Title
Using luminescence signals from bedrock feldspars for low-temperature thermochronology

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Using luminescence signals from bedrock feldspars for low-temperature thermochronology

A dissertation submitted in partial satisfaction
of the requirements for the degree
Doctor of Philosophy in Geology

by

Nathan David Brown

2017
ABSTRACT OF THE DISSERTATION

Using luminescence signals from bedrock feldspars for low-temperature thermochronology

by

Nathan David Brown

Doctor of Philosophy in Geology
University of California, Los Angeles, 2017

Professor Timothy Mark Harrison, Chair

Over the past several years, optically-stimulated luminescence signals (OSL) from quartz and infrared-stimulated luminescence (IRSL) from feldspar in bedrock have been investigated for their use in thermochronology. In this study, I propose using thermally-stimulated signals (thermoluminescence, or TL) from feldspar instead. Because TL is measured by gradually heating a sample, the luminescence emissions correspond to electron traps of increasing thermal stability. The primary goal of this dissertation is to describe how this signal can be optimally measured and interpreted to understand the recent thermal history of bedrock samples.

I first modified the laboratory luminescence reader to allow us to irradiate feldspar samples at a range of dose-rates, from $8.7 \times 10^{-5}$ to $1.2 \times 10^{-1}$ Gy/s to estimate the influence of dose-rate on the subsequent TL signals. Although less stable sites were not preferentially populated at higher dose-rates (an unexpected result), I did observe an increase in brightness at the lowest dose-rate, a result which may suggest that the dose-rate influences recombination or trapping competition probabilities. In natural TL signals, I observed the expected trend of greater site occupancy at lower measurement temperatures with higher dose-rates.

Next, I perform several experiments to relate the TL signal that I monitor to OSL and IRSL from feldspar. I propose that the TL signal preserves a more detailed structure of trapping stability than the optically-stimulated signals, which derive from the full range of TL stabilities. Moreover, preheating and phototransfer effects may redistribute trapped charge,
leading to potential inaccuracies in IRSL or post-IR IRSL thermochronology techniques.

The kinetic parameters involved in natural and laboratory conditions are of primary importance when using TL signals to quantify thermal history. I develop a novel method for determining the activation energy, effective frequency factor, and kinetic order values for natural and regenerative TL signals. This method, termed ‘post-isothermal TL’ analysis, reveals that for the blue-green emission of the low-temperature TL peak, the apparent trap depth in measured bedrock K-feldspar samples increases to a depth of about $\geq 1.9$ eV as measurement temperature increases, at which point it reaches a plateau in some samples. If this plateau value is the true depth of the trap, the frequency factors are measured to decrease as measurement temperature increases, an observation consistent with the recent conception that feldspar luminescence (IRSL and TL) results from excited-state tunneling to randomly-distributed centers.

Three archived drill cores were sampled at depths corresponding to burial temperatures ranging from -4.1 to 60.2 °C. The extracted feldspars from these samples yield TL signals that clearly relate to temperature. With higher ambient temperatures, there is a linear increase in the $T_{1/2}$ value (measurement temperature at half-maximum emission intensity) and a reduction in signal intensity. This behavior can be replicated by isothermal treatments in the laboratory. I interpret this behavior as reflecting the continuum of trap lifetimes present in feldspar TL, an observation that I substantiate with additive dose experiments and a numerical model.

How glaciers erode is an active research question that can be informed by feldspar TL thermochronology. I collected bedrock samples along vertical and longitudinal profiles within the Rock Creek glacial valley in the Beartooth Mountains of Montana to investigate their thermal history. Using the relationship observed with the drill core samples, I can predict the ambient temperature of these samples from their $T_{1/2}$ values. The calculated values are indistinguishable from the historical record of mean annual air temperature from the local weather station. The shapes of the resulting TL signals imply that the samples are in disequilibrium, i.e., that the signals are still growing through time. By measuring the single-aliquot regenerative (SAR) dose-responses of the $T_{1/2}$ values, I estimated the maximum time
that each sample has been at its current surface temperature. These ages correlate with periods of local glacial activity and offer insight into the erosional mechanisms involved. In particular, I observe post-glacial high-elevation plateau erosion, which supports a key prediction of the glacial buzzsaw hypothesis.

Although a maximum age is useful, a more desirable solution is a continuous $T - t$ history. The final chapter pursues this goal with samples taken from the Yucaipa Ridge tectonic block (YRB) of the San Bernardino Mountains in Southern California. I introduce a multiple-aliquot additive-dose (MAAD) measurement protocol that can be used to estimate the degree of dose saturation as a function of measurement temperature, $\frac{\alpha}{N}(T)$. This MAAD TL $\frac{\alpha}{N}(T)$ method capitalizes on the earlier observation of feldspar TL, that site stability increases with measurement temperature. Using the same kinetic model used to describe the drill core samples, I simulate two previously-proposed geologic cooling scenarios for the YRB (as constrained by apatite (U - Th)/He ages and catchment-averaged cosmogenic $^{10}$Be denudation rates) and the model is found to be sensitive enough to discriminate between them. I then measure MAAD TL signals for several YRB samples, convert these to $\frac{\alpha}{N}(T)$ functions, and use Monte Carlo simulations to invert for each sample’s thermal history. The resulting $T - t$ histories from these five samples tell an internally consistent story of samples nearest the fault-parallel valley cooling recently and those nearer the ridge having been at present temperature for a longer time. Despite the vertical relief being only about 0.4 km between the highest and lowest samples, the difference in trap saturation is significant, suggesting that this technique may be well suited to resolving Quaternary landscape evolution. I interpret the exhumation histories of these samples to reflect a combination of post-uplift relaxation of isotherms and a lagged erosional response in the form of fluvial downcutting.
The dissertation of Nathan David Brown is approved.

Edward John Rhodes
Ioanna Kakoulli
Edwin Arthur Schauble
Seul Gi Moon

Timothy Mark Harrison, Committee Chair

University of California, Los Angeles
2017
To my son, Arlen.
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PUBLICATIONS


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CHAPTER 1

Introduction

1.1 Introduction

Thermochronology is the study of the time-versus-temperature \((t - T)\) history of rocks. Most commonly in terrestrial applications this involves the cooling that happens as a body of rock moves towards Earth’s surface. Because the rate at which a rock is brought to the surface depends on the dynamic balance between rock uplift and exhumation, geologists commonly use thermochronometric systems to understand the interplay between tectonic uplift and erosion (Willett and Brandon 2002; Finnegan et al. 2008; Whipple 2009; Fox et al. 2015). Noble gas and fission-track systems are sensitive to a wide range of temperatures \((\sim 60-550^\circ C; \text{Fig. 1.1})\) which correspond to crustal depths of the order \(10^0-10^1\) km (Reiners and Brandon 2006), conditions well-suited for studying regional orogenic evolution.

Low-temperature thermochronology offers another intriguing application: the study of landscape evolution at surficial conditions. The thermal structure of the continental crust below several kilometers is primarily governed by radiogenic heat production, conduction of heat to the surface, and, in regions where the crust has vertical velocity, advection. Within the upper several kilometers, periodic topography (e.g., regularly-spaced ridges and valleys) can perturb the thermal structure of the crust; this effect decays exponentially in a depth proportional to the topographic wavelength (Chapter 4, Turcotte and Schubert 2002). A corollary of this relationship between topographic wavelength and thermal disturbance is that thermochronometers sensitive to very low temperatures \((T < 100^\circ C)\) can be used to investigate changes in topographic relief (Braun 2002b). To date, apatite fission-track (AFT) (Spotila et al. 2004), apatite \((U-\text{Th})/\text{He} (\text{AHe})\) (House et al. 1998) (often in conjunction
Figure 1.1: Commonly used thermochronometers compared with luminescence thermochronometers. Modified from Table 1.1 of Braun et al. (2006).

Source
Harrison (1981)
Hames and Bowring (1994)
Coyle and Wagner (1998)
Harrison et al. (1985)
Brandon et al. (1998)
Reiners et al. (2002)
Lovera et al. (1989)
Reiners and Farley, (1999)
Gleadow and Duddy (1981)
Wolf et al. (1998)
Guralnik et al. (2013)
This study
with its derivative technique apatite $^{4}\text{He}/^{3}\text{He}$; Shuster et al., 2005; Valla et al., 2011, and quartz optically-stimulated luminescence (OSL) (Herman et al., 2010) techniques have all been used to estimate changes in topographic relief.

A further consideration is the minimum detectable cooling age of a given thermochronometer. For noble gas systems, a finite cooling age can be measured if the target isotope has ingrown to within detection limits. In the case of AHe methods, this lower limit is about 0.5 Ma, depending on the concentration of parent isotopes and the degree of diffusive loss (Shuster et al., 2011). For AFT methods, the number of visible fission-tracks generated by $^{238}\text{U}$ within an apatite grain is the primary control on the minimum resolvable age (Hendriks and Redfield, 2005), about 0.5 - 1 Ma (e.g., Fuller et al., 2006).

Here lies the unique promise of luminescence thermochronology: a system sensitive to temperatures at Earth’s surface which accumulates on timescales of order $10^2 - 10^5$ years. The phenomena which could be interrogated with such a tool are intriguing: Neotectonic uplift rates, changes in Late Pleistocene-Holocene fluvial downcutting, the spatial evolution of glacial excavation, and the feedbacks between glacial-interglacial climate fluctuations and catchment-scale erosion rates.

The remainder of this chapter has three aims. First, a brief description of the luminescence dating of Quaternary sediments will be given. Second, it will be shown that the same charge traps which are used for sediment dating are sensitive to storage temperature. Once thermally emptied, these traps will refill to saturation after a few hundred thousand years. Third, the trajectory of this dissertation will be outlined.

1.2 Luminescence dating of sediment burial events

For more complete discussions of the luminescence dating of Quaternary sediments, the following summaries are excellent. As the progenitor of modern luminescence techniques, Aitken (1985, 1998) offers perhaps the most comprehensive descriptions of the discipline. Wintle (2008) gives the historical progression of the technique from its origin in the archaeology community to its current uses in Quaternary geology; Duller (2008) provides a concise
guide for first-time users; Rhodes (2011) enumerates the contemporary geologic applications of luminescence dating; and Preusser et al. (2009) describe the fundamental physical chemistry underlying the use of natural quartz for dosimetry; the author is unaware of an equivalent text for feldspar minerals, although Duller's (1997) description of feldspar luminescence systematics is excellent, as is the recent work of Jain et al. (2015).

Luminescence dating, along with electron spin resonance, belongs to the field of trapped-charge dating. As a mineral grain (e.g., quartz or K-feldspar) rests within a body of sediment, it is exposed to ionizing radiation from naturally occurring radionuclides (\(^{40}\text{K}, {^{238}}\text{U}, {^{235}}\text{U}, {^{232}}\text{Th}, {^{87}}\text{Rb}, \) and their daughter products) and cosmic rays. This radiation dislodges electrons from their host atoms, creating ions and free electrons. Point defects capture a fraction of these free electrons before they are able to relax to a ground state, and in this way the number of trapped electrons will increase with dose. Eventually, the number of unfilled defect sites will go to zero and the system will be saturated.

If the grain stays buried for a long time (\(\sim 10^5 - 10^6\) y), all traps will fill and the burial age will be indistinguishable from infinity. If, however, the grain is brought to the surface and exposed to sunlight, the ultraviolet and visible light from the sun will detrap all previously trapped electrons. Photons from sunlight have sufficient energy to liberate electrons bonded to point defects (i.e., optical activation energy or optical trap depth, \(E\)) but not enough energy to generate new free electrons. Upon burial, the grain will once again start to accumulate trapped electrons.

Under normal circumstances, the strength of the radiation field within a sedimentary deposit will remain effectively constant as all the electron traps fill. In other words, the dose that a grain absorbs is directly proportional to the radiation exposure time within that deposit. Therefore, two pieces of information are needed to determine the time since sunlight exposure for a buried grain: the geologic dose-rate (\(\dot{D}\)) at the location of the grain and the total radiation dose absorbed by the grain, known as the equivalent dose (\(D_e\)).

Before describing how absorbed dose is determined, a brief summary of luminescence is appropriate (Fig. 1.2). Consider a trapped electron. Microseconds after receiving an incident
Figure 1.2: (a) Following irradiation, natural minerals will contain many electrons trapped in higher-energy states. (b) Stimulation by light provides enough energy to free the electron into the conduction band. (c) From the conduction band, the electron can lose energy in the form of an emitted photon. This progression constitutes optically-stimulated luminescence.
photon, and thereby the energy required to escape its trap \cite{Denby2006}, the freed electron will conduct throughout the lattice before relaxing to a lower energy state, emitting a photon. Because the electron usually drops below the energy of the trapped state, the emitted photon has a shorter wavelength than the absorbed photon (i.e., anti-Stokes shift). This difference in wavelength allows one to isolate the emitted light through the use of detection filters.

Having established that the number of trapped electrons depends upon the absorbed dose and that the intensity of OSL derives from the number of trapped electrons, we can now determine the natural dose absorbed by a mineral grain during burial (Fig. 1.3). First, the OSL response of the naturally-dosed sample is measured. (Care must be taken to keep the sample dark before measurement, lest the trapped electrons be inadvertently liberated prior to measurement). A brighter OSL response can be crudely interpreted the result of long burial. Samples vary in their sensitivity to radiation, however, such that the dose-response behavior of each sample must be quantified. Second, the sample is given a known amount of radiation and the resulting OSL is counted. This is repeated for a range of doses, from zero to beyond the expected geologic dose. As the lab doses increase, the luminescence responses become brighter. The dose-responses are fitted to a saturating exponential function (cf. \cite{Duller2007}) of the form

\begin{equation}
I = a(1 - \exp(-D \cdot b)) + c
\end{equation}

where \( I \) is the luminescence intensity (often expressed as a ratio of the luminescence response, \( L \), over the response to a static, repeated ‘test dose’, \( T \), to correct for sensitivity changes throughout the measurement sequence; \cite{Murray1998, Wintle2006}), \( D \) is the dose administered, and \( a, b, \) and \( c \) are best-fit constants. The lab dose which would produce the natural luminescence intensity, the equivalent dose \((D_e)\), approximates the absorbed dose during burial. The burial age is then simply calculated as

\begin{equation}
\text{Age (ka)} = \frac{\text{Equivalent dose (Gy)}}{\text{Geologic dose-rate (Gy/ka)}} = \frac{D_e}{\dot{D}}
\end{equation}

That a dose-response curve follows the functional form of a single saturating exponential is a consequence of the limited number of available trapping sites, such that the ratio of
Figure 1.3: The natural dose received by a sample is estimated by first measuring the naturally-induced luminescence signal (red square) and then measuring the responses to known doses (blue circles), which should grow with dose as a saturating exponential function (purple curve). The lab dose required to produce the natural signal is known as the equivalent dose, $D_e$, e.g., 13.6 ± 1.6 Gy.
occupied traps, \( n \), over total traps, \( N \), follows the form

\[
\frac{n}{N} = \left(1 - \exp\left(-\frac{\dot{D}}{D_0}\right)\right)
\]

where \( D_0 \) is sample-specific dose at which saturation effects become significant (Wintle and Murray, 2006).

The determination of the mean geologic dose-rate experienced by a sample is exhaustively covered in Murray (1981). In short, the total dose-rate (\( \dot{D} \)) comprises contributions from alpha particles (\( \dot{D}_\alpha \)); beta particles (\( \dot{D}_\beta \)); and gamma rays, both extraterrestrial and lithogenic (\( \dot{D}_\gamma \)). Quantifying \( \dot{D}_\alpha \) depends upon the target mineralogy. Because alpha particles (He\(^{2+}\)) attenuate after traveling several microns, the alpha dose-rate to coarse quartz grains (which contain negligible internal potassium) is zero, once the outer surface has been removed by etching with hydrofluoric acid. For coarse-grained potassium feldspar grains, an internal potassium content of \( 10 \pm 2\% \) is usually assumed based upon laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) measurements of luminescent grains (while lower concentrations of potassium are common among dim grains, luminescence signals are dominated by the brighter, more potassic grains) (Smedley et al., 2012). The conversion from K-content to an internal dose-rate is straightforward (Adamiec and Aiken, 1998). To determine \( \dot{D}_\beta \), beta counting, mass spectrometry or neutron activation analysis of a representative portion of sediment are often used to determine the concentrations of radionuclides surrounding the sample. These concentrations are then converted to a beta dose-rate following Adamiec and Aiken (1998). While the measured concentrations of bulk U, Th, and K can also be used to determine the gamma dose-rate, a preferable approach is to measure this component in situ through the use of a portable sodium iodide gamma spectrometer which registers incoming gamma rays from \(^{40}\)K and daughter products within the \(^{238}\)U and \(^{232}\)Th decay chains. Less common approaches include the burial and recovery of synthetic dosimeters (at least a few months are required for an accurate measurement), and the use of high-resolution germanium gamma spectrometry or thick-source alpha counting to determine the elemental concentrations of radionuclides responsible for \( \dot{D}_\beta \) (Duller, 2008).
1.3 Luminescence signals within a cooling body of rock

It has long been known that luminescence signals are sensitive to temperature (Daniels et al., 1953). Indeed, thermoluminescence (TL) dating (stimulating the luminescence response by heating the sample rather than shining light upon it) was originally developed to determine the time since ceramics were fired (Aitken et al., 1964, 1968; Fleming et al., 1970) and has also been used in the study of hearth stones (Plachy and Sutton, 1982), burnt flint (Valladas and Valladas, 1987), and burnt stones (Mejdahl, 1983, 1985; Spencer and Sanderson, 1994).

Trapped electrons are, in other words, susceptible to detrapping by exposure to light or heat. Under first-order kinetics, a trapped electron has a lifetime, \( \tau \) (s), that exponentially decreases as the ratio of its depth beneath the conduction band, \( E \) (eV), divided by temperature, \( T \) (K), decreases (all scaled according to an attempt-to-escape frequency factor, \( s \) (s\(^{-1}\))) (Randall and Wilkins, 1945):

\[
\tau = s^{-1} \exp \left( \frac{E}{kT} \right)
\]

(1.4)

In the simple case of thermal-resetting, a luminescent mineral would be heated to a temperature such that the average trapping lifetime is less than the heating duration. For example, if we take the depth of the quartz TL peak centered at 325 °C (heating rate of 5 °C/s, UV emissions), the kinetic parameters \( E = 1.60 \) eV and \( s = 5.7 \times 10^{12} \) s\(^{-1}\); Spooner and Questiaux, 2000) can be used within Eq. 1.4 to predict the trap lifetime, \( \tau \), from 0 to 500 °C. The result is shown in Fig. 1.4. From this plot, we see that holding the sample at \( T > 300 \) °C would result in an average trap lifetime of < 1 minute, meaning that heatings lasting longer than this will deplete nearly all of these traps.

To consider a more general scenario, this concept of trapping lifetime should be considered alongside the opposite effect: the average time until an excited electron is captured by a trap. Here, it is conventional to reframe the discussion in terms of probabilities (trapping probability, detrapping probability), rather than lifetimes. The detrapping probability, \( p \) (s\(^{-1}\)), is defined as the inverse of the trap lifetime:

\[
p = 1/\tau = s \exp \left( - E/kT \right)
\]

(1.5)
Figure 1.4: The influence of temperature on trapping lifetime is calculated for the 325 °C TL peak within quartz (kinetic parameters from Spooner and Questiaux [2000]), a trap which exhibits simple, first-order kinetics.
Combining this expression with Eq. 1.3, we can describe the rate of change for a trap population as

\[
\frac{dn}{dt} = \frac{\dot{D}}{D_0} (N - n) - ns \exp \left( - \frac{E}{kT} \right)
\]

While this expression will be complicated by alternate detrapping pathways (e.g., quantum mechanical tunneling known to affect the main feldspar trap) or changes in trapping efficiency (e.g., competition from different trap sites), this simple form illustrates the balance between thermal detrapping and site filling that must be accounted for when considering the thermal evolution of a luminescence system.

Finally, the relationship between the trap population of interest and the measured luminescence signal deserves a brief description (see Chen and Pagonis, 2011, for a thorough treatment of this topic). As a preface to this description, the basic differences between optically- and thermally-stimulated luminescence should be detailed, which will clarify the purpose and meaning of the variety of luminescence signals which can be measured.

The Mott-Seitz mechanism (Seitz, 1939; Mott and Gurney, 1948) for electronic transitions within a semiconductor or insulator stipulates that the optical energy required for excitation into an excited trapping state or into the conduction band depends on the interatomic distance as shown in Fig. 1.5. The thermal energy required for activation (and thereby eventual radiative recombination) may be greater than or less than the optical energy required (Curie, 1963). More fundamentally, the differences in behavior can be described in terms of physical meanings. Optical excitation into the conduction band proceeds by the absorption of an incoming photon of some energy greater than or equal to the optical depth of the trap. The rate at which this absorption occurs depends on the flux of incoming photons (i.e., the power of stimulating light) scaled by the photoionization cross-section of the trap (which in turn depends on the stimulating wavelength and the degree of coupling to lattice vibrations) (Singarayer, 2002). By contrast, thermal activation into the conduction band occurs after coupling to one or more lattice vibrations (phonons) with a cumulative

1This scheme can be contrasted with the Schön-Klasens paradigm of discrete energy levels within the band gap (cf. Fig. 1.2 Schön, 1942 Klasens, 1946).
Figure 1.5: Two example configurational coordinate diagrams are shown for luminescence processes. a) Notice how the thermal energy required for excitation (e.g., into the conduction band) may differ from the optical excitation energy. (b) The emitted luminescence may have the same energy regardless of excitation type, or it may differ.
energy greater than the thermal depth of the trap (McKeever, 1985). Moreover, these effects can interact. For example, optical detrapping efficiency can be enhanced or diminished by increasing the temperature of the system (Bailey, 2001).

Given these complications, workers have developed many luminescence measurement techniques according to their manipulation of temperature and stimulating light intensity; these are shown in Fig. 1.6. Other types of luminescence measurements exist, for example, cathodoluminescence and radioluminescence, but these rely on stimulation mechanisms other than heat or light. While many of the signal shown in Fig. 1.6 were investigated in the early stages of this study, thermoluminescence ultimately proved to be best suited for our purposes and, with the exception of Chapter 3 which briefly considers the relationship between optical and thermal luminescence signals from feldspar, investigation will be limited to this signal.

1.4 Dissertation structure

The remainder of the dissertation is structured as follows:

Chapter 2 describes the construction of a dose-rate attenuator assembly which was incorporated into the existing luminescence reader and used to monitor the effect of irradiating feldspar samples at dose-rates ranging from $1.2 \times 10^{-1} - 8.7 \times 10^{-5}$ Gy/s. Chapter 3 discusses the relationship between the thermal and optical luminescence signals from feldspar samples. Chapter 4 introduces a novel technique for measuring the thermal trap depth, effective frequency factor, and kinetic order values for natural and regenerative TL signals. Most of this chapter was published in *Radiation Measurements* as Brown and Rhodes (2017).

