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VISIBLE AND ULTRAVIOLET REFLECTANCE AND LUMINESCENCE FROM VARIOUS SAUDI ARABIAN AND INDIANA LIMESTONE ROCKS

By

H. V. Watts

and

H. J. Goldman
IIT Research Institute
Chicago, Illinois

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WASHINGTON, D.C. 20242

Interagency Report
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Dr. Peter C. Badgley
Program Chief,
Earth Resources Survey
Code SAR - NASA Headquarters
Washington, D. C. 20546

Dear Peter:

Transmitted herewith is one copy of:

INTERAGENCY REPORT NASA-92

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Sincerely yours,

William A. Fischer
Research Coordinator
Earth Orbiter Program

*Work performed under NASA Work Order No. T-65757
**IIT Research Institute, Chicago, Illinois

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

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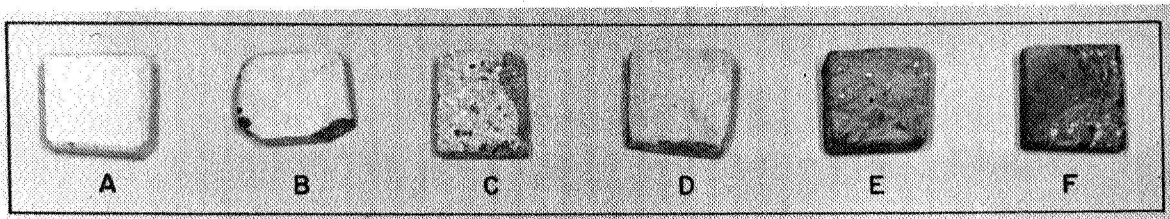
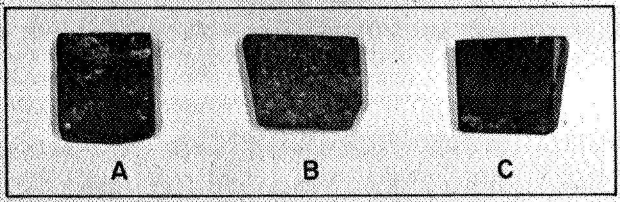
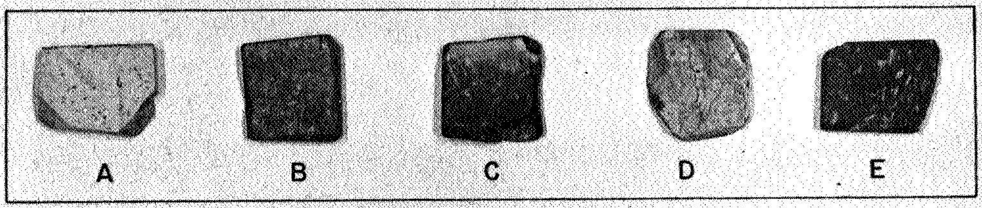
**IIT Research Institute, Chicago, Illinois, Contract No. 10360



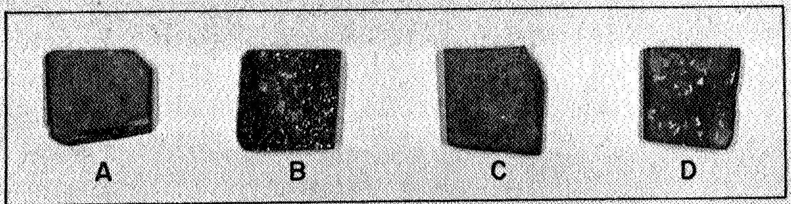
PHOSPHATE ROCK SAMPLES (DATA: FIG. 2)



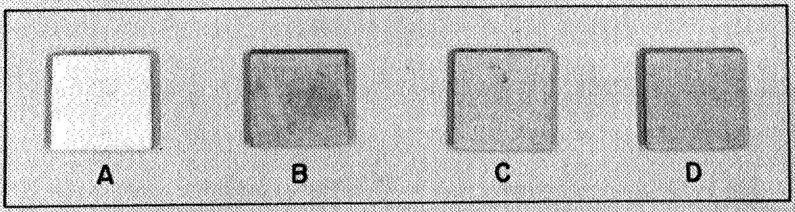
ANDESITE ROCK SAMPLES (DATA: FIG. 3)



RHYOLITE ROCK SAMPLES (DATA: FIG. 4)



FELSITE AND GREENSTONE ROCK SAMPLES (DATA: FIG. 5)



LIMESTONE ROCK SAMPLES (DATA: FIG. 6)

PHOTOGRAPHIC DISPLAY OF SAMPLES INVESTIGATED

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VISIBLE AND ULTRAVIOLET REFLECTANCE AND LUMINESCENCE FROM VARIOUS SAUDI ARABIAN AND INDIANA LIMESTONE ROCKS

I. INTRODUCTION

This study is a continuation of the work reported in "Reflectance of Rocks and Minerals to Visible and Ultraviolet Radiation," Technical Letter, NASA-32, July 1966, (Ref. 1), in which reflectance data were obtained for 38 samples of rocks and minerals. The overall objective of these studies is to determine if there are significant differences in the spectral reflectance or emission properties of selected natural materials which may be used for identification and/or differentiation purposes in remote sensing applications. In this report, 34 additional rock samples are studied. The samples include two suites: one from Saudi Arabia, and the other from selected limestone quarries in Indiana.

The Saudi Arabian samples were provided by U. S. Geological Survey personnel in that country. These samples include selected pre-Cambrian volcanic rocks because it was hoped that measurements of their ultraviolet spectral reflectance properties would provide information of direct importance in distinguishing rhyolite in andesite sequences in the field by airborne remote sensing methods. Anomalous metalliferous deposits are known to be associated with rhyolite in the Arabian shield area. The samples from Saudi Arabia also include phosphate rock from the northern part of the country where extensive prospecting for this commodity is currently underway. It was hoped that ultraviolet stimulated luminescence might be a measurable property that would permit detection of the phosphate from low aircraft altitudes.

The Indiana limestone samples were provided by personnel of the Geological Survey of Indiana in the hope that laboratory measurements of their ultraviolet reflectance and stimulated luminescence properties might provide information of direct importance in designing instrumentation capable of distinguishing limestone of varying quality along relatively inaccessible quarry faces. It was also hoped that some of the quarries would be suitable sites for field testing of a Fraunhofer line discriminator (Ref. 2) being designed and built under the auspices of NASA's Apollo Applications Program.

II. EXPERIMENTAL TECHNIQUES

A. Sample Surface Preparation

Each sample was cut to form a one-half inch thick slab about 1-1/2" x 1-1/2" in area. One surface of the slab was ground with 320 silicon carbide (30 micron particle size). The other surface was polished using W8 aluminum oxide and Linde "B". Only the ground surface was used in the measurements reported here.

Immediately after grinding, the surfaces were washed under running water to remove all abrasive. Before measurements were taken the sample surfaces were again washed and rinsed in absolute alcohol. Care was taken in subsequent handling of the samples to insure that the surfaces were not touched or contaminated.

B. Reflectance Measurement

A Cary* Model 14 MR recording spectrophotometer with a model 1411 diffuse reflectance accessory was used for all reflectance measurements. The instrument was used in the Type I illumination mode, i.e., a dispersed (monochromatic) collimated light beam is incident upon the sample surface, and the total diffuse reflectance is collected by an integrating sphere and detected by a DuMont type 7664 multiplier phototube. A tungsten lamp was used for the wavelength region of 3500 A to 7000 A, and a hydrogen arc was used between 2300 A and

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* Applied Physics Corporation, Monrovia, California

3500 A. The sample reflectance was measured relative to a magnesium carbonate block which in turn was periodically calibrated against freshly prepared magnesium oxide surfaces.

The incident beam size at the sample surface has a constant height of 15 mm and a width of from 1 to 2 mm, proportional to the slit width of the spectrophotometer, throughout most of the spectral range studied. At wavelengths below 2500A the beam width increases continuously to about 5 mm at 2300A. The spectral resolution varies from 10A to 20A throughout the visible and near ultraviolet, and rapidly widens at wavelengths below 2500A to about 45A at 2300A. All data were recorded at a spectral scan rate of 10A/sec.

The absolute values of reflectance used for the magnesium oxide standard reference are listed below. These

λ(A)	% Refl. of MO
7000 to 4000	97.0
3500	96.5
3250	96.0
3000	95.5
2750	94.8
2500	94.0
2400	93.0
2300	92.0

are selected from several references (3,4,5). There are uncertainties of the absolute values of reflectance in the ultraviolet spectral range. However, differences of a few percent in the absolute values of magnesium oxide reflectance would not change the reported data significantly.

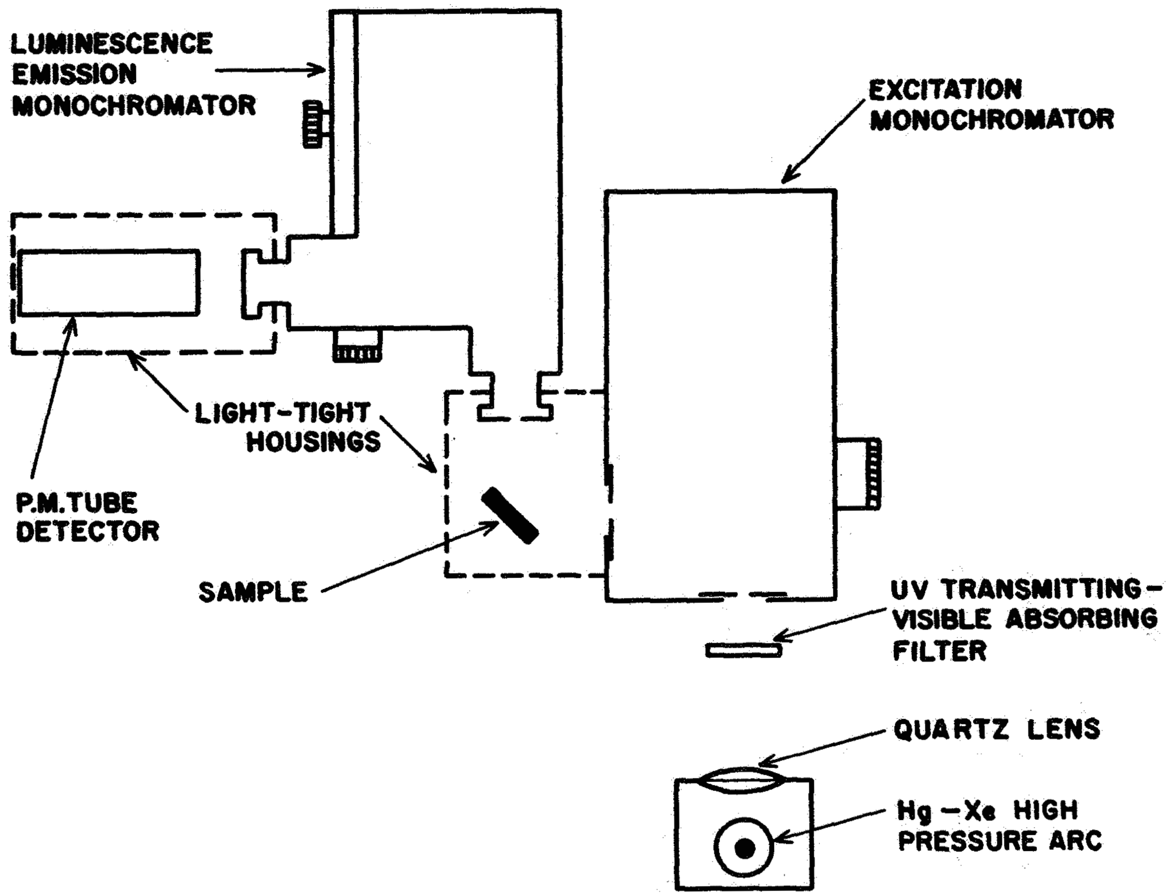
C. Luminescence Measurements

A double monochromator system was used to measure the luminescence. The system is shown in Figure 1. A one kilowatt Hanovia Xenon - mercury arc lamp was used as the primary source of excitation. The lamp output was filtered with a Corning 7-54 ultraviolet transmitting, visible absorbing glass filter before entering the Bausch and Lomb grating monochromator which served as the excitation monochromator. The luminescence emission was analyzed with a Gaertner Model L234-150 quartz prism monochromator using a ten stage multiplier phototube (DuMont Type K 1306) as the output detector. For all luminescence measurements the Gaertner slits were fixed at 1 mm.

Four different broadband excitation settings (designated as E1, ...) were used for the luminescence measurements. These are described as follows:

E1, 3500A to 3900A;
E2, 3000A to 3400A;
E3, 2600A to 3000A;
E4, 2400A to 2700A.

The E4 excitation band was narrower and much less intense than



LUMINESCENCE MEASUREMENT APPARATUS

Figure 1

the other three. This was caused by the comparatively low spectral emission of the hydrogen arc and the short wavelength cut-off of the Corning 7-54 filter which effectively reduced the throughput at these wavelengths. This experimental limitation is not critical however, because the solar ultraviolet transmitted through the earth's atmosphere is limited to wavelengths longer than 2950A.

The measurement system was checked by using a high efficiency ZnS:Ag phosphor and a plastic phosphor. The luminescence emission curves obtained from these materials were in agreement with the literature values.

Visible scattered light reflected from the sample surfaces was measurable. For the synthetic phosphors mentioned above the luminescence signals were 100 to 1000 times the reflected scattered light signal, and thus the scattered component was not significant. However, when measuring rock samples, whose luminescence emission is comparatively low, the reflected scattered light was of the same order as the luminescence. A correction for this signal was made by measuring the scattered light reflected from the magnesium carbonate block which was used as the reference in the reflectance measurements. Then, knowing the relative reflectance of the rock samples to the magnesium carbonate, a value for the reflected scattered light versus wavelength was obtained for each sample.

The luminescence intensity is the difference between the total detected intensity at a given wavelength and the value of the reflected scattered light at that wavelength. The error in calculated values of the reflected scattered light for a sample was roughly estimated at 10 percent. Because there was an appreciable increase in scattered light as the wavelength decreased, the probable errors in the luminescent measurements increase as the wavelength decreases and become large at wavelengths shorter than 4000A. These probable error values are given in the luminescence data tables (Tables 3 and 4), and are indicated by error bars on the luminescence emission curves.

Exact excitation curves, i.e., luminescence intensity versus monochromatic excitation wavelength, were not experimentally achievable because of the low luminescence efficiencies of the samples; attempts to obtain measurable luminescence with narrow bandwidths of excitation (e.g., 50A) were unsuccessful. However, the gross features of the excitation can be recognized by comparing the luminescence values obtained with the broad band (400A width) source.

III. DATA AND DISCUSSION

A. Rock Samples

The 26 Saudi Arabian rock samples and their locality of origin are listed in Table 1. In this suite are six phosphate rocks, ten rhyolite, six andesite, two greenstone, and two felsite. Also studied were eight Indiana limestone samples given by the code numbers DC66-95 to DC66-102 (Table 2). A calcite (Moorfield, West Virginia) sample whose luminescence had been examined previously by the Fraunhofer line-depth method (Ref. 2) was included in this suite for comparison purposes.

B. Diffuse Reflectance

Curves showing total diffuse reflectance plotted as a function of wavelength are presented in the Appendix for each sample individually. The reflectance curves are summarized for each rock type in Figures 2 through 6. To avoid confusion where several samples exhibit similar spectral reflectance, only a minimal number of curves are shown in each figure. These curves include samples which show maximum and minimum spectral reflectance intensities for each rock type. Other samples are noted by number to indicate similarity of their spectral reflectance to specific curves which are shown. Dashed lines are used to permit better visual differentiation where one curve crosses another.

The spectral reflectance curves, Figures 2-6, indicate some differences in response between rock types. The major differences are in their relative amplitudes of reflection and/or their rate of slope changes with wavelength. No sharp signatures such as narrow maxima or minima were observed.

Table 1
SAUDI ARABIAN ROCK SAMPLES

Rock Type	Sample Number	Source Locality
Phosphate	21232	29°44'N. x 38°12'E.
	21233A	29°56'N. x 39°27'E.
	21235	31°28'N. x 39°23'E.
	21237	31°37'N. x 38°59'E.
	21271	31°46'N. x 39°24'E.
	21272	31°45'N. x 39°21'E.
Rhyolite	10-L-10,130	20°06'N. x 41°49'E.
	10-L-10,151	20°00'N. x 41°50'E.
	00-Z-10,155C	28°18'N. x 35°37'E.
	4000	24°17'N. x 38°16'E.
	4196	27°47'N. x 35°31'E.
	7454	22°06'N. x 45°08'E.
	7456	22°06'N. x 45°10'E.
	7994	18°24'N. x 44°12'E.
	7997	18°18'N. x 44°15'E.
	30057	18°19'N. x 44°15'E.
Andesite	10-L-10,100	20°09'N. x 41°50'E.
	10-L-10,128	20°06'N. x 41°49'E.
	00-Z-10,155B	28°18'N. x 35°37'E.
	04-D-10,371	26°58'N. x 36°39'E.
	30052D	18°22'N. x 44°14'E.
Porphyritic Andesite	10A-1384	23°39'N. x 41°01'E.
Greenstone	4054	27°41'N. x 35°33'E.
	10G-13026	21°04'N. x 41°30'E.
Felsite	10B-1344	23°33'N. x 40°59'E.
Felsite Porphyry	10B-1373	23°25'N. x 40°46'E.

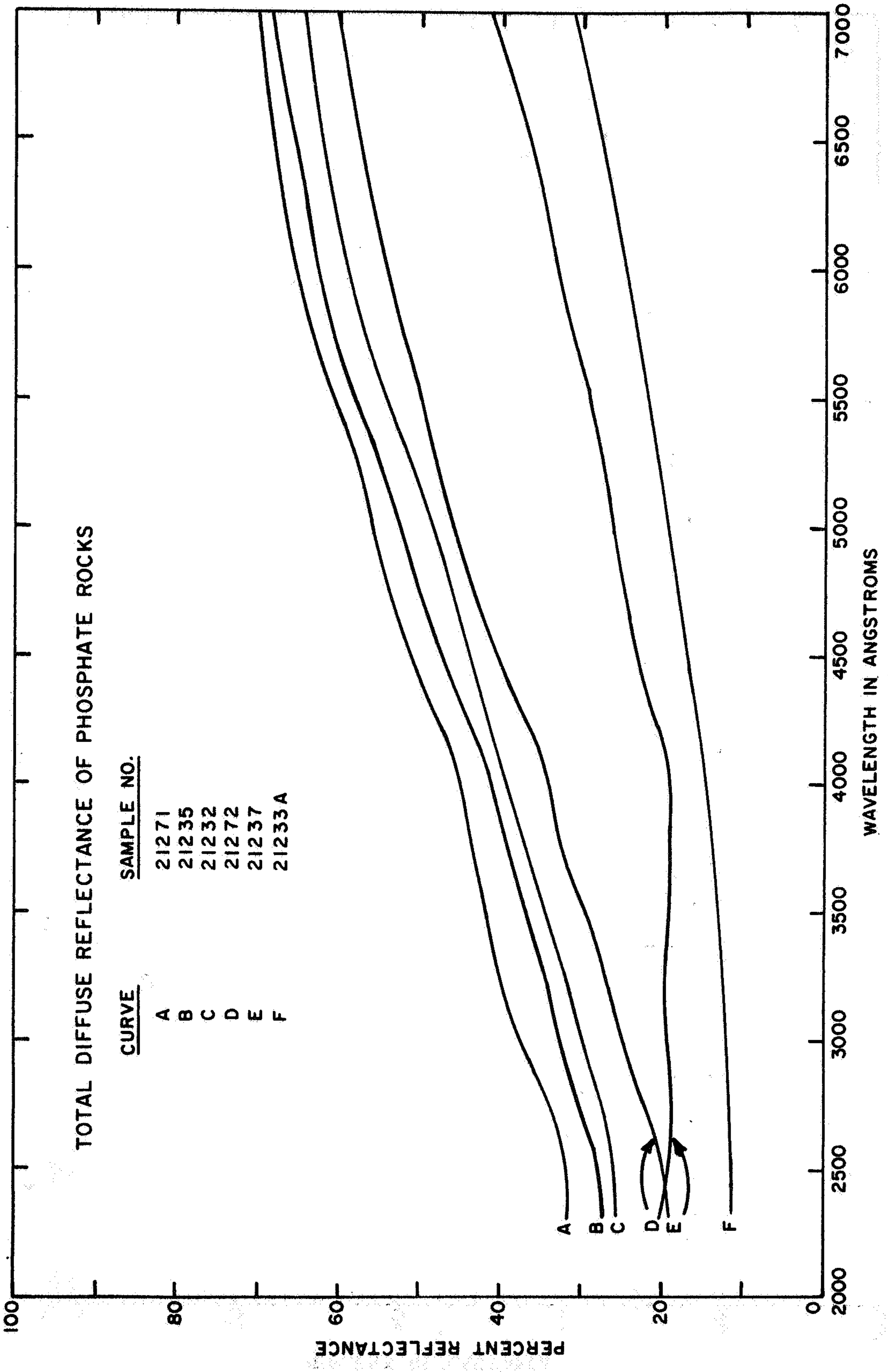

TOTAL DIFFUSE REFLECTANCE OF PHOSPHATE ROCKS
CURVE
SAMPLE NO.
A 21271
B 21235
C 21232
D 21272
E 21237
F 21233A
A
B
C
D
E
F
PERCENT REFLECTANCE
0
20
40
60
80
100
WAVELENGTH IN ANGSTROMS
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000

Figure 2

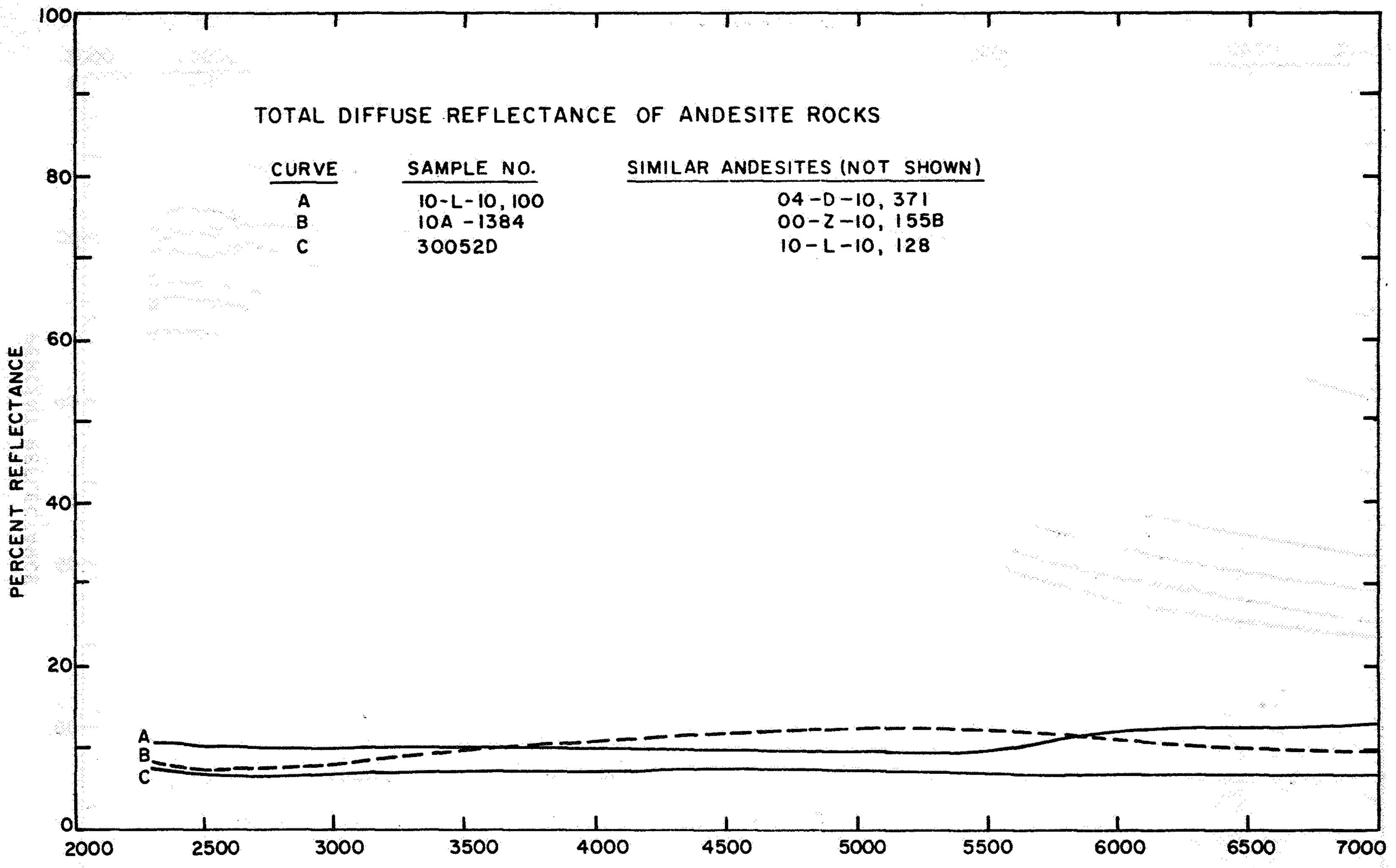

TOTAL DIFFUSE REFLECTANCE OF ANDESITE ROCKS
CURVE
SAMPLE NO.
SIMILAR ANDESITES (NOT SHOWN)
A
10-L-10, 100
04-D-10, 371
B
10A-1384
00-Z-10, 155B
C
30052D
10-L-10, 128
PERCENT REFLECTANCE
0
20
40
60
80
100
WAVELENGTH IN ANGSTROMS
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
A
B
C

