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SOIL THERMOLUMINESCENCE

**EFFECTS OF SOME CHEMICAL TREATMENTS OF SOILS
ON THEIR THERMOLUMINESCENCE**

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Table 1

Effect of pre-irradiation annealing at various
temperatures on the post-irradiation TL of
four soils

Soil	Glow Curve Area* (cm ²)				
	23°C.	100°C.	120°C.	140°C.	160°C.
Soil No. 4FF	236.9(8.9)	230.7(4.5)	235.6(11.7)	225.1(6.0)	215.5(11.6)**
Hanford s.l.	35.1(1.9)	34.3(1.6)	34.6(2.1)	32.6(1.9)	29.5(1.5)**
Soil No. 9RDG	19.8(1.8)	17.9(1.2)	17.7(1.8)	16.7(0.7)**	--
Yolo s.l.	65.9(2.8)	64.4(2.5)	63.8(3.9)	59.4(1.2)**	--

*Glow curve area (average of 4 readings (standard deviation)) was taken to represent soil TL. Readout time = 1 week. Instrument sensitivity setting = 900 + 3.0 for soil No. 4FF and 950 + 3.0 for the other 3 soils. Flush gas = Ar. The soils were irradiated to 1,000 R by Co60 photons.

**These values were significantly lower than those for 23°C. at the 95 per cent level (Dunnett's method) (5)).

Table 2

The TL ratios of soils that were chemically treated before
irradiation to 1,000 R with Co60 photons*

Soil	Treatment Ratios									
	<u>Untr.</u>	<u>I</u>	<u>II</u>	<u>II</u>	<u>III</u>	<u>III</u>	<u>IV</u>	<u>IV</u>	<u>V</u>	<u>V</u>
	Untr.	Untr.	Untr.	I	Untr.	II	Untr.	III	Untr.	IV
Soil No. 9RDG	1.00	1.37	1.87	1.37	2.33	1.25	7.55	3.24	6.34	0.84
Hanford s.l.	1.00	1.47	1.65	1.12	1.96	1.19	3.51	1.79	3.38	0.96
Yolo s.l.	1.00	1.17	1.34	1.15	1.33	0.99	2.13	1.60	1.96	0.92
Soil No. 4FF	1.00	1.16	1.10	0.95	0.76	0.69	0.93	1.23	0.59	0.63

*The TL was determined by measuring the total area under the glow curves below 450°C. All readout was done one week after irradiation. Untr. = untreated.

Table 3
Percentage loss of soil sample weight after each
chemical treatment*

Soil	Initial oven dry weight g.	Treatment					
		I %	II %	III %	IV %	V %	Total %
Soil No. 9RDG	9.898	0.29	0.69	1.44	2.82	0.52	5.76
Hanford s.l.	9.933	0.36	0.55	2.14	1.34	0.05	4.45
Yolo s.l.	9.725	0.12	1.52	2.20	1.55	0.45	5.85
Soil No. 4FF	9.844	0.14	22.43	5.39	2.06	1.00	31.02

*Percentage loss from the initial weight.

Table 4
Soil color in relation to chemical treatment
(Munsell Color)

Treatment	Soil			
	Hanford	No. 4FF	No. 9RDG	Yolo
Untreated	10 YR 5/3 brown	10 YR 7/3 very pale brown	5 YR 4/6 yellowish red	10 YR 5/3 brown
I	10 YR 5/3 brown	10 YR 7/4 very pale brown	5 YR 4/8 yellowish red	10 YR 5/3 brown
II	10 YR 6/3 pale brown	10 YR 7/4 very pale brown	5 YR 4/8 yellowish red	10 YR 6/3 pale brown
III	10 YR 6/4 light yellowish brown	10 YR 7/3 very pale brown	2.5 YR 5/8 red	10 YR 6/4 light yellowish brown
IV	5 Y 7/1 light gray	2.5 Y 7/0 light gray	10 YR 7/1 light gray	5 Y 7/1 light gray
V	5 Y 7/1 light gray	2.5 Y light gray	10 YR 7/1 light gray	5 Y 7/1 light gray

Footnotes:

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FIGURE LEGENDS:

- FIG. 1.** Thermoluminescence of Hanford sandy loam and soil No. 4FF in relation to various chemical treatments.
- FIG. 2.** Thermoluminescence of irradiated and unirradiated soil No. 4FF with and without leaching with 0.1 N HCl.
- FIG. 3.** Thermoluminescence of soil No. 9RDG in relation to various chemical treatments.
- FIG. 4.** Thermoluminescence of soil No. 9RDG after the removal of iron oxides before and after irradiation.

