Red thermoluminescence (RTL) in volcanic quartz: development of a high sensitivity detection system and some preliminary findings

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Abstract: *As part of a general study exploring the suitability of the RTL of quartz for dating volcanic events, a modified Risø Reader apparatus has been assembled and tested. Modification consisted of an alternative, cooled photomultiplier, and the incorporation of signal pass filters which have not previously been employed in RTL investigations. The use of an extended S20 9650 PMT provides a greater quantum efficiency in the wave range 600-800 nm than the traditionally used 9635 bialkaline tube. A substantially disadvantage of using such an extended tube relates to the relatively high thermal background generated with the photocathodes. To overcome this limitation we have tested the PMT response via cooling down by c. -17°C. This reduced the background to an order of magnitude (~ 200 c/s). A cooled (~-17°C) extended S20 Photomultiplier (PMT) demonstrated a signal increasing and background decreasing due to PMT cooling up to 400°C. A range of filter combinations was examined by both empirical experiments of RTL on quartz extracted from a late Holocene, New Zealand dune sand sample (OX_{OD}847/3) and a uv-vis spectrophotometer. Of the filter combinations examined, a Hoya 2-63 and Schott BG-39 provided the best IR suppression and therefore signal to noise ratio. However, as the BG-39 limits a substantial component of the 600-620 nm RTL peak emission , it may be inadequate for relatively young or insensitive samples. In such cases a new IR suppression filter (Corion FR-400S) is recommended.*

Introduction

Red Thermoluminescence (RTL) in quartz was first observed in samples collected from volcanic ash layers (Hashimoto et al., 1987). Since that time RTL in quartz has attracted considerable attention (e.g., Hashimoto et al., 1991, 1996; Pilleyre et al., 1992; Miallier et al., 1991, 1994 a, b). Previous research conducted on the RTL peak in quartz is summarised in Table 1. Unlike the more commonly employed ultra-violet and blue quartz TL emission bands which bleach readily in daylight, and occur frequently in quartz from a wide variety of geological settings, RTL has been recognised dominantly in quartz of volcanic origin and is only slightly sensitive to daylight bleaching (Miallier et al., 1994c). As a consequence, quartz RTL has been considered a potentially useful dosimeter for the dating of thermal resetting events (e.g., volcanic eruptions, baking of sediments & flint).

Despite over a decade of research into RTL of volcanic and other quartz, and the production of a small (<20) number of palaeodoses which have resulted in age estimates that compare favourably to independent age control, a number of important questions and research directions remain outstanding. These include:

1. The need for a systematic test of photomultiplier (PMT) and filter combinations in order to maximise RTL signal to noise.

2. Usually analysis of RTL, particularly of high (>300 °C) temperatures, has been complicated by high thermal background (e.g. Scholefield and

