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These studies were supported by Contract AT(04-1) GEN-12 between the Atomic Energy Commission and the University of California.

**Prepared for U. S. Atomic Energy Commission
under Contract AT(04-1) GEN-12**

**NATURAL THERMOLUMINESCENCE OF SOILS,
MINERALS, AND CERTAIN ROCKS**

H. Nishita, M. Hamilton and R. M. Haug

MASTER

Short Title:

NATURAL THERMOLUMINESCENCE

Complete Title:

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Table 1

Chemical characteristics of soils.

Soil Series	pH 1:1 H ₂ O Suspension	Lime as CaCO ₃ %	Organic Matter %	Cation Exchange Capacity me/100g	Extractable Cations*				E.C. Saturation Extract mmhos/cm	Clay**	Free Iron Oxides %	Remarks***
					Na me/100g	K me/100g	Mg me/100g	Ca me/100g				
Hanford	5.60	-	1.99	7.60	0.21	0.72	1.40	5.23	4.40	I	0.67	NS
Yolo	7.88	0.09	1.73	18.18	0.22	0.57	7.24	11.20	1.06	MK	1.68	NS
Egbert	3.92	0.25	32.89	45.30	1.62	1.06	7.89	23.66	4.40	-	-	SO
Aiken	6.13	-	3.60	25.00	0.12	0.99	1.37	10.17	0.50	K	5.40	NS
No. 4FF	8.62	33.00	0.45	9.98	0.48	2.32	6.58	83.56	0.66	M	0.35	NSC
No. 1SG	7.85	9.00	1.88	9.84	5.18	1.63	7.38	63.50	22.00	MK	0.60	SC
No. 16L	6.45	0.15	3.51	10.80	0.03	0.22	1.90	8.64	0.56	I	1.81	NS
Carlsbad	6.40	0.06	0.34	3.70	0.08	0.20	0.53	1.84	0.87	IM	1.47	NS
Redding	5.73	-	1.45	7.50	0.19	0.32	1.72	3.46	1.29	MK	1.97	NS
Alamo	6.20	0.17	1.33	31.19	0.15	1.16	9.00	17.78	0.46	IM	0.79	NS
Columbia	6.84	0.07	0.50	21.44	0.10	0.48	7.62	10.40	0.51	MI	1.77	NS
Hesperia	7.65	0.40	0.70	7.70	0.27	0.58	1.90	12.60	2.76	IM	0.58	NS
Fresno	5.85	0.06	0.27	1.46	0.04	0.14	0.26	1.06	1.00	IM	0.22	NS
Madera	6.85	-	1.29	23.61	0.13	0.65	6.88	15.23	0.68	IM	1.44	NS
Foster	6.20	0.16	0.98	11.47	2.06	0.72	2.96	14.07	19.70	IM	0.55	SC

* Extractable with neutral normal NH₄OAc.

** Main clay mineral: I = illite, M = montmorillonite, K = kaolinite, MK = montmorillonite and kaolinite, IM or MI = montmorillonite and illite (first clay in greater amount).

*** NS = nonsaline, SO = saline organic, NSC = nonsaline calcareous, SC = saline calcareous.

Table 2

The TL threshold temperature and the maximum relative glow intensity (highest peak) and their position on the soil glow curves.

Soil*	Threshold Temperature °C	Position of Maximum RGI** °C	Maximum RGI
Redding	215	328	1.9
Egbert	215	350	1.4
Alamo	218	370	2.3
Hanford	205	367	3.0
Columbia	221	402	3.2
Hesperia	205	392	5.0
Fresno	202	380	6.8
Madera	199	312	5.0
Foster	186	360	10.5
Yolo	179	344	13.0
Carlsbad	140	312	20.0
No. 16L	176	285	25.2
No. 1SG	186	312	59.9
No. 4FF	176	372	92.1
Aiken	-	-	-

* Aiken showed no TL.

** Highest peak of the glow curves. GRI = Relative glow intensity.

Table 3

TL
The/threshold temperature and the maximum relative glow intensity and its position on the mineral glow curves.

