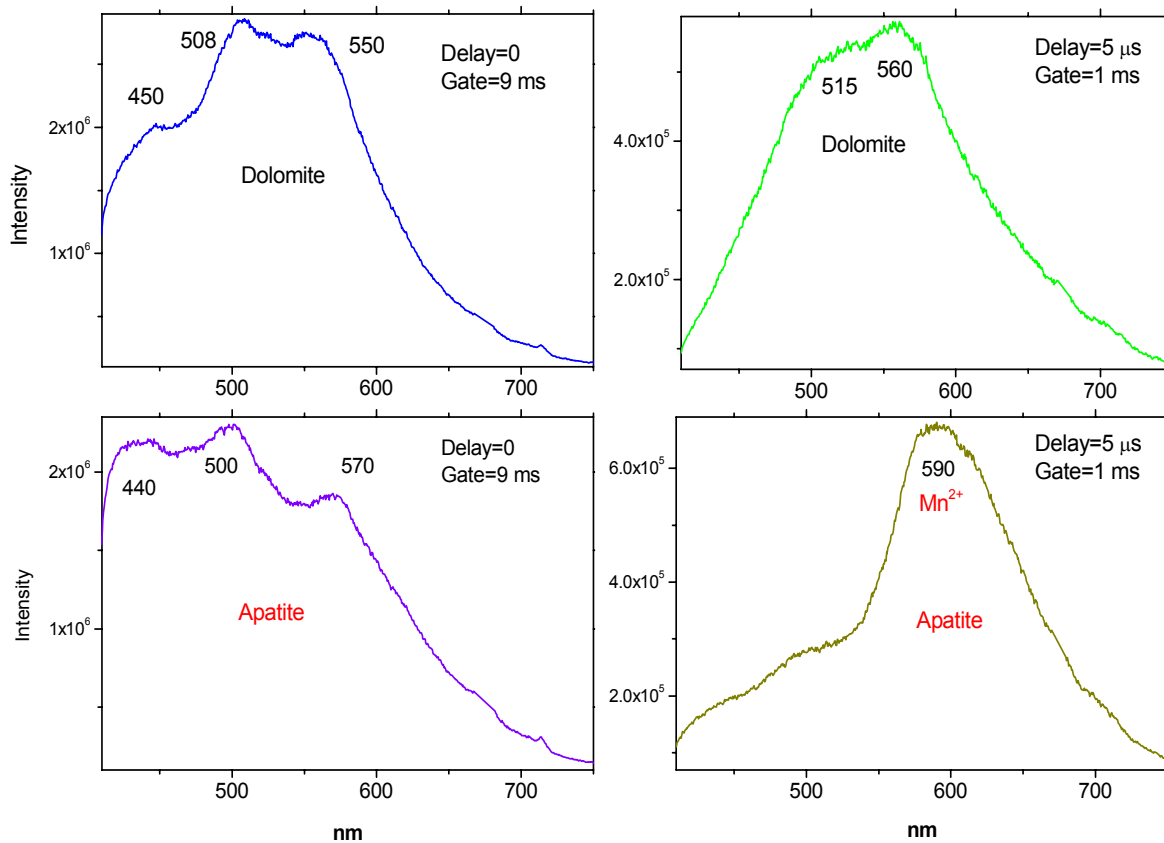
Figure 2. Florida Apatite and Dolomite Spectra Under λ $_{ex}$ = 337 nm.
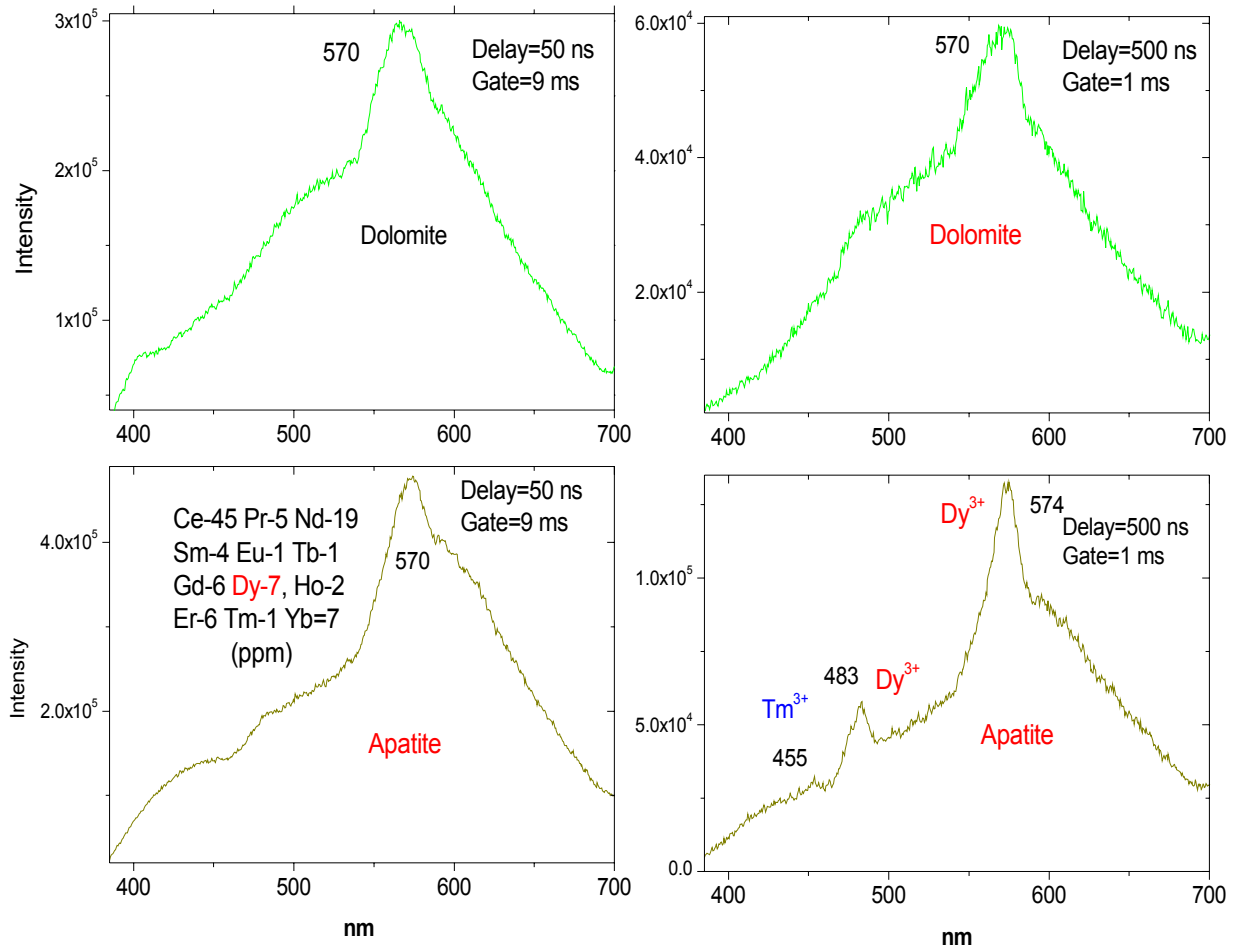
Figure 3. **Luminescence of Florida Dolomite and Apatite Under λ_{ex} = 355 nm.**

In the second stage, more than 200 samples were randomly chosen from those sent by IMC Phosphates. Two selective features were used: characteristic lines of Dy^{3+} and intensity ratios of 580 nm and 530 nm (I_{580}/I_{550}). The typical spectrum at 355 nm excitation is presented in Figure 4.

