Can temperature assisted hydrostatic pressure reset the ambient TL of rocks? – A note on the TL of partially heated country rock from volcanic eruptions

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Abstract
In the West Eifel Vocanic field of Germany, extensive fine grained tephra beds exist. These are derived from fragmentation of Lower Devonian siltstone. Analysis of fine grain TL and the IRSL of fine-grained tephra beds from independently dated tephra layers of 11 ka and ca. 20 ka suggested that their geological luminescence was reduced to near zero residual value during the eruption. This was despite the absence of any field evidence of heating above 400°C .

We examined possible resetting mechanisms and suggest that thermally assisted hydrostatic pressure can reset the latent geological TL of country rock fragments during phreato-magmatic maar eruptions. We also provide first evidence of the suitability for TL dating of such material. As anomalous fading experiments have not been completed so far, we cannot give definitive TL ages here, but as the apparent ages are underestimated as compared to the control ages, complete zeroing is inferred. However a fortuitous combination of incomplete resetting and anomalous fading, that yields the expected D_e, though unlikely in view of long D_e plateaus arguing for complete resetting, cannot be entirely ruled out.

Introduction
Thermoluminescence (TL) dating has often been tested for volcanic minerals (e.g. Fattahi and Stokes, 2003) but may face the problems of anomalous fading of luminescence of volcanic feldspars (Wintle, 1973) or of low TL sensitivity of other volcanic minerals, with the exception of quartz. Quartz does not occur in mafic volcanic rocks except in situations when xenoliths derived from older country rock in the direct vicinity of the vent are also present. We examined the TL of fine-grained silicoclastic country rock occurring in maar tephra beds to understand if, besides heating, other processes can reset the parent "geological" TL signal of such minerals.

Hydroclastic maar eruptions occurred in the entire Eifel Volcanic Field (Schmincke, 2000). In the West Eifel Volcanic Field maar tephra has >90% of country rock clasts (mainly Lower Devonian slates, siltstones and quartzites or quartzitic sandstones) and their TL is expected to be in saturation or in thermal equilibrium with corresponding palaeodoses in the range 2000 to 3000 Gy (Wagner, 1998, Fig. 79). Maar lakes are excellent archives of past climates (Negendank and Zolitschka 1993; Zolitschka et al., 2000; Sirocko et al., 2005) and this makes reliable dating of maar eruptions key for major advances in regional palaeoclimatology.

In the Eifel Volcanic Field, the youngest, well dated maar eruption is the Ulmen Maar dated to 11,000 varve years (before 1950 AD, Zolitschka 2000). Proximal Pulvermaar eruption has not yet been radiometrically dated, however the presence of a post-eruptive ice-wedge cast in the tephra suggests its antiquity to be at least the last glacial maximum (LGM; 21.5 ka calendar years; Büchel et al., 2000). Fine-grains (4-11 µm) extracted from cm to dm thick silty - sandy tephra beds in the exposed ramparts of these two maar lakes had a natural TL intensity (blue, 420±60 nm) that was far below saturation of the dose response function (Figs. 1-3). For such a deposit, optical bleaching during eruption can not be the resetting mechanism as big blocks of country rock embedded in tephra suggested a deposition by base surges (Lorenz and Zimanowski, 2000). Thermal resetting during the fragmentation phase just prior to the eruption cannot be ruled out but, the field evidence does not carry any signatures of heating above 400°C. We therefore examined another possible resetting mechanism through hydrostatic pressure, following earlier mechanoluminescence studies by Banerjee et al. (1999; see also Singhvi et al., 1994 and Porat et al., 2007).

