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DAT33   LUMINESCENCE EMISSIONS DURING FIRST STEP (150-400°C) NON-ISOTHERMAL DEHYDROXYLATION OF KAOLINITE

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Thermoluminescence (TL) measurements were recorded from a clean sample of natural kaolinite ($Al_2Si_2O_5(OH)_4$) of less than 4 μm in size, from room temperature to 500°C (non-isothermal dehydroxylation). A filter (FIB002) was placed in an automated RISØ TL system, model TL DA-12, to record light emissions in the UV-blue region with a heating rate of 5°Cs[-1]. The TL glow curve fits exactly the first thermal step (150-400°C) of the dehydroxylation process. An original glow curve analysis program was refined to analyse the TL glow curve; the main peak occurs at 285°C and has an activation energy of 1.13 eV. This first thermal step, which represents 70% of the dehydroxylation of kaolinite, produces a loss of intensity of the hydroxyl bands' emission spectra (3550-3750 cm^{-1}) in Fourier transformed infra-red spectroscopy (FTIR), following inhomogeneous mechanisms. This loss of OH⁻ can also be detected by X-ray diffraction (XRD). It is well known that isothermal dehydroxylation of kaolinite and other clay minerals produces thermo-induced mechanoluminescence emissions. The use of TL techniques to study the dehydroxylation of kaolinite is faster and more sensitive than XRD and FTIR methods.

DAT34   ENERGY DEPENDENCE OF EPR SIGNAL IN SYNTHETIC AND BIOLOGICAL HYDROXYAPATITE IRRADIATED WITH PHOTONS

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Radiation Electron Spin Resonance (ESR) has been widely used in ionizing dosimetry. Its applications include radioactive accident and retrospective dosimetry, accelerator and radioactive source dosimetry, reference dosimetry, identification of irradiated foods and geological and archaeological dating. Carbonated hydroxyapatite, the main component of the mineral part of the calcified tissue, is one of the most promising ESR dose indicator. Hydroxyapatite dose indicators are carbonate-derive radicals, CO_2^- and CO_3^{3-} induced from the decomposition of CO_3^{3-} groups. In this work we study the dose-response of CO_2^- radicals induced in synthetic carbonated apatite by photon irradiation as a function of the energy in the range of 50 keV up to 1.33 MeV. The energy dependence of the dose indicator radicals in synthetic apatite is compared with the one verified in apatite from calcified apatite. The potential of synthetic carbonated apatite for low energy photons dosimetry using ESR is discussed.

DAT35   ESR SIGNAL SATURATION AND COMPETITION IN TOOTH ENAMEL

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Synchrotron irradiation experiments have been conducted to study the radiation response of ESR signals in modern and fossil tooth enamel to synchrotron radiation between 8 keV and 25 keV. Samples of tooth enamel were exposed to the broad-band synchrotron beam. No further increase in either the peak-to-peak amplitude or the three deconvoluted component signals is observed after the initial five minutes of exposure, indicating that all signals are fully saturated. Furthermore, the fossil and the modern enamel samples used showed the same saturation values. As these are the saturation concentrations, the results can be interpreted as the number of receptor traps present in tooth enamel. The reproducibility across samples suggests that the trap concentrations may be universally constant. Samples

THERMOLUMINESCENCE OF KAOLINITE

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Abstract — Natural kaolinite (size < 5 μm) shows strong thermoluminescence (TL) which could be linked with water loss (~120°C peak) and dehydroxylation changes (~300°C peak). After 100 min of dehydration at room temperature, kaolinite displays microcracks, isothermal luminescence emissions and the starting point of a desiccation plateau. These phenomena were tested through 34 X ray diffractograms measuring the area increase of the (001) peak each 3 min. The DTA-TG analyses of natural kaolinite and the FTIR bands at 3696, 3668, 3652 and 3619 wave-number.cm^{-1} of preheated kaolinite show water loss, dehydroxylation and above 450°C, metakaolinite formation. TL glow curves after β irradiation of preheated kaolinite drop from 270 to 345°C, the maximum TL peak of kaolinite is around 300°C. These data fit well with the dehydration-related proton conductivity in kaolinite as follows: below 275°C the activation energy of kaolinite is 7–8 kcal.mol^{-1}, at 300°C the kaolinite produces the largest photon emission, later, between 300–450°C, the activation energy is 18–20 kcal.mol^{-1}.

