



Hydraulics Research
Wallingford

THERMOLUMINESCENT TRACERS -

Further Evaluation

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ABSTRACT

This report describes the continuation of our evaluation of the properties of certain thermoluminescent (TL) materials which may be of use as tracers in field sediment studies. A summary is given of some existing tracer techniques, including the use of radioactive, fluorescent and chemical tracers. A brief description is given of the property of thermoluminescence and the potential advantages of a thermoluminescent tracer material. The results of various laboratory tests are described and particular emphasis is given to the properties of fluorite which has appeared as the most promising of the minerals tested. Recommendations are given for further work.

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Durham University report on TL measurements

1 INTRODUCTION

In an earlier Hydraulics Research (HR) study (Ref.1) a preliminary evaluation was made of various minerals which were known to exhibit thermoluminescent (TL) properties and which had potential for use as tracer materials in field sediment studies. As a general introduction to this present report, parts of the earlier report are repeated as follows:-

"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.

A fairly typical experiment was that carried out at the Port of Brisbane, Australia in 1981. 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 μ m 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 Gray. (The Gray [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."

In the conclusion to the earlier report it was stated that:

"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. 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."

In this present report we describe more exhaustive tests carried out on some of the potential tracer materials. Most of the experimental work reported on was carried out by the TL Laboratory, Department of Archaeology, University of Durham. A report prepared by the University, which contains details of the techniques used and the various tests carried out is reproduced as an Appendix.

In the main body of the report we have drawn from the results obtained from the Durham tests to describe the properties of the mineral fluorite which has been identified as the most promising of the potential tracer materials examined.

2 LABORATORY TESTS

In these tests all samples examined were in the silt size range of 10 to 63 μ m.

Seven natural silts were examined. Six were from the following U.K. estuaries - Mersey, Nene, Ribble, Severn, Thames and Tees and the seventh was from the Port of Kuching, Malaysia. In addition, six TL minerals were examined viz - Anhydrite, Fluorite, Franklinite, Gypsum, Olivine and Willemite.

2.1

Mineralogical composition of the natural silts and TL measurements on the constituent parts.

The mineral composition of the various silt samples was determined by X-ray diffraction techniques. Having identified the various constituents, a series of experiments was carried out in which the initial TL emission from the composite silt was measured. Certain of the minerals were then leached from the silt using appropriate acids. TL measurements were then carried out on the remaining minerals. In this way the TL contribution from the various minerals within the silt sample was determined.

The results of these tests, which are detailed in the Appendix, show that acid treatment can effectively remove some of the brighter TL emitters. The treatment can however produce precipitates which are bright TL emitters. It is concluded that a significant reduction in natural background TL emission is unlikely to be achieved by acid pre-treatment of the silts.

2.2

TL emissions from silts and tracer materials after saturation radiation doses

In the earlier study (Ref.1) the TL characteristics of tracer materials was determined by subjecting small tracer samples to increasing radiation doses using a relatively small laboratory beta radiation source. These earlier results indicated an increasing TL emission with applied radiation dose. The laboratory source was too weak however to provide a saturation radiation dose which would give rise to the maximum TL emission from the sample.

In these present tests samples were subjected to saturation radiation doses in a Cobalt 60 gamma radiation facility. This facility, operated by a local commercial organisation, is used mainly for sterilisation of surgical products, food etc. The unit can if necessary handle large consignments on a conveyor belt system. For our purposes, irradiations were carried out in a small experimental facility. The initial samples were given a radiation dose of 10 k Gy, which was administered in approximately 30 minutes. In subsequent tests a 50 kGy dose was administered so as to confirm that the 10 kGy dose had saturated the samples.

Samples of each of the natural silts, as well as the six potential tracer materials, were irradiated in this facility. Each sample was contained in a polystyrene vial and vials were packed in a light-tight cardboard box and irradiated together. The irradiated samples were then dispatched to the TL laboratory at Durham for examination.

2.3

TL emission from the background and irradiated samples

The full experimental details are given in the Appendix.

The glow curve resulting from natural irradiation of the material over geological time was first determined for each of the silt samples. These "background" glow curves are shown in Fig. A2 of the Appendix. It is seen that there is very little TL emission from these samples at temperatures below 200°C. The glow curves from the irradiated silts and the irradiated tracer materials however show two characteristic peaks - one at about 200°C and the other at about 290°C (Fig A3). The best "signal to noise" ratio was achieved using measurements taken at the 200°C peak.

For comparison, the peak TL emission measured at 200°C for each of the background silt samples and each of the irradiated silts and tracer materials are tabulated below.

Sample Material	TL Emission at 200°C	
	Irradiated (MHz/mg)	Background (kHz/mg)
Kuching Silt	4.3 ± 0.3	< 0.2
Mersey "	11.7 ± 1.4	< 1
Nene "	19.8 ± 3.5	< 2
Ribble "	13.2 ± 0.2	< 3
Severn "	1.1 ± 0.06	< 0.2
Tamar "	14.0 ± 1.6	< 5
Tees "	10.0 ± 0.3	24 ± 3
Anhydrite	16.0 ± 1.9	
Fluorite	1080 ± 130	
Franklinite	0.67 ± 0.20	
Gypsum	0.27 ± 0.06	
Olivine	0.45 ± 0.15	
Willemite	2.3 ± 0.4	

TABLE 1. TL emissions at 200°C

Silt Type	Relative TL Emission Fluorite/Silt
Kuching	5.4 x 10 ⁶
Mersey	1 x 10 ⁶
Nene	5.4 x 10 ⁵
Ribble	4 x 10 ⁵
Severn	5.4 x 10 ⁶
Tamar	2 x 10 ⁵
Tees	4.5 x 10 ⁴

TABLE 2. Relative TL emissions at 200°C

From these results it is seen that fluorite is clearly the brightest TL emitter of the materials tested, being at least two orders of magnitude brighter than most of the other potential tracer materials. It is interesting to note also that many of the irradiated silts are brighter TL emitters than the other potential tracers.

To illustrate the potential sensitivity of fluorite as a tracer material, a comparison is made in Table 2 of the relative TL emission of irradiated fluorite against the background TL emission from the seven silts examined. In most cases a resolution of better than 1 part in 10^5 is indicated and in several cases a resolution of better than 1 part in 10^6 is achieved. This resolution still falls short of our objective of 1 part in 10^9 .

2.4

TL emission from single grains of fluorite

An alternative TL measurement approach was examined briefly. Samples of the irradiated fluorite were examined under a microscope and individual grains in the size range 40 to 60 μm were removed. These individual grains were then mixed with about 1 mg of natural silt and the resultant TL emission measured. In all cases the individual grains were readily detected. In the worst case where the tracer grain was mixed with the high background Tees silt a "signal to noise" ratio of 5 : 1 was achieved.

This grain counting technique appears to offer the potential for achieving high resolution detection. In a continuous flow system individual fluorite grains within the silt may be detected. A signal amplitude threshold set above the background noise level should enable the individual tracer grains to be counted and the background signal rejected.

2.5

Natural decay of the TL emission from irradiated fluorite

Exposure of TL emitters to optical irradiation of suitable intensity and wavelength can lead to a reduction in TL intensity.

In order to check the long-term stability of the TL emission from fluorite, a quantity of the irradiated material was exposed to ambient light conditions in the laboratory. Over a period of some seven weeks the TL emission from samples of this material was measured. No significant decay in intensity was detected over the period.

Samples of the irradiated fluorite were then exposed to more intense optical irradiation using an 80W mercury discharge lamp with a yellow glass filter to remove UV emissions below 280nm. The luminance of the optical radiation was estimated to be about one third of that present on a sunny summer day in Britain. Decay of TL emission was found to be rapid under these optical exposure conditions. The emission at the 200°C peak for instance had reduced to 7% of its initial value after 10 minutes of intense optical irradiation.

It is unlikely in a typical silt disposal study that the tracer, once incorporated within the natural silt, would ever be exposed to optical radiation more severe than the ambient laboratory conditions. These tests clearly indicate however that care must be taken to avoid exposure of the fluorite tracer to direct sunlight at any stage of the initial seeding of tracer and during subsequent sampling operations.