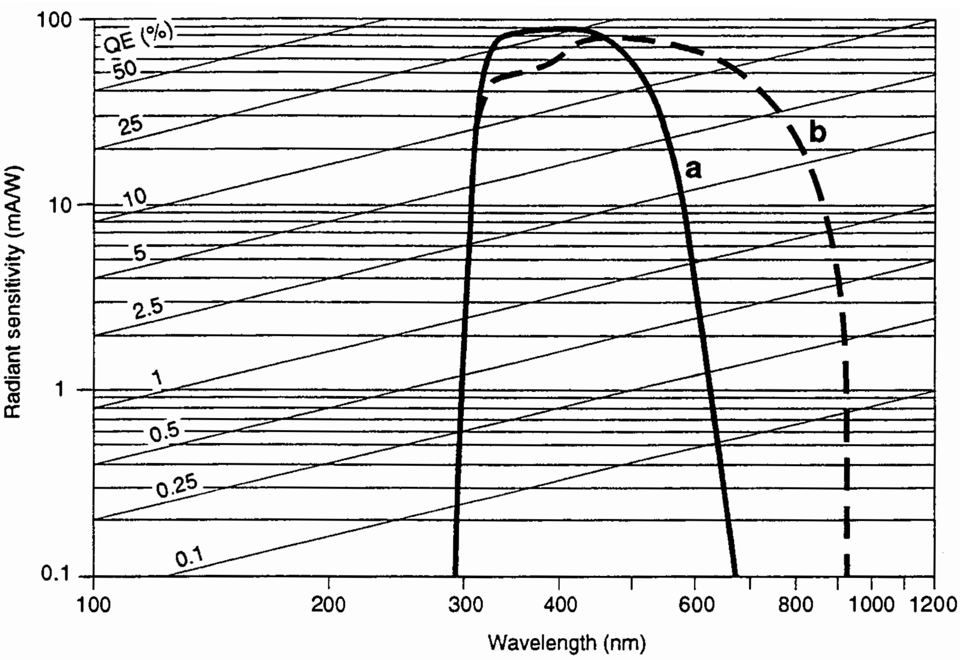

Figure 1. Quantum efficiency of Electron Tubes 9635Q and 9658 PMTs. Data from PMT catalogue.

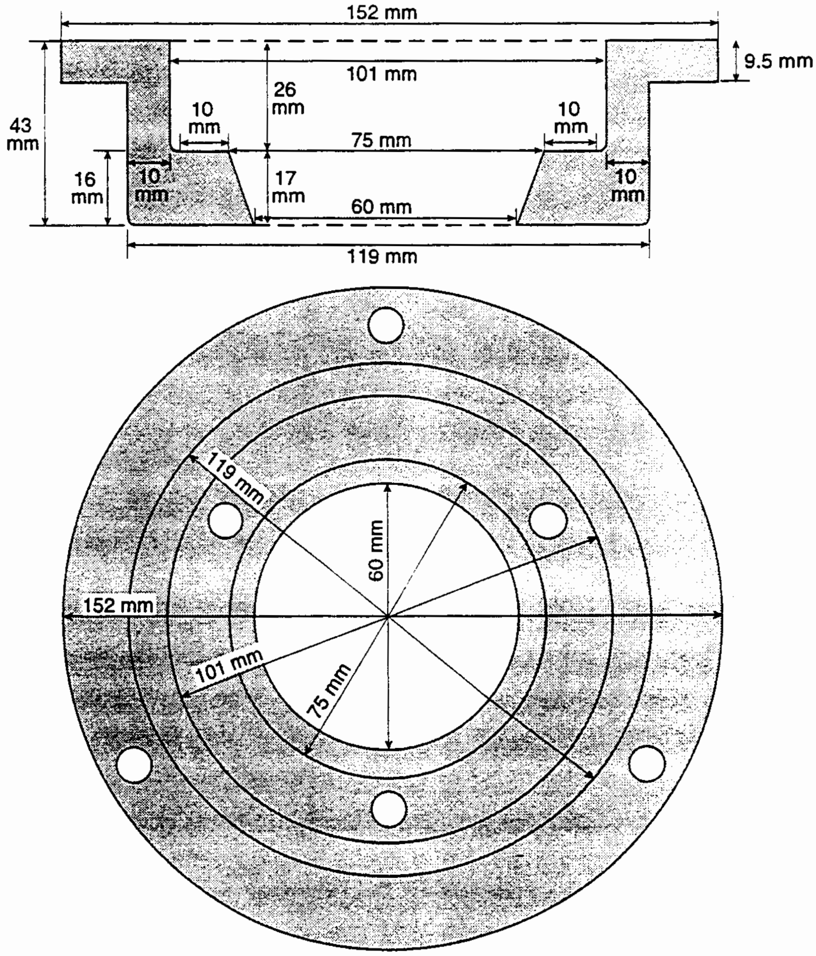

Figure 2. Adapted flange, which locates the S20 tube above the standard RISO OSL/IRSL collar.

Prescott, 1999). This has limited scope of RTL analysis typically to <450°C. While this is capable of primarily useful age-related information (e.g. Montret et al., 1992), the potential of higher temperature traps remains generally unknown.

3. The need for a survey of RTL for a range of volcanic deposits over a full (0-500°C) range of glow curves temperatures. Use of high (>300 °C) temperature peaks has to a large degree been prohibited by high temperature background and correspondingly poor signal to noise ratios (e.g., Scholefield and Prescott, 1999).

4. Tests on the potential of optical stimulation of the trap responsible for RTL.

5. The need for further systematic study of the thermal and optical stability of the RTL traps in quartz to complement existing research.

We have initiated a project, which seeks to explore additional physical aspects of RTL in quartz and assess its potential for dating volcanic deposits. Our approach was to first assemble and test apparatus to detect RTL in quartz, and it is subsequently intended to quantify some aspects of RTL properties in detail (peak temperature, dose effects, thermal stability, life time preheating and annealing effects, etc). This paper summarises the initial stages of the project, including an overview of the photomultiplier and filter combinations which we have tested.

