

EFFECT OF ADSORBED IRON ON THERMOLUMINESCENCE AND ELECTRON SPIN RESONANCE SPECTRA OF Ca-Fe-EXCHANGED MONTMORILLONITE

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Abstract—The electron spin resonance (ESR) spectra and the natural and gamma-induced thermoluminescence (TL) glow curves of a series of variably cation-exchanged Fe-Ca-clays prepared from SWy-1 montmorillonite were examined. The ESR signal ($g = 2$) intensity associated with the surface Fe was found to increase linearly with surface Fe content up to a nominal concentration of 50% exchangeable Fe. At >50% exchangeable Fe, no appreciable increase in the signal was noted. The TL intensity decreased linearly with increasing surface Fe up to 50% nominal exchangeable Fe. At >50%, the signal was not appreciably further diminished. The natural TL showed only a high-temperature peak, but irradiation produced an additional low-temperature peak. One month after gamma-irradiation, the integrated TL signal was still 10–100 times higher than that from the non-irradiated material. Thus, (1) surface iron clusters may form above a certain critical Fe concentration; (2) the Fe clusters are probably less effective in quenching TL than are single Fe atoms, implying interaction between surface Fe and the stored energy content of the material; and (3) the electronic energy stored in the material as the result of gamma-irradiation is only slowly dissipated.

Key Words—Electron spin resonance, Iron, Montmorillonite, Surface adsorption, Thermoluminescence.

INTRODUCTION

One of the principal photophysical properties of clay minerals is the capacity for electronic energy storage as evidenced by (1) thermal luminescence (TL) (Seigel *et al.*, 1968; Nishita and Hamilton, 1975; and Lemons and McAtee, 1983); (2) electron spin resonance (ESR); and (3) a variety of room-temperature luminescent phenomena related to dehydration, shock, and shearing which have been recently discovered and partially characterized (Coyne *et al.*, 1981a, 1981b; Lahav *et al.*, 1982; Coyne *et al.*, 1983, 1984; Lahav and Coyne, 1985; Coyne, 1985). This stored energy may alter surface reaction mechanisms and rates. To assess the extent and utility of the stored energy in surface processes of clays, it is paramount to characterize the storage sites and the luminescent centers and to quantify the relationships between stored and emitted photons and between bulk and surface energy levels.

Structural and compositional factors characteristic of the particular clay under examination must be considered to achieve a semiquantitative evaluation of the relationship between luminescence intensity and stored

energy. Among the more important composition-related factors is the quenching of radiative relaxation by intrinsic impurity centers, reabsorption of emitted light, both by intrinsic and by extrinsic impurity centers, and emission of light from extrinsic impurities. Fe is a ubiquitous intrinsic and extrinsic ingredient in clays and can act as a quencher (Leverenz, 1968; Medlin, 1968; Geake *et al.*, 1971); it can both absorb and emit light (Bell *et al.*, 1975). ESR is an appropriate companion technique to use with TL. ESR has been used to monitor ferric iron in clay structural sites (Jones *et al.*, 1974; Hall, 1980b; Komusinski *et al.*, 1981; Pinnavaia, 1979, 1981; McBride *et al.*, 1975a, 1975b); Fe complexes (Aasa, 1970), and solvated Fe ions (Levanon *et al.*, 1968). ESR has been used to detect electronic energy stored as O^- centers near structurally substituted sites (Angel *et al.*, 1974; Jones *et al.*, 1974; Hall, 1980a; Komusinski *et al.*, 1981; Pinnavaia, 1979, 1981) and dimers thereof, i.e., O_2^- (Kathrein *et al.*, 1984).

