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NATURAL THERMOLUMINESCENCE OF SELECTED CLAY
MINERALS AS INFLUENCED BY CHEMICAL TREATMENTS

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INTRODUCTION

Our previous paper reported the effects of five different chemical treatments on the thermoluminescence (TL) of soils (Nishita and Hamilton, 1972). It was found that selective removal of soluble organic matter and salts, organic matter and MnO_2 , and iron oxides consistently enhanced the soil TL. The removal of the carbonates and certain exchangeable cations and the silica, alumina and amorphous aluminosilicates decreased the TL. The removal of iron oxides had an especially great effect in enhancing TL, whereas the removal of the carbonates greatly reduced it.

This paper presents the effects of five chemical treatments on the TL of four selected clay minerals. The chemical treatments applied were the same as those applied on soils. The intent here was to study more homogeneous materials, since soils are heterogeneous mixtures of a number of minerals and other compounds. The effects of saturating the mineral exchange sites with single cations are also presented.

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MATERIALS AND METHODS

Four mineral samples (kaolinite No. 9 (Mesa Alta, N. M.); illite No. 35 (Fithian, Ill.); montmorillonite No. 26 (Clay Spur, Wyo.); and vermiculite (Transvaal) were examined. These 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 samples were passed through the 177-micron sieve before use. All minerals were pulverized with pestle and mortar to pass through the sieve.

The apparatus and the technique of measuring TL were as described previously (Nishita and Hamilton, 1970) with the sample heating rate of 500° C/min. All readouts were performed on 30 mg of air-dry samples in argon atmosphere. The total areas under the glow curves corrected for black body radiation were used to represent the sample TL.

Five chemical treatments were used to determine their effects on mineral TL. These treatments applied in sequence are often used to prepare soils for mineralogical analyses. The step-by-step details of each treatment were as prescribed by Jackson (1956). Each treatment is designed to remove selectively certain chemical components. Briefly, the principal substances removed under each treatment are as follows: Treatment I was centrifuge washing of the mineral samples with 25 per cent ethanol. This treatment was to remove soluble organic matter and salts. Treatment II was the digestion of the samples in pH 5 NaOAc buffer. This removed 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 pH 5 NaOAc and 99 per cent methanol to bring about the decomposition of organic matter, MnO_2 and additional carbonates. Treatment IV was the digestion of samples in Na-citrate- NaHCO_3 - $\text{Na}_2\text{S}_2\text{O}_4$ mixture to remove the iron oxides. Treatment V was boiling the samples in 2 per cent Na_2CO_3 to remove free alumina and silica and amorphous aluminosilicates. Organic matter that was not removed under treatment III may also be removed. These treatments were applied sequentially. After each step in the sequence, the samples were washed with 25 per cent ethanol, dried in an evacuated desiccator at room temperature, and prepared for TL measurement as described above. In applying each chemical treatment, the temperature of the reaction medium was monitored and always kept below 110°C when heat was applied. It has been shown previously that TL capacity of the soil minerals diminished at temperatures above 110°C (Nishita and Hamilton, 1972).

In order to determine the effect of sorbed cations on the mineral TL, the minerals were first carried through the five chemical treatments given above with one modification and then were treated to saturate their exchange sites with one cation. The chemical treatment sequence was modified in that 0.1 N HCl was used instead of pH 5 NaOAc buffer in treatment II. The end products after the application of the five chemical treatments were Na-saturated minerals, minus the components mentioned above. To obtain K-, Ca-, Mg-, Al-, or Fe-saturated minerals, 2 g. aliquots of the Na-saturated minerals placed in 50 ml centrifuge tubes were suspended in 25 ml. of normal solution of KCl, CaCl_2 , AlCl_3 , or $\text{Fe}(\text{NO}_3)_3$ and allowed to stand for 24 hr with occasional vigorous

mixing. The suspensions were then centrifuged and the supernatant liquid removed. Following this, the samples were resuspended and centrifuged in their respective solutions 3 times with occasional vigorous mixing during the 4 hr period between each centrifugation. After the salt treatments, the samples were washed in 95 per cent ethanol four times and dried in vacuum at room temperature. The compacted cakes that formed on drying were broken down to uniform material with pestle and mortar. The TL measurements were performed on the resulting materials:

The organic and inorganic carbon was determined by Allison's method (1960).