3 SOME RELEVANT PROPERTIES OF FLUORITE

Fluorite (also known as Fluorspar) occurs as a natural ore. It has a density of 3 to 3.2 g/cm³ which is similar to the main constituents of most estuarial silts eg. Quartz 2.6 - 2.7 g/cm³, Plagioclase 2.5 - 2.9 g/cm³, Dolomite 2.8 - 3.0 g/cm³, Calcite 2.7 g/cm³.

On the Mohs scale of hardness fluorite has a value of 4. On this scale each mineral listed is softer than (ie is scratched by) all those below it. Some comparative values for other minerals are: Gypsum 2, Calcite 3, Orthoclase 6, Quartz 7. Fluorite is therefore a reasonably durable mineral.

The solubility of fluorite was determined in the laboratory. A solubility of 0.012 g/litre in deionised water and 0.010 g/litre in 30% salt water was measured albeit under small-scale laboratory conditions. With this low level of solubility a fluorite tracer material is unlikely to dissolve by any significant amount during the course of a typical tracer experimental period.

The 1986 cost of fluorite in the U.K. (supplied as the natural ore) is approximately £12 per kilogram.

**SUMMARY AND
CONCLUSIONS**

In this latest series of tests we have:

- (a) determined the mineral composition of seven natural silts;
- (b) measured the background TL emission from these seven natural silts;
- (c) exposed samples of these silts and also six potential tracer materials to saturation gamma radiation doses in a Cobalt 60 irradiation facility;
- (d) determined the TL emission from the various constituents of the irradiated natural silts;
- (e) measured the TL emissions from the irradiated TL tracer materials;
- (f) measured the TL emission of single grains of irradiated fluorite against a background of natural silt;
- (g) measured the decay of TL emission as a result of exposure to optical radiation;
- (h) measured the solubility of fluorite under laboratory conditions.

These tests clearly identified fluorite as the most promising of the TL tracer materials. Significant reduction in the natural background TL emissions from the silts was not achieved by acid leaching procedures.

In the tests in which we compared the TL emissions from weighed samples of the various materials the "signal to noise" ratio ie. the TL emission from the irradiated fluorite compared with that from the natural silts ranged from $4.5 \times 10^4 : 1$ in the worst case to $5.4 \times 10^6 : 1$ in the best case. This resolution which appears to be the best that we can readily achieve, falls some way short of our objective of $10^9 : 1$. We have demonstrated however that it is possible to identify the TL emission from individual grains of irradiated fluorite against a background of natural silt.

This "grain counting" approach offers an almost infinite resolution, the resolution being limited solely by the quantity of silt examined. Existing TL detection systems are designed to examine very small samples (typically 1 mg). For large-scale tracer studies it is essential to have a detection system which can handle large samples (typically 1 Kg). It is proposed to examine the feasibility of producing such an instrument in the next phase of this research project.

Tests in the laboratory have indicated a low level of solubility of fluorite. Exposure of fluorite to ambient laboratory lighting conditions produced no measurable decay of TL emission. Exposure to a more intense optical source however produced a rapid decay of the TL emission.

It is proposed under the next phase of the project to investigate both the solubility and the decay of TL emission under representative field conditions.

5 ACKNOWLEDGEMENTS

The experimental work described in this report was supervised and the report compiled by Mr C B Waters, Head of Hydraulics Research Field Studies Section which is part of Dr A J Brewer's Technical Services Department.

The author wishes to thank Mr I Bailiff of the TL Laboratory, Department of Archaeology, University of Durham, who was responsible for the various TL measurements described in the report and who wrote the technical report contained in Appendix 1.

Thanks are also due to Mr P R Kiff, Head of Hydraulics Research Sedimentation Laboratory who was responsible for the preparation of the various tracer and silt samples and who carried out the solubility tests on the fluorite material.

6 REFERENCES

1. Thermoluminescent tracers - a preliminary evaluation. C B Waters. HR Report No. SR 19, March 1985.

Figure

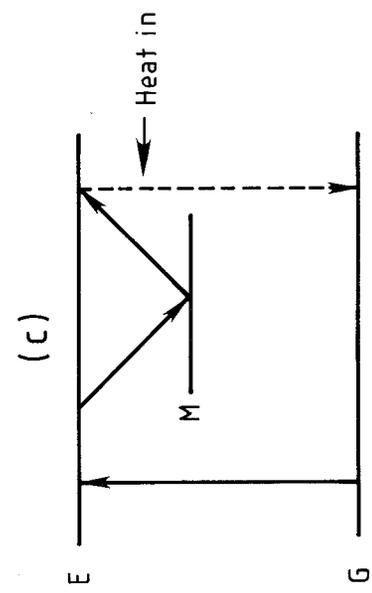
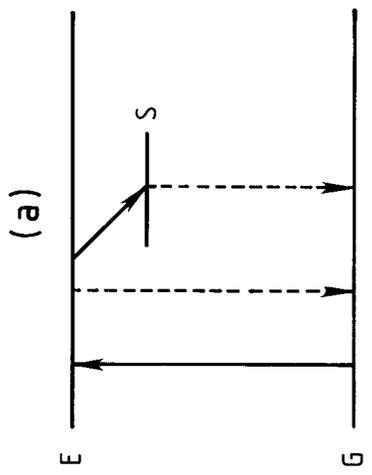
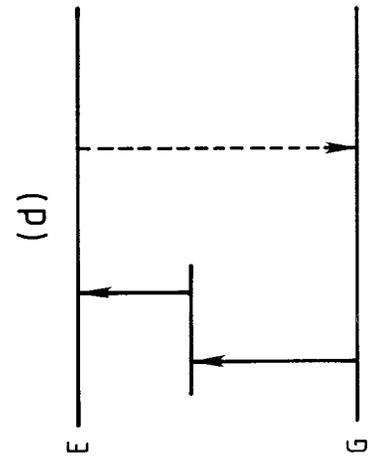
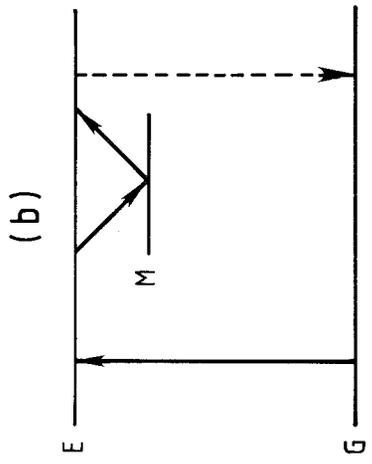


Fig 1 Simple examples of luminescent processes

APPENDIX

Report on TL measurements carried
out by University of Durham

THERMOLUMINESCENCE MEASUREMENTS ON NATURAL SILTS AND POTENTIAL TRACERS

Overview

In previous experimental reports (see Thermoluminescent tracers - a preliminary evaluation, C B Waters Rpt. SR 19), we have discussed the results of preliminary measurements on thermoluminescence (TL) emission from two natural silts and a number of TL minerals selected as potential tracers for sedimentation studies. In this report we discuss a more comprehensive programme of measurements on seven natural river silts and six TL minerals.

The TL emission was measured from sized fractions (10 - 63 μ m) of

- (i) untreated silts, to establish the level of natural background signal and
- (ii) similar silts and the selected TL minerals, following the administration of gamma doses sufficient to provide near saturating levels of TL signal, for the purposes of identifying suitably bright tracers.

A detailed examination of the TL emitters in the natural silts was performed to investigate means of minimizing its detection. Our previous measurements on the two natural silts had revealed that the TL emission was relatively bright. We attempted to determine the minerals contributing to the TL emission using TL and X-ray diffraction analysis on various components of the natural silt that had been isolated using acid treatments.

The levels of the TL signal from samples of gamma irradiated silts and selected TL minerals were measured periodically over two months to test the stability of the measured TL signal. For most TL minerals this stability is expected to be most seriously affected by irradiation with optical radiation; the effects of ambient laboratory illumination over the test period and short periods of intense artificial illumination were studied.

Since the ultimate aim of these investigations is the detection of single tracer grains located within a quantity of natural silt, measurements with single tracer grains were performed to test the feasibility of this method.

