

Hydraulics Research
Wallingford

THERMOLUMINESCENT TRACERS -

A PRELIMINARY EVALUATION

C B Waters

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Registered Office: Hydraulics Research Limited,
Wallingford, Oxfordshire OX10 8BA.
Telephone: 0491 35381. Telex: 848552

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ABSTRACT

This report describes a preliminary appraisal of the properties of certain thermoluminescent (TL) materials which may be used as tracers in long-term field sedimentation studies. A summary is given of some existing tracer techniques, including the use of radioactive, fluorescent and chemical tracers. A brief description is then given of the property of thermoluminescence and the potential advantages of a thermoluminescent tracer material. The results of various laboratory tests carried out on natural silts and on a number of common TL emitters are presented. Recommendations are given for further investigation.

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1 INTRODUCTION

Radioactive tracers have been used for many years by Hydraulics Research Limited (HR) for studying sedimentation processes in the field. Techniques have been devised for the measurement of shingle, sand and silt movements and many field experiments have been conducted worldwide.

One particular area of research in which HR has played a leading role is in the study of methods of disposal of dredged spoil from navigation channels. The efficiency of the disposal method is defined as the proportion of the material dredged from the navigation channel which does not return to the channel in a significant time. Clearly the disposal efficiency must be allied with the overall objective of removing the maximum amount of spoil from the channel in the minimum time and at the minimum cost. Some examples of such field studies carried out by HR are given in references 1 to 4.

A fairly typical experiment was that carried out at the Port of Brisbane, Australia in 1981 (Ref.3). One of the objectives of this study was to determine, within 5%, the proportion of the dredged spoil which returned from the spoil ground to the navigation channel within one year of dumping. The spoil ground in this case was some 27 km seaward of the upper limit of the navigation channel. The experimental procedure consisted of seeding six hopper loads of spoil with 10-20 μm diameter scandium glass radioactive tracer which were then dumped at the spoil ground in the normal manner. The total quantity of radioactivity (Sc46) injected at the spoil ground amounted to 20 Curies (7.4×10^{11} Becquerels). The deposition pattern of the dumped spoil was mapped after dumping using a towed scintillation detector. During the course of the following year routine collection of several 1kg bed sediment samples from the dredged channel was undertaken. These samples were taken to the laboratory for measurement of the Sc46 content using a high-sensitivity gamma ray spectrometer. The measurement sensitivity was such that quantities of Sc46 of 10^{-10} Curies (3.7 Becquerels) in the 1 kg sample could be detected. At the end of the one year experimental period, allowing for decay of the isotope, this minimum detectable activity, if spread uniformly throughout the length of the navigation channel, represented some 4% of the injected

tracer. It is seen therefore that in this case using a radioactive tracer enabled us to measure a tracer (and hence dredged spoil) dilution factor of 1 part in 5×10^{12} .

The radioactive tracer technique has two major merits: the in-situ measurement of the tracer deposit gives an immediate indication of the mobility of the deposit and this assists in the planning of the subsequent bed sampling programme. The high-sensitivity laboratory counting equipment facilitates the measurement of very dilute tracer quantities.

In the Brisbane experiment, the tracer preparation, sample counting etc was undertaken by the Australian Atomic Energy Commission who also obtained the necessary governmental authorisation for this particular use of radioactive materials. By involving the local Atomic Energy staff in this way the logistics of carrying out the radioactive study were greatly simplified.

In many of the emerging countries extensive port developments are taking place and the developments frequently involve the deepening of navigation channels and the consequent problem of maintenance dredging and disposal of the dredged material. Many of these countries do not have the facilities for producing radioactive materials nor the local expertise for handling large quantities of radioactivity. In addition, in some instances there are objections to the use of radioactive materials for environmental studies. There is clearly a need for a non-radioactive tracer method for use in these special circumstances.

The method should ideally:

- (a) be no more expensive than radioactive methods;
- (b) be non-hazardous and hence usable by relatively unskilled personnel and without objections on environmental grounds;
- (c) have a measurement sensitivity comparable with that achieved using radioactive tracers.

If the tracer costs are sufficiently low it is likely that a large initial tracer concentration could be used. A measurement resolution of 1 part in 10^9 of the initial concentration is therefore suggested as a reasonable objective.

Existing alternative techniques which have been used in sedimentation studies with varying degrees of success include:

1 Activation Analysis

This is a technique whereby an inactive chemical element is incorporated as the tracer. In order to detect the tracer element a bed sampling programme is undertaken, similar to that described for the Port of Brisbane study. These samples are subsequently irradiated in a nuclear reactor to produce a radioactive isotope of the tracer element. The quantity of tracer in the sample is then determined using a high-sensitivity counting system.

There are several major problems in using this technique:

- (a) the irradiation of the sediment samples produces not only the radioactive tracer isotope but also radioactive isotopes of the other constituents of the sediment sample. Some of these "background" elements have short half-lives compared with that of the tracer and after a period of decay the background contribution will decrease but will nevertheless remain significant;
- (b) in order to be uniquely identifiable, the tracer element should not be present in significant quantities in the natural sediments. This inevitably restricts the choice to very rare and hence very costly elements;
- (c) a nuclear reactor facility must be available to produce the radioactive samples. The irradiation of large-sized samples in a nuclear reactor is very costly and if carried out as a fully commercial exercise the cost of irradiating many samples would be prohibitively expensive.

Because of these inherent problems, the measurement resolution achieved using this technique is generally less than 1 part in 10^6 of the initial concentration.

2 Fluorescent tracers

In this method a fluorescent compound is used as the tracer. Many chemical elements fluoresce when exposed to ultra violet (UV) light. Techniques have been devised for coating sediment particles with fluorescent materials and a range of fluorescent colours are available.

The major drawback in using a fluorescent tracer in large-scale studies is that no instrument is available for automatically detecting small tracer particles. Recourse is therefore made to using laborious manual counting of samples whereby known weights of sediment are exposed to UV light and the fluorescent particles individually counted.

Because of the difficulty in detection, this technique has been used almost exclusively for measurements on large-sized sediments (sand and shingle) and can be a useful technique for small-scale beach studies.

3 Chemical tracers

A variety of techniques exist for determining the chemical composition of sediments and much work has been done in improving the sensitivity of detection of polluting elements such as heavy metals.

Most port areas are close to industrial complexes with high population densities. Sediments in the navigation channels are therefore generally heavily polluted with a wide range of chemicals. The prospect of finding a unique and cheap tracer element which can be used in these circumstances is very unlikely.

The shortcomings of the existing alternatives to radioactive tracers led us to consider the potential of thermoluminescent (TL) materials as a means of achieving our objectives.

THERMOLUMINESCENCE

Some simple examples of luminescence processes are illustrated in Fig 1.

- (a) Fluorescence: the prompt return of an electron from an excited state either directly to ground state or via an allowed transition from an intermediate state S.

- (b) Phosphorescence: return of an electron from an excited state to the ground state is delayed by the metastable state M. Direct transition from the metastable to the ground state is forbidden.
- (c) Thermoluminescence: the return of electrons trapped in the metastable state is speeded up by heating.
- (d) Anti-Stokes luminescence: the excitation of an electron is achieved by the absorption of two or more photons.

Thermoluminescence is the property of certain substances to absorb radiation and to release it, on application of heat, in the form of optical radiation of various wavelengths. The irradiation of the TL material by a radioactive substance does not produce a radioactive product. The TL material is not therefore radiologically hazardous. Many naturally occurring minerals exhibit TL properties.

The TL process is widely used for radiation dosimetry and specific TL "cocktails" have been developed for use as dosimeter materials. These dosimeters generally consist of either TL granules enclosed in a sealed plastic holder or powder incorporated in thin p.t.f.e. discs. Automatic dosimeter reading instruments are commercially available. These instruments consist of a small heated planchet on which is placed the TL dosimeter. Controlled heating of the planchet in an inert gas atmosphere causes emission of the optical radiation which is then detected by a photomultiplier/filter system. The photon output signal is amplified and recorded on a frequency meter. Each TL material has a characteristic glow curve ie. an amplitude versus temperature spectrum. The TL response of the dosimeter is generally linear within certain radiation dose limits. These dose limits for commercially available dosimeters range from 10^{-5} to 10^4 Grey. (The Grey [Gy] is the SI unit of absorbed radiation dose).

The amplitude of the TL signal is recorded as a frequency (Hz) and the TL response of the particular sample is usually described as a frequency per unit weight (Hz mg^{-1}).

As a point of interest most of the estimates of radiation dose resulting from the explosion of the atomic bombs on Hiroshima and Nagasaki have been obtained from an examination of the TL emission from building materials obtained from the sites.

Archaeologists also make use of the TL process for dating of ancient pottery, burnt clay, bricks etc. The clay often exhibits TL properties. Because of the high temperatures used in the firing process, any trapped TL in the clay would have been released at the time of firing, Subsequent exposure of the clay to the natural background radiation of the site would result in a gradual build up of TL in the material. Measurements of this TL emission, together with a careful calibration of the material and an assessment of the radiation exposure rate at the site allows the archaeologist to derive a date for the firing of the artefact.

A combination of factors, summarised below, lead us to consider the use of TL materials as tracers for sedimentation studies:

- (a) many commonly available materials exhibit TL properties, including some clays;
- (b) being common, the tracer cost is likely to be low;
- (c) the range of measurable absorbed radiation dose is high and hence the potential sensitivity of the method is high;
- (d) detection instrumentation is commercially available;
- (e) the TL tracer does not present a radiological hazard.

2 LABORATORY TESTS

The laboratory tests were carried out by the Department of Archaeology of the University of Durham. This department specialises in dating of archaeological specimens using TL techniques. The materials which they routinely study consist mainly of pottery, burnt clay, stones and flint which are ground to fine granular form before examination. The measurement techniques were thought therefore to be appropriate for the fine grained sediments which we wished to study.

Three separate studies were carried out and a short laboratory report was prepared by the University at the end of each. These individual reports are presented as appendices to this report.

2.1 TL characteristics of natural sediment

In the first study consideration was given to the possible use as TL tracers of the minerals found naturally in dredged sediments. The sediment used in this case was obtained from Port Qasim in Pakistan. For many years Hydraulics Research has been involved in the large-scale development work at this port and it was thought likely that techniques such as TL tracers could play an important part in studying and improving the spoil disposal practices used at the port.

The use of a naturally occurring tracer has dual attraction (a) any possible objections on the grounds of hydraulic similarity are removed and (b) the material is likely to be cheap and therefore usable in large quantities.

The full experimental details are given in Appendix 1.

The tests were carried out on the sand sized ($> 63 \mu\text{m}$) fraction of the sediment; this being the size of material normally used in dating work.

A qualitative determination of the mineral composition of the sample was carried out using X-ray diffraction techniques. The results indicated in relative order of abundance the minerals quartz, feldspar, muscovite, chlorite, kaolinite and calcite. Quartz, feldspar and calcite are known TL minerals and it was decided therefore to look more closely at the characteristics of the quartz fraction of the sample.

The glow curve resulting from natural irradiation of the material over geological time was first determined. This was followed by two calibration irradiations on samples which had been previously heated to remove the natural TL.

The results indicated some complexity in the behaviour of the TL response. At the peak TL position, corresponding to an excitation temperature of 325°C a background absorbed dose of 80 Gy was indicated. At higher temperatures of between 400 and 500°C a lower background dose of about 19 Gy was indicated.

The linearity of response of the quartz to increasing dose was determined from two irradiations, one of 20 Gy and the other of 180 Gy. It was not possible at the time, using the relatively small beta (β) irradiation source available at the University, to investigate the dose response to higher doses. The results indicate however that a dose of 2 MGy would be required to give a 1,000 : 1 tracer to background ratio, assuming that the response is linear up to this dose level.

A short test was then carried out on the untreated sand ie. sand containing the mixture of elements.

The "background" TL response of the sample was determined and this compared with the TL output of samples which had been irradiated in the laboratory. At a temperature of 325°C corresponding to the position of the peak TL response, the ratio of TL intensities ie. background + β irradiation: background appeared to saturate at a dose of about 100 Gy at a value of about 12 : 1. Some small gain in this ratio was indicated at lower temperatures. After some refinement of the measuring technique, a background TL response of about 9 kHz mg⁻¹ was found for the untreated sand.

2.2 TL Measurements on potential tracer materials

In the next series of short tests, detailed in Appendix 2, the TL properties of some potential tracer materials were investigated. The "short list" of materials was chosen after a preliminary literature search. As well as being cited as TL emitters the potential tracer materials were chosen on the grounds of availability and cost, similarity in density to natural sediments and low solubility in water. Eight materials were finally selected

viz - Anhydrite, Corundum, Fluorite, Franklinite, Gypsum, Olivine, Willemite, Glass + 1% Li Fl and Li Fl : Dy. The first six of these materials are naturally occurring minerals and the last two are commercially available compounds used widely for radiation dosimetry.