INTRODUCTION

Natural kaolinite displays thermoluminescence (TL) around 300°C (i.e. 14,000 arbitrary units) when recorded in a Risø TL reader. During the thermal interval of TL measurements (RT to 500°C) the kaolinite ($Al_2Si_2O_5(OH)_4$) structure suffer water loss and initial dehydroxylation processes which must be linked with the light emissions. During the dehydroxylation processes of kaolinite the original ordering is maintained along the a- and b- axes but disappears along the c-axis. The kaolinite lattice is composed of a sheet of SiO_4 tetrahedra in hexagonal array with bases roughly coplanar, bases and apices pointing in one direction and a gibbsite sheet, whose base is formed by apical oxygens of the SiO_4 sheet together with $(OH)^-$ ions positioned over the centres of the hexagons of the lower layer, and in which two-thirds of the octahedral sites are occupied by Al ions. The coordination of the aluminium changes from octahedral to tetrahedral during the dehydration reaction: $Al_2Si_2O_5(OH)_4$ (kaolinite) → $Al_2Si_2O_7$ (metakaolinite) + $2H_2O$ (vapour). The reaction takes place by consecutive and total dehydroxylation of the octahedral layers. According to the nuclear magnetic resonance (NMR) studies of Otero-Arean et al[1], the reaction occurs, layer by layer, from 0 to 70% of dehydroxylation. For the dehydroxylation >30% the protons left in the solid are distributed among two ensembles P′ and P″, P″ increasing at the expense of P′ as dehydroxylation increases. P′ is identified with patches of protons still linked to octahedrally coordinated aluminium.

Blue to near UV photons are emitted when a thin layer of an aqueous suspension of kaolinite ($Al_2Si_2O_5(OH)_4$) is dried over a desiccant or by gentle heating to 85°C[2]. Light release can be regenerated by repeated cycles of wetting and drying. Photon emission may well be associated with the formation of microcracks and their propagation inside the film during the dehydration period[3]. The sub-critical crack growth can be due to several competing mechanisms, such as stress corrosion, diffusion, dissolution, ion exchange, or microplasticity. Diffusional properties of minerals are often controlled by the effect of minor amounts of water. The response of minerals to ionising radiation is also influenced by hydrous components[4].

According to Suitch[5], using X ray diffraction, there is no appreciable dehydroxylation in kaolinite in the RT to 325°C range, and once kaolinite is heated above this temperature, the onset of dehydroxylation is shown through the loss in total X ray scattering by the kaolinite phase and the concomitant decrease in the magnitude of the IR absorption for the Al-OH, Si-O, Si-O-Al vibrations and the OH stretch modes. At 455°C to 465°C an amorphous hump, characteristic of the formation of metakaolinite was observed in the X ray diffraction pattern.

The dehydroxylation of kaolinite has been described extensively during the past 70 years by the XRD, DTA-TG, IR, etc., methods. The scarce number of studies concerning luminescence of kaolinite is due to: (a) the difficulties in explaining the TL emissions of kaolinite using the theory of valence conduction band, (b) the deficient results in geological dating of loess materials, (c) the damages in photomultiplier tubes from the water ejection from kaolinite, and (d) the recent use of automated TL systems. However, thermoluminescence (in Risø systems) is a sensitive technique up to 500°C which allows TL emissions in kaolin minerals to be detected. The TL results of kaolinite <5 μm here presented basically agree with the previous data following the kinetics of thermal decomposition of claystones which depends on the geometry of the crystal lattice, chemical bonds, grain size, crystal morphology, defects, pressure of gaseous products, specific reactions, etc.

EXPERIMENTAL

Measurements (TL, DRX, FTIR, DTA-TG) were carried out using natural white and clean natural kaolinite samples taken from the final overflow (sized <5 μm) of the industrial hydrocyclone of the Caosil Company (Poveda de la Sierra, Guadalajara, Spain). The kaolinite lattices at room temperature (RT) were tested by X ray diffraction using a Philips PW 1710 diffractometer with Cu Kα radiation. The patterns were obtained by step-scanning from 2° to 64°, 2θ in steps of 0.020° with a count of 6 s per step. Different lamps (12 v. halogen, 230 v. infrared, etc.) were fitted into the X ray chamber to obtain continuous structural measurements (areas of 001 peak every 3 min) whilst the sample was undergoing different irradiation temperature conditions (from room temperature to 130°C). All experiments were carried out in air atmosphere.

