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THERMOLUMINESCENCE OF THE MINERAL COMPONENTS IN GRANITE*

by

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ABSTRACT

The thermoluminescence (TL) of the minerals in Climax Stock (Nevada, USA) granite has been studied. The principal mineral constituents are plagioclase, quartz, potassium feldspar and biotite. Pyrite, sphene apatite and zircon occur at one percent or less. All exhibit TL except biotite. The TL kinetics were determined for plagioclase, quartz, potassium feldspar and pyrite. Plagioclase and potassium feldspar exhibit second order and pyrite first order kinetics. Natural TL of quartz follows second order and artificial TL first order kinetics. However, in these four minerals unrealistic kinetic parameters are often obtained; thus more general kinetics, e.g. interactive kinetics, may apply.

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The thermoluminescence of granite is of interest for purely scientific reasons, radioactive waste disposal applications and archaeological and geological dating, particularly the dating of quaternary deposits containing feldspars. There are numerous types of granites and no two deposits are precisely the same. By a natural process, which can be described—in an oversimplified way—as weathering and alteration, granites are the source of much of the clay and quartz in ceramic objects used for dating. Most importantly, the quartz originating in granites is fundamentally different from the quartz that has been used in almost all basic studies on the physical properties of natural quartz, especially thermoluminescence. Granitic quartz is "pyrogenic," i.e. it is formed by the solidification of a molten mass. Most studies on quartz have been made with the familiar terminated euhedral crystals seen in collections. In nature, as well as commercially, the more familiar crystal quartz is grown from solution (usually sodium carbonate) by a hydrothermal process. Thus, the physical and chemical properties, particularly the impurity content and distribution, of pyrogenic quartz can be quite different from that of hydrothermal quartz. The determination of thermoluminescence properties of a definitely pyrogenic quartz is one of the objectives of this study.

Sample and Sample Preparation

All of the thermoluminescence (TL) measurements described below were made on samples prepared from a single section of drill core from the Climax Stock, a granitic intrusion in the S.E. corner of Nye County, Nevada, U.S.A. This granite is more properly described as quartz monzonite. Two types of samples were prepared: polished slabs approximately 10×10×1 mm and powder samples of the principal mineral constituents. The latter were obtained by crushing and hand separating individual grains, using a low power microscope. After magnetic separation the separated material was sieved to obtain grains in the 212 to 250 μm range. Minerals were identified by microscopic and electron microprobe techniques. The principal minerals present are, in order of abundance, plagioclase, quartz, potassium feldspar (K-spar) and biotite. Pyrite, apatite, sphene, opaque iron oxides and zircon are present in quantities of a percent or less. Only quartz, K-spar, plagioclase and pyrite could be obtained in sufficient quantities to make detailed TL studies. Unfortunately, during separation the samples were exposed to light and consequently the natural TL may have been altered before TL measurement.

All irradiations employed Co-60 sources with the samples at 20-25°C. During and after irradiation the samples were protected from light and kept at room temperature. The TL measurements were made with the computer controlled, high-aperture "2-D" apparatus, i.e. the total light intensity (actually the phototube current) vs. temperature was recorded. It is intended that the spectral emission characteristics will be studied with the "3-D" apparatus.

Color of the Thermoluminescence Emission

After exposure to 10^7 R Co-60 irradiations, the TL of the 10×10×1 mm slabs was studied by photographing the emission, using high speed color film, as the sample was heated from 25 to 425°C. These pictures and electron microprobe measurements, which will not be described, established the mineral-emission relations described in Table I.

Table I

TL emission from the principal mineral constituents in Climax Stock (Nevada, U.S.A.) granite

Mineral	Color of TL Emission
Quartz: SiO_2	Light to Dark Blue
Plagioclase: $(Na,Ca)Al(Si,Al)Si_2O_8$	Green
Potassium feldspar (K-spar): $KAlSi_3O_8$	Violet-Purple
Apatite: $Ca_5(F,Cl,OH)(PO_4,CO_3)_3$	Dark Green
Biotite: $K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH)_2$	Not Detected

Glow Curve Analysis

Many of the glow curves obtained from the different granite components have been resolved into individual glow peaks using a procedure for determining the combination of individual first and second order glow peaks that provides a "best-fit" to the data. This procedure has been used since the late 1960's, e.g. see Mattern et al. (1970; 1975). It is based on the assumption that glow curves contain first and second order peaks that do not interact. More specifically the procedure does not include the interactive kinetics described in another article in these Proceedings (Levy, 1982a; see also Levy 1982b). The glow curves in Figs. 1 to 7 show: 1) data points, for clarity many fewer points are shown than were recorded, 2) the best-fit glow peaks and 3) the sum of the separate best-fit peaks, which usually lies close to the data points. Also shown, for the peaks from low to high temperature, are the pre-exponential factors--s for first order and $s^* = (n_0/N)s$ for second order, the activation energy E--in eV, a quantity n_0—which is proportional to the area of the separate peaks, and the full scale relative intensity. The fraction of traps containing charges when the measurement is initiated is n_0/N.

Natural Thermoluminescence

The natural TL of powdered but unseparated Climax Stock granite is shown in Fig. 1. It undoubtedly contains too many peaks to be meaningfully resolved into individual peaks. The natural TL glow curve from separated quartz and the best-fit resolution into individual peaks is shown in Fig. 2. Surprisingly, this curve is better fitted by second order than by first order kinetics. In contrast, the glow curves from irradiated quartz are better fitted by first order glow peaks.

The fact that the pyrite component exhibited TL, Fig. 3, was unexpected. The metallic appearance and lack of transparency of pyrite indicates that it should not exhibit TL. After TL was observed in Climax Stock pyrite, TL was detected from pyrite from a number of localities. Studies on samples crushed between measurements showed that the pyrite emission is not chemiluminescence.

