CHARACTERIZATION OF DEHYDRATION-INDUCED LUMINESCENCE OF KAOLINITE

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Abstract—Dehydration-induced luminescence (DIL), the emission of light from a clay paste upon dehydration, was characterized experimentally for a colloidal kaolinite. The relationship between total photon count of the emitted light and film thickness is linear up to a thickness of 30 μm. The photon emission was obtained over a critical range of water contents (25–60%) of the oven-dry clay, and the kinetics of photon emission was presumed to be closely associated with the kinetics of film dehydration. Whether drying proceeded throughout the bulk or via a moving front was undetermined, but in either mode it was preceded by the formation of a thin dry film at the interface with the atmosphere. Grinding of the kaolinite for several minutes by mortar and pestle before paste preparation resulted in an overall increase of photon emission compared to unground kaolinite and in the formation of more than one emission peak, as well as a prolongation of the light emission. This effect on the kinetics of light emittance was observed for about two months after the application of the mechanical stress and suggests a means of detecting the mechanical stress history of a clay.

An estimate was made of the spectral characteristics of the emitted light using optical filters and by incorporating tryptophan and salicylic acid into the kaolinite paste where they acted as fluorescent probes. The latter technique shifted the frequency of the light emitted by the kaolinite from the ultraviolet to the visible range where it was less effectively reabsorbed. The first method showed that the wavelengths of 97% of the emitted light was <460 nm and that 75% of the light had wavelengths <410 nm. The second method showed that the total intensity of DIL increased in the presence of fluorescence molecules, suggesting that the emittance was in the ultraviolet range.

Key Words—Dehydration, Fluorescent probes, Grinding, Kaolinite, Luminescence.

INTRODUCTION

Dehydration-induced luminescence (DIL) is the emission of light from a clay paste upon dehydration (Coyne *et al.*, 1980, 1981). It is typified by an initial low photon-emission rate which decays monotonically, followed by a sharp rise to a peak emittance, and then by a decay to the background level, the rise and fall occurring over a time scale of approximately 30 min. Under certain conditions (to be discussed below), the luminescence is typified by more than one peak and by a long tailing off of light emission.

Dehydration-induced luminescence is one of several novel luminescence effects first reported by the authors (Coyne *et al.*, 1980, 1981, 1983, 1984; Lahav *et al.*, 1982). The only other luminescence from kaolin to have been reported is thermoluminescence, first described by Seigel *et al.* in 1966. Thermoluminescence of several structurally related materials was reported by Ferraresso in 1967, greatly elaborated on by Nishita and Hamilton (1968, 1970, 1971, 1972, 1973, 1975) and Nishita *et al.* (1975), and others and recently reinvestigated by Lemons and McAtee (1982).

The atomic/molecular origins of the various luminescence effects have not yet been definitively assigned, although they have been tentatively associated with trapped electronic excitations centered near structural cation-substituted sites. Also, the mechanisms of radiative excitation and relaxation have not been completely enumerated or characterized for clay minerals, but it is thought that mechanical stress and/or interfacial effects on the energy level diagram may play a role in conjunction with, or independent of, the more traditionally studied gamma irradiation. To investigate this phenomenon and to observe the effects of different clay treatments on DIL, the phenomenon must be reproducible with a reasonable degree of accuracy. The purposes of the present work are to characterize further and to standardize the measurement of the DIL of a colloidal kaolinite, and to determine the effect of various treatments on the luminescence characteristics.

EXPERIMENTAL

Colloidal kaolin, lot 753828, from the Fisher Scientific Company was used without further purification. The surface area was measured by B.E.T. by Pacific Sorption Service, Chico, California, to be 15 m^2/g. The hygroscopic water content is 3–4% and the cation-exchange capacity of Fisher material is 1.03 meq/100 g, as reported by White and Erickson (1980). The trace metal composition of this material was reported in Coyne *et al.* (1983). L-tryptophan A-grade was ob-

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tained from Calbiochem AG, Switzerland. Salicylic acid A-grade was obtained from the Baker Chemical Company.