Further information concerning measurements

The TL emission is recorded as light intensity (pulses per second from the detector - Hz) vs sample temperature (raised linearly from room temperature, RT, to approximately 500°C) on an X-Y recorder, giving a TL glow curve. In this dynamic experiment the peaks of TL emission (see glow curves) that are obtained in certain temperature regions represent the thermal release of charge carriers from defect trapping sites within the crystal and their subsequent recombination at other sites with carriers of opposite charge. As illustrated in the schematic figure (A1) there is an energy difference between the two states and this gives rise to the emission of light (ranging from the UV to the red according to the nature of the recombination site). The long term stability of charge carriers (and hence the TL signal) at trapping sites is largely dependent upon the quantity of thermal energy (ie. temperature) required to release them - or as we discuss below, the optical energy that may be absorbed and cause trapped charge carriers to be released. The presence of trapped charge carriers at defect sites in the crystal arises because of the action of ionizing radiation (either natural or artificial). Consequently, TL minerals that have received a radiation dose release light when heated - minerals such as quartz are generally weak emitters, whereas fluorite is one of the brightest. Once the TL has been released during heating, a further radiation dose is required in order to observe TL emission from the sample in the same temperature region.

A considerable amount of work has been performed to study the kinetics of TL, however, in this report we will attempt to confine the discussion to an interpretation of the empirical data.

In this report we discuss the effects of exposure of samples to light. Two aspects of the light sensitivity of TL materials were studied; bleaching of the TL signal and photo-transferred TL (PTTL). The former, by means of photo-ejection of trapped charge carriers using suitable wavelength light, leads to a reduction of TL signal. The latter is more complex, and not observed in all TL minerals. If a sample of fluorite, for example, is exposed to light of suitable wavelength (at RT) after heating to approx. 500°C, a PTTL glow curve will be obtained on reheating the sample. In the case of fluorite the PTTL glow curve is slightly different to that obtained after exposure to ionizing radiation.

This phenomenon is believed to occur as the result of the transfer of charge carriers from deep traps that have not been emptied by the 500°C heating to shallow traps, the TL associated with which may be subsequently observed within the RT-500°C temperature region. Since there are two competing effects, we measured the TL emission after exposure to light for samples that had received no thermal treatments and for samples that had been previously heated to 450°C to remove the gamma-or natural- TL signal. The measurement of the PTTL also permitted an investigation of its potential for tracer work as an alternative to conventional TL.

1 SAMPLES

All samples were supplied by Hydraulics Research in the grain size range 10 - 63 μ m, packed in transparent polystyrene vials.

Natural Silts

The untreated silts were from the following U.K. estuaries - Mersey, Nene, Ribble, Severn, Tamar and Tees and from the port of Kuching, Malaysia.

Potential Tracers

Two types of material were tested to which had been administered a gamma dose (Co60 sterilising unit) of 10 kGy (1 Gray = 100 rads):

- (i) natural silts (as above)
- (ii) selected TL minerals: Anhydrite, Fluorite, Franklinite, Gypsum, Olivine and Willemite.

Further batches of fluorite were also tested, to which had been administered a gamma dose of 50 kGy.

2 SAMPLE PREPARATION

Portions required for measurement were taken from the material as supplied and deposited onto stainless steel discs (10mm diameter) that had been previously coated with a thin layer of silicone oil. The grains were spread by percussion within a circle of maximum diameter 8mm and this provided portion weights in the range 0.5 - 2mg. All portions were weighed (precision of ± 0.05 mg).

Where measurements on single grains were required, crystals were selected under a microscope, transferred to the measurement disc, and the presence of the grain verified by inspection. We estimated that the grains we selected were of 40 μ m diameter using this procedure. A number of "fine-grain" samples in the grain-size range approx. 10 - 20 μ m were also prepared by sedimentation in acetone onto 10mm diameter aluminium discs.

3 APPARATUS

The TL samples discs were heated at 10°C/s in an atmosphere of oxygen-free nitrogen using a simple resistive heater-plate oven system as used in TL dating measurements. The TL emission was viewed with a sensitive detection system comprising an EMI 9635Q photomultiplier (used in pulse counting mode) in conjunction with an optical filter system biased towards the violet/UV region of the spectrum. Where the TL emission was particularly intense (as for the tracers), neutral density filters were interposed between the detector and the sample.

A Hanovia 80W medium pressure mercury discharge lamp with Hanovia "yellow" glass filter interposed to remove UV emissions below 280nm was used for intense optical irradiations. From measurements made using a simple photometer, we estimated the luminance to be approximately 1/3 of that present on a sunny summer day in Britain.

4 MEASUREMENTS

Mineralogical Composition

TL and X-ray diffraction (XRD) measurements were performed on portions of natural silt as received, and after treatments selected from the following:

- (i) 30 min immersion in acetic acid (2%) + ultrasonic washes in distilled water (to remove calcite);
- (ii) 30 - 40h immersion in fluorosilicic acid (40% + ultrasonic washes in distilled water) to remove feldspar);
- (iii) 1h immersion in hydrochloric acid (15%) + ultrasonic washes in distilled water (to remove dolomite and any fluorides precipitated from the reaction of feldspar and fluorosilicic acid).

TL emission from natural silts and potential tracers

Natural silts: Measurement of the TL emission (RT-450°C) was made on four (unless indicated otherwise) portions taken from each sample. Each portion deposited on disc was heated to 450°C to record the TL glow curve, weighed, and then discarded.

10 kGy Dosed Samples: Measurement of the TL emission was made as above, approximately 10, 20 and 40 days after first testing the samples. Sample stocks were stored in transparent polystyrene vials under normal laboratory lighting conditions and agitated every 1 or 2 days to assist uniform illumination of the grains. Samples of gamma irradiated tracers and silts that had been stored under dark conditions since delivery were also tested (5th set in table below) after the last set of measurements, using the same measurement procedures.

The TL emission from "fine-grain" prepared samples was measured for the natural silts and gamma irradiated fluorite approximately 7 and 40 days after receipt of the samples respectively.

Samples of fluorite were also tested using stock (approx 3 mg in near monolayer) that had been exposed for two months to ambient laboratory lighting conditions, in addition to regular exposure to a 60W tungsten lamp. The stock material had been stored under a layer of cling-film to admit a greater quantity of short wavelength radiation (ie. higher energy). The use of neutral density filters was required when measuring the emission from tracers and the reduction factors were obtained in a set of subsidiary experiments.

50 kGy Dosed Fluorite: The 50 kGy gamma dose was administered to samples of fluorite that had:

- (a) received no further treatments and
- (b) been annealed at 500°C for 1 hour before the administration of the dose.

A fraction of preparation (a) was dissolved in NH_4OH (10%) and then recrystallized at 100°C to form preparation (c). These treatments were performed by Hydraulics Research.

Measurements on single grains of fluorite (from 10 kGy dosed stock)

TL glow curves from selected single grains of gamma irradiated fluorite were obtained under the following conditions:

- (i) after selection under the microscope (light from a 60W tungsten lamp was used for illumination for less than 5 mins) and transferred onto a sample disc from stock that had been stored under dark conditions;

(ii) single grains placed onto disc covered with approximately 1 mg of one of the brightest natural silts (Tees). The single grains were selected under the microscope using stock that had been exposed for two months to ambient laboratory lighting conditions under a layer of cling-film as described above;

(iii) single grains as in (ii) placed onto a disc covered with approximately 1 mg of one of the weakly emitting natural silts (Severn).

The effects of intense optical irradiation: natural silts and tracers

In addition to testing the effect of prolonged exposure of the gamma irradiated tracers to ambient lighting conditions, samples were also irradiated with intense artificial light for various periods ranging from 0.5 to 12 minutes. Two procedures were followed:

Procedure 1:

portions were deposited onto sample discs as described above and placed 7cm below the mouth of the lamp housing for the required irradiation period.

Procedure 2:

portions irradiated as in 1, but after measurement of the TL signal to 450°C and cooling to RT.

Procedure 1 aims to reveal the combined effects of optical bleaching and phototransferred TL (PTTL) and procedure 2 aims to reveal the nett effects of PTTL (some bleaching will take place) under the same illumination conditions.

5 RESULTS

General

It is most convenient for the purposes of comparisons to be made between the TL emissions from different samples in this report (ie. the peak heights for selected glow peaks within the glow curve). The results of measurement of TL emission are given, unless stated otherwise, as peak intensities for peaks that occur within specified temperature regions and normalized by weight - given terms of Hz/mg (using the scaling prefixes kilo and Mega where appropriate). The results are given as the mean of 4 measurements with their standard deviation, if different, the number of measurements is given in parentheses. Corrections for reduction in TL intensity obtained by the use of neutral density filters have been made for the results given below.