We report here the effect of variation of surface, i.e., exchangeable and extractable Fe, on the thermolumi-

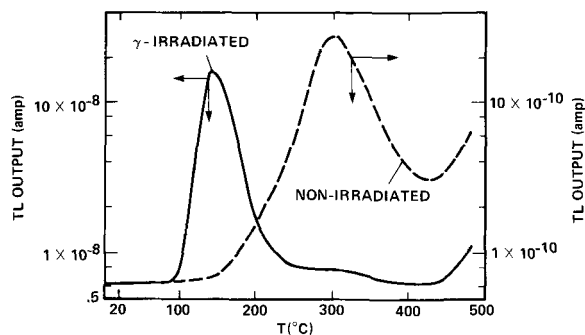


Figure 1. Representative thermoluminescence glow-curves: (a) Non-irradiated SWy-1 Wyoming montmorillonite, 100% Ca exchanged; (b) Same as (a) but after gamma-irradiation (1 Mrad). Note the difference in ordinate scales for two curves.

nescence of montmorillonite in comparison with its effect on the ESR spectra of the clay.

EXPERIMENTAL

Wyoming montmorillonite, SWy-1 from Crook County, Wyoming, obtained from the Source Clay Repository of The Clay Minerals Society (sample was described by van Olphen and Fripiat, 1979), was modified by the quantitative ion-exchange process of Banin (Banin, 1973; Gerstl and Banin, 1980) to contain varying proportions of surface adsorbed Fe and Ca. Samples were prepared with nominal surface Fe contents of 0, 25, 50, 75, and 100% of the cation-exchange capacity (CEC). Ferrous iron was used for the adsorption, but part of it oxidized during clay drying, so that a mixed $\text{Fe}^{3+}/\text{Fe}^{2+}$ clay powder was obtained. The exact content of surface-adsorbed Fe, i.e., exchangeable and acid-extractable, was determined by consecutive treat-

Table 1. Thermoluminescence peak temperatures of Fe-Ca-montmorillonites before and after gamma-irradiation.

Nominal exchangeable Fe ¹	Total exchangeable and acid-extractable surface iron (mmole Fe/g clay)	Temperature of glow-curve maximum (°C)			
		Non-irradiated clays		γ -irradiated clays ²	
0	0.038	304 (± 9) ³	(9) ⁴	136 (± 3)	(4) ⁴
25	0.091	274 (± 7)	(7)	128 (± 5)	(4)
50	0.193	289 (± 8)	(10)	137 (± 7)	(4)
75	0.287	295 (± 5)	(5)	135 (± 6)	(4)
100	0.375	286 (± 11)	(6)	138 (± 3)	(3)

¹ Complementary ion is Ca^{2+} .

² Value reported was that observed 24 hr after the irradiation. Peak temperature for the gamma-irradiated clay increased slightly over the one month in which the reported data were taken.

³ Standard deviation of the population.

⁴ Number of observations used for calculation of average and standard deviation.

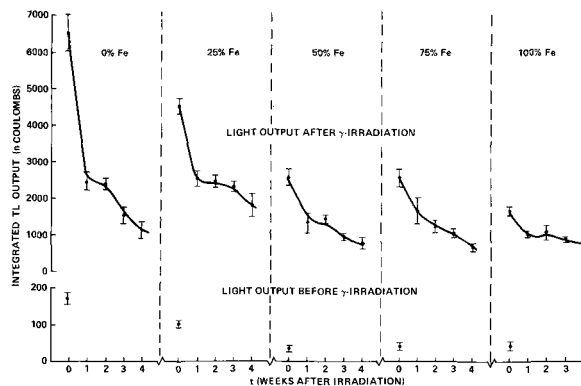


Figure 2. Time decay of thermoluminescence of irradiated, variably Fe-saturated, SWy-1 Wyoming montmorillonite. For comparison, thermoluminescence light-output for the non-irradiated clay is included.

ment with 1 M KCl and 0.5 M HCl, respectively, as detailed by Gerstl and Banin (1980).

Thermoluminescence measurements were made using a Harshaw Model 2000 thermal luminescence detector consisting of a Harshaw 2000A planchette-heating system and an RCA P4272 TA high-gain, low-noise photomultiplier tube with S-11 response and a Harshaw 2000B automatic integrating picoammeter. A few milligrams of the air-dried mineral powder was heated in air from ambient temperature to 480°C in 1 min ($\sim 8^\circ\text{C}/\text{s}$). TL was measured before and after gamma-irradiation in a ^{137}Cs irradiator to a dose of 1 Mrad. TL decay was followed at weekly intervals for one month after the irradiation. Data points shown in Figure 2 represent the average of 3–6 replicate samples. The error bars are the standard deviation from the mean value, i.e., the population, rather than the true, mean.

