

Direct and indirect luminescence dating of tephra: A review

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Received 11 March 2019; Revised 18 October 2019; Accepted 18 October 2019

ABSTRACT: In Quaternary studies, tephra are widely used as marker horizons to correlate geological deposits. Therefore, accurate and precise dating is crucial. Among radiometric dating techniques, luminescence dating has the potential to date tephra directly using glass shards, volcanic minerals that formed during the eruption or mineral fragments that originate from the shattered country rock. Moreover, sediments that frame the tephra can be dated to attain an indirect age bracket. A review of numerous luminescence dating studies highlights the method's potential and challenges. While reliable direct dating of volcanic quartz and feldspar as a component in tephra is still methodically difficult mainly due to thermal and athermal signal instability, red thermoluminescence of volcanic quartz and the far-red emission of volcanic feldspar have been used successfully. Furthermore, the dating of xenolithic quartz within tephra shows great potential. Numerous studies date tephra successfully indirectly. Dating surrounding sediments is generally straightforward as long as samples are not taken too close to the tephra horizons. Here, issues arise from the occurrence of glass shards within the sediments or unreliable determination of dose rates. This includes relocation of radioelements, mixing of tephra into the sediment and disregarding different dose rates of adjacent material.

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KEYWORDS: loess; Quaternary; red thermoluminescence; tephrochronology; volcanic glass.

Introduction

Tephra (Greek for 'ashes') are deposits of rock fragments and other particles ejected by volcanic eruptions. In Quaternary studies, tephra layers are widely used as isochrons, i.e. thin deposits with an effectively identical age, to correlate and date geological deposits (cf. Lowe, 2011). To synchronize records and transfer age data from one location to another, it is essential to identify the tephra securely, e.g. through geochemical fingerprinting, and to date it precisely. Several radiometric, age-equivalence, age-modelling and incremental dating techniques are available (see reviews by Lowe, 2011, and the example by Pillans *et al.*, 1996). Among these is luminescence dating, which determines the time since a mineral grain was last exposed to (sun)light or heat, or its crystallization (dated event; see e.g. Preusser *et al.*, 2008; Rhodes, 2011; Duller, 2015). The luminescence signal can be measured by thermal stimulation (referred to as thermoluminescence, TL) and optical stimulation (optically stimulated luminescence, OSL). The age is calculated by dividing the equivalent dose (D_e in Gy), i.e. the accumulated radiation dose since signal resetting (dated event), by the dose rate, i.e. the absorbed radiation dose per unit time (\dot{D} in Gy a⁻¹). Numerous measurement protocols are available using multiple or single subsamples (aliquots), as well as regenerative and additive approaches. As luminescence dating uses a wealth of acronyms for different measurement protocols or procedures, Table 1 summarizes full forms and the relevant literature. Advances in recent decades include the development of the single aliquot regenerative dose protocol (SAR; Murray and Wintle, 2000) for quartz minerals and the post-infrared infrared stimulated luminescence protocol (post-IR IRSL or pIRIR; Thomsen *et al.*, 2008) for feldspar minerals. For all measurement procedures it is important that any previously accumulated signal has been

reset through or shortly before the dated event (e.g. by exposure to sunlight during transport). Because tephra are the product of explosive eruptions, involving the cooling and ejection of melt but also explosive fragmentation of country rock and its exposure to heat, shock and/or light (which reset the signal), luminescence dating has the potential to date tephra directly. Moreover, sediments surrounding the tephra can be dated to obtain indirect age information. In this review we provide an overview of accomplishments and remaining challenges in dating tephra by luminescence techniques. We hereby focus on tephra as widespread time markers including airfall, pyroclastic flows and base surges, but excluding scoria cones.

Direct luminescence dating of tephra

Based on the main components of tephra, direct luminescence ages for this material can be obtained by individually targeting these constituents (Berger and Huntley, 1983):

1. volcanic-glass shards
2. volcanic quartz or feldspar which formed during or shortly after the eruption
3. quartz or feldspar fragments in the tephra originating from shattered country rock

All three approaches will be described in the following and examples are given on successful and unsuccessful dating attempts.

Volcanic glass

Because the glass shards contained in volcanic ash are formed through cooling of melted rock during the eruption, complete luminescence signal resetting during the event to be dated can be safely assumed (Berger and Huntley, 1983; Berger,

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Table 1. List of abbreviations.

Abbreviation	Full form	Exemplary reference(s)
BTL	Blue thermoluminescence	Ganzawa <i>et al.</i> (1997)
D_e	Equivalent dose	Aitken (1985)
FT	Fission track (dating)	Wagner and van den Haute (1992)
IR-PL	Infrared photoluminescence	Erfurt (2003); Prasad <i>et al.</i> (2017)
IR-RF	Infrared radiofluorescence	Trautmann <i>et al.</i> (1998, 1999); Erfurt and Krbetschek (2003); Frouin <i>et al.</i> (2017)
IRSL	Infrared stimulated luminescence	Hütt <i>et al.</i> (1988)
ITPFT	Isothermal plateau fission track	Sandhu <i>et al.</i> (1993)
MAAD	Multiple-aliquot additive-dose protocol	Aitken (1985, 1998)
MAR	Multiple-aliquot regenerative-dose protocol	Aitken (1985, 1998)
MET-pIRIR	Multiple-elevated-temperature pIRIR protocol	Li and Li (2011)
OSL	Optically stimulated luminescence	Huntley <i>et al.</i> (1985); Aitken (1998); Rhodes (2011); Duller (2015)
pIRIR (post-IR IRSL)	Post-infrared infrared stimulated luminescence protocol	Thomsen <i>et al.</i> (2008); Buylaert <i>et al.</i> (2009); Thiel <i>et al.</i> (2011)
PMT	Photomultiplier tube	
RTL	Red thermoluminescence	Fattahi and Stokes (2003); Yawata and Hashimoto (2004); Hashimoto <i>et al.</i> (2007); Ganzawa and Maeda (2009)
SAR	Single-aliquot regenerative-dose protocol	Murray and Wintle (2000)
TL	Thermoluminescence	Aitken (1985); Duller (2015); Preusser <i>et al.</i> (2008)

1985a, 1985b, 1991; Biswas *et al.*, 2013). The pioneering work by Berger and Huntley (1983) and Berger (1985a, 1991, 1992) on the TL properties of tephra showed that the most suitable target material for dating should be the glass fraction in the size range ~2–11 μm . According to the authors, the choice of this material was firstly based on the expectation that it is free from anomalous fading or at least less affected than, e.g., volcanic feldspar [although Berger (1991) states that ‘nothing is known of the physical nature of [the electron] traps in this glass’]. This assumption was inferred from the observation that the Mazama ash (British Columbia, Canada), consisting of almost 100% pure glass, did not lose TL signal over time. Anomalous fading was first described by Wintle (1973) for volcanic feldspar and is usually associated with loss of charge from their traps over time due to quantum-mechanical tunnelling despite the fact that kinetic analyses predict long-term stability of the measured luminescence signal (e.g. Visocekas, 1985, 1993; Spooner, 1994; Visocekas *et al.*, 1994). It should also be added that other (complementary) effects have been proposed to explain anomalous fading, such as localized transitions (Templer, 1986), electronic ‘hopping’ from trap to trap (Visocekas *et al.*, 2014; Guérin and Visocekas, 2015), defect diffusion (Wintle, 1977) or competition with radiationless transitions (Chen *et al.*, 2000). Secondly, the preferred size range of the glass particles is important because larger shards frequently contain microlites, crystallites and inclusions of foreign materials (e.g. volcanic feldspar). Beside the potential issue of anomalous fading, the presence of these ‘contaminants’ results in considerable heterogeneities in the radiation field, complicating the dose rate assessment for instance due to the internal dose rate from K-feldspar inclusions (Berger, 1991).

However, initial studies by Berger and Huntley (1983) and Berger (1985a) also revealed some methodological challenges associated with the use of TL for dating the glass fraction in tephra:

1. Most samples of supposed volcanic glass show anomalous fading, which is attributed to the presence of feldspar grains. Only one sample from the Mazama ash, consisting naturally of almost 100% glass, yielded a stable TL signal after laboratory irradiation over several weeks.
2. Glass shards are prone to hydration (attachment of water molecules), which induces ion mobility and may affect the TL properties, entailing potential dose underestimation.