+1/2 FRACTION

Twenty-two samples were randomly chosen from *the light colored part*: nine were identified by XRD as apatite and 13 as dolomite. By laser-induced time-resolved luminescence (LITRL), six apatites clearly demonstrate Dy^{3+}, while it is never detected in dolomite. The parameters using the I_{580}/I_{550} ratio are practically the same.

Thirteen samples were randomly chosen from *the dark colored part* and all were identified by XRD as apatite. Dy^{3+} appears only in 45% of the samples, while it was impossible to check the intensity ratio feature because we did not have dark dolomite for comparison.
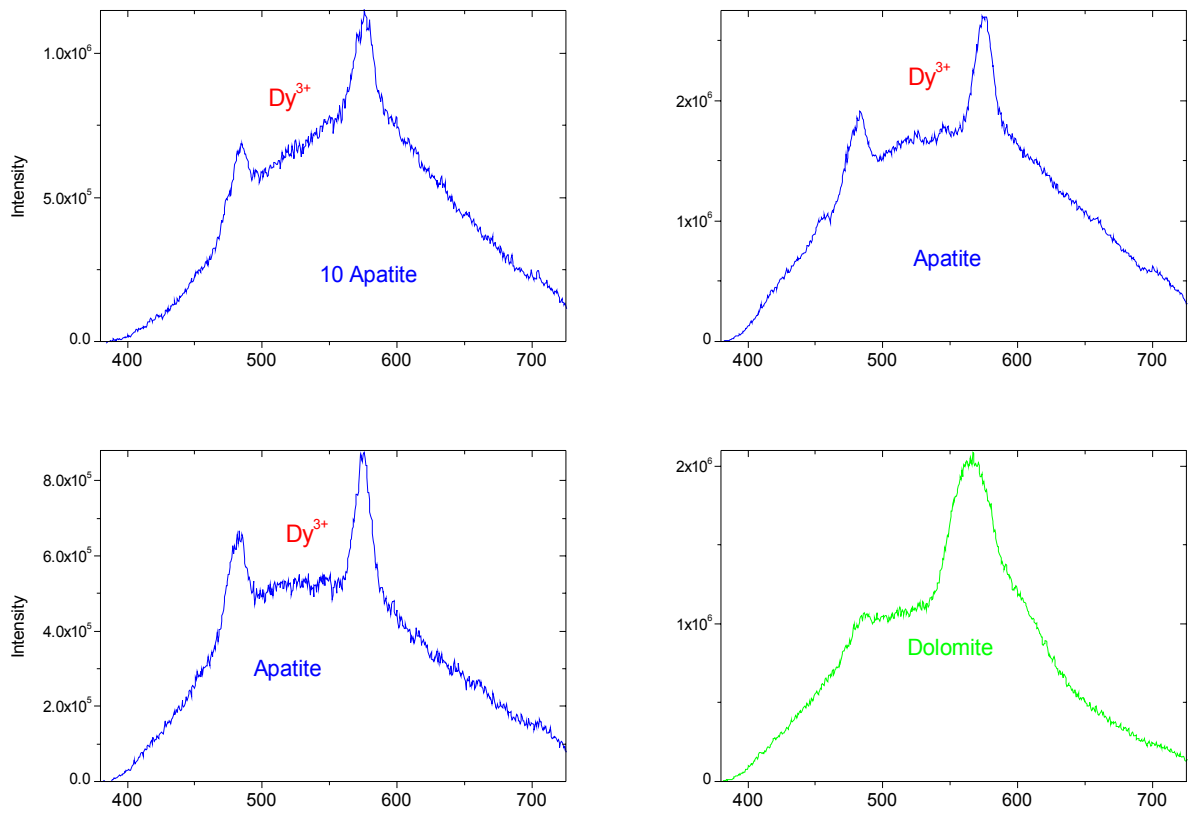
+3/8 FRACTION

Twenty-nine samples were randomly chosen from *the light colored part*: 15 were identified by XRD as apatite and 14 as dolomite. By LITRL, six apatites clearly demonstrated Dy^{3+}, while it was never detected in dolomite. The intensity ratio distinguishing feature enabled us to identify 12 apatite pebbles (80%), but one dolomite (7%) was also determined to be apatite.

Twelve samples were randomly chosen from *the dark colored part*: 10 were identified by XRD as apatite and two as dolomite. Dy^{3+} appeared only in two samples (20%), while the intensity ratio distinguishing feature enabled us to identify eight apatite pebbles (80%), rejecting dolomite.

+.156 FRACTION

Sixteen samples have been randomly chosen from *the light colored part*: 10 were identified by XRD as apatite and six as dolomite. By LITRL, eight apatites (80%) clearly demonstrated Dy^{3+}, while it was never detected in dolomite.

Twelve samples were randomly chosen from *the dark colored part*: 11 were identified by XRD as apatite and one as dolomite. Dy^{3+} appeared in nine samples (82%).

Figure 4A. Time-Resolved Luminescence of +1/2 Fraction at 355 nm Excitation.