The ESR spectra were measured over a range of magnetic field intensities from 0–10,000 gauss using a Varian Model E X-band spectrometer. The spectrometer was operated at 9.095 GHz and 0.5 mW of microwave power. The magnetic field was modulated by 1 gauss at 100 kHz.

RESULTS AND DISCUSSION

Typical thermoluminescence glow curves are shown in Figure 1. For the non-irradiated clay the curves are characterized by a broad peak having a maximum at about 290°C, an inflection at 250°C, and a broad asymmetric tail into lower temperature regions. After gamma-irradiation to a dose of 1 Mrad, the 290°C peak appears to be submerged under an asymmetric broad peak of higher intensity and a maximum at 150°C which tails into the high-temperature region. The surface Fe content and temperature of the TL maxima before and

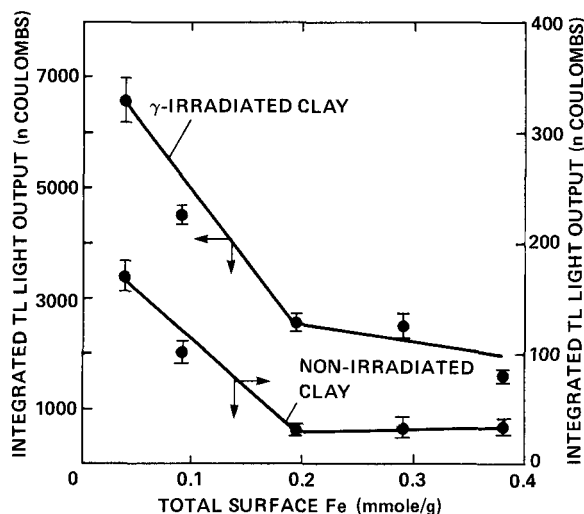


Figure 3. Effect of surface Fe content on total natural (lower points) and gamma-irradiation-induced (upper curve) thermoluminescence of SWy-1 Wyoming montmorillonite. Note the difference in ordinate scales for two curves.

after gamma-irradiation for each of the samples are shown in Table 1. The temperature of the maximum remained constant for increasing surface Fe substitution, indicating that the excitation traps for the material were essentially independent of the exchangeable cation.

The integrated intensity of the TL curves for the irradiated clays is plotted as a function of time after gamma-irradiation in the upper part of Figure 2. The lower part of the figure shows the light output from the materials prior to gamma-irradiation for comparison. Even one month after the radiation treatment, the intensity of emission was higher by one to two orders of magnitude than that from the non-irradiated clays, indicating relatively long-term storage of the recently applied energy. Presumably, most of the time-dependent energy dissipation resulted from Boltzman- or tunneling-induced recombination of charges stored in the shallow traps (140°C peak). The kinetics of redistribution of the energy in shallow traps to produce dissipation of the energy vs. transfer to lower energy centers was not investigated. To some extent the diminution of luminescence as a function of time after irradiation should be proportional to the gradual dissipation of stored energy.

In Figure 3 the integrated glow-curve intensities before and immediately after irradiation are plotted as a function of total surface Fe. As surface Fe increased the integrated TL intensity decreased, but a clear saturation effect was exhibited, in that the samples containing greater than about 50% Fe had an impact on light output that was less than linearly proportional to the change in surface Fe. On the other hand, the lu-