The natural TL from the plagioclase and K-spar components is shown in Figs. 4 and 5. Both glow curves are fitted best by second order kinetics. This is consistent with previous studies (Pasternack et al. 1977; Wintle and Huntley 1979, 1980; Levy 1979, 1980) indicating that feldspars exhibit second order kinetics.

Two general comments need to be made about the natural TL data shown above. First, some of the kinetic parameters obtained from the fitting procedure are physically unrealistic. Second, the natural glow curves, particularly that of the quartz, indicates that the granite may have received high natural doses and/or been heated to relatively high temperatures. This suggests that all of the natural TL may not have been removed from artifacts subject to low or medium temperature firing.

Radiation Induced Thermoluminescence

Samples of the separated minerals, quartz, plagioclase, K-spar and pyrite were exposed to various doses between 5×10^6 and 5×10^7 R and TL measurements made 24 and 72 hours and one week after irradiation, except for pyrite. More than 30 glow curves were recorded and resolved into component glow peaks. Space is available to describe only a few representative results. The TL of the quartz component, measured 24 hours after a dose of 5×10^6 R, is shown in Fig. 6. The peaks and inflection points in the glow curve require a minimum of 4 peaks. However a reasonable resolution could not be obtained until a fifth was inserted to account for the intensity in the wings of the highest peak. As the dose increases the low temperature quartz peaks decrease and the high temperature peaks increase in intensity. Also, the kinetic parameters obtained by fitting first and second order kinetics to the TL curve in Fig. 6 and other quartz curves are often physically unrealistic. This point is discussed below.

The TL from the plagioclase component, exposed to 5×10^6 R and measured 72 hrs. after irradiation is shown in Fig. 7. Again there are peaks and inflection points requiring at least 4 peaks. However, five second order peaks were required to fit the data. Also as the dose is increased the intensity of the low temperature peaks change relative to the high temperature peaks; but not in the systematic way observed with quartz.

Changes Occurring after Irradiation

All of the granite components investigated exhibited large glow curve changes as the time between irradiation and measurement was changed. This is illustrated by Fig. 8 showing glow curves for K-spar recorded 24 and 72 hours and one week after simultaneous irradiation. In almost all cases the decay of the quartz, K-spar and plagioclase TL are similar. First, the total area under the glow curves decrease as the time between irradiation and measurement increases. Occasionally the total area under the quartz glow curves change only slightly. Second, as time to measurement is lengthened the low temperature peaks decrease and the high temperature peak increases. These observations are significant. One expects ambient temperature charge untrapping to reduce the total TL emission. The relative increase in high temperature peaks can occur in several ways. Charges can be redistributed from low to high temperature traps, most likely by ambient temperature thermal untrapping and retrapping; tunneling is not excluded. Thermal untrapping may alter the charge distribution before the TL measurement so that interactive retrapping causes the higher temperature peaks to exhibit increased relative intensity during the TL measurement. Or, both of these processes may occur.

Thermoluminescence Kinetics of Quartz, Plagioclase and K-spar

The resolution of the radiation induced TL glow curves of quartz, plagioclase and K-spar into first and/or second order glow peak components leads to a number of similar conclusions. The quartz glow curves are well resolved into first order components. However, unrealistic s values are often obtained and the glow curves corresponding to different doses and/or times after irradiation were not fitted by a single set of glow peaks with the same E and s values and different n_0, i.e. intensity, values. This result is in accord with previous studies on hydrothermal quartz (Fuller and Levy 1977a, 1977b, 1978). The feldspar, i.e. the plagioclase and K-spar glow curves, are best fitted by second order kinetics. Also, in these cases unrealistic s* values are often obtained and the various glow curves were not fitted by a single set of peaks with the same E and s* values and different intensities. The plagioclase and K-spar results are similar to those obtained from albite, another feldspar (Pasternack et al. 1977).

Summary

Of the five principal constituents in Climax Stock granite, quartz, K-spar, plagioclase and pyrite exhibit strong natural and radiation induced TL. The biotite component is not thermoluminescent. The TL glow curves of all constituents depend strongly on dose and the time between irradiation and measurement. The changes occurring between irradiation and measurement can be attributed to thermal charge release and retrapping. All glow curves obtained can be resolved into first or second order glow peak components. The "fits" are very good. However, two important results regarding kinetics are obtained: 1) Physically unrealistic s and s* values are often obtained. 2) With few exceptions, the kinetic parameters, and occasionally the number of peaks, obtained from different glow curves for the same material are not in agreement. More specifically, the straightforward application of the fitting procedure did not produce a single set of glow peak parameters, i.e. a single set of E and s—or s*—values, which describe all of the glow curves from a given mineral by adjusting only the intensity, i.e. the n_0 values. Thus, the usual first and second order non-interacting kinetics apparently do not describe the TL of the minerals studied, at least for the doses used. However, the interacting kinetics (Levy 1982a--these proceedings; 1982b) appear to explain, at least qualitatively, these results.

A detailed description of this study is in preparation.

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Figure Captions

Figure 1. Natural thermoluminescence (TL) of powdered but unseparated granite, i.e. quartz monzonite, from the Climax Stock (Nevada, USA). The glow curve, which appears to contain only a few glow peaks, includes contributions from at least nine glow peaks associated with at least four different minerals, see Figs. 2-5.

Figure 2. Natural TL of the quartz component separated from Climax Stock granite. Shown are representative data points, best-fit individual peaks and the sum of the peaks. From top to bottom, the parameters apply to the glow peaks from low to high temperature. The data is best fitted by two second order glow peaks. In contrast, all radiation induced quartz glow curves are best fitted by first order glow peaks. Unfortunately, all material had to be exposed to light during separation and consequently the natural glow curves may have been altered by optical bleaching.

Figure 3. Natural TL of the pyrite component. Because of its opacity and metallic appearance, it is surprising that pyrite exhibits TL. The data is best fitted by two first order glow peaks. The s value for the high temperature peak is unrealistically low.

