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THERMOLUMINESCENCE OF CLAY MINERALS

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ABSTRACT

The thermoluminescence between −180 and 400°C of fundamental clay minerals groups kaolinite, halloysite, montmorillonite (bentonite, hectorite, pyrophyllite), talc and illite have been studied. The thermoluminescence of anhydrous and hydrated amorphous silica, quartz, cristobalite and alumina have also been studied. Each clay mineral group showed a characteristic glow curve. All the thermoluminescent peaks of the clay minerals, except the peak at 145°C in montmorillonite, coincided with the quartz and alumina peaks. Most of the observed thermoluminescent peaks are attributed to fundamental structural units of the clay minerals.

INTRODUCTION

The thermoluminescence of igneous and sedimentary rocks minerals has been studied for many years (Angino and Groegler, 1962). Recently, glow curves, between 20 and 400°C of naturally and artificially irradiated clay minerals have been published (Siegel, Vaz and Ronca, 1966) but no correlation between thermoluminescence peaks and structure have been considered. In this work, the study of the thermoluminescence of irradiated clay minerals between −180 and 400°C has been initiated to see if a relationship exists between glow curves and chemical composition and structure.

Such knowledge is particularly useful for the proposed application of glow curves for archeological dating of antique ceramic pottery.

Various fundamental types of clay minerals have been studied, and the dependence between glow curves from the type of structural unity has been ascertained.

EXPERIMENTAL

The materials under study were clay minerals supplied by the Ward's Natural Science (Rochester, N. Y.), bentonite (Ponza, Italy), illitic clay (M. Mario, Rome, Italy), quartz (Soriano C., Italy), cristobalite (Vicenza, Italy). Silica and alumina reagent grade have also been studied. The samples were powdered and the fraction between 100 and 200 mesh was selected.

In Table 1, the description and origin of the materials have been summarized.

The irradiation was performed either with a Co^{60} gamma source of 2.5×10^5 R/h, or an X-ray source (R. Seifert & Co.—Hamburg) of 4.8×10^5 R/h (measurements done at 6 cm from the anticathode by the Frike method). The effective flux of X-ray irradiation on the samples is about 3.85×10^3 R/min., this due to the shielding of a 3-mm thick perspex window and the greater distance of sample (11.5 cm) from the anticathode. Thermoluminescent glow curves between −180 and +20°C were produced by the cryostate previously described (Bettinali, Gottardi and Ferraresso, 1966). The linear heating rate (10°C/min.) was ob-

TABLE 1. DESCRIPTION AND ORIGIN OF MATERIALS

Sample	Materials	Description	Locality
1	Kaolinite	Very light, well crystallized	Bath, South Carolina
2	Kaolinite	Very light, well crystallized	Birch Pit., Georgia
3	Kaolinite	Very light, well crystallized	Mesa Alta, New Mex.
4	Dickite	Light, well crystallized	Chihuahua, New Mex.
5	Halloysite	Light, well crystallized	Bedford, Indiana
6	Halloysitic clay	Light grey, crystallized	Lazio, Italy
7	Montmorillonite	Light yellow, crystallized	Chambers, Arizona
8	Bentonite	White, poorly crystallized	Ponza, Italy
9	Hectorite	Selected from mixed minerals	Hector, California
10	Talc	White, well crystallized	Vicenza, Itlay
11	Pyrophyllite	Typical, light green	
12	Illite	Grey, crystallized	Fithian, Illinois
13	Illite	Grey, crystallized	Morris, Illinois
14	Illitic clay	Grey, well crystallized	Roma, Italy
15	Alumina	Synthetic product	C. Erba Inc., Italy
16	Silicic acid	Synthetic product (H_4SiO_4)	C. Erba Inc., Italy
17	Silica	From calcinated (H_4SiO_4) at 800°	C. Erba Inc., Italy
18	Silica	From calcinated $SiO_2 \cdot nH_2O$ at 800°	C. Erba Inc., Italy
19	Quartz	Natural sample, white	Soriano C., Italy
20	Quartz	Natural sample, white	Soriano C., Italy
21	Cristobalite	Natural sample, microcrystals	Vicenza, Italy

tained using a calibrated metallic mass, with established electrical resistance. The same criteria were employed in building the heating plate used to obtain glow curves in the temperature range between 20 and 400°C. In Figure 1, the heating cell used to perform the glow curve measurements at reduced pressure (10^{-4} mmHg) is shown. The light emitted was detected by an E.M.I. 6255 S photomultiplier, with a large spectral response having a peak between 3000 and 4500 Å. The signal was fed to a cathode-follower constructed with a radiometric Mullard ME 1501 triode, and supplied by dry-cell batteries. It was then amplified and registered with a Speedomax L & N recorder. Between the photomultiplier and the sample a thermal filter can be inserted in order to eliminate the black-body emission. The temperature was measured with a S.A.E. 10757 potentiometer and the temperature *versus* time path was registered by a Sargent SR recorder.