RESULTS AND DISCUSSION

The effects of chemical treatments on the natural TL of minerals were quite variable (fig. 1). This can be seen readily by comparing the relative heights of the glow curves for the 5 treatments among the minerals. For example, the height of the treatment I glow curve for illite was greater than that for the untreated sample, whereas that of the vermiculite glow curve (treatment I) was markedly less than that of its untreated sample. As indicated by the relative light output, treatment I (washing with 25 per cent alcohol) increased the TL of illite and montmorillonite, whereas it reduced that of kaolinite and vermiculite. Its effect on illite was relatively small (5 per cent increase), but was appreciable on montmorillonite (49 per cent increase). The TL of kaolinite was reduced 5 per cent and that of vermiculite 57 per cent.

The increase of TL shown by illite and montmorillonite might be explained as due partly to sample condensation. The removal of certain components has the effect of concentrating the residual sample if the material removed had only little or no TL, because constant weight (30 mg) of material was always taken for readout. If the amount of soluble material was large and if these materials had high TL, their removal could cause the reduction of TL capacity of the residual material. In the present case, the removal of soluble substances probably had only a minor effect, since the concentration of these materials was low. Perhaps, the more important factor was the removal of thin coating on the particles. The change of particle surface characteristics in the direction of increasing TL could be another factor. TL shown by vermiculite and kaolinite probably was due primarily to the change of the surface characteristics in the direction that caused the reduction. These statements imply that the increment or the decrement of TL depends on the characteristics of the particle surface. Some evidence for this is shown below.

Treatment II (digestion of pH 5 NaOAc buffer) reduced the TL of all 4 minerals. This is shown quantitatively in table 1, which gives the TL ratios between the chemically treated soils and between the treated and untreated soils. Note that both treatment II/Untr. and II/I TL ratios decreased. The effect of treatment II on reducing the TL of the minerals was in the following order: vermiculite > illite > montmorillonite > kaolinite.

The decrease of TL caused by the NaOAc buffer treatment was very likely due primarily to the change of surface characteristics of the minerals. Since vermiculite and illite contained some carbonate impurities, the effect of surface change probably was enhanced by the removal of carbonates. This is surmised from the fact that the carbonate compounds generally show high TL (Nishita and Hamilton, 1968, 1972). The treatment not only removed the carbonates, if they were present, but saturated the exchange sites of the minerals with Na. The effect of saturating the exchange sites with Na is shown below.

Treatment III (digestion in 30 per cent H_2O_2) had variable effects on the minerals. The III/II ratios (table 1) decreased for illite, vermiculite, and montmorillonite and increased for kaolinite. As indicated by the III/Untr. ratio, which was 0.95, the TL of kaolinite increased, but still remained less than that of the untreated sample. The TL of vermiculite was not measurable after treatment III.

The primary effect of H_2O_2 treatment seems to be the change of surface characteristics of the minerals. This change could be brought about by the oxidation of any oxidizable material on the surface. If present in large amount, the removal of organic matter can cause the increase of TL by the condensation of the residual sample. Organic matter itself is considered not to have appreciable TL. This is surmised from the fact that organic matter separated from a muck soil did not show measurable TL (Nishita and Hamilton, 1970). In view of its low concentration (table 2), organic matter probably had no influence in this situation. Concurrent with the destruction of

organic matter, the H_2O_2 will also cause the dissolution of MnO_2 , if present. Manganese dioxide is believed to be present as discrete particles and as partial coating on mineral particles (Anderson and Jenne, 1970).

Treatment IV (digestion in Na-citrate- $NaHCO_3$ - $Na_2S_2O_4$ mixture) increased the TL of illite, kaolinite, and montmorillonite, but had no apparent effect on vermiculite. The IV/III ratios (table 1) for illite, kaolinite, and montmorillonite were 1.36, 1.07, and 1.39, respectively. As indicated by the IV/Untr. ratios, the TL of the treated kaolinite and montmorillonite was raised above that of their corresponding untreated samples. The TL of illite was increased, but its IV/Untr. ratio remained less than one.