Figure 4. Natural TL of the plagioclase component. The data is best fitted by two second order glow peaks; which is usual for feldspars. The high temperature peak s* value is unrealistically low.

Figure 5. Natural TL of the potassium feldspar (K-spar) component. The width and an inflection point indicate that low temperature data contains two peaks. Three second order peaks fit the data but one s* value is unrealistically low.

Figure 6. Radiation induced TL of the quartz component, measured 24 hours after a 5×10^6 R Co-60 gamma-ray irradiation at room temperature. Inflection points suggest four peaks but the best-fit procedure requires five to account for the narrow upper part and wide lower part of the most intense peak. The s values for all but the low temperature peak are unrealistic.

Figure 7. Radiation induced TL of the plagioclase component, measured 72 hours after a 5×10^6 R Co-60 gamma-ray irradiation at room temperature. The data is best described by five second order peaks. However, only three s* values are definitely within the normal range.

Figure 8. Radiation induced TL of the K-spar component measured at various times following simultaneous 5×10^6 R Co-60 irradiation at room temperature. The total area decreases and the relative intensity of the peaks shift, primarily to higher temperatures.

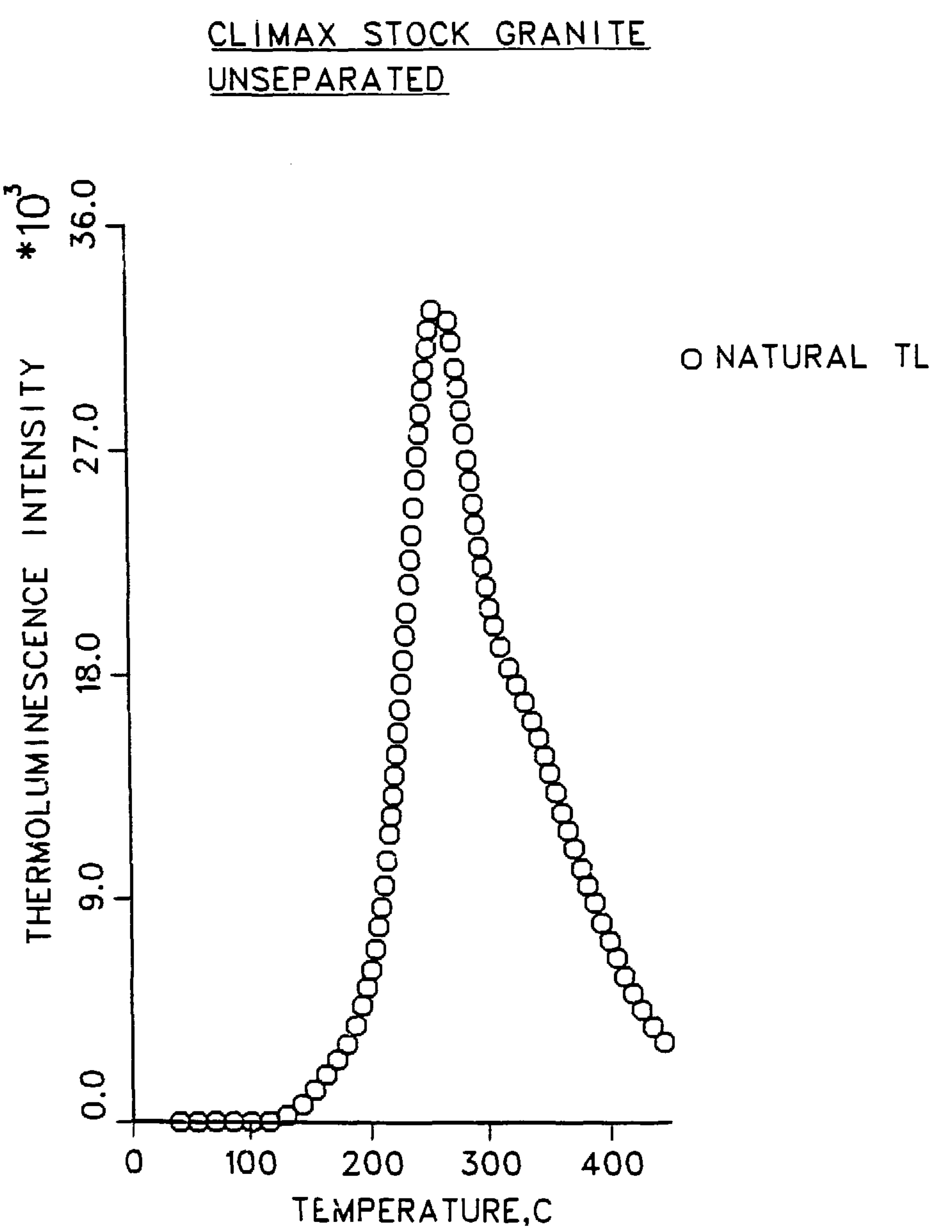
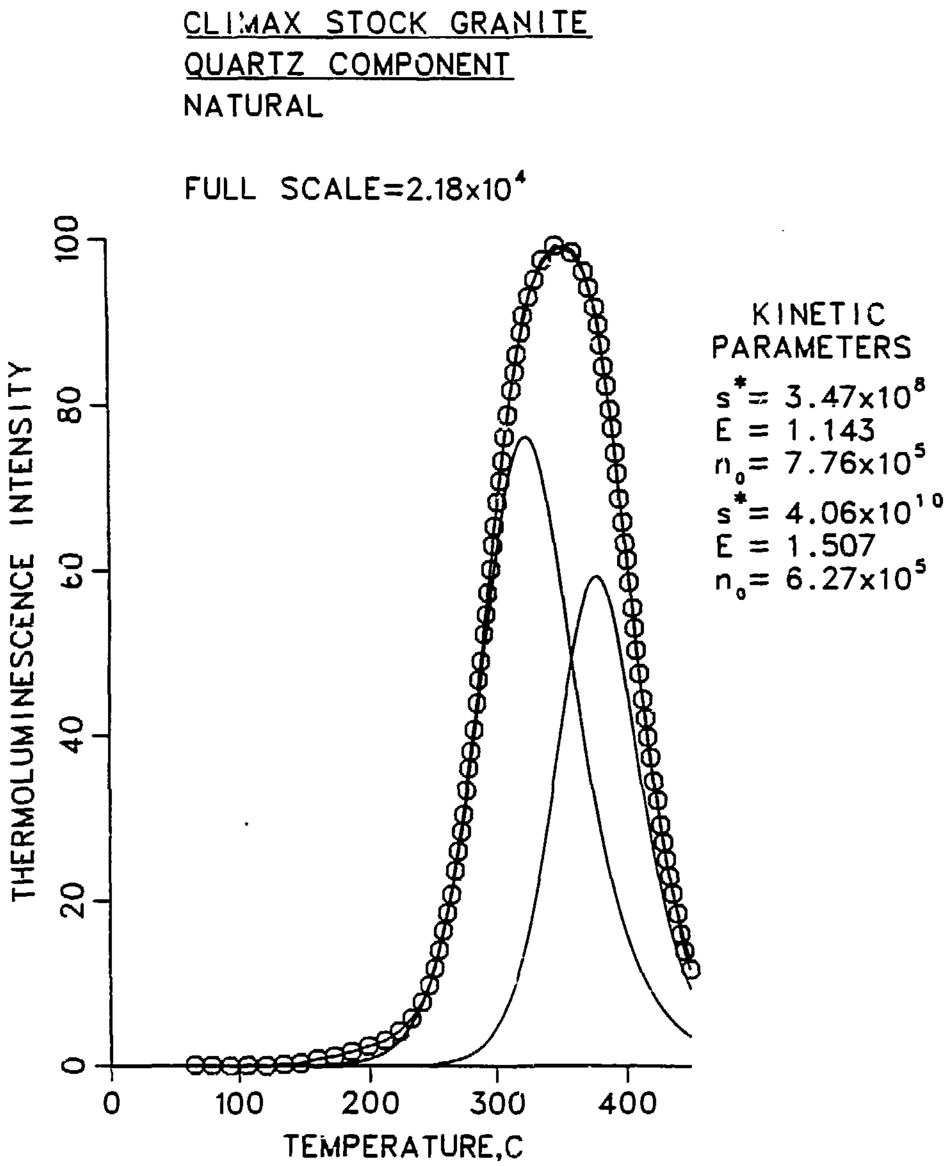