EXPERIMENTAL RESULTS

In Figure 2, the glow curves of the materials studied are reported, and in Table 2 (peak temperatures of thermoluminescence between 20 and 400°C) one sees particularly that the kaolinite and halloysite type minerals, constructed of a sheet of Si^{4+} tetrahedrons and one of Al^{3+} octahedrons, have a main peak at about 85°C; while the montmorillonite and illite minerals, composed of two silica tetrahedral sheets interlayered by a one alumina octahedral sheet, have a main peak at about 105°C.

The kaolinite- and halloysite-type minerals also have one peak of minor intensity and temperature; and another, common to both types of minerals, with a maximum around 320°C. This last peak disappears if the glow curves are obtained under a low gas pressure, with the cell described in Figure 1. The light emission around 320°C, seems in fact, to be due to the desorption of water and successive adsorption of gas on the surfaces, as has been demonstrated for other materials in previous papers (Bettinali, Ferraresso and Stampacchia, 1962; Bettinali and Ferraresso, 1963 and 1966a). The montmorillonite and illite minerals showed, beside the peak of 105°C, two more peaks found around 165 and 220°C. An exception is montmorillonite, which presents a peak at 145°C, and another wide peak with a maximum around 340°C instead of the peak at 165 and 220°C.

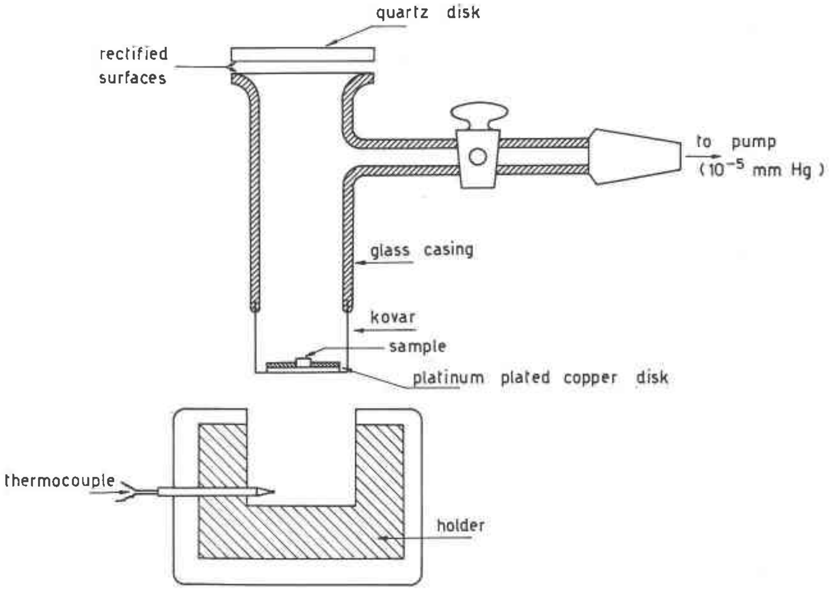


FIG. 1—Heating cell used to perform the glow curve measurements at low pressure (10^{-4} mmHg). The optical window must be made with a very pure silica glass. If the silica glass is not sufficiently pure, the irradiation produces a large amount of color centers. The glass casing is protected from irradiation by a shield of lead, but is not represented in figure.

Figure 2 also shows the glow curves of reagent grade products, such as amorphous silica and alumina, and the minerals quartz and cristobalite. These materials were studied to see if a simple relationship existed between the light emission of the clay minerals and that of materials having structural units similar to those present in the clay