Each sample was ground to the fine particle size range of 1 to 10 μ m diameter. For each material the background TL, produced by the previously accrued "natural" radiation dose was determined. Each sample was then subjected to known beta radiation doses, using a calibrated Strontium 90 plaque source. For each administered radiation dose, the TL response of the sample was determined.

The results of these tests are plotted in the Appendix and show that all samples exhibit some TL response over the small range of radiation dose investigated. The TL response to administered dose was found to be linear in each case. The saturation dose for the samples was not determined. The material showing the greatest TL sensitivity to dose was found to be fluorite. This material understandably also showed the highest background TL reading.

Having investigated briefly the TL properties of these various materials, additional tests concentrated on determining in more detail the TL properties of the fluorite material.

2.3 Further TL measurements on fluorite and natural silt

The final series of tests are detailed in Appendix 3.

Two forms of fluorite were examined: the natural one and a commercial grade of calcium fluoride; the latter being more readily available and its chemical properties thought likely to be more predictable than the naturally occurring one. In addition, a natural silt, this time from the Mersey estuary, was examined.

The TL characteristics of both tracer materials were examined by subjecting samples to increasing beta radiation doses and measuring the resultant TL glow curves. The background glow curve of the Mersey silt was also measured.

For both tracer materials the saturation beta radiation dose was approached at a dose level of about 18 kGy. At the dose saturation level the predicted peak TL response of the fluorite sample was 67 MHz mg^{-1} compared to 1.6 MHz mg^{-1} for the calcium fluoride sample. By comparison the background peak TL response from the Mersey silt sample was 6.4 kHz mg^{-1} . This figure was similar to the figure of 9.3 kHz mg^{-1} obtained from the Port Qasim silt studied previously. Assuming that the background absorbed dose on the Mersey and Port Qasim sand samples were representative, then the "signal to noise" ratio achieved using the fluorite tracer was approximately $10^4 : 1$.

3 **SUMMARY AND
CONCLUSIONS**

In this short series of tests we have:

- (a) investigated the background TL emission from natural sediment from Port Qasim, Pakistan and from the Mersey estuary, UK. In both cases a similar and relatively high background TL level was found from the untreated sediment;
- (b) identified a number of potential TL tracer materials and measured their relative TL sensitivities;
- (c) carried out more exhaustive tests on fluorite and determined its TL emission at a saturation dose level.

To date the best "signal to noise" ratio achieved ie. the ratio of the saturation dose TL emission from fluorite to the background TL emission from natural untreated silt is approximately 10^4 : 1.

It is likely that for a typical full-scale dredging disposal experiment, as outlined in the introduction to this report, a resolution of at least 1 in 10^9 will be required. Clearly after carrying out these initial tests we are a long way short of achieving this resolution.

There are two main problem areas - (i) the high background level from the natural silt and (ii) the resolution of the instrumentation used for detecting the TL emission.

In the case of the background contribution there is a need for a closer investigation into the mineral composition of the natural silts and the determination of the relative TL sensitivities of these constituents. It is possible that pre-treatment of samples could remove some of the background emission without adversely affecting the TL tracer material.

It is proposed also to carry out further investigation on other potential TL tracers. It is likely that the natural TL emitters found in the silts may be site specific and that a suitable tracer may need to be selected for a particular site. It is recommended that we determine the saturation dose TL emission from the selected TL materials described in Appendix 2. In order to achieve the

necessary high radiation dose levels we shall explore the possibility of sample irradiation at a local high-level radiation facility.

Commercial instrumentation used for detecting TL emission from samples has been developed largely for the specific purpose of personnel radiation dosimetry. The size of the individual dosimeter is small and sample weights of the TL materials used are consequently small. The sample holder/heating plate used in the typical commercial instrument is designed to contain sample weights of between 1 and 10 milligrams. This scale of measurement is consistent with the requirements of the archaeologist and TL dating of specimens is usually undertaken using the standard commercial dosimetry system. In our case however it would be advantageous to be able to measure much larger samples. For a uniform sediment particle size of $20\ \mu\text{m}$ diameter and a density of $2.6\ \text{g cm}^{-3}$ there are approximately 10^8 particles per gram of material. In order to detect 1 part in 10^9 we would need therefore to measure samples of at least 10 grams in weight. It is feasible to devise a detection system for larger samples. In the literature there are references to various means of stimulating the TL emission from samples such as heated gases and laser illumination. It is envisaged that a fairly simple "continuous flow" system could be used with the sample being heated within a chamber and using the existing optical detection equipment. It is not proposed to proceed to this stage of development until we have explored further the possibility of reducing the background TL emission of the natural silts.

Although it was not the purpose of this study it is worth mentioning that TL tracers could possibly be used in small-scale beach sediment investigations. At present, fluorescent tracer sand is frequently used for such studies. There is no automatic instrument for measuring fluorescent tracer concentration and a laborious manual process is used whereby fluorescent grains are counted. If a large quantity of "cheap" TL tracer were introduced a resolution of 1 in 10^4 may be adequate for some applications.

4 **ACKNOWLEDGEMENTS**

This preliminary evaluation was supervised and this report written by Mr C B Waters, Head of HR Field Studies Section which is part of Dr A J Brewer's Technical Services Department.

The author wishes to thank Messrs I Bailiff and I Watson of the Department of Archaeology, University of Durham, who were responsible for the various TL measurements described in the report and who gave valuable advice throughout the study period.

Thanks are also due to Mr P Kiff, Head of HR Sedimentation Laboratory who was responsible for the selection and preparation of the various tracer and silt samples.

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Figures

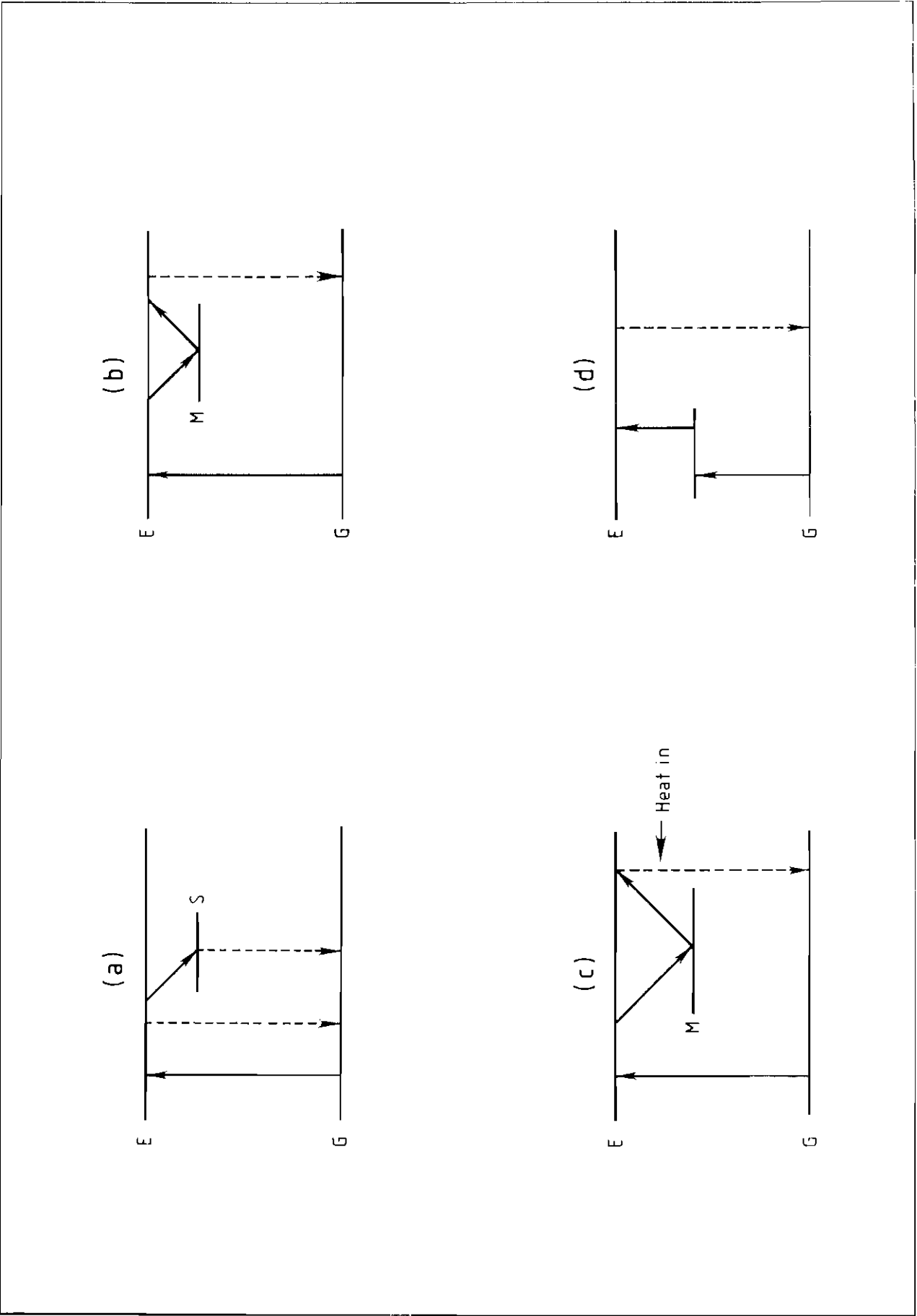


Fig 1 Simple examples of luminescent processes

APPENDIX 1

TL Measurements on Natural Silt

EXPERIMENTAL REPORT

SAMPLE: DREDGED SILT $> 63 \mu\text{m}$ FROM HYDRAULICS RESEARCH

A) Qualitative determination, by XRD, of mineral composition of the sample.

In relative order of abundance:

quartz	*
feldspar (plagioclase)	*
muscovite	
chlorite and kaol ⁱⁿ ite	
calcite	*

*TL minerals

B) Measurements to determine the absorbed dose from the quartz fraction.

A quantity of $> 63 \mu\text{m}$ spoil was etched in 40% HF acid for 30 min. and subsequently washed in an AlCl_3 solution to eliminate precipitated fluorides.

The TL glow curves are shown in fig. B1. The natural glow curve and glow curves obtained after the administration of beta doses of 20 Gy and 180 Gy are indicated as NAT-TL, β -TL(20 Gy) and β -TL(180 Gy), respectively.

The behaviour of the TL peaks is complex. Besides the shifts in peak temperature, the intensity of TL for the NAT-TL curve is expected to be lower than that for the β -TL curve in the lower temperature region of the glow curve if the curves match at higher temperatures. For dating work an evaluation of the "natural dose" would not be straightforward. However, a plot of the ratio of β -TL(20 Gy) : NAT-TL intensities vs temperature gives a measure of dose equivalence of the natural TL as a function of temperature - as shown in fig. B2. Although 19 Gy is required to match the NAT-TL intensity between 400 and 500 °C, 80 Gy would be required to equal the NAT-TL intensity at 325 °C, assuming linear growth of TL with dose at this temperature.

The variation in TL peak height (maximum intensity) with dose

is shown in fig. B3. A linear growth characteristic can be accommodated within $\pm 10\%$ error limits.- albeit with two points. As we discuss below, the growth characteristic needs to be investigated to much higher doses, for which the irradiation time would be too long to fit into our present schedule.

Further TL measurements have shown other TL complexities. If the filter system is changed, shifting the spectral window from the blue/violet towards the u.v. , the position of the natural and beta TL peak maxima move to lower temperatures [by 50°C]. The behaviour of the TL peaks with dose is similar to that described above , although the dose required to match the natural TL emission in the high temperature region of the glow curve is 30 Gy.

C) Variation in light output per unit weight

We compared the variation in light output of untreated silt and HF etched silt. Representative natural glow curves for both types of sample are given in fig. C1 .

[i] Using four portions of HF etched sample, the mean peak height was,

$$23.6 \pm 0.4 \text{ [s.e. 4] kHz mg}^{-1}$$

where the portions were in the weight range 1.8 - 2.7 mg.

[ii] Using four portions of untreated silt, the mean peak height was,

$$256 \pm 27 \text{ [s.e. 4] kHz mg}^{-1}$$

where the portions were in the weight range 0.65 - 2.7 mg.

By increasing the portion weight and introducing a 1.0 neutral density filter we found reduced scatter and the mean peak height from six portions was,

$$9.3 \pm 0.1 \text{ [s.e. 6] kHz mg}^{-1}$$

where the portions were in the weight range 1 - 10 mg.

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The variation in light output is very low for the HF etched sample (1.7% s.e.) and comparably low variation is obtained from the untreated sample if the portion weight is above 1 mg.

The results show that the quartz TL emission is a minor contributor to the natural TL emission from untreated silt, being an order of magnitude lower.

D) Maximum weight of sample

Using a monolayer of grains on a 1 cm diameter disc we can deposit up to 10 mg of sample. Larger diameters would probably give rise to undesirable temperature gradients across the sample. Greater mass could be accommodated in a pan, but we suspect that the variation in light output per unit weight would suffer as a result of multiple layering.

