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SOME EFFECTS OF PRESSURE ON THE THERMOLUMINESCENCE OF AMBLYGONITE, PECTOLITE, ORTHOCLASE, SCAPOLITE AND WOLLASTONITE

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ABSTRACT

The effects of shearing pressures on the natural thermoluminescence of several minerals have been studied. Pressure applied uniaxially and producing shear stress of unknown magnitude, decidedly affects the natural thermoluminescence of amblygonite, orthoclase, pectolite, scapolite and wollastonite. In all instances the peak temperatures of the natural glow curves are gradually shifted 40° to 60° C. with increasing pressure. (In some minerals the shift is upward, in others downward.) The ratio of light intensity of the middle (260° to 315° C.) to high temperature (335° to 405° C.) thermoluminescence after pressure treatment remained essentially constant.

It is suggested that detailed investigation of the effects of pressure and time on the thermoluminescent glow curve characteristics of different rocks and minerals may be useful in the study of pressure and temperature distributions in rock materials surrounding (and affected by) both underground nuclear explosions and also intrusive bodies.

INTRODUCTION

An investigation of the effects of nonhydrostatic pressures on the thermoluminescent properties of some compounds other than calcite and dolomite was made (Table 1). The results reported here are of a preliminary nature, however, and should be so considered. A description of the equipment and procedure employed in pressure thermoluminescence studies has been given by Angino (1959a) and will not be repeated here. In this procedure shear stresses of unknown magnitude are produced in the granulated material by the application of uniaxial pressures. Although the actual effects are the composite of several forces at work during pressure application, it is surprising that consistent changes of type reported here are obtained.

The first investigation of the influence of pressure on thermoluminescence was that of Zeller (1954), who found that the thermoluminescence of both fresh, chemically precipitated calcium carbonate ($CaCO_3$) and natural calcite (Tertiary in age) is changed markedly by high pressures followed by radiation treatment. Two principal effects were reported. Pressure and subsequent radiation significantly increased the high temperature ($>315°$ C.) thermoluminescence and decreased the low temperature (110° C.) thermoluminescence.

Later Zeller, Wray, and Daniels (1955) demonstrated that the high temperature, radiation-induced thermoluminescence of natural limestones *older* than 100 m.y. decreased upon high-pressure treatment.

Further work by Zeller *et al.* (1957) and Angino (1959a) showed that pressures of 508 to 3550 bars applied to powdered, *nonirradiated* calcite samples increased the amount of high temperature thermoluminescence in laboratory precipitates of Recent and Tertiary carbonates. Angino (1959a) suggested the feasibility of utilizing this phenomenon to date Tertiary limestones.

Additional studies of pressure-induced thermoluminescence have been reported by Handin *et al.* (1957), Debenedetti (1958), and Angino (1959b, 1961).

TABLE 1. Compounds Tested for Thermoluminescence

Name	Composition	Natural Thermoluminescence
Amblygonite	(Li, Na)$AlPO_4$(F, OH)	medium
Calcite[1]	$CaCO_3$	weak
Corundum	Al_2O_3	none observed
Halite	NaCl	none observed
Orthoclase	$KAlSi_3O_8$	medium
Pectolite	$Ca_2NaSi_3O_8(OH)$	medium
Scapolite	$Na_4Al_3Si_9O_{24}Cl$ (varies)	strong
Sphalerite	ZnS	weak
Spodumene	$LiAlSi_2O_6$	none observed
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	weak
Wollastonite	$CaSiO_3$	medium
Halides[1]	LiBr	none observed
	LiCl	none observed
	LiF	medium
	KBr	none observed
	KCl	weak
	KI	none observed
	NaBr	none observed
	NaCl	none observed
	NaI	none observed
	CaF_2	weak
Fluorite[1]		

[1] Analytical Reagent Grade.

RESULTS

Of the minerals studied (Table 1) only five (amblygonite, orthoclase, pectolite, scapolite and wollastonite) displayed any appreciable thermoluminescence. After reduction to a standard equipment setting, an arbitrary light scale of 10 chart units to 1 inch of recorded light intensity was used to measure the peak intensities.

