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Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

THERMOLUMINESCENCE IN THE EARTH SCIENCES AND ARCHEOLOGY

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Abstract

Over recent decades the uses of thermoluminescence have been expanding rapidly, as have advances in the equipment available for the determinations of this property shown by many materials. Despite this, the comparable growth of applications in the Earth and Archeological Sciences has been markedly overlooked in the mainstream thermal analysis literature, an omission this review sets out to rectify.

Keywords: archeology, earth sciences, thermoluminescence

Introduction

Thermoluminescence (TL) is one of a considerable number of thermal analysis methods where a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme, (Warne 1992).

There are also a number of different types of luminescence e.g. photo, cathodo, chemi, tribo, electro, bio, sono and ion beam induced which are not the same as TL which may be defined as 'the phenomenon whereby on heating a sample at a constant rate, it gives off energy in the form of visible light over a particular temperature range'. Such thermoluminescent light may be essentially white or coloured.

Further, TL is not the same as the light given off when a substance is heated to incandescence, but is the thermally stimulated emission of light following the previous absorption of energy from radiation. As such, a sample exhibiting TL, cannot be made to emit TL again by reheating, (McKeever 1985).

The amount of such emitted light when continuously measured and plotted against temperature forms a Glow Curve which is the standard way of recording TL data.

As the glow curve light is often coloured; further data may be acquired by obtaining a series of TL glow curves recorded for different wave lengths.

The areas under glow curves characteristic of particular substances have also been used to determine the mass fraction present in mixtures.

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In addition to such glow curves obtained with dynamic heating rates, similar measurements of the amount of light given off under different isothermal conditions may also be made, in this case against time.

Outside its immediate areas of application the method of TL has been grossly overshadowed by many other, now famous and very well established and accepted Thermal Analysis (TA) methods such as Thermogravimetry (TG), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Evolved Gas Analysis (EGA), Thermomagnetometry (TM) and the valuable technique of 'variable atmosphere thermal analysis' (Warne 1991).

This lack of wide spread attention is doubly surprising considering the large number of scientific publications using (TL) which describe applications in diverse but often potentially overlapping areas of investigation such as Chemistry, Solid-State Physics, Docimetry, Medicine, Biology, Earth Sciences, Mineralogy, Petrology, Extra-Terrestrial Geological Materials (Meteoritic & Lunar), Archeology, Dating and Pottery.

It is the topics including and following Earth Sciences, immediately above, which will be discussed below.

For an excellent coverage of theoretical background, causes of TL and detailed methods of analysis see McKeever (1985).

Instrumentation and Resultant Glow Curves

The modern *TL* equipment is quite sophisticated. It consists of a sample heater and its heating controller, an accurate and very sensitive light detecting system with associated amplifier and a recorder which may include a computer facility for glow curve data, storage, manipulation, assessment and hard copy production (Fig. 1).

If it is only the variation in the amount of such emitted light which is required, then this may be continuously measured and plotted against temperature to form a Glow Curve which is the standard way of recording TL data (Fig. 2).

However, if a glow curve is required for each of a number of different wave lengths of then light emitted, these may be obtained using different filters in the TL light path.

Further, by using double photomultiplier detector equipment, the composite glow curve, together with the glow curves of its different component wave lengths may be obtained simultaneously if required (Townsend *et al.* 1983).

The result in this case appears as a stacked array of glow curves, determined simultaneously from preselected closely spaced wavelengths obtained with the same constant heating rate (Fig. 3) (after Townsend *et al.* 1983).

Temperature ranges for TL determinations fall clearly into two groups, below and above ambient temperature, within the general range −100 to +600°C.

Facilities may also be required for heating the sample under test in vacuum or in oxygen (where, for the latter the term oxyluminescence has been used).