The photo detection system

While bialkaline tubes such as the EMI 9635Q have great utility for detecting UV-blue emission and have also been employed in RTL studies (e.g., Miallier et al., 1991), they have poor quantum efficiency at longer wavelengths (Figure 1). The S20 Trialkali (Na-K-Sb-Cs) tube (EMI 9658B) offers a response from UV to near IR, which is particularly suitable for the detection of red luminescence. In collaboration with Mr Henrik Christiansen (Risø labs) we have attached an S20 PMT to a Risø model TA-15a Automated TL/OSL reader (Bøtter-Jensen, 1997). A flange was designed that locates the S20 tube above the standard Risø OSL/IRSL collar which is fitted with a focussing lens system (Figure 2). This arrangement allows routine operation of the RISO reader while the red tube is mounted.

A disadvantage of the S-20 PMT is its relatively high dark count at room temperature (c. 2 kc.s^{-1}). This thermally-generated dark count can be reduced by an order of magnitude to levels comparable to that of a bialkali tube by active cooling down to ~ -15°C (Figure 3). For this purpose we use an S 600 PHOTOCOOL Thermoelectric Refrigerated Chamber. Maximum cooling (~Δ40°C) can be achieved with 1 hour of switching on, while the warm-up cycle takes the order of 3 hours.

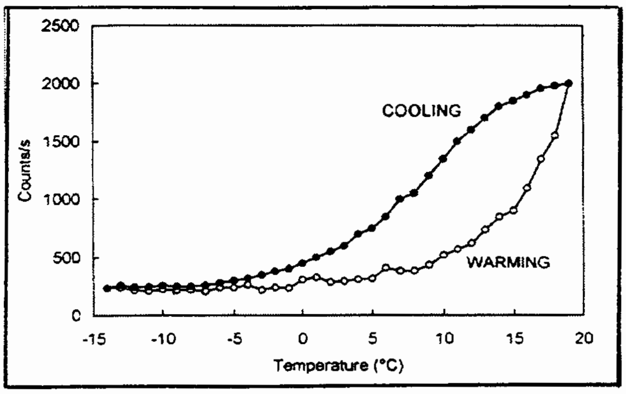

Figure 3. S20 PMT background versus photocathode temperature. Dark count was detected by combination of FR-400S+OG-590 filters.

Active cooling dramatically reduces the PMT background at low (<380°C) temperatures. At higher temperatures, somewhat surprisingly, the PMT background is greater for the actively cooled PMT than for the same PMT held at room temperatures. The response of the PMT increase by approximately factor of 2 which results in an enhanced level of black body radiation at TL measurement temperatures which exceed c. 300°C (Figure 4, Table 2). It is noted that the temperature at which the PMT background increases is different for each PMT temperature used (@ -17.7°C significant increases start at 300°C; @ 20°C significant increases start at 360°C). Actual RTL measurement show a similar enhancement (Figure 5, Table 3) which results in an enhanced signal to noise (S/N) ratio for glow curve temperatures below 350°C (Table 4). Above that glow curve temperature there is no specific S/N advantage, but the enhanced count rate of the cooled tube is advantageous.