The TL analyses were done by linear heating at 5°C.s^{-1} up to 500°C in N_2 gas using an automated Risø TL system model TL DA-12 developed by Risø National Laboratory. Signals were detected using a blue filter (FIB002) situated in front of an EMI 9635Q A photomultiplier tube (wavelength peaked at 400 nm +25,−0; FWHM at 80 ± 16 nm and 60% of peak transmittance (minimum)). Additional TL determinations were performed to observe the effects of β-irradiation exposure (^{90}Sr/^{90}Y source with a dose rate of 0.027 Gy.s^{-1}) on the light emissions of the natural and preheated kaolinite. Four aliquots of 5.0 ± 0.1 mg each of <5 μm kaolinite were used for each measurement.

FTIR spectra were recorded using a FTIR spectrometer (Perkin-Elmer 1720X) with a resolution of 2 cm^{-1}. For each spectrum a ratio of 10 sample scans and 10 background scans were used. The FTIR measurements were carried out adding one drop of Nujol between two KBr crystals using a microburette. The spectra were recorded between 4000 to 400 wavenumber.cm^{-1} using an HeNe laser of 633 nm (<0.4 mW). In addition, several DTA-TG analyses were performed in a simultaneous thermal analysis STA-409 Netzsch at 19°C.min^{-1}.

RESULTS AND DISCUSSION

Firstly, clean white natural kaolinite samples were analysed by X ray diffraction (XRD) and differential-thermogravimetric (DTA-TG) methods. The semiquantitative analysis of the disorganised kaolinite (powder) shows approximately a composition of 86% kaolinite, 13% quartz and 1% moscovite using as reflection factors: kaolinite 2, moscovite 2.8 and quartz 0.2.

DTA-TG data at 5°C.min^{-1} also confirm the presence of 87% of phyllosilicate in the sample, water loss and possible dehydroxylation. However, this technique does not offer brilliant results from RT to 400°C. This mineralogical composition is common for a sedimentary kaolinite for marketable coating uses. The first dehydration (water loss) of kaolinite was observed (Figure 1(a)) testing the area of the (001) peak, by a set of 34 diffractograms, which were obtained using a self-made X ray program (SIRDAT by Martin-Ramos). Additional sets of diffractograms whilst the sample was irradiated with halogen, UV and IR lamps (from 50°C to 130°C of temperature measured in sample) only show faster desiccation processes. According to different routines, the starting point of the desiccation plateau was obtained from 90 to 110 min. This agrees with the photon emission at this desiccation time[3]. In addition, both cases are linked with the formation of microcracks. The XRD procedure was also used to detect the well-known kao-
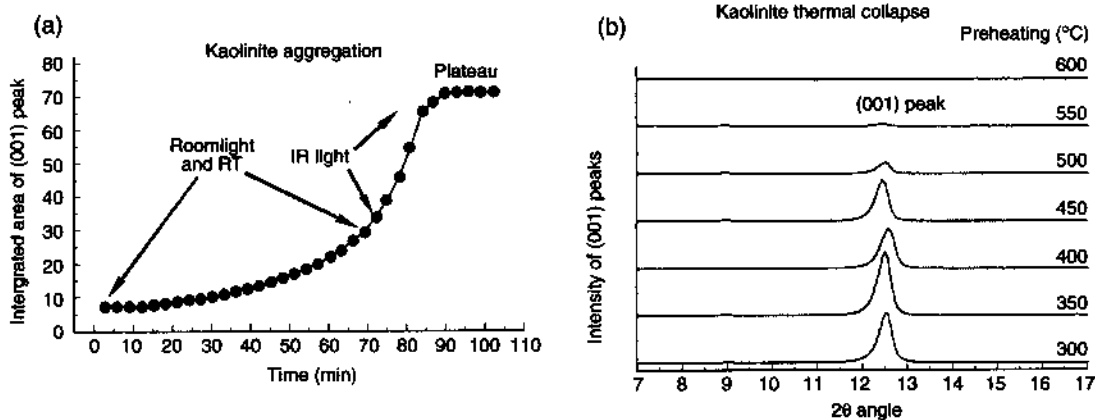