Chapter 5 investigates the natural TL signals of samples extracted from three drill cores in sedimentary basins with low exhumation rates during the Quaternary. These samples experienced burial temperatures ranging from -4.5 to 60.2 °C. These shape of these signals (specifically, the position of the $T_{1/2}$ value) is controlled by both burial temperature and also isothermal conditions in the laboratory, an observation that is then explained in terms of the probable underlying kinetics. The majority of this chapter is in review at *Quaternary*
Figure 1.6: Different luminescence measurement techniques, categorized according to their use of temperature and light (in this case, infrared light), as well as their purpose.
Chapter 6 considers samples from transects across and along glacial valley in the Beartooth Mountains near Yellowstone National Park in MT. A simple single-aliquot regenerative (SAR) technique is demonstrated for the recovery of minimum cooling ages based on the dose-response of the $T_{1/2}$ value. These ages compare well with existing records of local glacial activity.

Chapter 7 develops a more robust multiple-aliquot additive dose (MAR) technique for evaluated the integrated $T - t$ history of samples from the rapidly-uplifting Yucaipa Ridge tectonic block, part of the San Bernardino Mountains in Southern California. This technique is based on the fractional saturation values of the natural TL curve, termed $\frac{n}{N}(T)$. The sensitivity of this technique to realistic cooling scenarios is evaluated and the MAAD TL signals are used to interpret the recent exhumational history of this block.
CHAPTER 2

Dose-rate effects

2.1 The importance of dose-rate in thermochronology

Whether a set of traps accumulate or lose electrons through time depends on the balance between the rate of free electrons produced by ionizing radiation, i.e., the dose-rate, $\dot{D}$, and the average probability per unit time of detrapping, $p$, which is the inverse of the trap lifetime, $\tau$. This has an interesting consequence. Imagine that all traps in a crystal were emptied and then subjected to geologic burial. After some time there would exist some trap types that were in ‘field saturation,’ meaning that the rate of trapping at geologic conditions is the same as the loss rate (Kars et al., 2008). Other traps will still be experiencing net accumulation. If this crystal were analyzed and the equivalent doses ($D_e$) were determined for all trap types, the $D_e$ values for accumulating traps would be the time since traps were empty and the $D_e$ values for the static traps would be the average trap lifetime, as illustrated by the following equation (Grün et al., 1999):

$$D_e = \dot{D} \cdot \tau \left[ 1 - \exp(-t/\tau) \right]$$  \hspace{1cm} (2.1)

In other words, the magnitude of the dose-rate controls which sites will be saturated and the degree of site saturation, usually expressed as $n/N$, is the target measurement in most luminescence thermochronology efforts, this one included.

This chapter first describes the construction of a simple attenuator assembly that can reduce the dose-rate of a standard Risø TL/OSL luminescence reader by almost five orders of magnitude. Next, the dose-rate delivered to the sample stage is measured using a synthetic microdosimeter crystal. Then, TL measurements following each of the different dose-rates
are compared and analyzed. Lastly, measurements of natural TL signals are compared as a function of geologic dose-rate.

2.2 Dose-rate attenuator

2.2.1 Design and assembly

The basic design is shown in Fig. 2.1 and the finished pieces are shown in Fig. 2.2. The lead and brass rings function as spacers (to lift the source assembly 3/16 inches farther away from the sample stage) and as radiation shields. Copper and zinc, the two components of the alloy brass, have atomic numbers \( Z \) of 29 and 30, respectively. Elements with lower \( Z \) values efficiently stop beta particles without generating much braking, or ‘Bremsstrahlung,’ radiation. For this reason, the \(^{90}\text{Sr}\) beta source in the luminescence reader is primarily shielded with brass. Our spacer nearest the source is brass also. The braking radiation that is produced can be stopped by high-\( Z \) material, in the case of the luminescence reader and our added spacer, lead.

The pieces were all designed in AutoCAD and machined in the Physical Sciences student machine shop at UCLA.

The three remaining pieces are aluminum discs, all 3/4-inch in diameter and with thicknesses of 1, 2, and 3 sixteenths of an inch (standard units were used for ease-of-use concerns when using the CNC mill to machine the pieces). Aluminum was chosen for several reasons: it is cheap, easy to machine, and can attenuate beta radiation over short distances. For example, the maximum energy emission of \(^{90}\text{Sr}\) is 2.28 MeV. Standard calculations can be done to determine the energy lost to excitation, ionization, and Bremsstrahlung radiation as an electron moves through an elemental material such as aluminum(pp. 144 - 154 [Toulalanidis, 1995]). This calculation reveals that, for the source to sample geometry of our luminescence reader, adding 4.8 mm (~3/16 in.) should, by attenuation alone, reduce this component of radiation energy received by the sample by more than a factor of \(10^2\).

The pieces were all designed in AutoCAD and machined in the Physical Sciences student machine shop at UCLA.

The instructions for mounting the modification onto the Risø automated luminescence
Figure 2.1: The basic design for the dose-rate attenuator pieces are shown. Note that, because of the default programming of the CNC end mill, the units for this figure are decimal inches.
Figure 2.2: The finished dose-rate attenuator pieces are pictured. From left-to-right: the lead spacer, the brass spacer (with holes to accommodate bolts), and the three aluminum attenuators that sit on top of the beryllium window in front of the beta source.
reader are shown in Fig. 2.3 and described briefly here (see also the Risø TL/OSL Reader Manual[1]). After turning off the Controller and the Reader, disconnect the nitrogen line to the beta source assembly (used to pneumatically bring the source into active position). Next, loosen the top two bolts to remove the aluminum helmet (only on found on newer models). The lead shielding can then removed, first the cap, then the sleeve (remove a bolt from the side to remove the sleeve; this bolt will not fit back in while the source is modified). After loosening two additional bolts, the irradiator assembly can be removed (the reader manual shows a method for placing this assembly within the removed and stacked lead shield). At this point, the brass spacer and optionally an aluminum spacer can be placed as shown in Fig. 2.3.

The whole apparatus can then be reassembled, with two adjustments. After placing the lead sleeve around the irradiator but before placing the lead cap, the lead spacer should be added. Before adding the aluminum helmet add the modification to the wheel as shown in Fig. 2.3. In our case, this is simply a hose clamp with electrical tape added to the proper thickness. This can be fastened to the rotating wheel as shown (depress the rod beneath the wheel to add the clamp) to overcome the safety mechanism (which senses whether the rod is depressed when the reader is given power).

2.2.2 Dose-rate determination

To determine the dose-rate delivered at the sample position, an Al₂O₃:C microdosimeter was used [McKeever et al., 2004]. These single crystal dosimeters exhibit a linear dose response after doses as low as 10⁻⁶ Gy [Akselrod et al., 1990] and have been utilized for the quantification of both environmental dose-rates [Bøtter-Jensen et al., 1997] [Kalchgruber and Wagner, 2006] and dose-rate within Risø TL/OSL luminescence readers [Kalchgruber et al., 2002].

Following [Bøtter-Jensen et al., 1997], samples were irradiated, preheated to 100 °C for

[1] At the time of writing, the manual can be downloaded here: http://www.nutech.dtu.dk/english/products-and-services/dosimetry/radiation-measurement-instruments/tl_osl_reader/manuals
Figure 2.3: Step-by-step instructions are shown for incorporating the dose-rate attenuator into a Risø beta source. The controller and reader should be powered off before modifying the instrument.
30 s, and then the OSL response (blue diodes) was detected in the UV band for 40 s. The background-subtracted dose-responses of a Al$_2$O$_3$:C microdosimeter are shown in Fig. 2.4. Each of the experimental setups is shown in a different color: the unmodified source shown in orange; the 3/16” spacer added (no attenuator) in purple; the 1/16” aluminum attenuator in front of the source in green; and the 2/16” and 3/16” attenuators shown in red and blue. With the exception of the shortest two exposure times with the thickest attenuator in place, all other dose-response points fall on a linear trend as shown. Because the dose-rate of the unmodified source is well known, the equivalent time required to produce, for example, the 1 s response can be used to calculate the corresponding dose-rate with the spacer and different attenuators in place. These are tabulated in Table 2.1 and range from 1.2 × 10$^{-1}$ to 8.7 × 10$^{-5}$ Gy/s. (These rates apply for grains mounted on stainless steel discs, as is used in the Table 2.1 experiment. For aluminum discs, these rates will be divided by a factor of 1.2. The reason for this difference is the relative difference in backscatter enhancement of the beta dose (e.g., Fig. 5.5 of Aitken, 1985).)

2.3 TL measurements following different dose-rates

2.3.1 Different laboratory dose-rates

2.3.1.1 Methodology

To examine the effect of laboratory dose-rate on TL signals, the following experiment was performed (Table 2.1). A single aliquot of sample J0170 was preheated to 500 °C for 10 s twice to remove the natural signal. Next, the aliquot was exposed to the unmodified $^{90}$Sr/$^{90}$Y beta source for 10 s ($D = 1.20$ Gy). This exposure time is long enough to produce a bright TL response but short enough to avoid prohibitively long exposure times at lower dose-rates.

Instead of measuring the resulting TL immediately after irradiation, however, the aliquot was held at room temperature for 5071 s. The reason for this delay is to keep the effective fading time equal for all dose-rate experiments. The concept of effective fading time (usually notated as $t^*$, as developed in Appendix F, Aitken 1985) arises from the fact that some
Figure 2.4: The blue-light stimulated luminescence response to various irradiation times with: no modification (orange); the spacer added, but no attenuator (purple); the 1/16- (green), 2/16- (red), and 3/16-inch (blue) aluminum attenuator in front of the $^{90}$Sr beta source. These measurements are used, along with the known dose-rate when the source is unmodified, to calculate the dose-rate delivered at the sample stage by the source with different modifications.
Table 2.1: Protocol to monitor dose-rate effects on TL signal.

<table>
<thead>
<tr>
<th>Step</th>
<th>Treatment</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Two preheats ($T = 500^\circ C$, 10 s)</td>
<td>Remove natural signal</td>
</tr>
<tr>
<td>2</td>
<td>10 s exposure to unmodified source (1.20 Gy)</td>
<td>Populate traps at $\dot{D} = 1.2 \times 10^{-1} \text{ Gy/s}$</td>
</tr>
<tr>
<td>3</td>
<td>Pause at room temperature for 5071 s</td>
<td>Effective fading time to 5074 s</td>
</tr>
<tr>
<td>4</td>
<td>TL at 5 $^\circ C$/s to 500 $^\circ C$</td>
<td>Measure TL signal</td>
</tr>
<tr>
<td>5</td>
<td>TL at 5 $^\circ C$/s to 500 $^\circ C$</td>
<td>Measure TL background</td>
</tr>
<tr>
<td>6</td>
<td>25 s exposure to source with spacer (1.20 Gy)</td>
<td>Populate traps at $\dot{D} = 4.9 \times 10^{-2} \text{ Gy/s}$</td>
</tr>
<tr>
<td>7</td>
<td>Pause at room temperature for 5065 s</td>
<td>Effective fading time to 5074 s</td>
</tr>
<tr>
<td>8</td>
<td>TL at 5 $^\circ C$/s to 500 $^\circ C$</td>
<td>Measure TL signal</td>
</tr>
<tr>
<td>9</td>
<td>TL at 5 $^\circ C$/s to 500 $^\circ C$</td>
<td>Measure TL background</td>
</tr>
<tr>
<td>10</td>
<td>158 s exposure to attenuated (1/16” Al) source (1.20 Gy)</td>
<td>Populate traps at $\dot{D} = 7.6 \times 10^{-3} \text{ Gy/s}$</td>
</tr>
<tr>
<td>11</td>
<td>Pause at room temperature for 5016 s</td>
<td>Effective fading time to 5074 s</td>
</tr>
<tr>
<td>12</td>
<td>TL at 5 $^\circ C$/s to 500 $^\circ C$</td>
<td>Measure TL signal</td>
</tr>
<tr>
<td>13</td>
<td>TL at 5 $^\circ C$/s to 500 $^\circ C$</td>
<td>Measure TL background</td>
</tr>
<tr>
<td>14</td>
<td>Repeat steps 2 - 5</td>
<td>Check for reproducibility</td>
</tr>
</tbody>
</table>
amount of athermal fading occurs during irradiation. A mathematical convenience helps us out of this problem. For any continuous irradiation starting at some time $t_2$ and ending at $t_1$ (time before some luminescence measurement), the effective fading time for that dose population is defined as $t^* = t_1 + (t_2 - t_1)/e$ (e.g., Fig. 1 of [Auclair et al., 2003]). To deliver a dose of 1.20 Gy with the thickest attenuator (3/16”) in place would require an exposure time of 34 hrs; I have not yet performed this experiment. The next thickest attenuator (2/16”) produces a dose of 1.20 Gy after 13793 s (just under 4 hours). The effective fading time immediately after irradiation would be $t^* = (13793 - 0)/e = 5074$ s. Therefore, to normalize the fading response at all dose-rates, room temperature pauses were calculated to produce an effective fading time of 5074 s for all samples.

For example, with the 1/16” aluminum attenuator in front of the beta source, the dose-rate at the aliquot position is $\dot{D} = 7.6 \times 10^{-3}$ Gy/s, meaning that 158 s are required to produce 1.20 Gy. The effective fading time at the end of irradiation is $(158 - 0)/e = 58$ s. Therefore, a pause of $5074 - 58 = 5016$ s was added following irradiation to produce an effective fading time of 5074 s (Fig 2.5).

### 2.3.1.2 Results

The results of this experiment (Table 2.1) are shown in Fig. 2.6. The most obvious effect is that the lowest dose-rate has produced the brightest TL signal. A comparable reduction of TL intensity with increasing dose-rate has been observed previously in Brazilian quartz irradiated with $^{60}$Co γ-rays (factor of 5 decrease in intensity over the range $\dot{D} = 1.4 \times 10^{-3} - 3.3 \times 10^{9}$ Gy/s [Groom et al., 1978]. [Hsu and Weng, 1976] observed a sudden shift to lower TL intensity around $\dot{D} > 2 \times 10^{-7}$ Gy/s for various synthetic dosimeters (LiF, CaSO$_4$:Dy, CaSO$_4$:Tm, CaF$_2$:Dy). [Valladas and Ferreira, 1980] noticed that dose-rate effects in quartz (massive and granular) varied according to emission bands. By dosing samples at with $^{60}$Co and $^{137}$Cs ($1.5 \times 10^{-1}$ and $1.4 \times 10^{-3}$ Gy/s) observed that for the higher $\dot{D}$ value, the TL brightness increased in the ultraviolet band, decreased in the blue band, and, in the green band, brightness increased above about 350 °C and decreased below.
Figure 2.5: (Top panel) The beta source exposure times are shown according to the corresponding dose-rates. The same dose of 1.20 Gy was given for all $\dot{D}$ values. The effective fading time $t^*$ for all irradiations is shown to be equal, at 5074 s. The light blue vertical line is when fading effectively began and the light green line is when the TL measurement began.
Figure 2.6: The background-subtracted TL signals resulting from a dose of 1.20 Gy and an effective delay time of 5074 s are shown for all experimental dose-rate values (for \( \dot{D} = 0.1 \) Gy/s the solid curve ‘A’ was measured at the start of the protocol and dotted curve ‘B’ was measured at the end of the protocol; see Table 2.1), both in absolute intensity (a) and normalized (b).
By contrast, Kvasnička [1983] measured static and increasing TL responses for increasing
dose-rates in the 315 °C TL peak of natural Brazilian crystalline and milky quartz, respec-
tively. These samples were first annealed at 500 °C for 1 hr and then irradiated to 2.5 Gy
with $^{60}\text{Co} \gamma$-rays at $\dot{D}$ value of $2.10 \times 10^{-5}$ or $2.10 \times 10^{-2}$ Gy/s. These values are comparable
to our study: our 2/16" Al attenuator delivers $\dot{D} = 8.7 \times 10^{-5}$ Gy/s, with a spacer only
$\dot{D} = 4.9 \times 10^{-2}$ Gy/s, and I administered 1.20 Gy.

Perhaps the simplest explanation offered for changing TL brightness in quartz with in-
creasing $\dot{D}$ values was given by McKeever et al. [1980]. They demonstrated that, for a
one-trap-one-recombination-center (OTOR) situation, recombination during irradiation (i.e.,
free electrons are allowed to either trap or recombine) could produce either an increase or
decrease in TL brightness, depending on the ratio of relative probabilities for trapping or
recombination. This effect would also result from other types of trapping competition (e.g.,

The other interesting result is that I do not observe the expected shift in the leading edge
of emissions. There do seem to be some first-cycle effects, as evidenced by the different TL
responses to $\dot{D} = 0.1$ Gy/s at the beginning and end of the measurement sequence (notice
also the evolving behavior at higher temperatures, present in the first and second dose-
measurement cycles: steps 2 - 9 of Table 2.1). By considering only the final TL response,
I observe remarkable consistency between the intensity-normalized emissions (Fig. 2.6b).
This stands in contrast to our observation of a shifting $T_{1/2}$ value at geologic dose-rates, as
presented in the following section.

2.3.2 Different geologic dose-rates

Recalling equation 5.12 (rewritten here for simplicity)

$$\frac{dn(r)}{dt} = \frac{\dot{D}}{D_0} \left( N(r) - n(r) \right) - n(r) \exp \left( - \frac{\Delta E}{k_B T} \right) \frac{P(r) s}{P(r) + s}$$

we can see that the distance $r$ between the electron trap and the nearest recombination center
influences site stability. Nearer sites are more likely to recombine and will therefore have a
shorter mean lifetime. This effect is enhanced at higher temperatures as more electrons are
excited to higher-energy states where tunneling becomes more probable (see section 5.3.1 for a full description of this behavior). This temperature dependence is the underlying principle for feldspar TL thermochronology.

Assuming that all of the blue emissions\textsuperscript{2} from feldspar TL between measurement temperatures of about 130 - 330°C (Krbetschek et al., 1997) or below \(\sim 410\) °C (estimate of high-temperature dosimetric trap; Murray et al., 2009), are from the same defect (i.e., trap) and that the only difference between the TL measured at different temperatures is the stability of those detrapping sites, we can approximately describe the thermal stability of the bulk TL emissions by the position of the \(T_{1/2}\) metric (Fig. 2.7). Because the TL measurement temperature at which emissions become significant is a function of the occupied sites of minimum stability, and because the \(T_{1/2}\) value is a convenient and (usually) unambiguous measurement, I treat measured \(T_{1/2}\) values as representing the characteristic (minimum) thermal stability of the feldspar bulk TL signal.

In the case of widely varying steady-state temperatures, like in the drill core samples of Chapter 5, \(T_{1/2}\) values are shown to largely be a function of long-term rock temperature (see Figs. 5.1 and 5.3). If, however, a suite of bedrock samples have been held at a similar temperature, their natural \(T_{1/2}\) values may reflect higher-order influences (dose-rate variations, for example).

The bedrock samples collected from Rock Creek glacial valley lend themselves to this analysis. Collected from within a single valley and all from near the ground surface, these samples experienced roughly the same mean annual air temperature since their exposure (dry adiabatic lapse rate should result in a difference of about 8 °C between the highest- and lowest-elevation samples considered in this section). Furthermore, the geologic dose-rates for these samples vary by a factor of 4.9, an unusually high difference.

The natural \(T_{1/2}\) values measured at a heating rate of 5 °C/s are plotted as a function of geologic dose-rate (\(\dot{D}\)) in Fig. 2.8. The sizes of the error bars are determined by the between-aliquot variation, as TL curves were measured from three discs for most samples (only two

\textsuperscript{2}When measuring TL, I use a Schott BG3-BG39 filter combination which transmits between \(\sim 325 - 475\) nm.

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Figure 2.7: Thermoluminescence curves that would result following preheats of increasing temperature or duration are shown. The stability of the least stable occupied traps giving rise to the blue curve can be described with the $T_{1/2}$ metric (lower of the two measurement temperatures at half-maximum intensity) shown in red. Those least stable traps would have some mean lifetime $\tau$. In green are curves with lesser minimum lifetimes and in pink are curves with greater minimum lifetimes.
Figure 2.8: The $T_{1/2}$ values from natural TL curves ($\beta = 5 \text{ °C/s}$) show a linear dependence upon the geologic dose rate as predicted by theory: at higher dose-rates, the $T_{1/2}$ value for the leading edge of TL emissions shifts to lower temperatures. The interpretation is that traps of lower stability can remain occupied due to the high dose-rate. The vertical bars represent 1σ errors.

\[ T_{1/2} = (-2.96 \pm 0.56) \dot{D} + (244.7 \pm 2.8) \]
\[ \chi^2 = 9.50; \text{ dof} = 10 \]
discs were measured for samples J1007 and J1010). Samples J0999, J1008, and J1009 were excluded from this analysis, as the location of $T_{1/2}$ was ambiguous. A linear relationship is found, and as expected, as $\dot{D}$ increases the natural TL curves exhibit lower $T_{1/2}$ values. The interpretation is that these less stable sites (lower $T_{1/2}$ values) remain occupied because there are more free electrons roaming the lattice at any given moment due to the greater flux of ionizing radiation.

The best-fit line for the dependence of $T_{1/2}$ on $\dot{D}$ is given as

$$T_{1/2} = (-2.96 \pm 0.56)\dot{D} + (244.7 \pm 2.8).$$

(2.2)

The slope of this line, $-2.96 \pm 0.56$ °C Gy$^{-1}$ ka$^{-2}$ is particularly noteworthy, suggesting the magnitude of this dose-rate dependence. As a side note, the range in dose-rates observed for these samples is probably close the natural variation expected for bedrock feldspars, so this plot may prove useful in quantifying the maximum dependence of $T_{1/2}$ on dose-rate for a suite of samples.

### 2.4 Conclusions

Geologic and laboratory dose-rates typically vary by a factor of about $10^9$, so it is unsurprising that we observe different TL phenomena at both extremes. By placing aluminum attenuators in front of our radiation source, I was able to examine the effects of reducing the laboratory dose-rate by a factor of $10^3$. The TL curves following irradiation show remarkable similarity in their position and shape, an unexpected result. At the lowest laboratory dose-rate ($\dot{D} = 8.7 \times 10^{-5}$ Gy/s) there was an increase in TL intensity, suggesting that higher dose-rates may produce trapping competition effects.

The natural TL signals resulting from geologic dose rates of 1.7 - 8.4 Gy/ka show no relationship between $\dot{D}$ and brightness. There is, however, a linear relationship between $\dot{D}$ and the position of the leading edge, $T_{1/2}$. The slope of the best-fit line, $-2.96 \pm 0.56$ °C Gy$^{-1}$ ka$^{-2}$, provides a first approximation at the magnitude of this effect. This should prove to be a useful correction when differentiating between thermal and non-thermal controls on
natural TL shapes.
CHAPTER 3

Relating thermal and optical signals in feldspar luminescence

Understanding the relationship between feldspar IRSL and TL is of practical importance, as luminescence protocols often incorporate both thermal and optical treatments. In the context of feldspar luminescence thermochronology, most recent studies have employed a preheated IRSL signal (e.g., Guralnik et al., 2015a; King et al., 2016a,b). While more thorough investigations of these interactions can be found in other studies (Duller and Wintle, 1991; Duller, 1994, 1995; Murray et al., 2009; Wang and Wintle, 2013), this chapter investigates the effects of IR stimulation on the subsequent TL measurements as well as the reduction of IRSL intensity by preheating, in an effort to understand the implications for thermochronology protocols.