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Effects of Some Chemical Treatments of Soils on
Their Thermoluminescence

H. Nishita and M. Hamilton

Our previous reports have discussed several treatment factors that influence the thermoluminescence (TL) of soils. It has been reported that with one group of soils studied, the shallow electron (hole) traps were increased, while the deep traps were decreased by increasing annealing temperature before their exposure to Co60 photons (13). With another group of soils, the pre-irradiation annealing caused an increase of the traps of intermediate depths, while the shallower and the deeper traps decreased. In the former group of soils, the TL capacity was reduced at temperatures much higher than 100° C, whereas in the latter group, it was increased by heating. Pre-readout, post-irradiation heating at 100° C for 10 min caused only reversible electron (hole) transitions within the thermoluminescent particles. In other words, no apparent irreversible change involving the crystal lattice itself occurred under this heating regimen.

Another influencing factor is the temperature of the soil during its exposure to ionizing radiation (15). As might be expected, the higher the temperature of the soil during irradiation, the lower its TL. This factor could be eliminated by using an appropriate pre-readout, post-irradiation heating regimen or by allowing the thermoluminescent decay to progress for an appropriate length of time. The thermoluminescent decay rate is very high during the first 24 hours after the irradiation of soil, but becomes relatively very low after

a sufficient length of time, which depends on the soil. A factor that may have a direct bearing on the present study is spurious TL. This occurs when soil samples are read out in air (14). Spurious TL appeared to be related to the presence of oxygen and was considered to be the result of the surface state of the thermoluminescent particles.

This paper is concerned with the influence of several chemical treatments of soil on their TL.

MATERIALS AND METHODS

Four soils (Hanford sandy loam, Yolo sandy loam, No. 4FF, and No. 9RDG) were used for this study. Their chemical properties were reported previously (12). Hanford s.l. is a slightly acidic soil with illite as the predominant clay mineral. Yolo s.l. is a predominantly montmorillonitic, slightly basic soil. Soil No. 9RDG is an acidic kaolinitic soil. Soil No. 4FF is a non-saline, highly calcareous soil with montmorillonite as the predominant clay mineral.

The photon irradiations of the soils were done with the UCLA 10,000 curie Co60 source. The apparatus and the technique of measuring TL were as described previously (14). The sample annealing rate was $500^{\circ}\text{C}/\text{min}$, as in all of our previous work. The TL was determined by measuring the total area under the glow curve corrected for black body radiation.

Five chemical treatments were used on the soils in a sequential manner. The procedure was essentially that used in preparation for mineralogical analysis of soils. The step by step details of each

treatment were as prescribed by Jackson (6). Each treatment is designed to remove selectively certain soil components, however, as it will be discussed later, the removal of the various components was not always quantitative. In any case, the main substances that were to be removed under each treatment are given below.

Treatment I was centrifuge washing of the soil samples with 25 per cent ethanol. This treatment was used to remove soluble organic matter and salts. Treatment II was the digestion of the samples in pH 5 NaOAc buffer. This removed most of the carbonates and replaced the exchangeable cations with Na. Treatment III was the digestion of the samples in 30 per cent H_2O_2 followed by washing with 95 and 99 per cent methanol to bring about the decomposition of organic matter and the dissolution of MnO_2 . Treatment IV was the digestion of samples in Na-citrate- NaHCO_3 - $\text{Na}_2\text{S}_2\text{O}_4$ mixture. Iron oxides were removed in this step. Treatment V was boiling the samples in 2 per cent Na_2CO_3 to remove the free alumina and silica and amorphous aluminosilicates. Some organic matter that was not destroyed by H_2O_2 may also be removed. After each step in the sequence of chemical treatments, the samples were dried in vacuum at room temperature. This process formed compacted cakes which were broken down to uniform materials with pestle and mortar. The TL measurements were then done on the resulting materials and compared against that of the untreated soil. Spurious TL (14) that may have developed by grinding the samples is believed to have been avoided, because all TL readings were done in Ar atmosphere.