3. Inaccuracies in dose rate determination such as disequilibrium in the ^{238}U decay chain due to ^{222}Rn loss or ^{226}Ra excess (the latter built up during the eruption), or the difficulty of estimating the water content over the dating period. Due to its comparatively high stopping power, water in sediment pores absorbs radiation and therefore influences the dose rate. In addition, the moisture content may determine the degree of hydration to be expected.

Some of these methodological difficulties were eliminated in later investigations by Berger (1987, 1991) and Berger and Davis (1992). Thus, for the studied tephra from North America anomalous fading can be prevented or reduced by storing the samples after artificial irradiation for 8 days at 50–75 °C before measuring the TL. In addition, an improved sample preparation protocol was used which reduces the remaining non-glass components in the sample.

In practical terms, the extraction of volcanic glass of ~2–11 μm from bulk tephra is best facilitated by heavy liquid centrifugation ($\rho \sim 2.45\text{--}2.50\text{ g cm}^{-3}$) after having removed carbonates, oxidized organic matter and reduced the desired grain size range. This procedure usually yields >95% glass shards in a sample (Berger, 1984, 1991).

Following these routines, a number of multiple-aliquot additive-dose (MAAD) TL ages of North American tephra were obtained which correspond well with independent age control (mainly radiocarbon and fission track dating). For example, the Mazama ash gave a TL age of $8.18 \pm 0.53\text{ ka}$, in good agreement with a radiocarbon age of $7.66 \pm 0.10\text{ ka cal BP}$ obtained on turbidites from the Cascadia deep-sea channel by Adams (1990) (Fig. 1 for an exemplary dose–response curve). Similarly, the TL age of the Rockland ash of $460 \pm 120\text{ ka}$ is in accordance with a fission track age of $400 \pm 50\text{ ka}$ (Berger, 1991). For the Halfway House tephra at Fairbanks (Alaska), Berger (1987) obtained a direct TL age of $110 \pm 12\text{ ka}$ for the 4–11 μm volcanic glass fraction, which was supported by a TL age of $108 \pm 16\text{ ka}$ from loess overlying this tephra. This tephra age is in agreement (at 2σ) with fission track ages of $140 \pm 10\text{ ka}$ (Westgate *et al.*, 1990) and of $124 \pm 10\text{ ka}$ (Preece *et al.*, 2011). From these data, the author infers that reliable dating of volcanic glass from both proximal and distal tephra in the age range from a few hundred years to 400 ka is generally possible. Consequently, Berger and Davis (1992) presented TL results in the range 67–200 ka for tephra beds from Summer

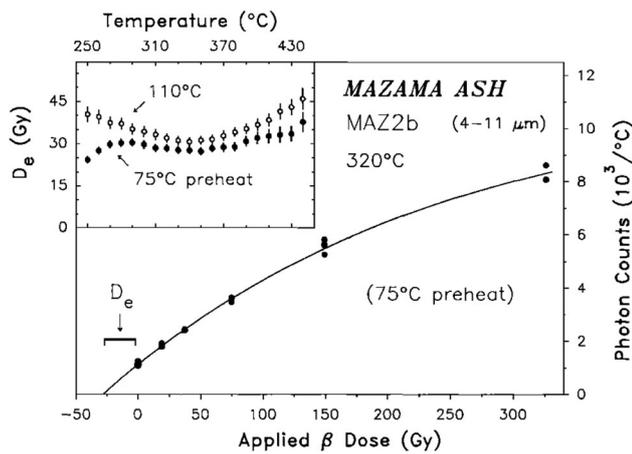


Figure 1. Multiple-aliquot additive-dose growth curve for volcanic glass extracted from the Mazama ash (taken from Berger, 1991). The temperature interval 310–320 °C from the glow curves was integrated to construct the dose–response curve. Dose points (at least three aliquots per dose) were fitted with a weighted saturating exponential. The inset shows the equivalent dose (D_e) calculated as a function of evaluated temperature interval for a preheat of 75 and 110 °C (for 4 days) [printed with permission from Wiley].

Lake (Oregon, USA) without previous age assignment. A TL age of 46 ± 5 ka for the glass fraction in tephra from Mount St. Helens sampled in Oregon, along with TL ages of bracketing loess, allowed Berger and Busacca (1995) to extend the formation period of this volcano back to at least 80 ka. A representative blue TL glow curve from this study is depicted in Fig. 2.

Despite these encouraging results, unsuitable TL behaviour of many other glass samples prevented their accurate dating. Major problems faced were the presence of anomalous fading even after elevated-temperature laboratory storage before TL measurement as well as poor fitting of the dose–response curve (plot of TL vs. added dose) by regression (Berger, 1990, 1991). In contrast to Berger (1985a), who attested to good TL sensitivity of most glass samples, Robertson *et al.* (1997)

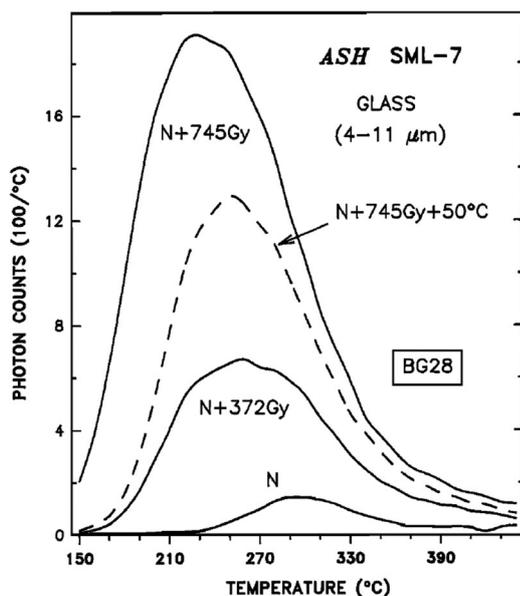


Figure 2. Representative smoothed blue TL glow curves for volcanic glass from the Mount St. Helens set Cy bed tephra (taken from Berger and Busacca, 1995). N denotes the natural TL, while additive doses as indicated in the plot are given on top of the natural dose in case of the other glow curves. The effect of preheating (50 °C for 8 days) is also shown [printed with permission from Wiley].

detected only weak TL insufficient for analyses of volcanic glass separated from tuff at Mount Gambier (South Australia).

Attempts by Berger and Huntley (1994) to date volcanic glass by OSL failed, except for the well-behaving Mazama ash. Two volcanic glass samples showed no or very low sensitivity to green (514 nm) and red (633 nm) stimulation, while the whole set of 15 samples yielded measurable but low response to IR (880 nm) stimulation. However, the obtained IRSL signal intensities did not correlate with the age of the samples. The fact that the highest luminescence output was obtained with IR stimulation led the authors to speculate on feldspar inclusions or crystallites in the glass fragments as the origin of the measured signal. Comparative spectrally resolved TL investigations of quartz, plagioclase and volcanic glass extracted from five Japanese tephras also indicate that the purification procedures applied by Kanemaki *et al.* (1991) did not result in 100% glass shards, but that the strong red TL (RTL) emission rather originates from 1- to 5- μm quartz microcrystals, as identified in electron scanning microscope images. In this study, a grain size range of 125–250 μm was used, but the dimension of the quartz microcrystals suggests that reducing the size range to ~2–11 μm as proposed by Berger (1985a) would not have resulted in pure glass TL signals either.

Huntley *et al.* (1988) tried to separate volcanic glass from feldspar by means of their characteristic TL emissions in a spectroscopic study with the ultimate aim of avoiding the need for mechanical separation of these mineral fractions. However, owing to low signal levels, no TL spectra of the four investigated samples (Mabton, Mazama, Salmon Springs and St. Helens Y ash, USA) could be recorded at realistic doses. Administering a 5-kGy dose resulted in TL spectra similar to those of feldspars with main emissions in the range 400–450 nm and 550–600 nm.