3.1 Reduction of regenerated TL signal by IR stimulation

To test the effect of IR stimulation following a beta dose, the following measurements were made using three aliquots of sample J0165. First, the discs were given a beta dose of 12.1 Gy and then held at 50 °C for 100 s before measuring the TL curves. This was repeated for hold temperatures of 150, 250, and 350 °C. Next, the discs were given the same dose, then stimulated with IR diodes for 100 s at 50 °C before measuring the TL signals. This was repeated for the three higher temperatures. Representative results for one of the aliquots are shown in Fig. 3.1(a).

By first measuring the TL signals following the isothermal loss at $T = 50$, 150, and 250 °C for 100 s, one can isolate the effect of IR stimulation at various temperatures (by subtracting
the stimulated-loss curves from the thermal-loss curves). This is shown in Fig. 3.1(b). The most salient feature of this experiment is that while IR stimulation preferentially depletes the lower temperature regions of the glow curve, the region of loss is broadly distributed. This broad region of loss has been recorded before (Murray et al., 2009).

### 3.2 Reduction of regenerated IR signal by heat treatments

The same aliquot was then given the same dose of 12.1 Gy, but instead of monitoring the effect of IR stimulation on the TL signal, I monitored the effect of heating on the IR signal. The aliquot was irradiated and then heated for 100 s at $T = 50, 150, 250, \text{ or } 350 \degree C$ before measuring the IRSL response for 100 s; the results are shown in Fig. 3.1(c).

Unsurprisingly, the higher the preheat temperature, the less subsequent IRSL signal is produced. More interesting is the change in shape: after 50 or 150 $\degree C$ for 100 s, the initial responses are of a similar magnitude ($I_0 \sim 9E3 \text{ cts/0.4s}$), but the post-150 $\degree C$ IRSL decays to a lower level by 100 s. The shape of decay after 150 and 250 $\degree C$ is similar, but after 350 $\degree C$ for 100 s, the IRSL decays to a constant background level after only about 20 s, suggesting that the IRSL source trap has been mostly emptied by this heat treatment.

Finally, one can compare the decrease in luminescence intensity following these treatments. Figure 3.1(d) shows the integrated luminescence response following IRSL (circles) or heating (diamonds). While a comparison between the absolute values of TL emissions and IRSL emissions is dubious, a comparison of depletion rates as a function of hold temperature is illustrative. Infrared stimulation, for example, reduces subsequent luminescence emissions more rapidly at lower temperatures, whereas the reduction in IRSL by preheating to higher temperatures appears to be linear.

### 3.3 Reduction of natural TL signal by IR stimulation

I tested the effect of IR stimulation on the natural signal by comparing six unbleached aliquots of J0165. In groups of two, the aliquots were either: a) stimulated with IR at 50
°C for 500 s; b) stimulated with IR at 290 °C for 500 s; or c) untreated (the two chosen hold temperatures represent the typical range for IRSL or post-IR IRSL sediment dating protocols). Following these treatments, the TL signals were measured at a heating rate of 5 °C/s (Fig. 3.2). Though the aliquots contained roughly the same number of grains, no sensitivity correction was performed.

Two observations can be made about Fig. 3.2. First, IR$_{50}$ stimulation does not significantly deplete the natural signal, an effect which has been measured previously and which may be especially prominent in orthoclase (Duller, 1995). Second, phototransfer seems to occur with charge present above the 50 °C hold temperature following IR stimulation. This phototransfer effect has also been documented with exposure to sunlight and for regenerated signals (Duller, 1995; Murray et al., 2009; Thomsen et al., 2011; Wang and Wintle, 2013).

### 3.4 Reduction of natural IR and BLSL signals by heat treatments

The thermal stability of the natural IRSL and post-IR IRSL signals was the subject of the next experiment. Two natural aliquots of J0165 were heated to 425 °C at 5 °C/s and then cooled to room temperature. The discs were then stimulated with IR diodes for 500 s at 50 °C (Fig. 3.3(a)) and then for 500 s at 290 °C (Fig. 3.3(b)). Two additional aliquots were stimulated with blue diodes ($\lambda = 470 \pm 20$ nm) for 500 s. These decay curves are not shown, though the signals were comparable to the IR$_{50}$ decays, with initial intensities at 200 and 500 counts per channel.

### 3.5 Phototransfer of preheated natural samples

The natural aliquots of J0165 that were heated to 425 °C and then stimulated with infrared or blue diodes for 500 s were then heated to 500 °C and the resulting TL curves are shown.
Figure 3.1: (a) An aliquot of sample J0165 (previously heated to 500 °C) was given a beta dose of 12.1 Gy and then either preheated or stimulated (IR diodes) for 100 s at a temperature of 50, 150, 250, or 350 °C. The remaining TL signal was measured at β = 5 °C/s. (b) By subtracting the post-IR glow curves from the post-preheat glow curves, I produce these four curves which represent the effect of IR stimulation on the TL glow curves and not the effect of isothermal loss. Whether this loss by stimulation is thermally-assisted, however, is not evaluated here (i.e., stimulation at higher temperatures may be more efficient). (c) The same aliquot is given the same dose of 12.1 Gy and is held at 50, 150, 250, or 350 °C for 100 s before measuring the remaining IRSL intensity. (d) The measured intensities following IRSL or preheating are plotted as a function of the initial hold temperature. To illustrate the meaning of these symbols, the shaded blue region in panel (b) is represented by the blue circle, and the shaded green region in (c) is represented by the green diamond.
Figure 3.2: To examine the effect of IR stimulation on the natural TL signal, I consider six unbleached aliquots of sample J0165, divided into pairs. Aliquots one and two (purple and green) are stimulated with IR diodes for 500 s at 50 °C (first 200 s shown in a). Aliquots three and four (dark blue and orange) are untreated. Aliquots five and six (red and light blue) are stimulated at 290 °C for 500 s (first 200 s shown in b). Finally, the TL signals are measured at 5 °C/s (c and d). Infrared stimulation at 50 °C appears to phototransfer charge to lower temperatures. Neither stimulation temperature appears to significantly deplete the natural glow curve after 500 s, aside from the isothermal loss induced by holding the discs at 290 °C.
in Fig. 3.4. The remarkable feature of these curves is the phototransfer that occurs during stimulation. The light-blue and red curves show the TL curves that result from heating to 425 °C; there is negligible signal up to about 300 °C measured during the subsequent TL. After heating and blue-light stimulation, however, an increase in TL signal of nearly two orders-of-magnitude is observed. This suggests that stimulation redistributes (i.e., phototransfers) charge to less stable traps (the stability threshold is controlled by the stimulation temperature; stimulation at 50 °C will never allow transfer into traps that would empty at 50 °C, for example).

3.6 Discussion and Conclusions

Feldspar thermochronology protocols that monitor an IRSL signal measure luminescence resulting from natural and regenerated trap populations that have been heated prior to stimulation. The primary reason for this preheat is to remove the unwanted lower-temperature charge populations, that are filled during regenerative doses but which fade quickly and are not found in natural signals (Duller, 1994; Thomsen et al., 2008). This preheat must also be applied to the natural signal to avoid differential thermal sensitization (Kars et al., 2014). An unintended consequence is that natural charge may be redistributed during this heating.

After preheating, the sample is stimulated at a low temperature, usually 50 °C. This offers a second opportunity for trapped charge to redistribute to other sites. If the low-temperature signal is the only measured signal, this does not matter. If, however, subsequent IRSL measurements are made at higher temperatures (e.g., the post-IR IRSL, or the multiple-elevated-temperature post-IR IRSL signals; Buylaert et al., 2009; Li and Li, 2011), this is significant, because the measured signals come from, at least in part, sites which were not filled naturally, but were filled by phototransfer. Our results illustrate how this effect could manifest as a redistribut ed TL curve following low-temperature IR stimulation (e.g., Fig. 3.2c) or as a robust post-IR IRSL signal following heating to 425 °C. While heating to this temperature should deplete this post-IR IRSL population, the region between the two sets of curves in Fig. 3.2d, the initial IRSL phototransfers charge that can then be measured during
Figure 3.3: Two aliquots of J0165 were heated to 425 °C at 5 °C/s and then cooled to room temperature. After this heating, the aliquots were stimulated at 50 °C for 500 s with IR diodes (a) and then again at 290 °C for 500 s (b). Notice that although the IR$_{50}$ signal is almost entirely removed by this preheat, the subsequent post-IR$_{50}$ IR$_{290}$ signal remains robust.
Figure 3.4: Following a heating at 5 °C/s to 425 °C, separate aliquots of J0165 are: immediately measured (blue and red curves); stimulated with blue light at 50 °C for 500 s (tan and salmon); or stimulated with infrared diodes at 50 and then 290 °C for 500 s each (yellow and light green) before measuring the shown TL curves. Notice how stimulation with blue light transfers charge into less stable traps (phototransfer).
post-IR IRSL (this latter effect is similar to that described by Wang and Wintle (2013)).
The degree to which this phototransferred population comprises the high-temperature signal
weakens the argument that such a signal represents charge naturally-located in more stable
sites.

The broad depletion of the TL signal by IR stimulation has been observed before (Duller,
1994). Despite the reduction in subsequent TL measurements, the IRSL trap is not signifi-
cantly emptied by heatings below, for example 350 °C for 100 s (Fig. 3.1), suggesting that
the IRSL does not derive from these regions in the TL curve that are depleted during IR
stimulation. One hypothesis is that the same recombination centers are used (Murray et al.,
2009), but this remains an open area of investigation.

The central observation from this chapter is that the act of heating or photostimulating
a sample prior to measurement depletes but also redistributes the trapped charge popula-
tion. In that regard, TL may be the preferable measurement over IRSL or post-IR IRSL
techniques, as emitted luminescence derives from the naturally-occupied sites and includes
neither phototransferred nor thermally-transferred contributions.
CHAPTER 4

Determining the thermal trap depth within alkali feldspars

4.1 Introduction

One critical parameter in understanding how the feldspar luminescence system will evolve in different thermal scenarios is the thermal activation energy required for recombination (E-value). A number of measurements can be used to constrain this parameter under first-order kinetics; however, in the case of feldspar luminescence, which exhibits a continuum of thermoluminescence (TL) signals (Grün and Packman, 1994; Visocekas et al., 1996) and is generally considered to exhibit non-first-order recombination kinetics (Ankjaergaard et al., 2006; Jain and Ankjaergaard, 2011), the determination of this parameter is not straightforward, nor is it necessarily a single trap being accessed during a TL measurement (Balescu and Lamothe, 1992; Murray et al., 2009).

The basic obstacle that must be overcome in order to measure the E-values of a sample, is that TL glow curves (following natural or laboratory irradiations) comprise overlapping emissions of different stability. For potassium-rich feldspars, this is complicated by the presence of a second TL peak at higher temperatures (centered around 330 °C for $\beta = 5$ °C/s, where $\beta$ is the experimental heating rate), such that the measured glow curve contains a broad, asymmetric peak at lower temperatures (apex near 100 °C), and a high-temperature peak (or two peaks; e.g., Murray et al., 2009), often embedded within the first (Duller, 1997). This range of stability in the broad, lower-temperature emission has been interpreted as representing multiple, discrete trap depths (Strickertsson, 1985; Kirsh et al., 1987) or a continuum of trap depths (Sanderson, 1988). Alternately, a continuum of recombination
distances may produce this behavior (Jain et al., 2012). Pagonis et al. (2014) recently concluded that either mechanism could produce the observed TL data. Regardless, to measure the kinetic properties for a portion of a feldspar TL glow curve (e.g., a single trap depth or a limited range of recombination distances), one must isolate that particular emission, either experimentally or mathematically.

To determine the thermal trap depths of the dosimetric traps producing the TL or IRSL signals, workers have relied chiefly upon: the initial rise method (hereafter, IRM), usually in conjunction with the fractional glow curve method (hereafter, FGC; Strickertsson 1985; Visocekas et al. 1996; Chruścińska 2001); isothermal loss measurements (Sanderson 1988; Guralnik et al. 2015a); and curve fitting methods (Pagonis et al. 2014; Jain et al. 2015) (for a full discussion of conventional methods, see pp. 101 - 130 of Chen and McKeever 1997). The following incomplete list of the resulting $E$-values can be broadly categorized as either singular, continuous, or multiple and discrete. The discrete estimates for the IRSL source trap include >1.5 (Jain and Ankjaergaard 2011), 1.66 (Li and Tso 1997), 1.72 (Li et al. 1997), 1.71 ± 0.08 (Murray et al. 2009), 1.92 - 2.06 (Li and Li 2013), and ~2 (Jain et al. 2015) eV. Pagonis et al. (2014) estimated a continuum of depths from 1.1 to 1.8 eV in plagioclase; Strickertsson (1985) assumed first-order kinetics to fit six TL peaks between 0.76 and 1.80 eV; and Kirsh et al. (1987) estimated five distinct peaks, ranging from 0.70 to 1.39 eV.

In this chapter, I estimate the apparent thermal activation energies responsible for natural and laboratory TL signals in feldspar crystals extracted from bedrock samples. First, I apply the initial rise method, the various heating rates method, and the fractional glow curve technique. Second, I develop a new $E$-value estimation technique based on the isothermal decay of TL curves: the post-isothermal TL (pI-TL) method. This method quantifies (by glow curve subtraction) the loss between hold times at various temperatures. By doing so, I quantify not only the magnitude of isothermal decay but also the shape of the TL signal that would have resulted during thermal stimulation. In other words, those emissions which are of lesser stability are stripped away, allowing for peak shape analysis of a narrow range of thermal stabilities. Finally, the pI-TL results are discussed in terms of recombination
kinetics, including the variation in kinetic order and frequency factor.

4.2 Sample composition

Electro-probe microanalysis (see section [B]) reveals the compositions of the feldspar samples discussed in this chapter, which are listed in Table 4.1. The analyzed grains of J0165 are K-feldspars, with an average composition of Or$_{89}$. Sample J0995 is high albite, An$_{0.1}$. Samples J0999 and J1001 both exhibit perthitic textures. In sample J0999, zones alternate between average compositions of An$_{25}$ and Or$_{96}$ and J1001 alternates between An$_{8}$ and Or$_{96}$.

4.3 Determining thermal trap depths in K-feldspar

The terms used throughout this thesis are described in Table 4.2.

4.3.1 Initial rise method

The initial rise method (IRM) plots the natural log of the normalized TL intensity as a function of the inverse temperature, analogous to an Arrhenius plot. If the concentrations of trapped electrons and recombination centers are effectively constant (a reasonable assumption for the low-temperature region of a stimulation curve), then the TL intensity with temperature should go as:

$$I(T) \propto \exp \left( -\frac{E}{k_B T} \right),$$

which implies that a straight line fitted to ln($I(T)$) plotted against 1/$T$ should have a slope of $-E/k_B$ ([Chen and Kirsh 1981](p.148)). The results of the IRM are shown for K-feldspar extract of Yucaipa Ridge bedrock sample J0165, for the natural luminescence signal (Figs. 4.1 and 4.3(a)) and following a laboratory beta dose of 64 Gy (Figs. 4.2 and 4.3(b)). A heating rate of 0.1 °C/s was used to minimize errors associated with thermal lag. Three aliquots were used in both cases and remarkable inter-aliquot consistency was found. The apparent activation energies of the natural (1.23 eV) and regenerative (0.83 eV) signals differ substan-
Table 4.1: Composition of feldspar samples discussed in this chapter, as determined by electron-probe microanalysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>n</th>
<th>Endmember composition</th>
<th>Elemental composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>An (mol%)</td>
<td>Ab (mol%)</td>
</tr>
<tr>
<td>J0165</td>
<td>4</td>
<td>0.3</td>
<td>10.5</td>
</tr>
<tr>
<td>J00995</td>
<td>4</td>
<td>0.1</td>
<td>99.6</td>
</tr>
<tr>
<td>J0999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-rich zones</td>
<td>3</td>
<td>18.5</td>
<td>78.5</td>
</tr>
<tr>
<td>K-rich zones</td>
<td>2</td>
<td>0.0</td>
<td>3.6</td>
</tr>
<tr>
<td>J1001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-rich zones</td>
<td>3</td>
<td>8.0</td>
<td>90.3</td>
</tr>
<tr>
<td>K-rich zones</td>
<td>3</td>
<td>0.1</td>
<td>3.8</td>
</tr>
</tbody>
</table>
Figure 4.1: (a) - (d) Thermoluminescence curves from separate natural aliquots are measured at the shown heating rates. The measurement temperatures of the maximum TL intensity at different heating rates are used to produce Fig. 4.3(c). The initial rise region of the TL curves measured at dT/dt = 0.1 °C/s are fitted as shown in Fig. 4.3(a).
Figure 4.2: (a) - (c) Three different aliquots of sample J0165 are given a beta dose of 64 Gy and then heated at different rates. The measurement temperatures of the maximum TL intensity at different heating rates are used to produce Fig. 4.3(d). (d) The initial rise region of these TL curves (dT/dt = 0.1 °C/s) are fitted as shown in Fig. 4.3(b).
Figure 4.3: Apparent thermal trap depths for sample J0165 are calculated using the initial rise method (natural signal in (a) and regenerative signal after 64 Gy in (b)) and the various heating rates method (natural in (c) and 64 Gy in (d)). Note that the values calculated with the various heating rates method (1.16 and 0.78 eV) are slightly lower than those from the initial rise method (1.23 and 0.83 eV).
Table 4.2: Nomenclature used in this chapter.

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>Thermal trap depth</td>
</tr>
<tr>
<td>$s$</td>
<td>Frequency factor</td>
</tr>
<tr>
<td>$b$</td>
<td>Kinetic order</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant ($8.617 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$)</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Temperature at maximum intensity</td>
</tr>
<tr>
<td>$T_{1/2}$</td>
<td>Temperature at half-maximum intensity</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Heating rate</td>
</tr>
<tr>
<td>IRM</td>
<td>Initial rise method</td>
</tr>
<tr>
<td>VHRM</td>
<td>Various heating rates method</td>
</tr>
<tr>
<td>FGC</td>
<td>Fractional glow curve</td>
</tr>
<tr>
<td>pI-TL</td>
<td>Post-isothermal TL</td>
</tr>
</tbody>
</table>
tially, with the $E$-value following 64 Gy being far too shallow to retain electrons for longer than a few days at room temperature.

4.3.2 Various heating rates method

The various heating rates method (VHRM) exploits the fact that the temperature of maximum TL emission intensity ($T_m$) can be expressed in terms of the heating rate, $\beta$:

$$\beta = \frac{(sk_B/E)T_m^2 \exp \left(-\frac{E}{k_BT_m}\right)}{k_B},$$

so that the plot of $\ln(T_m^2/\beta)$ versus $(1/T_m)$ can be fitted with a straight line of slope $-E/k_B$.

To measure the apparent trap depth of the natural signal, three aliquots were heated for each heating-rate: 0.1, 0.5, 1, 5, and 10 °C/s. For the apparent $E$ value after 64 Gy, the same 3 aliquots were heated at 0.1, 0.3, 1, 3, and 10 °C/s. The resulting $E$ values of 1.16 and 0.78 eV are shown for the natural (Figs. 4.1 and 4.3(c)) and regenerative (Figs. 4.2 and 4.3(d)) signals.

4.3.3 Fractional glow curve analysis

To probe multiple traps of similar depths (e.g., a continuum of depths or tunneling distances), researchers have developed the fractional glow curve (FGC) (Rudlof et al., 1978; Kirsh et al., 1987), which involves a series of preheats to progressively higher temperatures. After holding at a given temperature, the sample is cooled before heating to a slightly higher hold temperature and so on. In this way, the lowest temperature region is investigated (and thereby emptied) before the next-highest temperature region is investigated, thereby minimizing overlap from the lower-temperature region.

Although recent feldspar models (Poolton et al., 1995; Jain and Ankjaergaard, 2011) do not require a distribution of trap depths, the distribution in sub-conduction-band recombination distances should result in a similar effect of overlapping TL peaks (Jain et al., 2012). Therefore, the FGC for a single aliquot of J0165 was measured by first administering a dose of 12.8 Gy, then heating the sample at 5 °C/s to a hold temperature of $T$ °C for 100 s, with $T$
Figure 4.4: An aliquot of sample J0165 was given a beta dose of 12.8 Gy and then heated at 5 °C/s to a hold temperature of $T$ °C for 100 s, with $T$ ranging from 20 to 500 °C in increments of 20 °C. This measurement is known as a fractional glow curve.
Figure 4.5: (a) Normalized thermoluminescence intensity plotted against inverse temperature for TL curves measured from $T = 60$ to $320 \degree C$ in increments of $20 \degree C$ (sample J0165). (b) The data in (a) are fitted to calculate $E$-values for each of the TL curves within the fractional glow curve experiment.
ranging from 20 to 500 °C in increments of 20 °C (Fig. 4.4). Unfortunately, at \( T > 320 \) °C, the signal intensity was similar in magnitude to the thermal background, precluding analysis beyond this point. The initial rise regions of the individual heating steps following a single beta dose of 64 Gy (Fig. 4.5(a)) were then fitted with a straight line having a slope of \(-E/k_B\) (see section 4.3.1). These \( E\)-values are plotted against the corresponding hold temperature (Fig. 4.5(b); cf. Fig. 3.14 of Chen and McKeever [1997]).

Two observations can be made about Fig. 4.5(b). First, a relationship seems to exist between the final temperature and the \( E\)-value, representing a gradation in apparent site stability, perhaps due to increasing recombination distances (if the \( E\)-values are artifacts), or perhaps deeper traps are progressively accessed (if the \( E\)-values are real). Second, this linear increase in FGC \( E\)-values (0.97 - 1.51 eV) extends past the trap depth of the natural TL signal as calculated with the IRM and VHRM results (1.23 and 1.16 eV, respectively) (Fig. 4.3(a) and (c)).

4.3.4 Post-isothermal TL (pI-TL) curve analysis

An alternate approach is to monitor how the TL shape changes following isothermal treatments of various durations. For analysis of the regenerative signal, the same aliquot of sample J0165 was repeatedly given the same dose of 12.8 Gy and then held at \( T \) °C for \( t \) s, where \( T \) ranged from 100 to 350 °C in increments of 50 °C, and \( t = 0, 3, 10, 30, 100, 300, 1000 \) s. Following each isothermal treatment, the aliquot was cooled to room temperature before a TL measurement at 5 °C/s to 500 °C. These TL curves are shown with linear and logarithmic y-axes (Fig. 4.6(a) and inset, respectively). The advantage of this approach is based upon the ability to isolate the luminescence emitted during hold-times by subtracting one TL curve from another. In other words, each subtracted curve represents the pseudo-TL curve that would be depleted during that isothermal treatment. Fig. 4.6(b) shows the regenerative TL lost during the hold time of \( t = 3-10 \) s, 10-30 s, and so on, for all the hold temperatures.