Figure 1. X ray diffraction (XRD) measurements of the (001) peak of a natural sedimentary kaolinite from Poveda (Guadalajara, Spain). (a) XRD 3 min steps during a kaolinite desiccation process at room temperature. The kaolinite basal planes deposit during the water loss and the (001) peak increases in intensity up to the desiccation plateau. Note how the IR lamp speeds up the desiccation process. (b) Preheated kaolinites showing the kaolinite > metakaolinite reaction by thermal collapse of the XDR (001) peak.

linite>metakaolinite transformation using preheated samples from 300°C to 600°C (Figure 1(b)).

Preheated aliquots of <5 μm kaolinite (at 100, 270, 310, 345, 380, 415, 450°C) were analysed by FTIR and TL techniques (Figures 2 and 3). The evolution of the TL FTIR curves display some kaolinite dehydroxylation processes. The FTIR curves (Figure 2) could be classified in three groups:

(1) Preheated RT, 100, and 270°C samples, which show a clear FTIR curve evolution from water loss.
(2) Preheated 310, 345, 380, and 415°C samples where the 3668 band disappears and the others (3696, 3652 and 3619 wave-numbers cm^{-1}) decrease. These observations agree with the XY graph temperature against wave-number.cm^{-1} of the IR bands (3686, 3664, 3649 and 3620 cm^{-1}) of Frost and Vassallo[6] which shows a depletion in the 275–325°C gap which could correspond with these experimental TL glow curve maxima.
(3) The loss of signal due to the OH stretching modes between 3600 to 3800 cm^{-1} intensities of the hydroxyl bands over the temperature from 400°C to 540°C corresponds with the kaolinite-metakaolinite transformations (also seen by XRD, Figure 1(b)). The 270–345°C changes of the kaolinite are most visible using photonic techniques, e.g. the TL glow curves of preheated kaolinites from 270 to 345°C show the largest dip of intensity (~6000 arbitrary units) as shown in Figure 3(a).

A new set of TL determinations were perfomed using the same set of aliquot preheated samples after the former TL measurements (a second heating up to 500°C) and storage at RT. The result was new regenerated TL as shown in Figure 3(b). This new TL appears at differ-
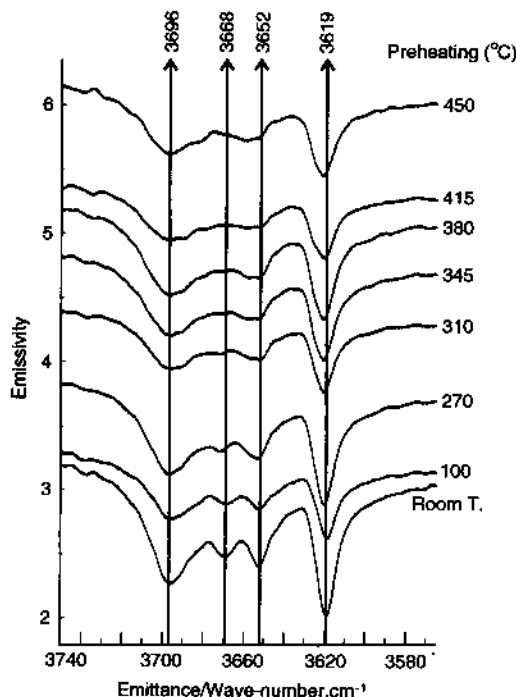