RESULTS AND DISCUSSION

Effect of pre-irradiation annealing

Table 1 shows the effect of pre-irradiation annealing at various temperatures on the post-irradiation TL of the four soils studied. Pre-irradiation heating of soil No. 4FF and Hanford s.l. to 160° C caused significant loss of TL capacity. The heating of soil No. 9RDG and Yolo s.l. caused a significant loss of TL capacity at 140° C. The effects of temperature on thermoluminescent materials are both reversible and irreversible. The reversible processes are believed to involve only the electron (hole) transitions without appreciable loss of the electron (hole) traps in the lattice structure, whereas the irreversible processes involve irretrievable loss of these traps. The present results indicate that soils may be heated up to 120°-140° C, depending on the soil, before the irreversibility of TL begins to occur. It will be noted, however, that even though only the higher temperatures gave mean values that are significantly different from 23° C (ambient), there was a general downward trend in the TL readings for all of the soils as temperature increased. Thus, it appears that soils should not be heated much above 100° C when the reversibility of TL is desirable. Consequently, in the chemical treatments that required heating, the temperature was monitored and always kept below 110° C in the present study.

Effect of chemical treatments on glow curves

The glow curves obtained after each chemical treatment of Hanford s.l. and the highly calcareous soil No. 4FF are shown in

figure 1. Note that the TL of Hanford s.l. increased progressively with each chemical treatment through treatment IV and then decreased slightly under treatment V. Although the glow curve shapes differed somewhat, the effect of chemical treatments on the TL of the other two noncalcareous soils (soil No. 9RDG and Yolo s.l.) was similar to that of Hanford s.l. Soil No. 4FF differed from the noncalcareous soils only in that its TL was reduced by treatment III instead of being enhanced. The relative TL between the chemically treated soils and between the treated and untreated soils are shown quantitatively in table 2. The treatment ratios give the relative effect between the treatments. Several consistent trends occurred between specific treatments among the soils studied. Treatment I (I/Untr. ratios) and IV (IV/III ratios) consistently increased the TL relative to their previous steps in the sequence of chemical treatments. Treatment V (V/IV ratios) consistently decreased the TL relative to treatment IV. The effect of treatment II (II/I ratios) and III (III/II ratios) varied with the soil.

Effect of the removal of soluble organic matter and salts

The consistent increase of TL after treatment I may be explained, at least in part, by the way the soil samples were handled. The removal of soluble organic matter and salts had the effect of concentrating the residual sample to some extent, since the same sample weight (30 mg.) was taken for TL readout before and after the chemical treatment. Assuming that the substances removed by treatment I had only little or no TL, they served in effect primarily as "diluting agents" in the original sample. As shown by the percentage loss of soil sample weight after

each chemical treatment (table 3), this effect may apply to a varying extent to all treatments used. Another factor involved may be the removal of the thin film of material coating the surface of the thermoluminescent particles, which in turn may improve the light transmittance from the particles. Also, the surface characteristics of the particles may be altered to some extent to change the surface TL. This latter factor will be discussed more in detail below.

Effect of the removal of carbonates

The treatment II/I ratios (table 2) increased for the noncalcareous soils and decreased for the highly calcareous soil No. 4FF. The enhanced TL shown by the 3 noncalcareous soils was probably due, in part, to the removal of additional "diluting agents" in the form of soluble salts. The replacement of the exchangeable cations with Na also could disperse the soil colloids, which in turn may increase the unmasked surface from which light is transmitted. The TL of soil No. 4FF probably decreased because of the large loss of TL capacity due to the removal of carbonates. This is surmised from the evidence that soil carbonates have very high TL compared to other soil components. This is shown in figure 2, which gives the glow curves that were obtained before and after leaching the irradiated and unirradiated soil No. 4FF with 0.1 N HCl. The large differences of the peak heights that occurred between curves A and B and between curves C and D are considered to be due almost entirely to the removal of the soil carbonates. By comparing the glow curves for the irradiated and

unirradiated soils, it can be concluded also that TL due to carbonates occurred almost exclusively in the temperature range above 200° C. The removal of carbonates from soil No. 4FF under treatment II can be inferred from the large weight loss (22.43 per cent, table 3).

