NOTE

PROLONGED TRIBOLUMINESCENCE IN CLAYS AND OTHER MINERALS

Key Words—Bentonite, Freezing, Grinding, Kaolinite, Triboluminescence.

During a study of luminescence in clay minerals and of its possible role in the early stages of prebiotic evolution (Coyne *et al.,* 1981), it was found that not only does the fracturing or grinding of certain clays bring about a burst of light during the time the mechanical stress is applied, but after the stress is removed a surprisingly high photon flux continues, although at a diminishing rate, for several days. The first burst of light can be observed by the unaided eye in a dark room; the latter process can be easily detected by a photomultiplier tube.

Light emission caused by the application of mechanical stress to crystals is known as triboluminescence and has been the subject of several studies (see Alzetta *et al.,* 1970; Hardy *et al.,* 1977). Although more than 350 substances are known to be triboluminescent, only a few of them have been studied spectroscopically, and the mechanism by which triboluminescence is excited is not completely understood (Hardy *et al.,* 1977). Luminescence as a function of time was reviewed by Leverenz (1968), and the decay characteristics of triboluminescence in arsenic crystals were studied by Stranski *et al.* (1955). As far as is known, however, no detailed studies of long-term photon emission in rock minerals have been carried out in which the photon emissions were excited by mechanical stress without subsequent heating.

EXPERIMENTAL

Samples of clays and other minerals were either ground with a mortar and pestle or fractured with a hammer and placed in pyrex vials. The emitted photons were counted using a Packard Tri-Carb Liquid Scintillation Spectrometer, Model 3320. Samples of (1) well-crystallized kaolinite, KGa-1, from Washington County, Georgia, and (2) poorly crystallized kaolinite, KGa-2, from Warren County, Georgia, were obtained in the form of powders from The Clay Minerals Society's Source Clay Repository. The powders had no detectable photon emission. Samples of Mesa Alta, New Mexico, kaolinite (Ward's Natural Science Establishment, Rochester, New York), and Umiat, Alaska, bentonite (Anderson and Reynolds, 1966) were prepared by forming cube-like chunks of known surface areas. Ground samples of chalk calcite, South England (Ward's Natural Science Establishment, Rochester, New York), sodium chloride, AR (Baker Analyzed Reagents), and quartz were filled up to half the volume of the Tricarb vials.

RESULTS

Figure 1 shows the decay curves of two triboluminescent-excited kaolinites. Grinding of the well-crystallized kaolinite (KGa-1) resulted in a higher photon-emission rate than that of the poorly crystallized kaolinite (KGa-2). The count rate of the latter did not appreciably increase with further grinding. The decay characteristics of the emitted light (Figure 1) continued for at least three days, and were very similar to those described by Stranski *et al.* (1955) for arsenic crystals. A rough estimate of the triboluminescence at the very first moments can be made by extrapolating the curves in Figure 1 back to time zero. It is estimated that the count rate of the well-crystallized kaolinite immediately after the grinding was of the order of several million counts per minute.

The decay curves of freshly filed, cube-like chunks of Mesa Alta kaolinite and Umiat bentonite are shown in Figure 2. The activity of kaolinite, which greatly exceeded that of bentonite, exhibited a similar decay characteristic in that the decay was very fast during the first few minutes followed by a slower rate; the slower rate gave a straight line on a log-log scale (Figure 2).

Considering the counting efficiency in the present work, it is estimated that the total amount of light emitted from a unit surface area of the Mesa Alta kaolinite, i.e., the light that was detected and counted by the scintillation spectrometer, was of the order of several tens of billions of photons per square centimeter of surface area. Obviously, part of the emitted light came from the surface, but the remainder originated at deeper layers in the solid phase. The total photon output of a unit mass of clay could not be estimated.

Adding water to either the kaolinite or bentonite preparations increased somewhat the count rate of emitted light. No effort was made to quantify this effect. When freshly filed
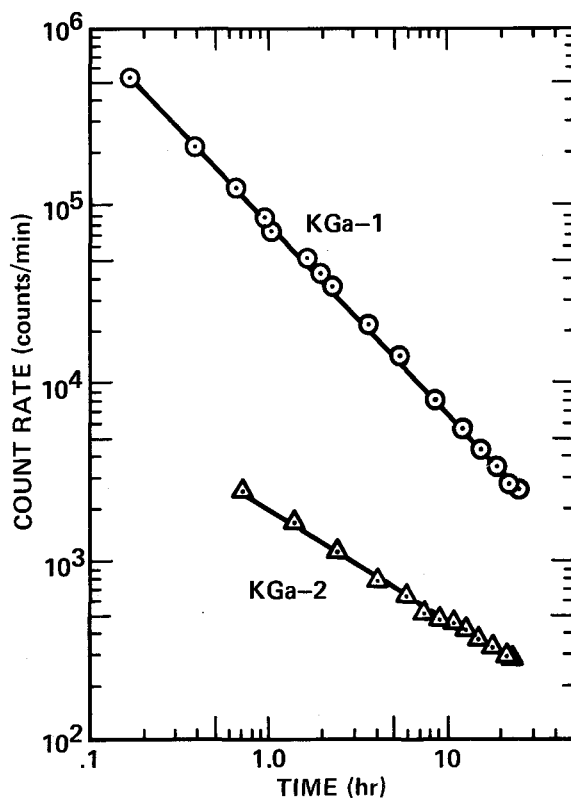