Table 1. Selected previous research conducted on the RTL peak in quartz

Authors	Deposits studied	PMT/filter combination	Comments
Hashimoto et al. (1987-1991-1993-1994-1996)	Natural quartz of dune sand, granite and fossil bones	R649 (Hamamatsu Photonics Co, Japan)/ IR cut-off filter (IRA-05) R-649	Red emission band at 330°C, at 620 nm (heating rate 1°C/s) was used for dating fossil bones, finding the relation between RTL and impurities, Colour images of different deposits
Kanemaki et al. (1991)	Volcanic Glass Fractions from tephra (Japan)	R649 (Hamamatsu Photonics Co, Japan)/ (Toshiba 0-58) 580 nm (Ealing 35-5420) 640 nm	Red emission band at 330°C, at 620 nm (heating rate 1.7°C/s). They attributed this to Quartz and Plagioclase microcrystals
Liritzis et al. (1996)	Materials extracted from a pyroclastic formation and consists of quartz which sets the boundary to the heterogeneous material of volcanic origin	EMI 9635 QA/ A blue filter and an IR rejection filter to detect 325°C peak of TL	Four samples were dated successfully. The mean age was 1460 (±460, ±595) yr B.C
Miallier et al. (1991-1994)	Xenolithic quartz grains heated by Volcanic Products of Gravenoire Volcano (France)	EMI 9635 QA/ ORIEL 610 FS RG610 (Schott)	A band at 380-395°C , at 610-620 nm (heating rate 5°C/s) was used for exploring the properties of quartz and dating Pumice eruption up to half a million years
Pilleyre et al. (1992)	Sediments heated by lava-flows (France)	EMI 9635 QA/ RG610 (Schott)	A band at 380-395°C, at 610-620 nm (heating rate 5°C/s). Samples 10-150 ka were dated successfully
Rendell et al.(1994)	Synthetic, hydrothermal, and volcanic quartz (England)	PMT(200-800nm)	3-D spectral measurements demonstrated: Red peaks at 135°C, 280°C, 400°C (heating rate 2.5°C/s)
Scholefield et al. (1999)	Samples of quartz extracted from a variety of sediments	EMI 9635 QA and EMI 9558 Q/	3-D spectral measurements demonstrated: Red peaks at 135°C(1.96 eV), 205°C(1.97 eV), 305°C(2.00 eV) and355°C(2.05 eV) (significant red at ~1.9 ev/650nm) heating rate 5k/s

Optical filter combinations

In designing filter combinations for RTL measurements, we have attempted to maximise luminescence transmission of 600-620 nm (Hashimoto et al., 1987; Miallier et al., 1991), while minimising passage of other photons (in particular photons which contribute substantially to thermal (blackbody) radiation). We have tested a range of filter combinations by both measuring transmission windows using a uv-vis spectrophotometer, and conducting empirical experiments of RTL on quartz extracted from a late Holocene, New Zealand dune sand sample (OX_{OD}847/3). The sample was collected from within a suite of prograding coastal dune features within the Bay of Plenty area, North Island, New Zealand. Construction of these dunes has occurred following the post Glacial sea level rise due to an abundance of volcanic detritus supplied (via coastal erosion and fluvial transportation) from the adjacent acid Taupo Volcanic Zone.

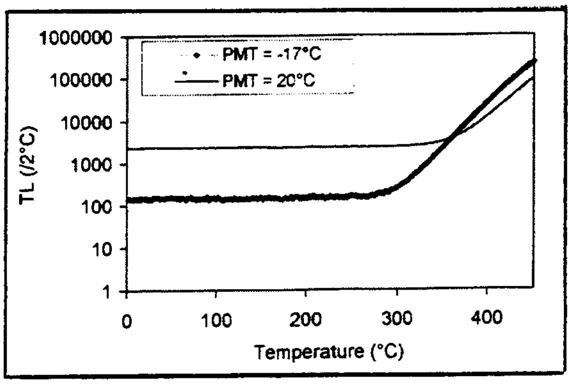

Figure 4. Dark count of a blank aluminium disc on RISO (0-450°C, heating rate 2°C.s^{-1}). Measurements are repeated 10 times while PMT temperature set to (1) 20°C and (2) -17°C. Average of measurements are showed for each experiment. Dark count was detected by combination of FR-400S+OG-590 filters.

The filters tested are primarily those which are widely available and in use in TL laboratories. Three heat rejection filters were incorporated in our tests (Table 5). The HA-3 and BG-39 are widely employed in TL and OSL applications for long cut filtering and heat rejection (Aitken, 1998). We additionally tested a multi-layer laminated, Corion FR-400S filter which according to the manufacturers possesses a sharp long cut at around 700 nm. This particular filter is supplied as a 52mm square which was cut down to the necessary 45mm diameter of the RISO filter holder. Corion produce a range of other small diameter (25mm) long and short pass filters which are potentially useful for RTL applications, but these have not been investigated at this stage due to the reduction in signal pass which would result from their size. There are a range of long pass filters capable of restricting wavelengths shorter than c. 600nm. Of these we have chosen to examine the characteristics of the Hoya 2-63, 3-67, and 2-61 and Schott OG-590 and RG-610 filters.