Figure 3

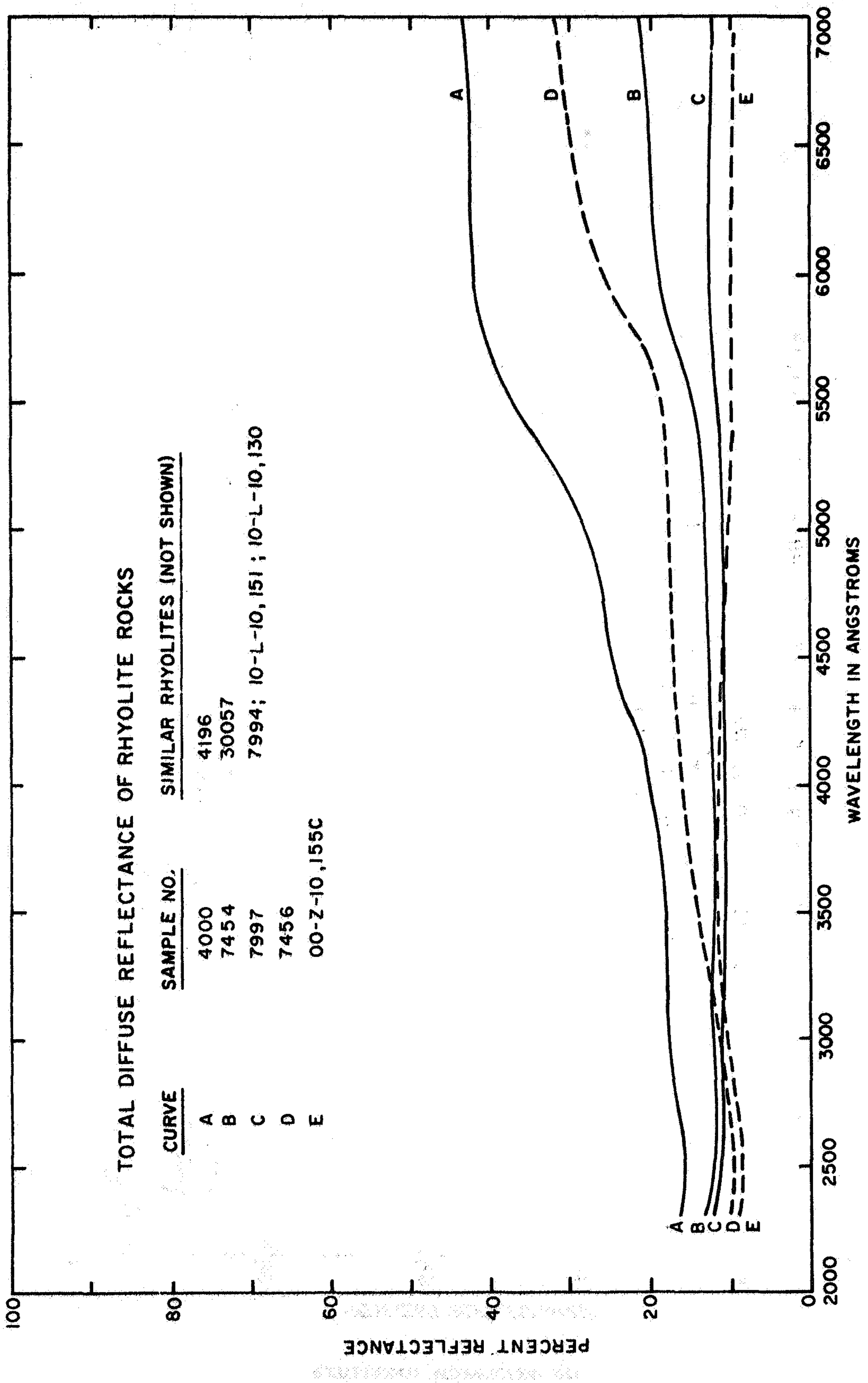

TOTAL DIFFUSE REFLECTANCE OF RHYOLITE ROCKS
CURVE
SAMPLE NO.
SIMILAR RHYOLITES (NOT SHOWN)
A 4000 4196
B 7454 30057
C 7997 7994; 10-L-10,151 ; 10-L-10,130
D 7456
E 00-Z-10,155C
PERCENT REFLECTANCE
100
80
60
40
20
0
WAVELENGTH IN ANGSTROMS
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
A
B
C
D
E

Figure 4

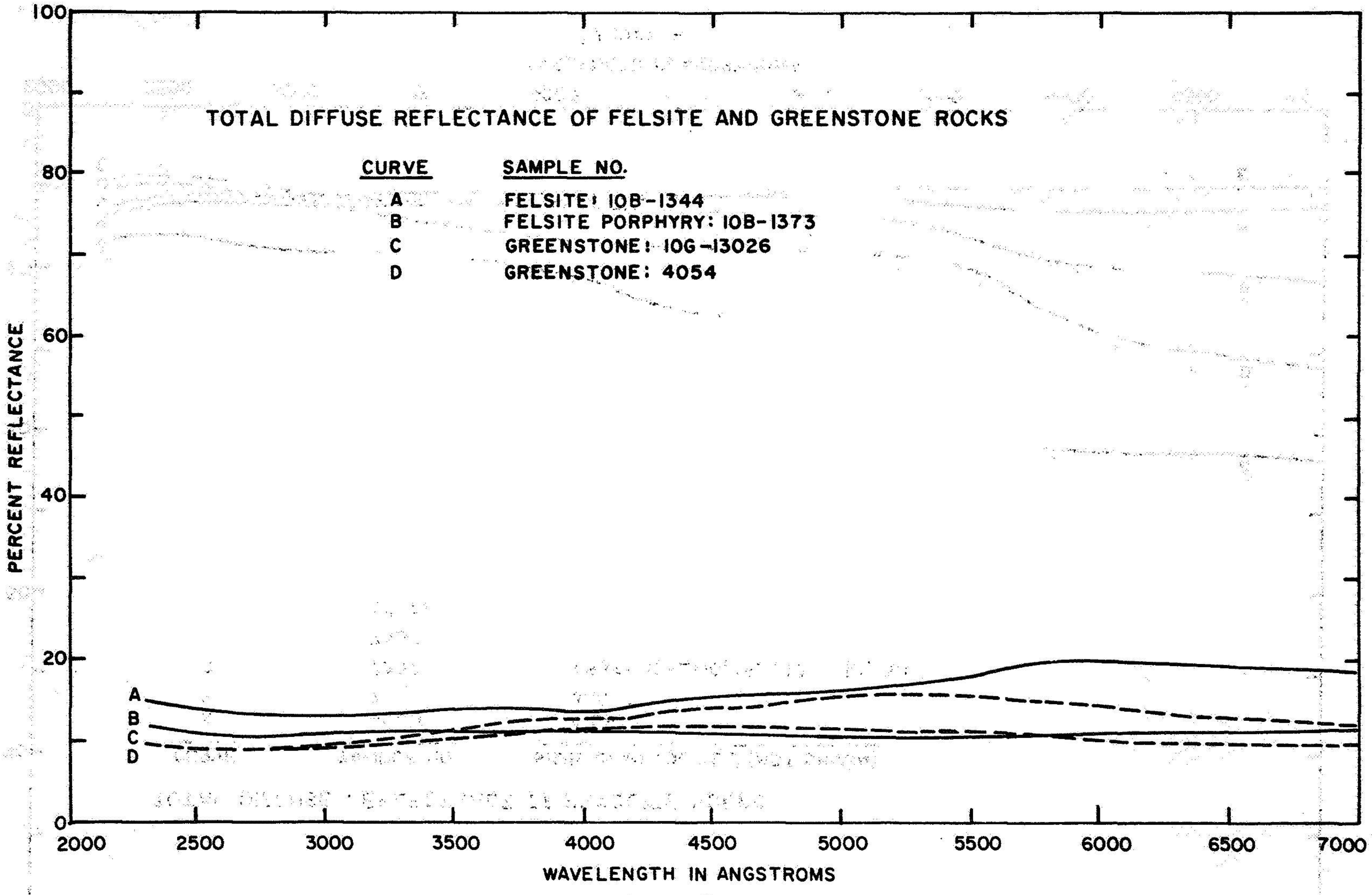

TOTAL DIFFUSE REFLECTANCE OF FELSITE AND GREENSTONE ROCKS
CURVE
SAMPLE NO.
A
FELSITE: 10B-1344
B
FELSITE PORPHYRY: 10B-1373
C
GREENSTONE: 10G-13026
D
GREENSTONE: 4054
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS
A
B
C
D

Figure 5

Table 2

INDIANA LIMESTONE SAMPLES

Sample Number	Formation	Source Locality
DC66-95	Salem Limestone	Acme Quarry, Indiana Limestone Co., Monroe County
DC66-96	Salem Limestone	Chumley Quarry, Empire Stone Co., Monroe County
DC66-97	Salem Limestone	Arlington Quarry, B.G. Hoadley Quarries, Inc., Monroe County
DC66-98	Salem Limestone	Arlington Quarry, B.G. Hoadley Quarries, Inc., Monroe County
DC66-99	Ste Genevieve Ls (unit directly above oolitic lens)	Radcliff and Berry Quarry, Orange County
DC66-100	Ste Genevieve Ls (oolitic unit)	Radcliff and Berry Quarry, Orange County
DC66-101	Ste Genevieve Ls (unit directly below the oolitic unit)	Radcliff and Berry Quarry, Orange County
DC66-102	Paoli Limestone (oolitic unit)	Outcrop along State Highway 46, 3.5 miles east of Spencer, Owen County

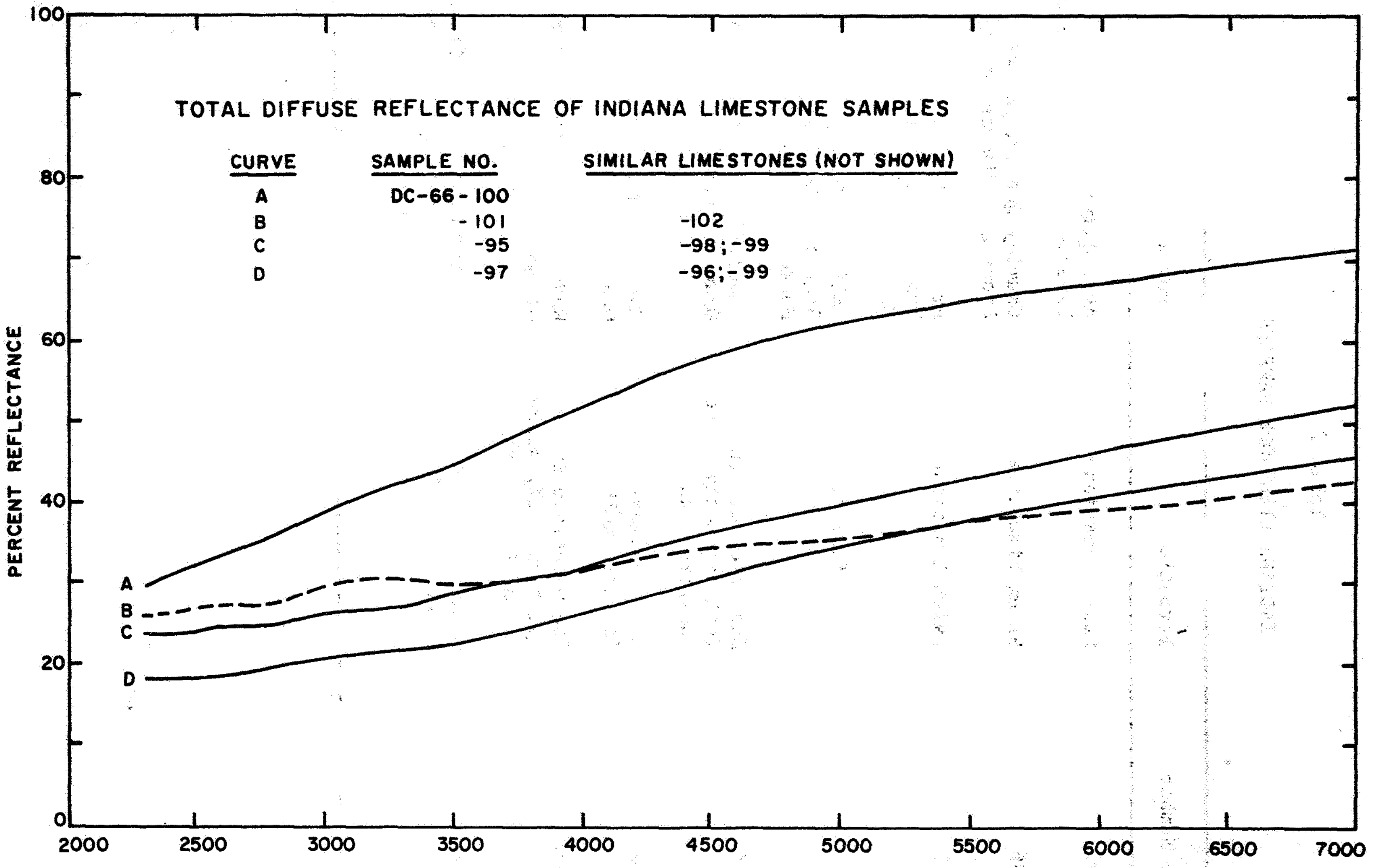

TOTAL DIFFUSE REFLECTANCE OF INDIANA LIMESTONE SAMPLES
CURVE
SAMPLE NO.
SIMILAR LIMESTONES (NOT SHOWN)
A
DC-66-100
B
-101
-102
C
-95
-98;-99
D
-97
-96;-99
A
B
C
D
PERCENT REFLECTANCE
0
20
40
60
80
100
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

Figure 6

The highest reflectance values, among all samples, were exhibited by phosphate rock samples 21232, 21235, 21271, and 21272 (fig. 2). Sample 21271, the highest reflecting sample, has reflectance values of 32% at 2500Å and 71% at 7000Å, for example. The curve slopes of all the phosphate rocks are very similar and essentially constant, showing a steady increase in reflectance value with wavelength. Samples 21233A and 21237 have similar slope characteristics, but with reflectance values that are approximately one-half of those phosphates cited above. Reasons for the observed differences in amplitude between these two phosphate groups have not been established, but could be due to differences in surface texture and/or composition of that part of the sample surface which was illuminated and observed.

On the other extreme are the andesite rocks (fig. 3) which have the lowest reflectance values and whose spectral reflectance curves are essentially flat. Andesite sample 30052D, for example, has a reflectance value of about 7% throughout the entire wavelength range. The highest reflectance value of any of the six andesites studied was 13% at 7000Å.

The set of ten rhyolite rocks exhibited significant differences in reflectance curve shapes (fig. 4). Five of these samples have rather flat and low valued reflectance curves similar to the andesites. (These samples are 7994; 7997; 10-L-10,151; 10-L-10,130; and 00-Z-10,155C). The other five rhyolite samples are distinctive in having noticeable inflections in the green-yellow region between 5000Å to 6000Å. It is noted that phosphate sample 21233A and rhyolite 7456 have very similar reflectance values with wavelengths, yet their observed colors are significantly different. The accentuation of the longer wavelengths introduced by the inflection around 5700Å of the rhyolite may be responsible for its definite red color whereas the phosphate appears brown.

The two felsites and two greenstones (fig. 5) have reflectance properties very similar to the andesites. Except for the fact that these samples, in general, have slightly higher reflectance values than the andesites, there is nothing distinguishable between their reflectance curves.

All of the Indiana limestones (fig. 6) are marked by relatively high reflectance values which increase with wavelength*. Sample DC 66-100 is anomalous in its very high reflectance at all wavelengths (72% at 7000Å) when constrasted with the other seven limestones investigated.

*All limestones and most phosphate rock samples have higher reflectance values at all wavelengths compared to the rocks studied in Reference 1.

C. Luminescence Emission

Spectral luminescence emission data for the Saudi Arabian phosphates, the Indiana limestones and a calcite reference used in earlier studies (Ref.1) have been obtained. Luminescence emission curves for each of these rocks samples are given in the Appendix on the same figures on which their reflectance curves are plotted. The luminescence curves shown are for the excitation band which provided the maximum intensity. The scale of emission intensity is an arbitrary one, but the relative intensities are consistent so that direct comparisons can be made between different samples.

C.1 Saudi Arabian Phosphate Rocks

A set of representative phosphate luminescence curves is presented in Figure 7; for comparison, a calcite curve is also shown in the same figure. These curves were obtained using the E2 excitation band (3000A - 3400A). Little change in emission curve shape was observed between 4200A and 6500A when other excitation bands were employed. In this region the emission is very broad in spectral character (the curve widths at half maximum are about 2000A). It was also observed visually that the emission was not of constant intensity over the sample surface; parts of the surface of some samples did not luminesce.

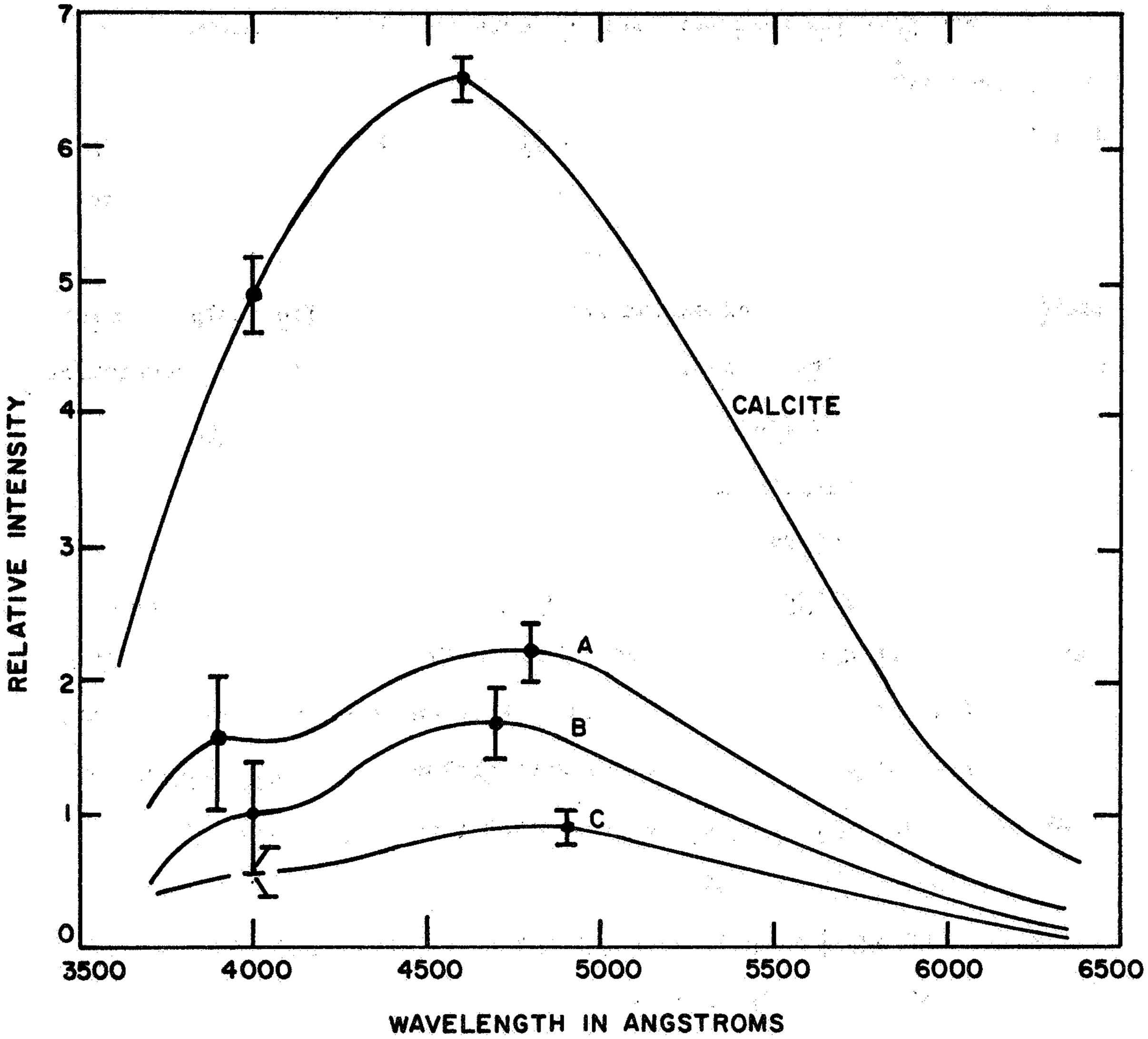


Figure 7

ULTRAVIOLET EXCITED LUMINESCENCE EMISSION FROM THREE SAUDI ARABIAN PHOSPHATE ROCKS AND THE CALCITE SAMPLE.

(EXCITATION BY 3000Å - 3400Å ULTRAVIOLET BAND)

CURVE	SAMPLE NO.
A	21235
B	21272
C	21233A

Most of the phosphate luminescence curves exhibit a primary peak at about 4800A and another around 4000A. The peak at shorter wavelengths is especially pronounced for sample number 21232 (Appendix A-1). At this wavelength, however, the probable error in the intensity value (see Section II. C) is quite large (twice that at 4800A) and thus the relative intensity of this secondary peak is questionable.

Table 3 lists the luminescence intensities observed from the phosphate rocks at the wavelength of their primary peaks. Intensities are listed only for the E2 excitation band which produced the strongest signals in all cases. To illustrate the effect of the different excitation bands we also tabulate the ratio of the peak intensities observed for the other three bands compared to the intensity for E2 excitation, i.e., I(E1)/I(E2), etc. In addition, the table includes data for calcite and the ZnS:Ag sample for comparison purposes.

An estimate of the energy conversion efficiency (luminescence energy/incident energy) of ultraviolet excited luminescence is based on an efficiency of 50 to 80 percent for ZnS:Ag (Ref. 6). Since calcite has a peak intensity value of about 0.01 that of ZnS:Ag and a total width of its emission curve which is about twice that of the synthetic phosphor, its overall energy conversion efficiency is estimated at between one and two percent. The phosphate samples have luminescent emission intensities that range between 0.14 to 0.34 that of the calcite sample.

Table 3

LUMINESCENT INTENSITIES VERSUS EXCITATION BANDS

- Phosphate Rocks and Reference Samples -

Sample	Wavelength of Primary Peak Emission (λ Max.)	Intensity at λ Max. as Function of Excitation*			
			Intensity Ratios		
		I(E2)	I(E1)/I(E2)	(I(E3)/I(E2)	I(E4)/I(E2)
Phosphates:					
#21232	4700 A	0.89 ± 0.26	0.75 ± 0.38	0.82 ± 0.38	0.10 ± 0.05
#21233A	4900 A	0.94 ± 0.08	1.01 ± 0.14	0.84 ± 0.14	0.16 ± 0.03
#21235	4800 A	2.25 ± 0.26	0.80 ± 0.17	0.85 ± 0.16	0.13 ± 0.03
#21237	4800 A	1.04 ± 0.12	0.88 ± 0.17	1.03 ± 0.17	0.18 ± 0.03
#21271	4700 A	0.90 ± 0.28	0.84 ± 0.48	1.00 ± 0.50	0.13 ± 0.07
#21272	4700 A	1.73 ± 0.22	0.91 ± 0.21	0.76 ± 0.18	0.15 ± 0.04
Reference Samples:					
Calcite	4600 A	6.56 ± 0.12	1.03 ± 0.03	0.80 ± 0.02	0.16 ± 0.01
ZnS:Ag	4650 A	680	0.61	0.90	0.09

* E1, 3500 - 3900 A
E2, 3000 - 3400 A
E3, 2600 - 3000 A
E4, 2400 - 2700 A

As mentioned previously, luminescence signals are too small to obtain true excitation spectra curves for the rock samples. However, comparison of the luminescence intensity ratios for the various excitation bands does indicate relative excitation efficiencies. Within probable errors of the emission measurements, there are no significant differences in the intensity ratios from sample to sample, and, thus, in the gross excitation properties of the calcite and the phosphate rocks. The reason for the consistently low ratio of I(E4) / I(E2) is due to the low intensity of available excitation energy in the E4 band as explained in Section II C.