Effect of the removal of organic matter, MnO_2 and residual carbonates

The III/II ratios (table 2) increased for two of the noncalcareous soils and decreased slightly for the third. The ratio for soil No. 4FF showed a definite decrease. The relative increase of TL was probably caused, at least in part, by the removal of soil organic matter, which acted as a "diluting agent." Soil organic matter was considered to be only a "diluting agent," since organic matter separated from a muck soil showed no detectable amount of TL (14). The influence that the dissolution of MnO_2 by H_2O_2 might have had is not known. Manganese oxide is believed to be present as discrete particles and as partial coating on soil particles (1). In the latter case, the dissolution of MnO_2 by H_2O_2 may have an effect by changing the surface characteristics of the thermoluminescent particles. The decrease of the III/II ratio for soil No. 4FF probably was due primarily to the decomposition of the residual carbonates, i.e., the carbonates that were not decomposed under treatment II. One evidence for this is the relatively large weight loss (5.39 per cent, table 3) under this treatment. Only a small fraction of this weight loss can be ascribed to the decomposition of organic matter, since the organic matter content of the original untreated soil was

relatively small (0.45 per cent). Further evidence can be seen by comparing the peak heights of curve III (fig. 1 B) with curve B (fig. 2), which was obtained after decomposing the carbonates more completely with 0.1 N HCl. Note that even though the glow curve III (fig. 1 B) was obtained after one-week decay period, its peak heights at temperatures above 200° C were much higher than curve B (fig. 2), which was obtained 30 min. after irradiation. In fact, as evidenced by curve V (fig. 1 B), some carbonates remained even after all of the subsequent treatments of the soil. Apparently the chemical treatments used in the sequential removal of soil components was not drastic enough to decompose some of the more resistant carbonates. Additional carbonates could be decomposed under treatment III, because acidic substances are produced as the organic matter and other substances are oxidized by H_2O_2 . Douglas and Fiessinger (2) have shown that the addition of H_2O_2 to a soil-water suspension could cause it to become quite acidic. Furthermore, additional carbonates could be exposed to dissolution as the soil organic matter that formed a protective coating on the carbonate particles was oxidized.

Effect of the removal of iron oxides

The removal of iron oxides caused marked increase of the IV/III ratios (table 2) of all soils studied. The increase was particularly marked for soil No. 9RDG (IV/III = 3.24). As it may be inferred from its greatest weight loss (2.82 per cent) under treatment IV (table 3), this soil contained the greatest amount of iron oxides among the soils studied. The relatively small increase of the IV/III ratio for soil

No. 4FF may have been caused by the removal of additional amounts of residual carbonates with the removal of iron oxides. In such event, the reduction of the TL capacity resulting from the reduction of the carbonate content could decrease the effective enhancement of TL due to the removal of iron oxides. The contrasting effect of the removal of iron oxides and carbonates is shown more clearly by comparing the IV/Untr. ratios. The IV/Untr. ratios (2.13 to 7.55) for the noncalcareous soils showed great enhancement of TL, whereas that (0.93) for the highly calcareous soil No. 4FF actually showed a net decrease.

Iron oxides are believed to occur as discrete particles and as partial coating and cementing materials for soil particles. They occur in microcrystalline forms as the unhydrated oxides Fe_2O_3 , hematite and maghemite, and also as magnetite Fe_3O_4 (10, 18). Hydrated iron oxides may occur as amorphous limonite and ferric hydroxide or as microcrystals of goethite and lepidocrocite. The free iron oxide particles themselves probably did not have much TL. This was surmised from the fact that reagent grade Fe_2O_3 irradiated to 1,000 R with Co60 photons showed no detectable TL. Two different samples of limonite (collected in Alabama and Georgia) showed no TL. These results may be due to the fact that unlike most other metal oxides, Fe_2O_3 has relatively high electrical conductivity. The magnetic Fe_3O_4 has exceptionally high conductivity (20). In a conductive material, the electrons could wander freely through the crystal lattice with an activation energy equal to zero. In the TL

process, an activation energy is needed to raise the metastably trapped electrons to the conduction band. The enhancement of TL by the removal of iron oxides could be caused by the uncovering of the particles surfaces, the dispersion of the soil particles, the alteration of the particle surface characteristics, and the change of soil color, which affects the reflectance of light. Among the chemical treatments used, the most marked color change (toward lighter color) occurred when iron oxides were removed (table 4).