Juvenile volcanic minerals

Volcanic feldspar

Numerous attempts have been undertaken at directly dating volcanic quartz and feldspar and hence to obtain chronometric control for the volcanic activity during which these juvenile minerals were formed. In an early study, however, Wintle (1973) observed severe TL age underestimation of labradorite, andesine, bytownite and sanidines extracted from basalt (Iceland and France) and rhyolite (Italy), respectively, as compared to ages obtained by other chronometric methods. This age discrepancy by up to one order of magnitude was attributed to anomalous fading (see above), which according to later studies appears to affect both the TL as well as the OSL and IRSL signals in the UV to red part of the spectrum from many types of feldspars (e.g. Spooner, 1994; Visocekas and Zink, 1995; Huntley and Lamothe, 2001). The presence and extent of anomalous fading has been correlated with the level of lattice disorder in feldspar: while low-temperature varieties of feldspars with a highly ordered crystal lattice (e.g. microcline) were reported to be free from anomalous fading (Spooner, 1992, 1994), volcanic feldspars such as sanidines belong to the high-temperature, disordered group that formed by rapid cooling and show the highest fading rates (Aitken, 1985; Spooner, 1992, 1994; Visocekas *et al.*, 1994; Visocekas and Zink, 1995). For example, TL fading rates of up to 30% per decade were determined for volcanic orthoclase and plagioclase (Guérin and Visocekas, 2015), whereas plutonic low-temperature feldspars as predominantly found in sedimentary deposits are characterized by IRSL fading rates <8% per decade (Huntley and Lamothe, 2001). Despite proposed correction routines for this effect (e.g., Huntley and Lamothe,

2001; Auclair *et al.*, 2003; Kars *et al.*, 2008), such high rates of anomalous fading in volcanic feldspars seem to generally preclude their accurate TL dating.

The only luminescence emission from volcanic feldspar less affected or even unaffected by anomalous fading is the far-red (~710 nm) emission during thermal stimulation. Zink and Visocekas (1997) obtained preliminary TL age estimates between ~9 and 11 ka for sanidine and oligoclase from two sites in the Chaîne des Puys, France, using this emission. These results agree with those from independent methods (K/Ar, U/Th, ^{14}C). Similarly, Visocekas and Guérin (2006) determined reasonable natural doses of plagioclases from two known-age eruption sites in the Chaîne des Puys using this TL signal. Notwithstanding these promising findings, the routine use of this far-red emission is hampered by low natural TL signal levels (even in signal saturation), which are hard to discriminate from the intense blackbody radiation at elevated temperatures (> 280 °C) in this spectral range (Visocekas *et al.*, 2014).

Using OSL and IRSL, Tsukamoto *et al.* (2010) investigated plagioclase in different grain size fractions extracted from an andesitic marker tephra (Hakone-Tokyo pumice) in central Japan, for which previous ^{14}C and K/Ar ages are available, placing the corresponding eruption between ~50 and 70 ka. Element composition analyses revealed that labradorite was relatively enriched in the larger sand-sized fractions, while rapidly crystallized bytownite dominated the smaller size fractions. General grain size-dependent differences in luminescence intensity and fading rates were therefore attributed to the crystallization history of the larger labradorite and the smaller bytownite grains. Since the OSL signal of all fractions proved unsuitable for accurate dose determination (due to intense thermal transfer), the IRSL signal of a smaller size fraction (150–212 μm) was used for age calculation, giving an age of 67.5 ± 4.3 ka after fading correction.

Recently, Biswas *et al.* (2015) produced pIRIR ages for sand-sized plagioclase extracts from three known-age Japanese marker tephra (Ikeda-ko: 6.4 ka; Aira-Tn: 30 ka; Aira-Iwato: 45–50 ka) using the violet–blue emission. Both multiple- and single-aliquot protocols in combination with a stimulation temperature of 300 °C result in age estimates consistent in most cases with independent chronologies, while the authors are in favour of single-aliquot figures due to their smaller uncertainty because of better signal-to-noise ratio and higher inter-aliquot reproducibility (Ikeda-ko: 7.8 ± 0.7 ka; Aira-Tn: 33 ± 4 ka; Aira-Iwato: 54 ± 6 ka). A similar methodology was applied by Biswas *et al.* (2013) to polymineral silt-sized extracts from rhyolitic volcanic ashes sampled at five different locations in India. Geochemical analyses suggest that all of these ashes can be associated with the Youngest Toba Tuff (YTT) constrained to ~74 ka (e.g. Chesner *et al.*, 1991; Westgate *et al.*, 1998). The pIRIR protocol at 300 °C stimulation temperature yielded fading-corrected average ages for three of the five samples of 81 ± 15 , 82 ± 13 and 71 ± 6 ka, in agreement with expectations. Laboratory tests indicated fading rates of the used signal between 0 and 1.6% per decade. Age inversions of two individual samples from the top and bottom of the ash layer at two sites are explained by the authors by vertical migration of radioelements. Furthermore, significantly underestimated pIRIR ages at two locations (<24 and <37 ka) were ascribed to post-depositional re-mobilization and hence bleaching of the YTT. Based on their methodological studies, Biswas *et al.* (2013) conclude that the pIRIR approach is a promising tool for accurate dating of volcanic ash in the age range ~1–150 ka. Other luminescence routines (multiple-aliquot TL in the violet–blue detection range, isothermal TL in the red detection range and IRSL) substantially underestimated the expected age.

Volcanic quartz

TL spectra of volcanic quartz are – in contrast to that of most plutonic or metamorphic types of quartz – mostly dominated by the red emission centred at ~620–630 nm (e.g. Hashimoto *et al.*, 1986a, 1986b, 1987, 2007; Rink *et al.*, 1993; Rendell *et al.*, 1994; Scholefield and Prescott, 1999; Nakagawa and Hashimoto, 2003; Ganzawa *et al.*, 2005; Hong *et al.*, 2008; see Fig. 3). Non-bridging oxygen-hole centres or peroxy radicals have been proposed to be responsible for RTL in quartz (Hashimoto *et al.*, 2007), but a certain correlation between a specific defect and this emission could not yet be established. In previous studies, the RTL signal of (volcanic) quartz showed distinguished features such as minor sensitivity changes in the course of repeated heating and irradiation (Yawata and Hashimoto, 2004; Ganzawa *et al.*, 2005; Ganzawa, 2010; Zöller *et al.*, 2014; Richter *et al.*, 2017), high dose saturation levels (>1.5 kGy; Pilleyre *et al.*, 1992; Fattahi and Stokes, 2000a; Hong *et al.*, 2008; Ganzawa and Maeda, 2009) and the existence of a signal component with sufficient thermal stability for dating on Quaternary timescales (Fattahi and Stokes, 2000a; Ganzawa *et al.*, 2005). More comprehensive reviews on RTL properties of quartz are given by Miallier *et al.* (1991), Fattahi and Stokes (2003), Stokes and Fattahi (2003) and Hashimoto (2008).

Technically, the measurement of RTL signals is complicated by interference with blackbody radiation above temperatures of ~300 °C. Although ‘conventional’ TL measurement equipment including a photomultiplier tube (PMT) designed to record the UV–visible range is principally suited for registering RTL (Miallier *et al.*, 1991; Krbeitschek *et al.*, 1997; Richter and Krbeitschek, 2006), the use of a cooled (~253 K) red-enhanced PMT in combination with appropriate optical filters offers better signal-to-noise ratios for RTL signals up to glow curve temperatures of ~400 °C (Fattahi and Stokes, 2000b; Richter *et al.*, 2015). Problems of instrumental background reproducibility in conventional TL measurements can be largely overcome by recording isothermal RTL in the range 370–410 °C (Toyoda *et al.*, 2006; Tsukamoto *et al.*, 2007; Ganzawa and Maeda, 2009). Additional modification of their experimental setup including a light-guide between sample and PMT and silver sample carriers with biotite shielding suppressed the recorded blackbody radiation further and enabled Yawata and Hashimoto (2007), Ganzawa and Maeda (2009) and Ganzawa and Ike (2011) to measure RTL signals of single grains of volcanic quartz with a minimum detectable dose of a few grays. Finally, good reproducibility of RTL glow curves in combination with these technical advances fosters the application of SAR routines down to a single grain level with the basic advantage of low amounts of required sample material (Fattahi and Stokes, 2000a; Ganzawa *et al.*, 2005;

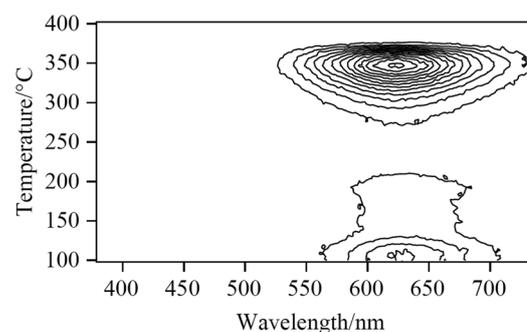


Figure 3. TL emission spectrum from unannealed volcanic quartz. The sample is called Medeshima and originates from the Miyagi Prefecture in Japan (taken from Nakagawa and Hashimoto, 2003) [printed with permission from Elsevier].