Figure 2. Fourier transformed IR (FTIR) measurements of preheated kaolinite from Poveda (Guadalajara, Spain). Note the three groups of FTIR curves: RT-270°C showing water loss, 310–415°C dehydroxylation changes and the metakaolinite formation above 450°C.
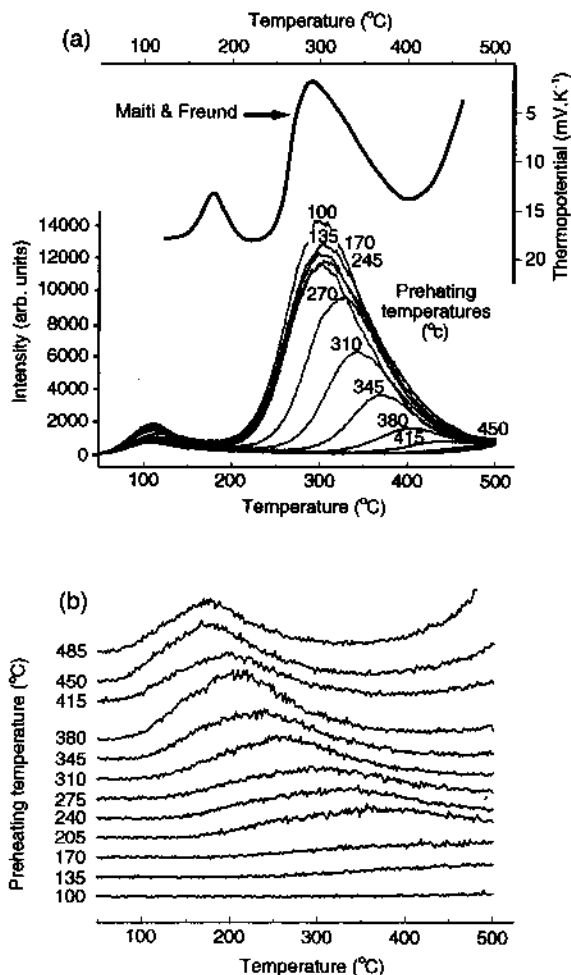

Figure 3. Thermoluminescence analyses after irradiation (5 Gy) of preheated kaolinite from Poveda (Guadalajara, Spain). (a) First set of TL measurements of preheated samples, natural kaolinite displays two TL peaks: 120°C (small) and 300°C (large). Note that the thermopotential curve of Maiti and Freund[7] fits (inversely) with the TL signal. TL and electrical conductivity are linked. (b) Second TL measurements using the same set of aliquot samples which had previously been preheated + 5 Gy + 500°C + moisture at RT. They were subsequently preheated + 5 Gy again. A new regenerated TL is displayed.

ent temperatures with a very different evolution of glow curves, Conversely, higher preheating produces high TL signals. Two important features must be considered, one is that over 500°C metakaolinite appears which has a different crystalline lattice and second, that these re-pre-heated samples easily rehydrate from environmental humidity.

Finally, the thermopotential curve for kaolinite published by Maiti and Freund[7] fits (inversely) very well with these TL results (Figure 3(a)). This interesting relationship between both signals (TL and electrical conductivity) could explain why kaolinite exhibits marked proton conductivity at pre-dehydration temperatures and also indicates a two-step (above and below ~275°C) defect proton–excess proton conductivity mechanism involving, in succession, two kinds of OH^- in the kaolinite structure: (a) OH^- located within the six-membered ring formed by SiO_4 tetrahedral sheet and (b) a close OH^- array formed by the octahedral sheet.

REFERENCES

1. Otero-Arean, C., Letellier, M., Gerstein, B. C. and Fripiat, J. J. *Protonic Structure of Kaolinite during Dehydroxylation Studied by Proton Nuclear Magnetic Resonance.* Dev. Sedimen. **35**, 73–85 (1982).
2. Coyne, L., Lahav, N. and Lawless, J. G. *Dehydration-induced Luminescence in Clay Minerals.* Nature **292**, 819–821 (1981).
3. Lahav, N., Coyne, L. and Lawless, J. G. *Characterization of Dehydration-induced Luminescence of Kaolinite.* Clays Clay Miner. **33**(3), 207–213 (1985).
4. Aines, R. D. and Rossman, G. R. *Relationships between Radiation Damage and Trace Water in Zircon, Quartz, and Topaz.* Am. Miner. **71**, 1186–1193 (1986).
5. Suitch, P. R. *Mechanism for the Dehydroxylation of Kaolinite, Dickite and Nacrite from Room Temperature to 455°C.* J. Am. Ceram. Soc. **69**(1), 61–65 (1986).
6. Frost, R. L. and Vassallo, A. M. *The Dehydroxylation of the Kaolinite Clay Minerals using Infrared Emission Spectroscopy.* Clays Clay Miner. **44**(5), 635–651 (1996).
7. Maiti, G. C. and Freund, F. *Dehydration-related Proton Conductivity in Kaolinite.* Clay Miner. **16**, 395–413 (1981).