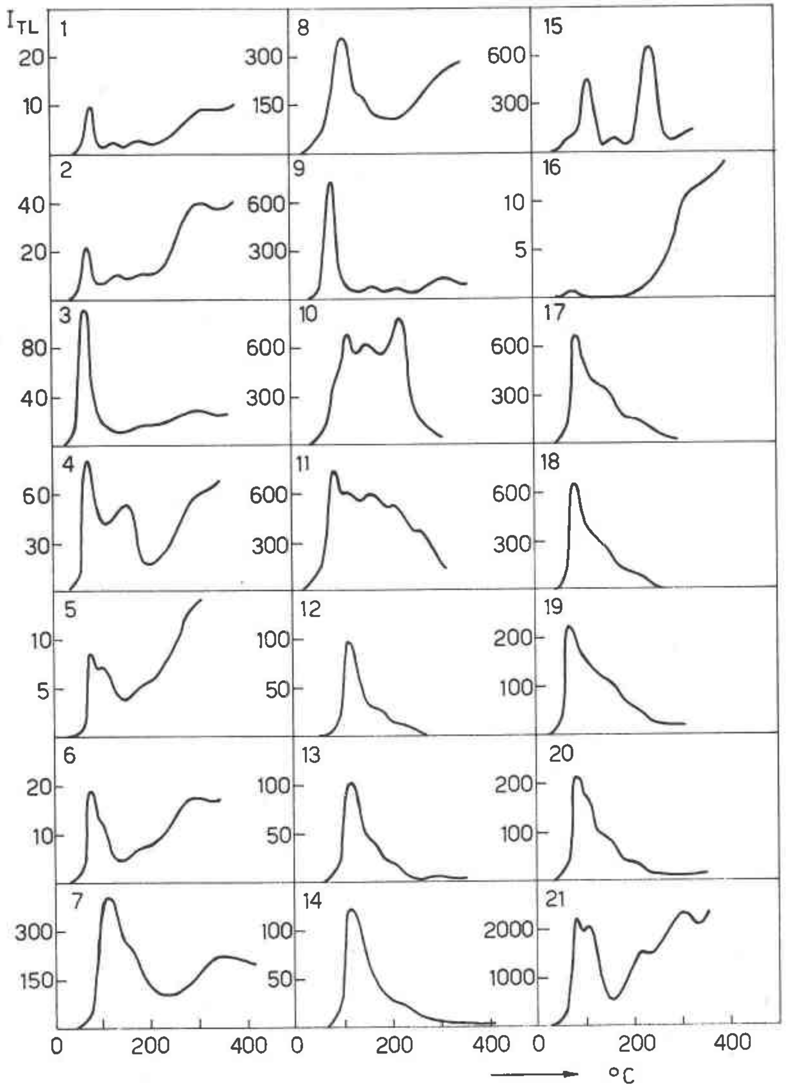


FIG. 2—Glow curves between 20 and 400°C of: 1, 2, 3—kaolinites; 4—dickite; 5—halloysite; 6—halloysitic clay; 7—montmorillonite; 8—bentonite; 9—hectorite; 10—talc; 11—pyrophyllite; 12, 13—illites; 14—illitic clay; 15—alumina; 16—silicic acid; 17—amorphous silica from silicic acid calcinated at 800°C; 18—amorphous silica from $SiO_2 \cdot nH_2O$ calcinated at 800°C; 19, 20—quartz; 21—cristobalite.

minerals. As shown in Table 2 the thermoluminescent peaks found in synthetic silica and in natural samples of quartz and cristobalite are also present in clay minerals. But, at the present stage of the research, it is not possible to establish a simple relationship which can explain in a certain mineral, the presence of certain peaks and the absence of others. Alumina presented a glow curve with four peaks at 80, 105, 165, 235°C, in accordance with the data of the previous literature (Rieke and Daniels, 1957; Moore, 1957; Atlas and Firestone, 1960; Gabrysh *et al.*, 1963).

TABLE 2. PEAK TEMPERATURES OF THERMOLUMINESCENCE

		A						B				
Sample	Materials	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
1	Kaolinite	−145	−110	−76	−61	−20	—	85	—	165	—	310
2	Kaolinite	−145	−110	−76	−61	−20	—	85	—	175	—	300
3	Kaolinite	−145	−110	−76	−61	−20	—	85	—	170	—	310
4	Dickite	−135	−110	−76	−61	—	—	85	—	160	—	300
5	Halloysite	−145	−110	−85	−61	−20	+5	85	105	—	—	320
6	Halloysitic clay	−145	−110	−85	−61	−20	+20	85	105	—	—	320
7	Montmorillonite	−145	−110	−85	—	−20	—	—	105	145	—	340
8	Bentonite	−145	−110	—	−60	—	+36	—	105	145	—	350
9	Hectorite	−135	−110	−70	—	—	+50	85	105	170	220	—
10	Talc	—	− 95	−72	—	—	+40	—	105	170	220	—
11	Pyrophyllite	−135	−110	−70	—	−15	—	85	105	165	220	235
12	Illite	−145	−110	−85	—	−20	—	—	105	165	220	—
13	Illite	−145	−110	−85	—	−20	—	—	105	165	220	—
14	Illitic clay	−145	−110	−85	—	−20	+50	—	105	165	220	—
15	Alumina	−150	—	—	−53	—	—	80	105	165	235	—
16	Silicic acid	—	—	−85	−35	—	—	85	—	—	—	320
17	Silica	−145	−110	—	—	—	—	80	—	160	220	—
18	Silica	−145	−110	—	—	—	—	80	—	160	220	—
19	Quartz	−145	−110, 95	−85	−35	−22	+ 0	80	—	160	220	—
20	Quartz	−145	−110, 95	−70	−30	−10	—	80	95	160	220	—
21	Cristobalite	−145	−110	—	−50	− 5	+40	80	95	160	220	—