Mineralogical composition

The results of XRD analysis performed for each of the natural silts are summarized in Table 1.

TL emission from natural silt

Examples of glow curve shape obtained from each natural silt are given in Figure A2a (they are not scaled according to specific TL output). The maximum TL emissions recorded from the natural silts and acid treated fractions are given in Table 2. The intensity of TL emission for the untreated silts at specific temperatures in the glow curve are also given, they are used below in comparisons with tracer measurements.

TL emission from gamma irradiated tracers

The glow curves for all gamma irradiated silts were of broadly similar form, exhibiting a dominant peak at 190 - 200°C, as shown in Figure A2b. The maximum TL emissions recorded for the 5 sets of measurements are given for each sample in Table 3A. The ratios of 4th/1st and 5th/1st sets of measurements are given in the last two columns of the table.

The glow curves for the gamma irradiated TL minerals were similar to the ATL glow curves given in Report SR 19 (see attached curves), with the absence of TL emission below 150°C, as expected. A representative glow curve for fluorite is also given in Fig.A2b. The maximum TL emissions recorded for the five sets of measurements are given for each mineral in Table 3B. With the exception of Anhydrite, all samples had TL peaks in the approx. 200 and 290°C temperature regions of the glow curve, consequently, the results for the two TL peaks are given in the table. In the case of Anhydrite, the peak emission recorded at 175°C and the TL intensity (peak obscured) recorded at 290°C is given in the table. As above, the results of 4th/1st and 5th/1st sets of measurements are also given in the table. The results obtained from fine-grain fluorite and from the fluorite stock exposed under "cling-film" for 2 months are also given in the table. The results of measurements on the 50 kGy dosed fluorite (10 - 63 m) are given in Table 3C.

TL measurements on single grains of fluorite tracer (10 kGy dosed stock)

The mean values of TL emission for the approx. 200°C and 290°C TL peaks of fluorite are given in Table 5, although weight normalized values cannot be given, they provide a measure of intensity limits using a small sample of single grains of approx 40 - 63 μm. The glow curves obtained from samples of Severn and Tees containing single grains gamma irradiated fluorite are given in Figs A3a and A3b respectively.

Effects of intense optical irradiation

The results obtained using the two procedures described above with samples of natural silt and irradiated tracers are given in Tables 6A - 6C and Figures A4a - A4d. In each table two sets of data are given corresponding to the two procedures used. (It should be noted that, with the exception of the unbleached samples, each result was obtained from a single measurement on a different portion taken from the same stock.

Procedure 1:

The maximum TL emission recorded in the noted temperature regions of the glow curve, after optical irradiation for the specified period, is expressed as a percentage of the maximum TL emission recorded in the same temperature interval for the unexposed samples. Hence these values represent the percentage signal remaining after optical irradiation (usually termed bleaching).

Procedure 2:

The values in parentheses represent the PTTL emission, expressed as the percentage defined above. The degree of peak structure in the glow curves obtained using this procedure varied between samples, but for the purposes of this report it will not be necessary to examine them in detail.

The absolute values of the peak TL emission recorded for each sample using procedure 1 (NB unbleached sample at $t = 0$) are given in Figures A4a and A4b. Although in some cases there were slight differences in the temperatures of the dominant TL peak after bleaching (as indicated in Figures A4c and A4d), we used peak emissions in comparisons with results from unbleached samples.

TL mineral composition of silts (Table 1)

All the samples contained quartz, plagioclase and calcite with the exception of Nene and Severn where calcite was not detected. Dolomite was also a principle component in Nene and Tees samples. Orthoclase was a candidate for Tees, but it was difficult to distinguish from the plagioclase signal. These minerals are expected to provide dominant TL signals since Muscovite and Kaolinite are not considered to be bright TL emitters. The acetic acid and fluorosilicic acid treatments applied to remove calcite and plagioclase respectively were successful in all cases except Severn and Tees where the plagioclase was resistant (or that we had incorrectly identified it).

The mineral fractions within the silt isolated by acid treatment (as confirmed by XRD) were then analysed by TL to determine the major components of the TL emission for untreated silt.

TL emission from natural silts (Figure A2a and Table 2)

The maximum TL emission from untreated natural silt ranges from 17 ± 5 (s.d 5) to 456 ± 112 (s.d 4) kHz/mg, the equivalent value for the silt tested in 1983 falls in the middle of this range. The values for TL emission measured after each acid treatment suggest that the dominant TL emitters in the natural silt are quartz in the case of Severn, Kuching and Ribble (the weakest silts), and plagioclase plus quartz in the case of Mersey and Nene. Calcite does not appear to be a significant contributor in the spectral range used in these experiments, except in the case of Tees where it contributed at least 25% of the TL emission. Results for Tees and Tamar are more difficult to interpret. The increase in TL emission with the removal of calcite could be due to increased plagioclase concentration - yet the application of HCl reduced the TL emission of the silt and it is not expected to attack the plagioclase. This behaviour, coupled with the maintenance of a high and variable level of TL emission after the application of fluorosilicic acid suggests that with our simple procedures complex precipitates may be formed which are strong TL emitters, but which have weak XRD signals. The results from the Tees sample are more consistent, calcite and dolomite are shown to be significant contributors to the TL emission from the results obtained after acetic and hydrochloric acid treatments. The significant increase in TL emission after fluorosilicic acid treatment is taken to be due to fluoride precipitates and their removal with HCl shows that plagioclase is also a major emitter in this sample.

Fluorite is clearly the brightest TL emitter, it is at least two orders of magnitude brighter than any of the other potential tracers (200 and 290°C TL peaks). The next brightest group are the gamma irradiated silts Nene, Tamar and Tees (approx. 200°C TL peak). No substantial loss in TL signal from fluorite was recorded over the 2 month test period, under ambient lighting conditions. Nene, Tamar and Tees samples showed approximately 45, 28 and 0% loss of TL signal under the same conditions. Further examination of the comparisons of fourth and fifth measurements relative to the first suggests that, in the case of Nene and Tamar, the loss in TL signal is substantially due to optical bleaching and thermal fading respectively.

Of the remaining potential tracer samples, the most severe losses in TL signal over the two month test period were found for the approx 200°C TL peaks, the greatest being a 60% loss for the 175°C TL peak of Anhydrite, this loss is not unexpected on the basis of known mean lives of traps in this temperature range and the effects of optical bleaching. The TL properties of Franklinite, Gypsum and Severn are evidently complex since they exhibited an increase in TL emission with storage time, which may be connected with optically/thermally stimulated charge transfer processes. However, the results from these and the remaining potential tracers do not merit detailed analysis in view of their inadequate levels of TL emission relative to those from the natural silts. This can be seen in Table 4, where the relative performance of the potential tracers can be compared using the ratios of the TL emission from the tracer to that from natural silt, calculated for each tracer (approx 200 and 290°C TL peaks) and the brightest (Tees) and the weakest (Kuching) emitting natural silts.

The results from measurements on 50 kGy dosed fluorite (Table 3c) reveal that only a slight increase in TL emission is available, confirming the closeness to saturation achieved by the 10 kGy irradiation. The 500°C pre-anneal did not improve the level of emission as expected - in fact, it was reduced. The TL emission from 50 kGy dosed fluorite was reduced by a factor of 25 by recrystallization.

Fine-grain samples

It is to be noted that TL emissions (per unit weight) from the fine-grain natural silt preparations were considerably lower than those for the full grain-size fraction (see Table 2), yet the reverse was found for the fine-grain fluorite emission (Table 3b). While this appears to offer advantages for tracer work, we found that the fine-grain fraction of the natural silt contained an appreciable amount of organic material (probably accounting for the differences observed), which left an opaque film over the window of the detector assembly and thus was not considered suitable for routine measurements. The fluorite results, however, confirm that the TL emission/unit weight was not reduced by surface-volume effects.

Single grains

The results (Table 5) from measurements on 16 selected single grains of 10 kGy dosed fluorite grains demonstrate that from an albeit small number of tests, no dull grains were found, which is an important point to consider in selecting potential tracers. Since weight normalization was not possible, and the grain sizes varied between an estimated 40 to 60 μ m diameter along their minor axis, the variations in emission appears reasonable. From the fluorite emission data given in Table 3b, the height of the 290°C TL peak from a single spherical grain of 50 μ m diameter is predicted to be 400 kHz using simple volume calculations - this compares well with the value of 900 \pm 400 kHz measured for the test group.