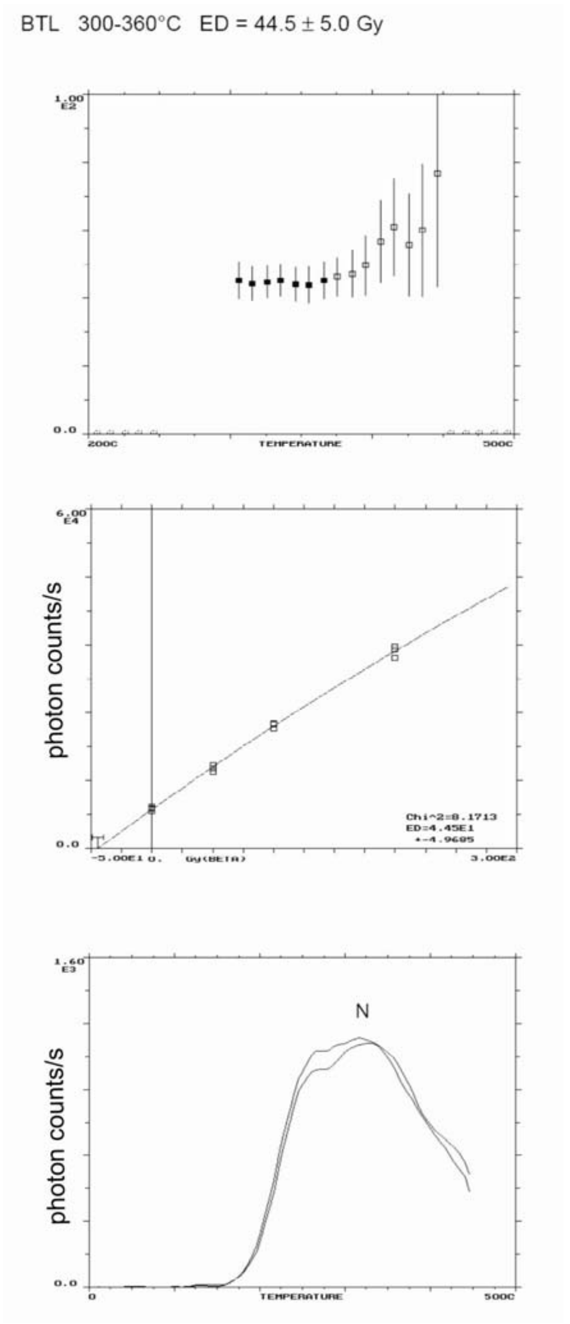

Figure 1: *D_e plateau test (top), TL growth curve 300-360°C (middle, saturating exponential fit, not corrected for anomalous fading) and two NTL glow-curves of #1 Ulmener Maar (bottom).*

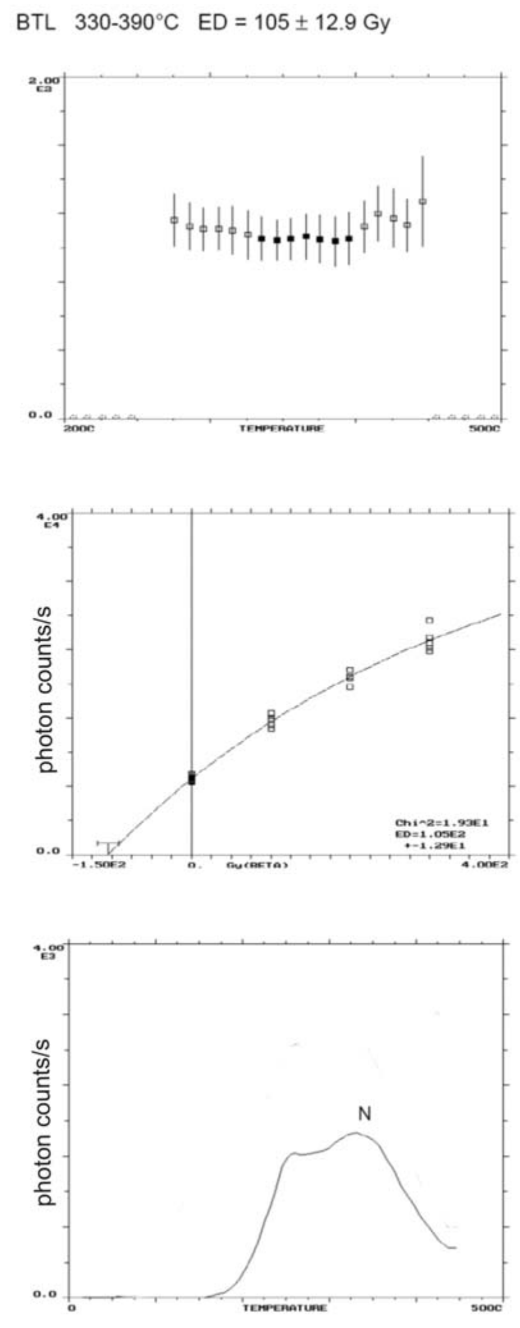

Figure 2: *D_e plateau test (top), TL growth curve 300-360°C (middle, saturating exponential fit, not corrected for anomalous fading) and NTL glow-curve of #2 Pulvermaar, bottom.*