Figure 1.   Luminescence rate as a function of time elapsed from the end of grinding: well-crystallized kaolin KGa-1 and poorly crystallized kaolin KGa-2.
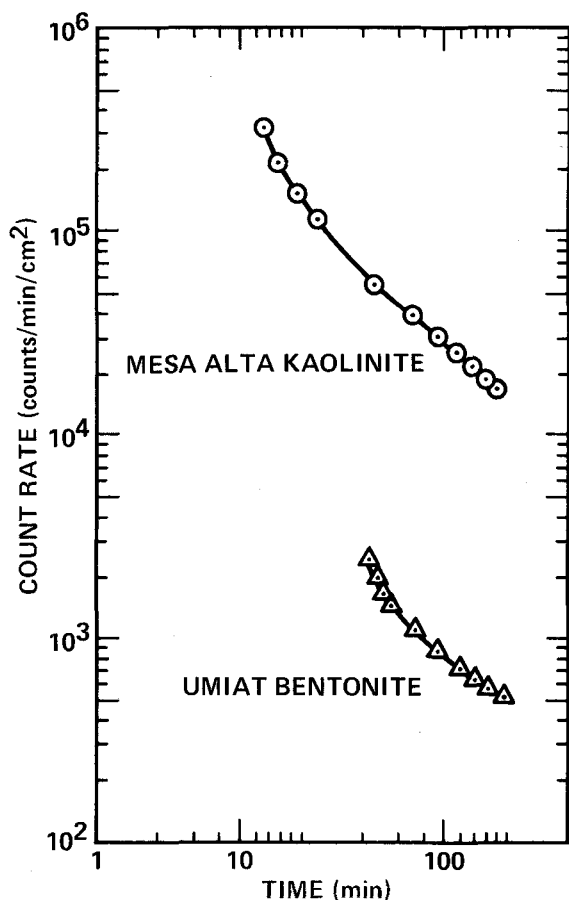
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Figure 2. Luminescence rate as a function of time elapsed from the end of filing of kaolinite No. 9, Mesa Alta, New Mexico, and bentonite, Umiat, Alaska.

Figure 3. Luminescence rate as a function of time elapsed from end of grinding of quartz, sodium chloride, and chalk calcite.

chunks of Mesa Alta kaolinite were dipped into a solution of the amino acid tryptophan and carefully drained, the count rate increased above that of the same kaolinite chunk wetted with water. Though the increased count rate induced by tryptophan was significant, it could not be quanitatively measured by the present method. A quantitative measurement of the effect of tryptophan on the count rate of kaolinite in a luminescence process is in progress.

Tryptophan, a fluorescent molecule, has excitation and fluorescence maxima at 287 μm and 348 μm, respectively (Underfriend, 1962). One possible interpretation of the tryptophan effect is that part of the triboluminescent light was in the UV or near UV range and was not counted by the photomultiplier both because of the high light absorbance and scattering of the kaolinite (Lindberg and Smith, 1974) and because of the light absorbance in this range of the spectrum by the Pyrex vials. However, the fluorescent amino acid was excited by these photons and consequently emitted photons at a higher wavelength. Because light transmittance of both clay and glass greatly increased with increasing wavelength in the UV or near UV range, the tryptophan molecules, according to this interpretation, served as probes for photons produced in the prolonged triboluminescence process, which otherwise would not have been counted. Triboluminescence in the UV and near UV range has been shown earlier (Stranski, 1955). Another possible interpretation for the tryptophan effect is nonradia-
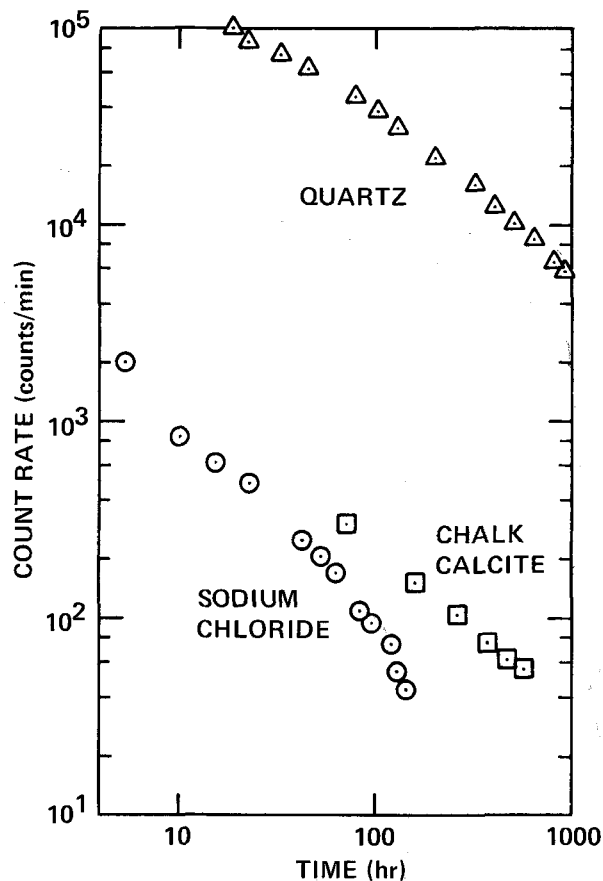
tive energy transfer between excited sites in the ground clay and the tryptophan molecules (see Fendler and Fendler, 1975).