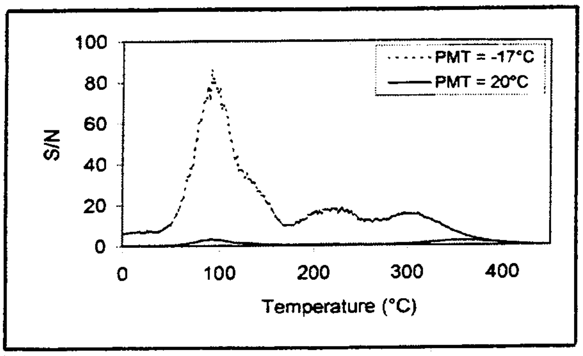

Figure 5. Average artificial TL measurement on RISO (0-450°C, heating rate 2°C .s^{-1}) of sample 847/3 after ~ 42 Gy dose. Measurements are repeated 3 times while PMT temperature set to (1) 20°C and (2) -17°C.

Spectrophotometer analysis

All spectrophotometer measurements were undertaken at room temperature on a Shimadzu uv-vis spectrophotometer model P/N 204-58000. Examination of the long cut filters reveals strong contrasts between filters (Table 5). While the HA-3 filter offers a broad transmission window passing from UV to red at levels in excess of 60%, its high (20%) transmission in to the IR renders it of limited utility for RTL studies. Of the two other filters tested the BG-39 offers the best (i.e., lowest) IR transmission characteristics, but transmits only c. 50% of that passed by the FR-400S in the red region of interest (c. 600-640 nm; Table 5).

Detailed examination of the FR-400S long cut characteristics has identified two minor IR pass window at around 720 and 900 nm. While the high signal pass levels are advantageous in RTL studies,

Table 2. Summary of dark noise measurements at different PMT temperatures.

Temp (°C)/ratio	Low temp. Average $_{(0\text{-}100°C)}$ dark noise (/2°C)	High temp. (@ 400°C) dark noise (/2°C)
-17.7	145.8	26046.8
20	2374.3	12466.6
-17.7/20	0.06	2.09

Table 3. Summary of sample 847/3 TL measurement at different PMT temperatures.

Temp (°C)/ratio	$TL_{(50\text{-}150)}$	$TL_{(350\text{-}450)}$
-17	325533	1324642
20	211707	623569
-17/20	1.5	2.1

Table 4. Ratio of signal TL to background (S/N) at different temperatures for sample 847/3 + β =40Gy.

Temp (°C)	$S/N_{(100)}$	$S/N_{(200)}$	$S/N_{(300)}$	$S/N_{(350)}$	$S/N_{(400)}$	$S/N_{(420)}$	$S/N_{(440)}$	$S/N_{(450)}$
-17.7	77.16	15.97	15.44	6.90	1.27	0.56	0.12	0.03
20	3.02	0.47	0.69	2.21	1.25	0.60	0.15	0.05

Table 5. Spectral characteristics of some long cut filters

Filters (mm)	Peak Transmission %	Peak Transmission λ (nm)	IR Transmission %	IR Transmission λ(nm)	Heat Rejection
HA-3 (3)	~ 80	340-620	>20	700->900	Poor
BG-39 (2)	~ 80	450-530	~ 0.2	760-900	Good
	~ 60	540-580			
	~ 30	580-620			
	~ 8	620-640			
BG-39 (1)	~40	400-580	~0.5	700-720	Good
	~30	580-620	~0.1	720-760	
	~15	620-660	~0.1	860-900	
FR – 400S (7)	~ 70	440-600	~ 2.0	700-720	Medium
	~ 60	600-640	~ 0.5	720-740	
	~ 10	680-700	~ 0.3	760-900	