Figure 3: *Road cut in the village of Ulmen, dark fine-grained maar tephra bed (hammer, sample 1) in the basal part of the rampart of the Ulmener Maar, topped by a diaclastic base-surge layer. Sample #1 was extracted at the tip of the hammer.*

Figure 4: *Exposure of tephra in the rampart of Pulvermaar. In the upper part, a 5-10 cm thick, light, fine-grained and more consolidated bed (A) sticks a bit out of the wall. This bed was sampled for TL and IRSL analysis (sample #2). In the lower part antidunes (B) and "swimming blocks" witness the deposition by base surges. The height of the exposure is 10 to 11 m.*

Samples

Samples were taken from the ramparts of two maar lakes in the West Eifel Volcanic Field, Germany, in the village of Ulmen (Ulmen Maar, Fig. 3), near the village of Gillenfeld (Pulvermaar, Fig. 4), and in the southern part of the city of Bonn in the Middle Rhine Valley (for details see below).

Two kinds of samples were collected, weakly consolidated fine-grained maar tephra-bed at Ulmen Maar, #1, (road cut in the village of Ulmen, 50°12' 38.10''N, 06°58'48.10''E, Fig. 3), and Pulvermaar, #2,(exposure 50°07'49.40''N, 06°55'05.40''E, Fig. 4), and a piece from Lower Devonian slate (sample #5) originating from the same epoch (Upper Siegenium) as country rock outcropping at Lake Pulvermaar. This was to test for zeroing experiments as the locality at the northern end of the Middle Rhine Valley at Bonn-Friesdorf is far away from any thermal overprint by volcanic activity during the Quaternary.

Experimental

Sample Preparation

The samples were processed under subdued red light (diodes, 620 nm) after removal of a minimum 2 mm outer rim using a knife or a handsaw. Sample #5 was carefully crushed in a bench vice and with an agate mortar and sieved (no natural TL below 200°C glow temperature indicative of triboluminescence was seen). Fine-grain samples were prepared using standard procedures (Zimmerman, 1971). From sample #2, the fraction 125-250µm was also extracted by wet sieving. Table 1 summarizes the experimental protocols for each sample. The fine-grain extracts from the Devonian slate (Bonn-Friesdorf, #5) were loaded in a silver tube of 3 mm diameter and 9 mm height and closed by a silver lid for subjecting it to high pressures.

High pressure and grinding experiments

The fine grains from sample #5 loaded in a silver tube were subjected to a static pressure of 1 GPa (10 kbar) for 19 h using the piston cylinder facilities of Bayerisches Geoinstitut (BGI) at Bayreuth. This static pressure corresponds to pressure conditions at the continental crust/mantle boundary. Two different runs of the experiment were conducted as follows:

Room temperature

a) natural sample held at 1 GPa for 19 h at room temperature;

b) natural sub-sample as received (without pressure).

Elevated temperature

a) natural sample held at 150°C for 19 h under 1 GPa pressure, and

b) natural sample held at 150°C for 19 h without pressure.

Furthermore, a sub-sample of rock sample #5 was homogenously spread between two steel plates. Strong hammer blows with a lump hammer (ca. 1 kg) were then administered to the upper plate for 3 minutes. Subsequently, the rock fractions were vigorously ground using an agate mortar for 15

Sample	Locality	Material	Expected age	Method	IRSL	Preheat
1	Ulmener Maar	fine-grain maar tephra, dark grey	11 ka	PM FG BTL ADD	max. ca. 72 cts/s	stage / cont. 220°C, 120 sec
2	Pulvermaar	fine-grain maar tephra, grey	18-24 ka	PM FG BTL ADD	max. ca. 75 cts/s	stage / cont. 220 °C, 120 sec
2	As above	As above	As above	PM 125-250um BTL ADD		stage / cont. 220 °C, 120 sec
5	Devonian Friesdorf	siltstone, Lower Devonian	400 Ma	PM FG BTL	max. ca. 650 cts/s	-

PM = polymineralic, FG = fine grains 4-11 µm, BTL = blue TL, ADD = additive dose (MAAD)

Table 1: *Description of samples and experimental details. For all samples a heating rate of 5°C/s was used, with measurements up to a maximum of 450°C. A filter combination of two BG-3 filters, a GG-400 and a BG-39 was used.*

minutes to see the effects of dynamic pressure in reducing the latent TL signal.