For analysis of the post-isothermal TL natural signals, a multi-aliquot approach is nec-
essary, where each heat treatment is performed on a different unbleached natural aliquot of sample J0165 (Fig. 4.7(a)). The TL emissions of each aliquot were normalized to a subsequent test dose response (maximum TL intensity following a dose of 1.3 Gy). Because the natural glow curve is not significantly eroded by the lower temperature treatments, the isothermal treatments of the natural signals were limited to $T = 250, 300, \text{ and } 350 \degree C$.

4.3.4.1 Trap depth

If we consider these subtracted TL curves to be the charge lost during specific hold-time ranges, then the shape of these curves should contain useful kinetic information. The initial rise portion of these subtracted TL curves was fitted in the same way as in Section 4.3.3 to determine the apparent thermal trap depth (Figs. 4.8 and 4.9); hereafter, this will be called the post-isothermal TL (pI-TL) method. The results for the regenerative and natural signals are shown in Fig. 4.10(a) and (e), respectively.

Just as with the FGC $E$-values following a regenerative dose (Fig. 4.5(b)), these pI-TL $E$-values steadily increase as deeper thermal regions are probed (Fig. 4.10(a)). Apparent $E$-values increase from about 0.73 eV to a seeming plateau around 1.86 (K-feldspar sample J0165). It is notable that the lowest value is similar to the values from the IRM and the VHRM for the 64 Gy irradiation in Sections 4.3.1 and 4.3.2. Additionally, this upper limit is higher than the highest FGC $E$-value (1.5 eV) observed for this sample.

The pI-TL regenerative $E$-values were also measured for samples J0995 (high albite), J0999 (perthite), and J1001 (perthite). A mean value of $E = 1.84 \pm 0.06$ eV was calculated from the final three hold intervals (30 - 100, 100 - 300, and 300 - 1000 s) at 350 °C for the regenerative signals of all four feldspar samples. While samples J0165 and J0995 may plateau at these durations, samples J0999 and J1001 exhibited a positive slope, suggesting that the maximum $E$-value may be higher for these two samples. (That structurally well-ordered feldspars like perthites should have greater maximum stability than those which formed at higher temperatures and exhibit more uniform composition (e.g., Ab and Or) is consistent with the observation of Visocekas et al. (1994) that athermal fading rates increase
Figure 4.6: (a) Thermoluminescence curves for sample J0165 following irradiation and hold times $t = 0, 3, 10, 30, 100, 300,$ and $1000$ s at $T = 100, 150, 200, 250, 300,$ and $350$ °C. The same data are shown on a semi-log plot in the inset. (b) The loss between adjacent time steps ($> 0$ s) are plotted as subtracted TL glow curves. Notice how loss between hold times resembles mixed-order thermoluminescence.
Figure 4.7: (a) The natural TL curve ($\beta = 5 ^\circ C/s$) is shown in black, as well as the natural curve following isothermal treatments $t = 3, 10, 30, 100, 300,$ and $1000$ s at $T = 250, 300,$ and $350 ^\circ C$ (multiple aliquots of sample J0165). The natural TL curves are normalized to subsequent test-dose responses. The areas between the adjacent TL curves are shown for $T = 250, 300,$ and $350 ^\circ C$ in (b), (c), and (d), respectively.
Figure 4.8: The initial rise regions of the curves shown in Fig. 4.6(b) (isothermal loss gotten by subtracting post-isothermal TL curves of laboratory-dosed aliquots) are fitted to determine the $E$-values shown in Fig. 4.10.
Figure 4.9: The initial rise regions of the curves shown in Fig. 4.7(b)-(d) (isothermal loss gotten by subtracting post-isothermal TL curves of naturally-dosed aliquots) are fitted to determine the $E$-values shown in Fig. 4.10.
Figure 4.10: (a) Thermal trap depths of sample J0165 estimated for the regenerative signal using the pI-TL method (curves shown in Fig. 4.6(b)). Notice the correspondence with Fig. 4.5(b) and the apparent plateau around 1.86 eV. (b) Regenerative dose frequency factors are estimated assuming general-order kinetics, using the analytical expression for the temperature at maximum intensity, $T_m$ (p. 11; Chen and Kirsh, 1981). (c) Identical to (b), except that the $E$-value is not calculated for each hold-time, but is instead set as 1.86 eV. This steady decrease in apparent frequency factor is consistent with the model for K-feldspar luminescence production wherein a trap of singular depth exhibits decreasing recombination probabilities as the tunneling distance increases (Jain and Ankjaergaard, 2011; Jain et al., 2015). (d) Kinetic order is estimated using the so-called geometrical factor, $\mu_g$, a peak-shape parameter, following Chen (1969). The same parameters are shown in (e)-(h), following isothermal treatments of the natural signal. The hold temperatures for the natural signal are limited to 250, 300, and 350 °C.
with greater structural disorder.) The average plateau value for J0165 and J0995 is only 1.86 ± 0.03 eV. Whether this plateau is real or apparent requires further investigation.

The trap depths measured for the natural pI-TL signals are generally consistent with the regenerative signals at the same isothermal conditions. Because of low signal intensity, the final subtracted curve at 350 °C (300 - 1000 s) was unsuited for analysis. The next two longest durations at 350 °C, however, give $E$-values of 1.81 and 1.86 eV and are in good agreement with the plateau found after regenerative doses, lending further support to the idea of a maximum value near 1.86 eV.

4.3.4.2 Kinetic order

The shapes of the pI-TL curves (Figs. 4.6(b) and 4.7(b)-(d)) resemble what would be expected under mixed-order kinetics. This conjecture can be quantified with the TL curve symmetry factor of Halperin and Braner (1960), $\mu_g$, which can be used to assign kinetic order to TL curves based on shape with little dependence on $E$ or $s$ values (Chen and Kirsh, 1981, pp. 159 - 167).

Calculated symmetry factors for the pI-TL curves (excluding the initial 0 - 3 s measurement) yield an average kinetic order of 1.6 ± 0.3 for the regenerative signals and 1.5 ± 0.5 for the natural signals (Fig. 4.10(d) and (h)). There is no apparent relationship between hold temperature and the kinetic order for most sets of hold temperatures. This relatively stable kinetic order with greater temperature is consistent with the interpretation that the pathways are unchanging, whereas the probed lifetimes increase with TL temperature.

The high $b$-values (i.e., kinetic order) for the natural signals lost at 250 °C between 3 - 10, 10 - 30, and 30 - 100 s ($b = 2.2$, 2.3, and 2.1, respectively) may be an exception to this uniformity. That kinetic order is higher as the natural signal is initially depleted may be caused by charge transfer to sites of greater thermal stability.
4.3.4.3 Frequency factor

Finally, given that each pI-TL curve has an apparent trap depth and kinetic order, we can estimate the corresponding frequency factors. The calculation assumes general-order kinetics, and requires kinetic order \((b)\), trap depth \((E)\), temperature at maximum intensity \((T_m)\), and heating rate \((\beta)\) to determine the frequency factor \((s)\) (p. 11; Chen and Kirsh, 1981):

\[
s(b - 1)/\beta \int_{T_0}^{T_m} \exp \left( -\frac{E}{k_B T} \right) dT + 1 = \left( sbk_B T_m^2 / \beta E \right) \exp \left( -\frac{E}{k_B T_m} \right).
\]

(4.3)

This calculation was performed under two different scenarios. In the first scenario, the \(E\)-value measured for each isothermal condition was used to calculated the corresponding frequency factor. In the second, the plateau value of 1.86 eV was used to calculate the apparent frequency factor for each pI-TL curve.

**Assuming individual \(E\)-values** If each pI-TL curve derives from different trap depth (or range of depths), the frequency factors for the regenerative and natural signals are shown in Fig. 4.10(b) and (f). The regenerative values seem to increase with hold time, especially those at \(T = 100, 300,\) and \(350 \degree C\), but the results from the other hold temperatures are less convincing. This result is unexpected if this broad regenerative peak represents an increase in recombination-by-tunneling distances; this mechanism should produce the opposite effect: a decrease in the apparent frequency factor as sites increase in stability (Jain and Ankjaergaard, 2011; Jain et al., 2015).

While both natural and regenerative frequency factors span a similar range \((\sim 10^{11} - 10^{13} \text{ s}^{-1})\), the former seem less organized. This may represent the lower signal intensities involved, resulting in poor fittings of \(E\) or \(b\) values. Alternately, the peak overlap from a higher temperature peak (e.g., Fig. 4.7 (b) - (d)) may sufficiently distort the \(T_m\) value or the position of \(T_2 (T_{1/2} > T_m)\).

**Assuming a shared \(E\)-value of 1.86 eV** If each pI-TL curve derives from a single trap depth of 1.86 eV (see Section 4.3.4.1), the frequency factors for the regenerative and natural

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signals are shown in Fig. 4.10(c) and (g). The consistent decrease in apparent frequency factor with increasing hold time and temperature is consistent with the interpretation that K-feldspar thermoluminescence derives from a single dosimetric trap via tunneling to centers at a variety of distances (Jain and Ankjaergaard, 2011). Such an interpretation would result in a range of apparent frequency factors which reflects the range of recombination probabilities (Jain et al., 2015). I favor this simple interpretation (i.e., one trap depth of 1.86 eV, many apparent frequency factors).

Finally, it is remarkable that the frequency factors for the natural and regenerative signals decrease at a similar rate and over a similar range. Such similarity supports the conjecture that the natural signal for sample J0165 contains the stable portion of the signal measured after laboratory irradiation and exhibits similar kinetic properties.

4.4 Discussion

4.4.1 Comparing the methods for $E$-value determination

To interpret the results from these four methods, it is helpful to consider their critical assumptions. The initial rise method assumes that detrapping, at least for the first portion of the emitted peak, is related only to the ratio of $E/k_B T$ (Eq. 4.1). In other words, effects like retrapping and changes in recombination efficiency should be negligible. The method also requires that the entire fitted region derives from the same trap and does not include overlapping peaks. With the IRM, a single $E$-value is produced that, for glow curves without overlapping emissions, corresponds to the first accessed trap. The various heating rates method also produces a single $E$-value and assumes that neither the trap depth nor the frequency factor change during the TL measurement. The fractional glow curve method incorporates the assumptions of the IRM but offers the possibility of measuring multiple trap depths, provided that each initial rise region is sufficiently separated for the chosen heating rate and stop-temperature increment.

The post-isothermal TL method is similar in approach to the FGC method: the TL curve
is progressively measured, allowing for multiple $E$-value analyses. Unlike the FGC, however, the pI-TL method is not inaccurate if there is trap overlap initially, as the next measured curve is subtracted before analysis (in the case of no overlap, the pI-TL method would reduce to the FGC method for $E$-value determination). Another advantage obtained by considering the emissions between hold times is that peak shape analyses can be performed, including the evaluation of $b$ and $s$ values for each isothermal time range. Because feldspar TL is known to exhibit overlapping emissions, I consider the pI-TL results least subject to error.

4.4.2 Comparing the measured $E$-values

Notable concordance is found between the initial rise method and the various heating rates method. For the VHRM, the data seem to be sub-linear rather than linear as would normally be expected. This effect probably reflects the asymmetric nature of the feldspar TL glow curve: the initial rise region of the curve would be less affected, but in measuring the $T_m$ value, the influence of overlapping, higher-stability traps biases the $E$-value determination. This effect should vary with heating rate, as lower heating rates will tend to minimize this trap separation effect. Importantly, the feldspar samples did not receive preheats prior to the measurement of apparent natural $E$-values.

The FGC $E$-values obtained compare well with experimental results reported elsewhere from sedimentary K-feldspars. Previous studies have reported values ranging from 0.4 eV at liquid nitrogen temperatures (Visocekas et al., 1996) to about 1.7 eV at temperatures above 280 °C (Strickertsson, 1985; Chruścińska, 2001). All of these studies also noted the linear increase in $E$ with FGC hold temperature.

Several observations can be made about the regenerative $E$-values derived from the post-isothermal TL method. First, just as with the FGC, a linear relationship exists between the isothermal duration and the corresponding $E$-value. A similar type of analysis on a museum specimen of plagioclase was done by Pagonis et al. (2014), who performed a general-order kinetics fitting of TL curves gotten by subtraction of post-isothermal TL curves where hold temperatures were varied but not durations. These authors found a range of $E$-values from
1.1 to 1.8 eV, with a generally decreasing kinetic order, from about 2.0 to 1.5. Measurements for our albitic sample (J0995) are comparable, varying over a slightly broader range, from 0.76 to 1.87 eV (omitting the 0-3 s measurement, the range becomes 0.97 to 1.87 eV).

There exists a plateau in regenerative pI-TL $E$-values at $1.86 \pm 0.03$ eV (J0165 and J0995; $1.84 \pm 0.06$ eV for all four samples) for the three highest $E$-values observed in our pI-TL method. I tentatively interpret this as the depth of the ground state for the main dosimetric trap (see also Section 4.4.4). Whether this is a maximum within a distribution of depths or the true trap depth (i.e., activation progresses up through the band-tail states finally into the conduction band) is unclear.

Another consideration is the difference between the FGC and pI-TL methods in the final values obtained for regenerative $E$-values. Both techniques yield final values which might be interpreted as plateaus: $1.49 \pm 0.03$ eV (FGC, last four values of J0165) and $1.84 \pm 0.03$ eV (pI-TL, last three values of J0165). Perhaps the best explanation for this discrepancy is that the reason for each ‘upper limit’ is different. In the regenerative fractional glow curve method, the sample receives a single dose before all measurements are performed. It seems reasonable to assume that above $320 ^\circ$C the source traps have been emptied and that further measurements are comprised mostly of thermal background emissions. The FGC upper limit may, in this interpretation, be understood as methodological, not directly characteristic of trap parameters. By comparison, the pI-TL method involves irradiation of the sample prior to each isothermal treatment, thereby replenishing the source traps. The upper limit for this technique is governed also by the low signal intensity relative to the thermal background, but this is true only after treatments of $350 ^\circ$C lasting 300 and 1000 s, which probe higher regions of the glow curve than those reached by the FGC method. Of course, the upper limit of this technique may also be limited by instrumental resolution and not by the maximum trap depth that would contribute TL at these measurement conditions.

Finally, it is encouraging that both the natural and regenerative doses yield similar $E$-values for J0165 when evaluated with the pI-TL method. This is true for both the rising values measured at $T = 250$, 300, and 350 $^\circ$C, and for the uppermost values: $1.86 \pm 0.03$ eV ($n = 3$) for the regenerative dose, and $1.84 \pm 0.04$ eV ($n = 2$) for the natural dose.
4.4.3 Kinetic order and frequency factor values

The pI-TL kinetic order values of $1.6 \pm 0.3$ for the regenerative signals and $1.5 \pm 0.5$ for the natural signals (Fig. 4.10(d) and (h)) compare well and show no obvious dependence on hold temperature. This may indicate that similar recombination pathways are utilized during the entirety of the TL measurement.

Assuming that a) the application of Eq. 4.3 to pI-TL curves is valid, and b) the TL emissions share an actual (i.e., not apparent) $E$-value of $\sim 1.86$ eV, the apparent frequency factor decreases regularly over the entire range of hold temperatures and durations (Fig. 4.10(c) and (g)). Even more striking is the correspondence between the natural and regenerative pI-TL frequency factors. This correspondence lends credence to the hypothesis that the natural and regenerative TL glow curves may receive contributions from the same trap population, with the natural signal missing the nearer trap-and-center pairs, i.e., a truncated $n(r)$ distribution in Jain et al.’s (2015) model. That a shared $E$-value produces expected behavior in apparent frequency factors may favor the interpretation of a single trap depth responsible for the lower-temperature blue-green TL emissions (Jain et al., 2015) instead of a continuum of trap depths (Sanderson, 1988).

Finally, it is worth suggesting that this interpretation may also explain the spectral shift to higher emission energies within the violet-to-blue detection window (like ours) as observed by Bailiff and Poolton (1991) and Rieser et al. (1994). If the trapped electrons had to be excited into progressively higher states to ultimately recombine, the recombination event would emit a higher energy photon, thus leaving this signature of higher energy emissions for more distant recombinations as the TL measurement progresses.

4.4.4 Relating the pI-TL $E$-value to IRSL signals

A primary concern when evaluating luminescence ages from K-feldspars is the thermal trap depth associated with the IRSL signal. Workers have investigated this parameter through the use of pulse-annealing experiments and the reduction of TL curves by IR stimulation (Li and Aitken, 1989; Duller and Wintle, 1991; Duller and Bøtter-Jensen, 1993; Duller, 1994)
The interpretation of these experiments has not been straightforward, however, for although exposure to IR light depletes a broad region of the regenerative TL curve at lower temperatures, the majority of the IRSL source trap does not seem to be depleted significantly until higher temperatures. This reduction in TL intensity at lower measurement temperatures (i.e., the region populated after irradiation and without preheating) following IR exposure has been explained as a reduction in recombination efficiency (Murray et al., 2009). (If the loss of efficiency is related to the depletion of a shared recombination center, this explanation reconciles the similar emission spectra for K-feldspar TL and IRSL (Huntley et al., 1988, 1991).) More recently, Jain and Ankjaergaard (2011) have suggested that the lower- and higher-temperature TL peaks commonly found in feldspars may derive from a) localized recombination via the excited state of the trap, and b) recombination from the band-tail states (transitioning eventually into the conduction band), respectively. Under this interpretation, and given that the excited state is thought to lie within the band-tail states (Poolton et al., 2009), the uppermost pl-TL $E$-value should represent the thermal depth of the main dosimetric trap measured in IRSL protocols.

### 4.5 Conclusions

The similarity of pl-TL kinetic parameters between natural and artificial TL signals is intriguing and merits further exploration. The implication that the natural TL signal represents the high-stability region of a trap continuum may be overly simple, especially given previous studies which demonstrate differential thermo-optical bleaching properties between the low and high-temperature regions of the TL curve. Nevertheless, the agreement between the uppermost $E$-values of about 1.86 eV offer insight into the maximum thermal stability that may be expected for alkali feldspars extracted from bedrock samples. Finally, the temperature-independent kinetic order values combined with the decreasing apparent frequency factor values at higher temperatures and longer hold times both support the recent hypothesis that feldspar TL (in addition to IRSL) derives from distance-dependent tunneling recombination.
CHAPTER 5

Thermoluminescence from drill core samples

5.1 Geologic context

Twenty samples were collected from split drill cores kept at the United States Geologic Survey Core Research Center (CRC), Lakewood, Colorado. The samples were chosen to represent a wide range of steady-state temperatures (−4.1 − 60.2 °C), within relatively uniform lithologies. The three cores sampled were from the North Slope of Alaska (CRC library code E802; n = 5; 69°50′18″N, 155°59′24″W), the Piceance Basin of northwestern Colorado (W219; n = 8; 39°53′36″N, 108°32′37″W), and the Greater Green River Basin of south-central Wyoming (R716; n = 7; 41°2′41″N, 108°6′39″W) (Fig. 5.1(a) and (b)).

Core E802 from the Colville Basin of North Slope Alaska is comprised of the Nanushuk Group: Lower and Upper Cretaceous sandstone, shale, and minor conglomerate deltaic wedge, all shed from the Brooks Range, a series of thrust sheets stacked during the Late Jurassic to Early Cretaceous arc-continent collision (Mull et al., 1987). Core W219 (Colorado) is comprised of the Green River Formation: Eocene interbedded mudstone and sandstone, carbonaceous shale, lenticular sandstones and thickly-bedded evaporites that were deposited in and around lacustrine basins formed during the Laramide orogeny (Irwin, 1977; Smith et al., 2008). Core R716 (Wyoming) contains Eocene basin-fill (Wasatch Formation): floodplain deposits of lenticular, parallel-bedded sandstones and mudstone (Roehler, 1992). Similar to W219, the R716 core was likely derived from Laramide basement (Fan et al., 2011).

We must estimate the undisturbed modern temperatures for each core. For E802, the geothermal gradients above and below the ice-bearing permafrost layer were interpolated
Figure 5.1: (a) Bedrock sample locations are shown for each of the three USGS CRC drill core sites: E802, W219, and R716. (b) Also shown are the steady-state temperatures for the drill core samples, according to their depths. (c) Representative natural TL signals are colored according to their steady-state temperature, $T_{SS}$. The $T_{1/2}$ values for these normalized TL curves are shown as solid circles in (c) and are plotted as a function of $T_{SS}$ in (d). The colored symbols in (d) derive from the TL curves shown in (c). The grey symbols represent all of the measured $T_{1/2}$ values (see also Fig. 5.3).
from nearby sites within the Colville Basin which were measured for a high-resolution temperature survey of wells considered to be in thermal equilibrium (Collett et al., 1993). For W219, a similar interpolation was performed using gradient-at-depth measurements from nearby sites within the Piceance Basin (Blackwell et al., 2011). For R716, a geothermal gradient map was used (Finn, 2005). From these geothermal gradient approximations, the modern temperature of each core sample was estimated (Fig. 5.1(b)). The following section offers further explanation.

5.1.1 Details of $T_{SS}$ estimation

5.1.1.1 Core E802

Subsurface temperatures for core E802 were estimated from the interpolated geothermal gradient maps of Collett et al. (1993). These gradients are shown in the top panel of Fig. 5.2. I estimate the gradient at the location of E802 to be 34°C/km, both within and below the ice-bearing permafrost layer, equivalent to a steady-state heat flow of 54.4 mW/m². I estimate the error associated with this gradient is about 0.5°C/km, given the density of isograds near core E802. The projected undisturbed surface temperature and permafrost layer thickness at this location are estimated in the same manner (data shown in Collett et al. (1993)) to be -9.5°C and 150 m, respectively (although the identical geothermal gradients make this thickness estimation unnecessary). Therefore, the final expression for temperature within core E802 as a function of depth (in km) is:

$$T(d) = -9.5\, ^\circ\text{C} + 34.0\, ^\circ\text{C/km} \cdot d$$  \hspace{1cm} (5.1)

5.1.1.2 Core W219

The $T_{SS}$ values at the site of core W219 were estimated using nearby measurements of geothermal gradient reported in the SMU Regional Heatflow Database of Blackwell et al. (2011). The gradient measurements as well as the borehole depths are plotted in the middle panel of Fig. 5.2. For reference, the extent of the Green River Formation (the formation
High-resolution temperature surveys near E802:

- Geothermal gradients (°C/km):
  - within ice-bearing permafrost layer
  - below ice-bearing permafrost layer

Geothermal gradient (°C/km):
- 25.5 - 29.2
- 29.2 - 32.8
- 32.8 - 36.5
- 36.5 - 40.1
- > 40.1

T control wells:
Figure 5.2: (Top panel) Based upon high-resolution temperature surveys, the interpolated geothermal gradients from Collett et al. (1993) are shown both within the ice-bearing permafrost layer (fuchsia curves) and below the layer (in light green). The temperature survey wells nearest the core are shown as black squares. I estimate the gradient at the location of E802 to be $34 \pm 0.5 \, ^\circ\text{C}/\text{km}$, within and below the layer. (Middle panel) Core W219 (and the depth range of samples) is shown along with nearby borehole gradient measurements (black squares) compiled by Blackwell et al. (2011); the depths for the reported gradient are shown in parentheses. Also shown in gray is the local extent of the Green River Formation (Johnson, 1981), the formation containing all measured samples. Assuming a simple set of isograds extending outwards from the constrained borehole sites (dashed blue lines), I can estimate the geothermal gradient at the location of W219 to be about $53 \, ^\circ\text{C}/\text{km}$. (Bottom panel) Core R716 is shown within the gradient field mapped by Finn (2005). Boreholes used in constructing the gradient map are shown as blue squares. The gradient at R716 is interpreted as $34.6 \, ^\circ\text{C}/\text{km}$. The entire map area lies within the Greater Green River Basin.
from which W219 samples were taken) is shown in gray.