Figure 3 shows the glow curves between −180° and +20°C, and in Table 2, it appears that all the materials (except dickite, pyrophyllite and talc) have two peaks at −145 and −110°C, whose relative intensity varies notably, as shown in Figure 3. Another peak, common to almost all the clay minerals, exists at about −20°C. Beside the common thermoluminescence peaks, there are others which characterize for maximum temperature and for reciprocal intensity ratio, the mineralogical types studied. The kaolinite type is characterised by two peaks at about −75 and −60°C, whose intensity ratio is very near to unity. An exception is dickite, which presents two peaks at −135 and −90°C, rather than at −145 and −110°C, and an intensity ratio between the peaks at −75 and −60°C very near to 1.5.

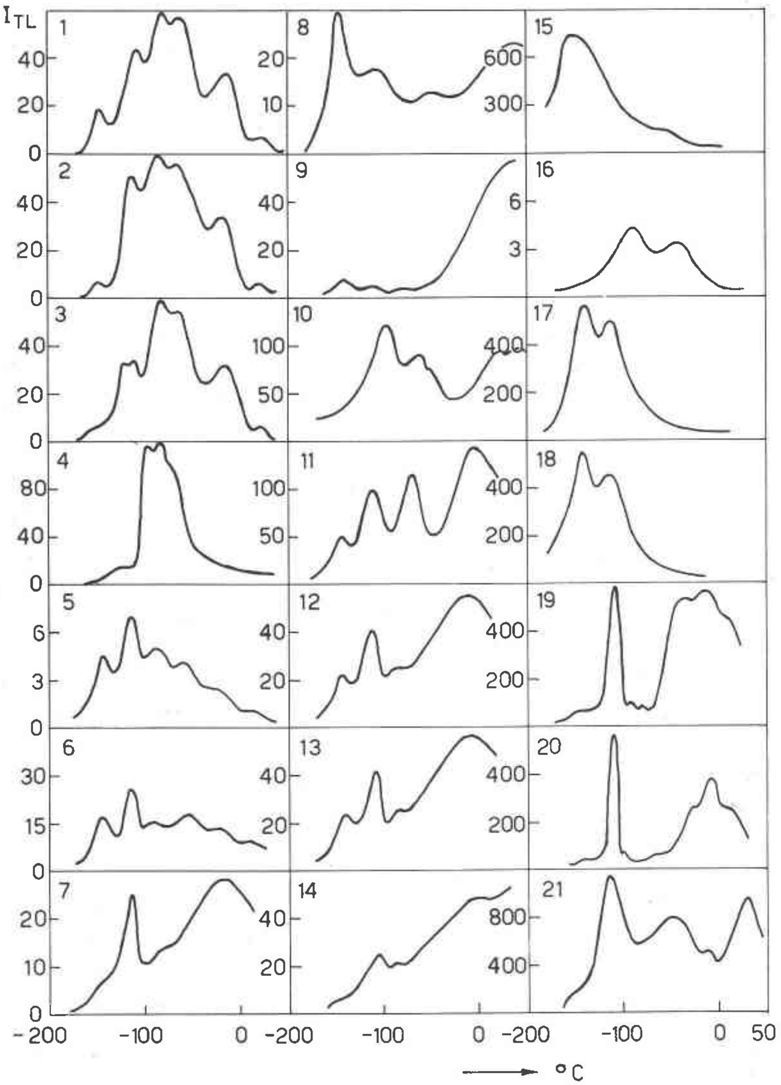


FIG. 3—Glow curves between −180 and +20°C of: 1, 2, 3—kaolinites; 4—dickite; 5—halloysite; 6—halloysitic clay; 7—montmorillonite; 8—bentonite; 9—hectorite; 10—talc; 11—pyrophyllite; 12, 13—illites; 14—illitic clay; 15—alumina; 16—silicic acid; 17—amorphous silica from silicic acid calcinated at 800°C; 18—amorphous silica from $SiO_2 \cdot nH_2O$ calcinated at 800°C; 19, 20—quartz; 21—cristobalite.

The glow curve of dickite is very similar to that of kaolinite since it presents a couple of peaks with intensity almost equal and at close temperatures (−90 and −75°C) which however, does not correspond to the characteristic couple of kaolinite (−75 and −60°C).