It is evident that the removal of free iron oxides can greatly enhance the TL of certain minerals. Vermiculite was unaffected by treatment IV probably because it had no free iron oxides. The iron oxides in themselves generally have little or no TL. Iron oxide minerals and soils usually show low TL (Nishita and Hamilton, 1972). This probably results from the fact that Fe_2O_3 has relatively high electrical conductivity compared to the other metal oxides. The magnetic Fe_3O_4 has exceptionally high conductivity (Verwey, 1951). The electrons could wander freely through the crystal lattice with an activation energy equal to zero in a conductive material. In the TL process, an activation energy is needed to raise the metastably trapped electrons to the conduction band. Consequently the removal of iron oxides influenced the mineral TL indirectly, i.e., by the uncovering

of the particle surface, the dispersion of the soil particles, and the alteration of the particle surface characteristics. The change of color could affect the TL by changing the reflectance of the light. However, this factor was of minor importance, since the minerals were of light color before the removal of free iron oxides, and there was only slight color change.

Treatment V (boiling in 2 per cent Na_2CO_3) decreased the TL of illite and montmorillonite, but increased that of kaolinite relative to treatment IV (compare V/IV ratios, table 1). As indicated by the increase of V/Untr. ratio, the kaolinite TL relative to that of the untreated sample was also increased by this treatment.

The decrease of TL may be ascribed, at least in part, to the loss of TL capacity with the removal of alumina and silica. Several sources of evidence indicate that silica and alumina could show TL. Acid washed silica was found to show considerable amounts of TL (Nishita and Hamilton, 1968). Natural quartz is known to show TL (Kikuchi, 1958; Yokota, 1958; Medlin, 1963; Ichikawa and Higashimura, 1968). Aluminum oxide and hydroxide compounds (corundum, bauxite, gibbsite, and diaspore) show appreciable amounts of natural TL (Nishita and Hamilton, unpublished data). In view of these facts, the increase of TL shown by kaolinite is difficult to explain. Perhaps, the amount of free silica and alumina contamination in the kaolinite was small, and the more important factors were the removal of amorphous aluminosilicate coating and the change of surface characteristics of the particles.

Figure 6 shows the effects of sorbed cations on the TL of minerals. The effects of sorbed cations vary and can be of considerable magnitude. The amount of mineral TL with respect to sorbed cations was as follows: illite, Untr. > Na > Al > Mg > Ca > K > Fe; vermiculite, Untr. > Na, K, Mg, Ca > Al, Fe (No TL); kaolinite, K > Na > Mg > Untr. > Ca > Al > Fe; and montmorillonite, Ca > Untr. > Na > Mg > K > Al > Fe. As shown by the relative light output, the treated samples showed less TL than the untreated sample in the majority of cases. These results show that the effect of sorbed cations depended on the saturating cations and the mineral species. However, one effect occurred consistently. Regardless of the mineral species, the saturation of the exchange sites with Fe drastically reduced the TL. This suggests that adsorbed Fe changed the electronic state of the mineral particle surfaces to the electrically conductive form much more effectively than other saturating cations. Aside from the light output, the shapes of the glow curves may be changed. For example, the distinctly two-peaked glow curve of untreated illite was changed to a broad one-peak curve after K saturation. Some treatments caused the increase of glow curve height (ordinate) in the low annealing temperature range, whereas others caused height increase in the high temperature range.

GENERAL DISCUSSION

The chemical treatments affected the TL of minerals by removing selected thermoluminescent and non-thermoluminescent substances and by changing the surface characteristics of the particles. As discussed above, the removal of thermoluminescent substances reduced the TL capacity. The removal of non-thermoluminescent substances had the effect of concentrating the residual thermoluminescent material, since a constant weight of material was always used for readout. The surface characteristics of the particles are important, because TL may occur at the surface as well as within the bulk (Nishita and Hamilton, 1970). Chemical treatments alter the surface characteristics by removing atoms and/or by exchanging sorbed ions or molecules on the particle surfaces. In this respect, chemisorption is more important than physical adsorption, since it involves electron transitions at much higher energy levels than physical adsorption (Nishita and Hamilton, 1972). These reactions alter the electronic energy levels that serve as electron (hole) trapping sites at the surface. However, the bulk properties also may be changed to some extent, because the perturbation at the surface could cause the migration of electrons (holes) and the crystal lattice defects in the bulk, particularly near the surface.