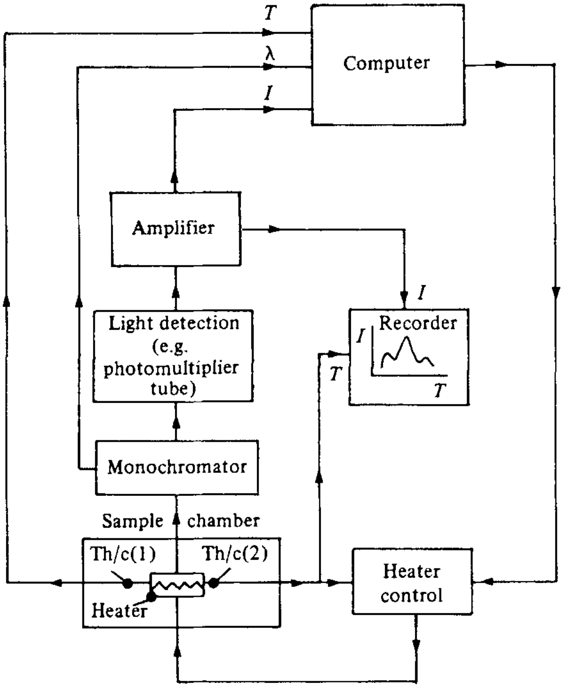

Fig. 1 Diagramatic representation of thermoluminescence equipment (after McKeever 1985)

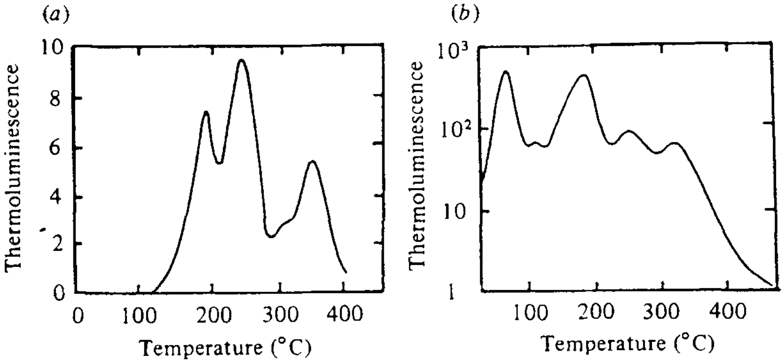

Fig. 2 Glow curves of (a) natural Brazilian quartz and (b) natural pink quartz (after Durrani *et al.* 1977 and David and Sunta 1981 respectively)

Applications

For convenience a list of the minerals and materials to which TL has been applied in the fields of Earth Science and Archeology is shown in Table 1.

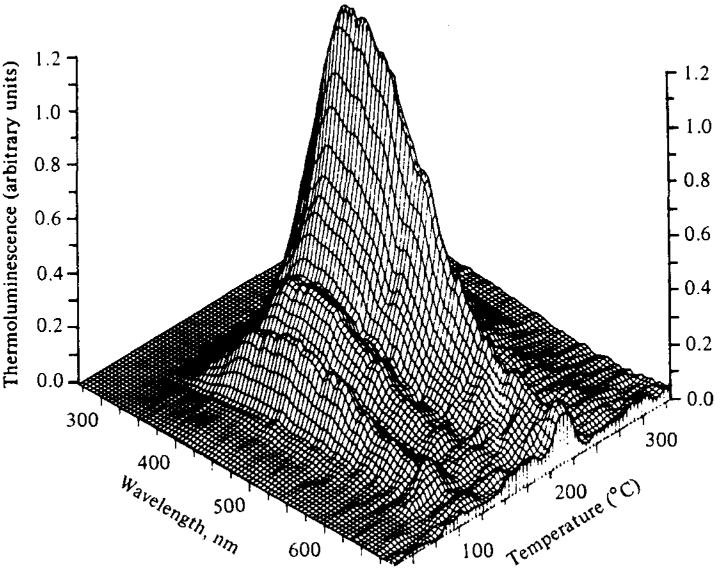

Fig. 3 Isometric plot of a stacked array of thermoluminescence spectra from X-irradiated LiF (after Townsend *et al.* 1983)

As dating (age determination) has applications in both Earth Science and Archeology it will be dealt with first.

The method is based on the discovery that the intensity of TL exhibited by specific materials is proportional to the amount of radiation absorbed. Thus, if this radiation, due to the natural radioactivity of uranium, thorium and potassium is at the constant background rate, its TL intensity gives a measure of geological time/age or on a shorter time span; archeological age.

Furthermore, if the intensity of radiation is different to background and particularly if variable, the intensity of TL provides a measure of radiation dosimetry (the amount or dose of radiation received) as described in the pioneering work of Daniels *et al.* (1953).

In fact this aspect viz. the search and evaluation of materials suitable for use as TL dosimeters constitutes a major field of TL applications, with LiF being a good example of a material being found to be very suitable for measuring radiation with a high degree of sensitivity (Daniels, *et al.* 1953). See also under Earth Sciences below.