Sample preparation

Kaolinite pastes of a specified water content were prepared, sonicated for several seconds to enhance dispersion and homogeneity, and stored at 5°C overnight. In all of the treatments reported herein the initial water content of the paste was 200% by weight [on the basis of oven-dry (110°C) matter]. Thin and rather uniform films of known weights and areas were prepared by smearing the paste on the inner wall of preweighed Pyrex vials with a spatula, and then spinning the vial to produce a uniform film. The initial average film thickness was calculated by measuring film weight and area and assuming a kaolinite density of 2.65 g/cm³ (Grim, 1968) and, thus, a bulk density of 1.26 g/cm³ for the wet film. Hand-grinding of air-dry kaolinite powders was carried out using a mortar and pestle for about 1 min.

Measurement technique

A Packard Tri-Carb liquid scintillation spectrometer, model 3320, was used for the luminescence measurements (Coyne *et al.*, 1980). Each sample was temperature-equilibrated in the instrument chamber, and the chamber was then opened for several seconds in partial darkness. A small amount of Drierite ($CaSO_4$) was placed in the bottom of the chamber, taking care not to touch the clay film. Photon counts of the vial were then made repeatedly over time intervals of either 100 or 120 sec until the peak of photon emission rate declined to the background level (usually several hours). The total number of detected photons was calculated by subtracting the background count rate (for more details, see Coyne *et al.*, 1981). A crude determination of the wavelength distribution of the light emission was made by wrapping the exterior surface of the counting vial in a flexible, plastic-coated, gel color filter before inserting the vial in the scintillation counter. Wrattan gel filters No. 8 and No. 2a supplied by Eastman Kodak Company were used to absorb varying portions of the ultraviolet spectral region.

RESULTS AND DISCUSSION

Figure 1 shows the total number of photons counted per film unit area during the drying-out period of each sample as a function of average film thickness. Each point represents a different sample preparation. With thinner films, <30 μm thick, the relationship between thickness and total count was more or less linear. For the thicker films, a deviation from linearity is observed. The explanation of this deviation requires further study, and, while theory would suggest saturation, experimental constraints complicate the measurement of light output from these thicker films. The relationship be-
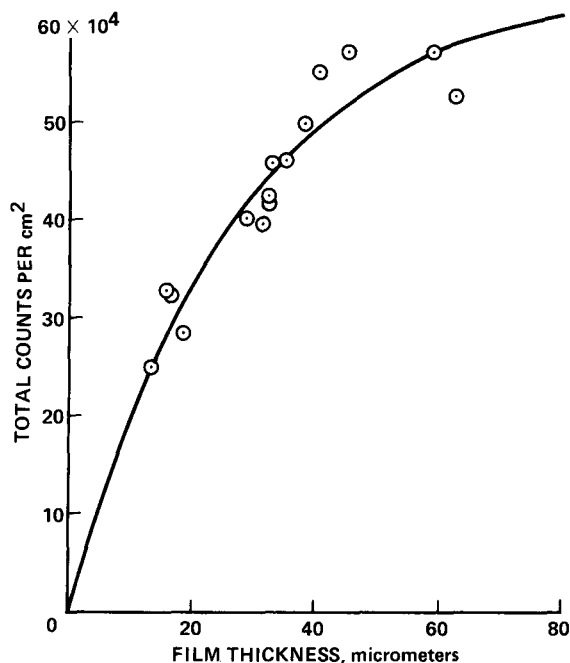

Figure 1.   Total count of the delayed peak as a function of average film thickness.

tween average film thickness and the time elapsed from commencement of dehydration to maximum count rate (Figure 2) seems to be linear over the range of film thickness studied, with the extrapolated straight line intersecting the axis at average film thickness of 8.7 μm.

In a separate experiment, the water content of the film, as determined gravimetrically 1 min after reaching the maximum count rate, was about 43% (oven-dry basis). The water content after about 95% of the photon output was emitted was found separately to be about 25%, and the final water content of clay films dehydrated for 1 day over Drierite was 10%. The dependence of water content at maximum emission rate on film thickness was not determined. Obviously the dehydration continued during the time of delayed peak formation. Assuming a constant evaporation rate, the average water content of the entire film, when the rising count rate was first observed, was about 60%. Presumably, photon emission was obtained over a certain critical, relatively low range of water contents; thus, the kinetics of photon emission must be closely associated with the kinetics of film dehydration. The range of water content in which the emittance takes place was between about 60% and 25%; however, because neither the dependence of water content on film thickness at maximum emission rate, nor the lower limit of initial wetness of the film that can produce light was determined, no firm conclusion can be reached about the
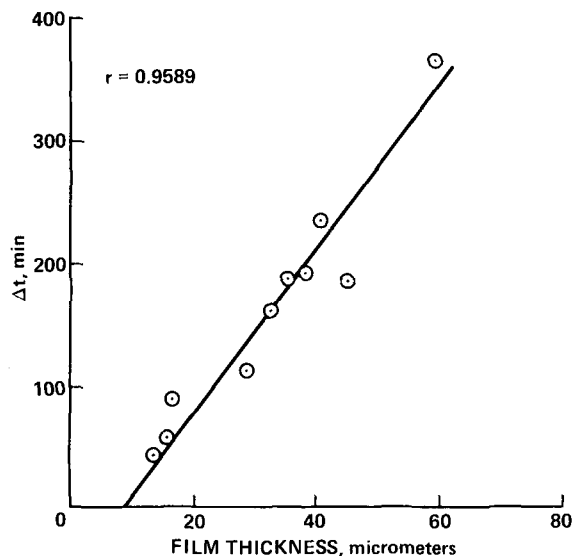
Figure 2.   Time elapsed from commencement of dehydration to maximum count rate (Δt) as a function of initial average film thickness.