Scapolite, by far, had the greatest amount of natural thermoluminescence (results summarized in Table 2). After determination of the natural thermoluminescence, four portions of the scapolite sample were pressed for 5 minutes at different pressures and the resulting curves compared with the natural glow curve.

TABLE 2. PEAK TEMPERATURE AND INTENSITY VARIATIONS OF THERMOLUMINESCENCE IN PRESSURE-TIME STUDIES

Nonirradiated Pressure-modified Specimens

Sample	Pressure, Bars	Time, Minutes	Peak Temperatures, ° C.		Intensity		R
			MTP	HTP	MTP	HTP	
Amblygonite	Natural	—	265	335	53	38	1.40
	2530	<0.5	305	—	27	—	
	2530	5	300	—	20	—	
	2530	10	—	325	—	20	
	2530	15	315	395	18	26	0.70
Orthoclase	Natural	—	255	—	10	—	
	1275	5	320	—	5	—	
	2030	5	308	—	6	—	
	2530	5	300	—	5	—	
	2530	<0.5	295	—	7	—	
	3050	5	285	—	8	—	
Pectolite	Natural	—	275	355	12	9	1.3
	2530	<0.5	288	380	11.5	11.5	1.0
	2530	2	315	395	10	9	1.1
	2530	5	310	375	11	9.5	1.1
	1530	10	290	370	12	12	1.0
	2530	15	287	367	14	14	1.0
Scapolite	Natural	—	260	355	380	680	0.56
	1275	5	290	385	420	680	0.62
	2030	5	280	385	330	550	0.60
	2530	<0.5	280	—	280	—	
	2530	5	310	400	260	350	0.74
	3050	5	310	405	310	500	0.62
Wollastonite	Natural	—	265	345	8	8	1
	2530	5	285	380	6	10	0.6

MTP = Middle Temperature Peak
HTP = High Temperature Peak

R = Ratio of Intensity $\frac{\text{MTP}}{\text{HTP}}$

Neither peak showed any change in light intensity (I-value) proportional to increasing pressure. An interesting point is that regardless of the respective I-values, the ratio of I-values of the MTP/HTP remained essentially constant in the pressed samples. MTP/HTP refers to middle and high temperature peaks respectively.

The natural thermoluminescence of pectolite is considerably less than that of scapolite. As indicated by Table 2, pectolite samples were treated somewhat differently from the scapolite ones. A pressure of 2530 bars for 2 minutes shifted both peaks upward 40° C (Fig. 1). Thereafter, with increasing duration of pressure application, these peak temperatures decreased steadily. In contrast to the peak temperatures, the I-values of the MTP and HTP increased slowly as the pressure time increased. The ratio of I-values of the MTP/HTP again remained essentially constant.

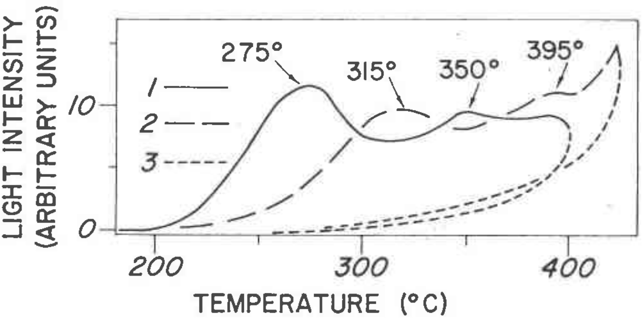

Fig. 1. Glow curves. (1) Natural curve of pectolite sample before pressure treatment. (2) Curve of same sample after 2530 bars for 2 minutes (3). Black body radiation curve.

Amblygonite exhibited medium intensity thermoluminescence. Pressure of 2350 bars for 0 to 10 minutes on amblygonite caused disappearance of both the 265° C, and 335° C. peaks; simultaneously, these peaks are replaced by one 305° C. which moved upward as the time of pressure increases (Fig. 2). After pressure of 2530 bars for 15 minutes, two peaks (not coincident with those in the natural curve) reappeared. This phenomenon was noticed only in amblygonite. In orthoclase, on the other hand, pressure treatment initially shifts the natural peak (255° C.) upward; thereafter, with increase of pressure, the peak temperature shifts slowly downward. The I-values remained essentially constant throughout. Result obtained on samples pressed and immediately released (0 time—<30 seconds) suggest that effects of pressure on natural thermoluminescence of these materials are immediate. Note the changes in amblygonite and pectolite especially.