Figure 4B. Time-Resolved Luminescence of +1/2 Fraction at 355 nm Excitation.
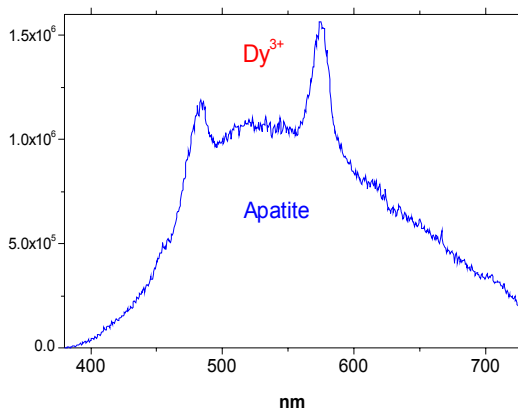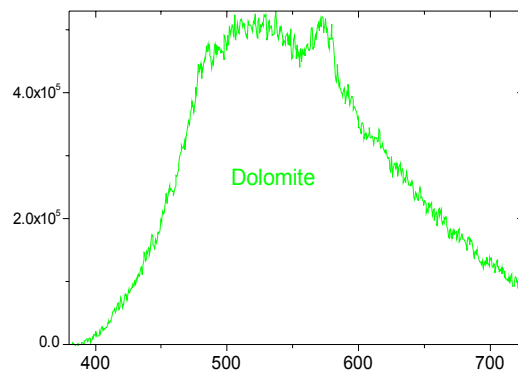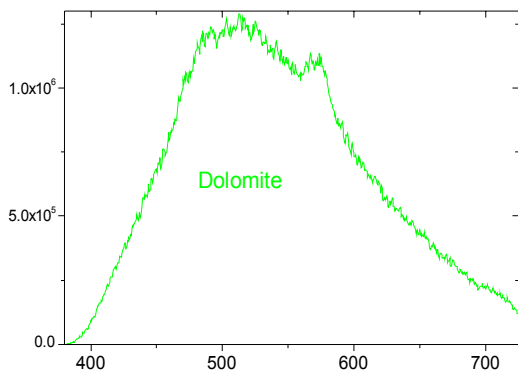
Figure 4C. Time-Resolved Luminescence of +1/2 Fraction at 355 nm Excitation.
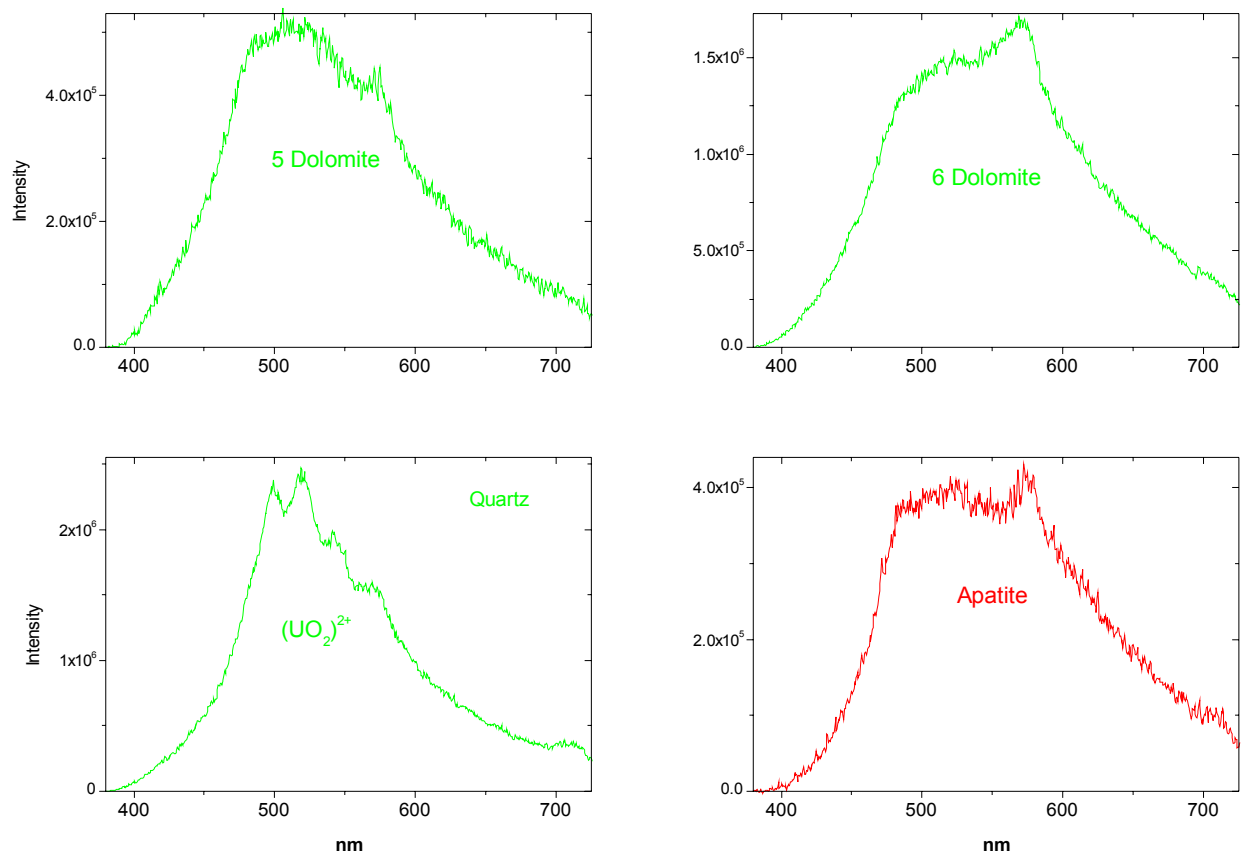
Figure 4D. Time-Resolved Luminescence of +1/2 Fraction at 355 nm Excitation.
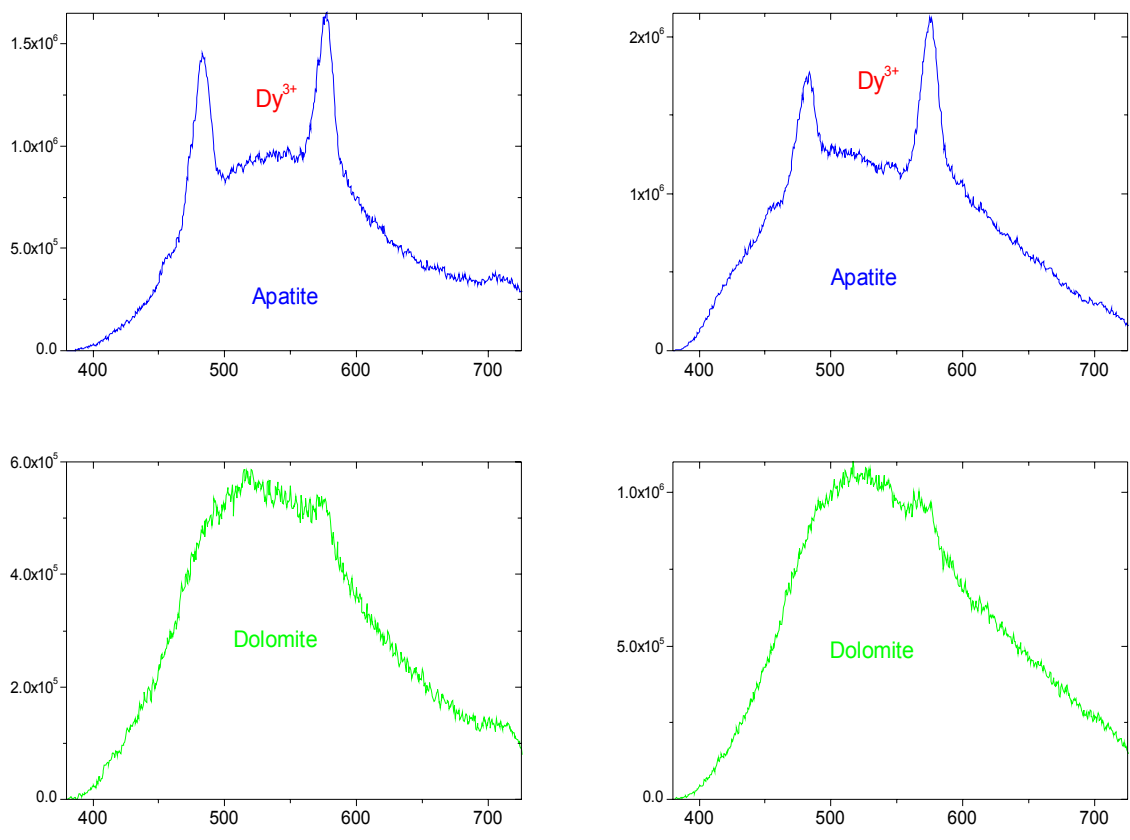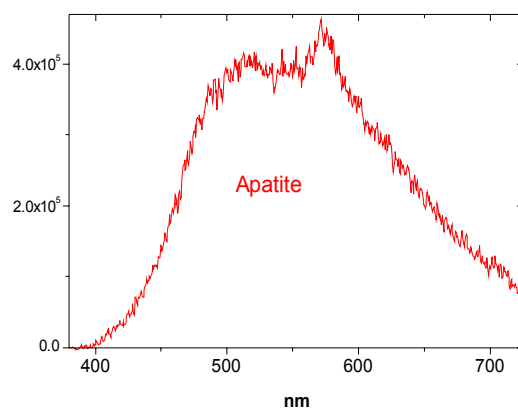
+16 FRACTION