exact range of water content for the emitting portion of the film.

The water content of the film should have been different between the side bordering the vial wall and the side exposed to evaporation. It is possible that the critical water content was obtained locally in the form of a transition zone and was not represented by the average water content; however, the extent of this localization and the pattern of the transition zone between the two sides cannot be evaluated at the present stage. The existence of such a transition zone between the wet and dry sides of the film during DIL implies the possibility of microcracks in that zone. Moreover, photon emission may well be associated with the formation of these microcracks and their propagation inside the film during the dehydration period.

Visual examination of drying kaolinite films revealed that an apparently dry layer formed on the film surface in a matter of less than 1 min. The formation of such a dry layer would have allowed photon emission to have taken place at the very beginning of the dehydration process.

The normal pattern of photon count rate vs. dehydration time in the kaolinite under study is an initial count rate somewhat higher than the background, which decays slowly and reaches a more or less constant value until the delayed peak starts to appear (Coyne et al., 1980; see also Figure 3a). The initial photon emission is normally less than 1% of the total count of the delayed peak and can be explained partially by artifacts such as the effect of light on the plastic caps of the vial, or the buildup of electrostatic charge on the vial (Cor-

mier et al., 1973). If the photons are emitted during the first moments of dehydration, a considerable part of this emittance may not be detected by the photomultiplier because of self-absorption by the film itself and the delay between the addition of the desiccant and the initiation of counting.

When the kaolinite film was applied to the external wall of a small cylinder placed in the counting vial, the self absorbance of emitted photons by the thin dry layer on the film was reduced. Indeed, such a preliminary experiment showed that the emittance during the first few minutes of dehydration increased from less than 1% to more than 10% of the total count of the delayed peak. These observations can be interpreted as an indication of the formation of a thin dry layer on the film surface. An initial, monotonically decaying emission independent of dehydration was produced by grinding or irradiation (Coyne et al., 1981). This monotonically decaying component of the emission also would be reabsorbed by the clay film. Therefore, this increased initial emittance, achieved by reversing the position of the drying front with respect to the bulk clay layer and the phototube, cannot be unambiguously attributed to more efficient collection of light produced by the drying of the initial layer. As a matter of fact, on several occasions when a physical contact was formed between the paste and the desiccant, the initial count rate increased substantially; presumably caused by the fast initial dehydration that was associated with the contact between the desiccant and the paste.

The formation of a thin, dry layer in the absence of a physical contact between the film and the desiccant may be inferred from Figure 2, where the linear regression line intersects the x-axis at a film thickness of 8.7 μm. It is tempting to interpret this relationship as an indication that at a certain finite film thickness no delayed peak will be produced; however, such a thin film might have been partially dried before the measurement was initiated. To determine the exact thickness and kinetics of formation of the dry layer, more experiments will be required.

The velocity at which the moisture-content profile further developed inside the film depended on the balance between evaporation rate, on the one hand, and the water flux across the film toward the dry end of the film, on the other. Presumably, soon after the establishment of the dry zone at the film surface the evaporation rate was somewhat reduced. At this time the water conductivity across the film should be relatively high, and water flux toward the drying zone should be high enough to delay the attainment of the above-mentioned critical water content. This time lag could have corresponded to the delay time before the appearance of the peak and is roughly proportional to Δt, Figure 2. As evaporation continued, the critical water content was reached inside the film, photon emission started again, and the delayed peak started to show up.