Luminescence and dosimetry measurements and data processing
TL and IRSL measurements were made using a Daybreak 1150 TL/IRSL reader equipped with infra-red diodes (870±30 nm), an EMI 9586Q photomultiplier (PM) coupled to a combination of detections filters (bottom to top: BG-3, GG-400, BG-3, BG-39, "blue combination" in Table 1). TL readout was at a heating rate of 5°C/s, to a maximum temperature of 450°C. The IRSL of sample #2 was recorded at room temperature.

For TL, preheat was done by holding the temperature at 220°C for 2 min followed by ramp heating to 450°C at 5°C/s. Laboratory irradiations were performed using a ^{90}Sr/^{90}Y beta source delivering ca. 0.17 Gy/s. Figs. 1-2, 5-6 provide the dose response curves using the MAAD protocol (Wintle, 1998). Owing to low IRSL sensitivity, no normalization beyond weight normalization (2 mg per disc) of aliquots was applied. Five aliquots per dose were measured. Tests for short term anomalous fading (7 days at 70°C, see Zöller, 1995) were carried out later to check for the occurrence of anomalous fading, but are not considered here as longer lasting fading tests at room temperature (required for correct estimation of burial dose) have not been executed so far. Estimation of the notional equivalent dose D_e (fading-uncorrected) required identification of the plateau range, (i.e. the glow curve temperature range exhibiting identical D_e within a given experimental variability of ca. 5%). As the growth curves were non-linear we used the D_e plateau test only.

Although definite TL ages were not the aim of this study, a check for significant age overestimates owing to incomplete TL resetting required dose rate calculations. Effective internal α- and ß-dose-rates for the samples were calculated using thick source alpha-counting of fine-ground bulk samples (Aitken, 1985; Zöller and Pernicka, 1989) for U and Th decay chains, and by ICP-MS and AAS measurements for K. Dose conversion factors of Adamiec and Aitken (1998) were applied. The γ dose-rate was calculated from U, Th and K concentrations of the maar tephras assuming homogenous 4π geometry. The cosmic dose rate was estimated with respect to sample depth below surface using Prescott and Hutton (1994). Present day interstitial water content was measured for samples #1 and #2 with due consciousness that this value may not be representative for the entire burial time. The a-value (alpha efficiency, see Aitken, 1985) was taken as 0.08±0.02 for polymineral fine-grain samples (representative value from Zöller, 1995). A secular equilibrium of U decay chains was assumed. In the absence of anomalous fading corrections, the notional ages of samples #1 and #2 do not provide the true eruption ages, but do provide an indication if these ages accord with the expected ages or, if these are overestimated resulting from incomplete zeroing. Underestimates of the apparent ages, of course, may result from anomalous fading, but this questions lies outside of the scope of the present study.

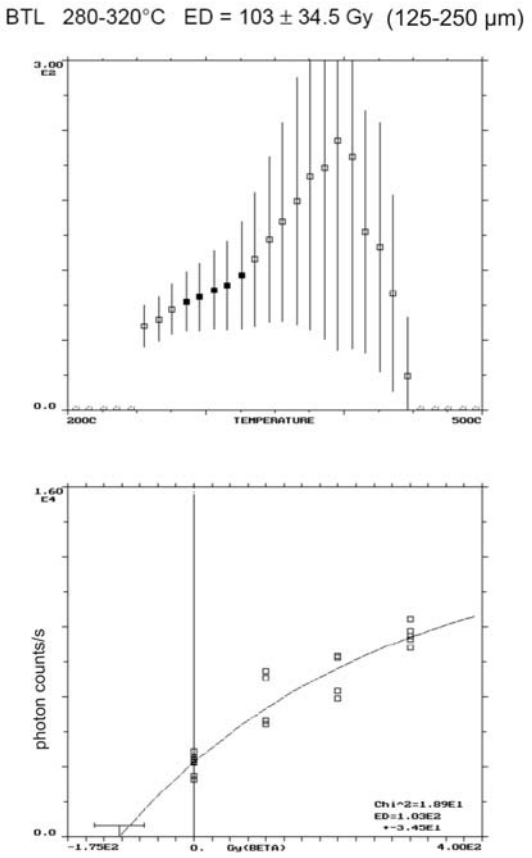

Figure 5: *D_e plateau test and TL growth curve of #2 Pulvermaar, 125-250 µm, 280-320°C (saturating exponential fit), not corrected for anomalous fading.*