Effect of the removal of silica and alumina

The treatment V/IV ratios (table 2) were consistently less than one among the soils studied. Thus, treatment V reduced the soil TL relative to treatment IV. The V/IV ratio for soil No. 4FF was appreciably lower than for the noncalcareous soils. This result plus the relatively high weight loss (table 3) suggests that there was further dissolution of the residual carbonates in soil No. 4FF in conjunction with the removal of silica and alumina. Although treatment V had a decreasing effect, the TL of the treated soils, except soil No. 4FF, still remained high compared to that of the untreated soils (V/Untr. = 1.96 to 6.34). The V/Untr. ratio for soil No. 4FF was 0.59, emphasizing again the influence of the loss of carbonates on soil TL. Aside from the dissolution of additional amounts of residual carbonates, treatment V caused soil particle dispersion, partial removal of free silica and alumina, and perhaps changes in

the surface characteristics of the thermoluminescent particles. Two per cent solution of Na_2CO_3 has a very favorable dispersion effect on soils and clay particles by the dissolution of amorphous cementing materials consisting of precipitated SiO_2 , Al_2O_3 , and alumino silicate (7). It is, however, ineffective in simultaneously dissolving appreciable amounts of both free silica and alumina from soils (4). Nevertheless, the partial removal of finely divided crystalline silica and alumina could contribute toward reducing the TL of the residual soil. Several sources of evidence indicate that silica and alumina in soils could show TL. Acid washed silica sand was found to show considerable amounts of TL (12). Natural quartz is known to show TL (5, 8, 11, 22). Rieke and Daniels (16) studied 30 samples of aluminum oxide representing various crystal phases, degree of hydration and chemical purity. They found that nearly all of the samples irradiated with γ -rays showed varying degrees of TL.

Effect of chemical treatments before and after irradiation

Thus far, the TL of soils that were chemically treated before irradiation with $\text{Co}60$ photons have been discussed. Figure 3 gives an example (soil No. 9RDG) of chemically treating the soils after irradiation. By comparing figures 3A and 3B several differences are evident. One difference is manifested by the shift of the threshold annealing temperatures toward higher temperatures. Also, a comparison of the relative light outputs under any given chemical treatment shows that they are always considerably less when the soil

was chemically treated after irradiation. Apparently each chemical treatment provided sufficient energy to cause a certain extent of electron (hole) transitions, which probably took place primarily at the surfaces of the thermoluminescent particles. Also, the distinct glow curve peak that occurred at 197°C under treatment IV when the treatment was applied before irradiation (fig. 3A) did not occur when the treatment was applied after irradiation (fig. 3B). Thus, significant differences in TL occurred depending on whether the chemical treatment was done before or after the exposure of the soil to ionizing radiation.

Upon re-irradiating the soil that was chemically treated after irradiation (fig. 4A), the 197°C peak reappeared (fig. 4C), indicating that the final states of the thermoluminescent particles were similar whether the chemical treatments were done before or after irradiation. The higher glow curve height at temperatures above the 197°C peak zone (fig. 4C) is, of course, due to the greater gamma dosage received by the re-irradiated soil. The loss of the 197°C peak that occurred under the post-irradiation chemical treatment could have been caused by the drainage of the metastably trapped electrons during the treatment (without appreciable loss of traps) and/or the removal of the chemically sorbed iron on the surface of the thermoluminescent particles. The exact mechanism has not been delineated. In view of the relatively high electrical conductivity of iron oxides, the removal of free iron oxides per se probably was not the cause of the loss of the 197°C peak.

GENERAL DISCUSSION

Except for treatment V, the chemical treatments used generally enhanced the TL of the noncalcareous soils. In this regard, the most important step was the removal of iron oxides. This was true also for the highly calcareous soil No. 4FF, even though the effect of iron oxide removal from this soil was somewhat masked by the concurrent loss of TL capacity caused by the removal of carbonates. The factors that may be involved in enhancing soil TL by the removal of iron oxides as well as other components were mentioned above. A factor that was mentioned but was not discussed to any extent was the change of the surface characteristics of the thermoluminescent particles due to chemical treatments.