E) Comments on the use of the quartz fraction as a tracer

The relatively low TL output of the quartz fraction provides a disadvantage (a factor of ten) unless all samples are HF etched before measurement. For a 'signal:noise' ratio of 1000:1, the growth characteristic in fig. B3 indicates that a dose in the region of 2 MGy is required. Since our source (40 mCi Sr90/Y90) delivers 1.3 Gy min^{-1} , we are not in a position to investigate the linearity of the quartz fraction into this dose region - unless the sample can be irradiated elsewhere.

F) Measurements on untreated silt

We measured the TL output of untreated portions of silt, each of which had received a laboratory beta dose in addition to the 'natural' dose. At the peak temperature of the natural TL glow curve (ca 325°C) the ratio of TL intensities (NAT + β) : NAT appeared to saturate by $\beta = 100 \text{ Gy}$ (Fig. F1) at a value of 12:1. However, a significant gain in this ratio is obtained at lower temperatures ($175 - 325^{\circ}\text{C}$), indicated by the shaded area, where the natural TL has faded over geological time. The stability of TL peaks

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above 180 °C should have sufficiently long half lives for use as a tracer. There is a stable peak at 280 °C from calcite, which may contribute to this glow curve. We have mentioned an instability of TL that is associated with some feldspars and its effect on the stability of the (NAT + β) glow curve would need to be tested.

I K Bailiff.

TL RESEARCH SERVICE LABORATORY
UNIVERSITY OF DURHAM.

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Notes on Experimental Conditions

1. The TL detection system comprises an EMI 9635QB photomultiplier with Chance Pilkington HA3 and Corning 7-51 or 5-60 Filters. The solid angle of collection is approximately π steradians.
2. Portions of sample supplied were deposited as a near monolayer on stainless steel discs.
3. Samples were heated in an atmosphere of oxygen-free nitrogen at a rate of $10^{\circ} \text{ s}^{-1}$.
4. Irradiations were performed with the sample located on the TL oven heater plate at RT using a calibrated Sr90/Y90 beta source.
5. Unless stated otherwise, an experimental error of $\pm 10\%$ is estimated for preliminary measurements.
6. The temperature shown on glow curve plots represent the temperature at the thermocouple, the junction of which is welded to the underside of the heater plate.

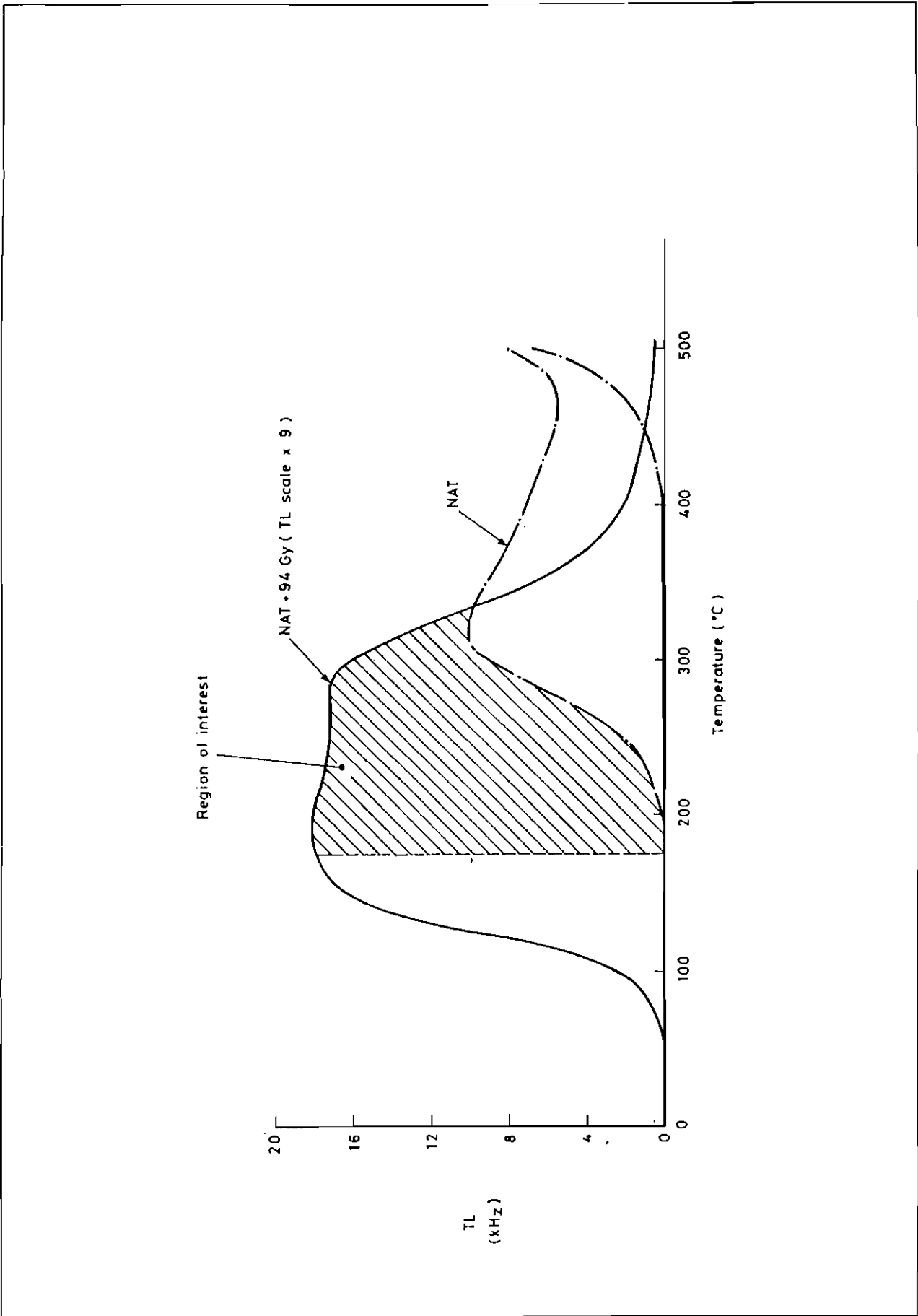
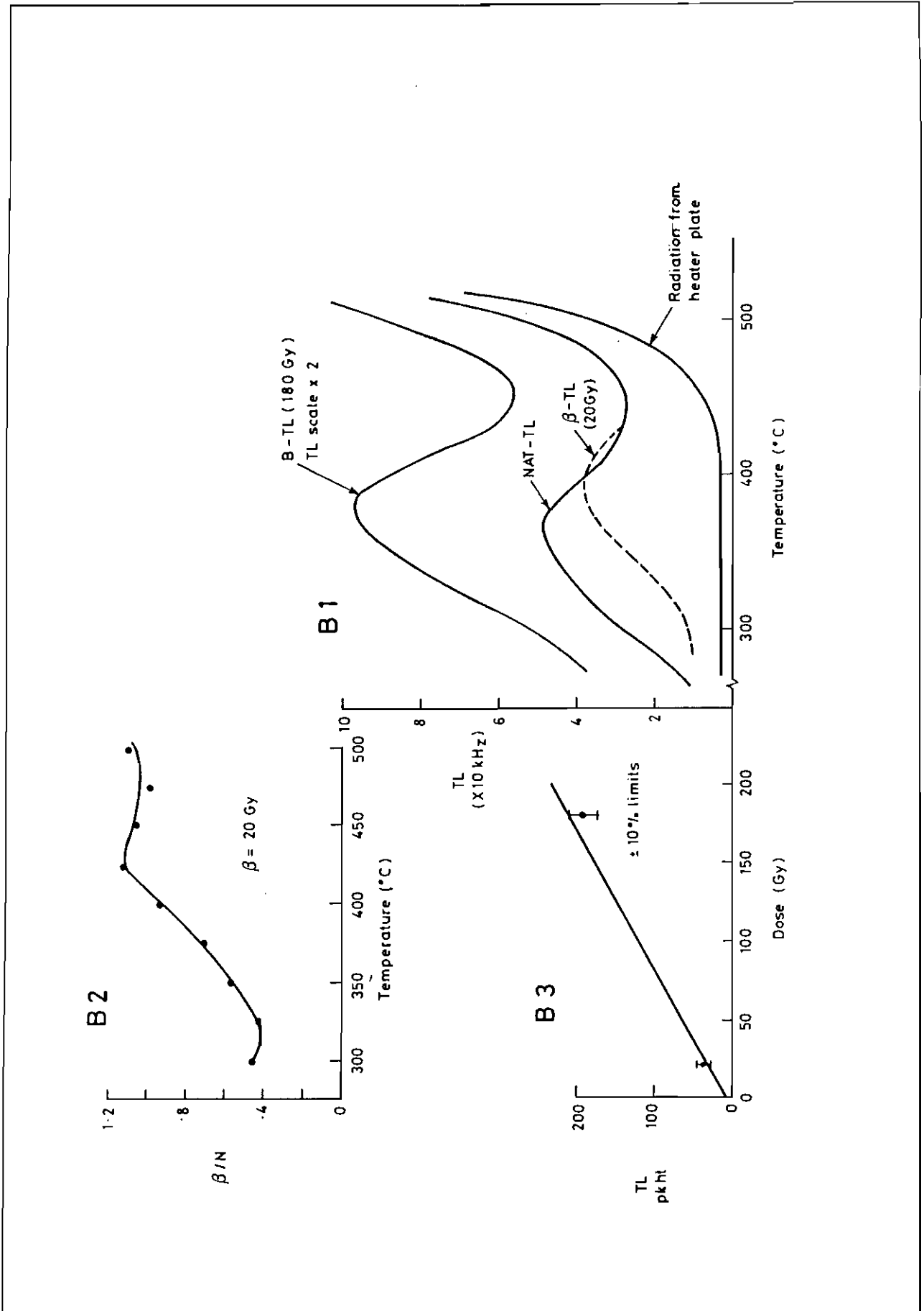
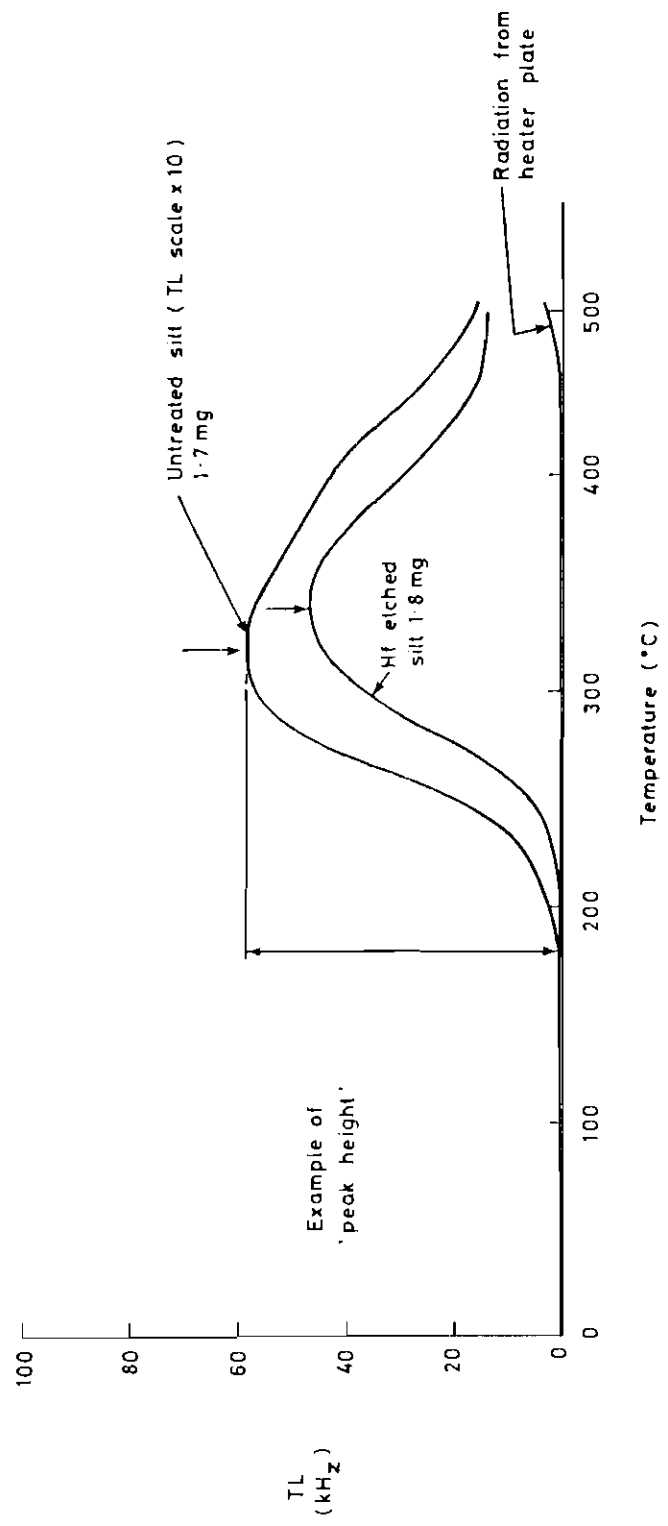


Fig F1 Comparison of (NAT + β) and NAT glow curves - untreated silt $> 63 \mu m$



Figs B1 - 3 Glow curves - Quartz fraction



Fig! C1 'Natural' glow curves > 63 μm silt

APPENDIX 2

TL Measurements on Tracer Materials

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REPORT: TL MEASUREMENTS ON TRACER MATERIALS

1. Sample Preparation

Material in the grain size range 1-10 μm was deposited by sedimentation onto four aluminium discs for each sample submitted, one disc carrying 1-2 mg of sample.