Halloysite presents a glow curve which is quite similar to that of kaolinite, although varying slightly at the peak temperature (−85°C for halloysite and −75°C for kaolinite) and notably the reciprocal relationships of the intensity of peaks.

Montmorillonite and illite present glow curves practically indistinguishable: the two mineralogical species have in common, in fact, both the temperatures of all peaks at −145, −110, −85 and −70°C approximately, and the reciprocal intensity ratio or the shape. Exceptions, are: pyrophyllite, which presents a temperature shift of the first peak at −145 to −135°C, and of the fourth peak at −20 to about −16°C; talc which presents four peaks at −95, −72, +20 and +40°C; hectorite which presents a temperature shift at the first peak from −145 to 135°C and the fourth, from −20 to +15°C.

Amorphous silica, from $SiO_2 \cdot nH_2O$ calcinated at 800°C, has only two peaks at −145 and −110°C, which coincide with those of the silica obtained by calcination of the silicic acid (H_4SiO_4) at 800°C. In contrast, silicic acid presents two peaks of low modest intensity at −85 and −35°C.

The glow curves of two different samples of natural quartz present, beside the peaks of the amorphous silica and silicic acid, other peaks at −50, −4 and +40°C.

Alumina presents a very intense peak with a maximum around −150°C and another, of a much lower intensity, around −50°C.

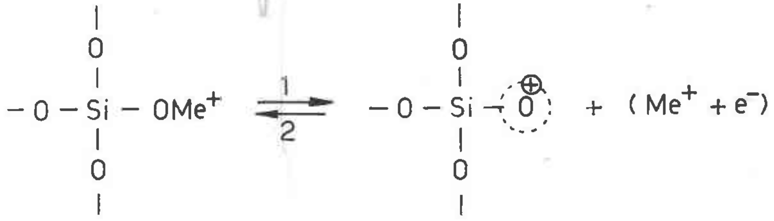
DISCUSSION

From Table 2, it is evident that the thermoluminescent maxima between −180 and +20°C found in clay minerals coincide with those present in quartz, according to literature data (Medlin, 1963). The maxima in quartz do not seem to have been derived from color centers formed by irradiation of pure silica (Cohen and Priqueler, 1963, 1964), but are connected more or less with impurities of various types such as Al^{3+}, Bi^{3+}, Ti^{4+}, Na^{+}, etc. It seems permissible to suppose that thermoluminescence between −180 and +20°C in clay minerals is connected with the tetrahedral layer of their structure.

From Table 2, it is evident that the maxima found at 85°C in kaolinite, in halloysite, in hectorite and in pyrophyllite; at 165°C in kaolinite, in hectorite, in pyrophyllite and in illite, coincide with those of quartz. The peaks present at 105°C in montmorillonite, pyrophyllite, hectorite and illite, seem to coincide with the peak of alumina at 105°C and therefore could be associated with recombination of the color centers produced by the irradiation on the octahedral sheet.

The substantial difference between montmorillonite and other clay minerals with triple-sheet layers is, as well known, an elevated capacity for a cation exchange due to substitution, either in tetrahedral or in octahedral sheets, with elements at lower valence. The peak at 145°C could be attributed to the substitution of Al^{3+} to Si^{4+} in tetrahedral sheets. This hypothesis is suggested from the glow curve of sodium aluminate, where Al^{3+} is tetracoordinated, which presents not only a 85°C peak but also another about 150°C.

The emitted light can be related to structural defects of the layers (substitutions, vacancies, slidings, etc.) and/or a recombination of electrons, trapped on changeable cations, with holes, following the scheme



$$\begin{array}{c} | \\ O \\ | \\ -O-Si-OMe^{+} \\ | \\ O \\ | \end{array} \quad \underset{2}{\overset{1}{\rightleftharpoons}} \quad \begin{array}{c} | \\ O \\ | \\ -O-Si-\overset{\oplus}{O} \\ | \\ O \\ | \end{array} \quad + \ (Me^{+} + e^{-})$$

(1: excitation; 2: recombination)

as supposed in a glass system of the type Me_2O-Al_2O_3-SiO_2 (Bettinali and Ferraresso, 1966b; Bettinali, Ferraresso and Bonetti, 1966).

CONCLUSIONS

Clay minerals present glow curves characteristic of each mineralogical type. The main thermoluminescence peaks seem to be related to the centers produced by the radiations on the SiO^{4+} tetrahedrons and the Al^{3+} octahedrons present in the structure.

Spectral compositions of the glow peaks, effects of different exchangeable cations types and surface effects are at present being studied in our Laboratory.

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