Surface characteristics of the particles are important because TL may occur at the surface as well as within the bulk (14). The existence of surface TL indicates the existence of electron (hole) trapping sites at the surface. These trapping sites are localized electronic energy levels resulting from the termination of the crystal lattice where the bonds are not the same and less numerous than in the bulk or are not completed, biographical or radiation-induced defects and imperfections, and adsorbed foreign impurity atoms or ions or molecules. Chemical treatments could change the surface characteristics by removing atoms and/or by exchanging adsorbed ions or molecules on the particulate surfaces. This may also change the bulk properties to some extent, since perturbation at the surface could cause the movement of electrons (holes) and

crystal lattice defects in the bulk, particularly near the surface. The electron (hole) transitions accompanying physical adsorption and chemisorption on the surfaces of the thermoluminescent soil particles perhaps could be explained by viewing the particles as semiconductors. This seems to be a reasonable approach, since to exhibit TL, a substance must have an ordered structure as in crystals or semiordered structure as in glass and be electrically an insulator or a semiconductor. On the basis of the band theory of solids, the only difference between an intrinsic semiconductor and an insulator is in the size of the forbidden energy gap. The electron (hole) transitions and the role of defects and impurities in the chemical transformations of semiconductor surfaces have been discussed in a number of excellent reviews (9, 17, 19, 21, 23).

With the chemical treatments used in the present study, the most important process that took place at the surface of the thermoluminescent particles probably was exchange adsorption. In considering adsorption, it is necessary to distinguish two types, viz., physical adsorption and chemical adsorption (chemisorption). The difference between physical and chemisorption amounts to the difference in the origin of forces that retain the adsorbed ions or molecules on the surface of solid. Physical adsorption is due to forces of electrostatic origin such as Van der Waals' forces and forces arising from electrostatic polarization. Physical adsorption implies that the electronic structures of the solid and the adsorbate are not changed

to any appreciable extent when the two are in mutual interaction. Chemisorption implies that a change in the electronic structures does occur. The forces producing the bond are covalent ones with perhaps ionic interaction to a varying extent. The bond energy of the adsorbed molecule with the surface of the solid in physical adsorption is 0.01 - 0.1 eV (21). For chemisorption, this energy is about 1 eV. From the point of view of TL, chemisorption is believed to be the important process, because it involves transitions of electrons at higher energy levels. Perhaps, part of the very marked enhancement of TL by treatment IV was caused by the removal of chemisorbed iron with free iron oxides. In any case, these results show that the surface states of the particles are important factors influencing soil TL.

SUMMARY

The influence of five chemical treatments of soils on their thermoluminescence (TL) were examined. Three noncalcareous soils representing different predominant clay mineral types and a nonsaline, highly calcareous one, were used for this study. The TL of each soil was examined after the removal of the following main components in a sequential manner: (a) soluble organic matter and salts, (b) carbonates and certain exchangeable cations, (c) organic matter and MnO_2 , (d) iron oxides, and (e) silica and alumina. The removal of components (a), (c), and (d) enhanced the soil TL, whereas the removal of components (b) and (e) decreased it. The removal of iron oxides had a markedly great effect in enhancing TL. The removal of the carbonates greatly reduced it. Among the factors believed to be involved in changing the soil TL are the removal of "diluting agents," the unmasking of the surface of the thermoluminescent particles, the dispersion of the particles, the change of the solid surface characteristics, the dissolution of the thermoluminescent material, and the change of color.

FIG. 1. Thermoluminescence of Hanford sandy loam and soil No. 4FF in relation to various chemical treatments.

A. HANFORD SANDY LOAM

B. SOIL NO. 4FF

FIG. 2. Thermoluminescence of irradiated and unirradiated soil No. 4FF with and without leaching with 0.1 N HCl.

FIG. 3. Thermoluminescence of soil No. 9RDG in relation to various chemical treatments.

A. SOIL TREATED BEFORE IRRADIATION TO 1000 R

B. SOIL TREATED AFTER IRRADIATION TO 1000 R

C. NATURAL THERMOLUMINESCENCE AFTER SOIL TREATMENT (NO IRRADIATION)

FIG. 4. Thermoluminescence of soil No. 9RDG after the removal of iron oxides before and after irradiation.