It is known that the excitation spectra of ZnS type phosphors (Ref. 6) increases nearly linearly to a maximum efficiency at about 3300A as the wavelength decreases, starting at about 4000A. The excitation spectra then remains nearly constant in efficiency (at room temperature) between 3300A and 2700A, and then slowly decreases as the wavelength decreases. All of the samples in Table 2 have intensity ratios higher than that of ZnS:Ag at the high and low wavelength regions, i.e., I(E1) / I(E2) and I(E4) / I(E2); this suggests that their excitation spectra tend to be nearly constant in efficiency throughout the 2400A to 3900A region.

C.2 Indiana Limestone

The Indiana limestone samples exhibit significantly different luminescent characteristics than the phosphate rocks. As the excitation wavelength is decreased from the E2 band (3000 - 3400A) to E3 band (2600 - 3000A), luminescence intensities and efficiencies of the limestone samples at 4000Å are increased. Some examples of limestone sample spectral luminescence curves are shown on Figure 8, along with the calcite reference. The curves shown here and in the Appendix are for the E3 excitation. Most of the samples are characterized between curve types B and C of Figure 8. Sample DC66-101 (curve A) is unique in having an apparent secondary emission band peak around 5000A.

The change in emission curve shape between the E2 and E3 excitation is illustrated by luminescence intensities at 4500A and 4000A for the two different excitation bands. These values are listed in Table 4 for all of the limestones. (Only E3 band excitation data were obtained for samples DC66-101 and 102.) Enhancement of the emission around 4000A for the shorter wavelength excitation is obvious. However, it should be noted that probable errors in measurement are large due to the scattered radiation from these highly reflective samples. Further refinements in the measurement system would be necessary to better establish the emission properties of these low efficiency luminescent rocks.

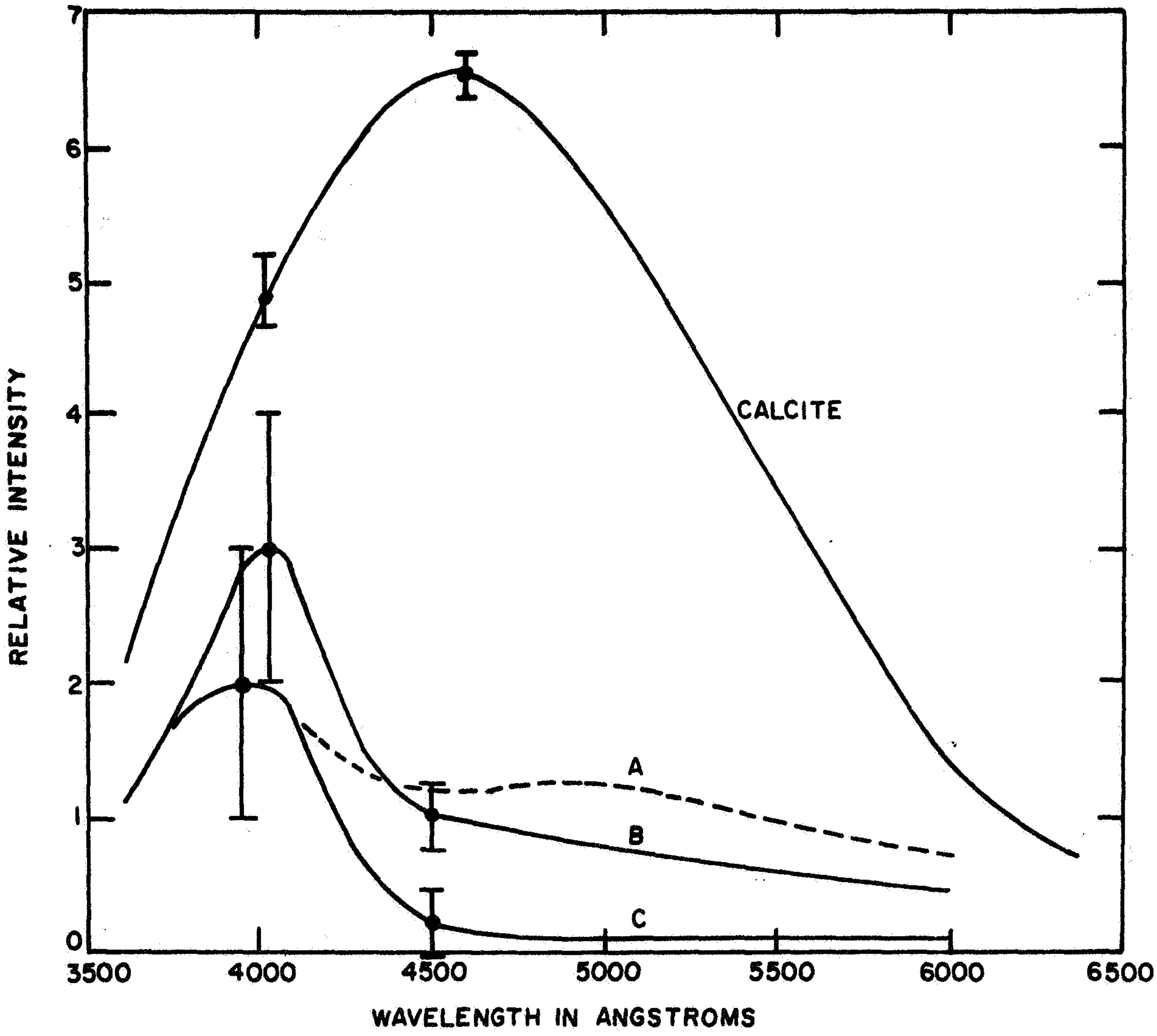


Figure 8

ULTRAVIOLET EXCITED LUMINESCENCE EMISSION FROM THREE INDIANA LIMESTONE SAMPLES AND THE CALCITE SAMPLE.

(EXCITATION BY 2600Å-3000Å ULTRAVIOLET BAND)

CURVE	SAMPLE NO.
A	DC-66-101
B	DC-66-99
C	DC-66-96

Table 4

LUMINESCENCE EMISSION INTENSITIES OF INDIANA LIMESTONES

Sample No.	Excitation Band*	I at 4500A	I at 4000A
DC66 - 95	E2	0.35 ± 0.23	0.60 ± 0.40
	E3	0.28 ± 0.27	2.0 ± 1.0
DC66 - 96	E2	0.36 ± 0.21	0.73 ± 0.35
	E3	0.19 ± 0.24	2.0 ± 1.0
DC66 - 97	E2	0.44 ± 0.21	0.77 ± 0.33
	E3	0.60 ± 0.23	2.3 ± 1.0
DC66 - 98	E2	0.59 ± 0.28	0.45 ± 0.32
	E3	0.61 ± 0.24	1.20 ± 0.81
DC66 - 99	E2	0.92 ± 0.20	1.43 ± 0.36
	E3	1.04 ± 0.24	3.0 ± 1.0
DC66 - 100	E2	0.49 ± 0.37	1.26 ± 0.65
	E3	0.46 ± 0.43	3.6 ± 2.0
DC66 - 101	E2	-	-
	E3	1.19 ± 0.23	2.0 ± 1.0
DC66 - 102	E2	-	-
	E3	0.77 ± 0.23	2.3 ± 1.1

* E2: 3000-3400A
E3: 2600-3000A

C.3 Luminescence Detectivity

Both the reflectance and the luminescence emission values at a given wavelength are necessary to evaluate the applicability of the Fraunhofer line-depth technique in detecting luminescence. In this technique (Ref. 2) the deduced parameter, p, is defined as

$$p = I_l/I_{sM}$$

where I_l is the luminescence emission intensity at the wavelength of the Fraunhofer line used, and I_{sM} is the intensity of the reflected incident light at the shoulder of the Fraunhofer line. Although the luminescence intensity values quoted in this report are not absolute, i.e., they have not been normalized to an assumed solar excitation spectra, they are useful in a relative sense.

Selection of the optimum Fraunhofer line regions for operation from the emission/reflectance data is illustrated by phosphate sample 21271 (Appendix A-5). The emission intensity (arbitrary units) shown on the luminescence curve at any wavelength, will be directly proportional to the emission intensity exhibited under actual solar excitation since the emission curve shape was found not to change significantly with the various excitation bands used. Thus, the arbitrary intensity shown on the curve, when multiplied by a constant factor, <u>a</u>, will correspond to the actual intensity, or I_l, under solar excitation; the factor <u>a</u> simply relates solar excitation to that which actually took place in the measurement reported. Multiplication of estimated solar incidence at the same wavelength (Ref. 7) by the reflectance shown on the curve, provides an estimate of I_{sM}. By noting the variation of the deduced I_l/I_{sM} ratios as a function of wavelength, one can thereby select the region (s) where the ratio appears to be maximized and the line-depth technique is most effective; the latter assumes the existence of a Fraunhofer line in the region. Some of the results are shown below for five isolated wavelength values for phosphate sample 21271 (Appendix A-5):

λ	3700A	3850A	4000A	4200A	4900A
Emission, I_1	8(a)	10(a)	10.5(a)	8.5(a)	10(a)
Incidence (microwatts per cm^2 per 50Å)	325	333	433	600	732
Reflectance	0.43	0.44	0.45	0.48	0.55
I_{sM}	140	147	203	288	403
$p = I_1 / I_{sM}$	0.051(a)	0.068(a)	0.052(a)	0.029(a)	0.025(a)

The above results indicate the K-line of calcium (3934A) as optimum for the line-depth method, assuming that a more complete plot at all wavelengths shown in Figure A-5 will substantiate the ρ maximum at 3850A.

Computations for phosphate sample 21235 (Appendix A-3) also indicates the K-line as optimum, despite peak emission near 4750Å. Computed luminescence values for sample 21235 are tabulated as follows:

λ	3700Å	3850Å	4000Å	4200Å	4500Å	4750Å	4900Å
$p = I_1/I_{sM}$	0.110(a)	0.138(a)	0.109(a)	0.082(a)	0.084(a)	0.075(a)	0.073(a)

These data illustrate that luminescence detectivity by means of the line-depth method is not necessarily maximized in wavelength regions where emission exhibits peak values, but instead depends on the ratio of luminescence to reflectance.

IV. CONCLUSIONS

Total diffuse reflectance of the Saudi Arabian rocks and the Indiana limestones generally increases in value as wavelength increases from 2300A to 7000A. All of the limestones and phosphate rocks have high reflectance values and show a significant increase in reflectance between the ultraviolet and visible range. Phosphate sample 21271, for example, has a 32 percent reflectance at 2500A and a 71 percent reflectance at 7000A. All andesite rocks, on the other extreme, have essentially flat reflectance curves with values ranging from 7 to 15 percent.

Based on the samples studies, it appears doubtful that it is possible to distinguish rhyolite in andesite sequences as indicated by spectral reflectance properties of these rocks in the near ultraviolet and blue-green region of the spectrum. All six andesite samples show a flat diffuse reflectance from 2300A to 7000A; 10 rhyolite samples are also generally flat, although four exhibit weak to moderate increase in spectral reflectance at longer wavelengths. Between 6000A and 7000A these four samples show two to four times the spectral reflectance of the andesite, and therefore, it may be possible by means of multispectral photography to discriminate some rhyolite outcrops in the red and near infrared.

Both the phosphate and limestone samples exhibit relatively high reflectivity throughout the ultraviolet where reflectivity values exceeding 25 percent are common. However, the extent to which this could be used as a distinguishing property in the field would depend upon the spectral reflectance of adjacent materials.

The spectral emission for ultraviolet excited luminescence from phosphate samples is broad, commonly exceeding 2000A at half intensity, with the emission maximum at or near 4800A in the visible. The energy conversion efficiency for luminescence appears to be nearly constant for excitation spectra between 2400Å and 3900Å.

Preliminary analysis of the phosphate luminescence and reflectance data indicates that Fraunhofer line-depth techniques are feasible and that maximum detectability can be achieved at the K-line of calcium at 3934Å. Data reported by Betz (Table 3, Ref. 2), using the line-depth method, have shown unambiguous detection of luminescence of both calcite and phosphate rock. His data indicate luminescence of one percent (H-line 3968Å) and three percent (K-line 3934Å) for the phosphate, and three and five percent respectively for the calcite. Our data obtained by conventional spectrometer techniques, indicate the same approximate 1:3 luminescence intensity ratios for some of the Saudi Arabia phosphates compared to the calcite sample. This implies that the Saudi Arabian phosphates exhibit the same order of luminescence detectability as that reported by Betz, and tends to corroborate the validity of the data obtained in both studies.

Calculations indicate that these luminescence and reflectance values are amenable to line-depth detection of phosphate from aircraft altitudes. Assuming shot noise of standard photomultipliers, and using a Fabry-Perot interferometer with an effective collecting aperature of 25mm, a signal-to-noise ratio of 100:1 is estimated. Computations are based on: (a) aircraft speed of 76 m/sec at an altitude of 2km; (b) a 1 degree field of view or a 35 m ground resolution; (c) a 0.25A spectral resolution; (d) a scan rate of 30/sec over a 4A range; and (e) an electronic band width of 500 cps. It is noted, however, that IITRI experience with the magnetostrictive drive used with this interferometer indicates an overheating problem for scan rates of this order. This problem may be obviated by narrowing the spectral scan range or by using a non-scanning servo-controlled system.* Also, in view of the high S/N ratios computed for a single spectral scan, the requirement for scan rates of 30/sec should be studied. Scan rate is a function of platform speed, desired ground resolution, and atmospheric fluctuation rates. These tradeoffs require further investigation.

The spectral emission for the limestone samples is also broad, commonly exceeding 600A at half intensity with the emission maximum at or near 4000A. The 2600-3000A band appears to be more efficient in stimulating luminescence than bands at longer wavelengths. In fact, with this excitation band the measured luminescence intensities near 4000A have about the same amplitudes as those peaks exhibited by the phosphates. However, relying on the sun as an excitation source is not appropriate in this case because the 2600-3000A band lies in the so-called solar blind part of the spectrum which does not penetrate the earth's atmosphere. For this reason, the Indiana limestone quarries would appear to be suitable sites for field testing

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*H. Betz, personal communication.

of the Fraunhofer-line discriminator only if an active UV system such as the Westinghouse prototype (Hemphill and Carnahan 1965) were used.

Further work is required to achieve a more detailed understanding of the reflectance properties which effect contrasts in both UV imagery and line-depth discrimination in field, aircraft, and spacecraft operations. This work would include such parameters as: rock surface texture (including powdered layers); incident and reflected angles with narrow fields of view; polarization components; and radiation aging.

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1. H. V. Watts, "Reflectance of Rocks and Minerals to Visible and Ultraviolet Radiation," Technical Letter, NASA-32, July 1966.

2. H. T. Betz, "Measurement of Luminescence by the Fraunhofer Line-Depth Method," Technical Letter, NASA-70, December 1966.

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4. G. A. Zerlaut and A. C. Krupnick, "An Integrating Sphere Reflectometer for the Determination of Absolute Hemispherical Spectral Reflectance," presented at 1st AIAA Annual Meeting, Washington, D. C., June 29 - July 2, 1964.

5. G. A. Zerlaut, (private communication of unpublished work).

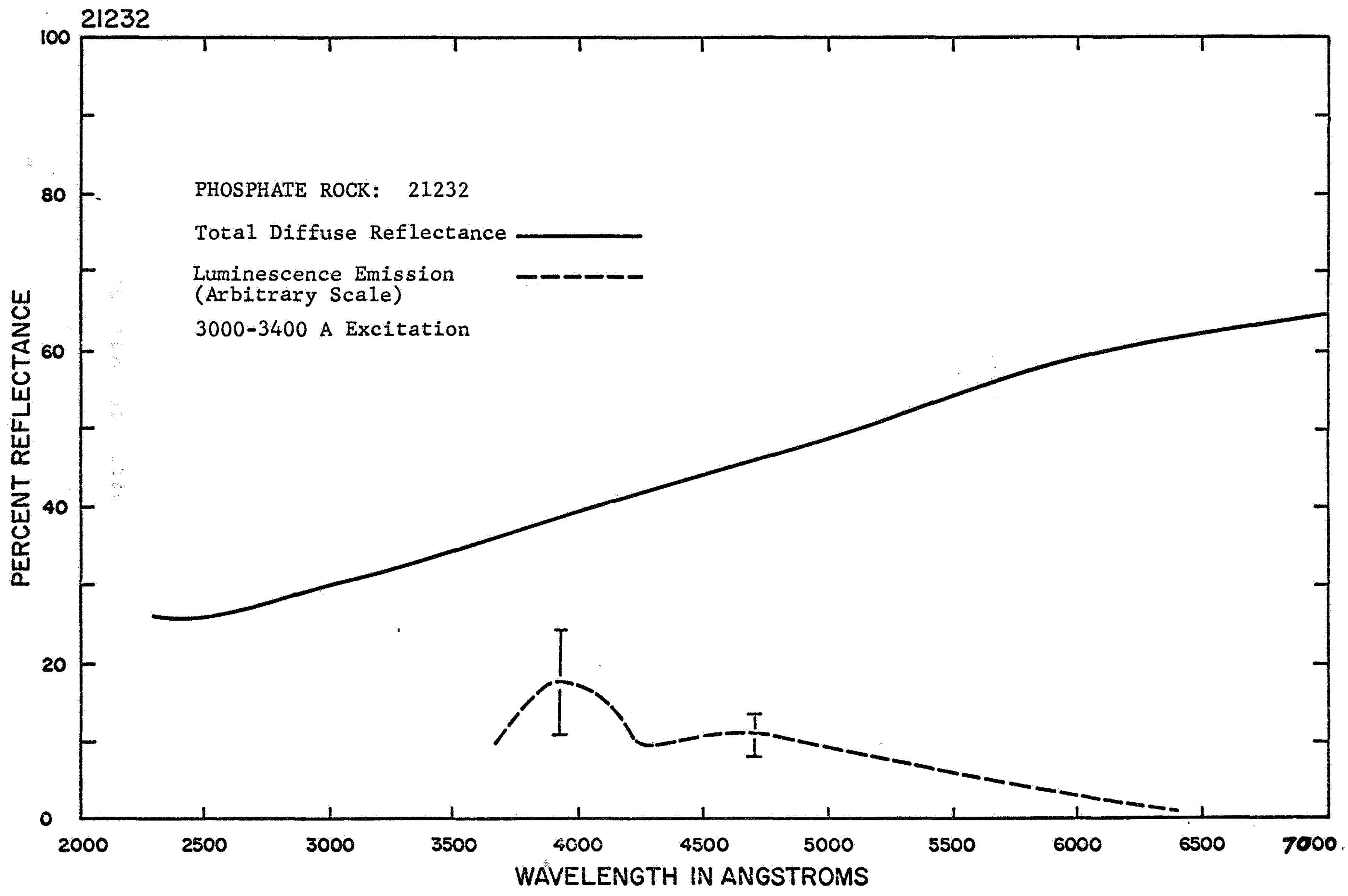
6. S. Shionoya, "Luminescence of Lattices of the ZnS Type,"Chapter 4 of Luminescence of Inorganic Solids, edited by Paul Goldberg (Academic Press, 1966).

7. L. R. Koller, "Ultraviolet Radiation," p. 133 (John Wiley and Sons, Inc., 1965).

8. Hemphill, W. R., and Carnahan, S. U., 1965, "Ultraviolet absorption and luminescence investigations progress report "U. S. Geological Survey Technical Letter NASA-6.

APPENDIX

DATA CURVES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Total Diffuse Reflectance
Luminescence Emission
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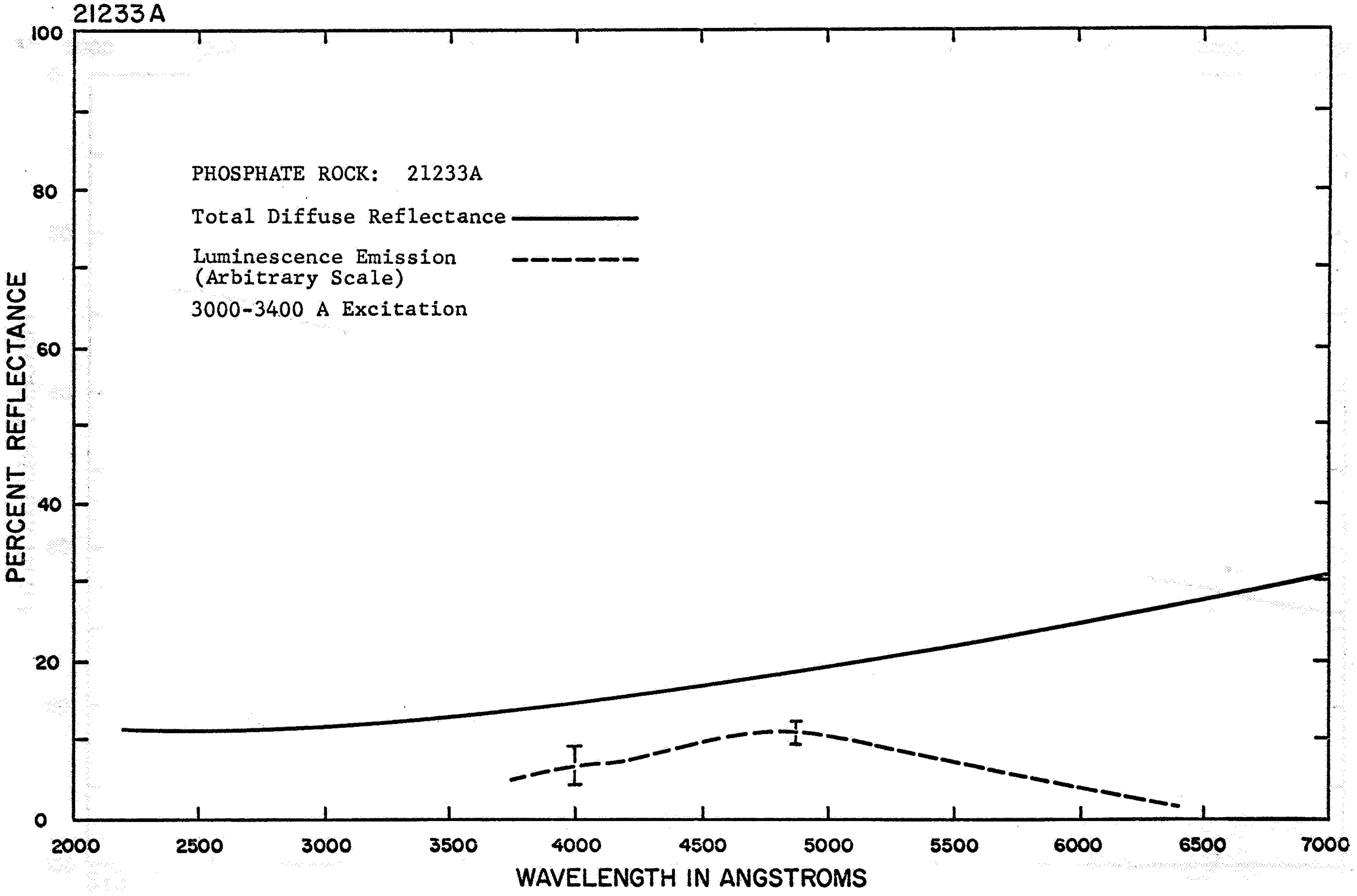
3000-3400 A Excitation
PERCENT REFLECTANCE
0
20
40
60
80
100
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS


21233A
PHOSPHATE ROCK: 21233A
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Luminescence Emission (Arbitrary Scale)
3000-3400 A Excitation
PERCENT REFLECTANCE
0
20
40
60
80
100
2000
2500
3000
3500
4000
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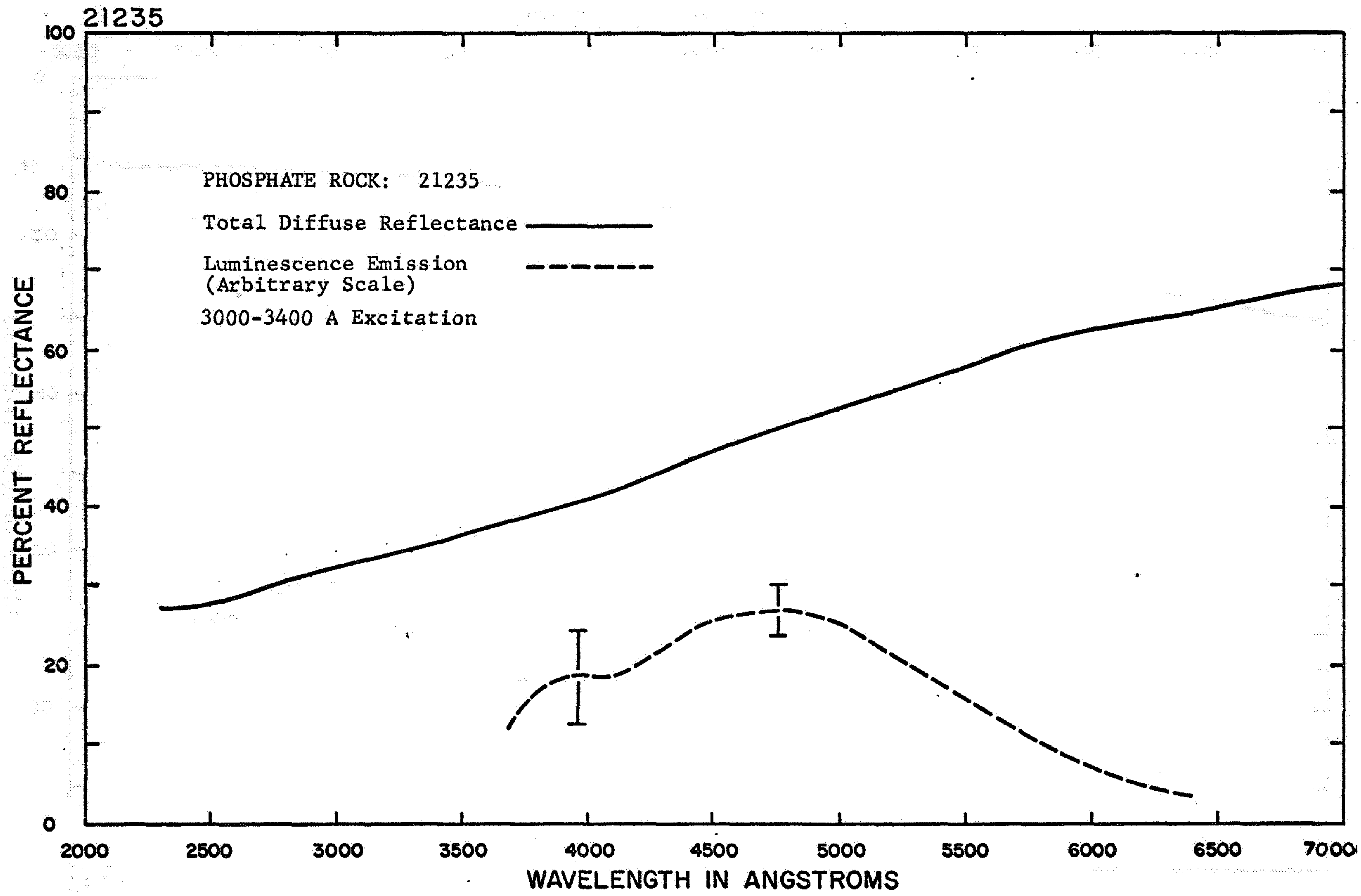
6000
6500
7000
WAVELENGTH IN ANGSTROMS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Luminescence Emission
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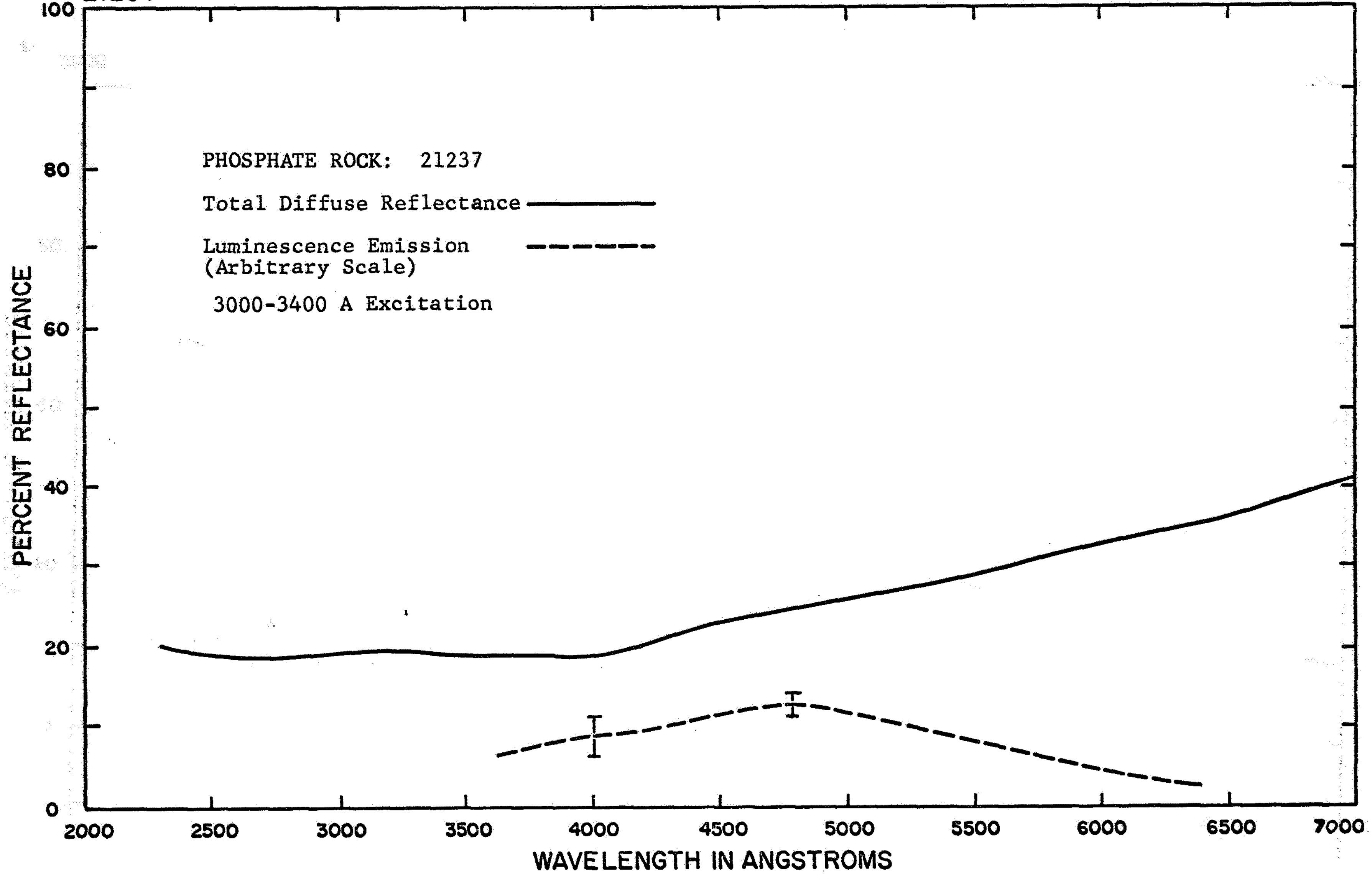
3000-3400 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

21237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Luminescence Emission (Arbitrary Scale)
3000-3400 A Excitation
PERCENT REFLECTANCE
0
20
40
60
80
100
WAVELENGTH IN ANGSTROMS
2000
2500
3000
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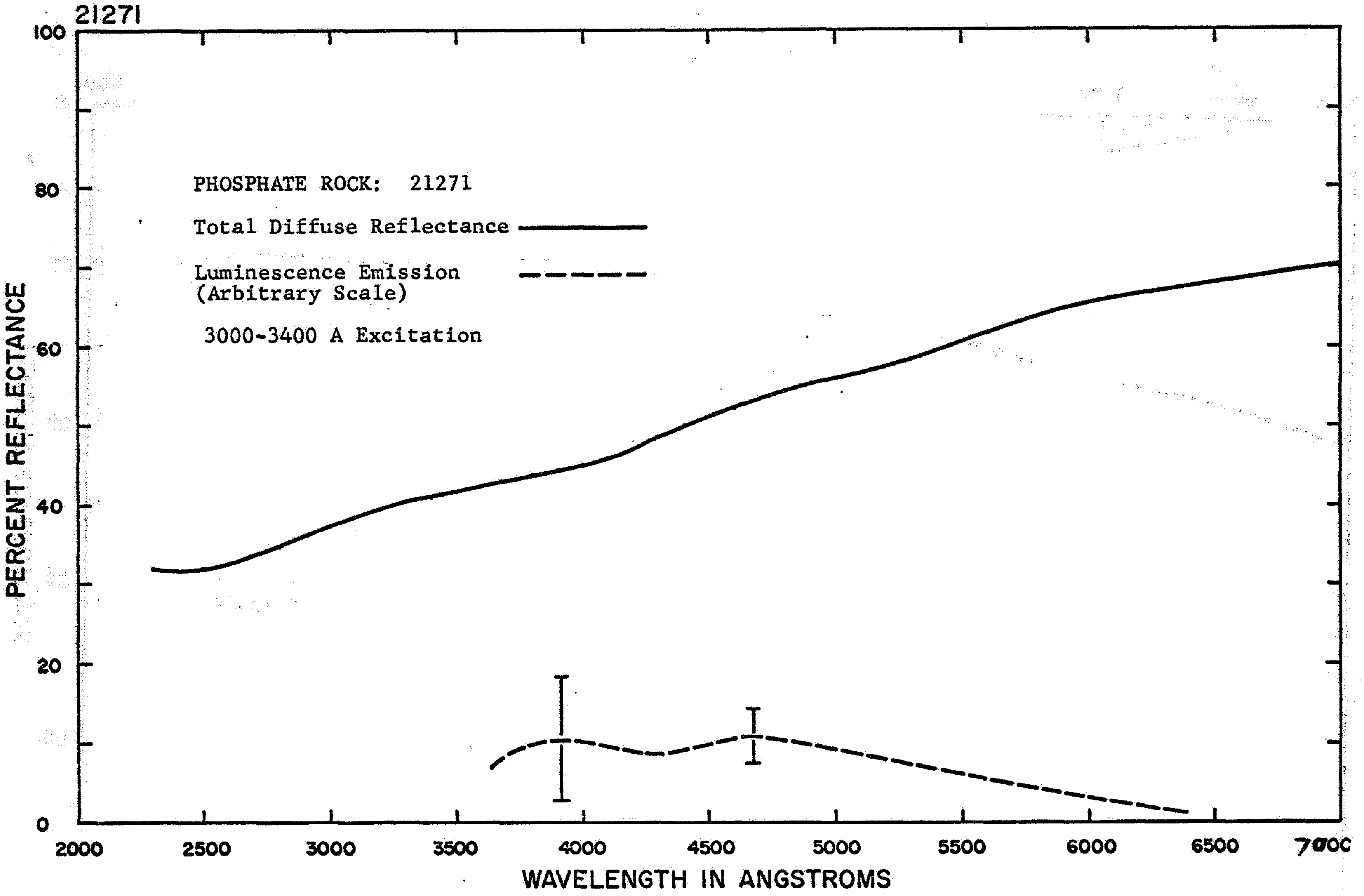
4000
4500
5000
5500
6000
6500
7000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Luminescence Emission
(Arbitrary Scale)
3000-3400 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
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6000
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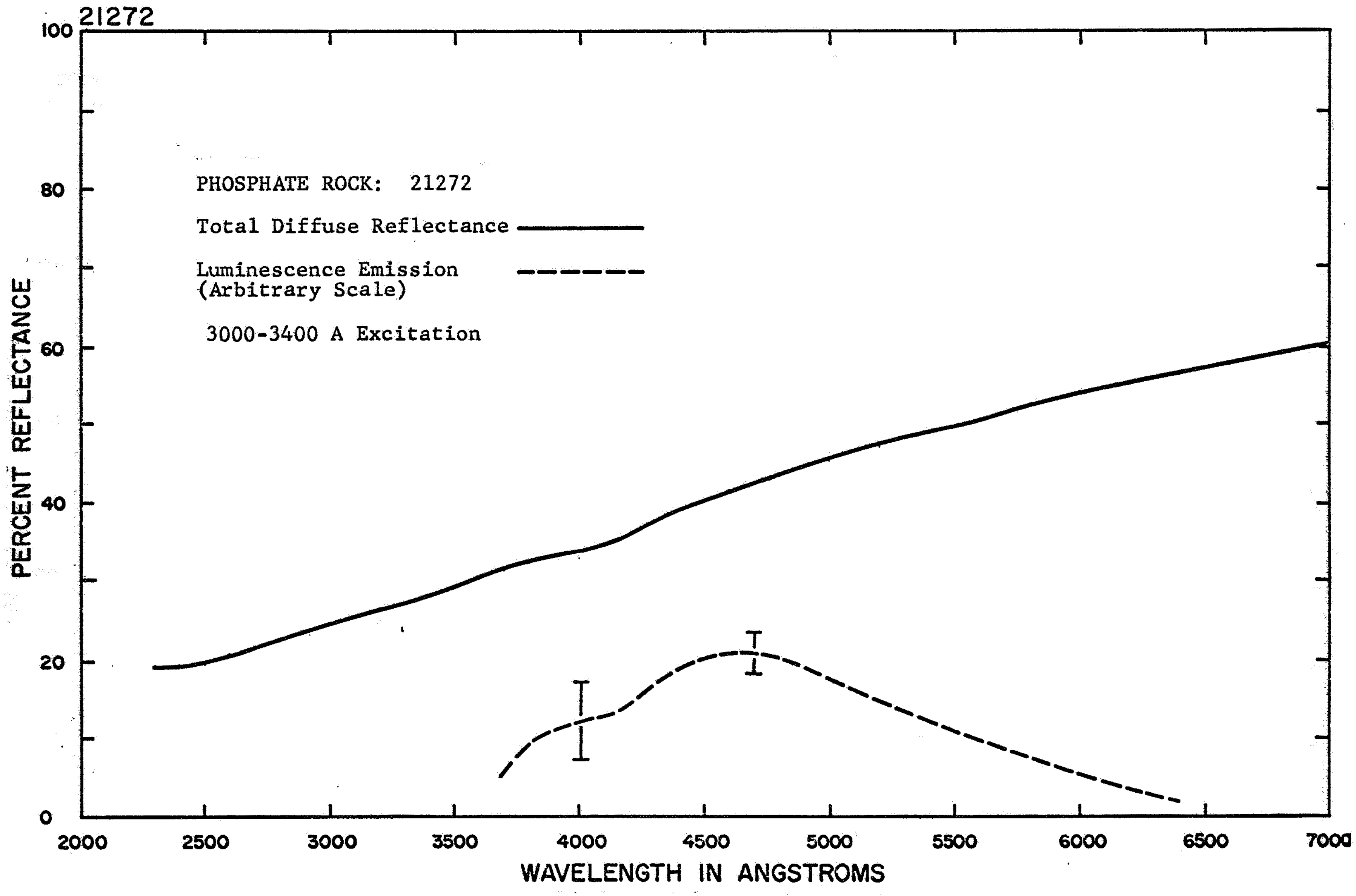
7000
WAVELENGTH IN ANGSTROMS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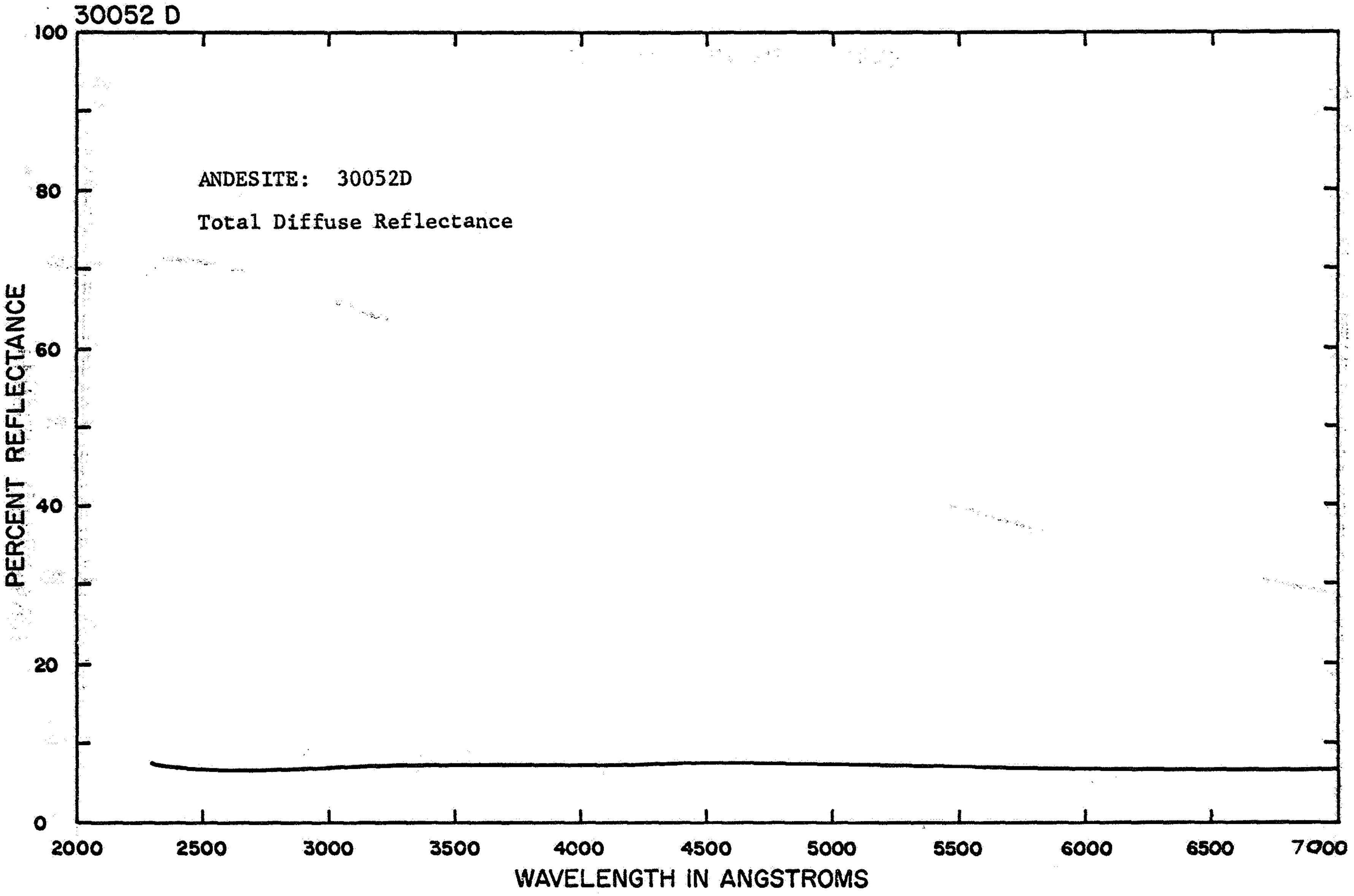
Luminescence Emission (Arbitrary Scale)
3000-3400 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS


30052 D
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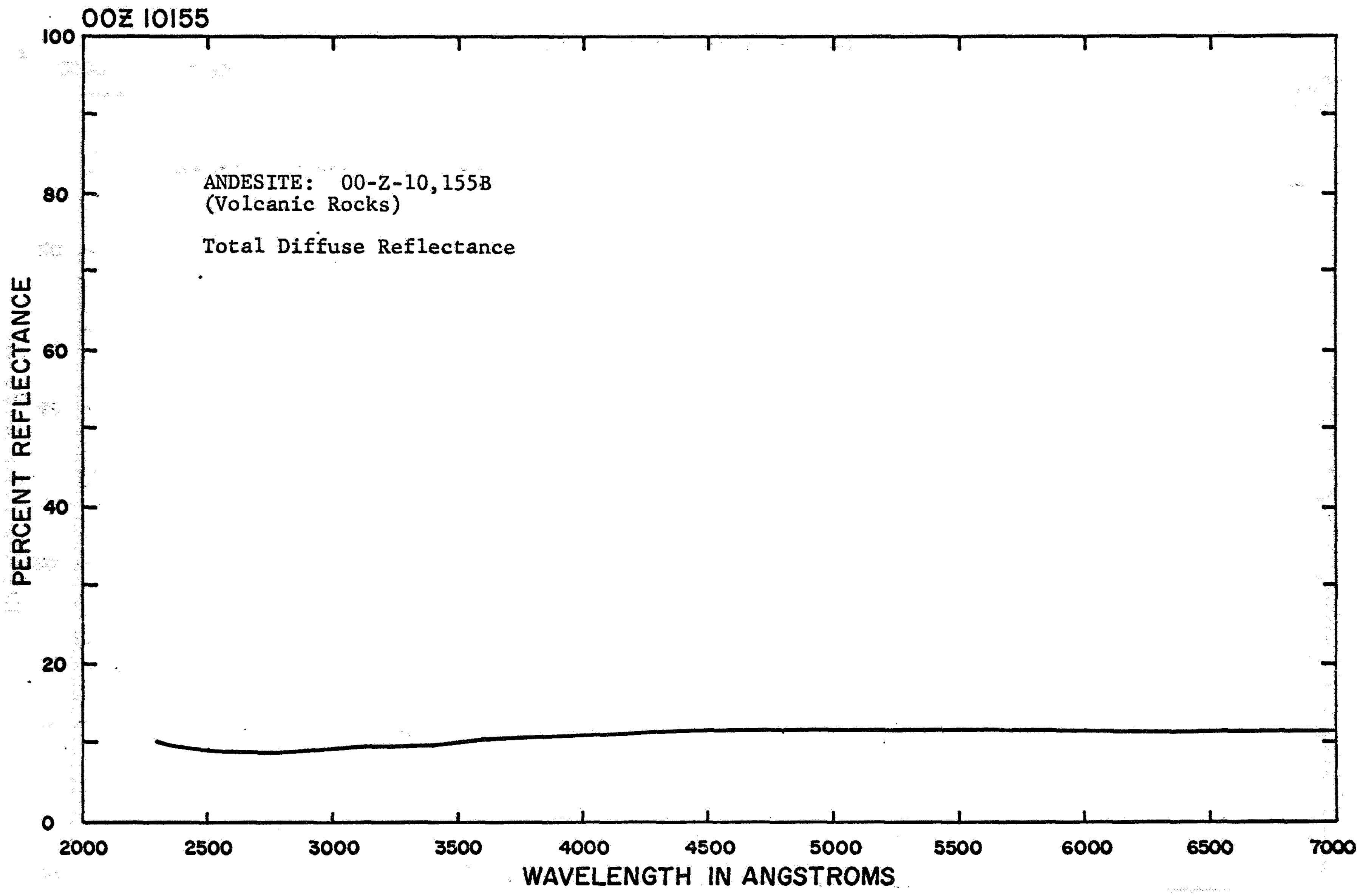
Total Diffuse Reflectance
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS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PERCENT REFLECTANCE
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80
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20
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2000
2500
3000
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4000
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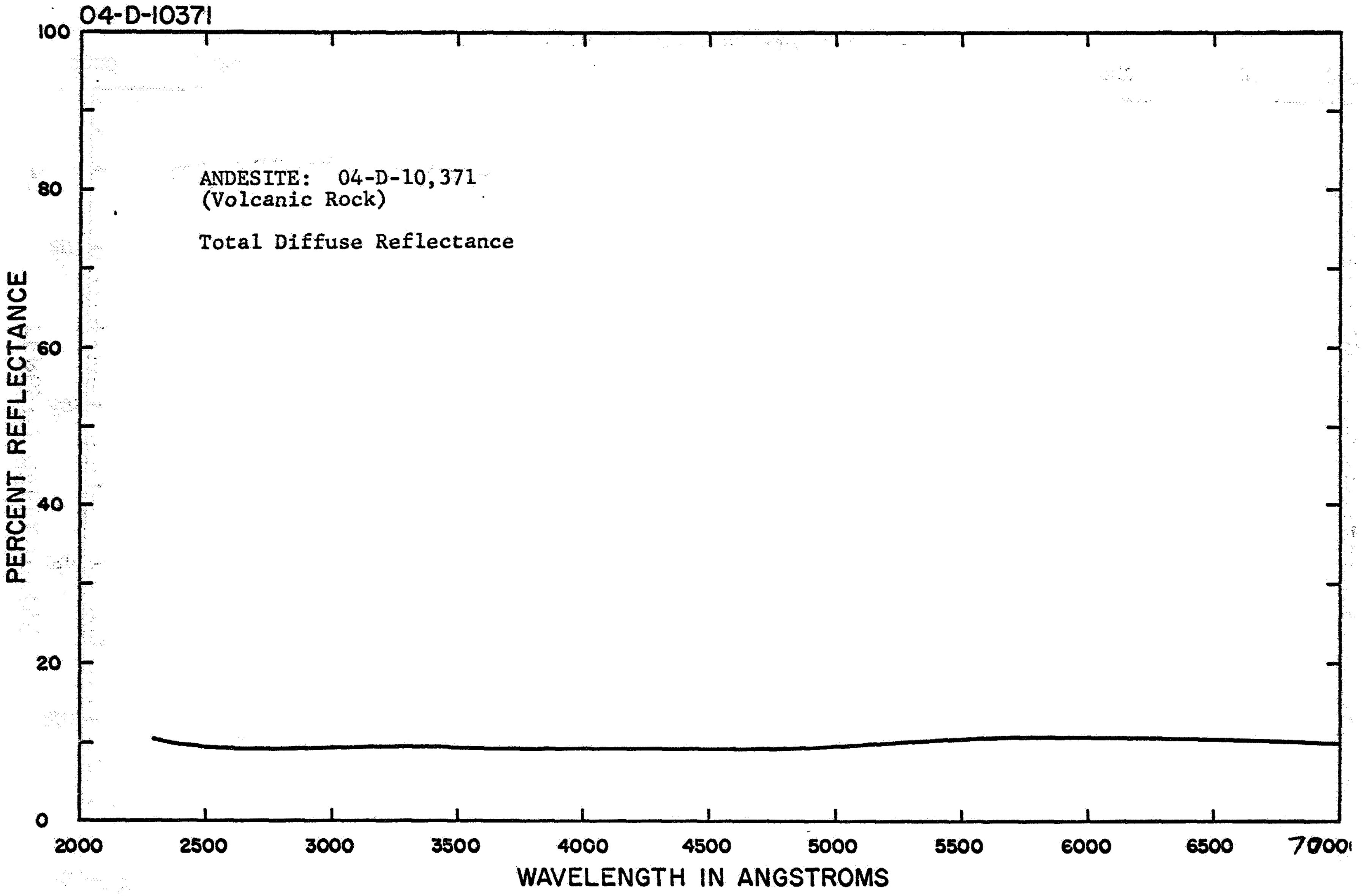
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS



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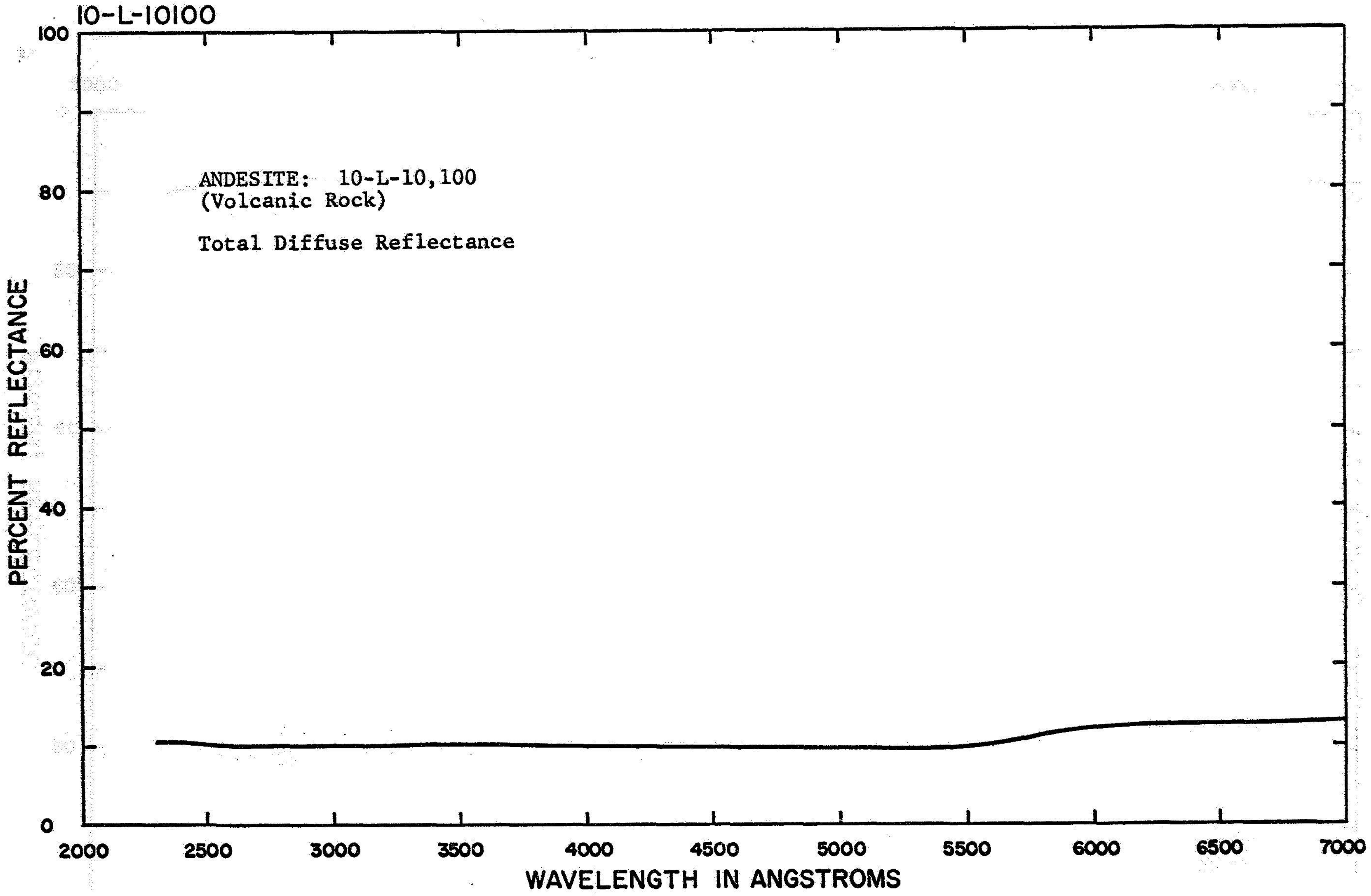
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2500
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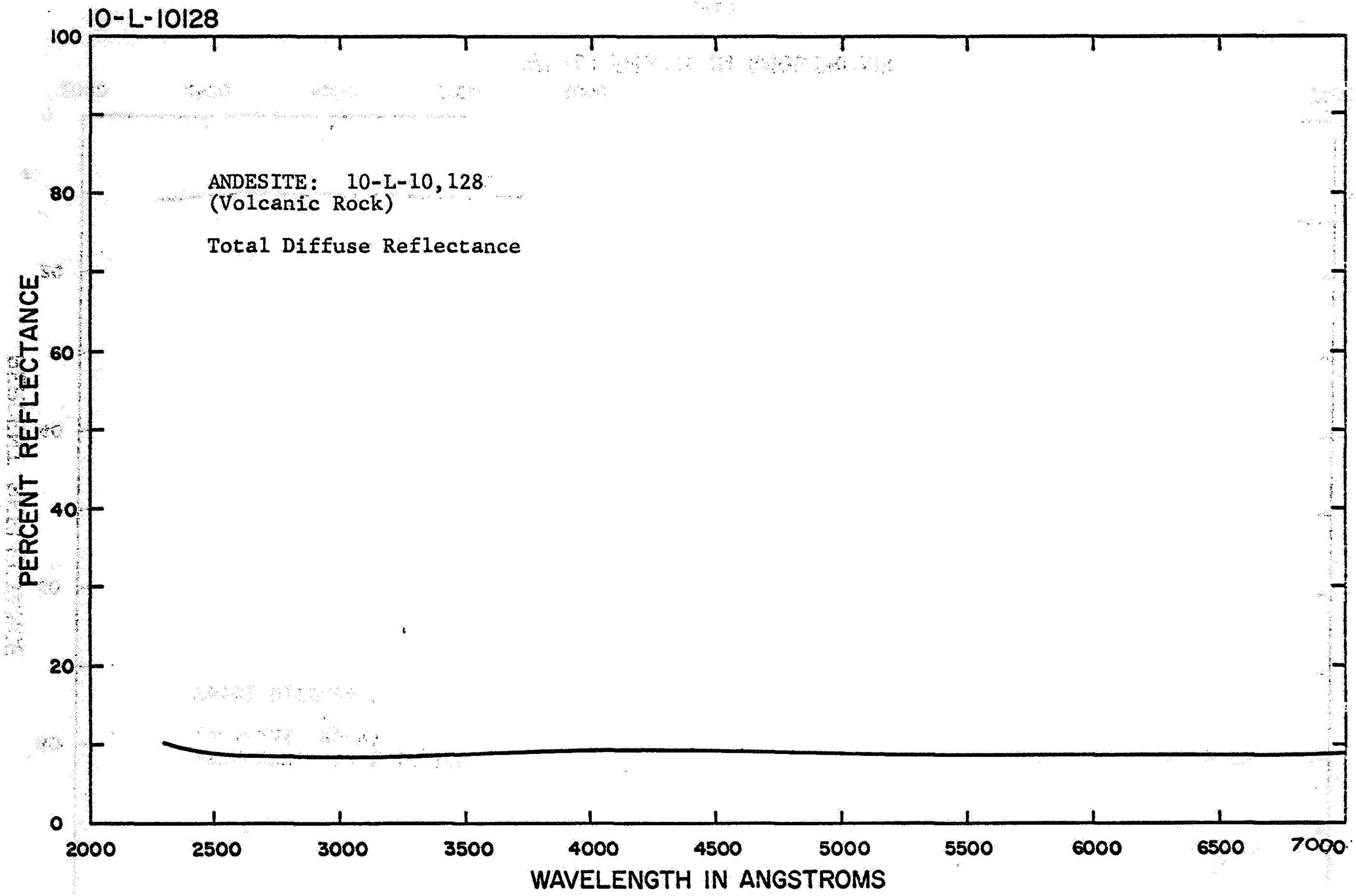
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PERCENT REFLECTANCE
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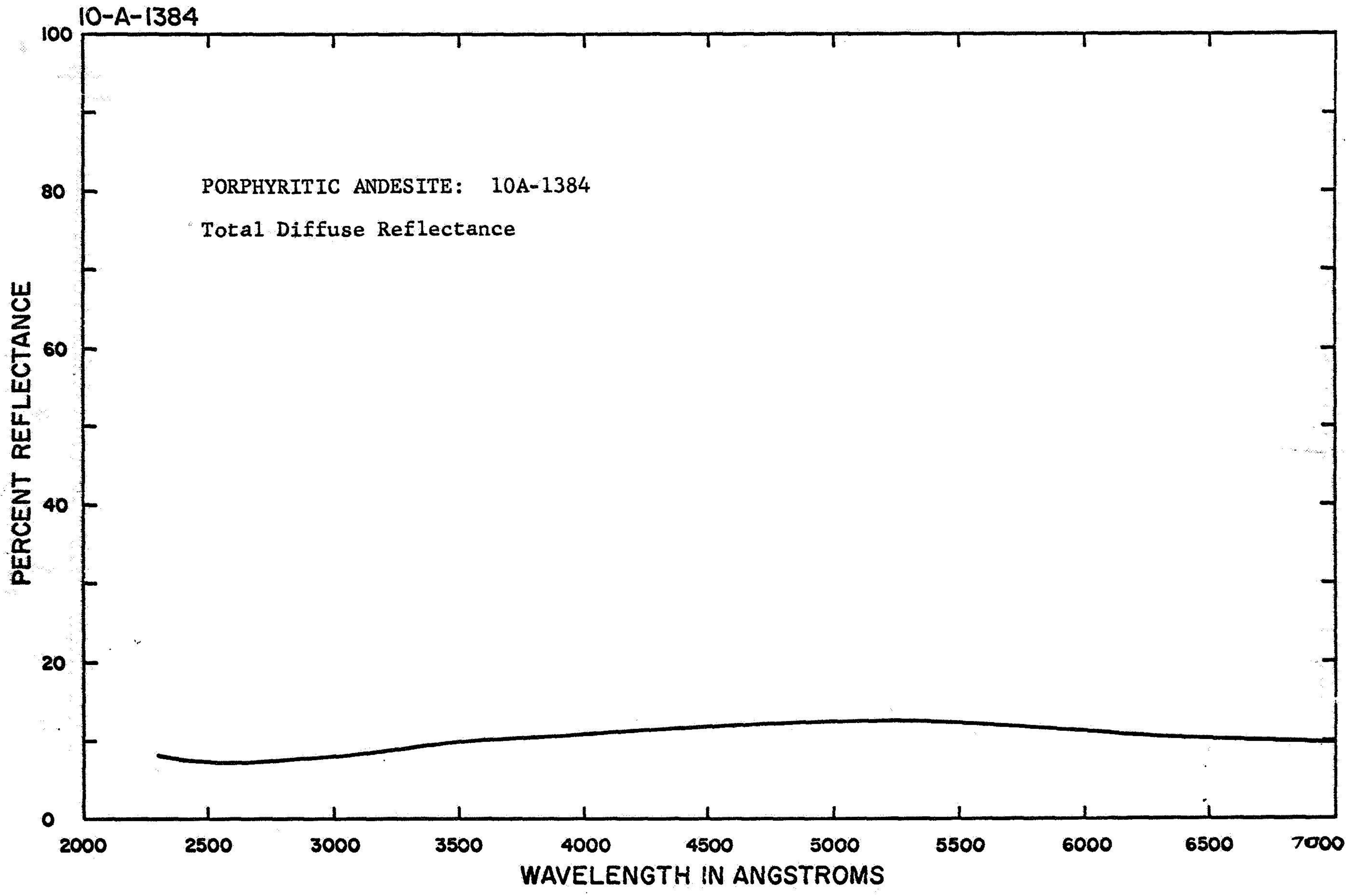

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PORPHYRITIC ANDESITE: 10A-1384

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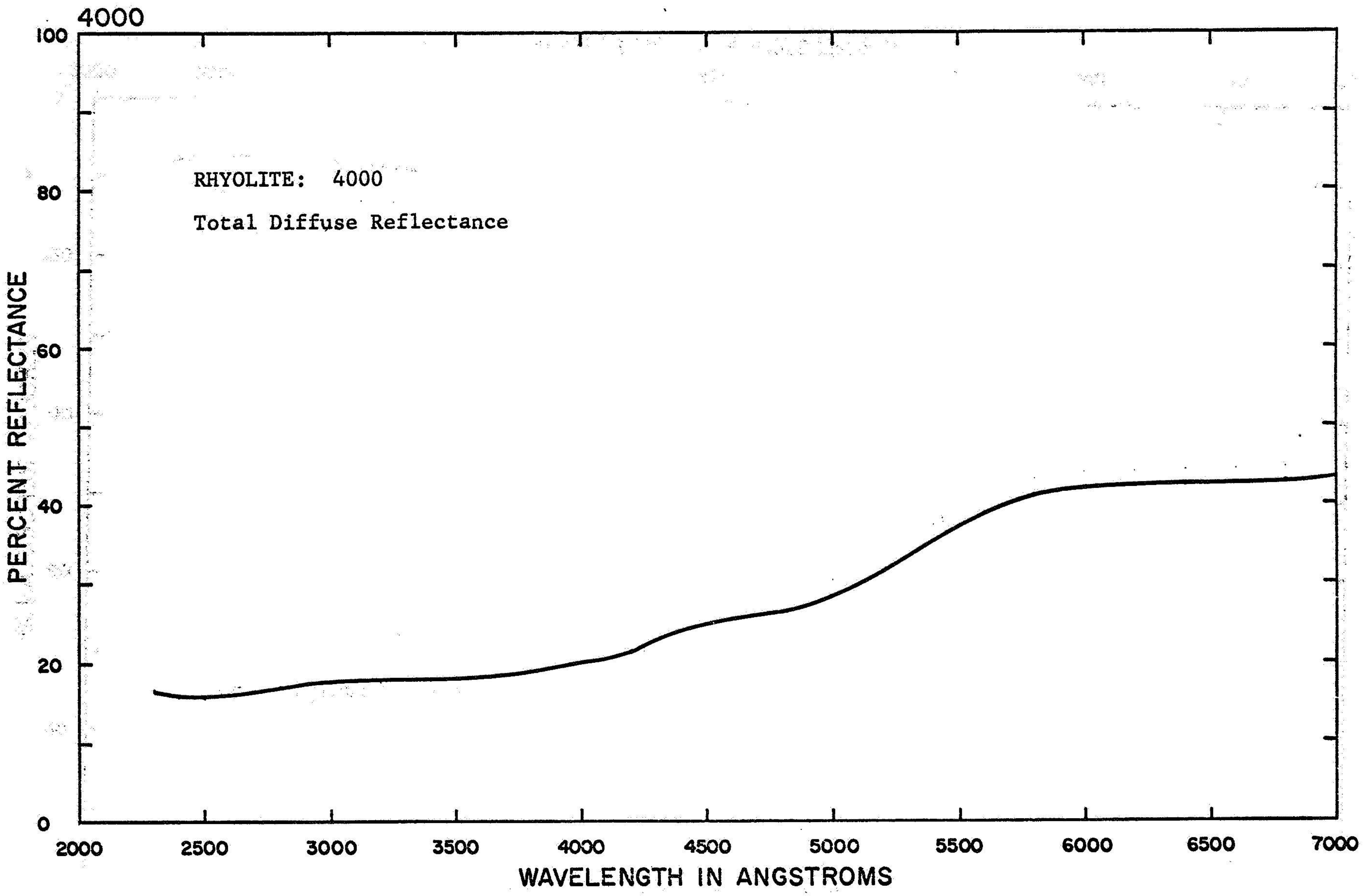
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Total Diffuse Reflectance
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4000
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5000
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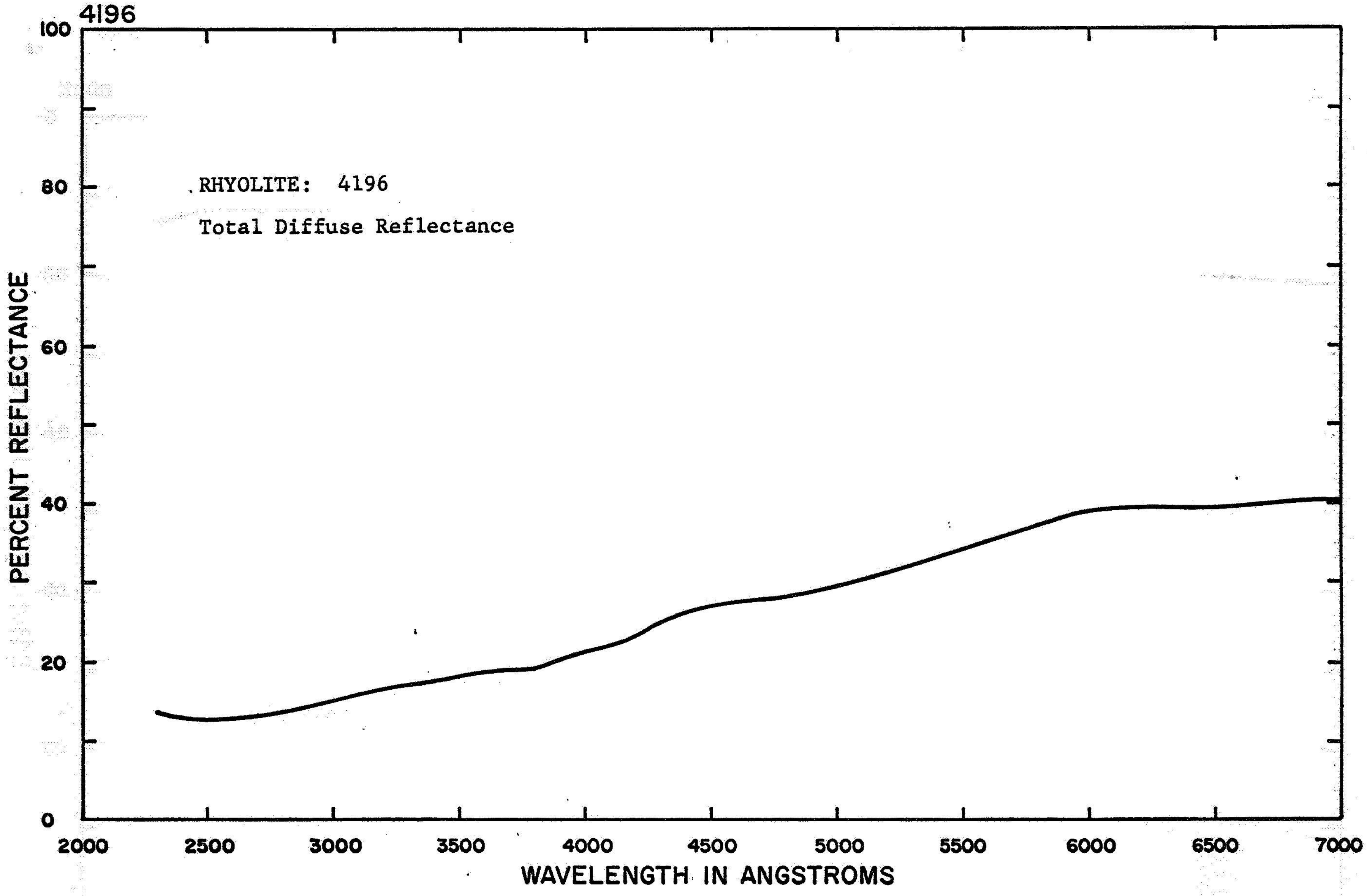
6000
6500
7000
WAVELENGTH IN ANGSTROMS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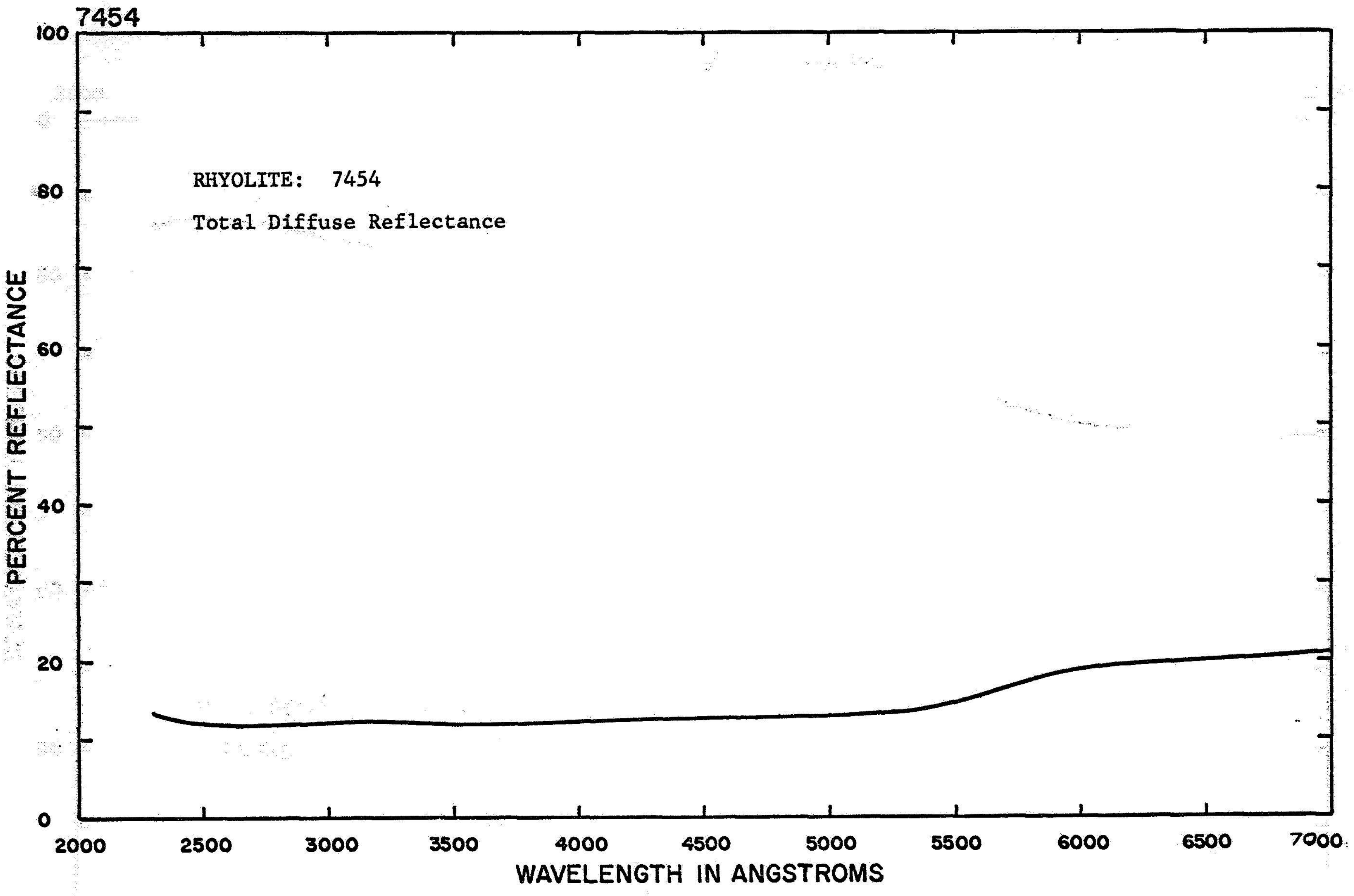
WAVELENGTH IN ANGSTROMS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6000
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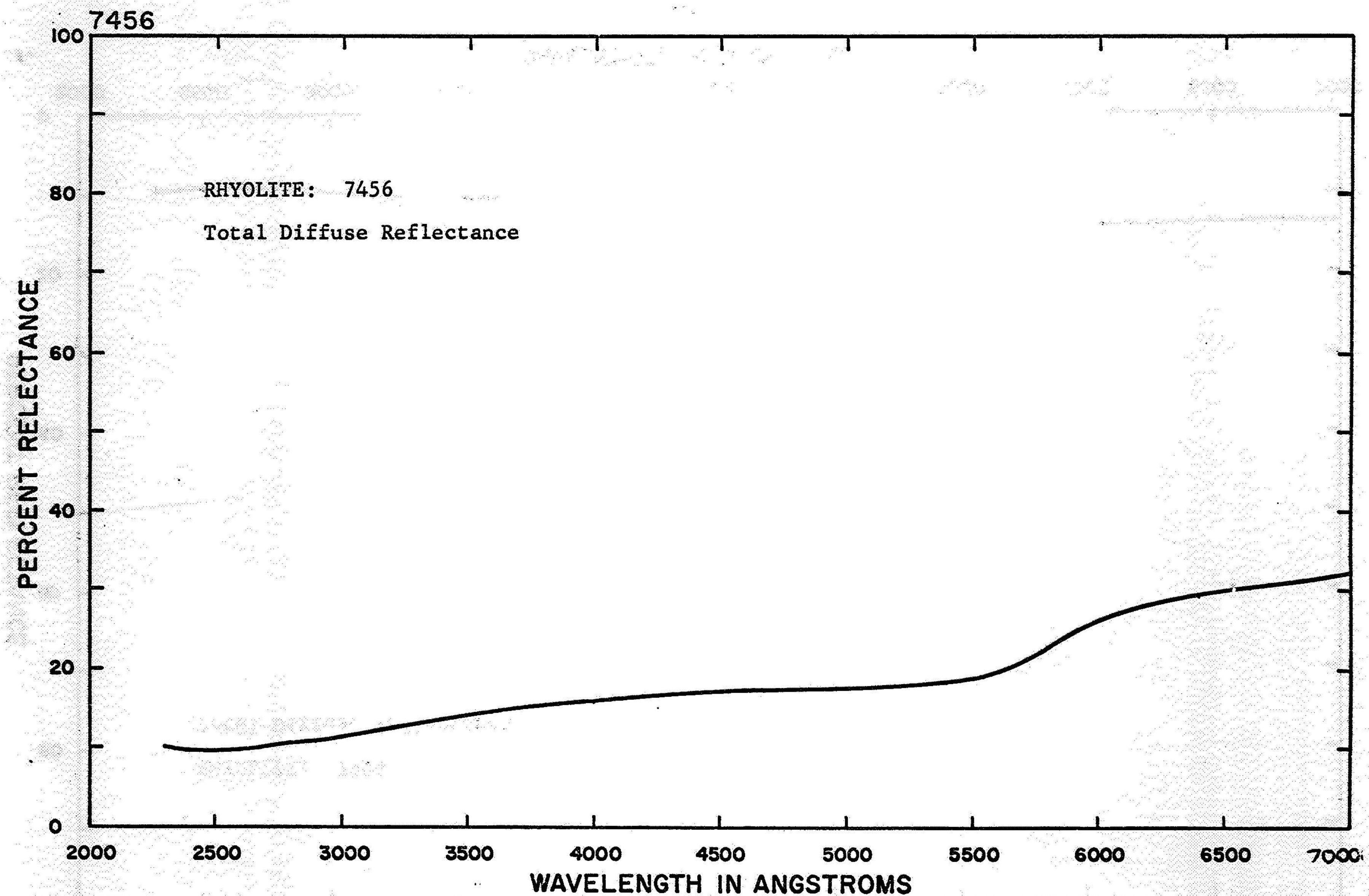
WAVELENGTH IN ANGSTROMS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WAVELENGTH IN ANGSTROMS
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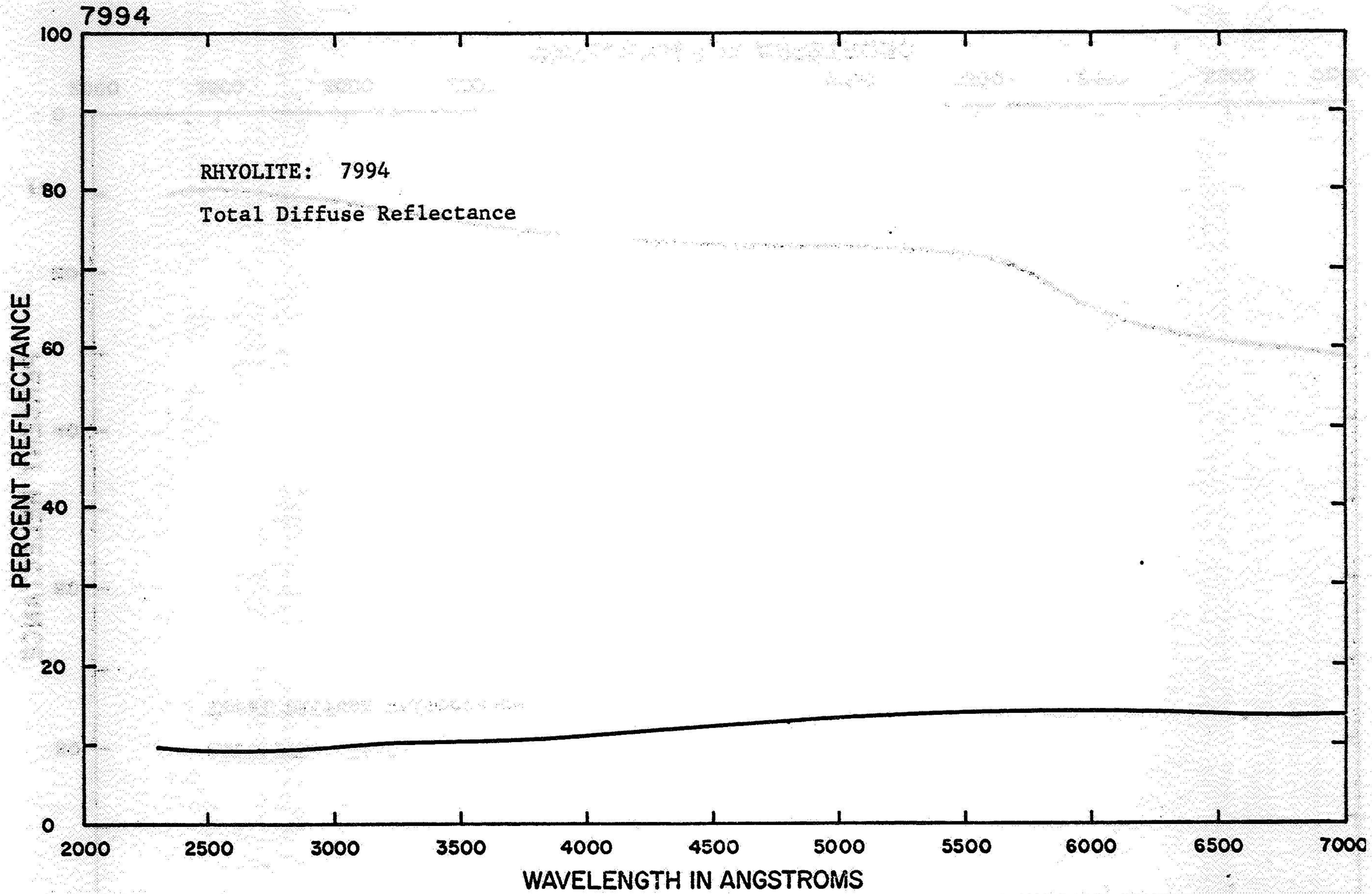
6500
7000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Total Diffuse Reflectance
PERCENT REFLECTANCE
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2500
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6000
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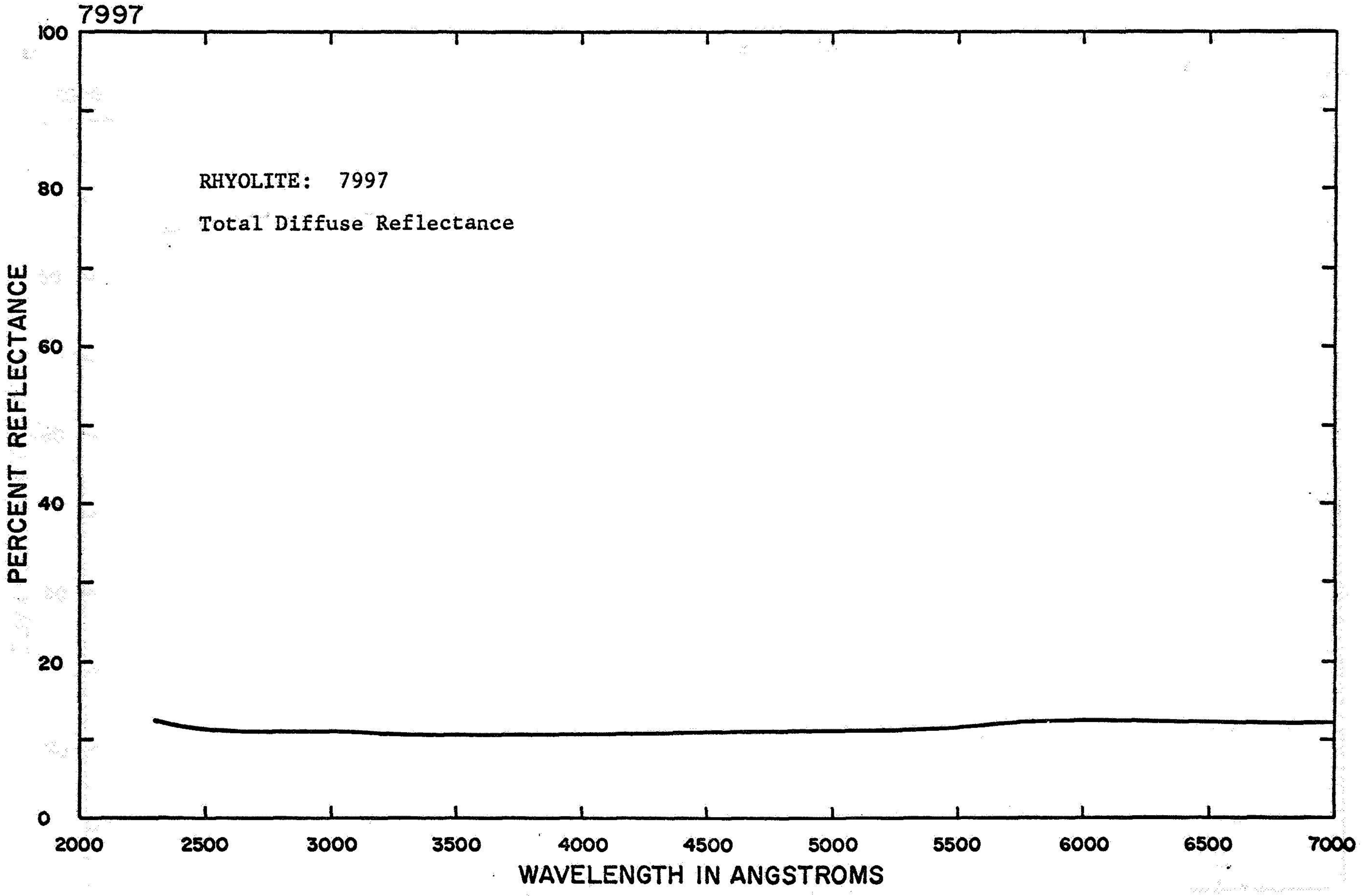
WAVELENGTH IN ANGSTROMS