Wollastonite was not studied extensively. Its natural glow curve showed two peaks, both of which were shifted upward by pressure with a slight change in light intensity (Fig. 3).

Clearly one of the effects of pressure on these materials is to induce a measurable shift in peak temperature of the glow curve. The exact mechanisms acting to cause these shifts is unknown. The permanency of the pressure-modified thermoluminescence effects was not determined. Such studies would be an interesting consideration for future work. A method for separating the effects of pressure-modified thermoluminescence from that of radiation induced thermoluminescence is given in Angino (1964).

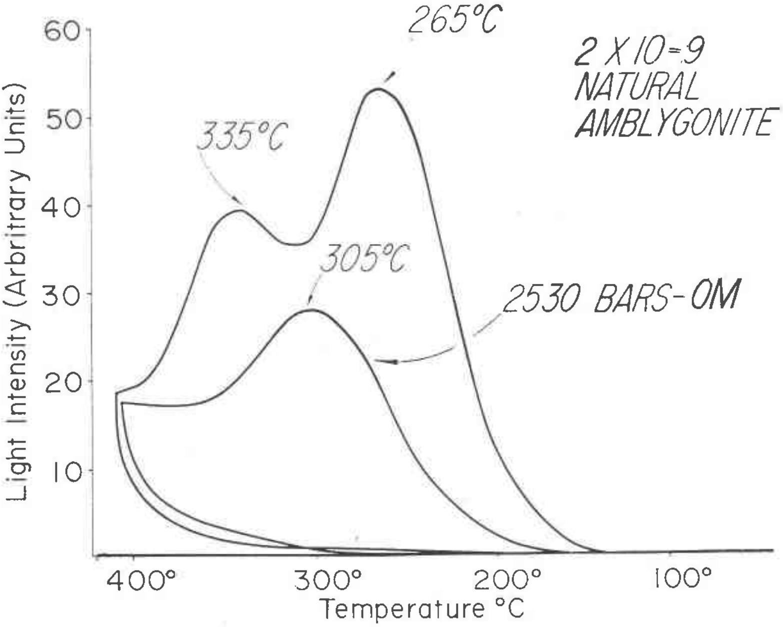

FIG. 2. Glow curve illustrating effects of pressure on natural thermoluminescence of amblygonite. See Table 2 for comparison of relative intensities.

In addition to the mineral specimens, several halides were tested (Table 1). Of these, only KCl and LiF displayed any natural thermoluminescence. LiF showed considerable high temperature thermoluminescence (around 325° C.); therefore, a set of experiments was run on this compound. One group of LiF samples was subjected to 2530 bars for increments of 2, 4, 5 and 10 minutes. Such treatment was sufficient to induce a shift in peak temperatures from 325° C. to 375° C. with increasing time of pressure; accompanying changes in I-values were erratic and followed no set pattern.

Analytical reagent grade $CaCO_3$ and CaF_2 (highly thermoluminescent in their natural equivalents of calcite and flourite) showed only slight pressure-modified thermoluminescence.

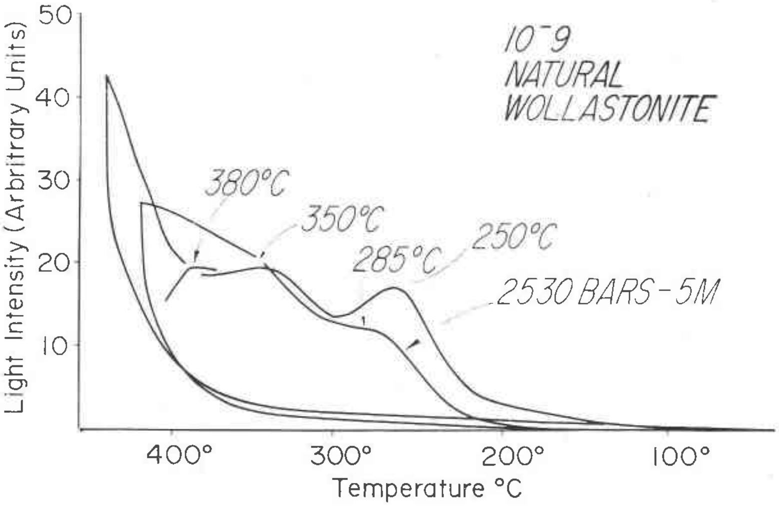

FIG. 3. Glow curve illustrating pressure effects on thermoluminescence of wollastonite. Table 2 gives relative intensities with other minerals tested. The 380° C. peak was resolved by subtracting the effects of black body radiations. Only the peak is indicated.