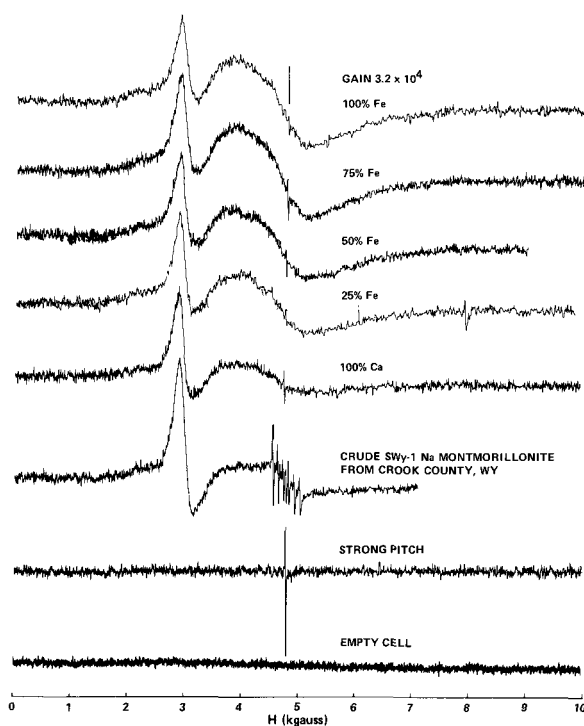


Figure 4. Electron spin resonance spectra of variably Fe-saturated SWy-1 Wyoming montmorillonite.

minescence was quenched in roughly linear proportion to the Fe content in the samples containing <50% surface Fe. Because Fe adsorbs appreciably in the visible and near-UV parts of the spectrum (Bell *et al.*, 1975; Burns, 1970), quenching of the TL output by surface Fe via emission-reabsorption is to be expected, but it should have been linear with Fe content. The nonlinearity thus indicates iron-iron interaction at higher surface concentrations and implies that the surface Fe clusters quenched less effectively, surprisingly, than single Fe ions.

Interaction between neighboring Mn^{2+} ions has been reported to produce intensity enhancement of the spin and parity forbidden d-d bands in several crystals, which was explained in terms of exchange interactions (Lohr and McClure, 1968). Intensity enhancement has been observed also in iron oxides (Sherman *et al.*, 1982). The 100% Fe form of a previously prepared set of these clays showed less reflectance in the short-wavelength visible region than did the 50% form (Banin *et al.*, 1985). As well as reabsorption from d-d transitions, $O_2^- - Fe^{3+}$ charge-transfer bands would be expected to reabsorb emitted light. In contrast to the d-d bands, the fully allowed charge-transfer bands would not be expected to show an intensity enhancement on $Fe^{3+} - Fe^{3+}$ interaction, but exchange interactions should serve to shift the absorption maxima for these transitions

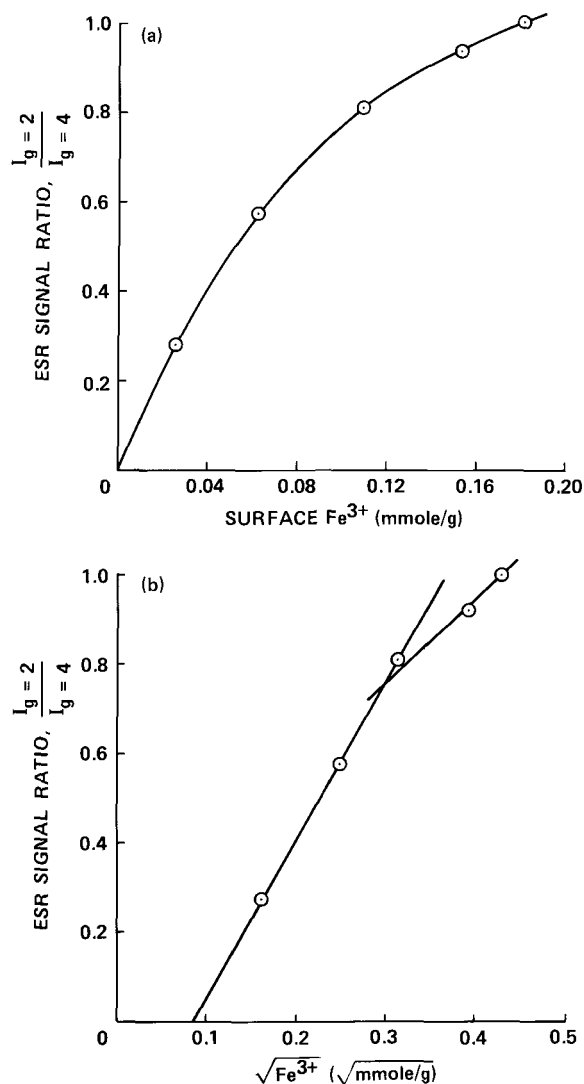


Figure 5. (a) Effect of exchangeable- Fe^{3+} content in SWy-1 Wyoming montmorillonite on the intensity ratio of the electron spin resonance peak associated with surface Fe ($g = 2$) to that associated with structural Fe. Intensity ratio was calculated as explained in text. (b) As above, effect plotted vs. the square root of Fe content in the clay.