7997
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Total Diffuse Reflectance
PERCENT REFLECTANCE
100
80
60
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2500
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4500
5000
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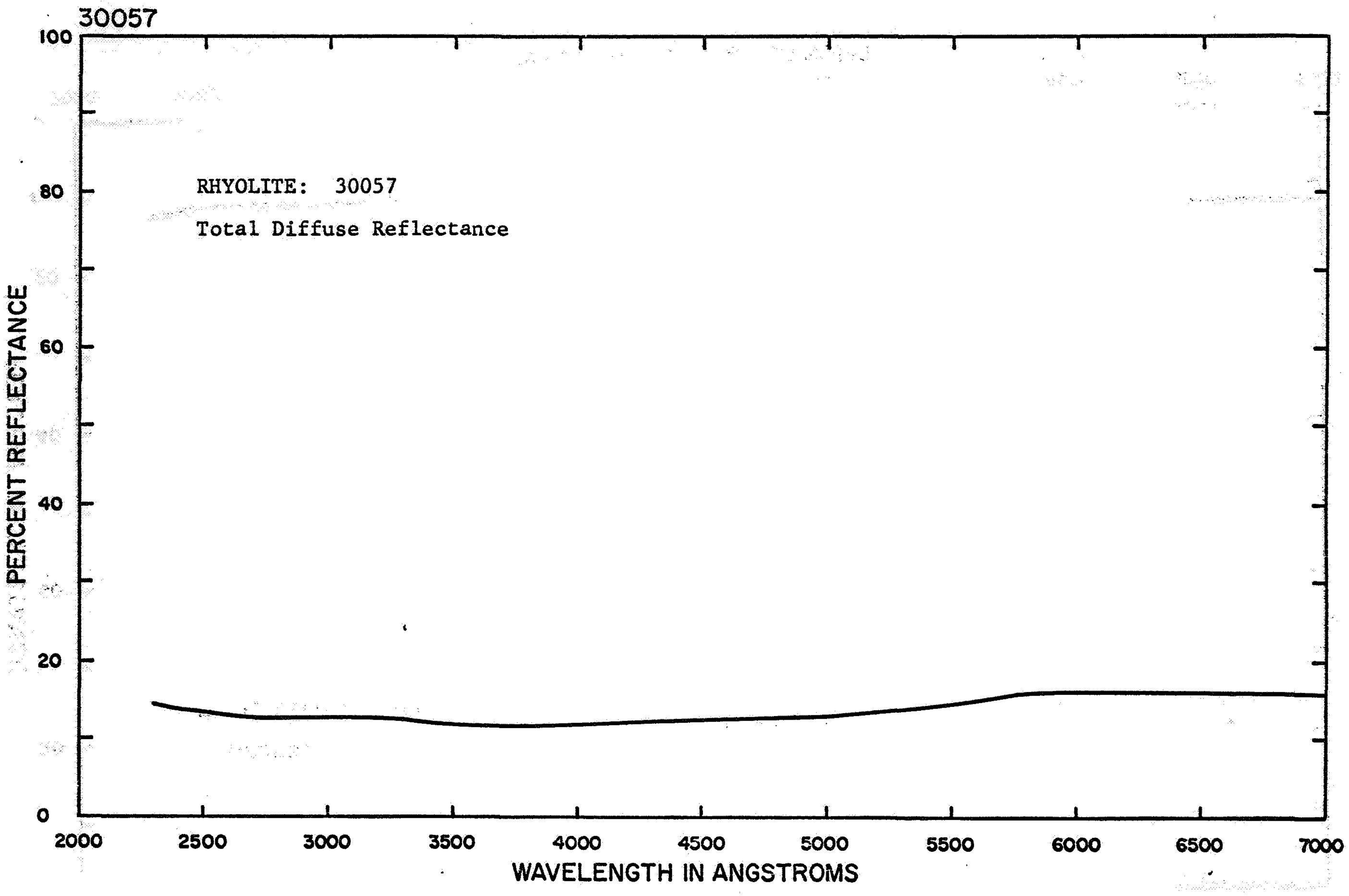
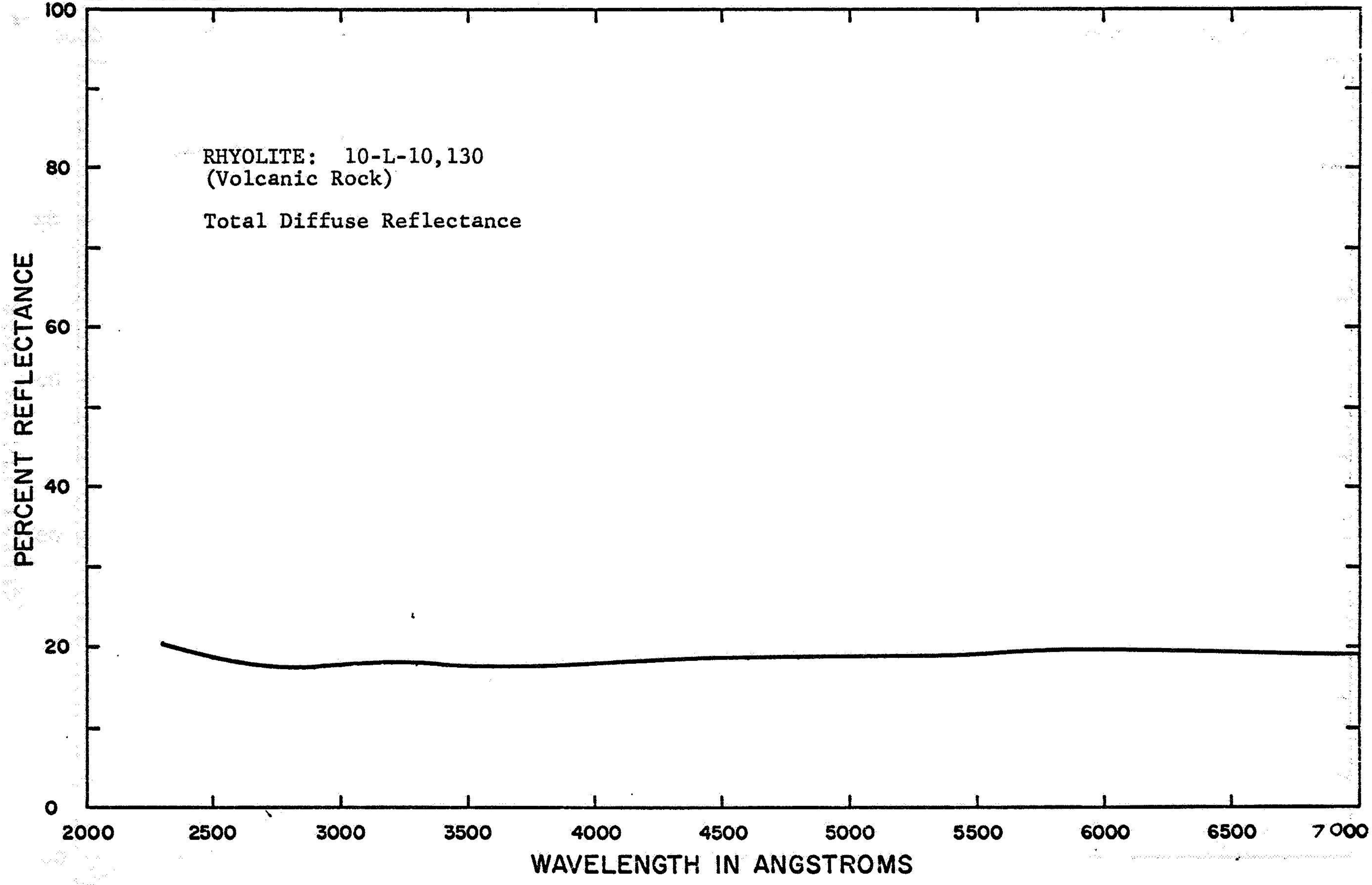
6000
6500
7000
WAVELENGTH IN ANGSTROMS