CLIMAX STOCK GRANITE
UNSEPARATED
THERMOLUMINESCENCE INTENSITY *10^3
36.0
27.0
18.0
9.0
0.0
O NATURAL TL
0
100
200
300
400
TEMPERATURE,C

FIGURE 1



CLIMAX STOCK GRANITE
QUARTZ COMPONENT
NATURAL
FULL SCALE=2.18x10^4
KINETIC PARAMETERS
s* = 3.47x10^8
E = 1.143
n0 = 7.76x10^5
s* = 4.06x10^10
E = 1.507
n0 = 6.27x10^5
THERMOLUMINESCENCE INTENSITY
0
20
40
60
80
100
0
100
200
300
400
TEMPERATURE,C

FIGURE 2

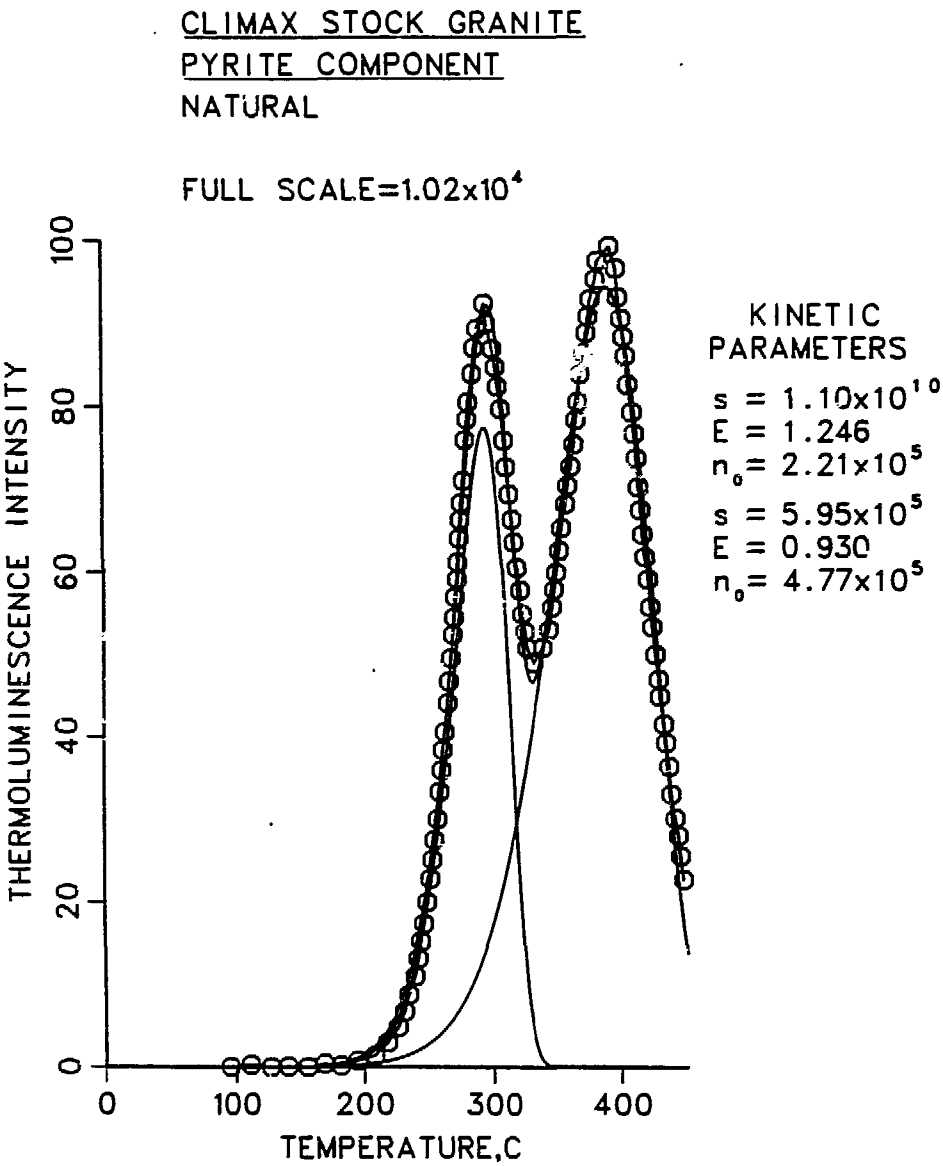
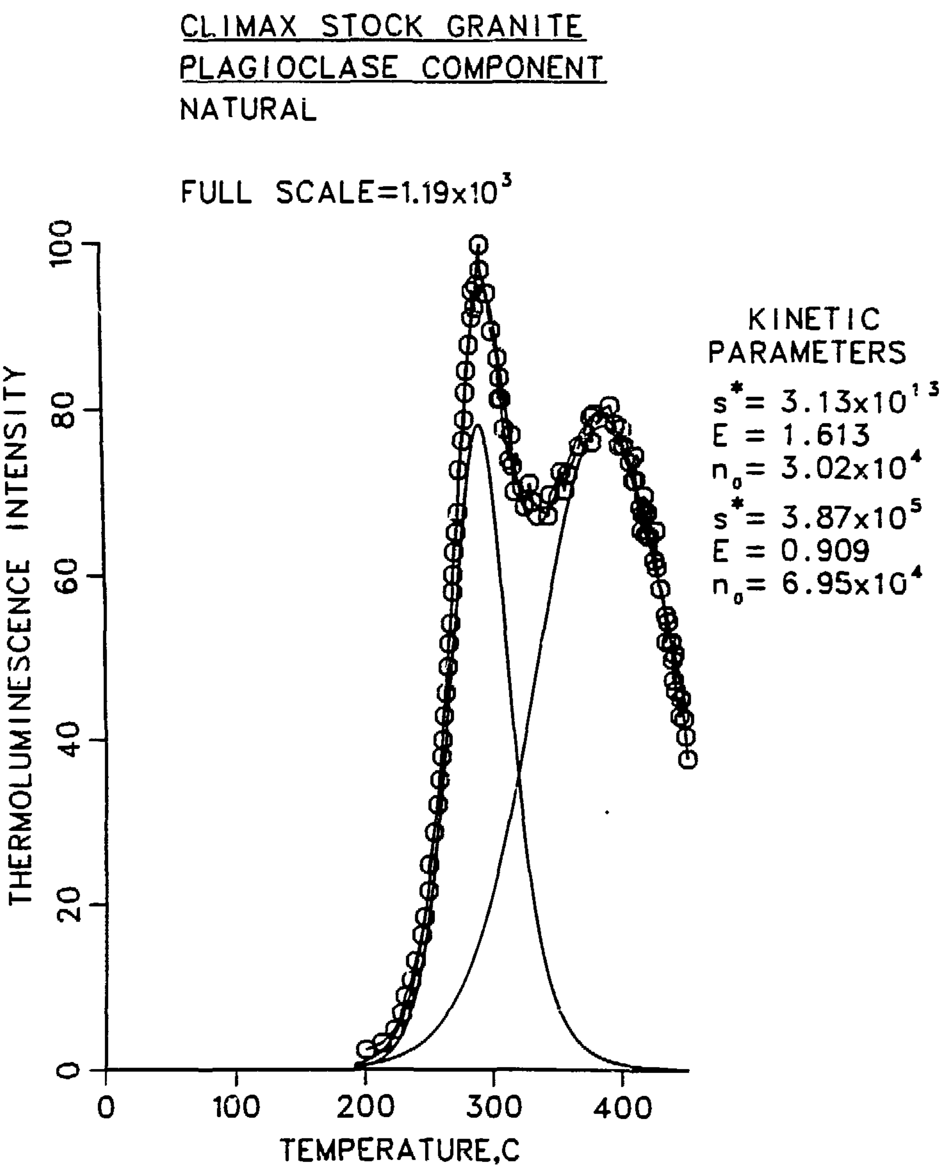
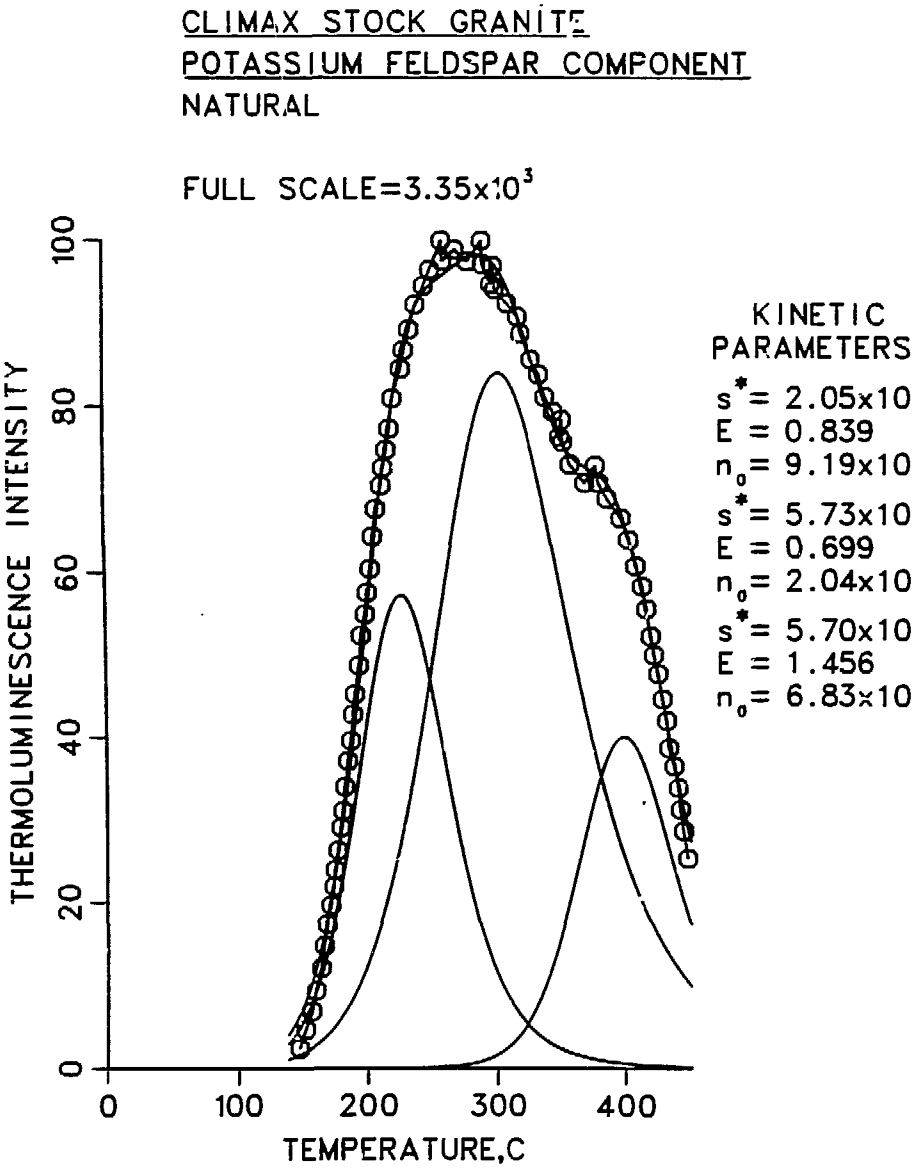