towards the red end of the spectrum. The net influence of increased Fe^{3+} - Fe^{3+} interaction should be to increase the absorption efficiency per unit Fe, rather than to produce a saturation effect, as observed.

The ESR spectra of the variably exchanged materials and the SWy-1 clay from which they were prepared are shown in Figure 4. The ESR signal from the clays is the composite of a low-field signal attributable to Fe substitution in the clay structure in sites of highly distorted octahedral symmetry (Aasa, 1970) and a high-field signal attributable to the hydrated surface iron (Levanon *et al.*, 1968). The broadness of this latter

signal at $g = 2$ appears to be due to several factors affecting the zero-field splitting parameter, one of which is dissociation of the waters of hydration (Levanon *et al.*, 1968). The presence of an additional transition metal impurity, probably Mn, in the untreated SWy-1 clay was observed as a six-line feature at $g = 2$.

The ESR spectra of the Fe-Ca-substituted clays show a clear progression of increased intensity of the high-field signal as a function of concentration of surface Fe, whereas signals due to the structural constituent were relatively constant in the various Fe-exchanged materials produced by the quantitative ion-exchange method (Banin, 1973; Gerstl and Banin, 1980). The marked decrease of the low-field signal after the initial purification by this method, which involved an acid wash, is believed to be attributable to the removal of admixed crystalline iron oxides or coatings.

The relative intensity of the $g = 2/g = 4$ signals, plotted in Figure 5, was estimated using peak heights rather than deconvoluted peak areas. Either method introduced quantitative, but not qualitative, uncertainties. Use of the peak height improves the accuracy of the estimation of the $g = 2$ intensity in the region of 4.5–5.5 kgauss, where it most sensitively reflects changing Fe content, because there is no contribution to the $g = 2$ intensity by the $g = 4$ peak in this region. Conversely, the $g = 2$ signal diminishes the peak to trough intensity of the $g = 4$ signal by about 20% over the range of the Fe concentrations studied. The effect of this error is to diminish, rather than enhance the clarity of the saturation effect seen in the plot. Were peak areas to be used, both the $g = 2$ and the $g = 4$ signal intensities would be subject to the approximations made in the shapes of the curves over the extensive regions of mutual overlap of signals. Were simply the $g = 2$ peak to trough signal used, no normalization would be provided for daily variations in machine response or for slight changes of packing densities of the samples in the ESR tube. The tendency of the signals towards saturation at high iron is clearly revealed, regardless of the method used for displaying it.

We attribute the saturation effect in the ESR to interaction of the surface Fe at some critical distance of interaction, i.e., effective area of occupation. The plot of ESR signal relative to the square root of Fe concentration, which is proportional to the effective area of occupation of an Fe atom, significantly, but not completely, linearized the dependence (Figure 5b).

The band shape of the ESR signal is not changed noticeably at $>50\%$ Fe-saturation. Thus, the ESR evidence does not support a fundamental change in the environment of Fe, but perhaps differences in the alignment of domains on increasing the Fe; however, the nature of the interaction is not yet fully characterized.

That both the TL output and the ESR from the surface Fe show a similar non-linearity in their depen-

dence on surface Fe content suggests some sort of "communication" between the surface Fe and the energy storage sites associated with the crystal structure.

In summary, the long-lived increase in thermoluminescence from clays after exposure to ionizing radiation suggests that electronic energy is stored in montmorillonite as a function of excitation by a penetrating energy source. Because the thermoluminescence and the component of the ESR signal attributable to surface iron both showed indication of a critical Fe content, an interaction between surface Fe and energy storage sites in the clay structure probably exists, beyond trivial quenching of luminescence by emission reabsorption.

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