Several desiccants, e.g., P_2O_5 and silica gel, were effective in producing DIL, but no comparison between them was made.

The presence of a thin dry layer on the external side of the film implies the existence of a moisture gradient across the film. The profile of this gradient could have two limiting cases depending on the balance of three factors controlling moisture flow: evaporation (gas phase transport), capillary motion, and diffusion (liquid phase transport). The two limiting cases are: (1) advancement of a moisture front through the film with continuous emission of light from a limited region throughout the drying process; and (2) a more uniform drying to an average moisture content, resulting in delayed emission from the bulk film over only a limited part of the total drying time. Should extensive microcracking occur, the actual profile might be rather more complex than those of either of the two limiting cases. The present data do not clearly discriminate between these limiting cases. To understand the details of the relationship between light emission and the moisture profile of the film, several factors must be considered, including (1) the elapsed time before the initiation of the delayed peak; (2) the relationship between this elapsed time and the thickness of the film (see Figure 1); (3) the duration of the delayed peak; (4) the spectral distribution of the initially released and the delayed light as a function of the different path lengths of these components of the emitted light through the drying film; and (5) the absorption/reflection characteristics of the drying clay film. A clear definition of the relationship is necessary to understand the physical process leading to the release of light and to determine precisely the critical moisture content at which light is produced.

It should be noted that during a photon-emission process the path length and possibly the optical properties of a film will change continuously. Thus, photons that are emitted from the side of a film exposed to the desiccant will have a longer path through the kaolinite film toward the photomultiplier detector. As a result, they will produce fewer counts compared with the same photon flux that is emitted from the film at the side of the vial wall. That is to say, the kaolinite film serves as a crude optical filter for the emitted light, inasmuch as a consistent feature of kaolinite is decreasing reflectance and increasing absorption coefficient with decreasing wavelength in the visible range of the spectrum (Lindberg and Smith, 1972, 1974). It is thus obvious that in addition to the evaporation rate and water mobility discussed above, kinetics of the photon release would reflect also the effect of different path lengths of the transmitted light during the emittance period. The details of this analysis will not be elaborated here, but it should be noted that the empirical relationship presented in Figure 1 is reproducible and valid for films of thickness where a linear output is observed.

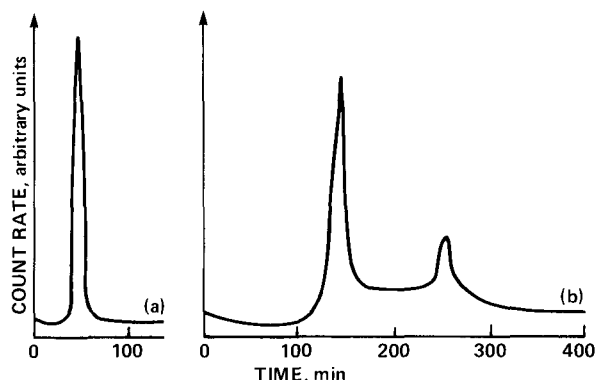In addition to detailing the changes in optical prop-

Figure 3. Dehydration-induced luminescence of Fisher kaolinite: (a) untreated kaolinite; (b) kaolinite ground 5 days before measurement.

erties and the kinetics of the development of the critical moisture content, a thorough modeling of the shape of the curve of photon output vs. time must consider the origin of the monotonically emitted portion of the light output. Although this light could derive from nonuniformities in drying, as elaborated above, it may result from any number of dehydration-independent radiative processes.

Calibration of the relationship between total photon count and film thickness for a given clay (Figure 1) is a prerequisite to quantitative interpretation, because it is practically impossible to prepare two films with the same area and film thickness in order to determine the effect of various treatments on the DIL.

Grinding

Coyne *et al.* (1981) noted that certain kaolinite samples, from different sources and of different particle size fractions, exhibited more than one emission peak and a rather prolonged photon emission period. Because all preparation procedures and size fractionation of kaolinite powders included grinding, some of these irregularities in photon-emission characteristics were perhaps related to prolonged triboluminescence (Lahav *et al.*, 1982).