CLIMAX STOCK GRANITE
PYRITE COMPONENT
NATURAL
FULL SCALE=1.02x10^4
THERMOLUMINESCENCE INTENSITY
0
20
40
60
80
100
0
100
200
300
400
TEMPERATURE,C
KINETIC PARAMETERS
s = 1.10x10^10
E = 1.246
n_0 = 2.21x10^5
s = 5.95x10^5
E = 0.930
n_0 = 4.77x10^5

FIGURE 3



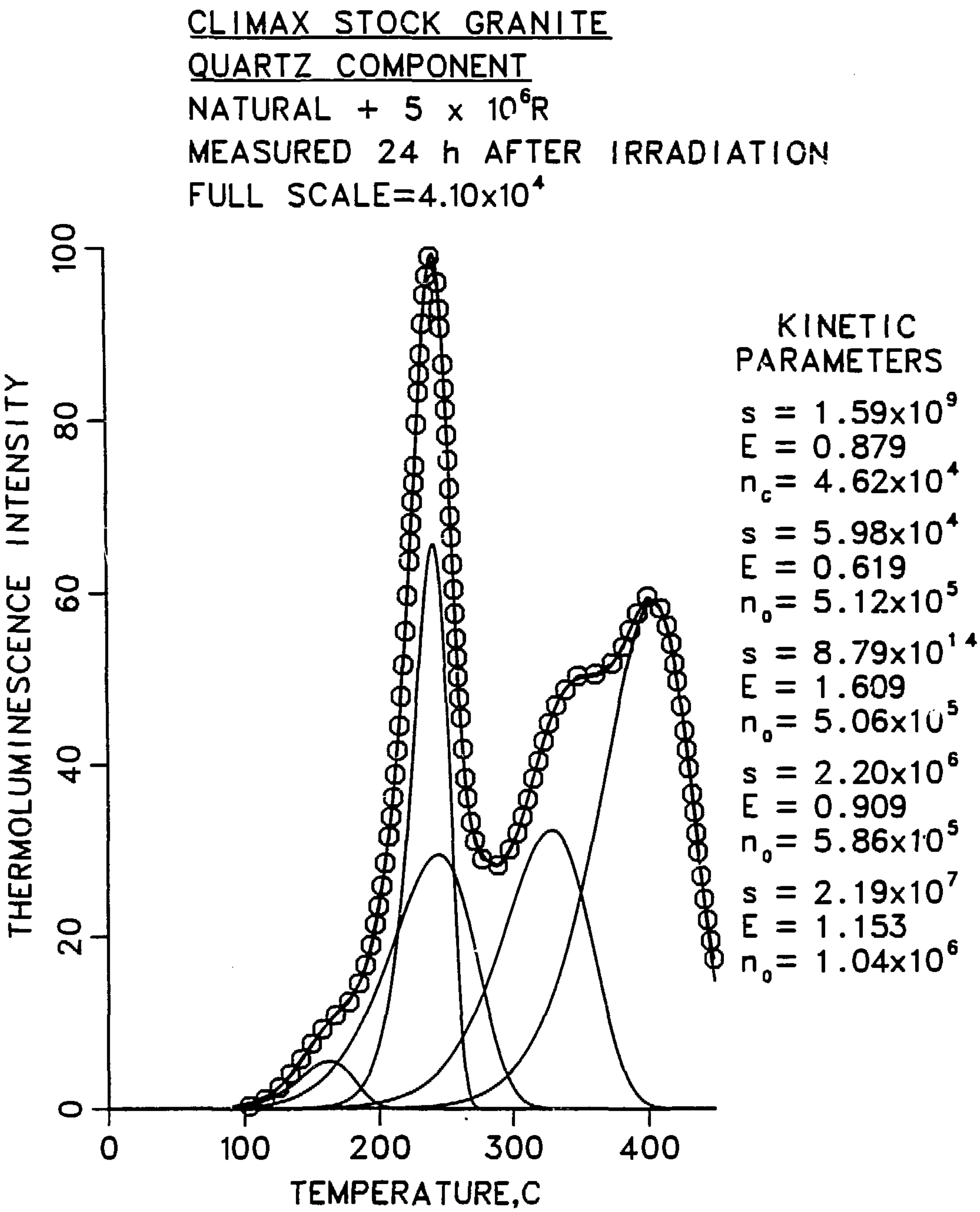
CLIMAX STOCK GRANITE
PLAGIOCLASE COMPONENT
NATURAL
FULL SCALE=1.19x10^3
KINETIC PARAMETERS
s*= 3.13x10^{13}
E = 1.613
n$_0$= 3.02x10^4
s*= 3.87x10^5
E = 0.909
n$_0$= 6.95x10^4
THERMOLUMINESCENCE INTENSITY
0
20
40
60
80
100
0
100
200
300
400
TEMPERATURE,C