Thirty-one samples were randomly chosen from *the light colored part*: 25 were identified by XRD as apatite and six as dolomite. By LITRL, 20 apatite samples (80%) clearly demonstrated Dy^{3+}, while it was not detected in dolomite.

Twelve samples were randomly chosen from *the dark colored part* and all were identified by XRD as apatite. Dy^{3+} appeared in nine samples (75%). However, it was impossible to check the intensity ratio feature because we did not have dark dolomite for comparison.

KINGSFORD FRACTION

Twenty-three samples were arbitrary chosen from *the light colored part*: 16 were identified by XRD as apatite and seven as dolomite. By LITRL, nine apatite samples (56%) clearly demonstrated Dy^{3+}, while it was never detected in dolomite. The intensity ratio distinctive feature enabled us to identify 13 apatite pebbles (81%).

Twelve samples were randomly chosen from *the dark colored part* and all were identified by XRD as apatite. Dy^{3+} appeared in nine samples (75%). However, it was impossible to check the intensity ratio feature because we did not have dark dolomite for comparison.

FORT GREEN FRACTION

Eighteen samples were randomly chosen from *the light colored part*: 15 were identified by XRD as apatite and three as dolomite. By LITRL, 11 apatites (73%) clearly demonstrated Dy^{3+}, while it was never detected in dolomite.

Twelve samples were randomly chosen from *the dark colored part*: 11 were identified by XRD as apatite and one as dolomite. Dy^{3+} appeared in nine samples (82%).

According to our data, the main object was the light-colored fraction, where the average dolomite content was 33%, while in the +1/2 fraction it was nearly 60% and in the +3/8 fraction more than 50%. The dark-colored fractions usually contained 1% dolomite. This being the case, we believed it would be possible to identify the dark pebbles as apatite according to the low intensity of the reflected laser beam.

Our results proved the assertion that Dy^{3+} lines are a good distinguishing feature between apatite and dolomite. They were not detected in a single dolomite sample and thus they allowed for 100% detection of dolomite pebbles. The problem is that Dy^{3+} luminescence intensity varies strongly from apatite to apatite and in certain samples it was not confidently detected under the existing experimental conditions. The average content of apatite with confident Dy^{3+} luminescence is slightly less that 70%. To

improve the distinguishing feature efficiency, the optimal excitation has to be chosen. It is well known that Dy^{3+} has very narrow excitation bands. It is confirmed by the fact that in apatite it is well excited by 355 nm, but absolutely not by 337 nm.

In order to determine the best excitation source for the Dy^{3+} distinguishing feature, excitation time-resolved spectroscopies were performed. For this task, the tunable dye laser pumped by excimer XeCl (308 nm) was used. The selected dye enables the tuning in the 345-365 nm spectral range, which corresponds to the $^4F_{9/2}$ excited state of Dy^{3+} responsible for luminescence lines at 480 and 573 nm. The excitation lines of f-f transitions for the trivalent rare-earth elements are extremely narrow and a change of several nm may be very substantial.

Luminescence spectra of magmatic apatite with very strong Dy^{3+} luminescence lines under different excitations revealed that the most effective excitation wavelength is under 351 nm, where Dy^{3+} luminescence is 3.3 times stronger than the previously used 355 nm excitation. The most important parameter for apatite and dolomite differentiation is the ratio of luminescence intensities at 482 and 500 nm (I_{482}/I_{500}). Figure 5 presents excitation spectra for Florida sedimentary apatite with weak Dy^{3+} luminescence lines. At 355 nm excitation for these samples, the I_{482}/I_{500} ratio is very close to 1, making it difficult to distinguish apatite from dolomite. At 351 nm excitation, this ratio is 1.2 times stronger and thus it will enable correct identification. This is extremely important for approximately 30% of Florida apatites, which have relatively weak Dy^{3+} luminescence under 355 nm excitation.

Besides being the optimal excitation wavelength for Dy^{3+} emissions, excitation at 351 nm exactly corresponds to the emissions wavelength of the excimer XeF laser. This state-of-the-art excimer has repetition rates up to 500 Hz, with maximum energy of 20 mJ per pulse. To check whether this energy is enough to effective Dy^{3+} excitation, the luminescence spectra of Florida apatite were studied as a function of the energy pulse. It was found that in the case of strong Dy^{3+} luminescence, it may be easily detected with a pulse energy of 5 mJ or even less. For weak Dy^{3+} luminescence, the lowest energy level may be 8-10 mJ, but for 351 nm excitation it must be lower.