To study the effect of grinding, a Fisher kaolinite paste was prepared from a freshly ground powder and films were prepared as described above. Using the relationship between total photon count and average film thickness shown in Figure 1, the effect of grinding on total count was measured. A comparison of the time profile of light output from a ground and an unground sample of Fisher kaolinite is shown in Figure 3a. For this clay, the ground sample differed from the unground one in that: (1) the overall photon yield was increased (not shown); (2) two delayed peaks were produced by the ground sample, compared with only one in the untreated sample; and (3) the emission tailed off markedly after the delayed peaks. The Fisher kaolinite stud-

ied here differed from Mesa Alta kaolin previously examined (Coyne *et al.,* 1981) in that no significant increase was produced in the initial monotonically decaying photon release by fresh grinding (this effect not shown).

The effects of grinding on both the monotonically decaying and the delayed portion of the DIL curves in these different kaolins bears a tentative relationship to results obtained in which the photon yield was enhanced by gamma irradiation (Coyne *et al.,* 1981). It appears that energizing the system by either mechanical stress or ionizing radiation affected both the monotonic and the delayed photon output. The effect of the mild grinding on particle size distribution was not determined.

The multiple peaks produced by the ground Fisher kaolinite more likely resulted from the population of distinctly different trapping sites rather than from any dramatic change in the particle size distribution caused by further mild grinding of the already ground kaolinite. Should it be possible to establish the mechanisms involved in the grinding effect, DIL may·be used for determining the history of mechanical stress of the clay. The Fisher kaolinite used here apparently aged in our laboratory sufficiently (more than 6 yr) to show a smooth and rather symmetric peak of DIL, and its recent history of mechanical stress resulted in readily apparent changes in DIL, as exemplified in Figure 3.

From the fact that grinding of the Mesa Alta kaolinite enhanced the monotonic component of the output (Coyne *et al.,* 1981) and that grinding of the Fisher kaolinite enhanced mainly the delayed peak, grinding appears both to effect solvent-independent luminescence and to affect the population of trapped states effecting DIL.

Effect of added fluorescent compounds

The wavelength distribution and photon yield of the emitted light are of great interest, not only because they are clues to the nature of the molecular state responsible for the emission, but also because of the possible relationship between emitted photons and energy available for promotion of prebiotic organic reactions (Coyne *et al.,* 1980). To assess the potential clinical significance of the available energy, it is necessary to determine the yield of these photons, their energy, and the modes by which energy in the clay can be transferred to neighboring organic molecules.

Direct quantitation of the photon yield is complicated by a number of intrinsic spectroscopic and extrinsic optical factors. Light absorbance of kaolinite is typified by absorption in the near-UV and UV (Karickoff and Bailey, 1973; Lindberg and Smith, 1974). Thus, DIL emitted in this spectral range will be substantially reabsorbed by the kaolinite film or by the containing vial. Tryptophan and salicylic acids were used as molecular probes to shift the frequency of the
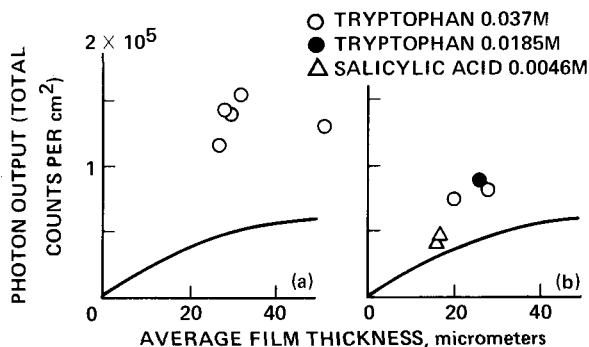

Figure 4. Effect of grinding (a) and tryptophan and salicylic acid addition (b) on total photon count of Fisher kaolinite paste in dehydration-induced luminescence process. The experimental points of the treatment are compared to the experimental relationship of total count vs. average film thickness shown in Figure 1 (smooth line).

emitted light to longer wavelengths to diminish problems of photon loss, by reabsorption, scattering, and internal reflection. The excitation and fluorescence maxima of tryptophan are 287 nm and 348 nm, respectively (Udenfriend, 1962). Salicylic acid has its corresponding maxima at 297 nm and 404 nm, respectively (Udenfriend, 1962). The two fluorescent molecules were presumably dispersed throughout the available liquid volume, with some adsorption on the clay particles. The measured total photon count increased in both cases (Figure 4b). The transfer of energy to the fluorescent probes may have been emission reabsorption, but could occur by nonradiative resonance transfer as well (Udenfriend, 1962). The relatively small effect of salicylic acid may be ascribed to one of several factors, including low concentration (see Figure 4) or the effect of pH on the quantum yield and fluorescence maximum (Udenfriend, 1962). This effect is under more extensive investigation.