FIGURE 4



CLIMAX STOCK GRANITE
POTASSIUM FELDSPAR COMPONENT
NATURAL
FULL SCALE=3.35x10³
THERMOLUMINESCENCE INTENSITY
0
20
40
60
80
100
0
100
200
300
400
TEMPERATURE,C
KINETIC PARAMETERS
s*= 2.05x10⁷
E = 0.839
n₀= 9.19x10⁴
s*= 5.73x10⁴
E = 0.699
n₀= 2.04x10⁵
s*= 5.70x10⁹
E = 1.456
n₀= 6.83x10⁴

FIGURE 5



CLIMAX STOCK GRANITE
QUARTZ COMPONENT
NATURAL + 5 x 10^6 R
MEASURED 24 h AFTER IRRADIATION
FULL SCALE=4.10x10^4
THERMOLUMINESCENCE INTENSITY
0
20
40
60
80
100
0
100
200
300
400
TEMPERATURE,C
KINETIC PARAMETERS
s = 1.59x10^9
E = 0.879
n_c = 4.62x10^4
s = 5.98x10^4
E = 0.619
n_0 = 5.12x10^5
s = 8.79x10^14
E = 1.609
n_0 = 5.06x10^5
s = 2.20x10^6
E = 0.909
n_0 = 5.86x10^5
s = 2.19x10^7
E = 1.153
n_0 = 1.04x10^6