Hong *et al.*, 2008). As a consequence of its unique luminescence properties, the RTL emission of volcanic quartz has frequently been used to date tephra during the last three decades.

Miallier *et al.* (1994a) applied an MAAD RTL protocol to sand-sized quartz grains from pumice deposits at Neschers (Massif Central, France), which were previously $^{40}\text{Ar}/^{39}\text{Ar}$ dated to 580 ± 20 ka (single-grain laser technique on sanidine phenocrysts). The slide technique (Sanzelle *et al.*, 1996) for natural dose evaluation yielded 3.25 ± 0.08 kGy and a corresponding RTL age of the pumice of 544 ± 42 ka, which is consistent with the $^{40}\text{Ar}/^{39}\text{Ar}$ age. Demonstrating the potential to extend the age range even further using the RTL method, Fattahi and Stokes (2000a) were able to calculate RTL ages of quartz contained in two ignimbrite formations from New Zealand of 279 ± 17 and 1280 ± 165 ka using the SAR protocol. These ages compare well with independently derived estimates of 330 ± 10 ka ($^{40}\text{Ar}/^{39}\text{Ar}$ dating) and 1.21 Ma (fission track dating), respectively. The presented results principally open up the possibility of dating volcanic activity over the entire Quaternary by means of RTL.

For pyroclastic flows from the Toya Caldera (Japan), Ganzawa *et al.* (2005) produced average RTL ages of 97 ± 13 ka for six single grains of volcanic quartz and of 94 ± 13 ka for eight multi-grain aliquots (see RTL glow curves in Fig. 4). These ages do not differ from an RTL MAAD age of 91 ± 12 ka obtained by the same authors. Furthermore, all RTL age estimates, which put the Toya eruption in marine isotope stage 5c, are supported by previous dating efforts by stratigraphic correlation, TL and pollen analyses, indicating an age of the Toya eruption younger than stage 5e. In a follow-up study, Ganzawa and Ike (2011) applied a similar methodology to four samples from Toya pyroclastic flows, which are in parts identical with previously analysed ones. The authors explain slightly older single-grain ages of 104 ± 15 to 118 ± 15 ka with sensitivity corrections applied in this study (but not in the previous one), and other minor differences in measurement routines. As a further outcome of this study, the RTL glow curve shape of the high-temperature peak could be used along with the scatter of determined D_e values as a diagnostic criterion to trace the origin of individual quartz grains from either the targeted Toya magma or from different source rocks of various ages. Finally, the same pyroclastic material was dated by Ganzawa and Maeda (2009) by means of single-grain isothermal RTL of volcanic quartz measured at

390 and 410 °C, giving average ages of 108 ± 10 and 112 ± 12 ka, respectively, for seven grains each (Figs 5 and 6).

Isothermal RTL was applied by Tsukamoto *et al.* (2007) to date volcanic quartz phenocrysts from three Japanese known-age tephra in the age range 30–400 ka. The SAR protocol yielded RTL ages consistent with previous chronometric control, and the additional measurement of the ‘conventional’ RTL signal of one of the samples resulted in indistinguishable ages. In an extension of that dataset, including an additional four Japanese tephra dated by independent methods to between 40 and 400 ka, Toyoda *et al.* (2006) obtained good agreement of isothermal RTL ages with the pre-assigned ages. In view of these results, Tsukamoto *et al.* (2007) conclude that ‘[isothermal RTL] dating of tephras using quartz is a very powerful tool for the age range beyond ^{14}C dating’.

Quartz extracted from andesitic or dacitic lava and pyroclasts was used by Hasebe *et al.* (2016) for chronologically constraining the eruptive phases of the Hakusan volcano in central Japan. Technically, they applied the coarse grain (125–355 μm) inclusion technique according to Fleming (1970) in combination with a TL SAR protocol. D_e values for 2–4 aliquots per sample were obtained by evaluating the 320 °C RTL peak. For part of the TL-dated stratigraphic units, previous K–Ar ages (Shimizu *et al.*, 1988) are available, which are in mutual agreement with the new TL ages as well as additional fission-track ages obtained by Hasebe *et al.* (2016). The TL ages were thus deemed reliable. Including the TL ages of previously undated pyroclastic rocks, the TL age groups of ~100, 35–60 and <10 ka summarized by Hasebe *et al.* (2016) call for a chronostratigraphic revision of the Hakusan volcanic deposits, whereas the youngest ages are maximum estimates due to low TL signal levels.

Studies in which luminescence signals other than the RTL emission were applied to volcanic quartz are rather rare. For instance, Takamiya and Nishimura (1986) extracted sand-sized quartz crystals from volcanoclastic materials for TL dating using the quartz inclusion method. The materials under study include pyroclastic flow and base surge deposits, pumice as well as volcanic ash from Japan. However, it is unclear whether juvenile volcanic quartz was dated or rather xenolithic quartz grains originating from the country rock. Employing the MAAD technique (including supralinearity correction), they arrive at TL ages ranging from 15 to 150 ka, all of them – except one from a base surge deposit – being in agreement (at 1σ) with independent age estimates obtained by ^{14}C and fission track methods as well as stratigraphic

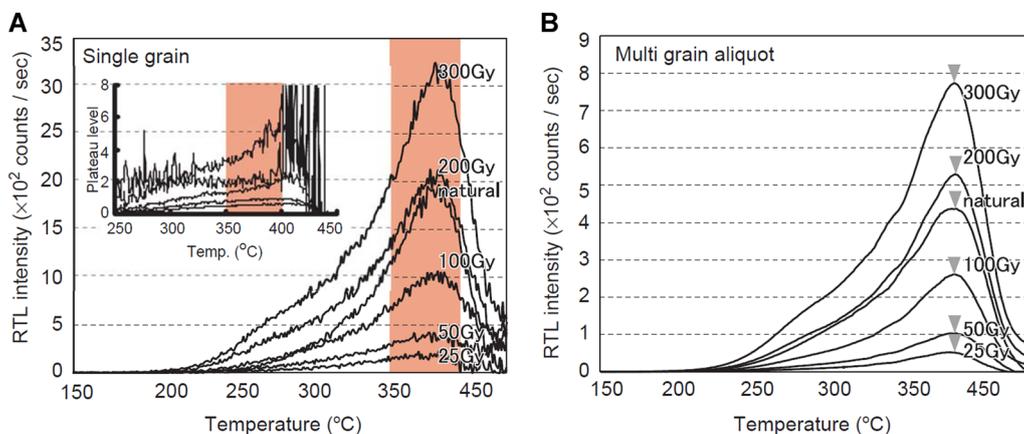


Figure 4. RTL glow curves obtained during regenerative dose method for a single grain (A) and a multigrain aliquot (B) composed of about 80 grains (taken from Ganzawa *et al.*, 2005). The heating rate was $1\text{ }^\circ\text{C s}^{-1}$. The plateau region (shaded area) between 350 and 400 °C in (A) was integrated for constructing the dose–response curve (DRC) with doses from 25 to 300 Gy. The inset shows a plateau test with the plateau region. The peak counts, shaded arrowheads in (B), were also used for constructing the DRC for multigrain aliquots. The data were obtained after application of a preheat at 220 °C for 3 min [printed with permission from Elsevier]. [Color figure can be viewed at wileyonlinelibrary.com].