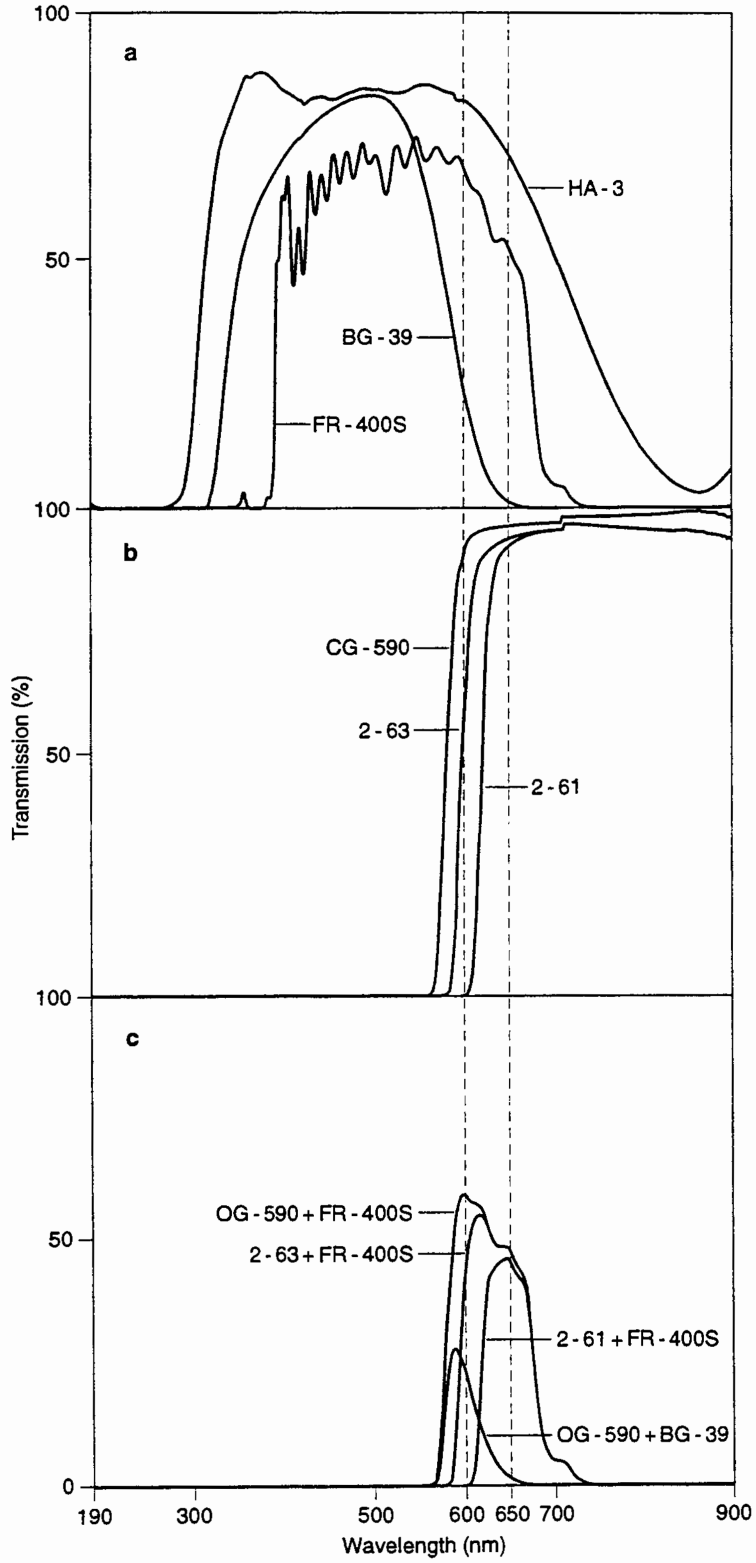

Figure 6. *Filter combination of long cut and short cut filters.*

Table 6. Spectral characteristic of combination of selected filters

Filters	Max Peak Transmission %	λ (nm)	Min-Max Wavelength λ (nm)
FR-400S + OG-590	60	600-620	570-730
FR-400S + 2-63	52	610-630	580-730
FR-400S +2-61	46	630-650	600-730
FR-400S +3-67	46	570-620	550-730
FR-400S + RG 610	44	620-640	590-730
BG-39 + OG-590	34	590-610	570-720
BG-39 +2-63	29	600-620	580-720
BG-39 +2-61	18	620-640	600-720
HA-3 + OG-590	60	610-630	530-900
BG-39 + RG 610	12	610-630	590-720
BG-39(1)+HA-3 + OG-590	20	580-600	560-720
BG-39(2)+HA-3 + OG-590	21	580-600	560-670
BG-39(1) + HA-3 + 2-63	12	600-620	580-710
BG-39(2) + HA-3 + 2-63	16	600-620	580-670
BG-39(1) + HA-3 + 2-61	8	620-640	600-710
BG-39(2) + HA-3 + 2-61	3	620-630	610-670
BG-39(1)+FR-400S+OG-590	14	590-610	570-680
BG-39(2)+FR-400S+OG-590	19	580-600	560-770

Table 7. Luminescence transmission characteristic of combination of selected filters