By constructing a set of isogradient lines from these boreholes, I can roughly estimate the gradient at the site of W219 to be about 53 °C/km (middle panel, righthand side of Fig. 5.2; heat flow of 100.4 mW/m²). These isogradient lines were drawn by first connecting the two survey wells with the same gradient values, and then assuming the other lines were parallel to this. Given that the gradient values decrease to the southeast across this line, I interpret the isogradient surface in this region to be trending as shown in Fig. 5.2. Of course, if the isogradient surface is more complicated, this estimate will be in error. For example, instead of assuming a downwarping plane, I could have assumed that the isogradient surface forms a basin (like the structure of the Piceance Basin comprising the local stratigraphy), in which case, the value at W219 would be closer to ~ 61 °C/km. I consider this to be a reasonable upper limit to the gradient value and doubt that the gradient would be much less than 53 °C/km. The Mean Annual Surface Temperature for the Piceance Basin at the elevation of W219 is estimated at 6 °C, a value which, based on paleobotanical data should not have changed more than about 5 °C in the past 10 Ma (Fig. 4 of Tong et al., 2016).

The temperature with depth function for W219 is thus:

\[ T(d) = 6 \, ^\circ\text{C} + 53 \, ^\circ\text{C/km} \cdot d \]  \hspace{1cm} (5.2)

### 5.1.1.3 Core R716

The geothermal gradient is well-constrained for core R716 using the map of Finn (2005).

At R716, the gradient is constrained tightly to be ~ 1.9 °F/100 ft., or 34.6 °C/km (bottom panel of Fig. 5.2; heat flow of 58.3 mW/m²). This gradient is used in conjunction with the mean annual ground temperature of 4.4 °C, the value used by Finn (2005) for calculating gradients in the Southwestern Wyoming Province. Temperature at depth within R716 is therefore:

\[ T(d) = 4.4 \, ^\circ\text{C} + 34.6 \, ^\circ\text{C/km} \cdot d \]  \hspace{1cm} (5.3)
5.1.2 Modern exhumation rates

Whether samples are in thermal equilibrium (i.e., trapping rate equal to detrapping rate) depends on the exhumation rate at each core site. The most rapid exhumation is at site W219. Although no measurements have been made at the core site itself, fluid inclusion microthermometry (Fall et al., 2012, 2015) and vitrinite reflectance data (Zhang et al., 2008) from the center of the Piceance Basin imply an exhumation rate of 0.16 - 0.24 km/Ma since 10 Ma, corresponding to a cooling rate of 3.8 °C/Ma within the Mesaverde Group, immediately below the Wasatch Formation (vitrinite reflectance data suggest heat-flow values similar to modern since the Miocene). Moreover, the exhumation at the northern basin edge is expected to be slower than in the center (Zhang et al., 2008).

Based on apatite fission track cooling ages, the exhumation rate for the Colville Basin (core E802) since the Paleocene has been about 0.05 - 0.06 km/Ma (Cole et al., 1997) and vitrinite reflectance data suggest an exhumation rate of 0.01 - 0.02 km/Ma since the Eocene for the Green River Basin (core R716) (Jagniecki et al., 2013), both of which are effectively static for the TL signal considered here. The modern geothermal gradients at these sites are also much lower than at W219: 34 and 35 °C/km compared with 53 °C/km, which would result in cooling rates of 1.9 and 0.5 °C/Ma for E802 and R716, respectively. Because simulations of cooling rates less than about 10 °C/Ma to some final temperature yield signals indistinguishable from samples held constant at that same temperature (using Eq. 5.12), the modern undisturbed core temperature measurements are reported as ‘steady-state’ temperatures \( T_{SS} \) hereafter.

5.2 Thermoluminescence signals from feldspars extracted from drill cores

5.2.1 Natural signals

Sixteen of the 20 measured samples produced natural TL signals suitable for analysis (Fig. 5.3). The four rejected samples were from core W219, were buried at temperatures \( \geq 23 \degree C \), and
yielded natural signals dominated by black-body radiation (approximated by measuring TL from the same aliquot after the natural signal has been removed). Two trends are notable from these natural signals. First, as steady-state temperatures \( T_{SS} \) increase, the leading edge of the emissions shifts to higher temperatures (Fig. 5.1c). Second, within a given core (each of which has a fairly uniform lithology), TL brightness tends to decrease at higher \( T_{SS} \) values.

### 5.2.2 Field saturation

A primary concern when considering the dose-response characteristics of luminescence signals is a change in sensitivity [Wintle and Huntley, 1982]. To avoid any such changes in dose-response sensitivity induced by heating, I tested the level of natural dose-saturation (i.e., ‘field saturation’; [Kars et al. 2008]) in samples J1012, J1026, and J1030 by using a multiple-aliquot additive-dose (MAAD) approach. Separate aliquots were given beta doses in addition to their natural doses. The subsequent TL curves (Fig. 5.4a - c) show which regions of the glow curve are saturated (and do not, therefore, grow with dose) and which regions are not saturated (and grow with dose).

Sample J1012 is almost fully saturated from about 270 to 370 °C, with an average ratio of 0.95 ± 0.02. The ratio for J1026 is 0.99 ± 0.01 within the range of measurement temperatures from 330 to 400 °C. Sample J1030 shows a similar degree of saturation, 0.95 ± 0.03, from 340 to 410 °C (Fig. 5.4c). The key observation from this experiment is that \( T_{SS} \) relates to the measurement temperature at which field saturation is complete \( (T_{SS} = -4.1 \, ^\circ C \text{ for } J1012, 19.8 \, ^\circ C \text{ for } J1026, \text{ and } 55.1 \, ^\circ C \text{ for } J1030) \). This indicates that burial temperature controls which regions within a TL curve are stable enough to accumulate. At higher measurement temperatures, all three samples show ratios greater than one. This may reflect dose-quenching (for a detailed description of this phenomenon in quartz, see [Bailey 2001]) of a high-temperature peak (e.g., 410 °C TL peak; [Murray et al. 2009]). Why the samples are > 1 at different temperatures is unclear, but likely relates to the variability in the position of the high-temperature peak.
Figure 5.3: The natural TL signals are plotted by drill core and colored according to the steady-state temperature, $T_{SS}$. Missing data points within a TL curve signify that the thermal background curve (TL measured after the natural signal and with no dose) is, at that time bin, larger than the natural signal. Notice the shift in the leading edge and the decreasing brightness as the natural $T_{SS}$ value increases. Notice also the logarithmic y-axes.
Figure 5.4: (a) The glow curve shown in blue is a natural aliquot of sample J1012 \( (T_{SS} = -4.1\, ^\circ C; \) core E802 \( ) (\beta = 5\, ^\circ C/s; \) the thermal background has been subtracted, so some data points are missing). In red is the TL curve of another aliquot of J1012 that has been given a dose of 242.2 Gy in addition to the natural dose. Notice that the low-temperature portion of the TL glow curve grows with dose, whereas no growth occurs above about 250 °C. The same measurements are shown for (b) two aliquots of sample J1026 \( (T_{SS} = 19.8\, ^\circ C; \) core R716) and (c) two aliquots of J1030 \( (T_{SS} = 55.1\, ^\circ C; \) core R716). (d) The ratios of the natural response to the added-dose response are plotted as a function of measurement temperature for both samples. A ratio of 1 (dashed line) indicates that the sample is in complete field saturation. Notice how the coldest sample is nearly saturated (ratio \( \sim 0.95)\) at lower measurement temperatures and as the burial temperature increases, saturation occurs at higher measurement temperatures. Above about 375 °C, we see a slight rise in the ratio, which may be attributed to a separate, high-temperature peak (Duller, 1997; Murray et al., 2009).
5.2.3 Signals following isothermal treatments

After the measurement of the natural signal, an aliquot of sample J1012 (core E802) was given a beta dose of 24 Gy and then subjected to a series of isothermal treatments: 50, 100, 150, and 200 °C for 10, 30, 100, 300, and 1000 s. Following these treatments, the TL signals were measured (Fig. 5.5). A shift of the leading edge and a reduction in intensity result from longer heat treatments and greater hold temperatures, an observation made also by [Spencer and Sanderson (1994)]. This resembles the effect of burial at higher natural $T_{SS}$ values (Fig. 5.3).

A higher temperature peak is evident, centered around 390 °C. High-temperature peaks (centered between ~ 310 - 410 °C) are well-documented for feldspar TL studies and exhibit different luminescence properties than the lower-temperature peak and must therefore involve a different combination of traps and/or recombination centers (Balescu et al., 1991; Duller, 1994, 1997; Murray et al., 2009). For that reason, our analysis is restricted to those regions unaffected by this higher-temperature peak.

5.3 A kinematic model of feldspar TL

5.3.1 Model description

Electron trapping during irradiation is expressed as

$$\frac{dn(r)}{dt} = \frac{\dot{D}}{D_0} (N(r) - n(r))$$  \hspace{1cm} (5.4)

where $n(r)$ is the concentration of trapped electrons with a recombination distance $r$; $N(r)$ is the concentration of trapping sites (occupied or empty) at that distance; $\dot{D}$ is the radiation dose rate (Gy/ka); and $D_0$ is the dose (Gy) at which $(1 - e^{-1})$ of the total traps are filled (i.e., the characteristic dose). In a lossless system, trapping would not depend on $r$ values, but the preferential depletion of traps near to centers (due to a high tunneling probability) has the consequence that the degree of saturation $(N(r) - n(r))$ increases with distance (Huntley and Lian, 2006). Under constant or no loss, the initial filling rate depends directly
Figure 5.5: (a) Measured TL curves are shown for sample J1012 (core E802), following isothermal treatments of durations 10, 30, 100, 300, and 1000 s at holding temperatures of 50 (purple curves), 100 (blue), 150 (green), and 200 °C (orange). (b) The $T_{\frac{1}{2}}$ values of these measurements are plotted as a function of hold time and colored according to hold temperature. Notice the shift towards higher $T_{\frac{1}{2}}$ values with longer hold times and higher temperatures.
on the environmental radiation intensity, but as the available traps fill, the rate of trapping decreases. If recombination centers are distributed randomly within a lattice in a density of \( \rho (\text{m}^{-3}) \), the concentration of trapping sites separated from the nearest center by a radial distance between \( r \) and \( r + dr \) is given as (Huntley, 2006; Jain et al., 2012)

\[
N(r)dr = N4\pi r^2 \rho \exp\left(-\frac{4\pi r^3}{3\rho}\right)dr
\]  

(5.5)

where \( N \) is the total concentration of trapping sites within the lattice. For comparison with other studies, it is convenient to introduce also the dimensionless recombination center density, \( \rho' \), defined by (Huntley, 2006) as

\[
\rho' \equiv \frac{4\pi \rho}{3\alpha^3}
\]  

(5.6)

where \( \alpha \) is the radial distance considered (in our case, this is the exponential term of Eq. 5.9 divided by \(-r\)).

Detrapping is treated according to a localized transition model (Halperin and Branner, 1960; Chen and Pagonis, 2011 pp. 55-57). In this model, electrons can thermally excite to a higher-energy state. Once excited, the electrons can tunnel to nearby recombination centers. To describe this pathway mathematically, we first note that the ratio of excited-state electrons, \( n_e \), to ground-state electrons, \( n_g \), depends on both the energy difference between the states, \( \Delta E \), and the absolute temperature of the system (Chen and McKeever, 1997 p. 458):

\[
\frac{n_e}{n_g} = \exp\left(-\frac{\Delta E}{k_B T}\right)
\]  

(5.7)

For the range of natural and experimental temperatures involved (\( T < 500 \) °C) and for \( \Delta E \gtrsim 0.3 \text{ eV} \), Eq. 5.7 shows that \( n_e << n_g \). Thus, since \( n = n_e + n_g \), we can make the approximations that \( n_g \simeq n \) and

\[
n_e \simeq n \exp\left(-\frac{\Delta E}{k_B T}\right)
\]  

(5.8)

Since tunneling occurs via the excited state, the rate of detrapping is simply the concentration of excited-state electrons multiplied by the probability of recombination. The
tunneling probability $P \, (s^{-1})$ depends on the thermal depth of the excited state beneath the conduction band, $E_e \, (eV)$, the effective mass of the electron within the feldspar lattice ($m_e^*; \text{Poolton et al. 2001}$), and the distance to the nearest recombination center, scaled by an attempt-to-tunnel frequency factor, $P_0 \, (s^{-1})$ (Chen and McKeever 1997, pp. 60-66):

$$P(r) = P_0 \exp \left( -2r \frac{\sqrt{2m_e^*E_e}}{\hbar} \right)$$  \hspace{0.5cm} (5.9)

where $\hbar$ is the Dirac constant. In the localized transition model, the probability of recombination is limited by either the attempt-to-escape frequency, $s$, or the tunneling probability, $P(r)$, whichever is smaller, summarized as

$$p = \frac{P(r)s}{P(r) + s}$$  \hspace{0.5cm} (5.10)

The final expression for detrapping probability is the concentration of excited electrons (Eq. 5.8) multiplied by the excited-state recombination probability (Eq. 5.10):}

$$-\frac{dn(r)}{dt} = n(r) \exp(-\Delta E/k_B T) \frac{P(r)s}{P(r) + s}$$  \hspace{0.5cm} (5.11)

Combining Eqs. (5.4) and (5.11), electron trapping and detrapping under the localized transition model is expressed as

$$\frac{dn(r)}{dt} = \frac{\dot{D}}{D_0} \left( N(r) - n(r) \right) - n(r) \exp \left( -\Delta E/k_B T \right) \frac{P(r)s}{P(r) + s}$$  \hspace{0.5cm} (5.12)

This trapped electron population, $n(r)$, is measured during TL. The expression for TL intensity is given as

$$I_{TL}(t) \propto \int_{t=0}^{t_F} \int_{r=0}^{\infty} n(r)drdt$$  \hspace{0.5cm} (5.13)

when a sample is heated from $T = 0$ to $T_F$ at $dT/dt = \beta \, ^{\circ}C/s$. All simulations presented in this work were evaluated with the ode23tb solver within MATLAB.

### 5.3.2 Justification of parameter values used in kinetic model

The purpose of this section is to demonstrate that the parameter values used to simulate natural and laboratory TL signals (Table 5.1) are all reasonable. While these values do

---

[82]
Figure 5.6: (a) Starting with empty traps, Eq. 5.12 is solved for isothermal geologic histories. The trapped populations at the final times then become the initial condition for another evaluation of Eq. 5.12 representing the TL measurement. These are the plotted curves. (Note that after 2 Ma, \( n/N \sim 1 \) for the most stable traps). (b) Instead of reproducing a geologic dose, this second experiment reproduces a laboratory dose followed by an isothermal treatment. Finally, the simulated TL measurements are shown according to the isothermal conditions. These simulation results can be compared with the positions of the natural and laboratory-induced TL peaks.
Table 5.1: Parameter values used in this chapter.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{D}_G$</td>
<td>Geologic dose rate</td>
<td>see Tables B.1 and B.2</td>
</tr>
<tr>
<td>$\dot{D}_L$</td>
<td>Laboratory dose rate</td>
<td>0.1 Gy s$^{-1}$</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Characteristic dose</td>
<td>1.6 kGy</td>
</tr>
<tr>
<td>$E_e$</td>
<td>Trap depth, excited state</td>
<td>0.8 eV</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Trap depth, ground state</td>
<td>2.1 eV</td>
</tr>
<tr>
<td>$P_0$</td>
<td>Tunneling frequency factor</td>
<td>$2 \times 10^{16}$ s$^{-1}$</td>
</tr>
<tr>
<td>$s$</td>
<td>Frequency factor</td>
<td>$2 \times 10^{16}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Luminescence center density</td>
<td>$1.7 \times 10^{26}$ m$^{-3}$</td>
</tr>
<tr>
<td>$\rho'$</td>
<td>Dimensionless $\rho$</td>
<td>$1.32 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
provide the best simultaneous fit for laboratory and natural $T_{1/2}$ values, I do not assert that these parameter values are all unique (of course, some values, like the laboratory dose-rate, are actually unique and well known), but rather, that they are consistent with all investigations and literature values reported here.

### 5.3.2.1 Geologic ($D_G$) and laboratory ($D_L$) dose rates

For the calculation of geologic dose rate, a 10 g portion of each sample was analyzed with inductively-coupled plasma mass spectrometry (ICP-MS) to determine the U and Th concentration, and with inductively-coupled plasma optical emission spectrometry (ICP-OES) to determine the K concentration. The conversion factors of Adamiec and Aiken (1998) were used, assuming a value of 12.5 ± 0.12 wt. % K content for the internal dose rate (Huntley and Baril, 1997). A water content of 1 ± 1 % was assumed.

The average environmental dose rate for all samples is 4.0 ± 1.5 Gy/ka, represented by our chosen $D_G$ value of 4 Gy/ka. The laboratory dose rate, $D_L$, administered by the $^{90}$Sr/$^{90}$Y beta source at UCLA has been measured to be 0.1 Gy/s at the sample location using the standard calibration quartz sample supplied from Risø DTU National Laboratory. This value is used to simulate laboratory irradiations.

### 5.3.2.2 Characteristic dose, $D_0$

The TL dose response of sample J1012 is shown in Fig [5.7]. Because we are concerned with growth in the region of the TL curve near the natural $T_{1/2}$ values, we examine the saturation behavior around 230 °C ($T_{1/2} = 222.6, 223.2, 227.4, \text{ and } 236.0 \degree C$ for J1012). In this region, we see an average $D_0$ value of 1.65 kGy. This value is consistent with previous additive dose observations (e.g., Balescu and Lamothe [1992]).

Three important questions should be addressed when considering this result. First, does this region of the TL curve fade? Given the multiple-aliquot additive-dose (MAAD) results reported in the main text, it appears as though the natural $T_{1/2}$ value demarcates those traps which are stable at the relevant geologic dose-rate and temperature. In this view, a more
Figure 5.7: (a) After heating the sample to 500 °C, an aliquot of J1012 was measured in a single-aliquot regenerative (SAR) TL sequence. The doses given were 60, 121, 242, 483, 967, 1933, 3867, and 60 Gy, and the TL curves measured immediately afterward ($\beta = 5 ^\circ C/s$) are shown in color. In gray are the same measurements, but with a preheat of 150, 250, or 350°C for 3 s prior to TL. (The subsequent TL response to $D = 0$ was measured and subtracted for every growth curve.) (b) Representative dose-response measurements are shown at $T = 230 ^\circ C$ (shown as a line in (a) and taken within the region of the curve corresponding to the natural $T_{1/2}$ values for sample J1012, shown as the shaded region in (d)) following a preheat at 150 °C. Notice the negligible sensitivity change in this region, suggesting no need for normalization. (c) The $D_0$ parameter fitted for the dose-response measurements at every measurement channel is plotted. Only growth curves for readout temperatures greater than the preceding preheat temperature are fitted. (d) The shaded region from (c) is enlarged to show the characteristic dose value within the region of the TL curve that corresponds to natural $T_{1/2}$ values, about 1.65 kGy.
conservative approach would be to examine the dose-responses at more ‘stable’ portions of the curve, though obviously this is subject to interpretation. I therefore report a $D_0$ value of 1.6 kGy, a value taken from the range $260 < T \, (^{\circ}\text{C}) < 270$.

Second, how generalizable is this to the other samples? As the length of exposure is so great for this experiment ($\dot{D} = 0.1 \, \text{Gy/s}$ requires $\sim 9 \, \text{h}$ irradiation for the highest dose-point), only two aliquots of J1012 were taken to 3.9 kGy. All samples from core E802 were given beta doses up to 485 Gy, however, and showed similar growth patterns, with all samples growing linearly with dose ($T = 270 \, ^{\circ}\text{C}$ and $\beta = 5 \, ^{\circ}\text{C/s}$) to the highest dose. Ultimately, this parameter will control the time required for a sample to equilibrate to thermal steady-state and should therefore be quantified thoroughly when addressing transient responses to thermal perturbation. For our study, where sites have been cooling very slowly for at least 10 Ma ($t >> 2D_0$), this parameter will not affect our drill core fitting results, though it does influence our cooling simulations of section 6.

Third, does heating the sample to 500 $^{\circ}\text{C}$ change the $D_0$ value before it has been measured? While it is difficult to say, the comparison between natural, SAR, and MAAD TL curves for sample J1012 hint that perhaps heating has the effect of sensitizing a high-temperature ($\sim 400 \, ^{\circ}\text{C}$) peak (Fig. 5.8). The effect of heating on the lower temperature region of the TL curve is less obvious, but the general shape of the curve after an added dose of, e.g., 484 Gy is congruent with the shape of the regenerative curve at similar doses, so I suspect that the dose-saturation behavior of the glow curve in the region of natural $T_{1/2}$ values is not significantly altered by heating to 500 $^{\circ}\text{C}$, though this merits further study.

5.3.2.3 Ground- ($E_g$) and excited-state ($E_e$) trap depths

Fitting ITL measurements [Jain et al. (2015)] introduced the following expression to describe isothermal TL from feldspars:

$$L \propto -\frac{dn}{dt} = 3n_0\rho'z(t')^{-1}\left(\ln(t'P_0) - \xi\right)^2 \exp\left(-\rho'\left(\ln(t'P_0) - \xi\right)^3\right)$$

(5.14)
Figure 5.8: (a) Multiple aliquots of sample J1012 are given additive doses of 0, 242, and 484 Gy before TL measurements ($\beta = 5 \, ^\circ C/s$). (b) The same aliquot of J1012 is given regenerative doses up to 3.87 kGy to produce the TL curves shown. Notice the prominent high-temperature shoulder (centered around 400 $^\circ$C) measured in the regenerative TL curves that seems absent in the additive dose TL curves (which are not heated to 500 $^\circ$C prior to measurement).
where

\[ t' = \tau_0 + zt \]
\[ \xi = \Delta E / k_B T \]
\[ \rho' = 4 / 3\pi \rho \alpha^{-3} \]
\[ z = d\tau_C / dt \]

The variables \( \tau_C \) and \( \tau_0 \) represent the critical lifetime at time \( t \), and the critical lifetime at the start of the measurement, respectively. Assuming that recombination proceeds by tunneling from the excited state to randomly-distributed luminescence centers, isothermal TL at any hold temperature should approximately follow Eq. 5.14.