Single grains of fluorite were placed on sample discs previously covered with natural silts to illustrate qualitative "best" and "worst" situations within the limitations of these laboratory experiments. The "best" and "worst" situations, as discussed in section 4, are illustrated in Figures A3a and A3b respectively.

"Best": The results show that for the weakly emitting silts (eg. Severn) and fluorite that has not suffered significant signal loss, both 200 and 290°C TL peaks are clearly distinguished against the silt background, an example of which is given in the figure (approx. 1 mg portion).

"Worst": The results show that the extremely bright natural emission from Tees is of a comparable level in the region of 290°C TL fluorite peak, and thus gives only a marginal means of differentiation. On the other hand, the 200°C peak is clearly discernible and provides an estimated signal background of at least 5:1 under the peak - this would be sufficient for detection purposes using a 1 mg silt sample.

Effects of intense optical irradiation (Figures A4a-d and Tables 6a-c)

It can be seen in the figures and tables that under the same optical irradiation conditions, the bleaching for the natural silts is considerably less than for the tracers. This is to be expected since the silts will have attained equilibrium TL levels through the action of previous exposure to light. It is a point worth noting when considering the stability of signal levels from irradiated tracers.

The irradiated tracers do not exhibit a single component in their bleaching characteristics (ie. a straight line on a log-lin plot) and this underlines the complexity of the bleaching process. The data in the figures may also be used to compare the relative strengths of the TL emissions since the TL emission is given in Hz/mg ($t=0$ for the unbleached samples). The general trend for the bleaching pattern for all tracer samples is an initial rapid component - within 0.5mins the majority of the samples had lost half their TL signal - and a decrease in rate of bleaching with (lamp) irradiation time. Of the potential tracers identified above as being of the second rank (gamma irradiated Nene, Tamar and Tees) an order of magnitude reduction in TL intensity may be obtained within approximately 10 min of lamp irradiation. The 200°C TL peak of Fluorite exhibits similar behaviour and the bleaching of the approx 300°C TL peak is half this value.

These limited bleaching experiments demonstrate the substantial reduction in TL emission that it is possible to achieve by the use of optical radiation of suitable intensity and wavelength. It is likely that the conditions are probably severe compared with those obtained for tracer grains in a silt matrix. The results from bleaching measurements using ambient laboratory light over two months with samples stored in containers of differing optical absorption properties, show that the degree of bleaching will, besides depending on intensity of irradiation, be highly dependent upon the spectral quality of the incident light. Consequently, the optical attenuation provided by the immediate surroundings of the tracer grains during the period of use will be of importance. In the case of Fluorite, where previous studies have shown that uv wavelengths are the most efficient in bleaching, it is likely that the surrounding silt medium would provide strong attenuation of these wavelengths. (The settling in water that would occur on deposition - if from the surface - would need further consideration and operation at night would be advisable if a problem).

PTTL: The main features to be noted from the results of the PTTL measurements are:

- i) The levels of natural TL emission in the high temperature region of the glow curve may be reproduced with short duration optical irradiation.
- ii) The levels of PTTL emission from the gamma irradiated tracers, compared with those from the natural silts, were not sufficient for the procedure to have promise for tracer work.
- iii) The increases in TL emission (or the lack of significant loss in TL signal in the case of Tamar) observed with the natural silts using procedure 1 may be connected with a phototransfer process which competes with the effects of bleaching, although this is not supported by the Mersey results.

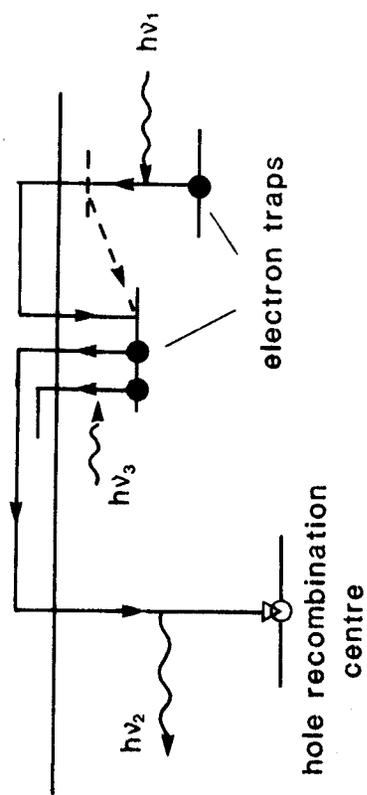
7 CONCLUSION

1. A wide range in maximum intensity of TL emission was measured from natural silts. The TL emission generally commenced and reached a maximum in the 200-250°C and 300-340°C temperature regions respectively. XRD and TL analysis on acid-treated fractions indicated that carbonates and plagioclase were responsible for a substantial proportion of the TL emission from the brightest silts, and that silts composed predominantly of quartz gave the lowest emission. Acid treatments can be used to remove the bright TL emitters, but we found that there is a risk of producing precipitates that are also bright TL emitters.
2. Gamma irradiated fluorite was at least two orders of magnitude brighter than the other tracers tested. Single grain measurements indicated that the brightness of the fluorite was uniform and that "dull" grains were not common. Irradiated fluorite, for the same weight, was at least 10^4 times brighter than the brightest natural silt (Table 5). Selected single grains (40-60 μm) of fluorite placed into 1 mg of the brightest natural silt were detectable using the 200 and 290°C TL peaks. (It should be noted that the single grains of smaller diameter are expected to yield less TL emission). The 200°C TL peak offered the best performance since the TL signal from the natural silt was considerably lower in this temperature region. An irradiated silt such as Tees may be of sufficient brightness for certain tracer applications if the host silt has weak TL emission.
3. All the potential TL tracers were sensitive to light, and this is a known feature of TL minerals. We were able to obtain substantial bleaching of the TL signals from all tracers by exposing near-monolayer portions of the sample to the radiation from an intense laboratory source of light, whereas similar losses were not observed with the natural silts exposed under the same conditions. However, the loss of TL from fluorite (200 and 290°C TL peaks) was negligible over a two month test period for material stored under ambient laboratory lighting conditions and contained in transparent polystyrene vials. These results are consistent with previous studies of the mean-lives of the two peaks (200°C peak, 39 y and 290°C peak, 10^7 y, both at RT) and of bleaching properties, where the maximum efficiency is in the uv/violet region of the spectrum.

4. The detection limits for a TL tracer system will be largely determined by the quantity of the sample portion used for TL measurement. This is not connected with the sensitivity of the TL detection system, but with the ability to resolve two TL emitting materials - host silt and the tracer. For fluortie tracer within a silt similar to Tees and measurement of the bulk TL emission, the maximum portion weight to detect a single grain would be several mg. For silts with TL emission similar to Kuching, the maximum portion size could be increased by a factor of 20. (It is worth noting that for a detection system with spatial resolution, the full brightness ratio for fluorite ($>10^4$) discussed above could be realised and in this case the maximum portion weight would be dependent upon how many grains could be heated and viewed by the detection system during the measurement period). Thus in principle, where single tracer grain detection is achieved (by selection of the maximum portion weight where bulk emission is detected), the measurement resolution of 1 in 10^9 - or a single $20\mu\text{m}$ tracer grain in an estimated 10g of silt - discussed in Report SR19 can be realised by simply testing enough portions (10^4 , 1mg portions!) It can be seen that a continuous flow system would be necessary where a number of kg of silt need to be analysed.