SC filter (mm)	LC filter (mm)	TL_{50-150}	$TL_{300-430}$	BG_{50-150}	$BG_{300-430}$	$TL_{390/110}$	$S/N_{(50-150)}$	$S/N_{(300-430)}$
OG-590 (2)	HA-3 (4)	1571241	4755374	10354	46278692	3.03	151.75	0.10
OG-590 (2)	BG-39 (2)	136070	353917	9019	63855	2.60	15.09	5.54
OG-590 (2)	FR-400S	325533	1324642	7382	2756975	4	44.09	0.48
2-61 (3)	HA-3, BG-39 (1)	188177	462180	9767	250566	2.46	19.27	1.84
2-63 (3)	BG-39 (2)	136381	406312	9326	51254	2.98	14.62	7.93
2-63 (3)	BG-39 (1)	38162	28065	67323	65721	0.74	0.57	0.43
2-63 (3)	FR-400S	418629	886934	19091	2501796	2.12	21.9	0.35
2-61 (3)	BG-39 (2)	29200	52503	10709	38118	1.80	2.73	1.38
2-61 (3)	HA-3 (4)	652287	477286	10240	45168705	0.73	63.70	0.01

these IR pass window complicate sample stimulation by IR.

The results for filter combinations are summarised in Figure 6. Of these the combination of FR-400S and OG-590 provide the greatest red transmission while limiting the principle IR transmission to levels lower than c. 720nm (Table 6). We note additionally, that in testing for phosphorescence or other malign effects, the orientation or ordering of the filters had no significant effect on the transmission window.

Actual RTL measurements using various filter combinations

To confirm the general patterns noted above we tested a range of filter combinations using a quartz sample which has been demonstrated to exhibit no significant TL sensitivity changes during repeated measurements (Fattahi and Stokes, 2000). An aliquot of the sample 847/3 was repeatedly given a c. 42 Gy test dose and its RTL measured (heating rate 2°C.s^{-1}) after changing the filter combination.

As it is shown in Table 7 the combination of 2-63(3mm) + BG- 39 (2mm) posses the best S/N at $TL_{300-430}$ (7.93) and the best ratio of $TL_{390/110}$ (2.9). The combination of HA-3 and Long pass filters demonstrated the poorest S/N at $TL_{300-430}$ (0.01) and the lowest ratio of $TL_{390/110}$ (0.73) and the highest S/N at TL_{110} (152). The combination of HA-3 + BG-39 + 2-61 demonstrated a poor S/N at $TL_{300-430}$ (1.84).

Conclusions

Quartz RTL has been considered a potentially useful dosimeter for dating volcanic deposits. In order to maximise RTL measurements, we have adapted a RISO model TA-15 Automated TL/OSL reader to a suitable apparatus to detect RTL in quartz. We have specifically tested a cooled (~-17°C) extended S20 and a range of filter combinations. The best combination found was the Schott OG-590 and Corion FR-400S filters. While these provide an enhanced signal level, the limited pass of 700-720 nm photon leaded to high (>1MC. S^{-1}) background at elevated (>450°C) temperatures.

Specific observations we have made include:

1- By cooling the Red PMT (~-17°C) background decreases at low (<380°C) temperatures and increases at high temperatures.

2- Signal increases due to PMT cooling.

3- S/N increases at temperatures lower than 400°C and decreases at higher temperatures (up to 0.03 @450°C).

4- A Corion FR-400S IR suppresser filter increases signal levels by comparison to the more commonly used Schott BG-39 (~100%), although the latter has better IR >700 nm rejection.

5- Of the various combinations of short cut and long cut filters tested via spectrophotometer, OG 590 and FR- 400 S provides the greatest red transmission while limiting the principle IR transmission to levels lower than c. 740 nm.

6- RTL measurements demonstrated that the combination of 2-63(3mm) + BG- 39 (2mm) posses the best S/N at 300-430°C (7.93) and the combination of OG-590 and FR- 400 S provide the best S/N at (200-300) °C (~30).

7- Filter orientation or ordering of the filters is not significant.

So, for measuring RTL of old or sensitive samples the combination of BG-39+2-63 is ideal. For RTL measurements on young or insensitive samples or studies, which are exploring the dating potential of the bleachable RTL, peak (Scholefield et al., 1999 in press; Fattahi and Stokes, 2000) a combination of OG 590 and FR- 400 S would appear more suitable.