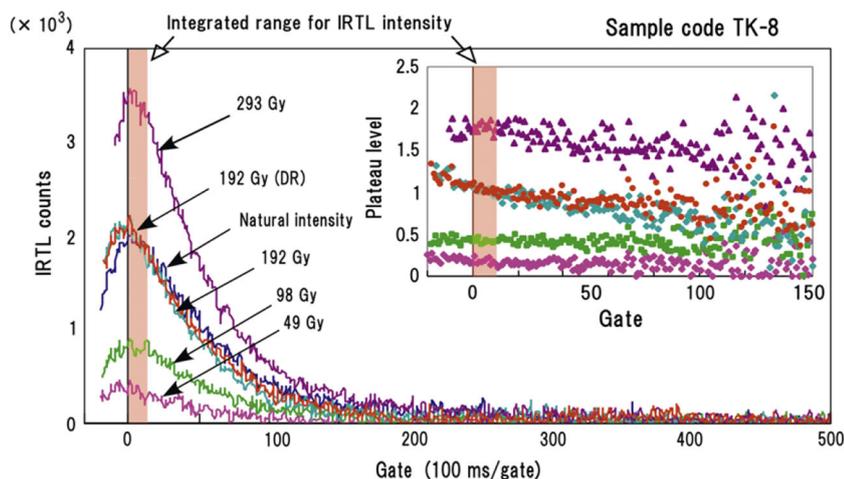


Figure 5. 410 °C IRTL natural and regenerative heat-down curves (HDCs) obtained for single grains using the SAR method (taken from Ganzawa and Maeda, 2009). The sum of IRTL signals for 1 s (10 gates) of the HDC (shaded area) is used in constructing the dose–response curve (DRC) [printed with permission from Elsevier]. [Color figure can be viewed at wileyonlinelibrary.com].

considerations. Similar investigations were undertaken in the early 1980s by Ichikawa *et al.* (1982) for pyroclastic flow deposits and by Ichikawa (1983, 1986, 1988, as cited in Nagatomo *et al.*, 1999) for the Hijiori–Obanazawa pumice at the Zazaragi archaeological site and for a further 14 tephra layers at the Babadan site. Both sand-sized quartz and feldspar grains from two tephra layers and quartz grains from the Shukunosawa pyroclastic flow at the Takamori palaeolithic site in central Japan were investigated by Nagatomo *et al.* (1999). They registered the TL in different detection windows ranging from blue (415 nm) to orange–red (595 nm) for quartz, while only the 630-nm emission was measured for feldspar. Obtained MAAD ages are consistent for different quartz emissions of the Shukunosawa sample (~280–320 ka) within comparatively large uncertainties. The two dated tephra layers at Takamori are stratigraphically meaningful and conform well to the tephrochronology of the Miyagi area as established with a range of chronometric methods (an overview of 22 dated tephra layers in that region is presented in Nagatomo *et al.*, 1999).

For dune sands from Niigata (Japan), Yawata and Hashimoto (2004) were able to distinguish between four different volcanic sources of 72 analysed grains due to their RTL D_e values. The grains of the smallest dose group could be attributed to the Numazawa volcano, because their dose value is close to that of grains extracted from the Numazawa pumice. As the

bleaching rate of the RTL signal is rather low (e.g. Miallier *et al.*, 1994b), optical exposure does not appear to affect the validity of the approach.

A further interesting application of TL not related to numerical dating is presented by Ganzawa *et al.* (1997): by comparing the ratio of RTL to blue TL (BTL) from quartz grains extracted from loess and tephra in Japan, they were able to trace the origin of quartz grains in deposits of unclear genesis. The ratio RTL/BTL is about one order of magnitude larger for volcanogenic material from Japanese eruptions compared to aeolian dust coming from inland China. In general, this application might be of relevance to distinguish between volcanic and xenolithic/detrital quartz in tephra based on their differing RTL properties.

In contrast to the TL emissions of volcanic quartz, OSL has failed to provide reliable age estimates for tephra. Investigations by Bonde *et al.* (2001) on quartz grains of assumed aeolian and/or volcanic origin from a palaeosol beneath the Cape Riva ignimbrite (Santorini, Greece) showed variable and generally low OSL sensitivity to blue light stimulation. Application of the SAR protocol for dose determination resulted in ages underestimating the independently known eruption age by 90%. Although the dated material behaved like quartz in luminescence analyses, laboratory storage tests indicated signal instability due to anomalous fading. Owing to the unidentified origin of the dated material, Bonde *et al.* (2001) could not give conclusive reasons for the failure of the OSL method in that study.

Tsukamoto *et al.* (2007) carried out detailed measurements on the OSL signal stability of sand-sized quartz grains from the Chichibuyama pyroclastic surge deposits and from the Omachi A_1Pm tephra (both central Japan). Their results confirm that the OSL signal of the investigated samples is affected both by anomalous fading (athermal instability, see Fig. 7) and insufficient thermal stability (lifetime of ~1.7 ka at 20 °C). These observations provide a good explanation for the significant age underestimation of the SAR OSL age (~5 ka) for one of the two Chichibuyama samples as compared to a ^{14}C age of ~29 ka.

The only promising OSL dating attempt of volcanic quartz was presented by Biswas *et al.* (2015). They were able to measure an SAR OSL age of coarse grains from a Japanese marker tephra (Aira-Tn) of 28 ± 3 ka, which is in line with an expected age of 30.0 ± 0.2 ka.

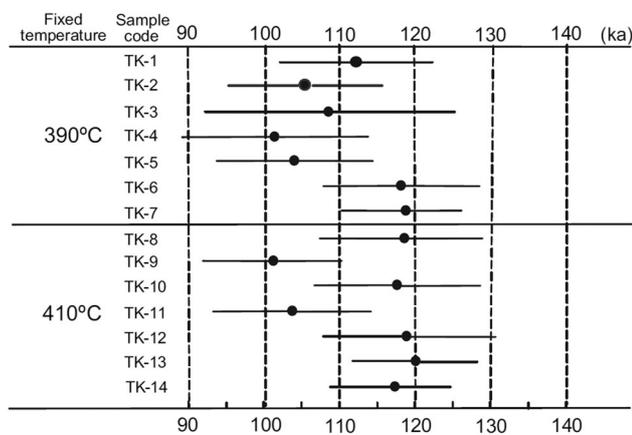


Figure 6. Results of IRTL dating of single quartz grains (taken from Ganzawa and Maeda, 2009). Two fixed temperatures (390 and 410 °C) to readout were tested to determine the equivalent doses (D_e). An annual dose rate of 1.95 mGy was used for the dating. All the obtained IRTL ages with systematic errors shown by bars are concordant with the expected age of 112–115 ka for the Toya pyroclastic flows [printed with permission from Elsevier].

Quartz and feldspar from fragmented or volcanically heated country rock (xenoliths)

As outlined in the previous section, luminescence dating of juvenile volcanic minerals (glass, quartz, feldspar) is often

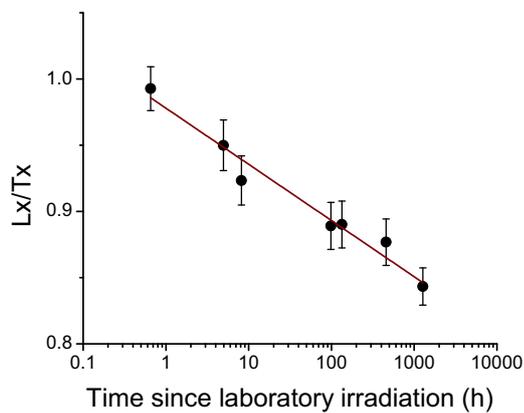


Figure 7. Loss of OSL signal, i.e. fading, from volcanic quartz from the Chichibuyama pyroclastic surge deposit-B (Cb-B) with storage periods (redrawn from Tsukamoto *et al.*, 2007) [printed with permission from Elsevier]. [Color figure can be viewed at wileyonlinelibrary.com].

hampered by low signal-to-noise ratios and instable signals, mainly due to anomalous fading. One way of circumventing these problems is to switch to (non-volcanic) country rock minerals in tephra, the luminescence signal of which was reset during the time of the eruption by either heat, high-pressure shock or a combination of these factors. While it is obvious that country rock or sediments closely underlying a lava flow were sufficiently heated during its emplacement to fully zero the previously accumulated dose (cf. Rufer *et al.*, 2012), it has been debated whether full signal resetting can also be expected during phreatic or phreatomagmatic explosions and in pyroclastic surges and ash plumes. Figure 8 provides an overview of relevant processes during a phreatomagmatic eruption and possible sampling sites around a maar crater.