Fig. 5.9 shows the isothermal decay of an aliquot of J1012 held at 250, 300, and 350 °C for 1000 s (400 s of which is shown). These data are fitted with Eq. 5.14 using the same parameters used in the main text to fit the \( T_{1/2} \) values for all drill core samples at natural and laboratory conditions, namely: \( \Delta E = 1.3 \text{ eV} \) (2.1 - 0.8 eV); \( \rho = 1.7 \times 10^{264} \text{ m}^{-3} \) (which, given the \( \alpha_g \sim \alpha_e \) value of 8.15 \( \times 10^9 \text{ m}^{-1} \) corresponds to a dimensionless value of \( \rho' = 1.32 \times 10^{-3} \)); and \( P_0 = 2 \times 10^{16} \text{ s}^{-1} \). A \( z \)-value of 1.8 was used, following Huntley (2006) and Jain et al. (2012).

The fitting residuals are not random, suggesting that the decay shape is not entirely captured by Eq. 5.14 (the observed rate of decay for 300 and 350 °C is slower than predicted). Nevertheless, the fitting is approximate for all temperatures and these parameter values seem plausible.

**pI-TL analysis** Determination of the thermal trap depth for feldspars is notoriously difficult, and has been attempted with the initial rise method, often in conjunction with the fractional glow curve method (Strickertsson 1985; Visocekas et al., 1996; Chruścińska 2001), isothermal loss methods (Sanderson 1988; Guralnik et al., 2015a), and curve fitting methods (Pagonis et al., 2014; Jain et al., 2015) (for a full discussion see pp. 101–130 of Chen and McKeever, 1997). I use the recent method of Brown and Rhodes (2017), where post-
Figure 5.9: The isothermal decay data from sample J1012 following a beta dose of 121 Gy are plotted for a hold time of 400 s at hold temperatures of \( T = 250, 300, \) and \( 350 \) °C (solid circles). These decays are fitted to the expression for isothermal decay (Eq. 5.14) from Jain et al. (2015) (‘J+15’), using the parameters listed in Table 5.1 and varying only the initial population \( (n_0) \) and the initial lifetime \( (\tau_0) \) values from one temperature to the next (lines).
isothermal TL glow curves are subtracted from each other to identify the region of TL lost during isothermal treatments between different hold times.

For this experiment, the same aliquot of J1012 was given a beta dose of 121 Gy, and then held at temperature $T$ for a duration $t$, where $T = 250, 300, or 350 \, ^\circ C$ and $t = 3, 10, 30, 100, 300, or 1000 \, s$. Immediately after isothermal treatment, the TL glow curve was measured to 500 $^\circ C$ at a heating rate of 5 $^\circ C/s$. These curves are shown in Fig. 5.10. The loss between curves was then fitted to determine the apparent activation energy during each isothermal holding period (Fig. 5.11). It is clear that the $E$-value increases systematically with heat treatment up to the maximum treatment of 350 $^\circ C$ between 300 and 1000 s. Beyond this point, fitting becomes difficult, as the thermal background is significant in the region of initial rise. What is apparent, however, is that $E > 2.0 \, eV$, consistent with our value of $E_g = 2.1 \, eV$.

**Literature values** The ground- and excited-state activation energies chosen to fit the drill core $T_{1/2}$ values (0.8 and 2.1 eV, respectively) both agree with previously reported values. For the ground state, 2.1 eV is on the higher end of reported values: >1.5 (Jain and Ankjaergaard 2011), 1.66 (Li and Tso 1997), 1.72 (Li et al., 1997), 1.71 ± 0.08 (Murray et al. 2009), 0.76 - 1.80 (Strickertsson 1985), 1.1 - 1.8 (Pagonis et al. 2014), 1.92 - 2.06 (Li and Li 2013), ∼1.86 eV (Brown and Rhodes 2017), and ∼2 (Jain et al. 2015) eV. Few reports exist on the value of $E_e$, but our estimation is consistent with the 0.9 eV estimate of Jain and Ankjaergaard (2011).

**5.3.2.4 Frequency factors, $P_0$ and $s$**

The pI-TL data reported in Sec. 5.3.2.3 and shown in Fig. 5.10 can also be investigated with peak-shape analysis. A full description of this approach is found in Brown and Rhodes (2017). The calculation assumes general-order kinetics, and requires kinetic order $b$, trap

\[ b_{\text{trap}} = \frac{1}{2} \left( \frac{E_g}{kT} \right)^{1/2} \]

Figure 5.10: (a) An aliquot of J1012 was given a dose of 121 Gy and then heated to 250 °C for the time values shown, and then the post-isothermal TL (pI-TL) response was measured at $\beta = 5 \, ^\circ\text{C}/\text{s}$. (b) Adjacent glow curves are subtracted (TL after $t = 3$ s minus TL after 10 s) to show the TL regions lost during isothermal holding times. (c) The initial rise regions of the subtracted TL curves are fitted to determine the activation energy for each holding interval. These plots are also shown for hold temperatures of 300 °C ((d) - (f)) and 350 °C ((g) - (i)).
Figure 5.11: The apparent $E$-values corresponding to the pl-TL fittings in Fig. 5.10 are plotted as a function of the upper-bound of the isothermal hold time (e.g., the loss from 3 to 10 s is plotted as a hold time of 10 s). Notice the increase in values, with the highest measured value at 2.0 eV. The lower panel shows the apparent frequency factors from pl-TL peak shape analysis. These values assume a fixed $E$-value of 2.1 eV, and range from $2.9 \times 10^{14}$ to $7.6 \times 10^{18}$ s$^{-1}$. 
depth \((E)\), temperature at maximum intensity \((T_m)\), and heating rate \((\beta)\) to determine the frequency factor \(s\) \citep{chen1981modeling}:

\[
s(b - 1)/\beta \int_{T_0}^{T_m} \exp \left( -E/k_B T \right) dT + 1 = \left( sbk_B T_m^2/\beta E \right) \exp \left( -E/k_B T_m \right)
\]

The calculated frequency factors are shown in the lower panel of Fig. 5.11, assuming an \(E\)-value of 2.1 eV. Values range from \(2.9 \times 10^{14}\) to \(7.6 \times 10^{18} \) s\(^{-1}\), inclusive of \(2 \times 10^{16}\), the value fitted to the drill core \(T_{1/2}\) measurements. Although I used the same fitting value for \(P_0\) and \(s\), it should be restated that these two parameters have different physical meanings and may differ by orders of magnitude \citep{Jain2015}.

5.3.2.5 Luminescence center density, \(\rho\)

To evaluate the density of recombination centers, curve fitting is the conventional approach. I fit the ITL decay of sample J1012 to Eq. 5.14 of \cite{Jain2015} as described in Sec. 5.3.2.3. Fig. 5.9 shows a reasonable fit with a \(\rho\)-value of \(1.5 \times 10^{26} \text{ m}^{-3}\) \((\rho' = 1.16 \times 10^{-3})\). This value also compares well literature values of \cite{Kitis2013} \((5 \times 10^{-3} \text{ for TL of feldspar})\), \cite{Jain2015} \((\rho = 10^{-3} \text{ for IRSL decay following different preheats})\), and \cite{Sfampa2015} \((\text{order } 10^{-3} \text{ for post-IR TL})\).

5.3.3 Thermoluminescence responses following isothermal geologic histories

Using Eq. 5.12 and the parameter values listed in Table 5.1 (with the average geologic dose rate for all samples of 4 Gy/ka), I modelled the evolution of \(n(r)\) for hold temperatures of 0, 10, and 20 °C, and durations of 20 ka, 200 ka, and 2 Ma. After 800 ka \((2D_0/D_G)\), assuming the parameters listed in Table 5.1, the most stable traps will be effectively saturated, i.e., \(n/N \sim 0.86\). After 2 Ma, these traps should be entirely full \((n/N \sim 1)\) (see also Fig. 5.12). The final distribution of \(n(r)\) after each treatment was then evaluated using Eq. 5.13 to produce a synthetic TL curve; these are shown in Fig. 5.6a.

Two features are remarkable. First, and most relevant for this study, the TL peaks are emitted at higher stimulation temperatures when trapping occurs at higher tempera-
tures. This is because those sites which are nearer to centers (i.e., have lower $r$ values) are unstable at higher ambient temperatures, and are therefore empty during the natural TL measurement. Second, the integrated emissions are greater for those simulations at lower temperatures. The reason for this is that the concentration of excited-state electrons depends exponentially on temperature (Eq. 5.7) and the ratio of excited-to-ground-state electrons controls the rate of detrapping.

5.3.4 Thermoluminescence responses following isothermal treatments

The same approach was used to predict the effects of short duration heat treatments. For each of these simulations, laboratory irradiation was reproduced by changing the dose rate, $\dot{D}$, to 0.1 Gy/s (the dose-rate received by grains exposed to the $^{90}$Sr/$^{90}$Y beta source at UCLA) and allowing the $n(r)$ distribution to evolve for 200 s ($D = 20$ Gy) at 20 $^\circ$C. Next, this $n(r)$ distribution was used as the initial condition of an isothermal heat treatment. The simulated hold times were 100, 300, and 1000 s; and the temperatures were 100, 150, and 250 $^\circ$C. Finally, the $n(r)$ distribution was evaluated with Eq. 5.13, producing the TL curves shown in Fig. 5.6b.

The effects of heating are to shift the TL emissions to higher measurement temperatures and to reduce the peak intensity. This reason for this behavior is the progressive thermal erosion of those sites which have lower recombination distances; the more stable sites comprise the higher temperature regions of the TL measurements.

5.3.5 Trapping at a single recombination distance

Equation (5.12) can also be used to illustrate the evolution of trap populations under different scenarios. To begin with, we consider a trapping site with a dimensionless distance, $r'$, defined by Huntley (2006) as

$$r' = \left( \frac{4\pi \rho}{3} \right)^{1/3} r$$  \hspace{1cm} (5.16)
where $\rho$ is the density of recombination centers. An arbitrary recombination distance of $r'$ (e.g., 1.5) and a constant temperature of $-4.1{ }^\circ\text{C}$ (e.g., sample J1012) are examined within a 2 Ma simulation (Fig. 5.12a). The results are shown as the fraction of traps which are filled (when $n/N = 1$, all available traps are filled). Once about 86% of traps are filled, even small variations in the measured luminescence response will lead to large or infinite errors in age determination and the trap is effectively saturated \cite{Wintle and Murray 2006}. This saturation level is described with the $D_0$ parameter (effective saturation occurring at doses $> 2D_0$). In our case, I prescribe a value of $D_0 = 1.6 \text{kGy}$ based on dose response measurements of sample J1012; higher values result in later saturation.

In our simulation, trap filling through time progresses as expected for a discrete trap (Fig. 5.12a). As the available sites fill, the fractional saturation behaves as a saturating exponential function. Notice that at the chosen temperature, this site will not fill entirely ($n/N < 1$). In other words, a thermal steady-state is reached which is incompletely saturated \cite{Christodoulides et al. 1971}. Of course, with randomly-distributed luminescence centers many recombination distances will occur, as discussed in the following section.

### 5.3.6 Trapping at all recombination distances

Considering all recombination distances present in the lattice, assuming randomly distributed centers, we can visualize trapping as a function of both time and recombination distance. Using Eq. 5.12, trapping is simulated at $T = -4.1{ }^\circ\text{C}$ for durations of 0.25, 0.5, 1, and 2 Ma (Fig. 5.12b). The results shown in Fig. 5.12 are indicated with the light blue line for reference. Those traps with centers nearer than about $r' = 1.7$ will not saturate completely (given the prescribed temperature and dose rate) and sites at $r' \lesssim 0.8$ will not accumulate a significant concentration of electrons. Such sites would accumulate appreciable charge, however, if the temperature were lowered sufficiently. This is illustrated in Fig. 5.13.
Figure 5.12: (a) For an arbitrary recombination distance of $r' = 1.5$, trap filling is simulated for 2 Ma at -4.1 °C ($T_{SS}$ for J1012) by assuming an initially empty $n(r)$ distribution that evolves with time according to Eq. 5.12. After about 1 Ma, the sites at this distance are effectively saturated. Notice that in steady-state at this temperature, not all of the traps will be full, even though they are in steady-state. I illustrate this steady-state limit $((n/N)_{SS})$ with a green line. This represents the upper-limit for the concentration of trapped electrons at this temperature. (b) This process is then shown for a range of recombination distances within a lattice, at the same constant temperature. The sites with the greatest recombination distances saturate first, while those with nearer recombination centers remain unsaturated. All distances have reached their steady-state concentration after about 2 Ma, and will not fill any further unless the temperature lowers. (The single distance illustrated in (a) is shown in light blue.) (c) The saturation domain $(n/N > 0.86)$ is modeled for three burial temperatures experienced by the drill core samples (the same samples for which MAAD saturation measurements are shown in Fig. 5.4). Notice that with higher burial temperatures only the trapping sites with high $r'$ values are occupied.
a) trapping through geologic time

b) TL measurement representing trapping history

C) trapping at the scale of angstroms

KEY:
- recombination center
- recombination event
- trapped electron; total number is n
- minimum possible tunneling distance

cooling through time
Figure 5.13: (a) The evolution of the feldspar luminescence system can be considered in terms of recombination distance. Each distance will evolve according to its respective stability at a given temperature (illustrated with green curves). For example, imagine a cooling scenario as shown by the solid red line segments. During the stage 1, the constant temperature is high enough to keep all the traps empty. An instant drop in temperature allows the most stable traps to begin accumulating at stage 2. The linear cooling during stage 3 would promote trapping at progressively less stable sites, which would continue to grow during stage 4. Stage 5 would represent cooling to surface temperature, opening up those traps which are stable at room temperature. Some sites remain open because their lifetime at room temperature is less than the de-trapping rate. This history can be summarized by the final distribution of trap populations by distance, $n(r)$. The imagined cooling history shown in (a) would result in a TL curve similar to the one shown in (b), where the increasing measurement temperature causes radiative recombination at progressively greater distances. The influence of cooling on recombination probability is shown at an interatomic scale in (c). As the thermal energy of the lattice decreases, fewer electrons can excite and therefore the tunneling probability decreases, resulting in a decrease in the minimum tunneling distance required for recombination.
5.3.7 Trapping at drill core temperatures

Finally, the simulation conducted in Section 5.3.6 is repeated for the steady-state temperatures experienced by drill core samples J1012, J1026, and J1030 ($T_{SS} = -4.1, 19.8, \text{ and } 55.1$ °C, respectively) (Fig. 5.12c). The $r'$ values greater than about 1.48 reach effective saturation ($n/N > 0.86$) after some amount of time (sites nearer to centers than $r' = 1.48$ experience thermally-assisted tunneling at a rate higher than the filling rate). The more stable sites saturate shortly after 800 ka, but some of the less stable sites reach saturation later. This is because the detrapping rate is greater for these sites.

Higher mean temperatures result in a trapped population with greater minimum $r'$ values. In other words, the nearer sites that would be occupied at lower temperatures remain empty at higher temperatures. This trend in site occupancy with temperature can be examined in the measured TL signals from drill core samples discussed in the following section.

5.4 Comparing measured and modeled behaviors

5.4.1 Comparing natural signals to modeled signals

Because the low-temperature TL peak in feldspar is generally asymmetric with overlapping peaks at higher temperatures, it is common practice to describe natural TL curves according to the measurement temperature at half of the maximum TL intensity (i.e., the position of the ‘leading edge’ of the main peak in a TL glow curve), or $T_{1/2}$ (e.g., Spencer and Sanderson, 2012). The $T_{1/2}$ values for all drill core natural TL signals are shown as open symbols in Fig. 5.14a.

Also shown as filled red triangles in Fig. 5.14a are the $T_{1/2}$ values simulated at natural conditions. To produce these values, I first solve Eq. 5.12 for the time range $t = 0$ to $2$ Ma at $T_{SS}$, each sample’s burial temperature. The resulting $n(r)$ distribution for each sample as evaluated with Eq. 5.13 to determine the TL that would result after burial at $T_{SS}$ for 2 Ma. The $T_{1/2}$ values for these simulated TL curves are shown in Fig. 5.14a. A remarkable concordance is found, suggesting that the measured relationship between natural $T_{1/2}$ values
Figure 5.14: The modelled and observed $T_{1/2}$ values are shown for natural (a) and post-isothermal (b) TL curves. For the natural signals, the $T_{1/2}$ values result from 2 Ma of burial (enough time to reach thermal equilibrium) at the shown temperatures (triangles). These are shown alongside the natural $T_{1/2}$ values measured for the drill core samples (circles, diamonds, and boxes). (b) Measured (circles) and modelled (triangles) $T_{1/2}$ values are also shown following real and simulated isothermal treatments (the same kinetic parameters are used in natural and post-isothermal TL simulations). The fitting residuals are shown above each panel.
and the steady-state temperature is explainable in terms of site stability.

5.4.2 Comparing isothermal decay of TL signals to modeled response

The $T_{1/2}$ values following laboratory irradiation and heat treatment are plotted as open symbols in Fig. 5.14b. Also plotted are the $T_{1/2}$ values that are simulated with Eqs. 5.12 and 5.13 given the same kinetic parameters used in Fig. 5.14a. It is encouraging that the same kinetic parameters that reproduce the natural drill core $T_{1/2}$ values also resemble the high-temperature measurements. Broad agreement between observed and modeled TL behaviors over timescales ranging from $10^{-7}$ to $>10^6$ years and temperatures ranging from $-4.1$ to $200 \, ^\circ C$ lends support to this conception of the position of the lower-temperature TL peak in feldspars as a useful record of thermal history.

This concordance between measured and simulated $T_{1/2}$ values gets stronger at longer durations and higher temperatures, which may suggest that our model fails to incorporate transient luminescence phenomena occurring at room temperature. Ground-state tunneling is omitted from the current model, but this effect should only decrease the minimum stability distance, shifting the $T_{1/2}$ value higher. This discrepancy deserves further consideration in future work.

5.5 Application to cooling systems

Having reproduced the behavior of the natural TL signals in tectonically quiescent settings, we consider briefly how this signal would accumulate in settings where exhumation is more rapid. I simulate four simple cooling scenarios (Fig. 5.15). In each scenario, the sample is first cooled at a fixed rate ($dT/dt = -1, -10, -100,$ or $-1000 \, ^\circ C/Ma$) for 2 Ma and then held at $10 \, ^\circ C$ for 0.5 Ma (simulated as an evolving $n(r)$ distribution using Eq. 5.12 assuming initially empty traps and a dose rate of 4 Gy/ka). In addition to monitoring the evolution of $n(r)$ through time, I also simulate the TL that would be measured a) immediately after cooling, and b) after linear cooling followed by 0.5 Ma at $10 \, ^\circ C$. Given the sample parameters reported in Table 5.1, a cooling rate of $-1 \, ^\circ C/Ma$ would produce a TL signal at equilibrium.
Figure 5.15: Electron trapping is simulated at different cooling rates. For all four simulations (a) - (d), the sample is cooled at a rate $dT/dt$ for 2 Ma and then held at $T = 10 \, ^\circ\text{C}$ for 0.5 Ma. The cooling rates are $dT/dt = -1$ (a), -10 (b), -100 (c), and -1000 (d) °C/Ma. The results of these simulations are presented as the degree of fractional saturation $n/N$ through time for all dimensionless recombination distances $r'$. The color scale goes up until the sample is effectively saturated $n/N \sim 0.86$; at values greater than this, only white is shown. Finally, the TL signals that would be measured after the initial cooling (red curves) and after the 0.5 Ma at 10 °C (blue curves) are shown. Notice that at a cooling rate of -1 °C/Ma, these curves are effectively indistinguishable, indicating that the $n(r)$ distribution (and therefore the TL signal) is in equilibrium with the ambient temperature during cooling. At the other extreme of -1000 °C/Ma, the sample is not yet in equilibrium after 500 ka at 10 °C.
(i.e., indistinguishable from the signal measured 500 ka later). The TL following cooling at \(-10\, ^\circ\text{C/Ma}\) is only marginally distinct from the later measurement, but by \(-100\, ^\circ\text{C/Ma}\), the signal is clearly in disequilibrium. Following cooling a rate of \(-1000\, ^\circ\text{C/Ma}\), the system is entirely unsaturated even 500 ka later.

These results are encouraging, as they suggest that cooling rates around \(-100\, ^\circ\text{C/Ma}\) or faster should be in disequilibrium for \(\sim 10^3 - 10^6\) years, depending on sample parameters. While this prediction remains to be demonstrated, it would suggest that TL thermochronometry could resolve slower exhumation rates than optically-stimulated luminescence techniques in feldspar (e.g., \(dT/dt < -200\, ^\circ\text{C/Ma}\); Guralnik et al., 2015a). The time over which the signal grows before reaching equilibrium would also be quite useful for geomorphic and neotectonic applications.

5.6 Discussion and Conclusions

Thermoluminescence signals from bedrock feldspars show a systematic dependence on ambient temperature. During burial, the electron traps within these grains were filled according to the stability of each trapping site. Because this stability should depend on the distance to the nearest recombination center, a distribution of trap saturation as a function of distance develops, \(n(r)\), which characterizes a sample’s thermal history. In the case of thermal steady-state, some sites are entirely filled \((n/N \sim 1)\), some are partially filled, and some remain empty (Fig. 5.12b). This partially-occupied recombination distance controls the position of the \(T_{1/2}\) measurements shown for the natural signals and for signals following isothermal treatments (Figs. 5.14a and b).

The systematic dependence of natural \(T_{1/2}\) values on ambient temperature (Fig. 5.14a)) coupled with the multiple-additive dose results (Fig. 5.4) give convincing evidence that \(T_{SS}\) controls the location of the leading edge in feldspar TL, a behavior that can be explained in light of recent advances in our understanding of feldspar luminescence kinetics (e.g., Jain et al., 2015). Within this context, the role of anomalous fading should be considered. In our formulation (Eq. 5.12), athermal fading is incorporated, though only in the excited-state
(i.e., thermally-assisted tunneling). Thermally-activated tunneling would produce the phenomenon of anomalous fading as commonly measured in sediment studies (e.g., a decrease in luminescence intensity after storage at room temperature; Huntley and Lamothe 2001). Moreover, such a recombination pathway is consistent with the observation of Visocekas (2000), that the anomalous fading of the feldspar TL signal detected in the blue range (as in this study) exhibits a temperature dependence. The observed fading rate will depend primarily upon the activation energy required to access the excited state, the ambient temperature, the effective frequency factor, and the density of recombination centers.