MATHEMATICAL TREATMENT

Another way to improve sensitivity is via computerized spectra analysis. All spectra measurements are accompanied by background and noise, thus all individual or group parameters need preliminary data processing for background estimation and for the smoothing of the raw spectrum data. The principal problem in background modeling is finding a suitable analytical function to model the background behavior. Most analytical background functions involve polynomial approximation based on the least-squares method.
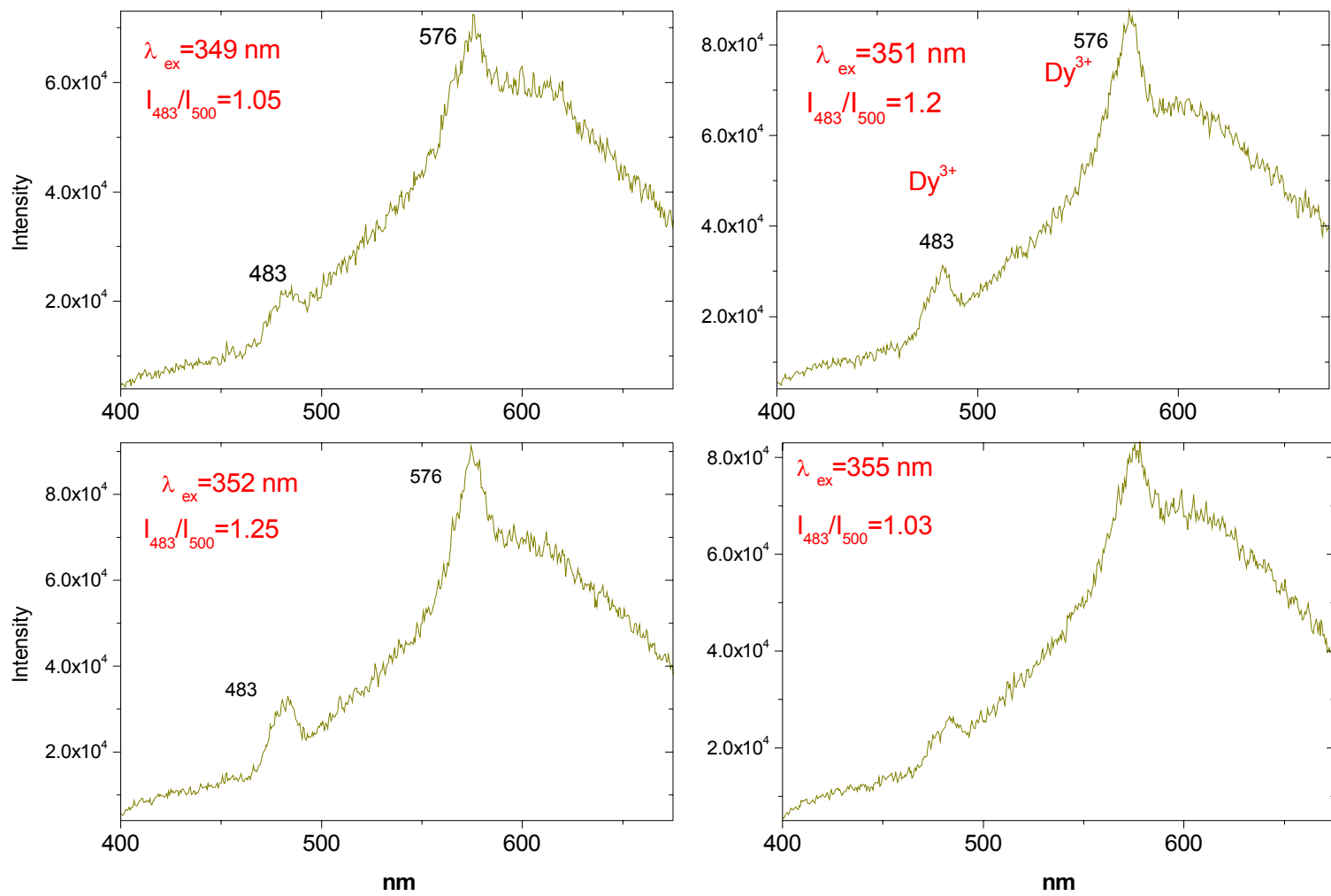
Figure 5. Excitation Spectrum of Dy^{3+} (2 ppm) in Phosphate from Florida.

Smoothing is the improvement of the signal/noise ratio by the mathematical processing of the raw data. The most widespread method of spectrum data smoothing is the "moving window" and polynomial curve fitting (the Savitzky-Golay method). This method also includes simultaneous processing of data to locate peaks by the calculation of the spectrum derivatives. Moving window scans spanning M data points move along the data and create an estimate of a smoothed spectrum or its derivation in the inner window point. The window may be symmetric or asymmetric. In the former case we get the estimation in the central point of the window; in the latter case, we get the estimation in the first or last point, accordingly. The parameter M defines the degree of smoothing; the different noise characteristics of the raw data require different degrees of smoothing.

For the computerized analysis of spectrum data, a Visual Basic application has been written. This application contains the following components:

- Reading the ASCII spectrum data files
- Smoothing by the Savitzky-Golay method
- Calculation of the first and second derivations of spectrum data by the Savitzky-Golay method
- Calculation of the background by the least-squares method
- Peaks searching
- Calculation of the exceedances of peak amplitude above the background
- Storing the results in Microsoft Excel files

The significant difference between apatite and dolomite is the presence of a peak near 483 nm, which is present in the apatite spectrum but not in that of dolomite. We analyzed 97 digital spectra of minerals (51 apatite spectra and 46 dolomite).

The purpose of the first step of the analysis is the smoothing of spectra and checking for peak existence in the 483 nm area. The five-point Savitzky-Golay method was used for smoothing and it gave effective results in increasing the signal/noise ratio. It was defined that all apatite spectra have peaks in the 483 nm area (the average wavelength of the peak maximum is equal to 483.250 nm with a standard deviation equal to 1.572 nm). At that time, only seven of the dolomite spectra had peaks in this area (average wavelength of 483.219 nm, standard deviation of 2.144 nm).

The next step was the calculation of the background by the least-squares method. The parabolic approximation of the background gave satisfactory results, and the exceedances of peak amplitude above background were calculated for all of the spectra. This analysis shows that the exceedance of peak amplitude above background for the apatite spectra is much higher than the exceedance for the dolomite spectra. For apatites, the average value of the exceedance is 9.74% with a standard deviation of 6%, while for dolomites the average value of the exceedance is 0.91% with a standard deviation of 2.21%.

It is important to emphasize that according to the XRD data, the remaining apatite without a clear Dy^{3+} emission very often contains an elevated quartz content. It is well known that quartz has strong laser-induced luminescence, which may conceal the Dy^{3+}

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lines. Thus it is possible that by using Dy^{3+} luminescence as a distinguishing feature, we will be able to reject the quartz and calcite portions before grinding, which is good for flotation efficiency.

DETECTION SYSTEM BASED ON PHOTOMULTIPLIER TUBES

The registration device (InstaSpec, Andor Technology Ltd.) used in our laboratory experiments is based on a cooled intensified CCD time-gated system. A possible alternative to such a complicated device may be photomultiplier (PMP) tubes combined with the appropriate filters. To check such a possibility, decay parameters and luminescence spectra of Florida apatite and dolomite were studied using PMP. The light pulse of the third harmonic of the Nd:YAG laser (355 nm, 30 ns) was used for luminescence excitation. Luminescence light transmitted through the monochromator was registered by the PMP, the electric pulse of which was fed to a memory oscilloscope. The luminescence pulse at 480 nm consists of an intense, fast component and a much weaker, slow component.   Our estimation showed that the pulse current of the fast component is about three orders of magnitude higher than that of the slow component. The decay time of the fast component is about 30 ns and the slow component decays with a time constant of about 800 µs.   At 500 nm there are only fast luminescence components. The spectrum of the slow component is shown in Figure 6. The spectrum was obtained using an oscilloscope and the amplitude of the signal was measured at a time delay of 500 µs.   The spectrum and decay time of the slow component confirmed that these results are due to Dy^{3+} ions in apatite. The luminescence spectrum of the fast component is about the same as those for apatite and dolomite and evidently results from adsorbed water-organic matter.