Measurement of the wavelength distribution of the luminescence by optical filters

The integrated photon count rate under the delayed peak was normalized to unit weight of kaolinite film in the linear range of total count versus film thickness (Figure 1). Values for the normalized total count rate of the delayed peaks were compared for samples with no color filter and samples in which Kodak Wrattan gel filters Nos. 8 or 2a intervened between the sample and the photomultiplier tubes (Table 1).

Examination of the integrated count rate in the first 20 min of the dehydration process yields a preliminary indication that the monotonically decaying region of the emission process is essentially unaffected by any of the filters and thus may occur at longer wavelengths than that of the delayed peak.

The results show that 97% of the emitted light is in

Table 1. Effect of color filters on dehydration-induced light output from kaolin.

Filter	UV cutoff λ (od = 2) (nm)	Photon output of 1 g clay, $\times 10^{-6}$	σ_m^1 $\times 10^{-6}$	Light absorbed (%)
None	—	9.4	1.4 (n = 5)	—
Kodak No. 8	460	0.30	0.032 (n = 2)	97
Kodak No. 2a	410	2.5	0.20 (n = 2)	73

Note: The Student t-test applied to the above data indicates that any of the reported means is significantly different from any of the others to a confidence limit of >99%. From data published by Eastman Kodak on the absorbance characteristics of Wrattan filters, it was determined that ~97% of the emitted light is of wavelength <460 nm and ~73% is of wavelength <410 nm.

^{1} σ_m is the calculated standard deviation of the mean of the measured population. It is related to the standard deviation of the sample population, σ_p, by $\sigma_m = \sigma_p/\sqrt{n}$ where n is the number of replicate measurements. σ_m is used as defined in Brewer *et al.* (1974).

the wavelength range below 460 nm, and that 75% of this emission is in the wavelength range below 410 nm. This observation corroborates the results of the experiments using molecular probes.

In conclusion, (1) the photon output of dehydration-induced luminescence in Fisher kaolinite pastes is reproducible and is related experimentally to average film thickness for an appreciable range of film thicknesses; (2) mechanical stress in the form of grinding increases the photon output of this process and brings about extensive changes in the emission kinetics; (3) a direct check of the emission wavelength dependence (by using color filters) indicates that roughly 75% of the emission occurs in the wavelength range below 410 nm; and (4) incorporation of fluorescent molecules into the kaolinite paste increases the photon output and may indicate the transfer of ultraviolet photons to the fluorescent probe.

ACKNOWLEDGMENTS

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Резюме—Люминесценция, вызываемая дегидратацией (ЛВД) т.е. эмиссия света глиновой пасты во время дегидратации, определялась опытным путем на коллоидальном каолините. Взаимодействие между полным счетом фотонов излучаемого света и толщиной фильма является линейным в диапазоне до величины толщины равной 30 μm. Величина эмиссии фотонов была определена для критического диапазона содержаиия воды (25–60%) в глине после сушки в печи, а кинетика эмиссии фотонов предполагалась быть близко связанной с кинетикой дегидратации фильма. Неустановлено происходила ли сушка во всей массе или путем движущегося фронта, но в каждом случае формирование тонкого сухого фильма на поверхности контакта с воздухом предшествовало этому процессу. Результатом растирания каолинита перед подготовкой пасты в течение несколько минут при помощи ступки и пестика было увеличение полной эмиссии фотонов по сравнению с величиной для нерастертого каолинита и формирование более, чем одного пика эмиссии, а также продолжение эмиссии света. Этот эффект на кинетику лучеиспускательной способности света, наблюдался примерно в течение двух месяцев после применения механического напряжения. Это указывает на способ выявления истории механического напряжения в глине.

Сделано оценку спектральных характеристик излучаемого света при помощи оптического фильтра и путем включения в каолинитовую пасту триптофана и салициловой кислоты, где они действовали как флуоресцентные образцы. Последняя техника перемещала частоту излучаемого каолинитом света из ультрафиолетовой в видимую область, в которой свет был менее эффективно реабсорбирован. Первый метод указывал на то, что длины волны 97% количества излучаемого света были <460 нм и что 75% количества света имело длину волны <410 нм. Второй метод показал, что полная интенсивность ЛВД увеличивалась в присутствии молекул флуоресценции, указывая на то, что лучеиспускательная способность находилась в ультрафиолетовой области. [E.G.]