Of particular note is the agreement that we observe between model predictions and measured TL responses following natural and laboratory heating conditions (Fig. 5.14). The same kinetic parameters (Table 5.1) can be evaluated with Eq. 5.12 to reproduce the \( T_{1/2} \) position resulting from 1000 s at 200 °C \( (T_{1/2} \) measured to within about 15 °C) and thermal steady-state \( (t \gg \text{order } 10^5 \text{ ka}) \) at -4.5 °C \( (T_{1/2} \) measured to within about 5 °C).

I emphasize that this model is one of the simplest justifiable models for feldspar luminescence. Additional pathways that could be incorporated in the future might include activation into the band-tail states (up to the conduction band) or ground-state tunneling, both of which have been adopted for IRSL thermochronometry with feldspars (e.g., Guralnik et al. 2015a; King et al. 2016a). The main elements of this kinetic model are identical to those used in Jain et al. (2015) and have been used in that and other studies to explain both optical and thermal features of feldspar luminescence. Thermoluminescence signals may be preferable over optical luminescence for feldspar thermochronology applications, however, as the full range of thermal stability is monitored during a single TL measurement. Additionally, TL measurements avoid the complications arising from preheating and phototransfer effects (see Chapter 3).

Moving forward, many questions remain to fully develop this method. Does the feldspar TL response become more sensitive to radiation with prolonged heating or metamorphism? What is the maximum steady-state temperature that can be identified using the leading edge of TL emissions? How should one handle low-temperature shoulders when identifying the natural \( T_{1/2} \) value? What is the natural variation in \( D_0, \rho' \), trap depth, and frequency
factors? Can we analytically define the closure temperature for a $T_{1/2}$ age at different cooling conditions, or can this only be defined numerically?

Our results illustrate the potential utility of the feldspar TL signal for geothermal studies. The $n(r)$ distribution is sensitive to a wide range of ambient temperatures: -4.1 to 60.2 °C. This distribution responds to thermally dynamic scenarios as well and initial simulations suggest that the signal should be useful for monitoring rapid ($dT/dt \sim -100$ °C/Ma, depending on sample parameters) exhumation during the Quaternary. This combination of low-temperature sensitivity and measurable signal growth between $10^2$ to $10^6$ years is promising for tectonic and geomorphic applications involving short-wavelength, upper-crustal thermal perturbations, and could prove useful in resolving questions of recent bedrock exhumation rates.
CHAPTER 6

Estimating the thermal history of Rock Creek glacial valley using SAR TL

6.1 Introduction

Landscape evolution phenomena are ideal targets for low-temperature thermochronometers, as has been demonstrated with, for example, apatite fission-track and apatite (U- Th)/He dating (Fox et al., 2015; Adams et al., 2015). The range of ages that can be recovered with luminescence thermochronology (∼10² – 10⁵ y), however, is better suited for studying processes such as glacial and fluvial erosion. Fundamental questions can be addressed at these timescales. Under which conditions will fluvial knickpoint migration dominate over uniform down-cutting (Schildgen et al., 2010)? Does glacial erosion increase (Montgomery, 2002; Valla et al., 2011; Sternai et al., 2012) or decrease (Whipple et al., 1999; Mitchell and Montgomery, 2006; Egholm et al., 2009) topographic relief? Numerical studies have made specific and testable predictions about these mechanisms. For example, workers have recently hypothesized that at full glacial conditions erosion is focused at low elevations. This down-valley steepening generates a locus of erosion which migrates headward thereby increasing relief (Shuster et al., 2011; Sternai et al., 2013). Such claims could be directly addressed with luminescence thermochronology. In this chapter, I examine the thermal evolution of the Rock Creek glacial valley using feldspar single-aliquot regenerative (SAR) TL signals measured from 18 bedrock samples in hopes of gaining insight into these important geomorphic questions.
6.2 Geologic context

The Beartooth uplift is a 60 × 125 km block of Precambrian crystalline basement which was initially exhumed during the Laramide orogeny (Wise, 2000). Apatite fission-track results from a 2.5-km-deep exploratory well indicate a two-stage uplift history, with the first stage beginning around 61 Ma and resulting in 4 - 8 km of uplift, and the second stage beginning between 15 and 5 Ma and producing about 4 km of uplift, which continues to the present (i.e., 0.3 - 0.8 mm/yr) (Omar et al., 1994).

Though located south of the Cordilleran ice sheet, the Rock Creek valley (just south of Red Lodge, MT) experienced multiple alpine glaciations throughout the Pleistocene. The resulting glacial landforms within this region have been qualitatively described in some detail, but there remains a scarcity of absolute age constraints for major advances and retreats. Graf (1971) classified terminal moraines according to morphology, spatial distribution, and weathering features. He concluded that the area contained evidence of multiple Pinedale interglacials and Bull Lake glaciation, which have more recently been correlated with marine oxygen-isotope stages (MIS) 2 and 6 (or perhaps 5d), respectively (Pierce, 2004). Bull Lake moraines south of the Beartooth uplift pre-date the West Yellowstone rhyolite flow dated as 122.3 ± 2.2 ka by about 30 ka based on the thickness of hydration rinds within obsidian clasts which were cracked by glacial pressure, putting the age of the Bull Lake glaciation around 150 ka (Obradovich, 1992). Cosmogenic $^3$He, $^{10}$Be, and $^{26}$Al surface exposure ages from boulders within moraines (Phillips et al., 1997; Gosse and Phillips, 2001; Licciardi et al., 2001; Licciardi and Pierce, 2008) and U-series dating of subaerial travertines (Sturchio et al., 1994) and pedogenic carbonates within glacio-fluvial terraces (Sharp et al., 2003) demonstrate significant activity up through the Last Glacial Maximum (LGM), with pronounced activity around 20 ka.

Within the Rock Creek glacial valley, 18 bedrock samples were collected from vertical and longitudinal transects (Fig 6.1). The longitudinal profile spans nearly 17 km, from the valley mouth to the head. The vertical profile represents about 690 m of relief, from the top of the plateau on the south side, down the southern wall to the valley bottom and back up.
Figure 6.1: The Rock Creek glacial valley is depicted within the Beartooth uplift (upper-left corner), and individual sample locations are shown within the valley.
the northern wall. These samples were collected to compare luminescence cooling ages with regional glacial chronologies and to elucidate sub-valley-scale erosion mechanisms.

The chief difficulty in identifying ideal sample locations was simply finding an exposed, in situ outcrop. The landscape of the Rock Creek glacial valley is roughly divided into high summit flats, steep rock walls, drift-mantled slopes, and valley bottom [Ballantyne, 2002]. The summit flats are relatively easy to sample (e.g., J0994 and likely the original location of J1008), but sampling the other environments is difficult. For high rock walls, the base of the wall can be sampled (J1001, J1007, J1010), but unlike with fluvial valleys, there are few if any spurs that can be hiked to gain elevation, such that rope-aided climbing may be the only viable alternative. In the case of this valley, the highway snaked up the valley wall, allowing for easy identification of fresh surfaces and relatively direct access. Of course, fluvial tributaries provide an alternative route up the mountain side. The difficulty here comes not with sampling but with interpretation: how much erosion should be attributed to glacial versus fluvial activity? In the same way, the valley bottom is largely comprised of till, perhaps exacerbated by overdeepenings [Preusser et al., 2010], perhaps simply a combination of alluviation and debris flow. Of the entire valley, only one sample was taken from near active channel of Rock Creek, J1002.

6.3 Motivating observations for cooling age determination

6.3.1 Experimental results

6.3.1.1 Stability continuum

The most basic observation about feldspar TL is that it exhibits a continuum of stabilities. Figure 6.2 (sample J0165, from the Yucaipa Ridge block) demonstrates the effects of storage at room temperature for about a minute to 8.4 h (green curves). Notice the shift of the leading edge of emissions and also the decrease in intensity relative to the first measurement following a 75 s delay. Compare this with the effect of preheating to temperatures of $T = 100 - 350 \degree C$ for a few to several-thousand seconds. This results in a similar leading-edge shift, but the
intensity does not diminish to the same degree. Rather, the remaining signal at higher measurement temperatures (e.g., 250°C) is nearly the same following preheats of different temperatures and durations.

This suggests that while the charge at sites of lesser stability is lost, the higher stability sites remain occupied during heat treatment. The measured curves may also reflect the process of trapped-charge not only simply detrapping, but sometimes transferring from sites of lesser stability to sites of greater stability (i.e., thermal transfer). At room temperature, by contrast, it appears that fading operates over a wider range of stabilities, depleting TL curves over a wider range of measurement temperatures.

6.3.1.2 Overprinting the TL signal

Next, we consider how this TL signal gets overprinted in three experiments (Table 6.1). In the first experiment, this same sample (J0165) was given a lab dose of 12 Gy and then left at room temperature for 30 s up to 30,000 s (about 8.3 h). The sample was then given the same dose again before measuring the TL curves shown in Fig. 6.3(a). Notice how the first irradiation produces a TL signal which migrates to higher $T$ values but is still resolvable within the bulk TL signal even after a pause of 8 hr. A simple prediction from these results would be that higher fading rates (e.g., higher $\rho'$ values) would have the effect of lowering the slope of the initial rise, of broadening the low-temperature edge of TL emissions.

The second experiment (Fig. 6.3(b)) is similar to the first, except instead of an intervening pause there is an intervening heat treatment at 250°C for a range of times, from 3 to 3000 s. This has the effect of shifting the preheated population to higher temperature domains before the second dose is given (without any further heating prior to TL measurement). That the first signal persists after almost one hour at 250°C is remarkable. These results are provocative in that they suggest that prior heat treatments may be remembered in the form of a higher-temperature shoulder.

These results prompt the final experiment (Fig. 6.3(c)). Sample J0165 is given a lab dose of 12 Gy, heated to $T_1$ (250°C for the green curve; 300°C for the yellow curve) for 100 s,
Figure 6.2: The natural TL response of sample J0165 (blue curve) is compared with the regenerative TL responses following a beta dose and: a) a range of room-temperature delays ranging from 75 s to 8.4 hr (green curves); b) progressive preheating to the temperatures shown (red curves); or c) isothermal holding from 100 to 350 °C for a range of times (grey curves; same data as in Fig. 4.6). All TL measurements were performed at a heating rate of 5 °C/s. While the relative heights for same-colored curves are real, the different sets have been scaled for comparability.
Table 6.1: The protocols used in section 6.3.1 to illustrate how feldspar TL can be used to infer multi-step thermal histories.

<table>
<thead>
<tr>
<th>Step</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
<th>Experiment 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$D = 12$ Gy</td>
<td>$D = 60$ Gy</td>
<td>$D = 12$ Gy</td>
</tr>
<tr>
<td>2</td>
<td>Pause for $t$ s</td>
<td>250°C for $t$ s</td>
<td>$T_1$ °C for 100 s</td>
</tr>
<tr>
<td>3</td>
<td>$D = 12$ Gy</td>
<td>$D = 60$ Gy</td>
<td>$D = 12$ Gy</td>
</tr>
<tr>
<td>4</td>
<td>TL (5 °C/s)</td>
<td>TL (5 °C/s)</td>
<td>$T_1$ °C for 100 s</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>$D = 12$ Gy</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>TL (5 °C/s)</td>
</tr>
</tbody>
</table>
Figure 6.3: (a) Sample J0165 is given a beta dose of 12 Gy, kept at room temperature in the dark for $t$ s to allow for fading, and then given another dose of 12 Gy before measuring the TL curves shown. (b) The same disc is given a dose of 60 Gy, preheated to 250 °C for the duration shown, given another dose of 60 Gy and then heated to measure the TL responses shown. (c) The disc is then given the same dose of 12 Gy three times, with two preheats intervening as shown in the legend (e.g., 12 Gy, PH at 250°C for 100 s, 12 Gy, PH at 300°C, 12 Gy, TL measurement). Panels (d) - (e), the simulated TL curves, show comparable TL shapes produced assuming discrete trap populations defined by $r_{min}$ and $n_0$ values. Notice that all upper panels (actual measurements) are closely approximated in our simple model by assuming that fading and heating have the effect of increasing the minimum occupied recombination distance.
given a dose of 12 Gy, heated to $T_2$ (150 or 100 °C) for 100 s, given a dose of 12 Gy, and then the TL is measured. As with the previous experiment, the dose populations comprising the TL curve reflect the heat treatment(s) they received. More specifically, we can make out that the subpopulations comprising the TL curves are empty during measurement up until the same temperature as the isothermal treatment. So, not only can we observe three distinct populations ($D$ before $T_1$, $D$ before $T_2$, $D$ after $T_2$), we can estimate the temperatures of the heat treatment(s).

To offer further support to this hypothesis, the TL experimental data in Fig. 6.3(a)-(c) are approximated with a simple kinetic model which assumes that TL proceeds from one or more discrete populations of traps sharing the same kinetic pathways, differing only in their minimum occupied recombination distance ($r_{min}$). A population was used for each experimental dose-population (e.g., the traps populated following $T_1$ but preceding $T_2$) and these were scaled only in intensity and $r_{min}$. In all three examples (Fig. 6.3(a)-(c)) a single higher-temperature population (centered around 375 °C) was added to account for this separate feldspar TL trap. The results are shown in Fig. 6.3(d)-(f). That such close agreement is observed lends credence to our interpretation of discrete ‘legacy’ populations preserved in the final TL measurement.

### 6.3.1.3 Dose response after heating

Before moving to the shapes of natural TL signals, we should examine how the regenerative TL signal grows following heat treatment (Fig. 6.4). In this experiment, J0165 was given a beta dose of 25 Gy and then heated to either 150 (solid curves) or 250 °C (dashed curves) for 100 s. Next, the sample was given a second dose before the TL response was measured. As with Figs. 6.2 and 6.3 we observe that the heating forces the initial dose population to higher-temperature regions. The second irradiation then preferentially fills these recently-emptyed sites.

Two important observations should be made about Fig. 6.4. First, by isolating the initial dose population within the measured TL curve (in this case, the higher-temperature peak),
Figure 6.4: Sample J0165 is given a lab dose $D = 25$ Gy and then heated to $T = 150$ (solid curves) or $250$ °C (dashed curves) for 100 s and then given a second dose (displayed as a fraction of the original dose) prior to TL measurement at 5 °C/s.
one could calculate the post-heating dose received. Second, after a greater post-thermal
dose, this will become increasingly difficult to do, as the first signal is overwhelmed by the
second.

6.3.2 Similarity to natural TL shapes

The observations from the previous section pose an obvious question: can the natural TL
signals be fitted to discrete components, and if so, can these be used to estimate geothermal
history? In this section, I illustrate this fitting with three natural TL signals, and, in the
rest of the chapter, I address the question of interpreting geothermal history.

Figure 6.5 shows the measured and modelled natural TL signals from samples J0994,
J0999, and J1001 (Fig. 6.9). Each curve is fitted to three components, that is, three trap
populations. The first is the highest temperature trap, which is thought to have markedly
different kinetic properties than the trap investigated in this study (Duller 1997; Murray
et al. 2009). In the simplest interpretation, the middle signal would be interpreted as the
signal prior to geologic cooling, and the component at the lowest temperature would be the
charge that has trapped during or since cooling.

Not only are the natural TL signals well approximated by discrete populations, but this
exercise suggests a simple way forward for interpreting thermal history: identify the locations
of the lower-temperature peaks and then evaluate the dose needed to populate them to the
natural degree. That will be the focus of the next section.

6.4 Estimating the thermal history of a bedrock sample using the
SAR TL

A reconstruction of the thermal and dosimetric history of a sample can be subdivided into
four tasks. First, the \(T_{1/2}\) values for the leading edges of any natural TL peaks should
be identified. In many cases there will be a single edge, but if the sample is not in thermal
equilibrium, there may be multiple preserved edges. Second, an isothermal decay experiment
Figure 6.5: The TL signals from samples J0994, J0999, and J1001 (Fig. 6.9) are shown in the top panel and then fitted (lower panel), each curve approximated by the sum of three trap populations (dashed curves).
should be carried out in order to a) determine the $T, t$ combination which will produce this natural $T_{1/2}$ value for the subsequent dose response experiment, and b) produce a dataset from which the natural $T_{SS}$ can be extrapolated. Third, a dose response experiment should be conducted to determine the radiation dose that would reproduce the same TL intensity at this $T_{1/2}$ value. This equivalent dose can be divided by the geologic dose rate to determine a finite age. Using this age as the $t$ value, the $T_{SS}$ value will be extrapolated from the experimental $T, t$ data. This section will detail this procedure for sample J1002, taken from floor of the glacial valley. Lastly, the meaning of this age will be discussed.

6.4.1 Isothermal decay of $T_{1/2}$ value

Sample J1002 was held at temperature $T \degree C$ for a duration of $t$ s. The hold temperatures were $T = 50, 100, 150, 200,$ and $250 \degree C$, and the hold times were $3, 10, 30,$ and $100$ s. At $50$ and $100 \degree C$, the discs were also subjected to longer hold times of $300, 1000,$ and for $T = 50 \degree C, 3000$ s. The results are shown in Fig.6.6(a). With the exception of the $3$ and $10$ s hold times at $50 \degree C$, all of the $T_{1/2}$ values for a given hold temperature show a logarithmic dependence on hold duration. The thermal age (as described in the following subsection) is plotted according to the natural $T_{1/2}$ value; notice the discontinuity of the $x$-axis.

6.4.2 Dose growth of $T_{1/2}$ value

The geologic dose since cooling was estimated with the protocol listed in Table 6.2. First, a dose was given. This dose should be sufficiently large to reproduce magnitude of the upper peak, when present; I chose $122.9$ Gy for sample J1002 (with each SAR cycle, this dose will remain the same). After administering the dose, the sample was heated to increase the laboratory $T_{1/2}$ value to approximate the higher of the two natural $T_{1/2}$ values (e.g., $250 \degree C$ for $226$ s to reproduce the approximate upper $T_{1/2}$ value of $310 \degree C$; Fig.6.6(a) and (b)). At this point in the protocol, between Steps 2 and 3, the sample resembles the natural state immediately following instantaneous cooling. Steps 3 and 4 then mimic the dose since cooling: a dose followed by a heating to $200 \degree C$ for $18$ s to reproduce the natural lower
Figure 6.6: (a) Sample J1002 was repeatedly given a beta dose of 3.1 Gy then subjected to isothermal treatments at the temperatures and times shown. After isothermal treatment, the TL was measured ($5 \degree C/s$) and the $T_{1/2}$ value was calculated. (b) The isothermal data were used to recreate TL curves with similar $T_{1/2}$ values following doses from 0 to 245.8 Gy. (c) Integrated TL intensities at $T = 234.2 \degree C$ were then used to produce a dose response curve from which the laboratory equivalent dose ($D_E$) could be determined to be 102.7 Gy. Divided by the geologic dose rate of 5.4 Gy/ka, this yields an age of 18.9 ka. (d) The age of 18.9 ka can then be used to extrapolate to the steady-state temperature which would produce the natural $T_{1/2}$ value; in this case, $T_{SS} = 4.1 \degree C$. 
$T_{1/2}$ value of 234.2 °C (gotten by mapping the position of the upper leading-edge to the isothermal conditions necessary to produce this $T_{1/2}$ position; Fig. 6.6a). The TL response was then measured. The entire protocol was repeated for a range of doses in Step 3: 0, 30.7, 61.4, 92.2, 122.9, 153.6, 184.3, 215.0, and 245.8 Gy. Finally, the TL responses at the natural, lower $T_{1/2}$ value of 234.2 °C were plotted as a function of administered dose to estimate the geologic dose since cooling, 102.7 Gy. Divided by the geologic dose rate of 5.4 Gy/ka, this gives a cooling age of 18.9 ka.

6.4.3 Estimating the modern $T_{SS}$ value

6.4.3.1 By extrapolation

Once the cooling age of 18.9 ka was estimated for J1002, the $T_{SS}$ value since cooling was estimated at 4.1 °C (Fig 6.6(d)). The isothermal decay results from Fig 6.6(a) were extrapolated to calculate the $T_{1/2}$ value which would be produced following a hold time of 18.9 ka at various steady state temperatures. While the predicted $T_{1/2}$ values produced by most laboratory $T_{SS}$ values are unphysically high, the extrapolation to lower $T_{SS}$ temperatures should remain valid.

6.4.3.2 By comparison with drill core samples

An alternative approach is to test whether the natural $T_{1/2}$ values would map to realistic mean annual temperatures when interpreted with the fit of drill core $T_{1/2}$ results to steady-state temperatures that was developed in Chapter 5. The results of this exercise are shown in Fig. 6.7, which compares both the drill core results fitted to a linear regression and the $T_{SS}$ values evaluated from the TL signals of the Rock Creek glacial valley samples.

The resulting mean annual (air) temperatures vary but are all reasonable for this location. The Western Regional Climate Center offers minimum, maximum, and mean monthly temperatures for the town of Red Lodge, MT (station located at N45° 11’ W109° 15’, elevation 1

1 http://www.wrcc.dri.edu
Table 6.2: The protocol for estimating the geologic dose at the present temperature is calibrated according to the isothermal decay characteristics of the sample and the location(s) of the natural $T_{1/2}$ value(s). Steps 1 and 2 maybe neglected if the shoulder of the upper peak does not interfere with the lower peak.

<table>
<thead>
<tr>
<th>Step</th>
<th>Treatment</th>
<th>Significance</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Dose of $D$ Gy (constant for every SAR cycle)</td>
<td>Prior geologic dose</td>
</tr>
<tr>
<td>4</td>
<td>Heat at $T$ °C for $t$ s (produce higher $T_{1/2}$)</td>
<td>Prior geologic temperature</td>
</tr>
<tr>
<td>3</td>
<td>Dose of $D$ Gy (various)</td>
<td>Recent geologic dose</td>
</tr>
<tr>
<td>4</td>
<td>Heat at $T$ °C for $t$ s (produce lower $T_{1/2}$)</td>
<td>Recent geologic temperature</td>
</tr>
<tr>
<td>5</td>
<td>TL measurement to 500 °C</td>
<td>Measurement</td>
</tr>
<tr>
<td>6</td>
<td>TL measurement to 500 °C</td>
<td>Thermal background</td>
</tr>
</tbody>
</table>
**a**

Drill core:
- E802 (purple circles)
- W219 (green diamonds)
- R716 (orange squares)

\[ T_{1/2} = (1.34 \pm 0.05) T_{ss} + (235.0 \pm 1.4) \]

**b**

Monthly MAT for Red Lodge, MT (1894 - 2012)

predicted from \( T_{1/2} \) values

Month abbreviations:
- M (March)
- A (April)
- J (June)
- S (September)
- O (October)
- N (November)
- D (December)

Sample codes:
- J1001
- J0994
- J1002
- J1000
- J0997
- J1003
- J1006
- J0995
Figure 6.7: Using the observed relationship between steady-state temperature and $T_{1/2}$ values of drill core samples discussed in Chapter 5 (a), we can convert the measured $T_{1/2}$ from the Rock Creek glacial valley samples into apparent mean annual air temperatures (b). The monthly mean air temperatures for the town of Red Lodge, MT (1697 m above sea level) constitute an instrumental record from 1894 to 2012. These data were taken from the Western Regional Climate Center website (www.wrc.dri.edu).
558 m) for an instrumental record spanning from 1894 to today. The apparent steady-state temperatures for these samples are strikingly consistent with the instrumental record from the nearby climate station, if slightly colder (as would be expected at slightly higher elevations). This approach for determining burial temperature from TL data seems preferable to the extrapolation of $T_{1/2}$ isothermal data to geologic conditions (e.g., Fig. 6.6(d)).