FIGURE 6

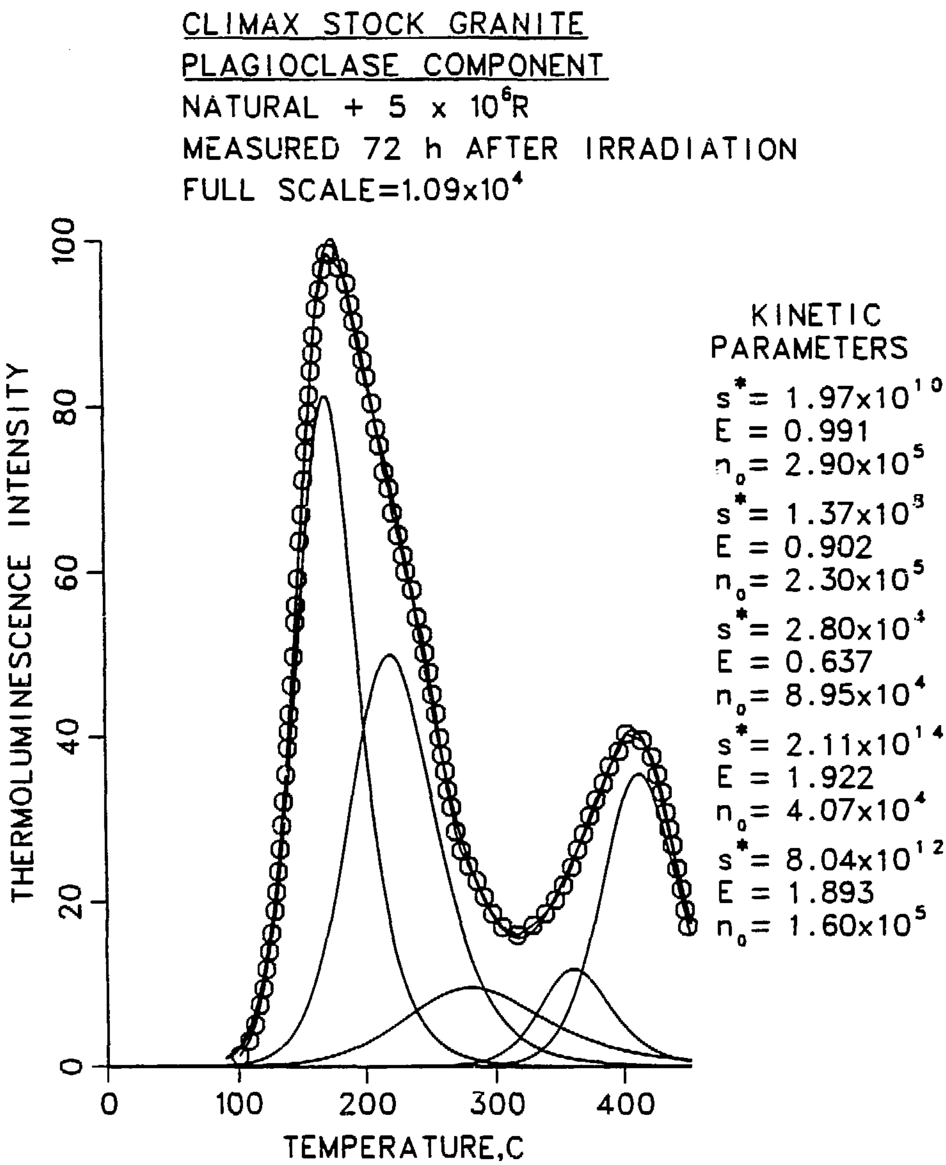
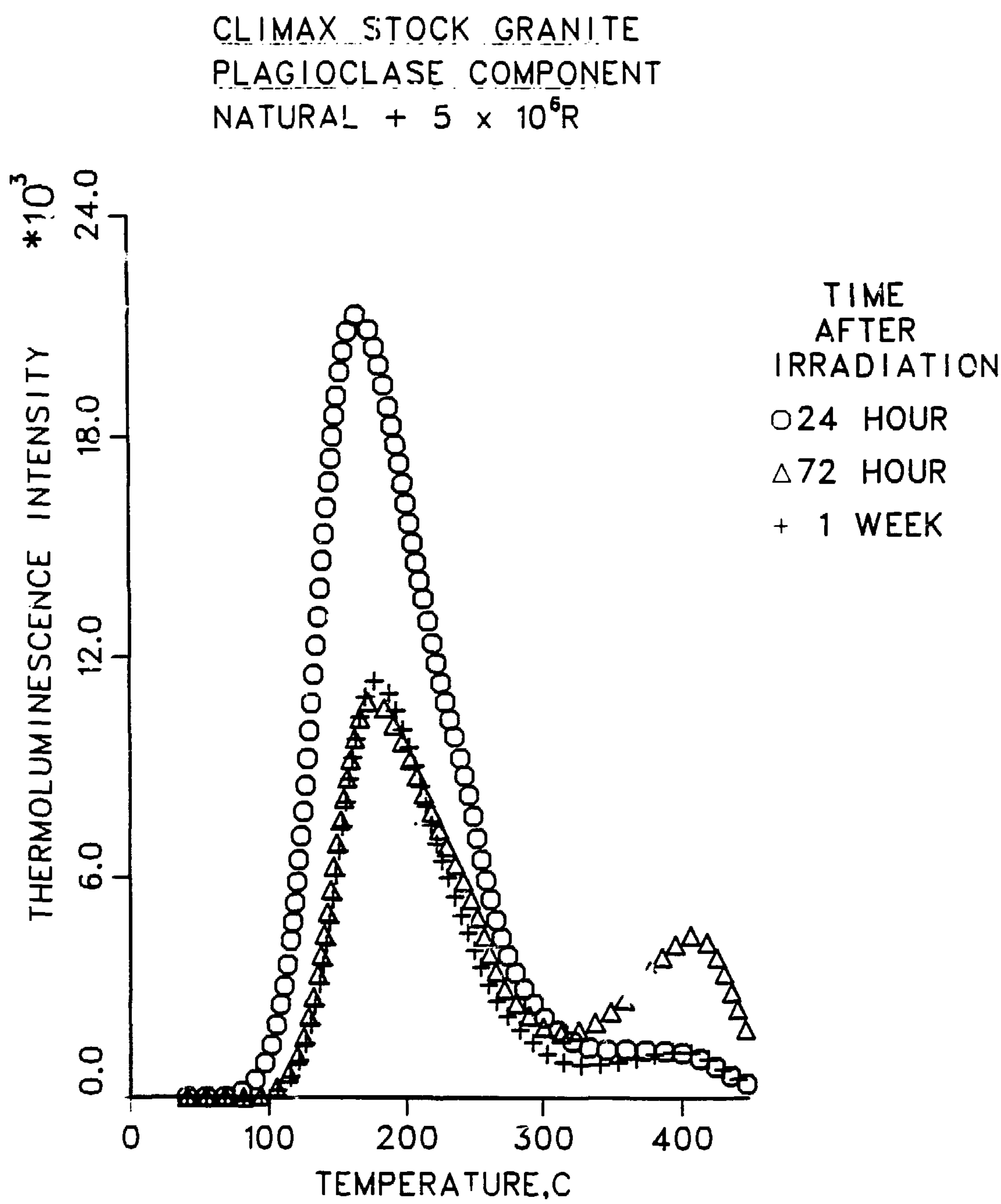

CLIMAX STOCK GRANITE
PLAGIOCLASE COMPONENT
NATURAL + 5 x 10^6R
MEASURED 72 h AFTER IRRADIATION
FULL SCALE=1.09×10^4
THERMOLUMINESCENCE INTENSITY
0
20
40
60
80
100
0
100
200
300
400
TEMPERATURE,C
KINETIC PARAMETERS
$s^* = 1.97 \times 10^{10}$
$E = 0.991$
$n_0 = 2.90 \times 10^5$
$s^* = 1.37 \times 10^8$
$E = 0.902$
$n_0 = 2.30 \times 10^5$
$s^* = 2.80 \times 10^4$
$E = 0.637$
$n_0 = 8.95 \times 10^4$
$s^* = 2.11 \times 10^{14}$
$E = 1.922$
$n_0 = 4.07 \times 10^4$
$s^* = 8.04 \times 10^{12}$
$E = 1.893$
$n_0 = 1.60 \times 10^5$

FIGURE 7



CLIMAX STOCK GRANITE
PLAGIOCLASE COMPONENT
NATURAL + 5 x 10^6 R
THERMOLUMINESCENCE INTENSITY
*10^3
24.0
18.0
12.0
6.0
0.0
0
100
200
300
400
TEMPERATURE,C
TIME AFTER IRRADIATION
24 HOUR
72 HOUR
1 WEEK

FIGURE 8