A further quite widely used method is the characterization of artificially induced TL. This type of TL is produced in the laboratory under strictly reproducible conditions by subjecting samples to precisely known doses of radiation. In this way the TL caused by various doses of radiation (which corresponds to different periods of time in the natural environment) may be used to elucidate the TL behaviour of different materials and the effects of metamorphism etc. on them (McKeever 1985).

Table 1 List of relevant minerals and materials to which TL has been applied

Albite	(see feldspars)	Grossular	(see under garnets)
Amethyst	(see quartz)	Halite	
Andesine	(see feldspars)	Hydroxyapatite	
Anhydrite		Ilmenite	
Anorthite	(see feldspars)	Labradorite	(see feldspars)
Apatite		Lavas	
Aragonite	(see carbonates)	Limestone	(see calcite under carbonates)
Bytownite			
Calcite	(see carbonates)	Maskelynite	(Feldspathic glass, see under feldspars)
Carbonates			
Aragonite		Melilite	
Calcite (limestone)		Metamorphics:	rocks and minerals
Dolomite		Meteorites	
Chlorapatite		Obsidian	(Black volcanic glass)
Cristobalite		Olivine	
Dolomite	(see carbonates)	Fayalite	
Diamond		Forsterite	
Enstatite	(see pyroxene)	Oligoclase	(see feldspars)
Fayalite	(see olivine)	Orthoclase	(see feldspars)
Forsterite	(see olivine)	Orthopyroxene	(see pyroxene)
Feldspars		Plagioclase	(see feldspars)
Albite		Pottery	
Andesine		Pyroxene	
Anorthite		Enstatite	
Labradorite		Clinopyroxene	
Oligoclase		Orthopyroxene	
Orthoclase		Quartz	
Plagioclase		Amethyst	
Maskelynite	(Feldspathic glass)	Citrine	
Sanidine		Cristobalite	
Flint		Tridymite	
Fluorapatite		Sanidine	(see feldspars)
Fluorite		Spinel	
Garnets		Tridymite	(see quartz)
Grossular		Zircon	

Archeology

Of prime importance in archeology is the major and long established TL dating method based on different types, styles, decoration and glazes used in antiquity.

The mechanism here is that because the temperatures of firing pottery are more then sufficient for the constituents of pottery, mainly clay, to give off their stored TL energy they are 're-set' back to zero. In this way any new pot, once cooled, is immediately exposed to the natural radiation and starts to accumulate at a constant rate an ever increasing dose, the magnitude of which, as TL, when released on subsequent heating is proportional to age.

As the preservation of the broken remains of ceramic pots in large amounts, as 'pot sherds', is often very wide spread in archeological sites, this TL method of dating has proved particularly useful. Firstly, for confirming stratigraphic age sequences based on pottery types. Secondly, for dating the same type of pottery in widely separated locations where they are essentially the same age, but re-located by trading OR are significantly different in age due to the time taken for new fashion or technology to arrive in a distant city or country.

Specifically it is grains of the minerals quartz and feldspar naturally occurring in the pottery clay and subsequently in the fired pottery which exhibit the strong TL upon which dating is based (McKeever 1985).

Thermoluminescence has also been applied to the dating of the age of flint artifacts, not with regard to the age of the original flint nodule locations, which is too great, but to the age of the working of the flint artifacts.

The TL dating of the time of working of the flints comes about due to the fact that the knapping quality of flints is often markedly improved by a pre-treatment by heating (Melcher and Zimmerman, 1977), which again 're-sets the TL clock' as for pottery. Not all flints have however been heated and there are other difficulties (Bowman and Sieveking 1983). The limit in time due to 'saturation effects' is at ≈50.000 years before present.

Similarly again the dating of 'burnt' or hearth stones can be achieved from the TL that has accumulated since the last heat re-setting (use). Again this mainly depends on the presence of quartz and feldspar in the rocks used in hearths.

As described below under 'earth science', lava flows once cooled and solidified, may by TL of contained quartz or feldspar, give dated time lines in archeological investigations of deposits immediately below. But note clearly the proviso that an age limit in thousands (max.≈50.000), not millions, of years applies.

A secondary effect of this is the heating of pre-existing rocks below by very hot lava flowing over them to give material similar to 'hearth stones' suitable for TL dating.

As carbonate cave deposits including stalagmites and stalactites are usually relatively young and because they sometimes are deposited over or include archeological deposits their ages by TL are often useful.