These experiments confirm the possibility of constructing a laboratory prototype of a system for apatite sorting. This sorting must be based on a comparative time-delayed measurement of the luminescence intensity at some spectral points, for example at 480 nm and 520 nm. In order to detect the Dy^{3+} signal, which is very weak compared to background emissions, its longer decay time must be used. In order to do this, we started from the PMP with a timed delay. We constructed the system based on the delayed opening of the PMP anode output for a certain time period, which may be electronically regulated along with the gate width. This system was built and checked on the samples that were previously studied on the InstaSpec and were analyzed by the XRD technique. It was found that the ratio of luminescence intensities at 480 nm-500 nm measured by the PMP with time delay enabled confident differentiation between apatite and dolomite if the Dy^{3+} lines were relatively strong.
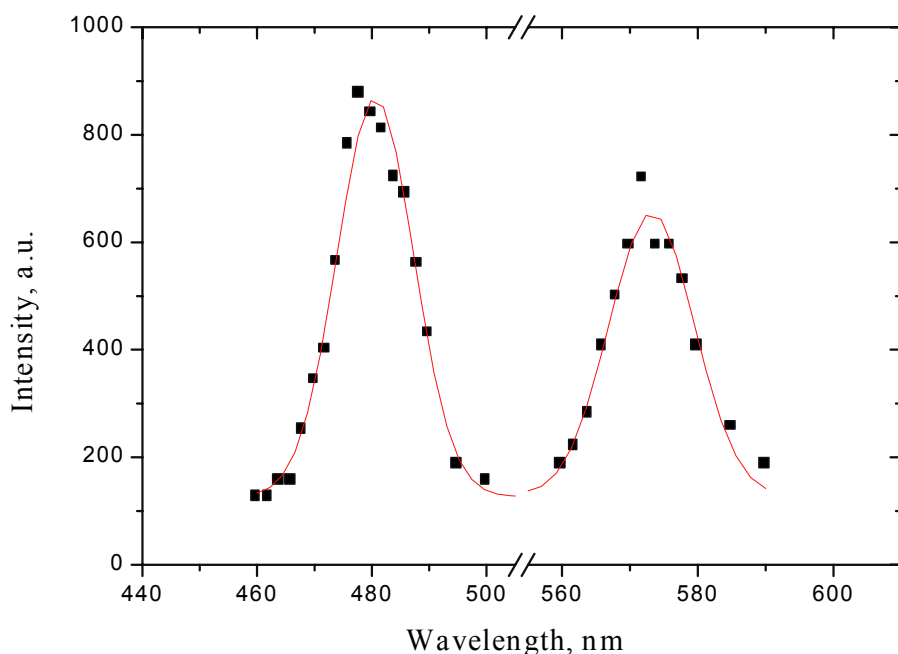
Figure 6. Time-Resolved Luminescence of Dy^{3+} Received with Gated PMP.

One problem still remains unresolved in this delaying system. Due to the large resistance of the output PMP, the "tail" from the fast non-characteristic luminescence component still hides the weaker Dy^{3+} luminescence, with a resulting reduction in sensitivity. As an alternative approach two PMP gated systems, which were found suitable for our task, were ordered and received from Electron Tubes Ltd. The gating is based on switching out the PMP high voltage at the PMP cathode for the time needed for delay (the so-called "gating time"). A PMP housing, filter holder and double PMP power supplier for the field test system were designed and produced. This system included coupled fiber connectors that enabled us to use fibers to simultaneously detect two luminescence intensities at different wavelengths, 480 and 520 nm.

A comparison of these systems revealed that in the first case, the strong background emission with the short decay time became approximately 10^3 weaker, while in the second case it was only approximately 200 times weaker. This is enough for apatites with relatively strong Dy^{3+} lines, while in both systems the "tail" from the fast background still hides the Dy^{3+} in apatites with relatively low Dy contents. In an attempt to overcome this, we developed an electronic circuit which enables us to combine both types of delay--on the input and on the output of the PMP. In any case, apatites with very weak Dy^{3+} luminescence, which represent approximately 12-15% of the studied samples, will be counted as dolomite.

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PLASMA-INDUCED TIME-RESOLVED LUMINESCENCE SPECTROSCOPY (PITRLS)

In addition to the originally proposed approach, we checked the possibility of using plasma-induced time-resolved luminescence spectroscopy (PITRLS) for our task. According to our data, plasma-induced luminescence, better known by the name laser-induced breakdown spectroscopy (LIBS), enabled confident dolomite and apatite identification even without time-resolved measurements (Figure 7). It can be clearly seen that the line at 604 nm, which is connected with P and F, belongs only to apatite, while the line at 518 nm, which is connected with Mg, belongs only to dolomite. These results have been confirmed on all 208 studied samples. Thus PILS (or LIBS) enables confident dolomite and apatite identification, using the same pair of PMPs as for Dy^{3+} detection, but the ratio of the 604 and 518 nm lines. For this method, the first harmonic of YAG may be used for plasma formation and the detection system is extremely simple, with the usual PMP without delay and gating. The signal is very strong, thus the scanning and collimating systems will also be much simpler. The energy of the laser pulse before focusing is approximately 15 mJ.
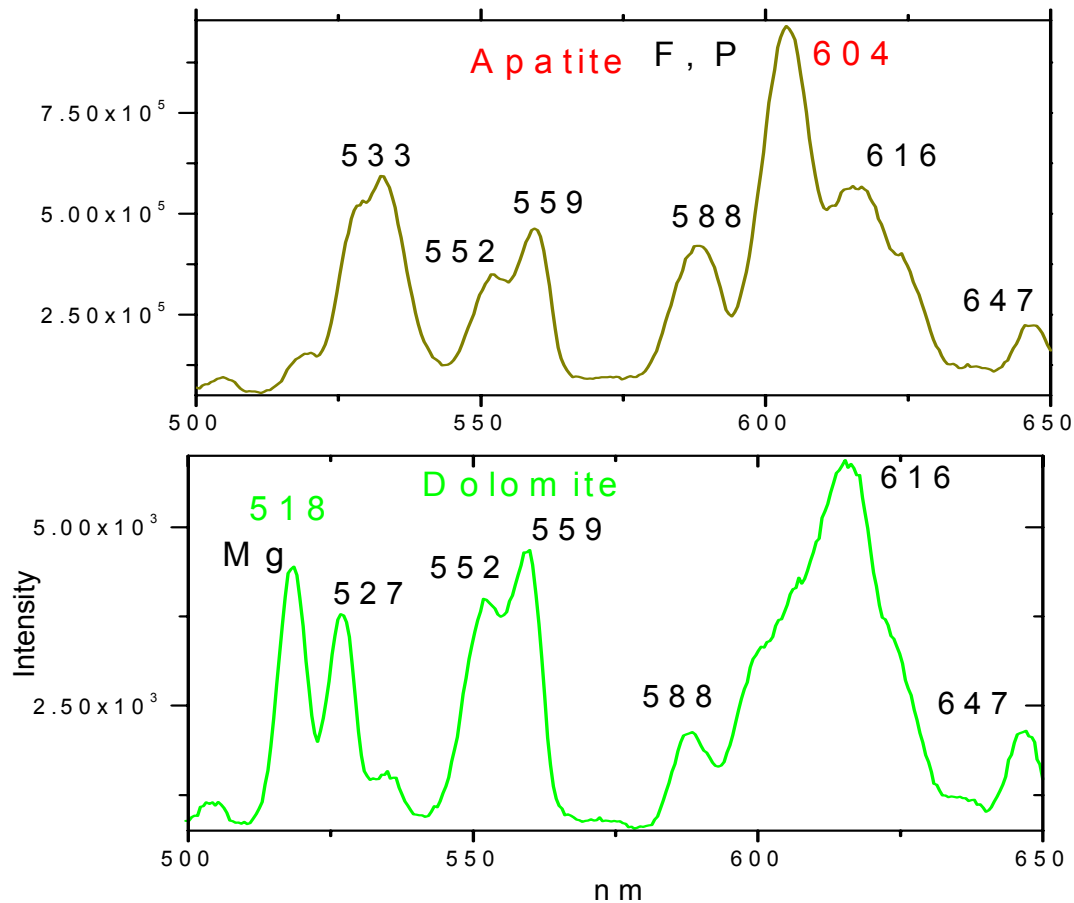

Figure 7. LIBS of Florida Apatite and Dolomite at 355 nm Excitation, 15 mJ/Pulse.