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21 March 1986



Valence Band

SCHMATIC ENERGY BAND DIAGRAM- showing three different charge carrier pathways:

- (i) TL (thermal stimulation)
- (ii) Bleaching (optical stimulation)
- (iii) Phototransfer (optical stimulation)

Fig A1 Conduction band

Mersey
Tees
Nene
Severn
Kuching
Tamar
Ribble

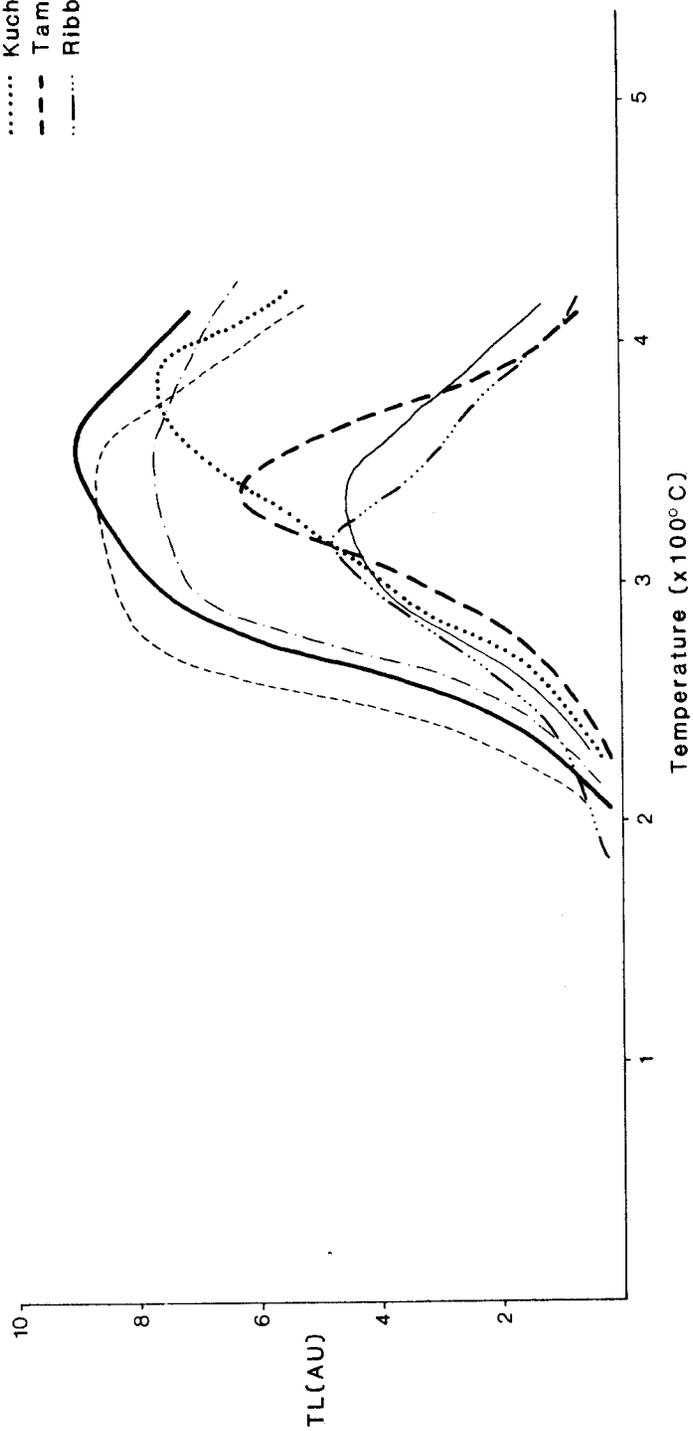


Fig A2a Glow curves from natural silt

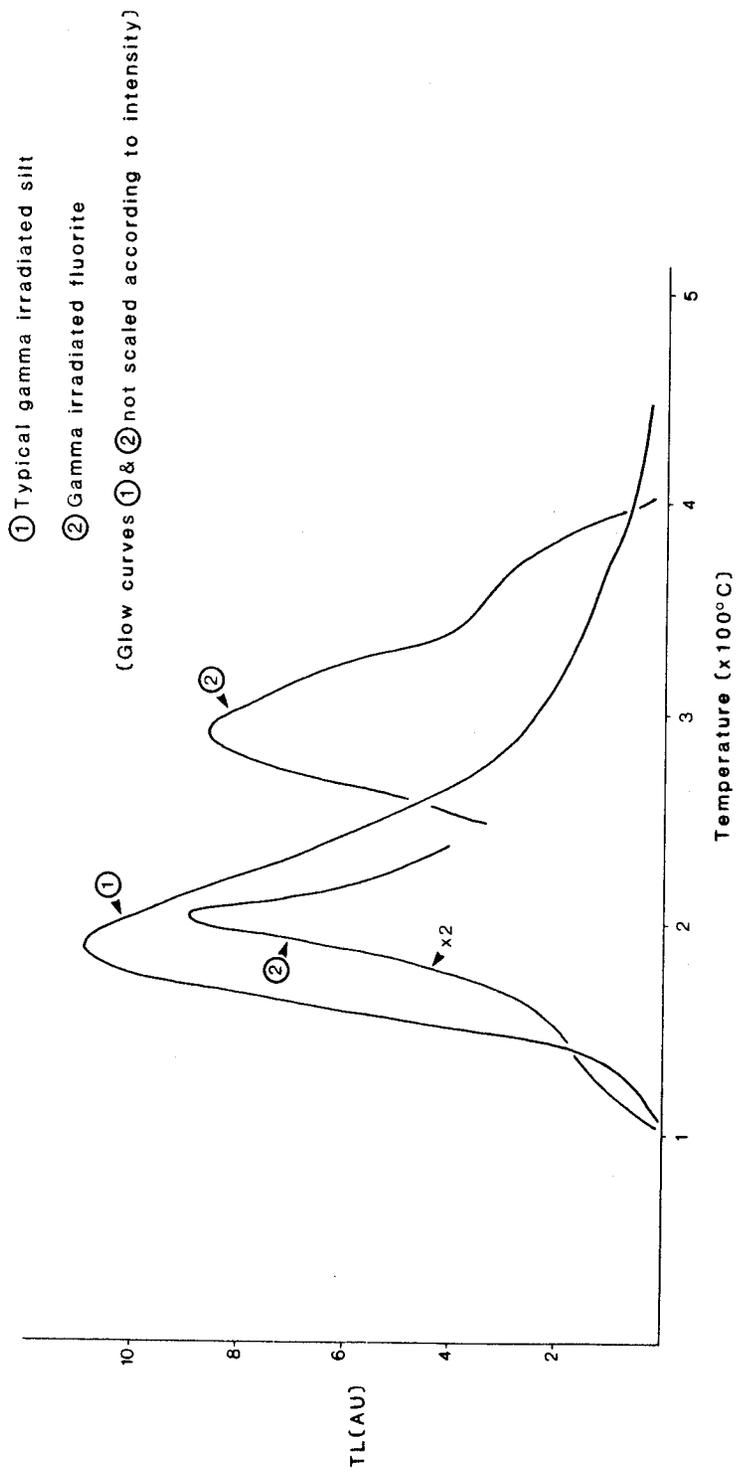


Fig A2b Examples of TL glow curves

Examples of glow curves obtained:

- ① Brightest
- ② Weakest single grains placed onto ~1mg Severn silt samples
- ③ 1mg Severn silt only