Resümee—Durch Dehydratation induzierte Lumineszenz (DIL), die Lichtemission von Tonpasten aufgrund Dehydratation, wurde experimentell für einen kolloidalen Kaolinit charakterisiert. Die Beziehung zwischen der gesamten Photonenzahl des emittierten Lichtes und der Filmdicke ist bis zu einer Dicke von 30 μm linear. Die Photonenemission wurde für einen kritischen Bereich des Wassergehaltes (25–60%) von Ofen-getrocknetem Ton gemessen, und es wurde angenommen, daß die Kinetik der Photonenemission sehr eng mit der Kinetik der Filmdehydratation zusammenhängt. Ob die Trocknung im ganzen oder über eine sich bewegende Front erfolgte, war unbestimmt, aber in jedem Fall ging ihr die Bildung eines dünnen trockenen Films an der Grenzfläche mit der Atmosphäre voraus. Das Mahlen des Kaolinites mit Mörser und Pistill während einiger Minuten vor der Herstellung der Paste führte zu einer generellen Zunahme der Photonenemission im Vergleich zum ungemahlenen Kaolinit und zur Bildung von mehr als einem Emissionspeak, sowie zu einer Verlängerung der Lichtemission. Diese Auswirkung auf die Kinetik der Lichtemission wurde bis zu über zwei Monaten nach der Anwendung der mechanischen Beanspruchung beobachtet und bedeutet eine Methode, die Geschichte der mechanischen Beanspruchung eines Tons aufzudecken.

Es wurde eine Schätzung der spektralen Charakteristike des emittierten Lichtes durchgeführt, indem optische Filter benutzt wurden und indem Tryptophan und Salicylsäure in die Kaolinitpaste eingearbeitet wurden, wo sie als Fluoreszenzmittel wirkten. Die letztere Methode verschob die Frequenz des vom Kaolinit emittierten Lichtes vom Ultraviolett in den sichtbaren Bereich, wo es weniger wirksam readsorbiert wurde. Die erste Methode zeigte, daß die Wellenlängen von 97% des emittierten Lichtes <460 nm waren, und das 75% des Lichtes Wellenlängen <410 nm hatten. Die zweite Methode zeigte, daß die Gesamtintensität des DIL bei der Anwesenheit von Fluoreszenzmolekülen zunahm, was darauf hindeutet, daß die Emissionsfähigkeit im ultravioletten Bereich liegt. [U.W.]

Résumé—La luminescence induite par déshydration (DIL), l'émission de lumière d'une pâte d'argile lors de la déshydration, a été caractérisée expérimentalement pour une kaolinite colloidale. La relation entre le compte total de photons de lumière émise, et l'épaisseur du film est linéaire jusqu'à une épaisseur de 30 μm. L'émission de photons a été obtenue pour une gamme critique de teneurs en eau (25–60%) de l'argile sechée au four, et les kinétiques d'émission de photons ont été présumées être associées de manière proche avec les kinétiques de déshydration de film. On n'a pas déterminé si le sechage s'est produit à travers la masse ou via un front avançant, mais dans les deux modes, il a été précédé par la formation d'un film fin et sec à l'interface avec l'atmosphère. Lorsqu'on mout la kaolinite pendant plusieurs minutes à l'aide de mortier et pilon avant la préparation de pâte, le résultat est un accroissement général d'émission de photons comparé à la kaolinite non-moulue, et la formation de plus d'un sommet d'émission, ainsi que la prolongation de l'émission de lumière. Cet effet sur les kinétiques d'émission de lumière a été observé pendant à peu près deux mois après l'application du stress mécanique et suggère un moyen de détection de l'histoire de stress mécanique d'une argile. On a estimé les caractéristiques spectrales de la lumière émise en employant des filtres optiques et en incorporant de la tryptophane et de l'acide salicylique dans la pâte kaolinite où elle se sont comportées comme des probes fluorescentes. Cette dernière technique a deplacé la fréquence de la lumière émise par la kaolinite de la gamme ultraviolette à la gamme visible où elle était moins effectivement réabsorbée. La première méthode a montré que les longueurs d'onde de 97% de lumière émise étaient <460 nm et 75% de la lumière avait des longueurs d'onde <410 nm. La seconde méthode a montré que l'intensité totale de DIL a augmenté en la présence de molécules de fluorescence, suggérant que l'émission était dans la gamme ultraviolette. [D.J.]