2. Measurements

Sample discs were heated at 10deg/s in an atmosphere of oxygen-free nitrogen and the TL emission observed using a detection system comprising an EMI 9635Q photomultiplier in conjunction with an optical filter system biased towards the violet/uv region of the spectrum.

For each sample the following TL measurements were performed:

- 1) TL due to previously accrued dose - NTL
- 2) TL due to laboratory administered beta dose for three levels of dose (1, 5 and 10 minutes of irradiation) - ATL
- 3) stability of ATL after 4 days storage in dark at RT
- 4) tests for spurious TL comprising 1 min exposure to ambient atmosphere and light.

The laboratory beta doses are given in minutes of irradiation: the source used delivered a dose of 2Gy/min to all samples except fluorite where a different source was used, delivering 1.4Gy/min. These dose-rates are calibrated for quartz grains in the size range of 2-10 μm and to calculate the exact dose administered to materials of different mean atomic number, small corrections (less than 10% in most cases) are required to account for differences in stopping power.

3. Results

NTL and ATL glow curves recorded for each sample in the temperature region RT-500 deg.C are given in figure 1 (reproducibility better than $\pm 10\%$). Table 1 contains the measured heights (as photon rate) of the TL glow peak marked by an arrow in the NTL and ATL glow curves, and these values have been plotted in figure 2. We also checked the suitability of the optical filters by repeating these measurements using an optical filter system biased towards the blue region of the spectrum and observed no gain in TL peak height, except for olivine where a threefold increase in TL peak height was measured.

No significant fading of TL was detected for any of the samples, the greatest being in the case of the LiF tracers where $10 \pm 5\%$ loss was recorded. Sensitization of the marked peak was also tested for each sample: LiF:Dy and fluorite both exhibited sensitivity enhancement (approximately 30% after the administration of 30 Gy), while for the other samples, the alteration of sensitivity of the marked peak was within $\pm 10\%$ limits.

No significant spurious TL was detected for any of the samples using the 1 min exposure test.

4. Discussion

The TL emission from fluorite is significantly higher than from any of the other samples. Its nearest competitor is gypsum, the TL emission from which is lower by a factor of 300. Assuming linearity of TL with dose, a beta dose of approx. 500 Gy is required to match the intensity of the marked TL peak. This peak has been studied in a natural fluorite and has a mean lifetime in excess of $10E^8$ years at RT. We have not explored the linearity of TL emission beyond the level of the NTL and a dose in excess of 2.5 kGy would be required to test for saturation effects (28 h irradiation with our source).

A rough comparison can be made of the TL emission from fine-grain fluorite with that from the silt that we tested in 1983. If we assume that the TL output from untreated silt and fine-grain material is similar, the ratio of NTL intensities per unit weight is,

$$\frac{TL(FLU)}{TL(SILT)} = \frac{1.6 \cdot 10E5}{4.5 \cdot 10E2} = 3.6 \cdot 10E2$$

in the temperature region 300 - 350 deg.C of the glow curve (a correction for the differences in TL detection efficiency has been made in the case of the silt result of 1983).

The amount by which this ratio may be increased will depend on the saturation level of NTL emission from fine-grain silt samples. On the basis of examination of the NTL glow curves for the larger grain silt, an order of magnitude increase in this ratio would probably be obtained by using the 200 deg.C fluorite TL peak. Further gain may be available if the difference in NTL emission for HF etched and untreated silt is substantially due to calcite, which could be eliminated by treating samples in a weak acid solution.

Suggestions for further work:

* Determination of saturation level of TL emission from fluorite using a dose in excess of 2.5 kGy and test NTL emission from fine-grain silt.

* Investigate linearity of NTL and ATL response from silt doped with various concentrations of tracer.

* Reduction of NTL using weak acid treatments if further gain required.

N.B. We have assumed that the relative TL outputs for the samples tested broadly reflect the relative differences in the maximum TL output per unit weight that would be obtained after the administration of a saturating radiation dose.

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TL LABORATORY, DURHAM TL DATING AND RESEARCH SERVICE.

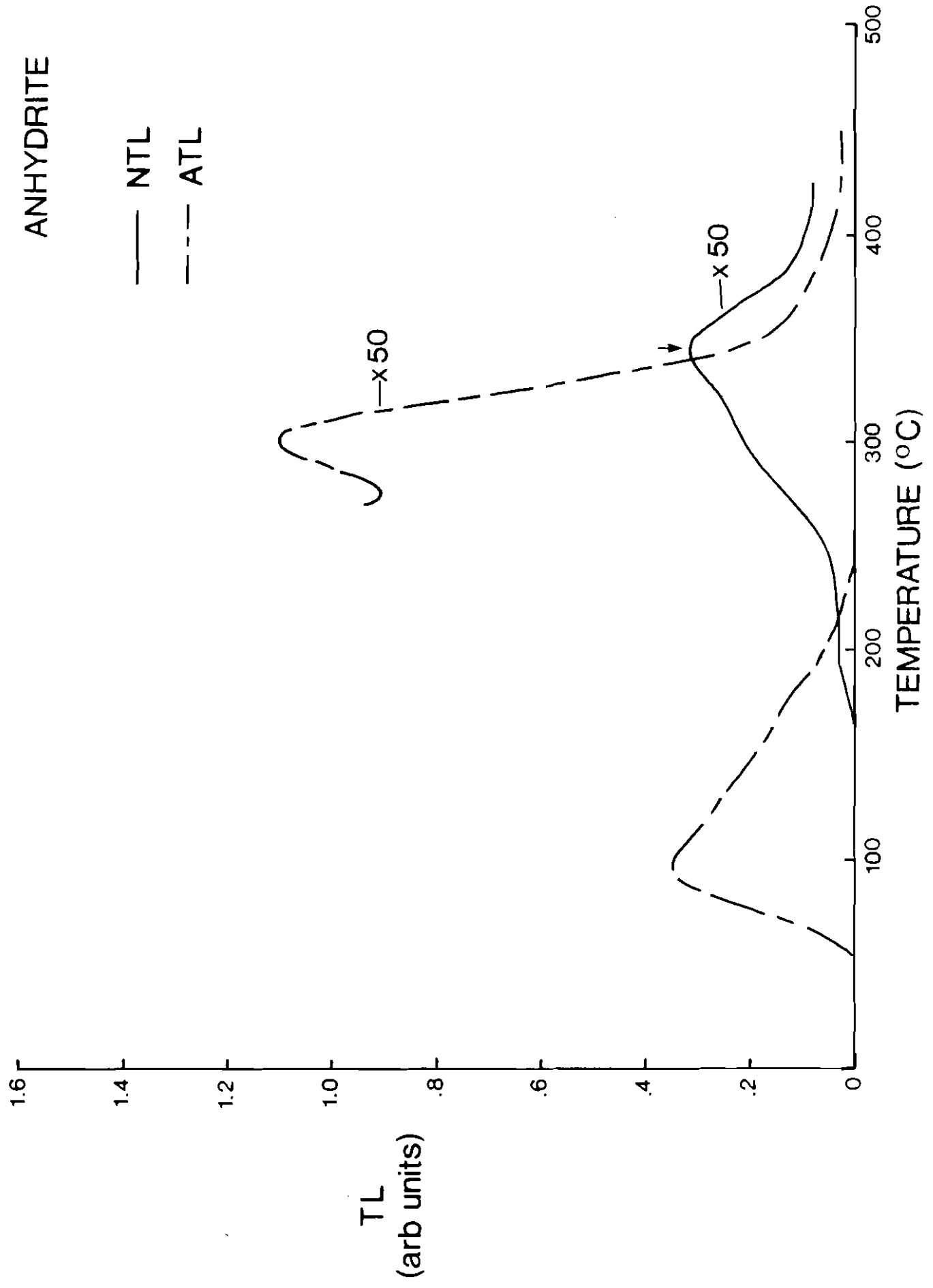
FIGURE 1.

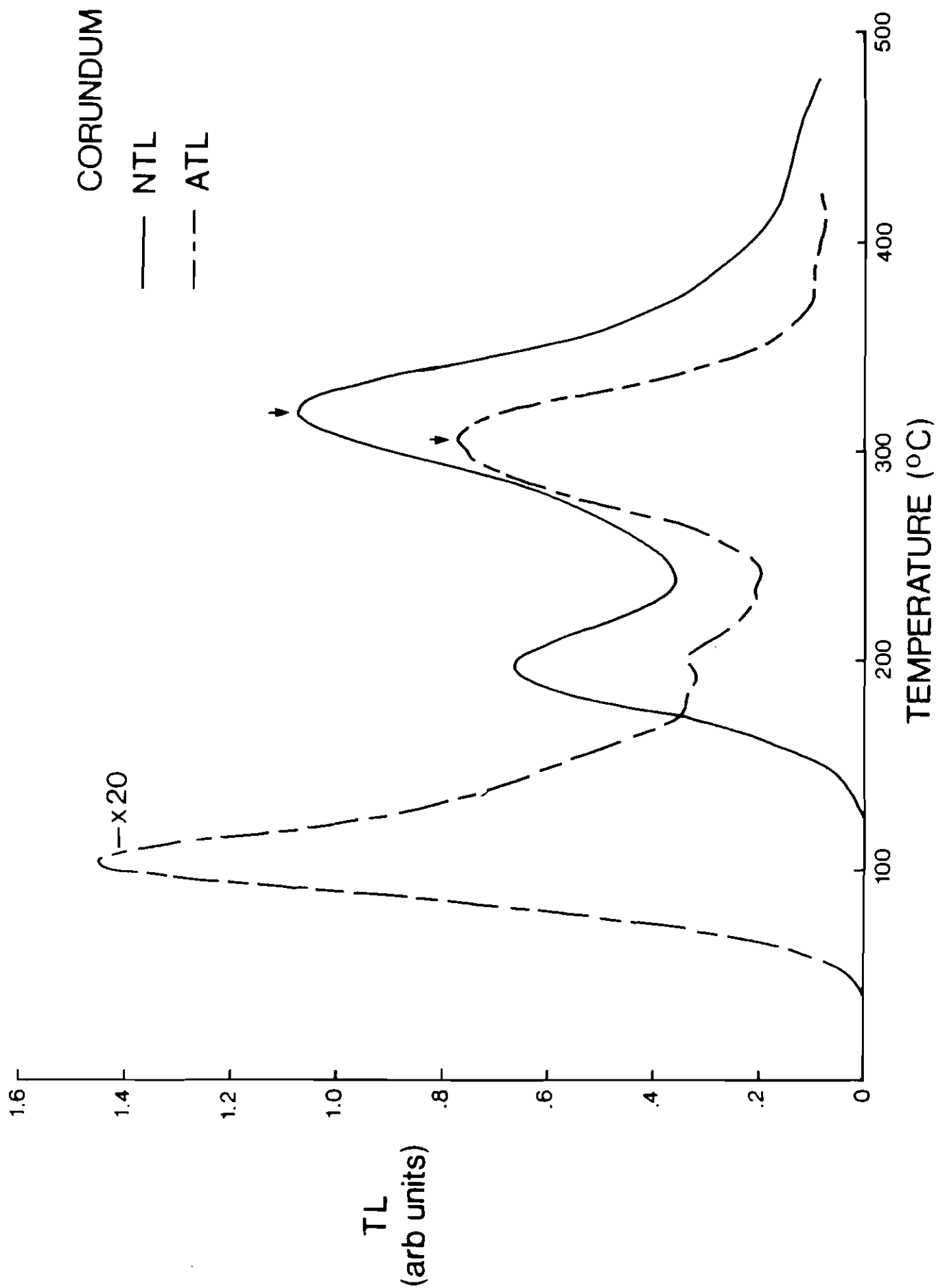
TL GLOW CURVES: FINE GRAIN SAMPLES

ANHYDRITE
CORUNDUM
FLUORITE
FRANKLINITE
GLASS +1%LiF
GYPSUM
LiF:Dy
OLIVINE
WILLEMITE

Note: The ATL glow curves were obtained after beta irradiations of 1 minute with the exception of glass +1%LiF and olivine samples, where the irradiation period was 5 minutes.