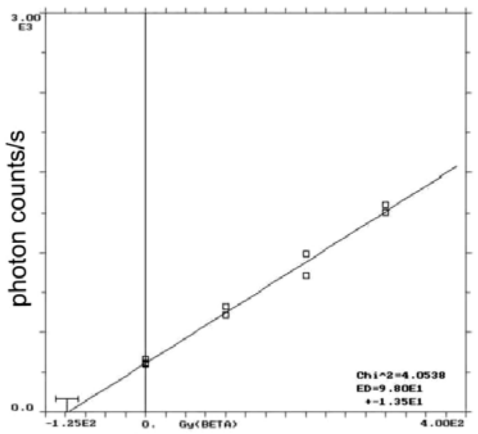

Figure 6: *IRSL MAAD #2 Pulvermaar, fine grains, linear fit, not corrected for anomalous fading. Within error bars, the D_e (98±13.5 Gy) is identical with the D_e from TL measurements (see Fig. 2)*

Results

Results of high hydrostatic pressure and grinding experiments

The aliquot to aliquot reproducibility of TL glow-curves from the first experiment (high pressure at room temperature) was ± ca. 25% compared to ± ca. 10% in the second experiment (high pressure at 150°C). However, loss of TL intensity after high pressure at room temperature (not shown) was not detected. The ratio of intensities was not significantly different from 1. The grinding experiment increased the natural TL via triboluminescence by ca. 7% rather than draining it.

High pressure at elevated temperature, however, resulted in a partial decay of the natural TL beyond thermal draining (Fig. 7). The TL signal loss affected the entire natural glow peaks and up to 36% of the signal was lost when compared to the natural TL after an identical thermal wash of 19 h at 150°C. This suggests that high hydrostatic pressure at elevated temperature is able to at least partially reset the latent TL and thermal assistance enhances the effect. Such conditions of moderately elevated temperature (ca. 150°C or more) and high pressure may exceptionally occur at shallow crustal depths typically <3 km in a maar explosion chamber during the fragmentation stage. For such a rock of Lower Devonian age, the geological dose is computed to be 2 MGy.

TL results from fine-grained maar tephra

Sample #1a (TL from Ulmener Maar tephra) yielded a long D_e plateau which was not expected a priori due to absence of any field evidence of heating that could erase the geological luminescence. The dose response was almost linear up to 30 Gy of additive dose (Fig. 1). This suggested a near complete resetting of TL (of fine grains) at eruption in the D_e plateau range (up to 360°C) as partial resetting would have implied finite initial dose and hence chances of nonlinear growth increases (as is evident from Fig. 2 and from TL growth curves of older maar tephra beds not mentioned here, onset of sublinearity can be seen from 200-300 Gy on). Supra linearity intercept (Aitken 1985) was not determined as its magnitude was expected to lie within the error bars of D_e.

The apparent TL age for Ulmener Maar was calculated to be 7.3 ± 1.0 ka (not corrected for observed short term fading of ca. 13% within 7 days at 70°C). The apparent TL age is significantly lower than the independent age (11 ka, Zolitschka et al., 2000), but as it is not higher than the expected age, a plausible inference of zeroing could be made. Age overestimation would be expected in the case of incomplete TL zeroing during eruption. As the apparent TL age of sample #1, calculated from the D_e

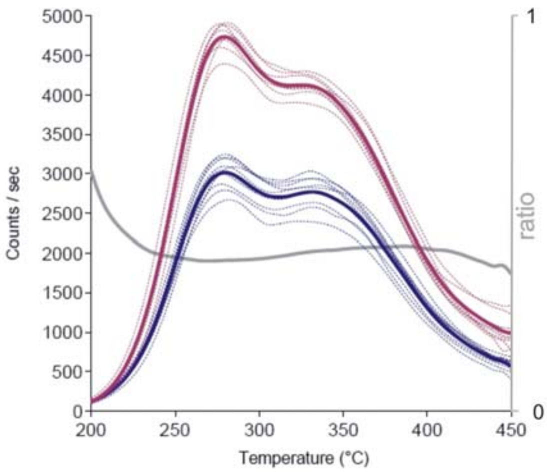

Figure 7: *TL glow-curves of sample 5 (Devonian siltstone). Upper curves (thick line: mean) NTL after 150°C preheat for 19 h only (T). Lower curves: (thick line: mean) NTL after 150°C preheat for 19 h and simultaneous 1 GPa pressure (P+T). Grey line: ratio of (P+T)/T.*

corrected for short term fading (8.4±1.1 ka) would still underestimate the known age (11 ka) significantly it is unlikely that a more rigorous fading correction would result in a significant age overestimate.