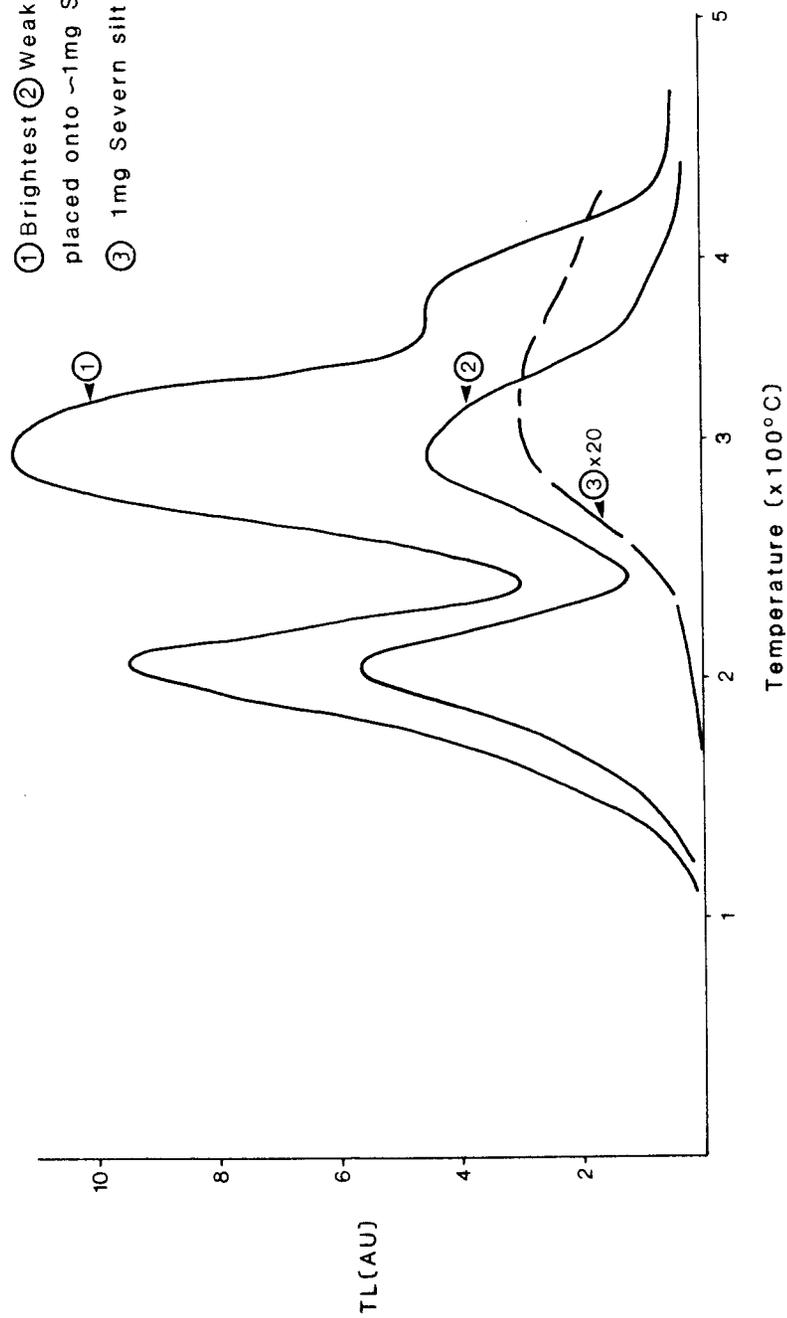


Fig A3a Single fluorite grains in Severn silt

Examples of glow curves obtained:

- ① Brightest
- ② Weakest single grains placed onto 1mg Tees silt samples
- ③ ~1mg Tees silt only

Intensity ② < Intensity ③ in high temperature region of glow curve reflects variability in emission from natural silt