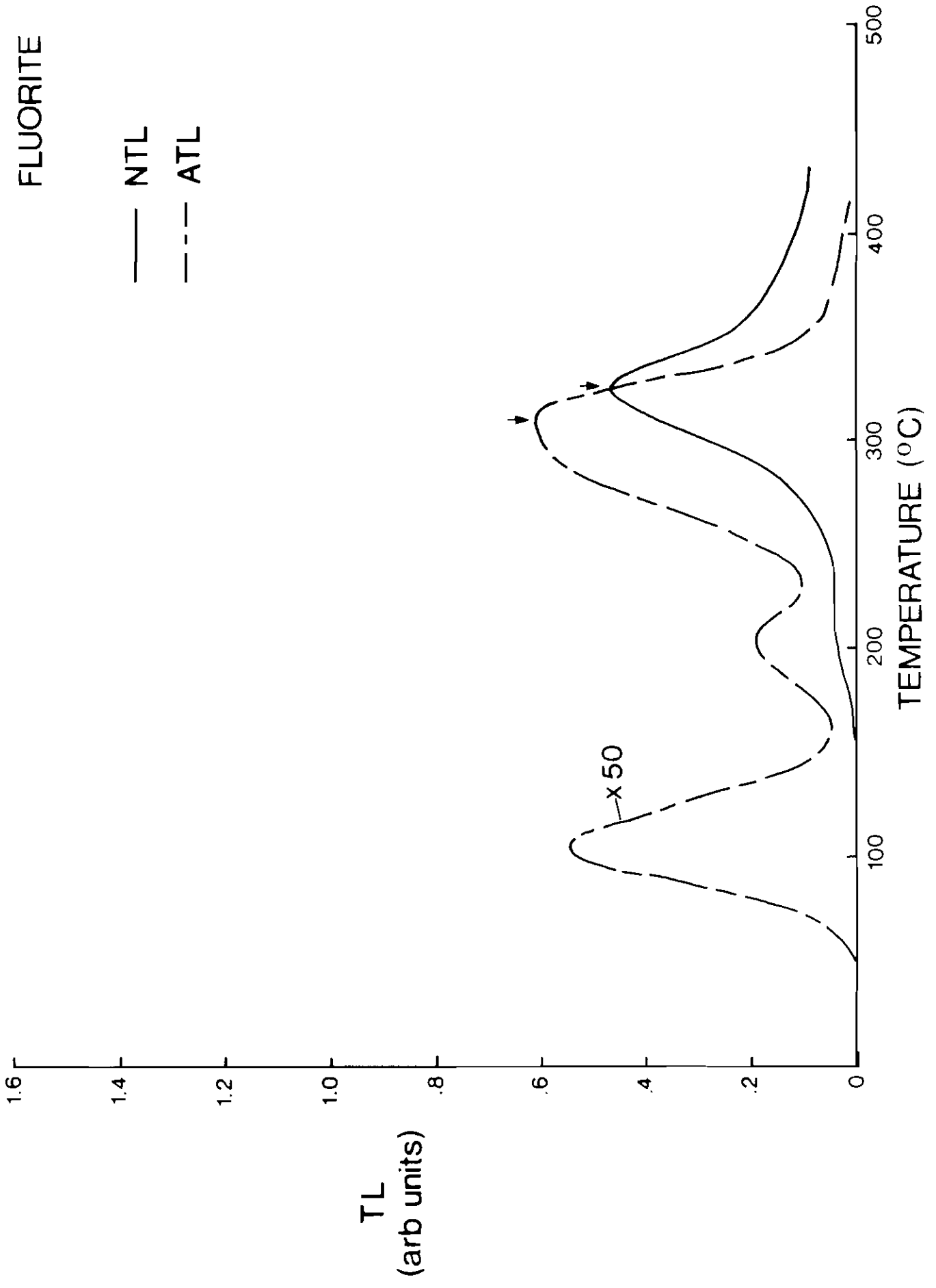
ANHYDRITE



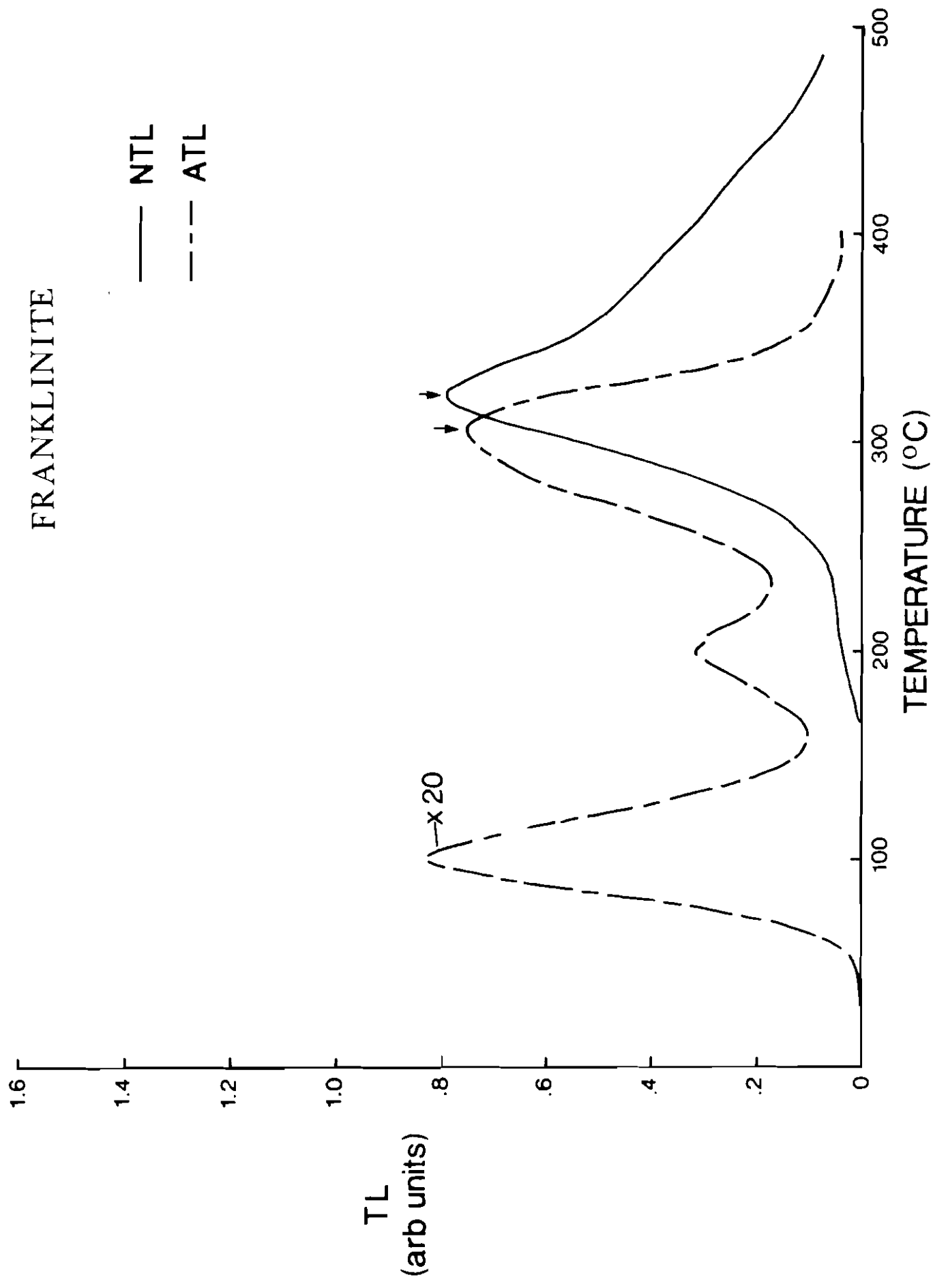


FLUORITE

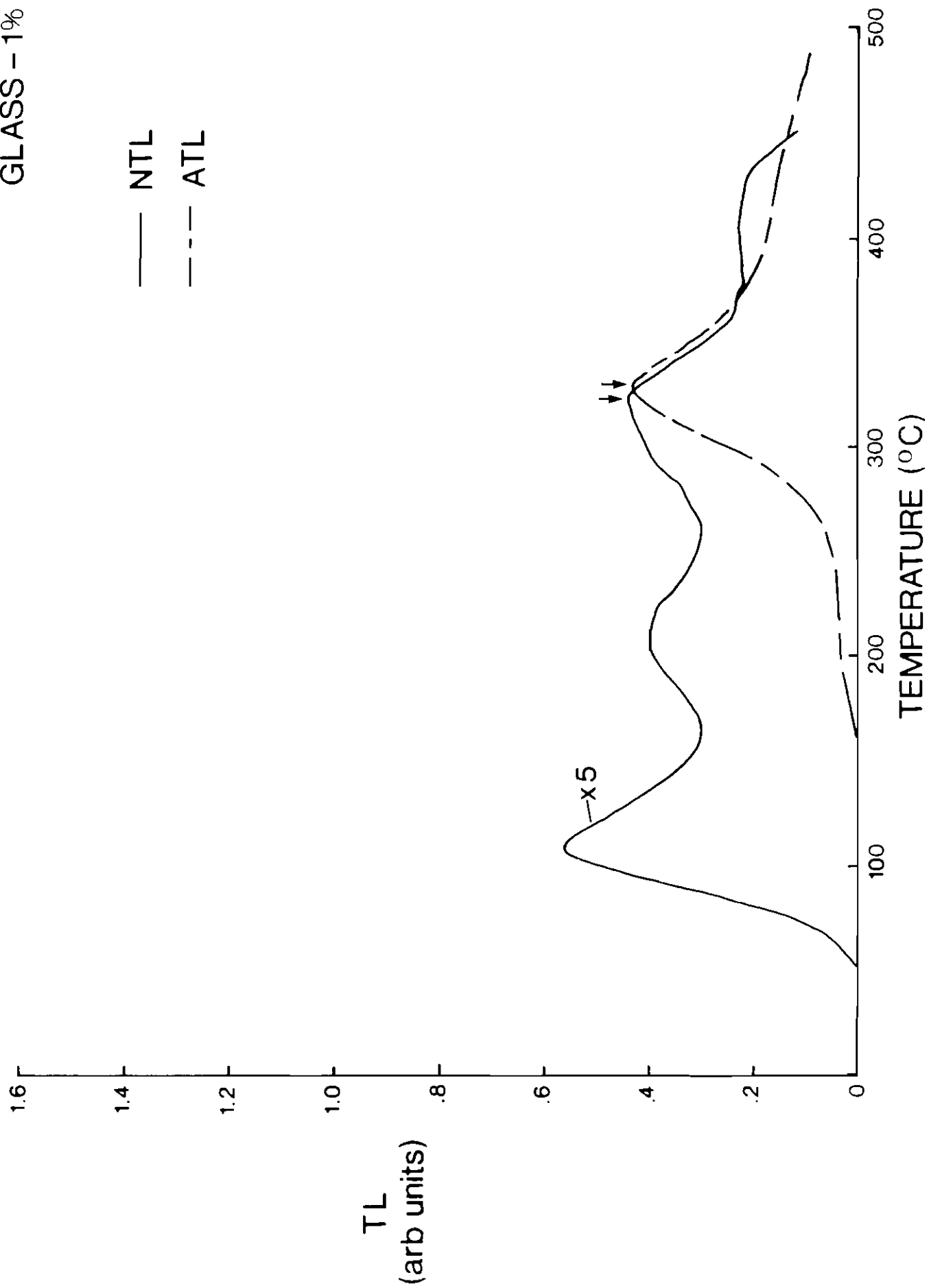
— NTL
- - - ATL



FRANKLINITE

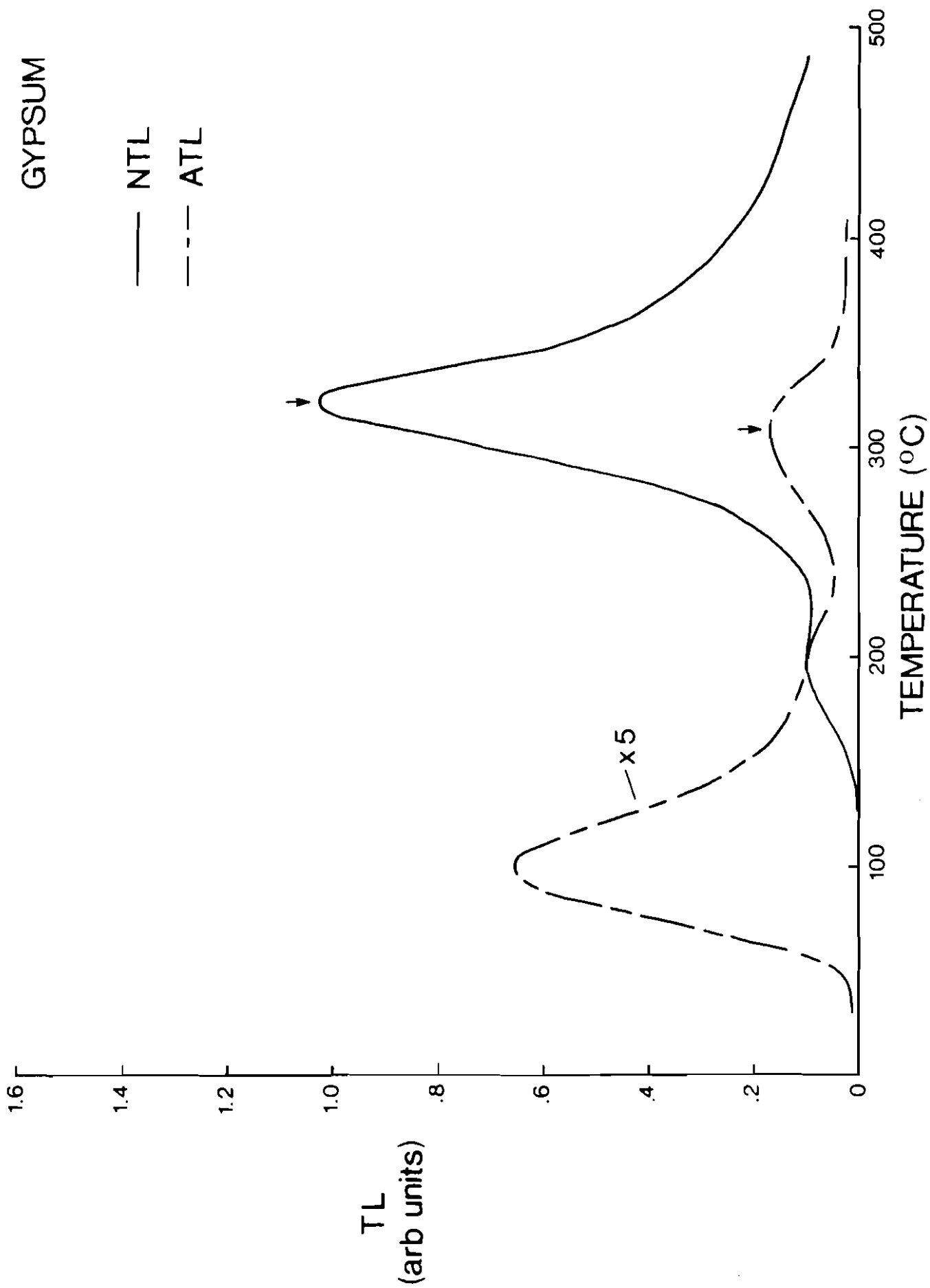


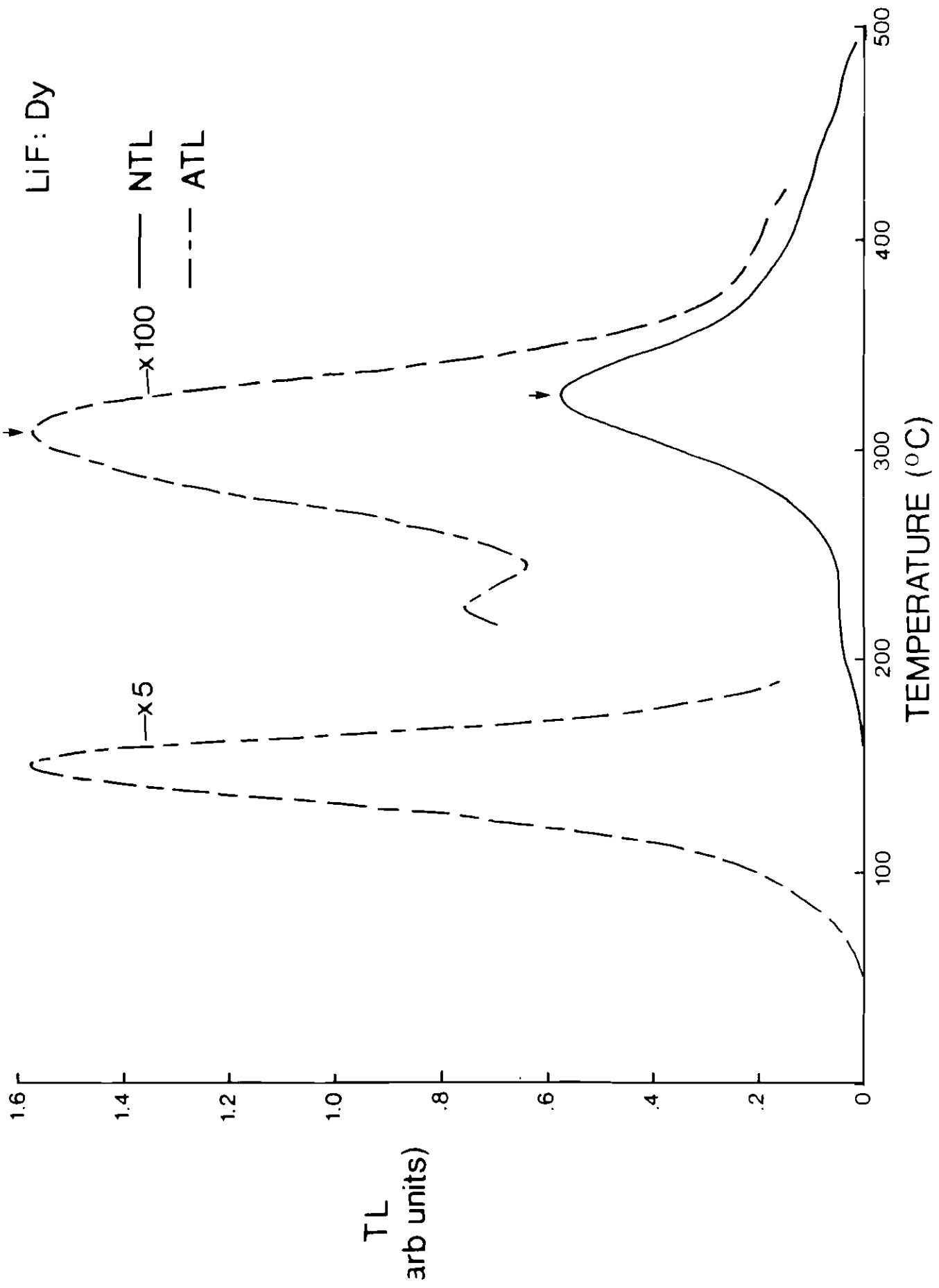
GLASS - 1% LiF



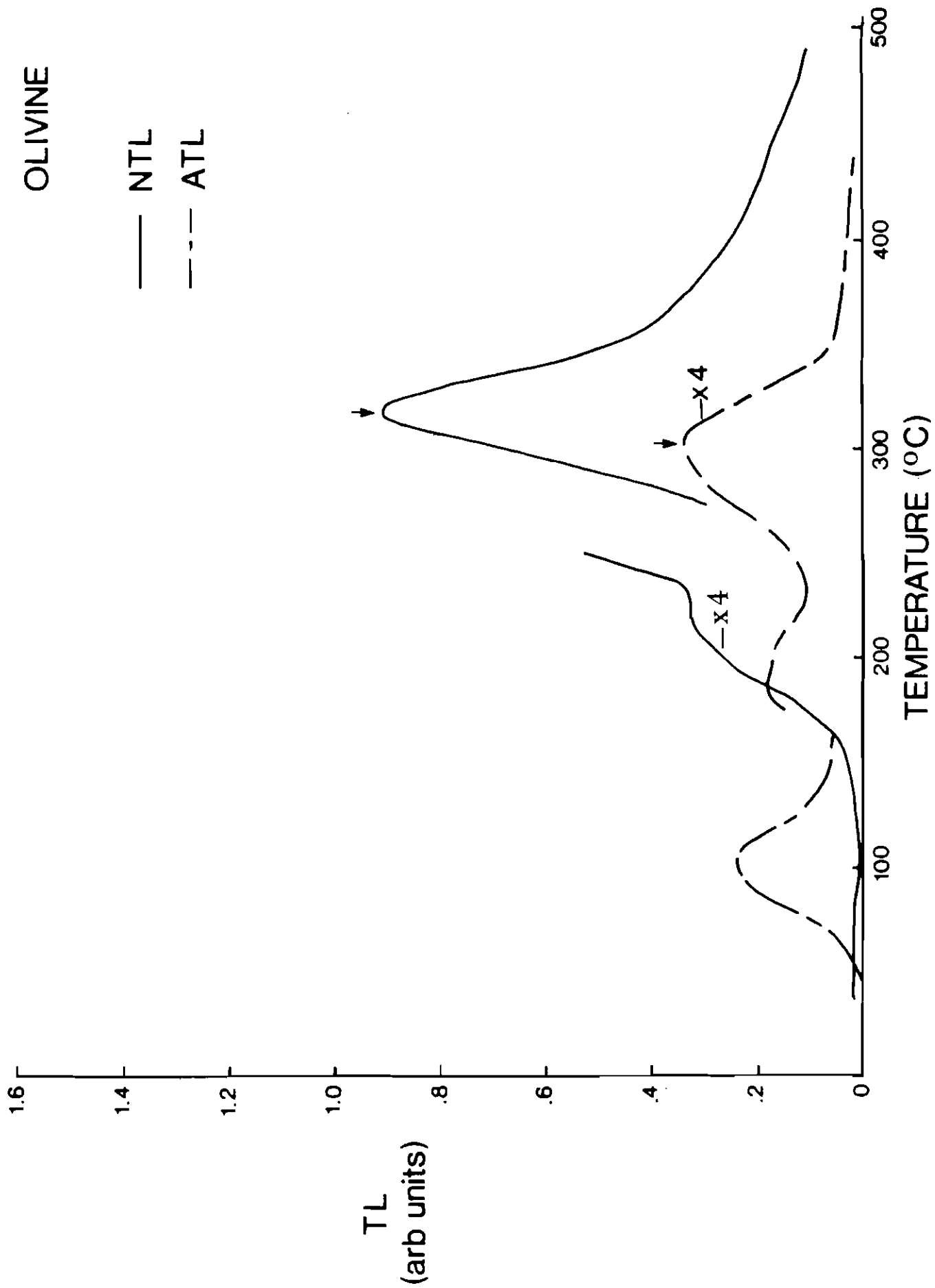
GYPSUM

— NTL
- - - ATL

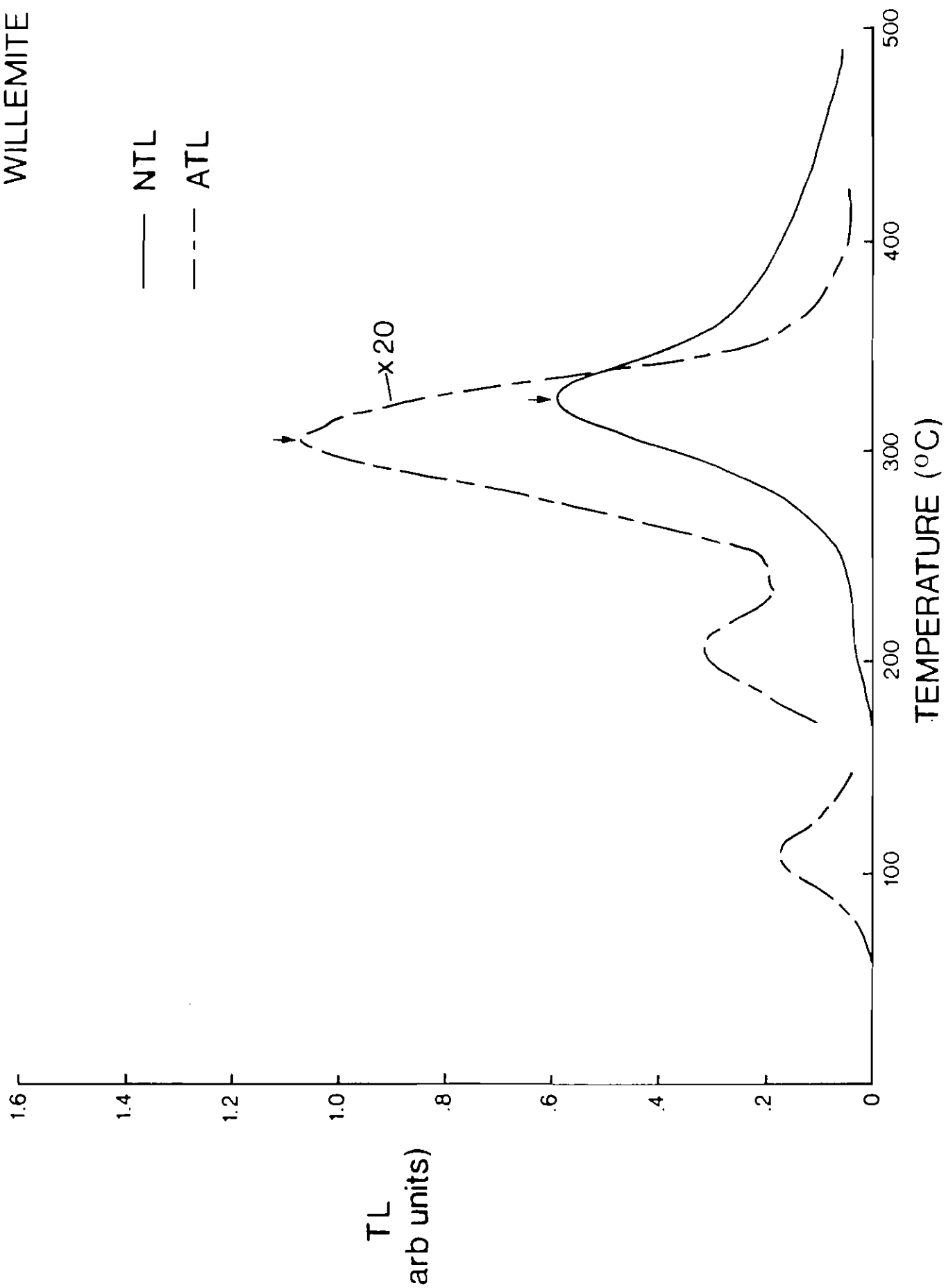




OLIVINE



WILLEMITE



HYDRAULICS RESEARCH

Comparison of TL intensity and linearity of response to dose

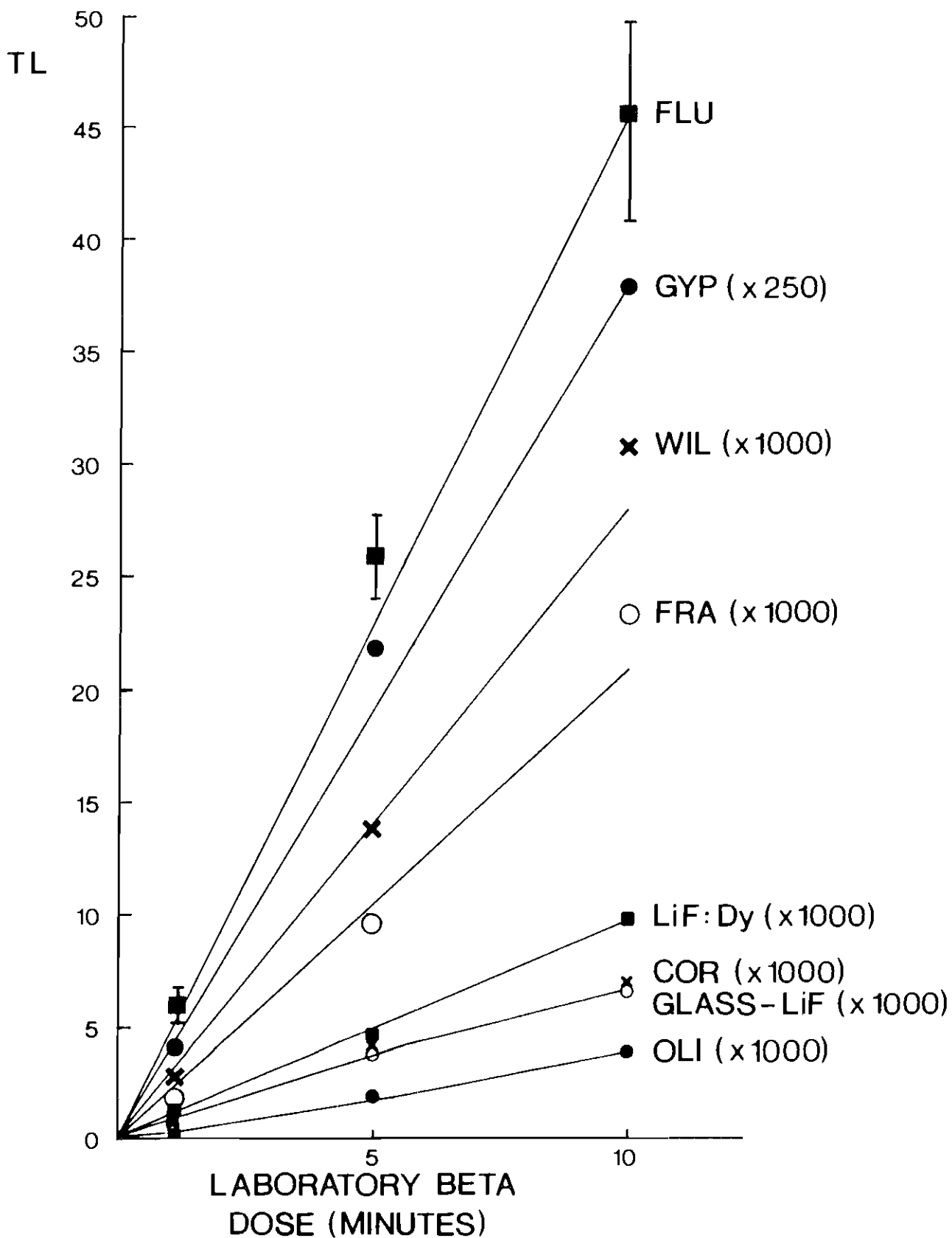


Table 1

SAMPLE	NTL	LABORATORY BETA DOSE		
		1min	5min	10min
ANHYDRITE	3.2	poor peak structure		
CORUNDUM	52	0.9	4.2	7.3
FLUORITE ¹	1.6×10^5	6×10^3	2.6×10^4	4.6×10^4
FRANKLINITE	84	2.2	10.0	23.4
GLASS +1%LiF	21.5	0.9	4.3	7
GYPSUM	675	17.6	88	152
LiF:Dy	66	1.7	4.3	9.9
OLIVINE	4.5	0.4(5)	2.0	3.9
WILLEMITE	29.5	2.7	13.9	30.7
		TL PEAK HEIGHT (kHz)		

1. Measured intensities increased by a factor of 200 to allow for reduction by 2.0 neutral density filter

APPENDIX 3

Further TL Measurements on Tracer Materials and on Natural Silt

46 Saddler Street, Durham, DH1 3NU, England

Telephones:

Day -- Durham 64466 (STD code 0385)

Night -- Durham 65997 (STD code 0385)

Coin Box -- Durham 62311 (STD code 0385)

Professor Rosemary Cramp

HYDRAULICS RESEARCH

REPORT: TL MEASUREMENTS ON TRACER MATERIALS

SAMPLES:

- | | |
|--------------------------------|------------------|
| 1. Fluorite | Our ref. HRIII-1 |
| 2. Calcium Fluoride | HRIII-2 |
| 3. Natural silt/Mersey | HRIII-3 |
| 4. Fluorite (10%) + silt (90%) | HRIII-4 |
| 5. Fluorite (1%) + silt (99%) | HRIII-5 |

TL SAMPLE PREPARATION

Portions, in the supplied grain size range 20-38 μm , were deposited onto stainless steel discs that had been previously coated with a thin layer of silicone oil. They were spread by percussion within a circle of approximately 8 mm diameter (10 mm diameter discs) and this provided portion weights in the range 0.5 - 1.5 mg.

EXPERIMENTAL

Sample discs were heated at 10°C/s in an atmosphere of oxygen-free nitrogen and the TL emission viewed with a detection system comprising EMI 9635Q photomultiplier in conjunction with an optical filter system biased towards the violet/uv region of the spectrum; neutral density (Kodak, gelatin) filters were additionally interposed where required. Beta

doses were administered using a calibrated Sr90/Y90 plaque source; they are given below in terms of minutes of irradiation and the nominal dose-rate for these samples may be taken to be 1.4 Gy/min.

MEASUREMENTS AND RESULTS

Determination of Saturation Level of TL emission of HRIII-1&-2

The following measurements were performed on single portions, each taken from samples HRIII-1 and -2;