Combining laboratory experiments and dating results for polymineral silt from Ulmener Maar and Pulvermaar tephra (Eifel Volcanic Field, Germany), Zöller *et al.* (2009) conclude that hydrostatic pressure at elevated temperature (here at 150 °C) may result in at least partial signal resetting, which could act in combination with thermal resetting and resetting due to frictional heat (Takeuchi *et al.*, 2006) during hydroclastic maar eruptions. For other maar eruptions in the Eifel Volcanic Field, Preusser *et al.* (2011) found empirically that the luminescence signal has more likely been fully reset during

phreatic explosions rather than phreatomagmatic ones due to the higher impact of high-pressure shock waves.

Because obviously not all volcanic explosions result in complete thermal and/or shock-induced signal resetting, additional optical bleaching of xenolithic clasts in tephra should be considered. Cheong *et al.* (2007) argue that the light conditions in pyroclastic surges and ash plume are favourable for complete optical resetting of xenolithic quartz grains due to the only slightly increased optical density compared to the atmosphere. Furthermore, it is supposed that those quartz grains fall back in the volcanic vent multiple times before finally being ejected, thus elongating the potential time for bleaching of the OSL signal. This is in strong contrast to Zöller *et al.* (2009) and Rufer *et al.* (2012) who doubt that optical signal resetting is possible in eruption columns and base surges due to the high opacity.

A summary of methodological aspects with regard to luminescence dating of xenolithic minerals in tephra is provided by Rufer *et al.* (2012). Numerous applications of this approach during the past more than three decades, from which a selective overview is given in Table S1 in Supporting Information, demonstrate its large potential for accurately constraining the time of formation of tephra layers.

Challenges and recommendations for dating

While TL dating of volcanic glass was considered as a reliable technique by Berger (1991, 1992), further and independent studies demonstrating the general applicability of the method are pending. Major challenges to be overcome for directly dating volcanic glass by luminescence methods comprise its purification processes, avoiding or correcting for anomalous fading and potentially the geochemical instability of volcanic glass.

Anomalous fading and hence age underestimation also constitute the main problem in the accurate dating of volcanic feldspar and quartz, which can be correlated to rapid cooling during mineral formation and increased lattice disorder. However, specific luminescence emissions and protocols may provide access to stable signals. For feldspar, far-red (710 nm) TL emission appears to be a promising candidate despite technical challenges in signal acquisition (Zink and Visocekas, 1997; Visocekas *et al.*, 2014), as is the recently developed pIRIR protocol (e.g. Biswas *et al.*, 2013, 2015). For

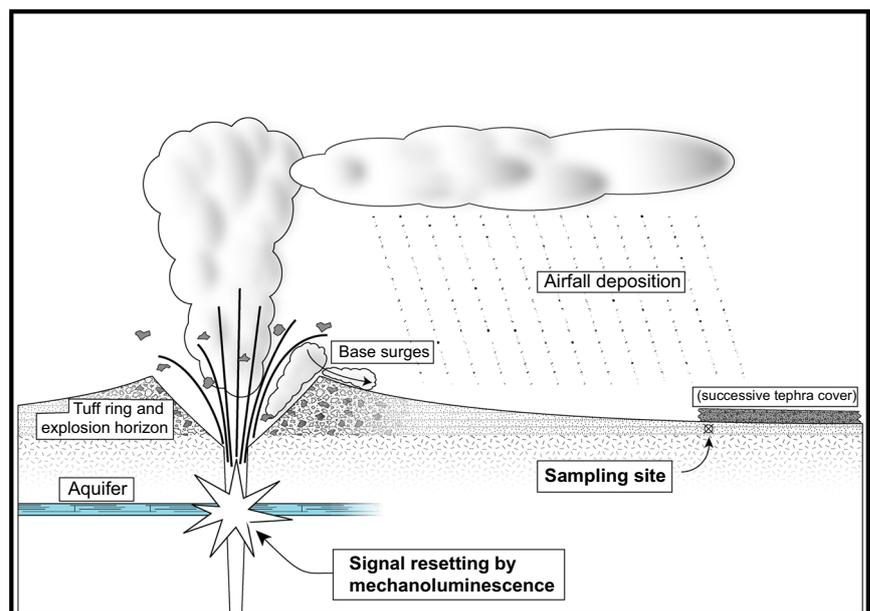


Figure 8. Overview of relevant processes during a phreatomagmatic eruption and possible sampling sites around a maar crater (taken from Rufer *et al.*, 2014) [printed with permission from Springer Nature]. [Color figure can be viewed at wileyonlinelibrary.com].

volcanic quartz, RTL emission in combination with SAR protocols has proved to be the best choice with the additional benefit of considerably extending the dating range (e.g. Fattahi and Stokes, 2000a; Ganzawa and Maeda, 2009).

Depending on bedrock lithology, targeting xenoliths ejected during the eruption can be a good alternative to juvenile volcanic material. Rates of anomalous fading are expected to be lower (feldspar) or absent (quartz) and numerous studies have verified complete signal resetting of bedrock clasts through heating and/or shock during the volcanic explosion and thus the large potential of this approach (e.g. Preusser *et al.*, 2011; Onken and Forman, 2017; Schmidt *et al.*, 2017).

Indirect luminescence dating of tephra by bracketing sediments

To overcome the methodological issues that arise while dating tephra directly, numerous studies date sediments that bracket them. Dating these sediments is generally straightforward, but some issues arise regarding dose rate determination or the occurrence of glass shards in samples that frame the tephra layers too closely. Here, only major challenges are presented, while a more extensive summary is given in the Supporting Information alongside a table containing >140 ages of samples bracketing tephra layers. Only the special case of Japanese loess deposits is elaborated in more detail in the last part of this section. Table S2 demonstrates the widespread applicability of luminescence dating. Reported ages spread globally from North America across Europe and eastern Africa to Japan and New Zealand. They also indicate a remarkably wide dating range of ages from 8 to 660 ka which exceeds other indirect dating methods such as radiocarbon dating by far, highlighting the strength of the luminescence dating method. Finally, the table is available in an editable format, so the reader can use and extend it easily.

Dating accuracy

Most studies that try to date unknown tephra indirectly or use tephra deposits as independent age control for their geochronological investigations work with aeolian sediments, in particular loess and dune sediments (Hilgers *et al.*, 2001; Westgate *et al.*, 2008; Demuro *et al.*, 2013; Fitzsimmons *et al.*, 2013; Veres *et al.*, 2013; Klasen *et al.*, 2015; Bösken *et al.*, 2017). However, research on lacustrine (Shulmeister *et al.*, 2001; Shane *et al.*, 2002; Blegen *et al.*, 2015; Karatson *et al.*, 2016), marine (Sugisaki *et al.*, 2010; Buylaert *et al.*, 2012a), and glacial sediments (Kondo *et al.*, 2007) was also conducted successfully. Dating sediments that bracket tephra layers poses the following challenges: some studies report age underestimation (e.g. Zeeden *et al.*, 2018) with regard to other dating methods, which is sometimes accompanied by field or laboratory saturation of the luminescence signal and therewith is problematic for older samples (e.g. Schmidt *et al.*, 2014; Thiel *et al.*, 2014). Samples of the New Zealandian Birdling Flat loess for instance underestimate radiocarbon ages of pedogenic carbonate and the independent Kawakawa/Oruanui tephra age by at least 20% (Almond *et al.*, 2007). In other studies, several tephra in this region were luminescence-dated (Lian and Shane, 2000; Berger *et al.*, 2001; Grapes *et al.*, 2010a), but the age differences with regard to radiocarbon or other dating techniques led to severe discussions about the reliability of the luminescence results (see Grapes *et al.*, 2010b; Lowe *et al.*, 2010; Vandergoes *et al.*, 2013). In contrast, age overestimation is also reported, for example by Shulmeister *et al.* (2001) who investigated sediments of Lake Poukawa, New Zealand. While

the Tahuna tephra was dated successfully (Table S2), the Kawakawa/Oruanui tephra was extremely overestimated (60 ± 18 ka; ^{14}C age: 25.4 ka cal BP; Vandergoes *et al.*, 2013). The authors explain this overestimation by incomplete bleaching before deposition.