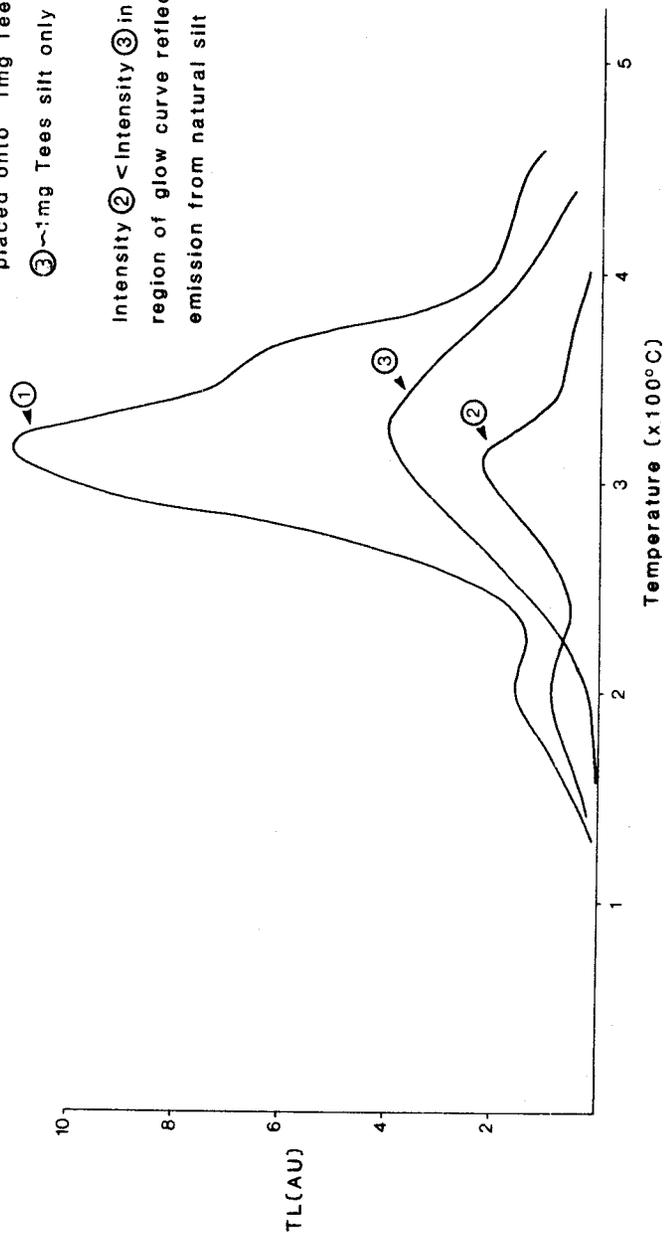


Fig A3b Single fluorite grains in Tees silt

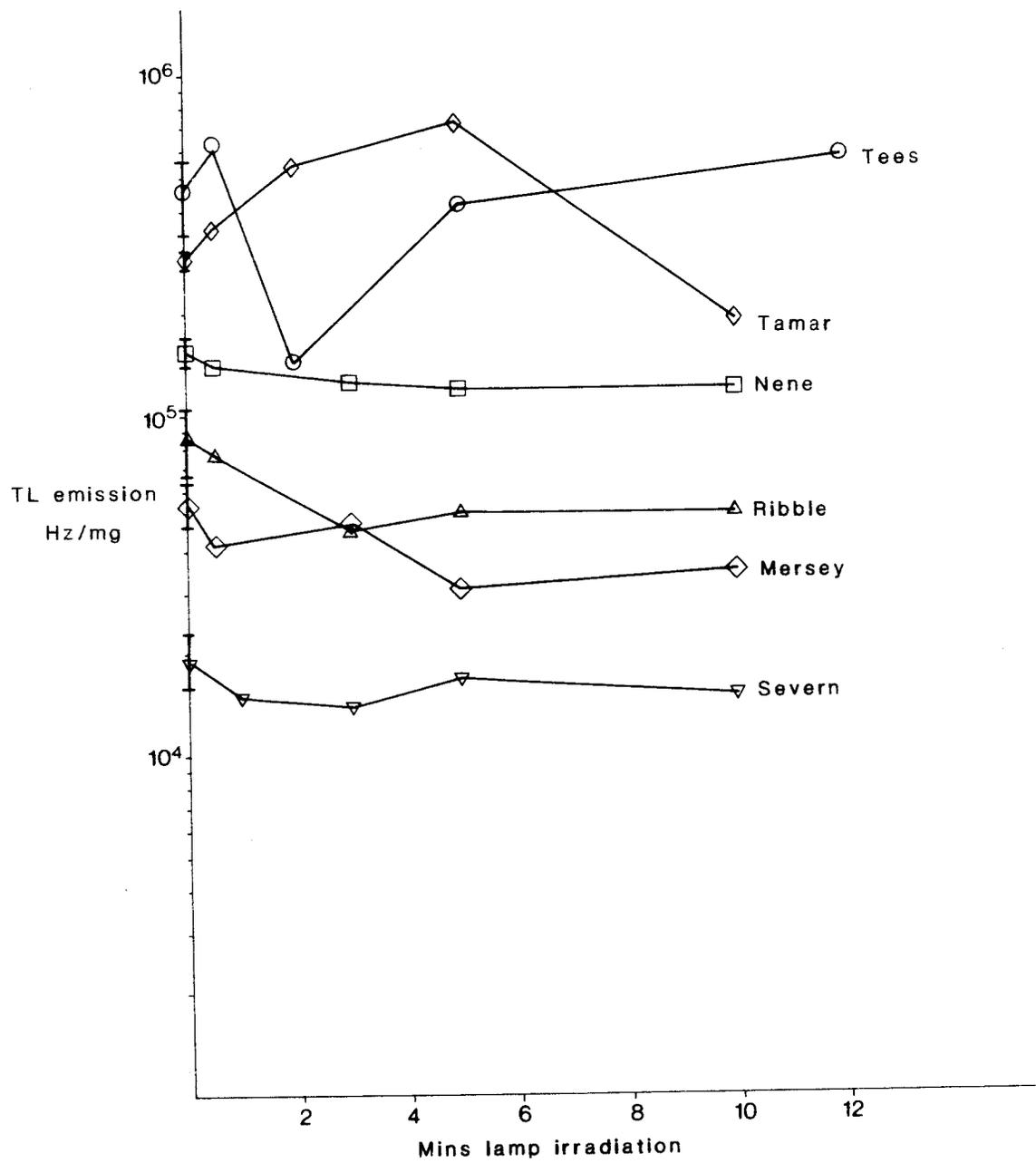


Fig A4a Optical bleaching of TL peaks (~300-400°C): Natural silts

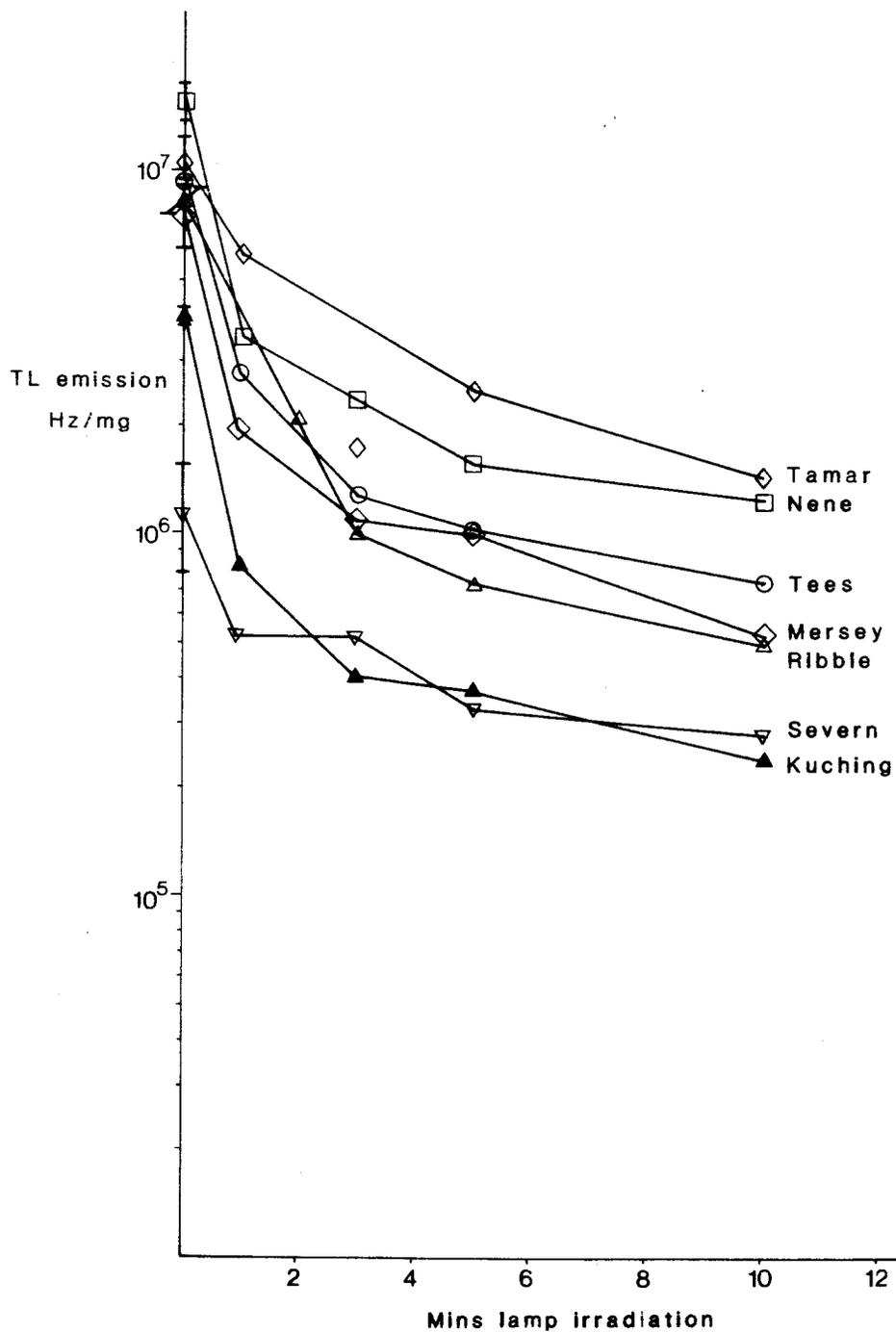


Fig A4b Optical bleaching of ~200°C TL peaks: γ irradiated tracers (silts)

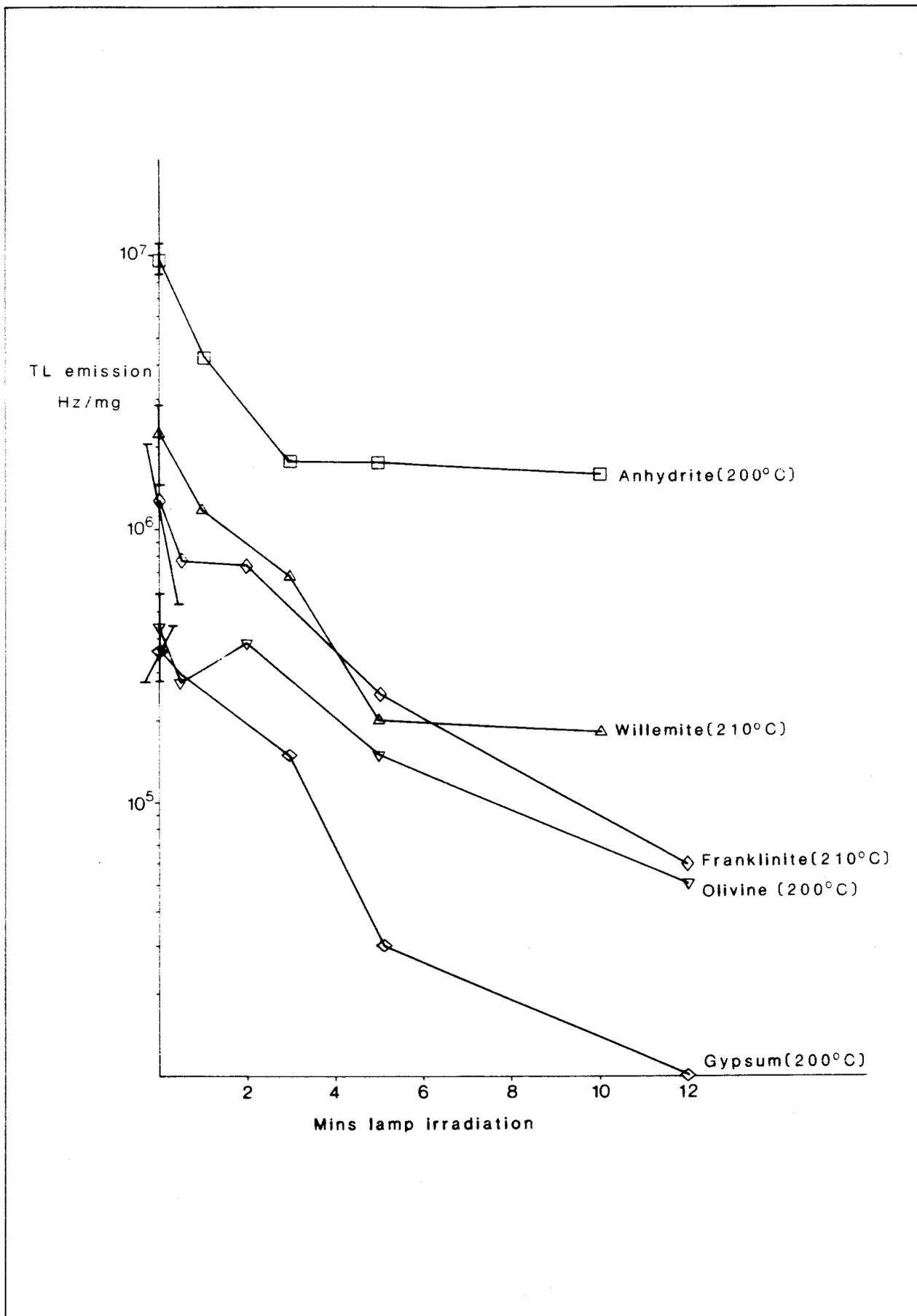


Fig A4c Optical bleaching of ~200°C TL peak: γ irradiated tracers (selected TL minerals)