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This method was checked out on all the samples with two PMPs, and the identification was absolutely accurate. To check the possibility of using plasma-induced luminescence spectroscopy on preliminary unknown samples, 160 pebbles were randomly selected on the moving belt of the Four Corners facility. They were analyzed in conditions similar to those on the moving belt, namely from a distance of 1 m, using only one laser pulse. Three samples taken from the belt after time intervals of approximately 10 minutes were divided into two categories, "bad" (dolomite) and "good" (apatite). All products were subjected to chemical analyses in the IMC-Agrico analytical laboratory. The results are presented in Table 1. It can be clearly seen that the "bad" fraction contains mainly dolomite with a mean MgO/P_2O_5 of 0.7, while the "good" fraction is mainly apatite with a mean MgO/P_2O_5 of 0.015, nearly 50 times lower. Besides, the dolomite products contain elevated concentrations of Fe_2O_3, Al_2O_3 and insoluble residue compared to the apatite products (by 1.5, 2.5 and 4.7 times, respectively). Consequently, the removal of the rock with elevated dolomite content results in a lower concentration of not only Mg, but also other harmful impurities.

Table 1. Comparison Between Spectroscopic and Chemical Analyses.

LIBS Results	No. Pebbles	MgO	P_2O_5	BPL	F	Fe_2O_3	Al_2O_3	Insoluble
Reject	20	2.2	3.5	7.6	0.4	1.1	2.2	70.4
Accept.	31	0.5	28.6	62.5	3.6	0.7	1.1	12.9
Reject	18	2.5	5.9	12.9	0.5	1.1	3.8	63.9
Accept.	33	0.4	28.1	61.42	3.3	0.8	0.8	13.3
Reject	13	4.6	4.5	9.81	0.3	1.3	2.0	56.5
Accept.	45	0.3	27.4	59.80	3.4	0.8	1.4	14.2

Identification may be further improved by using time-resolved spectroscopy. Our results demonstrate that the analytical line of Mg at 518 nm is characterized by a very short decay time of approximately 200 ns, while the decay time of F/P at 604 nm is longer (Figure 8). Thus the line at 518 nm may be emphasized in a time-resolved spectrum with a narrow gate of 1 µs. Under such conditions, the intensity of the relatively broad band in the range of 600-630 nm connected with carbonate is substantially lower and the ratio of I_{518}/I_{606} will be higher. The decay time of the F/P characteristic line at 604 nm of approximately 500 ns is still relatively strong, with a gate of 1 µs, enabling easy detection of apatite.