RHYOLITE: 30057

Total Diffuse Reflectance

10-L-101130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(Volcanic Rock)
Total Diffuse Reflectance
PERCENT REFLECTANCE
100
80
60
40
20
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2500
3000
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4000
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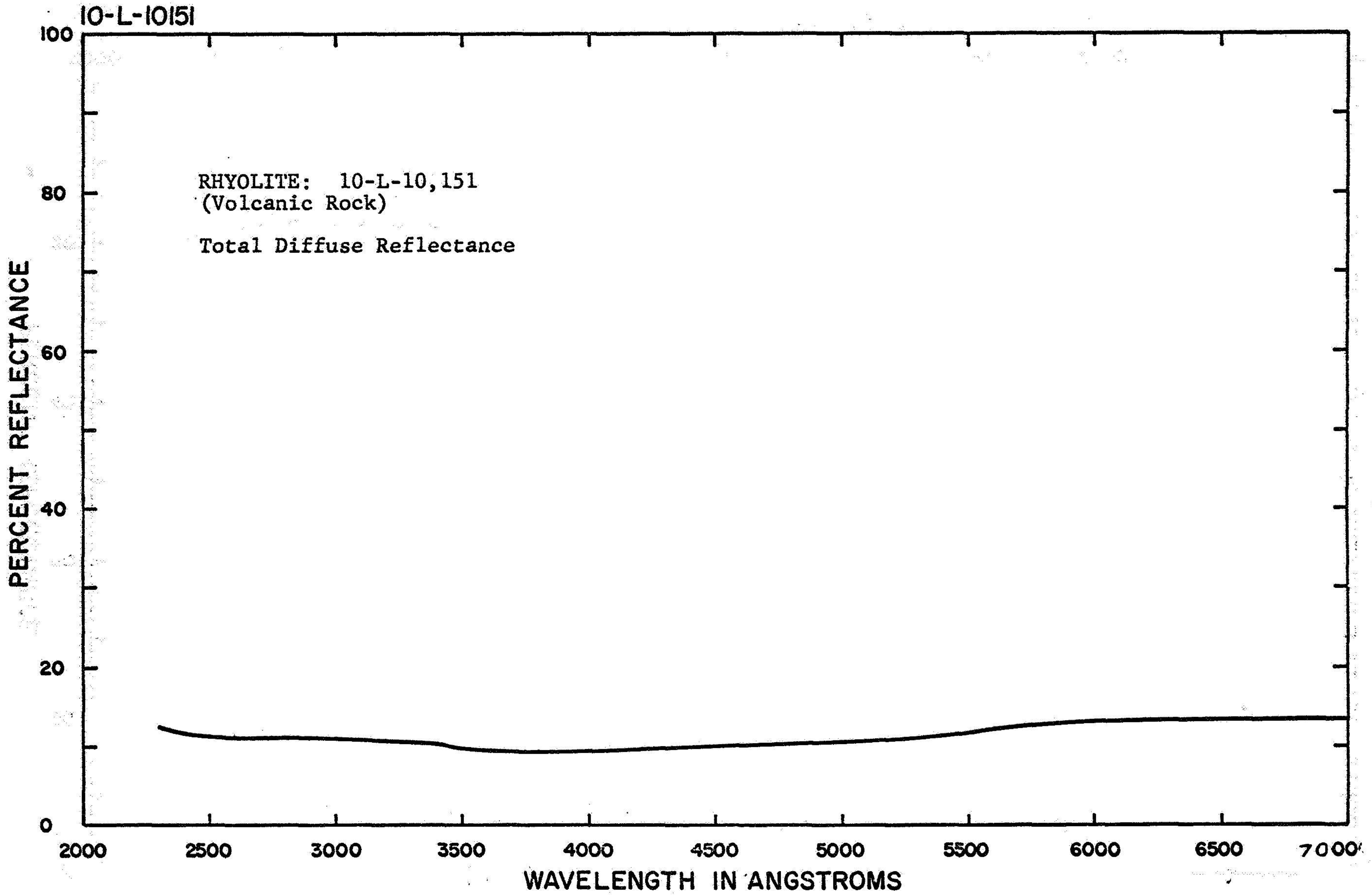
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS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(Volcanic Rock)
Total Diffuse Reflectance
PERCENT REFLECTANCE
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40
20
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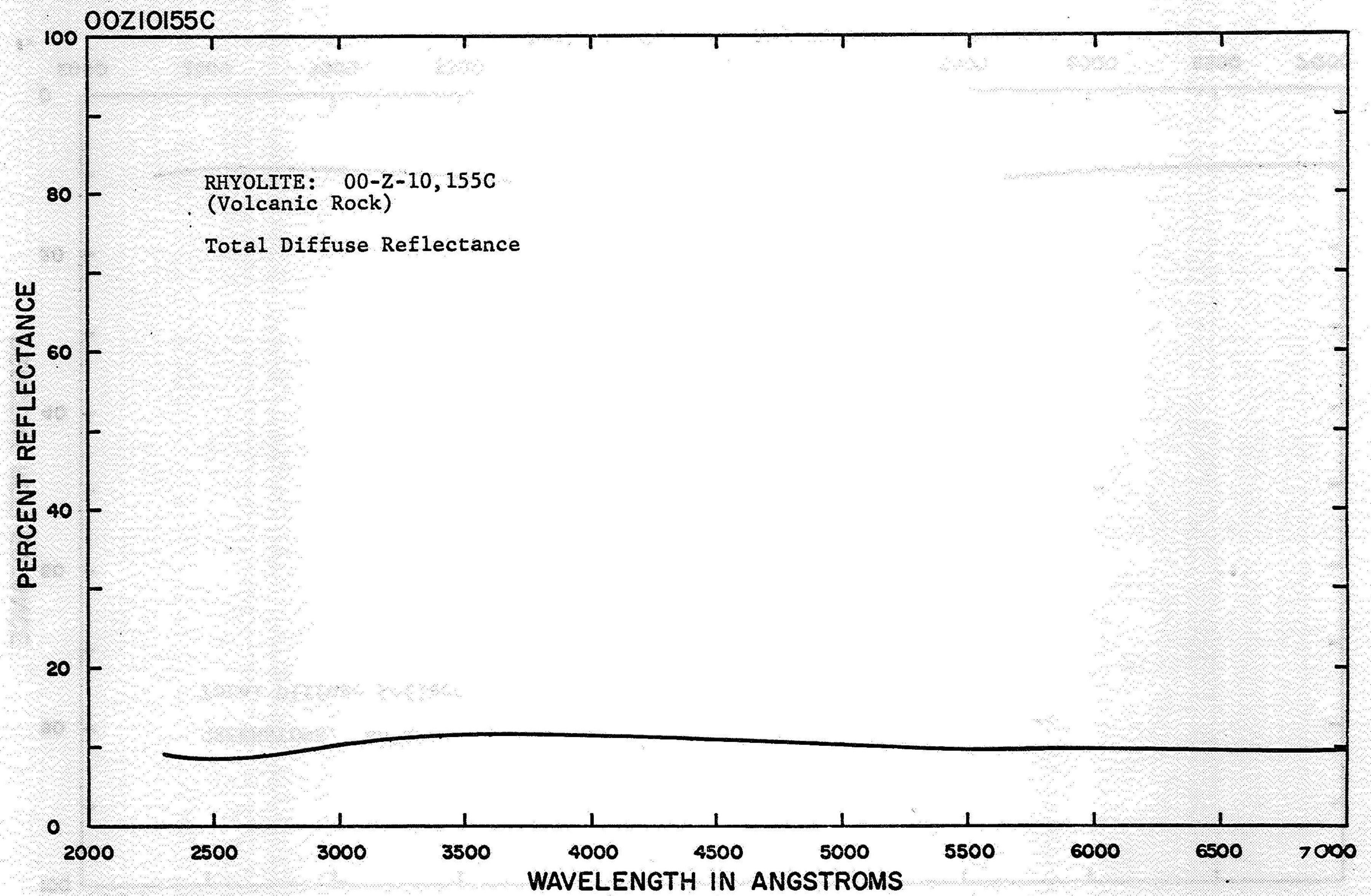
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS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RHYOLITE: 00-Z-10,155C
(Volcanic Rock)
Total Diffuse Reflectance
PERCENT REFLECTANCE
100
80
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2000
2500
3000
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6000
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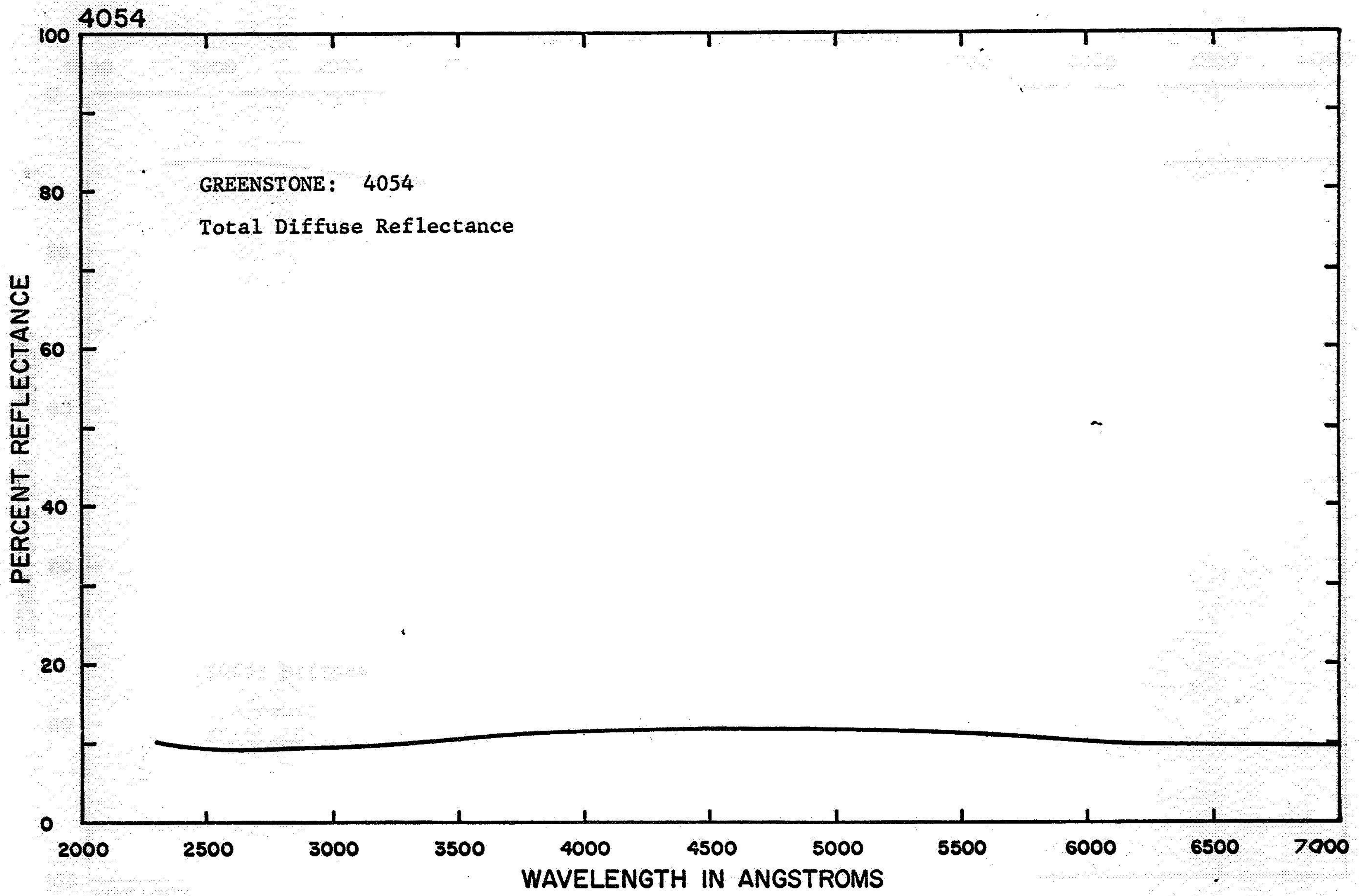
7000
WAVELENGTH IN ANGSTROMS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GREENSTONE: 4054
Total Diffuse Reflectance
PERCENT REFLECTANCE
100
80
60
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2500
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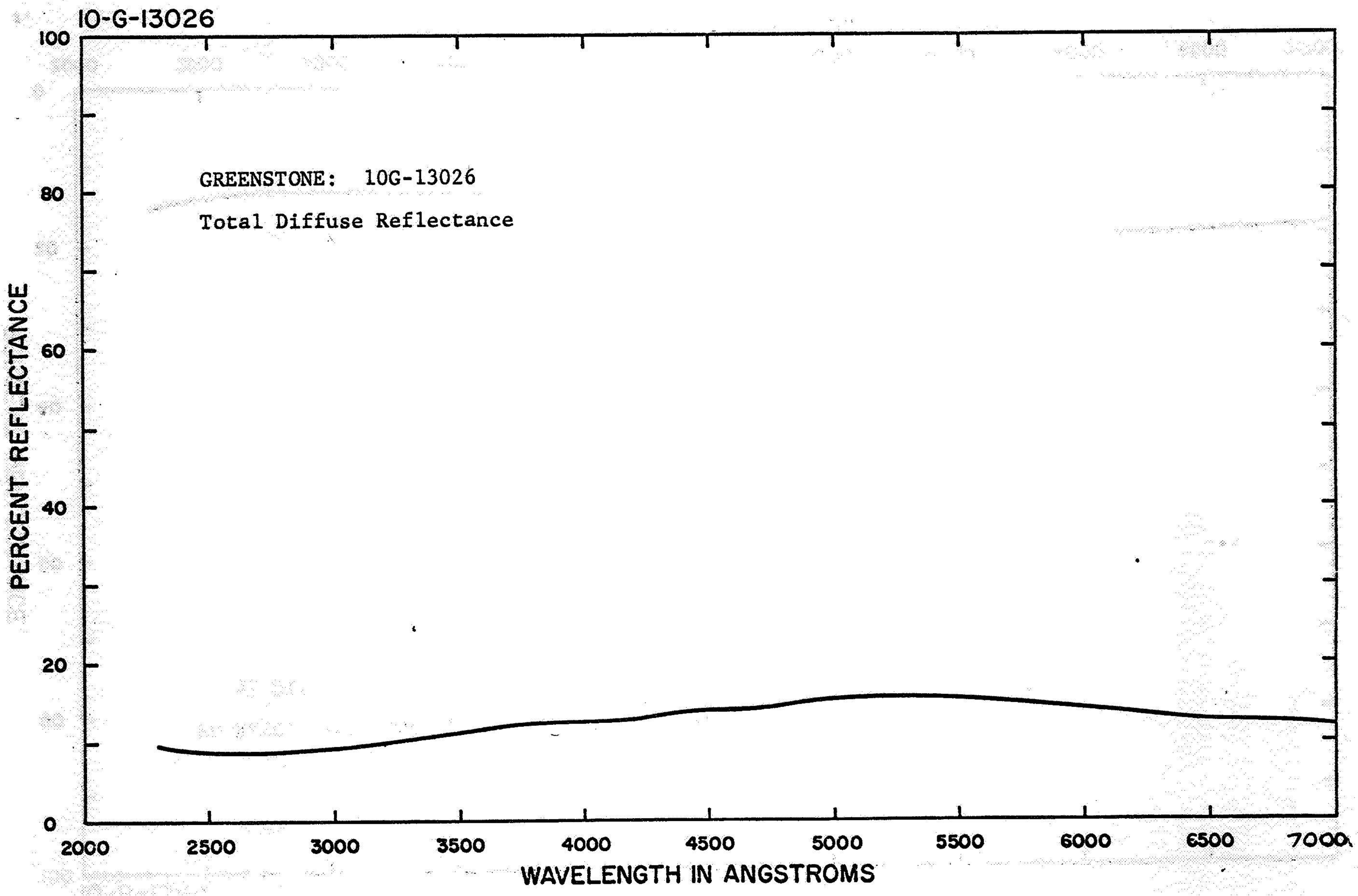
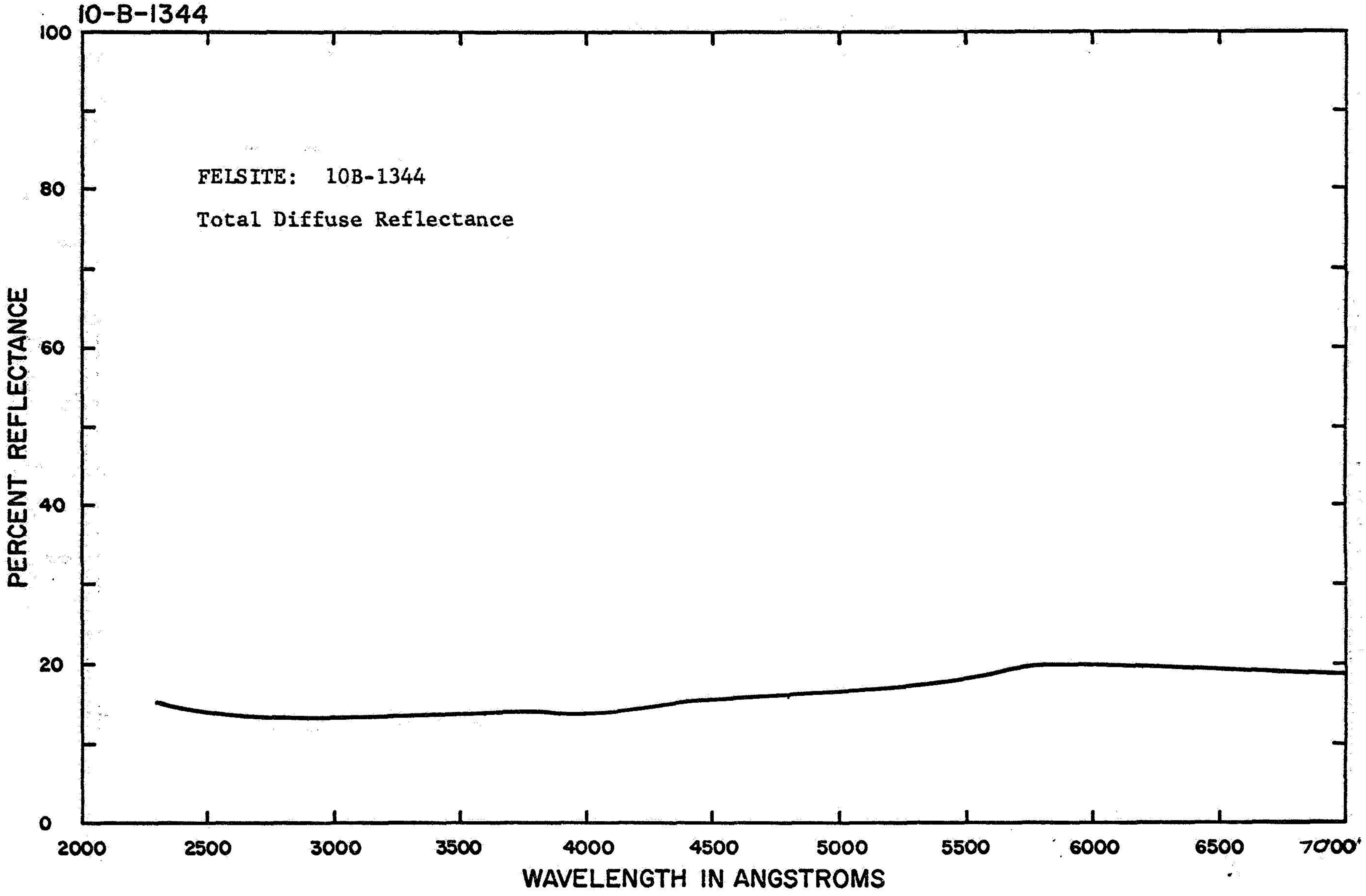
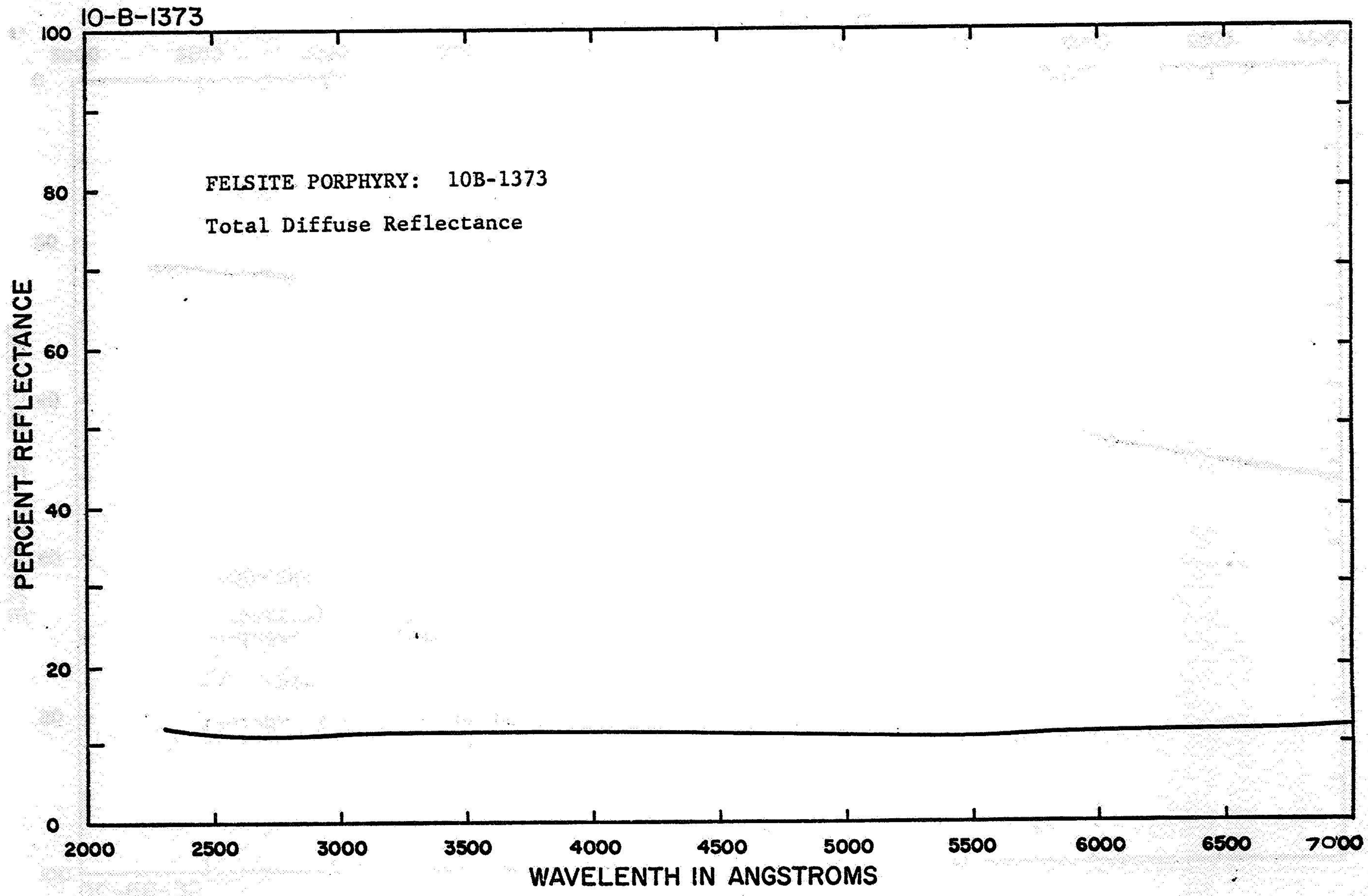
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

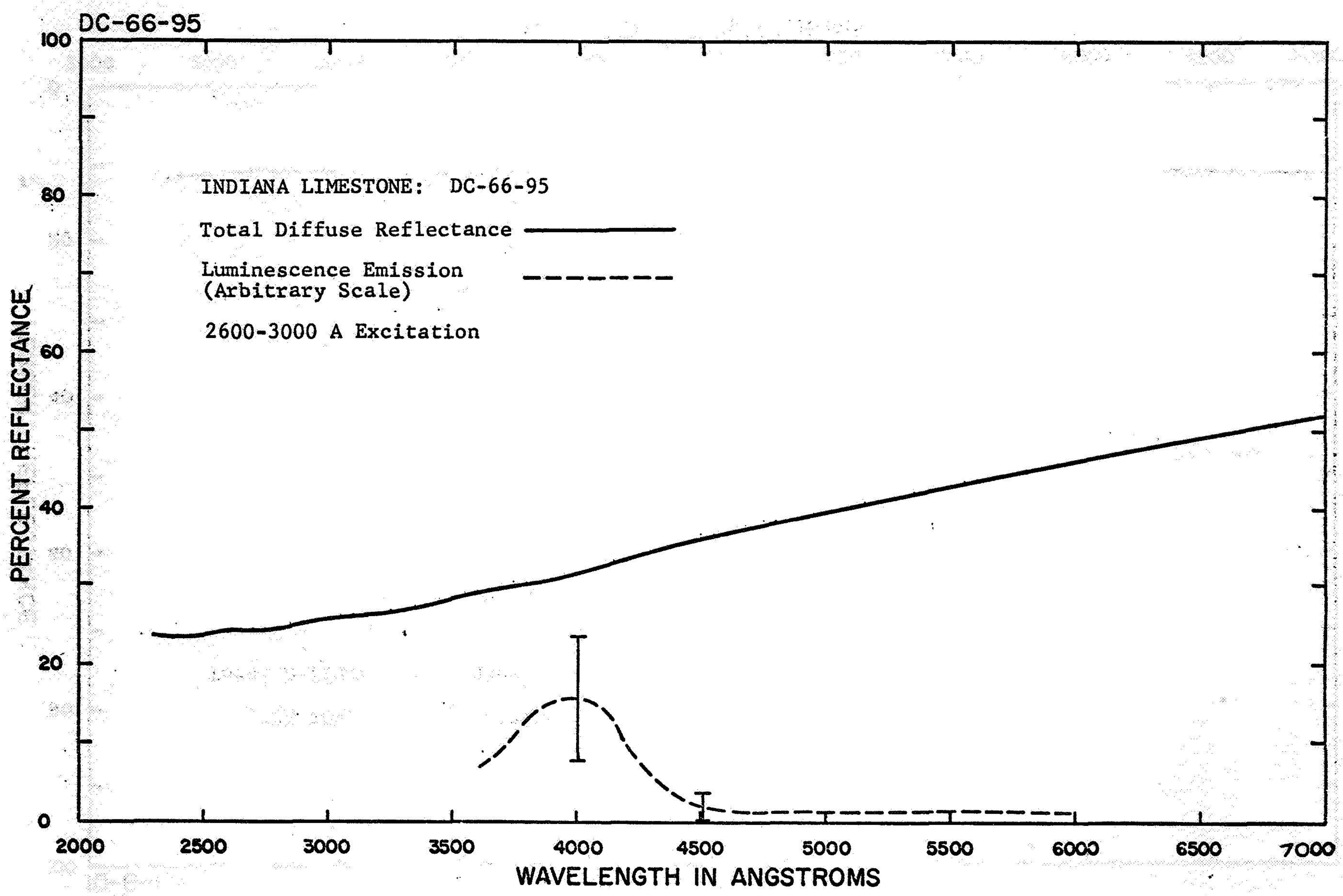

10-G-13026
GREENSTONE: 10G-13026
Total Diffuse Reflectance
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

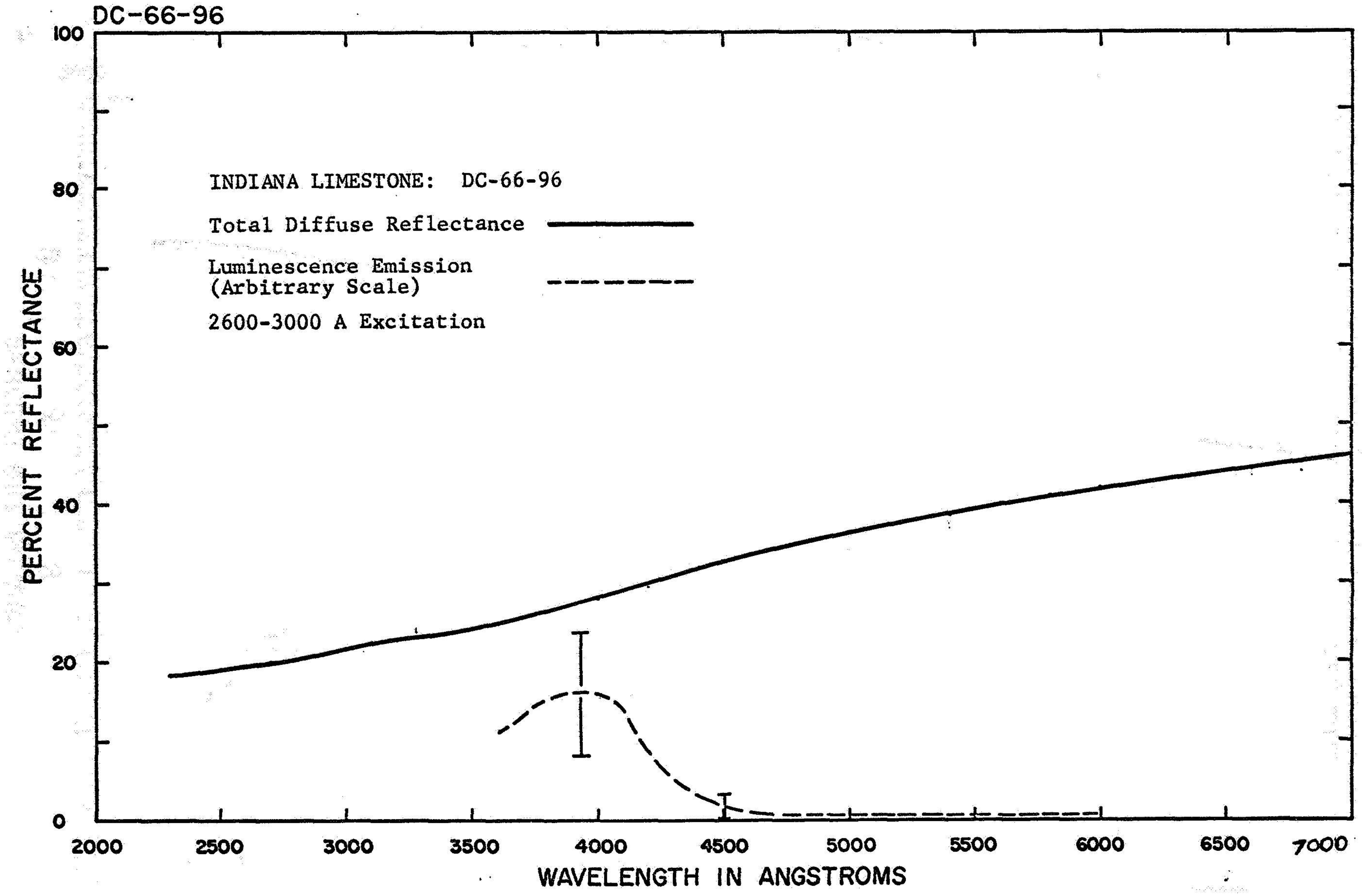

10-B-1344
FELSITE: 10B-1344
Total Diffuse Reflectance
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