- 1) Measurement of natural TL (NTL) glow curve (arising from any previously accrued dose).
- 2) Administration of beta dose at RT and subsequent measurement of the β TL glow curve to 450°C for four levels of beta dose ranging from 10 to 1220 minutes.

The NTL and BTL glow curves for sample HRIII-1 are shown in figure 1; the glow curves for sample HRIII-2 were qualitatively similar. The height of the marked peak III of the β TL glow curve, plotted against irradiation time (minutes), is given for both samples in figure 2. Since the data cannot be fitted to single exponential functions, we have simply joined the data points with linear curves. The peak height of the dominant peak (marked) of the NTL glow curve is indicated on each β -TL growth curve for comparison.

TL emissions for samples HRIII-1-5

The NTL and β TL glow curves were measured using a number of weighed portions. A representative glow curve obtained from sample HRIII-3 is shown in figure 3 (note similarity of NTL glow curve shape for silt, fluorite and calcium fluoride. For samples HRIII-4 and -5 the forms of the NTL and β TL glow curves were similar to those shown for samples HRIII-3 and -1 respectively. The heights of the marked peaks per unit weight

are listed in table 1 and in the case of the β TL glow curves, 10 minute irradiations were administered to all portions to permit comparison of the β TL glow curves between samples.

DISCUSSION

1. Multiple Layering of Samples

The sample portions, as deposited on the discs in the manner described above, were found to comprise several layers of grains by inspection under a microscope. This, as expected, affected the precision of weight normalized results and in a few cases outliers were excluded from the calculation of the results that appear in table 1. The grain size range provided was too large for use with our sedimentation procedures and too small to easily obtain monolayers, as we can achieve with 100 μ m grains. Consequently, while the sample deposition procedures were adequate for the purposes of these experiments, a procedure to obtain monolayers would be desirable in further work.

2. Peak Height Comparisons: NTL and β TL

For simplicity in the discussion below we will make comparisons of the peak heights of the third β TL peak at $\sim 310^{\circ}\text{C}$ and the dominant TL peak at $\sim 330^{\circ}\text{C}$ of the NTL glow curves, rather than the TL intensity at a particular temperature, or integrated TL emission between two temperature limits. It should be noted that if the comparison is made at $\sim 310^{\circ}\text{C}$, the β TL:NTL ratio is increased by a further factor of 2 because of the relative displacement of the two peaks.