Curve No.	I °C	III °C	III RGI	Curve No.	I °C	II °C	III RGI	Curve No.	I °C	II °C	III °C
A1	166	278	52.4**	E5	118	320	19.2	I3	128	300	50.8**
A2	166	289	24.9**	E6	176	404	42.6**	I4	134	254	46.9**
A3	166	323	16.0	E7	95	310	7.0	I5	115	265	95.0*
A4	170	341	20.0	E8	250	409	12.7	J1	202	328	43.2
A5	173	392	22.0	E9	250	338	3.2	J2	178	273	27.2
B1	263	344	1.8	E10	206	344	8.6	J3	244	367	0.9
B2	241	344	2.3	F1	115	363	91.0	J4	170	368	35.5
B3	239	334	1.0	F2	195	292	41.6*	J5	296	376	1.4
B4	205	334	7.0	F3	63	268	56.0**	J6	202	425	18.2
B5	195	354	15.1	F4	200	336	48.9	J7	215	409	2.8
C1	186	289	82.7***	F5	NT			J8	NT		
C2	183	273	77.0	G1	292	386	8.7	J9	NT		
C3	189	277	37.9	G2	118	434	15.4	K1	202	279	17.4
C4	159	292	21.5	G3	265	409	1.1	K2	300	383	1.0
C5	150	276	62.0	G4	257	383	4.0	K3	215	279	3.7
C6	82	270	69.0	G5	296	376	0.9	K4	NT		
C7	202	305	3.0	G6	166	378	37.9	L1	118	315	79.2*
D1	115	328	52.3*	G7	273	405	6.9	L2	199	394	56.0*
D2	166	347	22.3*	H1	226	386	13.1	L3	176	283	73.5**
D3	166	331	32.2**	H2	160	454	24.9**	L4	183	376	94.0**
D4	150	360	49.0**	H3	270	412	2.2	L5	219	381	89.9****
E1	260	409	2.7	H4	134	360	36.9	L6	263	418	4.3
E2	312	409	2.6	H5	118	283	31.1**	L7	183	499	53.0****
E3	218	376	3.7	I1	134	319	70.3**				
E4	263	376	3.6	I2	124	298	91.1				

I = TL threshold temperature. II = position of maximum RGI. III = maximum RGI with instrument setting of 950 + 3.0. RGI = relative glow intensity. The asterisks represent instrument setting as follows: * = 850 + 3.0, ** = 800 + 3.0, *** = 750 + 3.0, and **** = 550 + 3.0. NT = no TL.

Footnotes:

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University of California, Los Angeles, California 90024. These
studies were supported by Contract AT(04-1) GEN-12 between the Atomic
Energy Commission and the University of California.

Figure Legends:

FIG. 1. Natural TL glow curves of soils.

FIG. 2. Natural TL glow curves for montmorillonite, hectorite, metabentonite, and illite samples.

FIG. 3. Natural TL glow curves for samples of attapulgite, pyrophyllite, and the members of the kaolinite and mica groups.

FIG. 4. Natural TL glow curves for samples of the feldspar group members and the oxides and hydroxides minerals of Al and Si.

FIG. 5. Natural TL glow curves for samples of the oxide, hydroxide, carbonate, sulfate, and phosphate minerals.

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NATURAL THERMOLUMINESCENCE OF SOILS, MINERALS, AND CERTAIN ROCKS

H. Nishita, M. Hamilton and R. M. Haug

Geologic materials show various amounts of natural thermoluminescence (TL). Kohler and Leitmeier (1934) have shown the natural TL of a number of minerals and rocks. More recent works have shown the natural TL of alumina (Rieke and Daniels 1957), quartz (Medlin 1963), calcite (Medlin 1954, 1967; Johnson 1965; Vaz and Zeller 1966), clay minerals (Ferraresso 1967; Siegel, Vaz and Ronca 1968), and soils (Nishita and Hamilton, 1968, 1970). Natural TL results from trapping of charge carriers at crystal lattice imperfections in the geologic materials. The crystal lattice imperfections were formed during the crystallization process and by the continuous low-level irradiation by the penetrating cosmic radiation from space and the radioactive impurity elements (particularly K40 and the uranium and thorium decay series) present.

The objectives of this investigation were to determine the different glow curve shapes that the natural TL of soils may take and the natural TL of minerals and rock materials that may be the source of natural TL of soils. Also, the minerals were examined to determine whether or not certain minerals can be identified or grouped on the basis of their natural TL.