Only LiF, of those reagent grade compounds examined for pressure-produced thermoluminescence (piezothermoluminescence) showed a measurable amount of such thermoluminescence. The testing procedure on these samples was similar to that outlined in the preceding paragraph. After a pressure of 2530 bars, the peak temperature of LiF was displaced from 350° C. in the 2-minute pressed sample to 380° C. in the 15-minute pressed sample. No relationship between peak intensity and pressure time was evident.

DISCUSSION AND CONCLUSIONS

The accuracy of the temperature values reported in the above data is ± 5° C. Such values would vary somewhat from one laboratory to another owing to different performance characteristics inherent in the types of measuring equipment used. Of real importance, however, are the trends indicated by both the shifts in peak temperature and the essentially constant MTP/HTP intensity ratios induced by pressure treatment.

It is possible that some of these pressure effects may be due to dislocations produced in the samples by pressure treatment (Angino, 1961). If so, some of these effects may be the result of a complicated annealing mechanism which operates when the sample is heated. Although the fundamental mechanisms at work must involve dislocations, it may be quite difficult to define these mechanisms more precisely. The equipment used provided no means of ascertaining the spectral distribution of light emitted by the samples; as a result, no information is available on the luminescent centers associated with the respective glow curve peaks.

In the studies described several samples of the same mineral were measured with similar results; however, the same mineral but from a different locality and with a different thermal and/or pressure history may behave differently.

Some of the halides may not require much additional pressure to induce a phase transition. It would be interesting (as suggested by several colleagues) to follow any changes in glow-curve shape accompanying phase changes. Such studies might contribute considerable information to elucidating the underlying mechanism of pressure-induced thermoluminescence.

It is suggested that pressure thermoluminescence may provide a useful tool in geologic studies where the normal indicators of deformation and temperature are questionable or lacking. Detailed thermoluminescence studies of pressure-induced changes in the glow curve characteristics of different rock and mineral species may be a possible tool for investigating pressure and temperature distribution both in areas of intrusive rocks and in rock materials surrounding an underground nuclear explosion.

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REFERENCES

ANGINO, E. E. (1959a) Pressure effects on thermoluminescence of limestone relative to geologic age. *Jour. Geophys. Res.* **64,** 569–574.

——— (1959b) Some effects of pressure on thermoluminescence of limestone. *Jour. Geophys. Res.* **64,** 1638–1640.

——— (1961) Pressure thermoluminescence. *Proc. 1960 Inter. Conf. Color Centers and Crystal Luminescence, Bull. Instituto Elettrotech. Naz., Turin, Italy*, 95–110.

——— (1964) The effects of non-hydrostatic pressures on radiation-damage thermoluminescence. *Geochim. Cosmochim. Acta.* in press.

DEBENEDETTI, A. (1958) On mechanical activation of thermoluminescence in calcite. *Il Nuovo Cimento*, **7**, 251–254.

HANDIN, J., D. V. HIGGS, D. R. LEWIS, AND P. K. WEYL (1957) Effects of gamma radiation on the experimental deformation of calcite and certain rocks. *Bull. Geol. Soc. Am.* **68**, 1203–1224.

ZELLER, E. J. (1954) Thermoluminescence of carbonate sediments. *Nuclear Geology*, ed. by Henry Faul. John Wiley & Sons, New York, 180–188.

——— J. L. WRAY, AND F. DANIELS (1955) Thermoluminescence induced by pressure and crystallization. *Jour. Chem. Phys.* **23**, 2187.

——— J. L. WRAY, AND F. DANIELS (1957) Factors in age determination of carbonate sediments by thermoluminescence. *Bull. Am. Asso. Petrol. Geol.* **41**, 121–129.

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