Related materials such as shell, bones and teeth have been used with varying success, shells show considerable TL variation with taxonomy and with compositions of calcite being much better than aragonite. Further, complications are also due to the presence of residual organic matter, mainly collagen which has to be chemically extracted first.

Two excellent books on dating in archeology have been written by Fleming (1979a) and Atiken (1984) and should be referred to for further details.

An interesting aside is that the TL of ceramics can indicate their incorrect age of manufacture and therefore their detection as fakes, recent forged additions to sets or later repairs which are too young (Fleming 1979a & 1979b) and for authenticity testing of various types of art, see review by Wintle (1980).

In this area TL has proved invaluable because although the material may look 'right' due to excellent workmanship it will have an age which is too young. Such disparate ages are not always very recent as repairs have sometimes taken place at times long after manufacture but still well back into antiquity.

Some idea of the scope of forgeries may be gained from the work of Atiken, Moorley and Ucke (1971) where the TL examination of 66 artifacts showed that almost 3/4 were forgeries.

Earth Science

In the same way that the firing of pottery destroys any TL that may have previously accumulated and readies the material to build up TL again with time, so does once molten magma. Minerals in the resultant lava flows, on cooling and solidification, also build up TL, with time, as they are slowly irradiated. This provides a measure of the period elapsed since solidification (see above also for subflow baking effects).

On the one hand, the age involved needs to be within the time range of archeological investigations because over times much longer than this the radiation induced TL reaches a saturation level above which it does not increase.

Conversely once TL saturation has been reached the characteristics of the resultant glow curve of specific mineral/geological materials may also differ due to compositional variations (particularly phosphors) and including trace elements. Thus it may be useful in indicating the divers geographic places of origin of specific types of materials.

Applications are also in the fields of geothermometry and palaeothermometry, that is to say in relation to the temperature of formation of present and past geological materials. Variations being due to the incorporation of impurities which may be dependent on the temperature of formation, of the geological material under investigation (David and Sunta 1981)

Similarly increased TL variations have been described in rocks surrounding hydrothermal ore bodies i.e. forming a zone or envelope around them which constitute a prospecting or exploration tool, particularly for obscured deposits.

Such TL 'envelopes or aureoles' must also be considered in relation to metamorphism which is dealt with under a separate heading below and with particular regard to the proximity (often obscured) of once hot igneous bodies.

Further prospecting and evaluation applications lie in the areas of detection and assessment of natural radioactive mineral deposits. Here the increased radiation levels round these ore bodies cause increased TL of key minerals in the surrounding rocks. Such minerals are thus acting as natural 'dosimeters'.

Metamorphism

Although if the background radiation is at the constant rate the TL intensity it produces gives a measure of time under 'normal' conditions, another factor may come into play. This is the fact that the absorption of heat from the surrounding environment (if it does not completely destroy the expected TL) causes a reduction in the expected intensity of TL and thus provides a method of assessing the degree of metamorphism based on its thermal history. This aspect is applicable to the 'glow intensity fall off' approaching both igneous intrusions and underneath extrusions.

In addition it is clear that this aspect of the application of TL applies equally to terrestrial and extra-terrestrial materials available to us in the form of meteoritic materials.

Further, it has been determined that pressure effects on minerals can influence their TL properties, Sears (1980). If the shock is sufficiently intense to cause physical, optical, electronic, structural, polymorphic, melting and associated vaporization modifications the term 'shock metamorphism' may be applied.

Such severe shock effects and their associated TL modifications are dominantly caused by large meteor impacts, the presence of which may be indicated in the surrounding rock even after the original impact crater has been eroded away. However, shock metamorphic effects may also be produced by massive explosions and faulting, so that care must be taken when attributing such TL shock metamorphism effects to a particular cause such as meteor impacts.

Similar variations in emission of natural TL from minerals in natural rocks effected by hydrothermal alteration and emplacement are applicable. They are regarded as potentially useful for prospecting as they often constitute an anomalous halo of TL values surrounding such ore bodies.

Further, TL variations of gypsum and anhydrite occurrences have been used to indicate palaeotemperatures at various intervals down oil and gas exploration wells. This in turn casts light on the important concept of maturation temperatures vital for the formation and preservation of liquid and gaseous hydrocarbon deposits.

Conclusions

It is now clear that TL has much to offer in many aspects of Earth Science and Archeology, will yield increasingly valuable results if more widely applied and has the potential for considerable expansion particularly as its merits become increasingly widely known and appreciated.

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