MATERIALS AND METHODS

Fifteen soils representing widely different chemical types were used (Table 1). They include saline-organic, saline-calcareous, non-saline-calcareous, and nonsaline-noncalcareous soils with different predominant clay minerals. The pH measurements were performed on 1:1 H₂O suspension with a glass electrode assembly. Lime and organic matter were determined by the wet combustion procedure of Allison (1960). The cation exchange capacity of the soils was determined by the method of

Peech et al. (1947). The soils were NH_4^+ -saturated by leaching with neutral normal ammonium acetate (NH_4OAc) and the adsorbed NH_4^+ was then extracted with acidified NaCl solution and assayed by the Kjeldahl method. The saturation extracts were obtained by the method of Richards et al. (1954) and their electrical conductivities were determined with a Leeds and Northrup conductivity bridge. The free iron oxides were determined by Coffin's method (1963). All chemical analyses were performed on soil materials passed through 2-mm sieve. The TL measurements were done on soils passed through 1-mm sieve.

Seventy-three mineral and rock samples, which are listed in figures 2 through 5, were examined for their natural TL. These minerals were selected to include all important minerals that may be found in soils. They include the members of the montmorillonite, kaolinite, mica, and feldspar groups and the oxide, hydroxide, carbonate, sulfate, and phosphate minerals of Mg, Ca, Al, Si, Ti, and Fe. The minerals were obtained from Ward's Natural Science Establishment, Inc. The clay minerals that appear with number designations correspond to those of the American Petroleum Institute Clay Minerals Standards Project No. 49. All mineral and rock samples were passed through a 177-micron sieve before use. The samples were pulverized to pass through the sieve when necessary.

The apparatus and the technique of measuring TL were as described previously (Nishita and Hamilton 1970) with the sample heating rate of $500^\circ\text{C}/\text{min}$. All readouts were performed on 30 mg of air-dry samples in argon atmosphere.

RESULTS AND DISCUSSIONS

Figure 1 shows the glow curves of the natural TL of soils. It is evident that the glow curve shapes vary considerably among the soils. Some have two distinct peaks, whereas some give only a suggestion of two peaks. Others show only one broad peak with their maximum relative glow intensity (RGI) in either the lower ($\leq 325^{\circ}\text{C}$) or the higher ($> 325^{\circ}\text{C}$) temperature range. The maximum RGI (the major peak in case of the 2-peaked curves) of each glow curve is listed in table 2. Except soil No. 16L, all soils showed the maximum RGI at 312°C or greater. It is also evident in figure 1 that the soils showed only little, if any, TL below 200°C . This appeared to be a general phenomenon also of all other soils that we have examined during the course of our investigations. The threshold temperatures at which the TL began are listed in table 2. Except the Carlsbad soil, all soils showed threshold temperatures greater than 175°C . Comparisons of the areas under the glow curves show that the TL of the highly calcareous soils (No. 4FF and No. 1SG) was markedly greater than that of the other soils. The lime content of soil No. 4FF and No. 1SG was 33 and 9 percent, respectively (Table 1). Soils containing large amounts of carbonate compounds generally show high TL (Nishita and Hamilton 1968, 1970, 1972). The Aiken soil did not show TL. Note in table 1 that this soil contained very high amount (5.40 percent) of free iron oxides compared to the other soils. It has been shown previously (Nishita and Hamilton 1972) that soils high in iron oxides are likely to show only little, if any, TL.

Figures 2 through 5 show the glow curves of the natural TL of 73 mineral and rock materials. To allow intra- and inter-group comparisons, the glow curves of the same mineral species or classification groups are displayed together insofar as it is possible. It is evident that the glow curve peaks of the different minerals overlapped and that the glow curve shapes varied widely. In fact, the shapes varied considerably among the minerals of the same groups. For example, some of the members of the montmorillonite group (Fig. 1) showed at least two peaks whereas the others showed only one broad peak. Furthermore, the positions of the maximum RGI of each member of the same mineral group varied. These results are interpreted to indicate that the amounts and the kinds of crystal lattice defects are more important in determining mineral TL than the crystal lattice structure.