3. TL Saturation Levels: HRIII-1 and -2

The saturation level of the marked peaks (figure 1) for fluorite (HRIII-1) and calcium fluoride (HRIII-2) was approached for doses in the region of 18 kGy and above. This

level of saturation emission represents $\sim x 13$ and $\sim x 18$ the height of the marked NTL peak and $\sim x 30$ and $\sim x 38$ the height of the marked β TL peak (10 min β irradiation) for samples HR1111-1 and -2 respectively. In terms of TL emission per unit weight, the predicted saturation peak heights are;

Sample	HR1111-1	67 MHz mg ⁻¹
Sample	HR1111-2	1.6 MHz mg ⁻¹

It should be noted that these results refer to measurements that were performed on the samples after the NTL glow curve had been recorded.

4. TL emission from natural silt HR1111-3

From table 1, the NTL peak height from natural silt (HR1111-3) was found to be 6.4 ± 0.9 (s.d. 7) kHz mg⁻¹ which represents 10^{-4} of the saturation emission level of the marked peak of the fluorite sample.

5. TL emissions from fluorite-spiked silt samples HR1111-4 and 5

In considering the TL emission from the fluorite-spiked samples HR1111-4 and -5, we may compare both the NTL and β TL (10 minute irradiation) peak heights for each sample.

Thus using data from table 1;

$$1) \text{ NTL: } \frac{\text{peak height (10\%FLU)}}{\text{peak height (1\%FLU)}} = \frac{1000 \pm 76}{88.7 \pm 5.5} = 11.9 \pm 1.2$$

$$2) \beta\text{TL: } \frac{\text{peak height (10\%FLU)}}{\text{peak height (1\%FLU)}} = \frac{295 \pm 23}{24.8 \pm 1.7} = 11.3 \pm 1.1$$

(Small increases in these ratios occur if an allowance is made for the host silt emission, assuming the silt is of similar composition to sample HR1111-3.

Within experimental error (using standard deviation at 68% level of confidence), the two results are similar and they show that the TL peak height per unit weight is approximately

proportional to fluorite tracer content. However, the difference between the expected value of 10 and the measured values is significant at the 95% level of confidence if the standard error is considered. Although this difference needs to be confirmed by further measurements, it is worth noting that it is not expected to occur in the direction found (as indicated above) on the basis of a significant under-estimate of the TL emission from the host silt.

However, multiple layering of the sample is likely to result in a relatively higher average attenuation of TL emission (due to overlying translucent silt grains) with decreasing tracer concentration, thus increasing the ratio as defined above. A method of monolayer sample deposition would be required to avoid such an effect.