However, there are numerous studies in which luminescence ages agree well with independent age control (e.g. Berger, 1987; Auclair *et al.*, 2007; Buylaert *et al.*, 2012a; Roberts, 2012). A challenging example is given by Demuro *et al.* (2008) who investigated ice-rich loess deposits that frame the Dawson tephra in the eastern Beringia region. In their SAR measurements, quartz grains were dim and dose-response curve shapes varied greatly between aliquots. Nevertheless, unsuitable grains (showing low signals, significant IR depletion ratios and early onset of saturation) could be rejected through single-grain measurements leading to OSL ages of 30 ± 4 and 28 ± 5 ka that agree well with radiocarbon dating of *in situ* macrofossils ($30\,433\text{--}30\,014$ cal a BP, 2σ).

Optical dating provides a range of different measurement techniques and protocols that often tend to give various results, especially when different sample material is used. Zens *et al.* (2017) showed this impressively in their compilation of sediment ages bracketing the Eltville tephra in central Europe. A total of 87 dates yield luminescence ages between 13.5 and 49.6 ka, which were subjected to a Bayesian approach to obtain a common age between 23.2 and 25.6 ka, that fits well with stratigraphic and palaeoenvironmental data. At the lacustrine/fluvial/aeolian sediment sequence of Caciulatesti in south-western Romania, Constantin *et al.* (2012) investigated two samples bracketing the CI/Y5 tephra (39.85 ± 0.14 ka, $^{40}\text{Ar}/^{39}\text{Ar}$, Giaccio *et al.*, 2017) using the SAR protocol on different grain size fractions of quartz. Ages from the underlying sand layer range from 38.5 ± 2.8 ka (4–11 μm) to 44.6 ± 3.8 ka (90–125 μm), while the overlying loess gave ages between 36.2 ± 3.3 ka (125–180 μm) and 44.4 ± 3.4 ka (4–11 μm). Although age estimates differ by grain size, weighted means of 40.4 ± 1.3 and 40.7 ± 1.2 ka agree well with the independent age. Different age results depending on the grain size fraction used were also obtained by Trandafir *et al.* (2015) and Timar-Gabor *et al.* (2017). Figure 9 shows the extent of tephra deposits in south-eastern Europe and investigated loess deposits containing these tephra (cf. Table S2).

Proximity and dose rate assessment

Some studies encounter difficulties when dating samples that were taken in too close proximity to a tephra layer. This can cause problems because geologically fresh volcanic deposits are prone to relocation of radioelements and therewith dose rates are not assessed accurately (cf. Krbetschek *et al.*, 1994; Biswas *et al.*, 2013). At Rasova Valea cu Pietre for instance, another Romanian site, one sample above the CI/Y5 tephra showed unusually high radionuclide concentrations (Anechitei-Deacu *et al.*, 2013), suggesting enrichment in radioelements due to upward mixing of the magmatic mineral assemblage of the tephra layer. This is also supported by a noted gradual upper boundary of the tephra. In addition, the D_e of the sample below the tephra is high, but this is not reflected in the dose rate data, leading to an overestimated age of 81 ± 8 ka. Therefore, the authors decided to neglect these samples. Two other samples 38 cm above and 50 cm below the CI/Y5 tephra gave fine-grain quartz ages consistent with independent age control (44.4 ± 4.5 ka; 41.4 ± 4.2 ka). By contrast, dated dune sediments containing the central European Laacher See tephra in Mainz-Gonsenheim, Germany, delivered most reliable results for the sample within the

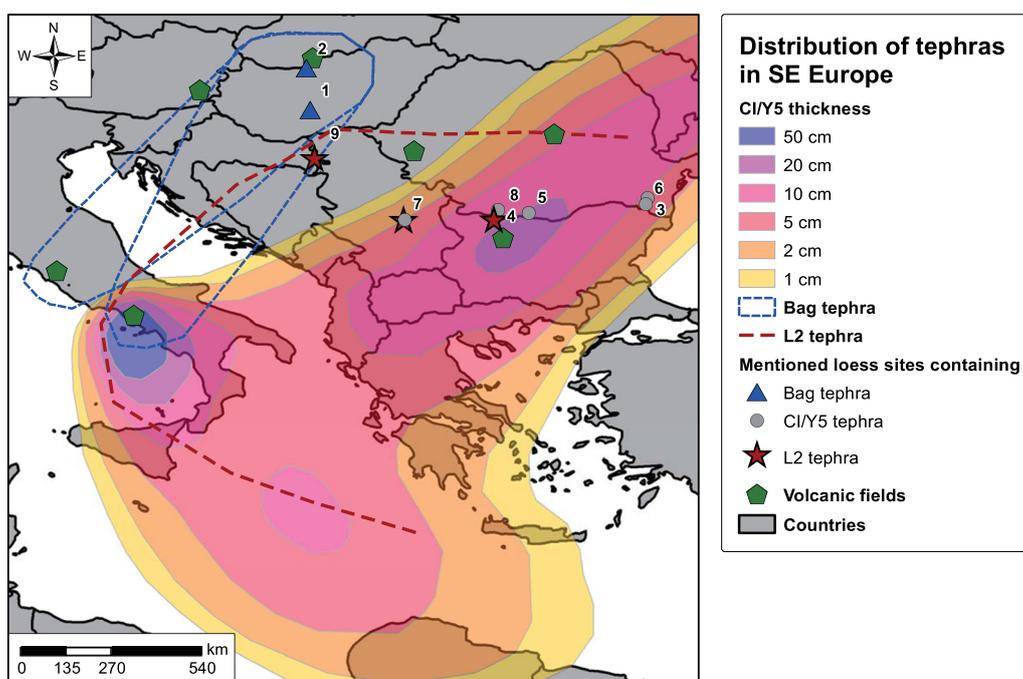


Figure 9. Map showing the distribution of the bag (after Pouclet *et al.*, 1999), CI/Y5 (after Marti *et al.*, 2016) and L2 (after Laag *et al.*, 2018) tephras in south-east Europe. For the CI/Y5 tephra also modeled tephra thickness is depicted (see Marti *et al.*, 2016). As the origin of the bag tephra remains unclear, two possibilities are shown. Moreover, several volcanic fields (after Pouclet *et al.*, 1999) and the following loess–paleosol sequences discussed in the text are indicated: Paks (1; Thiel *et al.*, 2014), Basaharc (2; Frechen *et al.*, 1997), Rasova-Valea cu Pietre (3; Anechitei-Deacu *et al.*, 2013; Zeeden *et al.*, 2018), Caciulatesti (4; Constantin *et al.*, 2012), Lunca (5; Veres *et al.*, 2013), Urluia (6; Fitzsimmons *et al.*, 2013; Obrecht *et al.*, 2017), Stalač (7; Böskén *et al.*, 2017), Harletz (8; Lomax *et al.*, 2019), Garjanović (9; Wacha and Frechen, 2011). [Color figure can be viewed at wileyonlinelibrary.com].

tephra layer (11.9 ± 1.0 ka), while the samples above (13.4 ± 1.2 ka) and below (14.6 ± 1.5 ka) overestimate the independent tephra age of 12.9 ka slightly (Brauer *et al.*, 1999; Radtke *et al.*, 2001). Although this seems surprising, it can be similarly explained by higher dose rates within the tephra layer that influence the surrounding sediments but that might not have been fully considered for the two bracketing samples.

Japanese tephric loess

While most studies reviewed here deal with ‘common’ issues in optical dating, the luminescence behaviour of Japanese loess is distinct. In Japan, several loess sequences with interbedded tephra horizons of known age are found (e.g. Watanuki and Tsukamoto, 2001), which are excellently suited to test the reliability of luminescence dating approaches. While numerous tephra deposits are independently dated by fission track dating and other techniques (e.g. Watanuki *et al.*, 2005), problems arise from the presence of volcanic glass shards scattered within the loess deposits. This so-called tephric loess is widely distributed in Japan. It probably consists of a mixture of tephra from small-scale eruptions and Asian aeolian dust (Tsukamoto *et al.*, 2003). Research on tephric loess reports strong recuperation after preheating and high recycling ratios for some samples (e.g. Tsukamoto *et al.*, 2003; Watanuki *et al.*, 2005). These samples tend to show a slower signal decay during optical stimulation, suggesting a higher contribution to the signal from other than the fast component (i.e. medium or slow components, cf. Jain *et al.*, 2003). Tsukamoto *et al.* (2003) showed that the OSL signal of such a sample is dominated by the medium and slow 1 components, suggesting the existence of volcanic quartz within the problematic samples. Watanuki *et al.* (2005) demonstrated that the measured high recuperation is related to the medium component of their samples by using linearly modulated OSL. However, by separating the fast component, Watanuki *et al.*

(2005) obtained ages which agree closely with independent age control. Tsukamoto *et al.* (2003) suggest a less time-consuming method: after determining D_e values and recuperation at different stimulation intervals, a plot of D_e vs recuperated signal was built (Fig. 10). Resulting points were fitted with an exponential decay curve and extrapolated to the point of zero recuperation. This ‘corrected D_e ’ agrees excellently with independent age control.