We have adjusted our system within the structural limitations of the RISO reader to optimise the detection of RTL emission. While this represents a significant development on apparatus previously used to detect RTL we would welcome any additional comments or advice, which practitioners may have. On the basis of our spectral observations on the HA-3 filter we would further suggest that it performs a limited function in TL (and OSL) applications. To minimise black body emission for either bialkaline or extended red tubes such as the S-20 there would appear to be little merit in using this filter in preference to a BG-39 or similar filter (e.g., Schott BG-38).

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References

Bøtter-Jensen L. (1997) Luminescence technique: Instrumentation and methods. *Radiation Measurements* 27, 749-768.

Fattahi M. and Stokes S. (2000) Extending the time range of luminescence dating using red TL (RTL) from volcanic quartz. *Radiation Measurements* 32, 479-485.

Hashimoto T., Yokosaka K. and Habuki H. (1987) Emission properties of thermoluminescence from natural quartz - blue and red TL response to absorbed dose. *Nuclear Tracks and Radiation Measurements* 13, 57-66.

Hashimoto T., Sakai T., Shirai N., Sakaue S. and Kojima M. (1991) Thermoluminesence spectrum changes of natural quartzes dependent on annealing treatment and aluminium-contents. *Analyt. Sci.* 7, 687-690.

Hashimoto T., Yokosaka K., Notoya S., Ojima T. and Sakaue S. (1993) Dependence of red thermoluminescence on Eu-anomaly in natural quartzes. *Nuclear Tracks and Radiation Measurements* 21, 209-215.

Hashimoto T., Sakaue S., Aoki H. and Ichino M. (1994) Dependence of TL-property changes of natural quartzes on aluminium contents accompanied by thermal annealing treatment. *Radiation Measurements* 23, 293-299.

Hashimoto T., Sakaue S., Notoya S., Arimua. and Konishi M. (1996) Changes in Luminescence color images from quartz slices with thermal annealing treatments. *Radiation Measurements* 26, 233-242.

Liritzis I., Michael C. and Galloway R.B. (1996) A significant Aegean volcanic eruption during the second millenium B.C. revealed by thermoluminescence dating. *Geoarchaeology* 11, 361-371.

Miallier D., Faïn J., Montret M., Pilleyre T., Sanzelle S. and Soumana S. (1991) Properties of the red TL peak of quartz relevant to thermoluminescence dating. *Nuclear Tracks and Radiation Measurements* 18, 89-94.

Miallier D., Faïn J., Sanzelle S., Pilleyre T., Montret M., Soumana S. and Falguères C. (1994) Attempts at dating pumice deposits around 580 ka by use of red TL and ESR of xenolithic quartz inclusions. *Radiation Measurements* 23, 399-404.

Miallier D., Sanzelle S., Falguères C., Faïn J., Montret M., Pilleyre T., Soumana S., Laurent M., Camus G. and De Goër de Hervé A. (1994) Intercomparisons of red TL and ESR signals from heated quartz grains. *Radiation Measurements* 23, 143-154.

Miallier D., Faïn J., Montret M., Pilleyre T., Sanzelle S. and Soumana S. (1994) Sun bleaching of the red TL of quartz: preliminary observations. *Ancient TL*, 12 No1.

Montret M., Miallier D., Sanzelle S., Faïn J., Pilleyre T. and Soumana S.TL (1992) Dating in the Holocene using red TL from quartz. *Ancient TL*, 10.

Pilleyre TH., Montret M., Faïn J., and Sanzelle S. (1992) Attempts at dating ancient volcanoes using the red TL of quartz. *Quat. Sci. Rev.* 11, 13-17.

Rendell H.M., Townsend P.D., Wood R.A. and Luff B.J. (1994) Thermal treatments and emission spectra of TL from quartz. *Radiation Measurements* 23, 441-449.

Scholefield R.B.and Prescott J.R. (1999) The red thermoluminescence of quartz: 3–D spectral measurements. *Radiation Measurements* 30, 83-95

Reviewer

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Comments

Systematic research on the RTL of quartz seems to be fully justified because this signal has already proved to have remarkably reproducible features whatever the geographical origin of the quartz. Since it seems that difficulties of measuring this signal hinders generalisation of its use, the technical data given by Fattahi and Stokes are very welcome.