A potential problem with plasma-induced luminescence may be the wetness of the samples. Damp samples of apatite and dolomite from the moving belt were checked and practically the same spectra were detected (Figure 9).
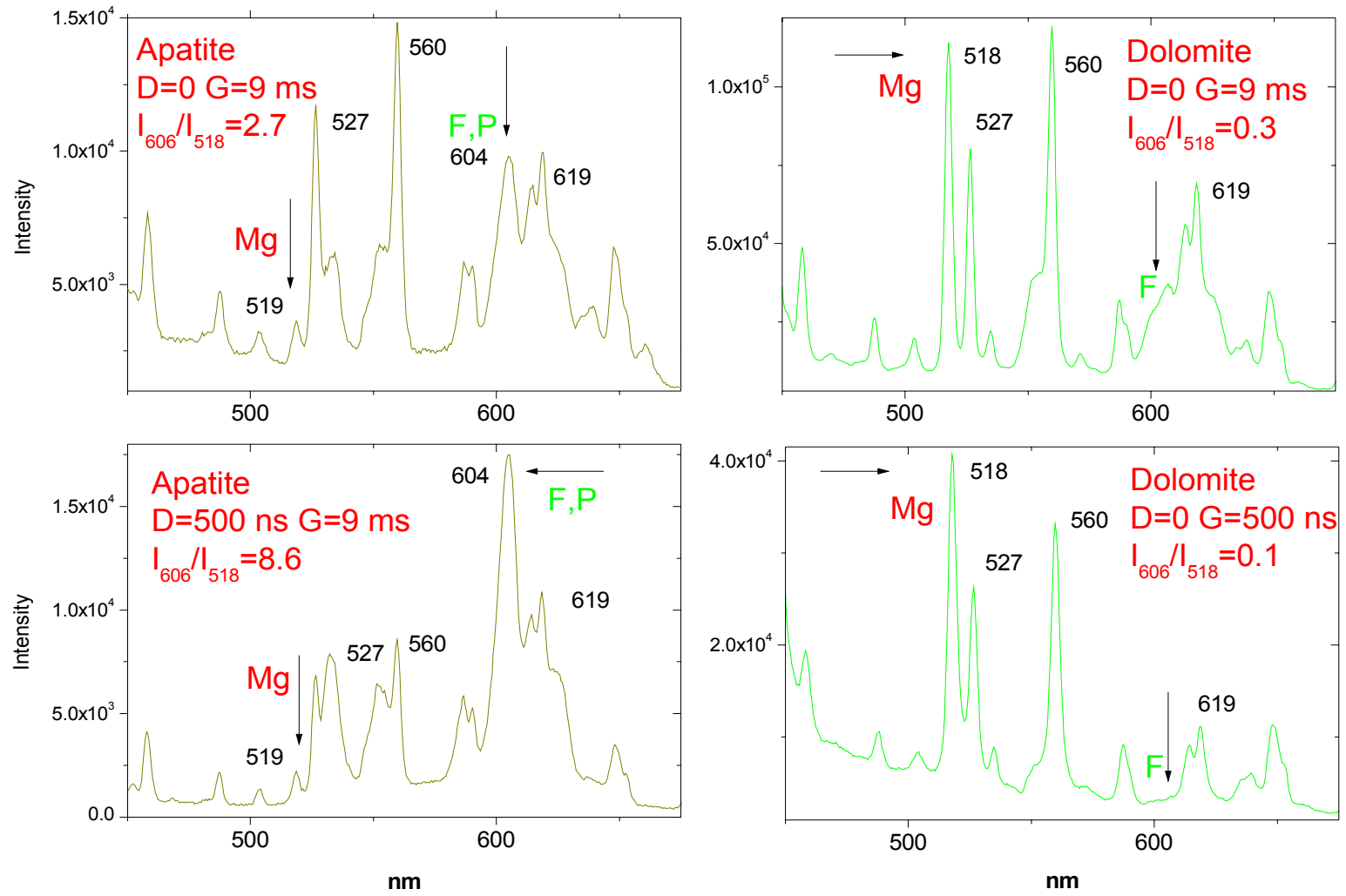
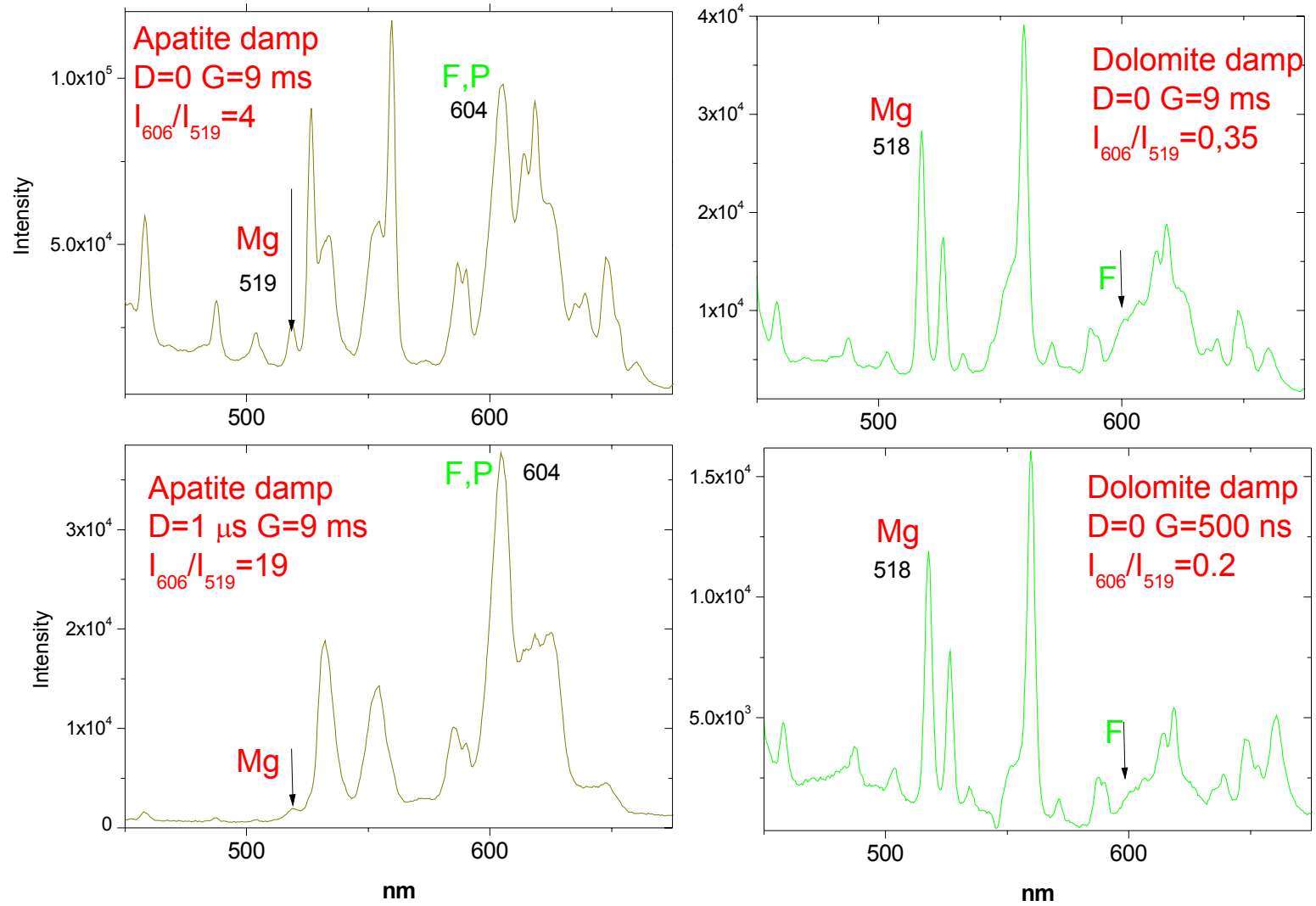**Figure 8. Time-Resolved LIBS of Florida Apatite and Dolomite.**

Figure 9. Time-Resolved LIBS of Wet Apatite and Dolomite from the Moving Belt.

ANALYSIS OF OPTICAL CONCEPTS FOR MOVING BELT ANALYSES

CALCULATION OF REQUIRED PULSING FREQUENCY OF THE LASER

The detection limit of the MgO has to be less than 1%, which corresponds to approximately 5% of mineral dolomite. If it is possible to suppose that dolomite distribution is absolutely uniform, the probability of each laser pulse striking the apatite is 95% but only 5% for dolomite. The probability that two pulses strike only apatite is 0.95 x 0.95 = 0.9025, that three pulses strike only apatite is $(0.95)^3 = 0.857$, and so on. Consequently, the probability that the first 60 laser pulses will detect only apatite is approximately 5%. Thus, there is a probability of 95% that one out of each 60 pulses will strike dolomite and detect it.

The width of the strip of rock and stones was 100 cm. The number of 1.0 cm diameter pebbles that can be placed in a strip 100 cm wide is therefore equal to 100. If the velocity of the strip is 200 cm/sec, the number of stones moved per second is 200 x 100 = 20,000. The representative sampling must be approximately $(20000)^{1/2} \approx 150$.

Thus, a laser with a repetition rate of 200-400 Hz, which enables analyses of 200-400 pebbles per second, will be suitable for our task even without a scanning system. For Dy^{3+} luminescence analyses we need a UV laser with a power of 10-15 mJ, while for PITRLS it must be 5-10 mJ before focusing. Such lasers are quite common on the market.

SOFTWARE

An electronic card has been developed which enables one to synchronize the laser beam, the scanner and PMPs; to measure two luminescence signals from the PMPs simultaneously; to calculate their ratio; to identify apatite or dolomite according to this ratio; to display the place of the corresponding mineral on the computer screen; and to calculate the dolomite content.

CONCLUSIONS

1. The optimal method for dolomite content analysis on a moving belt is plasma-induced time-resolved luminescence based on characteristic lines of F/P in apatite at 604 nm with a relatively long decay time of 500 ns, and of Mg in dolomite at 518 nm with a shorter decay time of 200 ns.

LIBS has never been used for such a task.

2. The apparatus for practical use includes a laser source with a pulse energy of 5-10 mJ and a frequency rate of 400-500 Hz, a focusing lens, fiber optics for luminescence detection, an ICCD-based spectrometer capable of detecting 500 spectra per second, an electronic card, and a computer. Such a system enables dolomite content analyses starting from 1% MgO even without the scanning system across the moving belt.

The approximate price (in U.S. dollars) is as follows:

- Laser – $50,000
- ICCD spectrometer plus optical components – $40,000
- Electronic card and computer – $10,000
- Mechanical parts – $10,000
- Total: $110,000