The dose response curve of #2 (fine grains) shows a sub-linear shape but also stays far below saturation. A fit to a saturating exponential curve yielded a D_e plateau extending over 80°C (Fig. 2). The D_e found by the IRSL MAAD protocol (Fig. 6) is identical within error bars, thus arguing for a total resetting of the IRSL at eruption as well. A good shine plateau (not shown here) was obtained.

The notional TL age of Pulvermaar (19.2 ± 2.7 ka, not corrected for short term fading of ca. 9% within 7 days at 70°C) lies within the LGM as expected (Lorenz and Zimanowski, 2000). Nevertheless, the true age is expected to be older due to observed anomalous fading. If corrected for short term fading the apparent age would be 21±3 ka which still lies within the LGM. But again, there is no evidence for TL age overestimation.

From Pulvermaar we also used the TL of the 125-250 µm fractions to check for possible grain size-dependant zeroing. This fraction consists of platy slate clasts. As shown in Fig. 5, a D_e-plateau is not obtained using extrapolation of the dose response curve to zero level. This suggests that TL-zeroing of this fraction during the fragmentation phase in the explosion chamber of the maar was not as complete as for the fine silt fraction (see Discussion).

These preliminary observations suggest that fine-grained maar tephra derived by hydroclastic fragmentation of country rock may be dated reliably by TL. Strategies to achieve this are discussed below. Coarser grains from maar tephra, however, may suffer from incomplete resetting at eruption and are easily subject to age-overestimation.

Discussion

The observed total or partial resetting of TL glow peaks in maar tephras derived from non-volcanic country rock may have several reasons: (a) thermal only zeroing (questionable, but in addition to hydroclastically frictioned rocks), (b) thermodynamic friction by dynamic pressure (frictional heating), and (c) hydrostatic high pressure at elevated temperatures.

High pressure experiments gave no evidence for resetting of the latent TL at room temperature; whereas high pressure at elevated temperature (150°C) partially drained the latent TL in addition to thermal bleaching. This thermally assisted resetting due to hydrostatic pressure is similar to the phonon-assisted bleaching of infra-red stimulated luminescence of feldspars (Hütt et al., 1988; Aitken, 1998). Our grinding-by-hand experiment was not able to reset the latent TL signal, but recently Takeuchi et al. (2006) reported successful resetting of the TL in milled quartz grains clearly showing a grain-size effect. The TL of smaller grains (<500 nm), corresponding to the surface disordered layer, was the more effectively reset. This coincides with our findings from the Pulvermaar tephra bed (sample 2: 4-11µm fraction totally reset; 125-250 µm fraction partially reset). Mere thermal resetting of the TL during or prior to maar eruption due to heat transfer from the rising magma into the adjacent non-volcanic rock is expected to affect all rock clasts. Our results, however, provide evidence for grain size dependent resetting in maar tephra, arguing for a resetting by thermally assisted hydrostatic pressure, or both, rather than merely thermal resetting by heat transfer.

Although one of the motivations to use non-volcanic minerals for dating volcanic events was to circumvent the anomalous fading often observed from volcanic feldspars, anomalous fading still is a major problem. Corrections for anomalous fading as suggested by Auclair et al. (2003) and Lamothe et al. (2003) are needed. An alternative strategy may be TL from pure fine-grained quartz extracts, in particular if the orange-red emissions (much higher saturation dose) are used despite their lower detection efficiency.

Conclusions and Outlook

High hydrostatic pressure and elevated temperatures (but too low for total annealing of the geological TL) may occur at low crustal depths (<2 km) in the root zone of hydroclastic maar eruptions during the fragmentation phase just prior to the opening of the maar eruption vent. In addition to frictional heating (Takeuchi et al., 2006) and to heat transfer from the rising magma to neighbouring country rock, we propose another reasonable mechanism for at least partial resetting of the geological TL (and IRSL), which may be termed phonon-assisted mechano-luminescence. Further high pressure experiments with varying pressure and temperature will be useful to better understand the preconditions and efficiency of this resetting mechanism.

Circumventing or correcting for anomalous fading may still be a limiting factor for reliable TL dating of volcanic feldspars (and other volcanic minerals). Fine-grained quartz extracts from fine-grained maar tephra beds are expected to overcome the fading problem (e.g. Richter and Krbetschek, 2006), the applicability of the resetting mechanism as discussed here for polymineralic fine grains, however, remains to be tested for pure quartz separates.

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