Thiel *et al.* (2011) investigated the same samples as used in Watanuki *et al.* (2005) employing the pIRIR₂₉₀ protocol. While

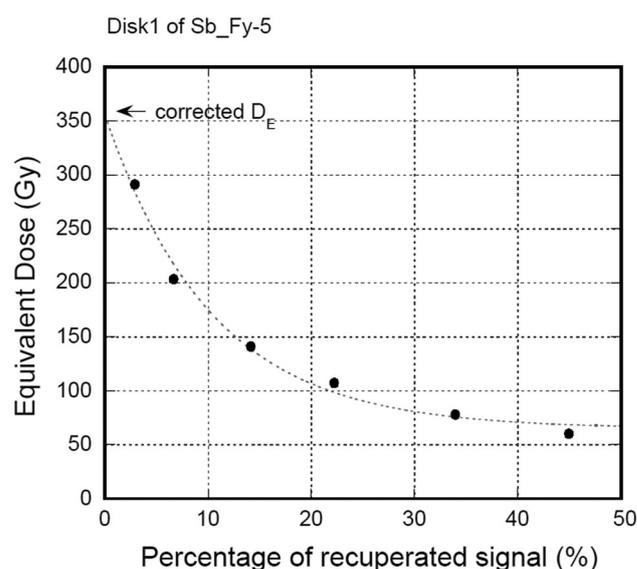


Figure 10. The relationship between equivalent dose (D_e) and percentage of the recuperated signal for sample Sb Fy-5 (taken from Tsukamoto *et al.*, 2003). The correct D_e is obtained by fitting the plot to an exponential curve and extrapolating the curve to the point at which R_0/R_N equals zero [printed with permission from Elsevier].

recycling ratios are within 10% of unity and recuperation is low, results of the dose recovery tests vary greatly. Nevertheless, non-fading-corrected ages agree well with previously published quartz ages and independent age control (although some exceptions are reported). pIRIR ages for the younger samples overestimate the quartz ages, which is probably related to small residual doses <20 Gy. Older pIRIR ages overestimate the quartz ages, but fit better to independent dates. This agrees with Watanuki *et al.* (2005) who proposed a slight underestimation of the older quartz ages. Later, Ito *et al.* (2017b) built upon the previous studies on Japanese tephric loess to constrain the eruptive history of the Towada volcano. They also found the bulk OSL signal of quartz to be unsuitable for dating and extracted the fast component for D_e calculations. With the exception of one outlier, ages are in stratigraphic order and agree with independent dates where available. They relate the age overestimation of the outlier to incorrect assessment of the dose rate. Moreover, they report larger scatter in their three oldest samples, which might be related to a small uncertainty during deconvolution of the bulk signal that seems to begin when D_e values surpass D_0 at ~70 Gy.

Challenges and recommendations for dating

Dating sediments that surround tephra poses the usual issues that also non-tephra-related dating approaches face, such as age disparities with regard to other dating techniques or between different measurement protocols or measured grain sizes. More tephra-related problems may be encountered when samples are taken in too close proximity to the tephra. This might be associated either with the existence of glass shards in the sample due to mixing of tephra and sediment or with unsuccessful assessment of the dose rate. To avoid glass shards in the sample it is advisable to take (another set of) samples >30 cm distance to any visible tephra particles. Additionally, the data should be screened carefully for any signs of odd behaviour (recuperation, stronger medium and slow components, poor dose recovery) and D_e values can be corrected by extracting the fast component or by Tsukamoto *et al.*'s (2003) 'zero recuperation method' as demonstrated for tephric Japanese loess deposits. While it is difficult to account for the migration of radioelements through the sediment, one should take extra care to assess the current dose rate carefully. We suggest applying *in situ* dose rate measurements for each sample or if this is not feasible to take several samples to assess the amount of radionuclides not only for the luminescence sample but also for the surrounding layers, such as the tephra layer itself. Afterwards dose rates can be calculated considering all radionuclide data and the distance of the single samples to the luminescence sample, for example using the *scale_GammaDose*-function in the R-package 'Luminescence' (Kreutzer *et al.*, 2012; Riedesel *et al.*, 2019). Finally, modelling radionuclide migration might be an option for difficult cases (cf. Zander *et al.*, 2007).

Conclusion and future directions

The review of previous studies has shown that the reliable direct dating of volcanic quartz and feldspar as a component in tephra is still methodically difficult, mainly due to anomalous fading that occurs in both materials. Only the RTL of volcanic quartz and the far-red emission of volcanic feldspar appear to be exceptions here, the further methodological exploration of which seems promising. Largely successful dating attempts have also been conducted on xenolithic material in tephra, where quartz is clearly preferred over feldspar to avoid age underestimation due to anomalous fading. Where xenolithic and juvenile tephra components cannot be

physically separated, the RTL signal of quartz might be an appropriate choice, as this signal has turned out to be stable for both volcanic and xenolithic/plutonic quartz. A comprehensive and systematic study of the conditions of luminescence signal zeroing in different pyro- and hydroclastic settings and considering both proximal and distal tephra deposits could provide further insights into the best sampling positions of xenolithic material. Moreover, this review summarizes the challenges that are encountered when dating tephra indirectly by sampling the surrounding sediment. An overview of indirectly dated tephra across several types of deposits and regions is given in the Supporting Information. While the dating of sediments that bracket tephra deposits is generally straightforward (except for the usual challenges in luminescence dating), some issues arise regarding reliable dose rate determination or the occurrence of glass shards within the samples when they are taken too close to the tephra horizons. Recommendations for dating include the avoidance of glass shards either by increased sampling distance from the tephra layer or by extraction of the fast component (in the case of quartz dating). Furthermore, increased care should be taken in assessing the dose rates by using *in situ* measurements or by taking several dose rate samples.

Especially with luminescence dating of feldspar, considerable progress has been made in the last 10 years in searching for long-term stable signals. For example, consistent ages in accordance with independent dating results could be achieved using the pIRIR method (Thomsen *et al.*, 2008; Buylaert *et al.*, 2012a; Ito *et al.*, 2017a; Klasen *et al.*, 2017; see Li *et al.*, 2014 for an overview), although there still seem to be methodological challenges in the age range >100 ka (e.g. Lowick *et al.*, 2012; Lomax *et al.*, 2019). Nonetheless, the results obtained by pIRIR on feldspars from tephra (Biswas *et al.*, 2013) are promising and warrant further studies applying this method to similar contexts.

Luminescent signals that have not yet been used for tephra dating include infrared radiofluorescence (IR-RF) (Trautmann *et al.*, 1998, 1999; Erfurt and Krbetschek, 2003; Frouin *et al.*, 2017) and infrared photoluminescence (IR-PL; Erfurt, 2003; Prasad *et al.*, 2017) of K-feldspar. For these methods, the signal is recorded during ionizing irradiation (IR-RF) or during stimulation with IR radiation, respectively, but it is assumed that the sampled electron trap is the same (Kumar *et al.*, 2018). Although both methods require further basic research (see Buylaert *et al.*, 2012b), the signals do not seem to be affected by anomalous fading, and their comparatively large saturation doses should allow reliable dating of tephra (far) beyond the last glacial cycle.

Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web-site.

Acknowledgements. Part of the research was carried out in the frame of the CRC 806 'Our way to Europe', funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Projektnummer 57444011 – SFB 806. We thank Dr Sumiko Tsukamoto and Dr Daniel Rufer for providing the figures used in this review article. We thank Yunus Baykal and Christian Laag for their support concerning Fig. 9.

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