Because mechanical stress in the form of grinding was so effective in exciting triboluminescence in kaolinite and montmorillonite, freezing should have produced similar effects under conditions that brought about breaking and distortion of the crystal structures. To investigate this effect, pastes of kaolinite and montmorillonite were smeared on the inner walls of vials, frozen in either liquid nitrogen (fast freezing) or in a $-10°C$ salt-ice mixture (relatively slow freezing), thawed, and the emitted photons counted. Freezing by either method excited montmorillonite to produce luminescence and produced a decay curve similar to the one shown in Figure 2. This freezing-induced triboluminescence was repeated simply by further freezing and thawing the bentonite paste. A quantitative comparison between the two processes has not been attempted. In contrast, freezing excited no measurable triboluminescence in kaolinite. Obviously, more work is needed to understand the difference between the two clays in their response to freezing. Presumably, the different responses are related to both particle size and interparticle distances and forces, as well as to surface-water interaction.

Prolonged triboluminescence has been examined in many other solids, including several kaolinites and montmorillonites, quartz, "pure" sand, calcite, marble, illite, nontronite, talc, pyrophyllite, ilmenite, vermiculite, apatite, asbestos

(Jade mine), sodium chloride, and sugar. Several examples are shown in Figure 3. All of these materials showed prolonged triboluminescence, but the apparent intensities of the effect differed considerably. For example, nontronite exhibited very weak activity; quartz, "pure" sand, talc, and pyrophillite showed a considerable effect; and montmorillonite samples exhibited a rather low level of prolonged triboluminescence. Vermiculite gave no apparent triboluminescence, presumably because the method of grinding was not effective in breaking its sheets.

The intensity and decay rate of prolonged triboluminescence depend on both the properties of the material under study and on the method of sample preparation and measurement. To compare different materials and to elucidate the roles of chemical composition, crystallographic properties, environmental conditions, and method of sample preparation, the method of excitation must be standardized as well as the measurement procedure. Obviously the grinding applied in the present study cannot be easily standardized. On the other hand, development of a standardized polishing technique is easier and would permit measurements of triboluminescence excitation under comparable conditions (see also Lewis, 1968).

It should be noted that the effects of chemical composition and crystallographic properties on prolonged triboluminescence are not easily separated. For example, the two kaolinites shown in Figure 1 differ considerably not only in their degree of crystallinity, but also in their chemical composition, cation-exchange capacity, surface area, and thermal analysis (Van Olphen and Fripiat, 1979), and, presumably, in impurities content. Thus, because of light absorbance (Diehl *et al.*, 1968), the higher iron content of the KGa-2 kaolinite may be at least partially responsible for its lower triboluminescence activity.

The possible significance of the prolonged triboluminescence should be investigated in connection with processes in which it is either naturally formed or artifically induced. An example of a natural process is rock fracturing, whether by expansion-contraction, the impact of meteorites, or during tectonic movement (see Wakita *et al.*, 1980). Artificially induced prolonged triboluminescence is probably very common in mines and quarries.

It should be noted that prolonged triboluminescence and the surface phenomena related to it immediately suggest a possible connection between human exposure to freshly powdered materials such as those produced in mines (e.g., asbestos and silica) and certain respiratory diseases (e.g., asbestosis and silicosis). Preliminary studies on this possibility are in progress in the Department of Radiobiology, Stanford Medical School.

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