The chemical treatments showed two consistent effects, i.e., the removal of iron oxides always increased the TL in the residual

material and the saturation of the mineral exchange sites with Fe always markedly reduced it. As mentioned in the introduction, the chemical treatments of soils showed other consistent effects in addition to that due to iron oxide removal. The difference between the minerals and the soils probably was due to the fact that the soils had much higher concentration of the materials that were removed.

SUMMARY

The natural thermoluminescence of four clay minerals as they are affected by chemical treatments was examined. The application of chemical treatments designed to remove various components selectively had variable effects among the minerals. Depending on the mineral and the chemical treatment, the mineral thermoluminescence was enhanced or reduced. Iron appeared to have the greatest effect. The removal of iron oxides drastically increased the thermoluminescence of the residual sample. The saturation of the mineral ion exchange sites with Fe consistently reduced the thermoluminescence markedly more than saturation with Na, K, Mg, Ca, or Al.

RESUME

La thermoluminescence naturelle de quatre minéraux argileux alors qu'ils réagissaient à des traitements chimiques fut examinée. L'application de traitements chimiques destinés à soustraire selectivement certains composants eût des effets variés parmi les minéraux. Selon le minéral et le traitement chimique respectif, la thermoluminescence minérale fut augmentée ou réduite. Le fer apparut avoir le plus grand effet. La soustraction d'oxyde de fer intensifia énergiquement la thermoluminescence de l'échantillon résiduel. La saturation des points d'échange du minéral avec le fer réduisit uniformément la thermoluminescence de façon beaucoup

plus prononcée que grâce à la saturation avec Na, K, Mg, Ca, ou Al.

ZUSAMMENFASSUNG

Die natürliche Thermolumineszenz von vier Tonmineralien wurde unter der Einwirkung chemischer Behandlungen untersucht. Durch die Anwendung chemischer Behandlungen wurde beabsichtigt, auswählend verschiedene Bestandteile zu entfernen, und dies hatte unterschiedliche Wirkung auf die Mineralien. Je nach Mineral und der jeweiligen chemischen Behandlung wurde die Mineralthermolumineszenz erhöht oder reduziert. Eisen schien den größten Einfluß zu haben. Durch die Entfernung von Eisenoxiden wurde die Thermolumineszenz der Restsubstanz in drastischer Weise erhöht. Die Sättigung der Adsorptionspunkte der Mineralien mit Fe reduzierte die Thermolumineszenz in allen Fällen wesentlich stärker als die Sättigung mit Na, K, Mg, Ca oder Al.

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Table 1

The natural TL ratios of minerals that were chemically treated.*

Mineral	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
Illite No. 35	1.00	1.06	0.61	0.57	0.46	0.75	0.62	1.36	0.61	0.99
Vermiculite	1.00	0.42	0.03	0.06	0.00	0.00	0.00	0.00	0.00	0.00
Kaolinite No. 9	1.00	0.95	0.90	0.95	0.95	1.06	1.02	1.07	1.18	1.16
Montmorillonite No. 26	1.00	1.50	1.18	0.79	0.97	0.82	1.35	1.40	1.16	0.86

*The TL was determined by measuring the total area under the glow curves below 473° C.

Table 2

Organic matter and carbonate contents of the
four minerals on an oven-dry basis.

Mineral	Organic-C %	Carbonates* %
Illite	0.40	6.51
Kaolinite	ND	ND
Montmorillonite	ND	ND
Vermiculite	T	2.98

*Carbonates as CaCO_3 . ND = not detectable

T = trace

Fig. 1. Natural TL of four minerals in relation to various chemical treatments.

Fig. 2. Effect of sorbed cations on the TL of minerals.