Concluding Remarks

1. The saturation value of the peak height of the 310°C TL peak of fluorite compared to the height of the dominant peak of the NTL glow curve obtained from the silt supplied provides a ratio of at least $10^4:1$.
2. The results from initial experiments with fluorite-spiked silt samples were encouraging and we consider that with refinement of sample deposition procedures, results closer to the predicted values could be obtained.
3. Before we can recommend further measurements we need to discuss the minimum level of tracer content required to be detected.

I.K. Bailiff
14.2.85
Durham TL Laboratory

TABLE 1. Results

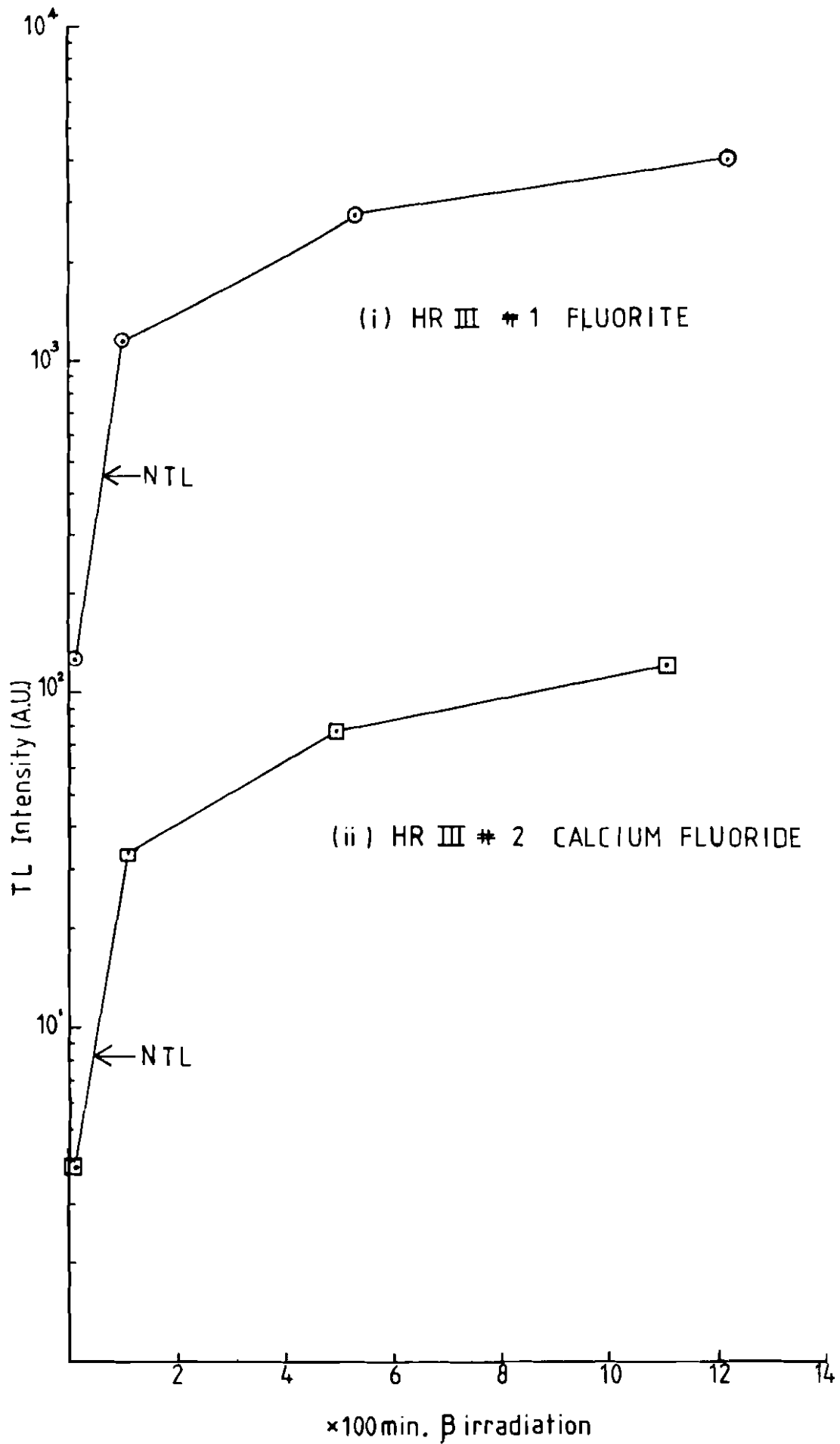
SAMPLE	TL PEAK HEIGHT (kHz mg ⁻¹)		COMMENTS
	NTL	β TL	
HRIII -1	5435 \pm 600(6)	2235 \pm 180(6)	{ Corrected for 2ND Filter
-2	86 \pm 10(3)	41 \pm 8(3)	
-3	6.5 \pm 0.9(7)	-	
-4	89 \pm 6(3)	25 \pm 2(3)	
-5	1000 \pm 75(3)	300 \pm 23(3)	

Notes.

1. NTL peak @ $\sim 330^{\circ}\text{C}$.
2. β TL peak @ $\sim 310^{\circ}\text{C}$ obtained after the administration of a 10 minute beta irradiation.
3. Errors given represent the standard deviation at the 68% level of confidence and the number of results used is included in parentheses.
4. TL emissions were reduced by the use of a 1ND filter.

FIGURE 2.

TL peak height vs beta dose for samples HR III -1 & -2



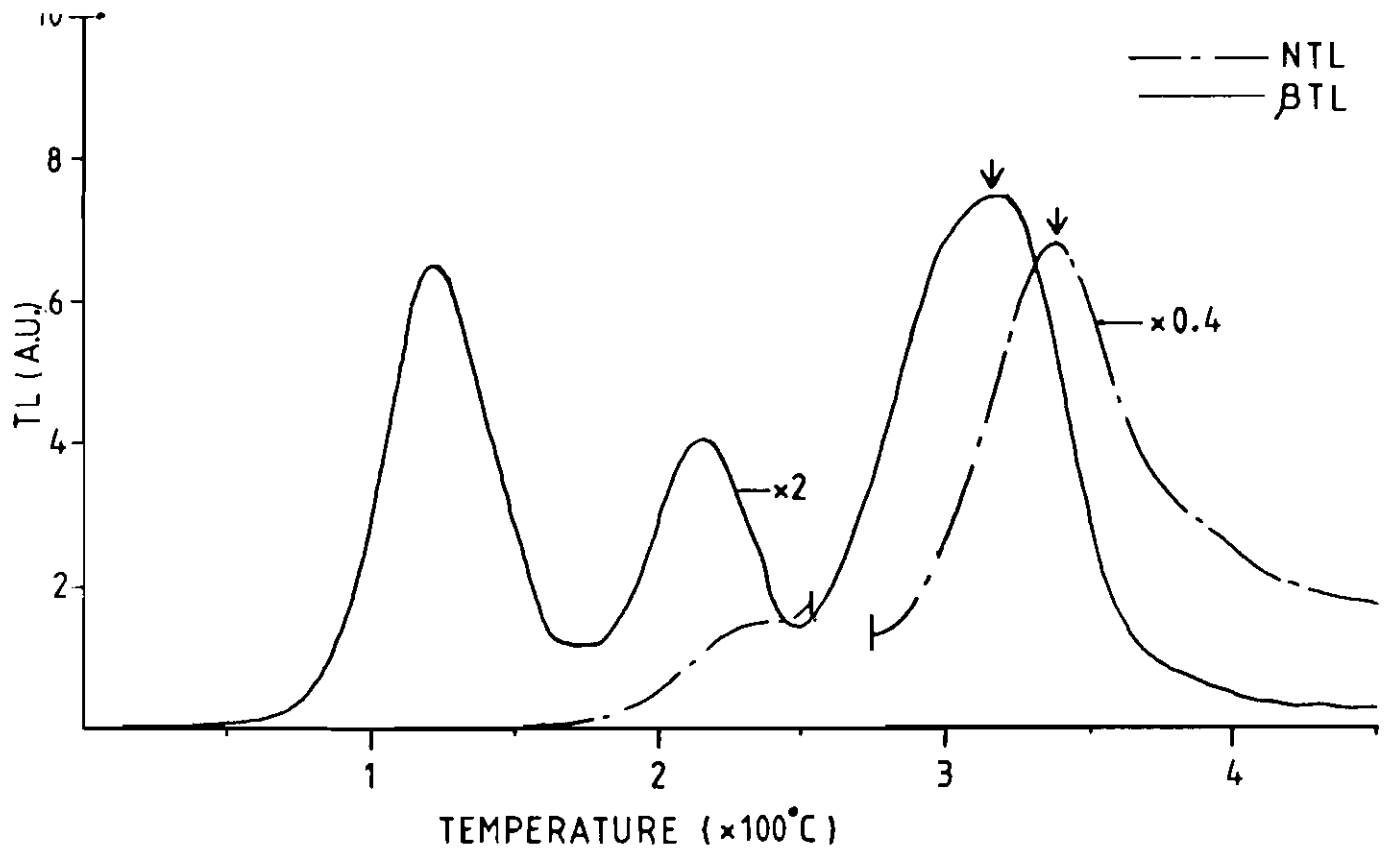


Figure 1

N- and β - TL glow curves obtained from fluorite

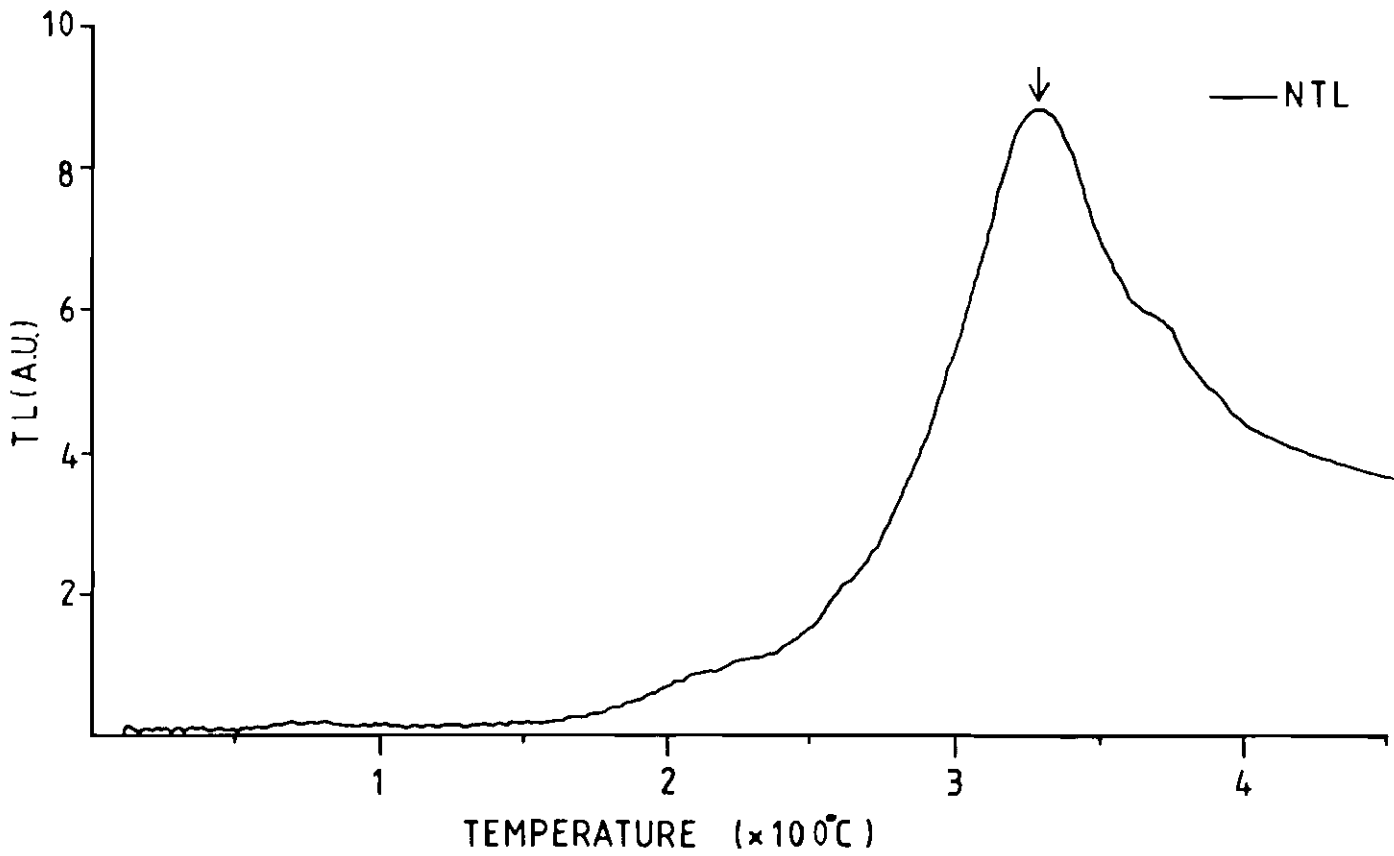


Figure 3

NTL glow curve obtained from silt sample HRIII-3.