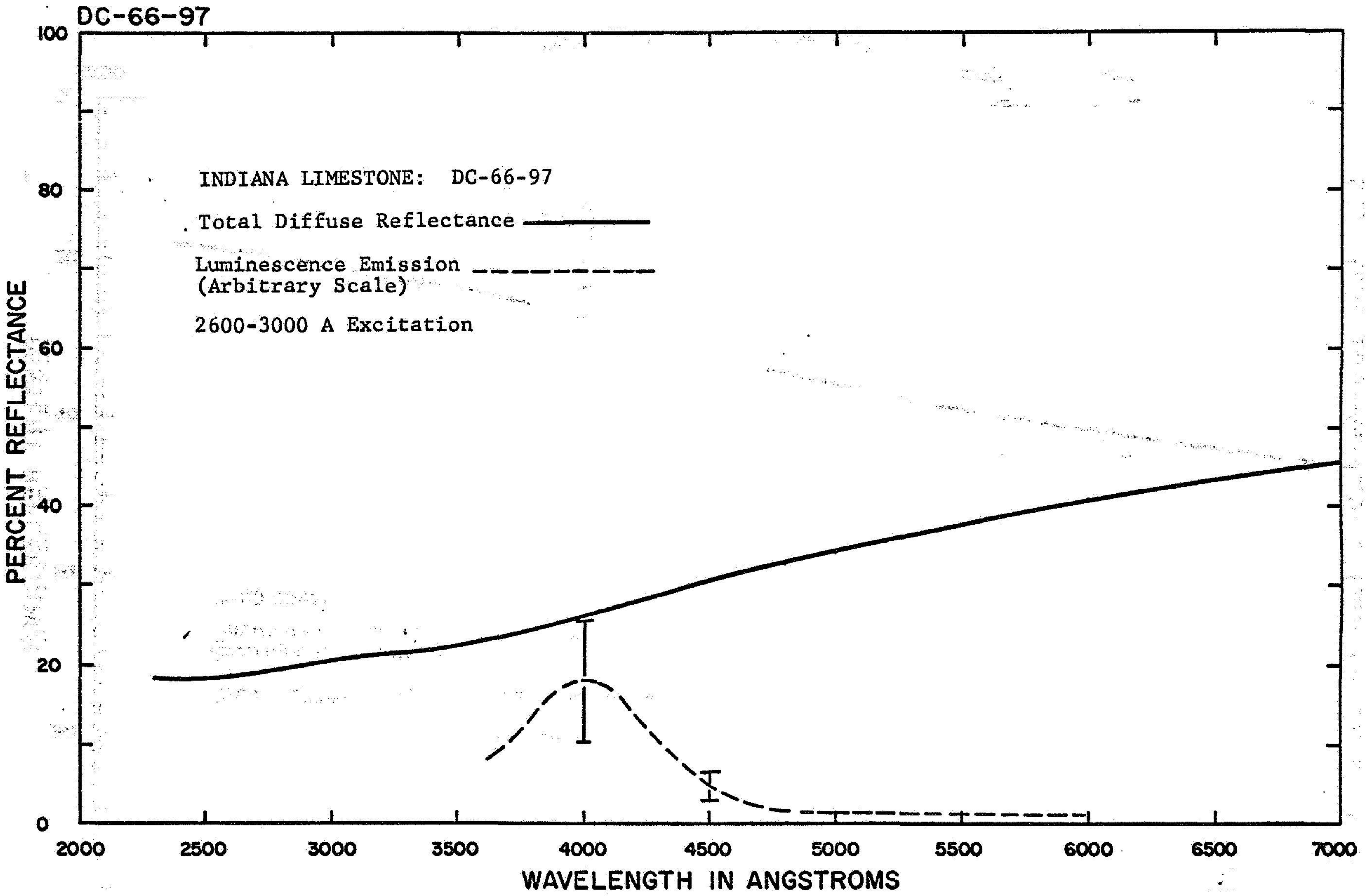


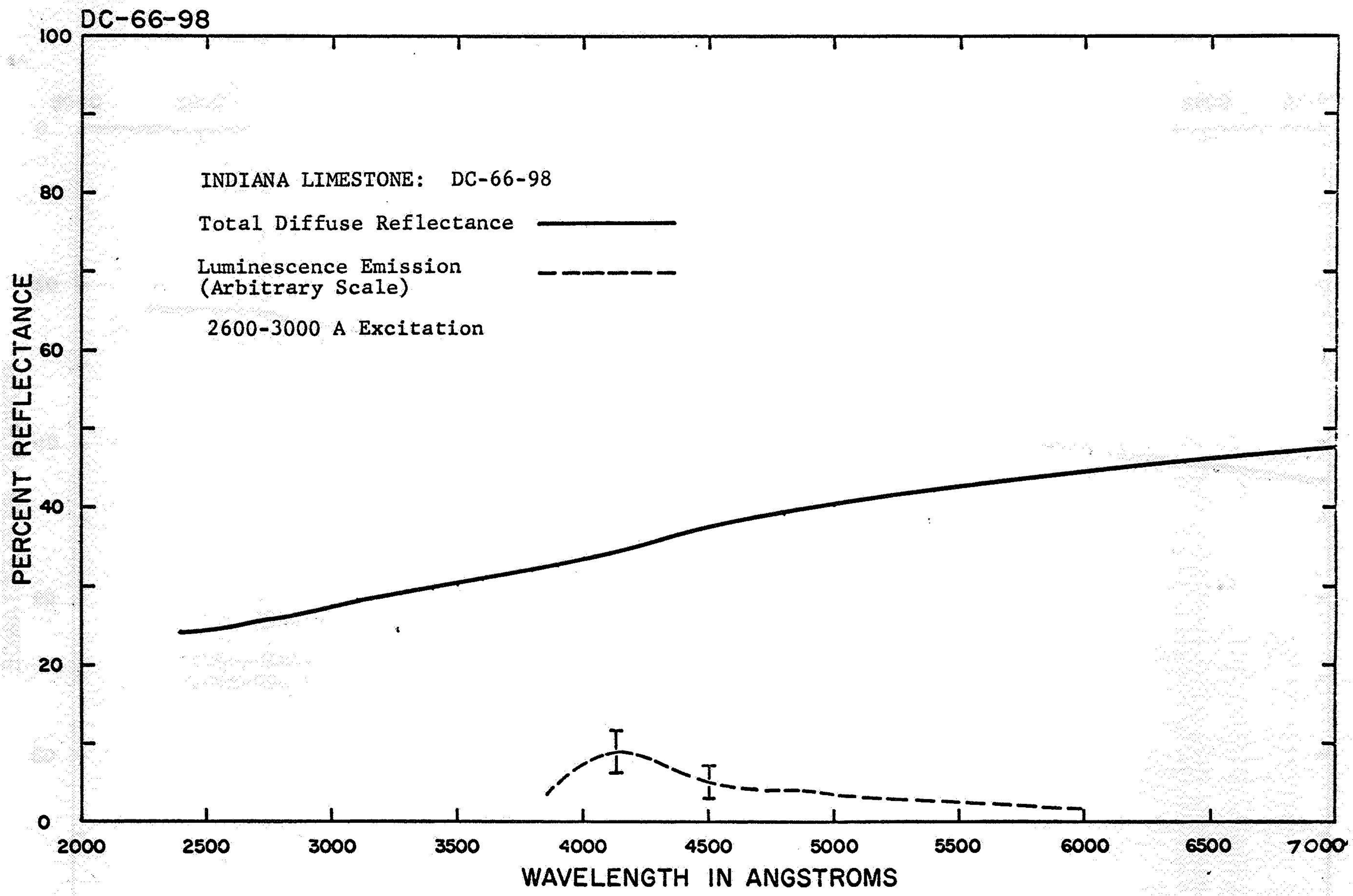
FELSITE PORPHYRY: 10B-1373

Total Diffuse Reflectance

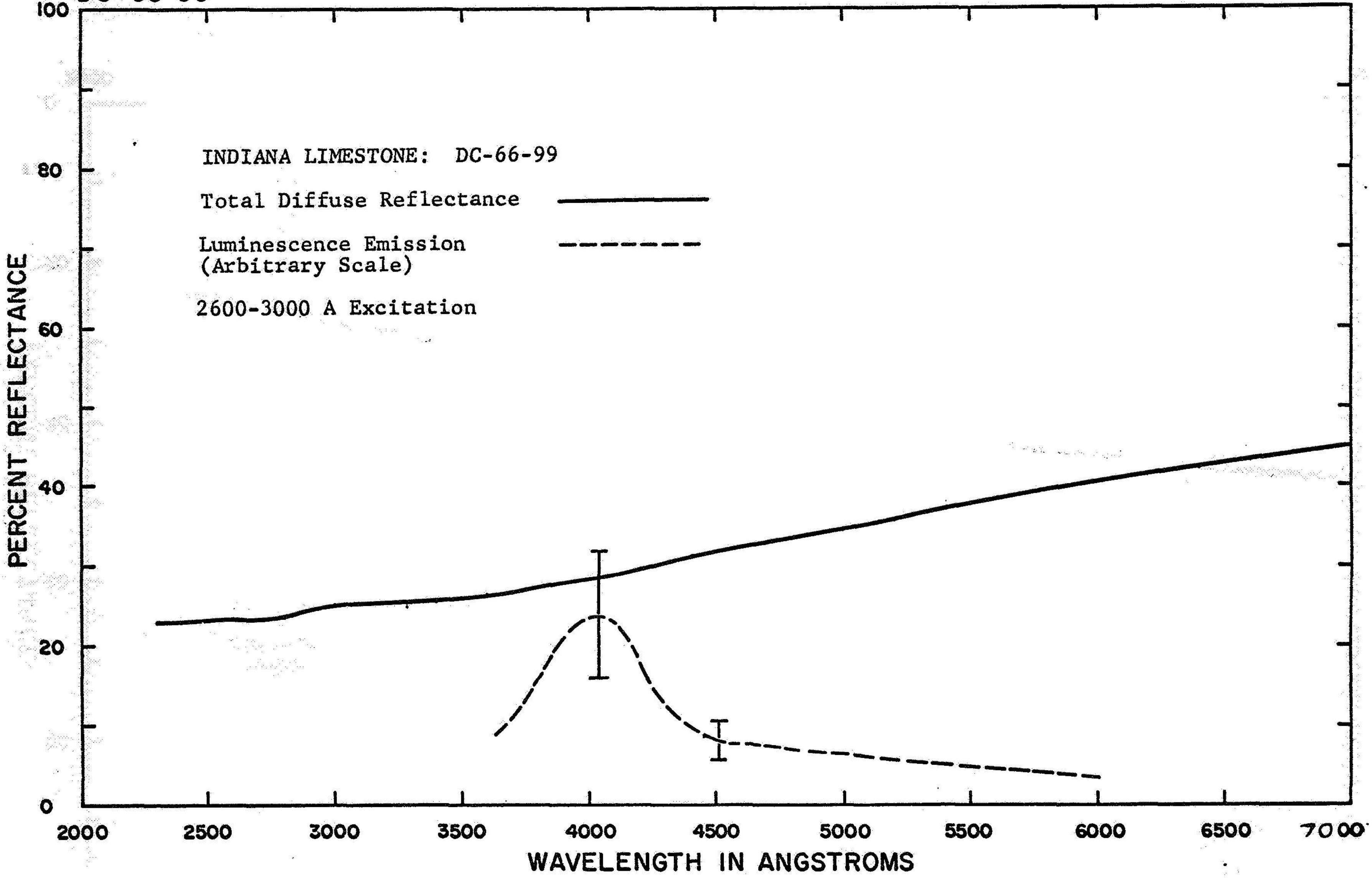

DC-66-95
INDIANA LIMESTONE: DC-66-95
Total Diffuse Reflectance
Luminescence Emission
(Arbitrary Scale)
2600-3000 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

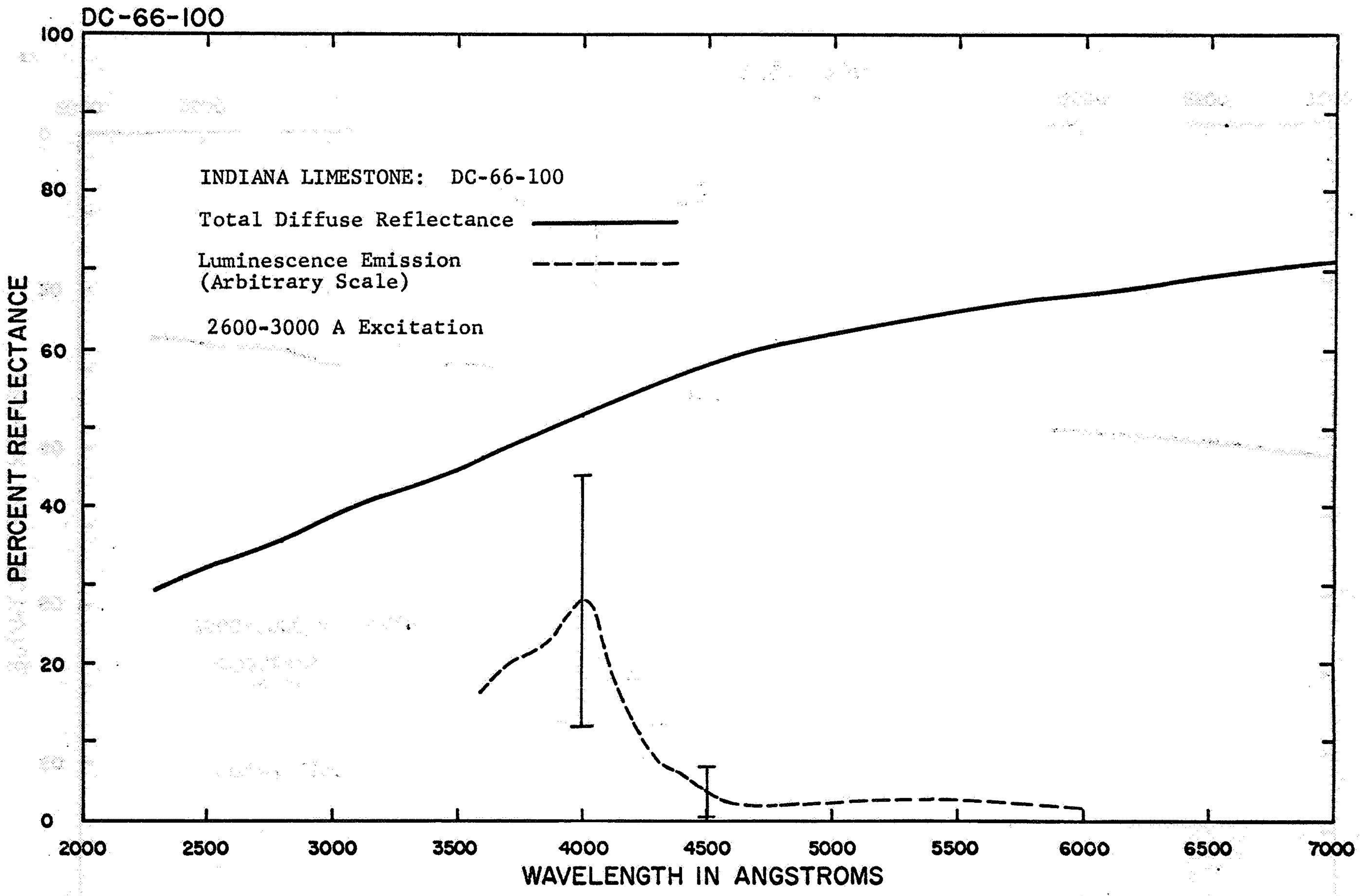

DC-66-96
INDIANA LIMESTONE: DC-66-96
Total Diffuse Reflectance
Luminescence Emission (Arbitrary Scale)
2600-3000 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

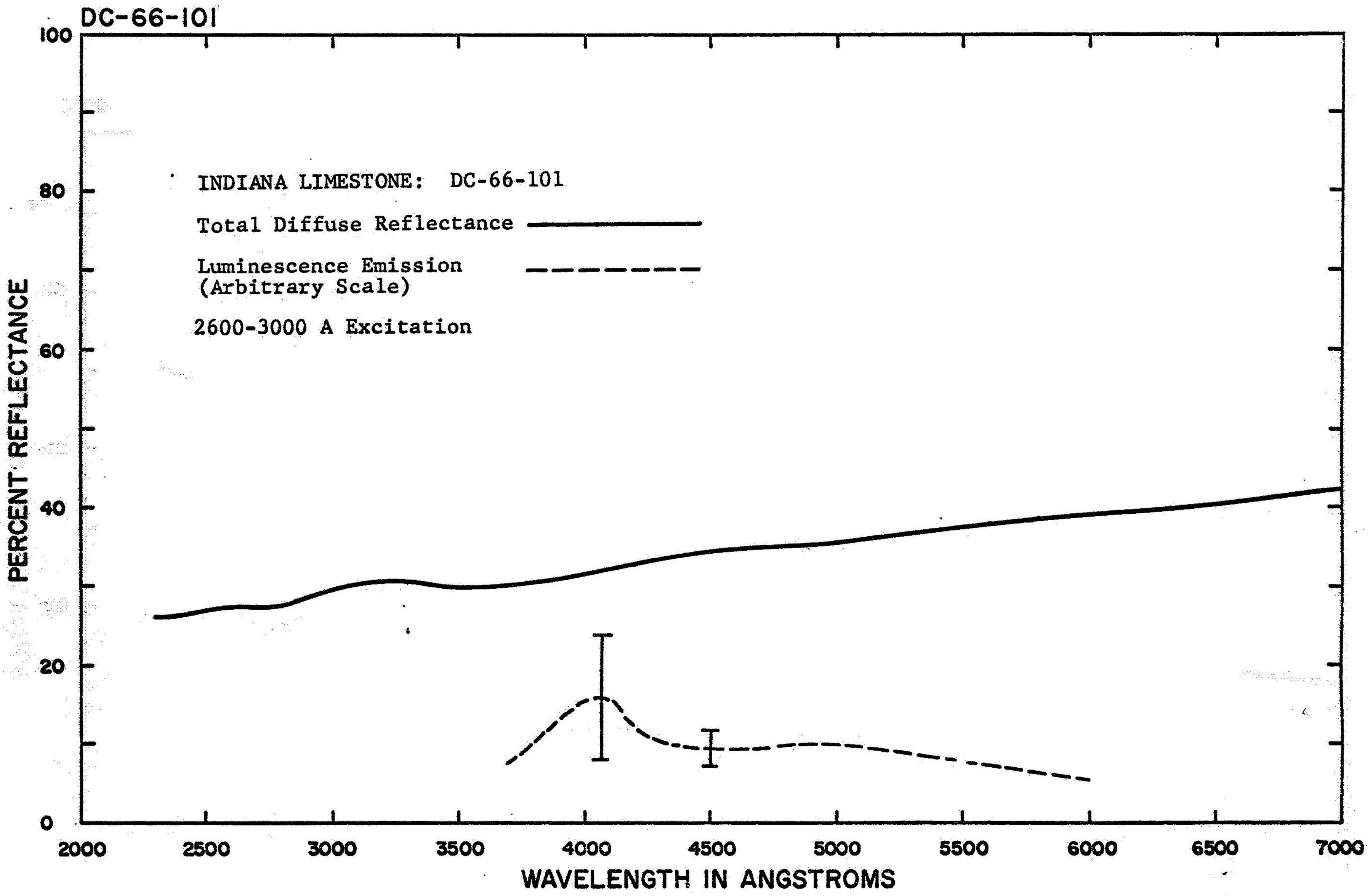

DC-66-97
INDIANA LIMESTONE: DC-66-97
Total Diffuse Reflectance
Luminescence Emission
(Arbitrary Scale)
2600-3000 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

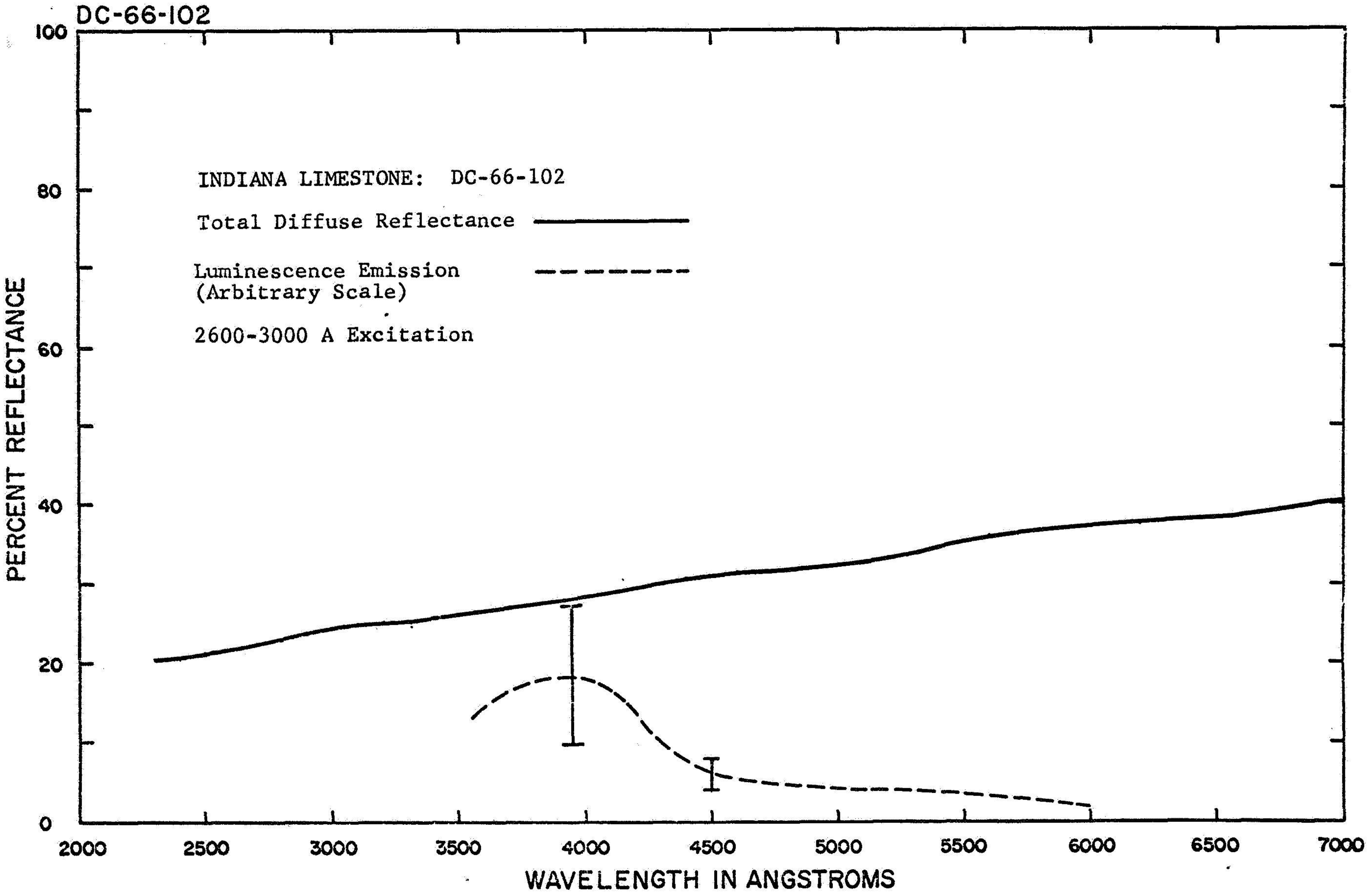

DC-66-98
INDIANA LIMESTONE: DC-66-98
Total Diffuse Reflectance
Luminescence Emission (Arbitrary Scale)
2600-3000 A Excitation
PERCENT REFLECTANCE
0
20
40
60
80
100
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS

DC-66-99


INDIANA LIMESTONE: DC-66-99
Total Diffuse Reflectance
Luminescence Emission (Arbitrary Scale)
2600-3000 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS


DC-66-100
INDIANA LIMESTONE: DC-66-100
Total Diffuse Reflectance
Luminescence Emission
(Arbitrary Scale)
2600-3000 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS


DC-66-101
INDIANA LIMESTONE: DC-66-101
Total Diffuse Reflectance
Luminescence Emission (Arbitrary Scale)
2600-3000 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS


DC-66-102
INDIANA LIMESTONE: DC-66-102
Total Diffuse Reflectance
Luminescence Emission
(Arbitrary Scale)
2600-3000 A Excitation
PERCENT REFLECTANCE
100
80
60
40
20
0
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH IN ANGSTROMS