Table 3 lists the TL threshold temperature and the position and the magnitude of the maximum RGI. The TL threshold temperature (col. I) ranged from 82° to 312°C . Most (78.3 percent) of the minerals showed thresholds above 150°C . All maximum RGI (col. II) occurred in the temperature range of $254 - 499^{\circ}\text{C}$. Most of the maximum RGI (col. III) listed are for the glow curves read out with instrument setting of $950 + 3.0$, which was the most sensitive setting. However, twenty-two samples were read out at lower sensitivities, because their light outputs were above the recording capacity of the instrument. These samples included the following minerals: montmorillonite (curves A1 and A2), hectorite No. 34 (curve C1), attapulgite (curves D1, D2, D3), pyrophyllite (curve D4), dickite (curve E6), phlogopite (curve F2), lepidolite (curve F3), anorthoclase (curve H2), microcline (curve H5), albite (curve I1), oligoclase

(curve I3), perthite (curves I4 and I5), dolomite (curves L1 and L2), calcite (curve L3), limestone (curves L4 and L5), and apatite (curve L7). To make the readings of these samples comparable to those read at 950 ± 3.0 , they must be increased by the following multiplying factors: 850 ± 3.0 , 1.9; 800 ± 3.0 , 14.4; 750 ± 3.0 , 19.3; and 550 ± 3.0 , 224.5.

The limestone sample (curve L5) showed the greatest TL. Biotite (curve F5), limonite (curves J8 and J9), and chlorite (curve K4) showed no TL. Our previous work with soils indicated that those with high carbonate contents generally show high TL and those with high Fe contents show low or no TL (Nishita and Hamilton 1968, 1972). The relatively high TL shown by dolomite, calcite, and limestone in the present study confirm the fact that materials of high carbonate contents tend to show high TL. The relatively low or no TL shown by goethite, magnetite, and limonite tend to confirm that materials high in Fe content show low or no TL.

GENERAL DISCUSSION

The survey of minerals indicates that if present in soils, all but a few may contribute to the natural TL of soils. In this respect, the concentrations of the minerals in the soil are important, since minerals differ widely in TL capacity. Obviously, low concentration of a highly thermoluminescent mineral could make an appreciable contribution to soil TL, whereas the contribution of the relatively high concentration of a lowly thermoluminescent one may be practically nil. As pointed out above, iron oxide minerals tend to show low TL. The carbonate minerals usually show high TL. It is possible that a

number of the minerals that showed relatively high TL contained an appreciable amount of carbonate impurities.

There appear to be no criteria by which minerals can be identified or grouped on the basis of their natural TL. Minerals even of the same group or classification showed wide variation of TL capacity and glow curve shapes and overlapping peaks. Siegel, Vaz, and Ronca (1968), who worked with natural and radiation-induced clay minerals, came to the same conclusion. However, the glow curves of natural TL could be used to differentiate different lots of unknown minerals, since each lot would have its own characteristic glow curve. Difficulty may possibly be encountered when the glow curve shapes and heights are nearly the same. In such event, chemical treatments of the samples such as those described previously (Nishita and Hamilton 1972) may help to differentiate them.

SUMMARY

The thermoluminescent characteristics of fifteen soil and seventy-three mineral and rock samples were examined. The soils of widely different chemical types showed wide range of thermoluminescent characteristics. Generally, soils high in lime content showed very high TL. One soil, which was relatively high in free iron content exhibited no TL. The natural TL of soils appeared to be affected by the kinds and the amounts of mineral and rock materials present. Since the TL of the different samples even of the same mineral species varied widely, there appeared to be no criterion by which minerals can be identified or classified on the basis of their natural TL. Different lots of samples, however, might be differentiated from each other. Most soils and minerals showed only little, if any, TL below 200°C.

FIG. 1. Natural TL glow curves of soils.

FIG. 2. Natural TL glow curves for montmorillonite, hectorite, metabentonite, and illite samples.

FIG. 3. Natural TL glow curves for samples of attapulgite, pyrophyllite, and the members of the kaolinite and mica groups.

FIG. 4. Natural TL glow curves for samples of the feldspar group

members and the oxides and hydroxides minerals of Al and Si.

FIG. 5. Natural TL glow curves for samples of the oxide, hydroxide, carbonate, sulfate, and phosphate minerals.