6.4.4 What does this SAR $T_{1/2}$ age represent?

In this section I have described a SAR TL protocol for determining the equivalent dose ($D_e$) at the position of the natural $T_{1/2}$ value. This $D_e$ value divided by the geologic dose-rate gives a finite age, but how should this age be interpreted? The answer is actually quite intuitive. Remember the primary observation of Chapter 5: the position of the $T_{1/2}$ value is directly related to the burial temperature. Put another way, the TL signal will accumulate up the leading edge, the least stable sites that can still accumulate at some ambient temperature. If that temperature decreases, the signal will begin to accumulate at sites that are luminescent at slightly lower measurement temperatures (see Fig. 6.8). Because of this effect, ages calculated in this way should be interpreted as the maximum amount of time spent at the present temperature. (In the next chapter, I will develop a method for evaluating a more complete thermal history).

6.5 Interpreting the SAR TL ages from the Rock Creek glacial valley

6.5.1 SAR TL ages

By applying the technique described in section 6.4.2, I estimated the maximum cooling ages for samples J0994, J0999, J1001, J1002, J1007, and J1008 (Fig. 6.9(a)). With the exception of J0999 (0.5 ± 0.3 ka), these ages are consistent with periods of significant local glacial activity, as inferred by cosmogenic $^{10}$Be surface exposure ages of the Clarks Fork moraine, 18 km to the southeast ([Licciardi and Pierce 2008]) and $^{230}$Th/U dating of pedogenic
Figure 6.8: As an example TL curve accumulates through time, the intensity at the $T_{1/2}$ location gradually increases. Under this conception, the age estimate that would be calculated from the dose-response at $T_{1/2}$ would represent the maximum amount of time that the sample has been at its present temperature (an endmember scenario wherein cooling was instantaneous). The other endmember scenario would be slow geologic cooling resulting in gradual signal accumulation at $T_{1/2}$, with only a fraction of time spent at the present temperature.
carbonates within glacio-fluvial terraces within the Wind River Basin, about 200 km to the south (Sharp et al., 2003) (Fig. 6.9(b)).

Two samples require additional explanation: samples J0999 (≥ 0.5 ± 0.3 ka) and J1008 (≥ 82.3 ± 3.9 ka). Sample J0999 was detached from bedrock within a draw. About 350 m below this sample location is a fully-vegetated debris flow with a surface area of ~0.2 km² (Fig. 6.10). One possible interpretation is that the bedrock cooled to its present temperature when it was exhumed by a landslide 500 years ago.

For sample J1008, the age of ≥ 82.3 ± 3.9 ka is surprising because of its position near the active river channel on the valley floor. Aerial imagery (September, 1980; 1: 32000 scale; courtesy of the U.S. Geological Survey), however, reveals that the bedrock block sampled (380 m² visible surface area) sits within a larger landslide apron, and likely derives from the exposed valley wall, nearly 830 m above (Fig. 6.11).

6.5.2 Post-glacial erosion

A post-glacial landscape is essentially unstable, prone to rapid modification (Ballantyne, 2002). To evaluate how the modern paraglacial topography of the Rock Creek glacial valley may be evolving, we start with two end-member approaches to the problem of understanding topographic evolution. The first describes the form of the landscape in its current form (Seidl et al., 1994; Montgomery, 2002; Wobus et al., 2003). The second uses physical laws to simulate the evolution of imaginary topography with the aim of reproducing topographic features similar to those observed naturally (Kirkby, 1971; Howard, 1994; Braun and Scherler, 2014). Of course, these approaches are often used in conjunction, and increasingly workers use an inversion approach wherein the modern topography is taken as the boundary condition towards which landscape evolution models must evolve (e.g., PECUBE; Braun, 2003; Sternai et al., 2012); see Braun et al. (2012) for a concise summary.

In this study, I use the first approach, though the additional incorporation of landscape evolution models could also prove illuminating. To begin with, I use the TopoToolbox MATLAB package (Schwanghart and Kuhn, 2010; Schwanghart and Scherler, 2014) to calculate
Maximum TL cooling ages

- 59.0 ± 10.7 ka [J1010]
- 20.1 ± 1.7 ka [J1002]
- 19.3 ± 7.8 ka [J1001]
- 0.5 ± 0.3 ka [J0999]
- 11.2 ± 2.0 ka [J0994]
- 24.5 ± 1.4 ka [J1007]
- 82.3 ± 3.9 ka [J1008]

Elevation (m):
- 2212
- 3554

This study
L&P '08
S+ '03 (WR4)
S+ '03 (BLN)
S+ '03 (L)
S+ '03 (BR)
S+ '03 (WR1)
Figure 6.9: (a) Maximum feldspar TL cooling ages for bedrock samples within the Rock Creek glacial valley. (b) Comparison of maximum cooling ages from this study (purple diamonds) with cosmogenic \(^{10}\)Be surface exposure ages of the Clarks Fork moraine, about 18 km to the southeast (blue squares; Licciardi and Pierce 2008), and \(^{230}\)Th/U dating of pedogenic carbonates from within glacio-fluvial terraces (Wind River 4, Bull Lake North, Lenore, Boysen Reservoir and Wind River 1) in the Wind River Basin of Wyoming, about 200 km to the south (Sharp et al. 2003).
Figure 6.10: The lefthand panels show two different USGS aerial images. Both sample locations and the photo perspective for the righthand panels are shown for reference. Notice the apparent landslide outlined in the lower-left and lower-right corners. Minimum cooling ages are also shown.
Figure 6.11: Lefthand panels: An aerial photo shows sample J1008 in a larger context, within a landslide apron. Righthand panels: the sampled block of rock is outlined orange, with a full-sized backpack for scale.
Figure 6.12: The normalized steepness index values ($k_{sn}$) are plotted for the drainage network calculated for the stream outlet at the northeast corner of the map. Notice that the steepest regions are often located at hanging valleys; glacial activity has left the landscape in topographic disequilibrium.
the drainage-area-normalized steepness values, \( k_{sn} \) \cite{Wobus2006}, for the drainages within the glacial valley (Fig. 6.12).

Channel steepness is often used to locate stretches of bedrock rivers with abnormally high erosive capacity due to the increase in shear stress. Normalization according to drainage area allows comparison across catchments, as the greater contributing surface area will increase stream discharge and therefore its erosive ability \cite{Whipple1999}.

(It has recently been suggested, on the basis of \(^{10}\)Be concentrations in alluvial sand, that topographic metrics such as \( k_{sn} \) may not correlate well with denudation rates in post-glacial landscapes \cite{Moon2011, Moon2015}. Given the significant difference in precipitation regime between those studies, set in the Cascade Mountains of Washington, and the present one, it is unclear how influential channel steepness will be for evaluating post-glacial erosion.)

Examination of Fig. 6.12 reveals that while the main trunk of Rock Creek seems not to be overly steepened, many of the tributaries are quite steep adjacent to the main channel. This is expected in many cases, as many of these tributaries are found within hanging valleys, which become isolated from the main valley glacier as it erodes downward with greater ice discharge and therefore greater erosional efficiency \cite{MacGregor2000}. I expect post-glacial fluvial erosion to be highest along these stretches with high \( k_{sn} \) values.

The most obvious observation of the spatial distribution of these steepness values is that the tributaries seem to be in disequilibrium, still adjusting to the lowering of the valley bottom. Aside from the stretches connecting hanging valleys to the main stem, the drainages at higher elevations also exhibit steep stretches.

To investigate this further we can use the \( \chi \) plot of Perron and Royden \cite{Perron2013}, which transform the longitudinal elevation profiles of river networks into a system where the horizontal coordinate relates the balances between uplift and erodibility. These plots allow for the identification of fluvial steady-state according to the stream-power law, but also they enable the identification of transient knickpoint clusters migrating upstream \cite{Schmidt2015, Chen2016}, which present as overlapping lines. In Fig. 6.13, I show a \( \chi \) plot for the same drainage network shown in Fig. 6.12. Two features are remarkable. First,
Figure 6.13: Chi plot of stream network shown in Fig. 6.12. The overlap of values about 900 m above base level may imply the presence of a migrating knickpoint (dotted circle). The red dashed line would be the profile expected under topographic equilibrium; clearly the profile is in disequilibrium.
the network does not lie on the regression line \((m/n = 0.308)\), indicating disequilibrium. This is unsurprising, given the dramatic post-glacial topography. Second, there does appear to be a shared knickpoint around 900 m above the base-level (circled in blue), possibly indicating the presence of transient erosional wave with a common origin. The tributaries connected to this clustered region are found in approximately the lower half of the main stem of the channel.

Another important post-glacial erosion mechanism is mass wasting (Moon et al., 2015). Hillslope angle exerts a nonlinear control on the sediment flux of mass wasting processes (Dadson and Church, 2005) and is simple to extract from digital elevation models. Figure 6.14 shows the hillslope angles near Rock Creek. The general pattern that emerges is of steeper headwalls to the southwest that become more gradual moving downvalley. Presumably, the valley expands to the northeast due to prior hillslope mass wasting (Hovius et al., 1998), a process which is operable during and after glaciation (Guillon et al., 2015).

Given this current state of erosion that I interpret from topography, how might the valley have evolved during glaciation? That is the question addressed in the following section.

### 6.5.3 Glacial erosion

Although the mechanisms involved in active glacial erosion are complicated, especially in alpine settings (Egholm et al., 2011), basal erosion is considered greatest at the equilibrium line altitude (ELA), where ice accumulation exactly balances loss and ice sliding velocity is greatest (Anderson et al., 2006). An intriguing recent numerical (Sternai et al., 2013) and thermochronometric (Shuster et al., 2011) finding is that the long-term position of the ELA focus of glacial erosion may propagate up-valley through time, resulting in an erosional wave analogous to the concept of fluvial knickpoints. The basic sequence put forward by Sternai et al. (2013) is that a glacier initiates at the lower stages of the valley early on and as glacial mass accumulates, the erosive front moves headward along with the ELA.

Another view is that, while subglacial erosion is focused at the ELA position, there are peripheral geomorphic processes at work which promote erosion at higher elevations.
Figure 6.14: The hillslope angle is shown relative to the river network of Fig. 6.12. Notice the steepest regions are generally found near the headwaters and as the valley widens downstream, the angle of the valley walls becomes shallower.
undercut cirque walls lead to overly steepened headwalls, primed for collapse; toe removal from hillslopes above the ELA facilitates an increase in diffusive transport downhill, and so on (Mitchell and Montgomery, 2006). Moreover, this mean ELA position is argued to set an upper limit to mountain height, even in the presence of rapid uplift (Brozović et al., 1997; Montgomery et al., 2001). This paradigm is known as the glacial buzzsaw hypothesis.

As a tool for investigating how the position of the ELA relates to landscape development in and around glacial valleys, workers often investigate the relationships between modern ELA, ELA during full glacial conditions, and hypsometry (the frequency distribution of land surface area with elevation) (Brocklehurst and Whipple, 2004; Egholm et al., 2009); this is shown in Fig. 6.15. The hypsometry of Rock Creek glacial valley (specifically, the map area of Fig. 6.12) was extracted with a built-in script in QGIS (open-source geographical information system software), using an elevation bin width of 100 m. The few existing cirque glaciers found in the drainage system were used to estimate the modern ELA as about 3415 m. Simulations of glacial erosion imply that the mean position of the ELA during glaciation lies about 1/3 of the distance from the headwall to the valley terminus (Anderson et al., 2006). I plot the corresponding elevation in this valley, 2500 m, as the ELA during glaciation. The elevation of the mean Quaternary ELA is also often identified with the elevation of cirque outlets (Porter, 1989). I get a consistent result of 2546 ± 171 m for the 16 valley cirques. This difference between modern and mean Quaternary ELA is also consistent with erosional simulations and global topographic surveys, which find that just less than 1 km of separation is typical (Egholm et al., 2009; Pedersen and Egholm, 2013).

The characteristic signature of topography controlled by the glacial buzzsaw mechanism is a peak in surface area found between the elevation of the modern ELA and the ELA during glaciation (Egholm et al., 2009). In fact, we do observe this pattern at our location (Fig. 6.15). The accompanying interpretation for regions with high plateaux dissected by deep glacial troughs is that, at the modern snowline\(^2\) atop the plateau, snowfall is widely

\(^2\)Often snowline and ELA are used interchangeably in discussions about glacial buzzsaw. Though the concept of annual snowline is less physically relevant in terms of erosional dynamics, it is often more readily identifiable (e.g., Brozović et al., 1997).
Figure 6.15: The percent area as a function of elevation, i.e., hypsometry, for the map region of Fig. 6.12 is shown with elevation bins of 0.1 km. The modern ELA (measured directly from cirque glaciers), and the mean ELA during full glaciation (estimated as the elevation 1/3 of the distance from the headwall to the valley termination) are shown as dashed blue and red lines, respectively. The elevations of dated samples are shown on the right. Sample J1008, which was taken from a landslide block, is shown as the range of likely original elevations.
distributed over undulating topography. Unable to erode much below mean snowline, glaciers instead erode local highs in topography, which become ‘topographic lightning rods’ (Brozović et al., 1997). In this way, the plateau slowly and steadily flattens and lowers. A more recent addition to this theory comes from numerical simulations involving long-term glacial erosion of a plateau morphology (Pedersen et al., 2014). Their intriguing result is that, providing that the main valley is not entirely filled with ice, the edges of the plateau will be subjected to focused basal shear stress and will erode towards the interior of the plateau.

6.5.4 The recent evolution of the Rock Creek glacial valley

Given the reported SAR TL ages, their meaning (maximum time at present temperature), and the expected erosional mechanisms during and after glaciation, I can now suggest a realistic history for this valley. Prior to the LGM, we have little resolution, as only samples J1008 and J1010 give pre-LGM ages, at 82.3 ± 3.9 and 59.0 ± 10.7 ka, respectively. It is noteworthy that sample J1010, which was taken from the base of the southeastern wall, is so old, given how low in the valley it sits. An older age at the valley mouth might be expected if glaciers initiate at the lowest reaches of a drainage basin before migrating up-drainage (Sternai et al., 2013). After all, the valley mouth should have been in roughly the same position, going back to the inherited fluvial topography. So, even as glaciers make further headward erosional progress from one glacial cycle to the next, each glaciation should begin at about the same location. I therefore interpret this age as consistent with the idea for an initial ELA near the valley mouth.

Sample J1008 was inadvertently taken from what appears to be a landslide block (Fig. 6.11). The pattern of the landslide apron surrounding the block points directly to a small horn about 500 m above (see the red arrow in Fig. 6.9). If we assume that 82.3 ± 3.9 ka is the maximum time that the horn surface has been at present temperature, the implication is that headward erosion reached at least this far up the valley before the LGM but not before the last full interglacial (~130 ka; Lisiecki and Raymo, 2005). Technically, our age, as a maximum, does not preclude the horn being exposed as late as the LGM, but the apparent
thermal sensitivity of the other samples to more recent erosion suggests that this 82 ka signal would have been overprinted if erosion of similar magnitude were experienced; so, the horn was probably not eroded much more recently than about 80 ka.

The rest of the samples provide more detailed spatial information about the evolution of glaciation during, and after, the LGM. (For the remainder of this discussion, I assign an age range of 16.9 - 23.2 ka for the LGM, a result from proxy-based simulations of Cordilleran ice sheet advances during the last glacial cycle (Seguinot et al., 2016).) The first observation is the presence of headward erosion, potentially as early as 24.5 ± 1.4 ka (J1007). This may suggest a rapid headward propagation of the ELA for the main valley glacier, which would provide an important constraint in the time required for mass accumulation. Alternately, the cirques above may have been occupied, eroding their hanging walls.

The samples from the vertical transect reveal an interesting trend of younging upwards. Samples J1002 (20.1 ± 1.7 ka) and J0994 (11.2 ± 2.0 ka) reveal this trend best, as J1001 is too imprecise (19.3 ± 7.8 ka), and J0999 (0.5 ± 0.3 ka) is probably related to paraglacial erosion (e.g., mass wasting). The age of J1002 is interesting in terms of erosional timing. Namely, basal erosion was probably most active here close to this time.

The age of J0994 is probably the most exciting finding. At 11.2 ± 2.0 ka, this sample definitively postdates the LGM. Interestingly, its timing corresponds to the Younger Dryas cooling event, an abrupt cooling period which lasted from about 12.8 to 11.5 ka (Alley et al., 1993). The main valley may have been occupied by a glacier during this temperature excursion, but that glacier would not have been nearly thick enough to erode the plateau, ∼690 m above. Given that the sample was taken on a fresh bedrock platform, I interpret this young plateau-surface age as direct evidence of the near-edge plateau erosion hypothesized by Pedersen et al. (2014). I take this finding to be supportive of glacial buzzsaw mechanism to the extent that I demonstrate significant lowering of high-elevation, low-relief topography in a stadial period.
6.6 Conclusions

I began this chapter by noticing how regenerative TL shapes from bedrock feldspars can record successive heating events in the form of low-temperature shoulders. This observation was compared with the shape of natural TL signals and I hypothesized that for the lowest-temperature shoulder (or peak) embedded within the bulk TL signal, the time taken to accumulate should represent the maximum time that a sample has been at its present temperature, and the position of the rising edge of emissions, the $T_{1/2}$ value, should be controlled by the present temperature (a primary observation from Chapter 5). A single-aliquot regenerative (SAR) protocol was then developed to reproduce the TL shape and measure the TL dose-response function at the $T_{1/2}$ position. By mapping the natural $T_{1/2}$ intensity to the dose-response function, I can determine the geologic dose accumulated. Divided by the measured dose-rate, this gives us a SAR TL age, which I interpret as representing the maximum time that the sample has been at the surface temperature.

The ages from longitudinal and vertical transects within the Rock Creek glacial valley were then compared with regional proxies for glacial activity and were shown to be coeval with: a) cosmogenic $^{10}$Be exposure ages of cobbles within terminal moraines, deposited by a glacier which accumulated within the Beartooth Mountains (Licciardi and Pierce, 2008); and b) $^{230}$Th/U dating of pedogenic carbonates from glacio-fluvial terraces 200 km to the south, in the Wind River Basin (Sharp et al., 2003).

Lastly, I interpreted the erosional history based on the sample ages. As expected from weathering intensity differences between moraines (Graf, 1971), the valley carries signatures of erosional activity before, during, and after the LGM. Near to the head of the valley, sample J1008 suggests that a glacial horn cooled nearly 80 ka and down near the valley mouth the cooling age of sample J1010 is about 60 ka. Sample J0999, dated at $0.5 \pm 0.3$ ka, may have been exhumed a post-glacial mass wasting event. Along the vertical transect, the valley bottom sample (J1002) corresponds to the LGM ($20.1 \pm 1.7$ ka), but the plateau age (J0994) is markedly younger: $11.2 \pm 2.0$ ka. I interpret this to reflect an erosional wave propagating toward the interior of the plateau, possibly initiated during the Younger Dryas.
cooling event. If this interpretation is valid, this constitutes an important confirmation of a glacial buzzsaw erosional mechanism that was recently predicted by numerical models of high-elevation landscape evolution (Pedersen et al., 2014).
CHAPTER 7

Developing a MAAD TL thermochronology protocol to resolve uplift history along the San Andreas fault

7.1 Introduction

The foremost goal of this work is to develop a protocol that allows a user to quantify the $T-t$ history of a bedrock sample. This chapter pursues that goal and outlines why a multiple-aliquot additive-dose (MAAD) TL protocol is the most promising method for bedrock feldspar luminescence thermochronology. This protocol is then applied to several drill core samples as well as samples from the Yucaipa Ridge tectonic block (YRB). The resulting signals are shown to be diagnostic of thermal history and the recent exhumation rate of the YRB is estimated.

Of all the luminescence signals that have been considered so far, TL seems to be the most sensible for this application. The nature of the measurement is a natural fit: the gradual heating of a sample which progressively releases trapped charge according to thermal stability. The measured luminescence is therefore organized in a sense, such that the intensity measured at lower instrumental temperatures corresponds to sites which would fill at lower geologic temperatures.

A multiple-aliquot additive-dose procedure involves the irradiation of several naturally-dosed aliquots to produce a single dose-response curve and equivalent dose ($D_e$) estimate (Fig. 7.1). By contrast, the currently popular single-aliquot regenerative-dose (SAR) protocol produces a dose-response curve and $D_e$ estimate from a single aliquot which, after the natural measurement, is repeatedly irradiated and measured, each time filling the traps
a) Single-Aliquot Regenerative-Dose (SAR) protocol:

![Diagram showing the SAR protocol.](image)

- Luminescence intensity vs. Laboratory dose
- $D_e$ as the threshold dose
- $n = 1$ aliquot:
  - $\bigcirc$ = Natural dose
  - $\bullet$ = $0 +$ lab dose
- Saturation point

b) Multiple-Aliquot Additive-Dose (MAAD) protocol:

![Diagram showing the MAAD protocol.](image)

- Luminescence intensity vs. Laboratory dose
- $D_e$ as the threshold dose
- $n = 4$ aliquots:
  - $\bigcirc$ = Natural dose
  - $\bullet$ = Natural + lab dose
- Saturation point
Figure 7.1: The basic differences between a single-aliquot regenerative-dose (SAR) protocol and a multiple-aliquot additive-dose (MAAD) protocol are shown. (a) The SAR protocol measures (and therefore empties) the natural luminescence signal from an aliquot and then administers a lab dose to regenerate a signal. This is repeated with increasing doses until a dose-response curve is created which maps the natural intensity to the laboratory equivalent dose ($D_e$) which would produce this intensity. (b) The MAAD protocol involves several naturally-dosed aliquots. The first is measured. The second is given a small dose in addition to the natural and then measured, and so on. In this way, the dose-response curve beyond the natural dose is mapped out experimentally. By extrapolation, the dose-response curve at lower doses is projected backwards to identify the equivalent dose.
before emptying them. Probably the greatest advantage of a SAR protocol is that each disc offers an independent $D_e$ estimate, which can be measured to optimal resolution by incorporating many dose points, usually with higher precision than in a MAAD protocol. This ensures that with even small amounts of material a date can be gotten (e.g., when dating a pottery shard or a target mineral of low natural abundance). The caveat is that any sensitivity changes which occur during a measurement sequence must be accounted for. In optical dating, this is achieved by monitoring the response to some uniform ‘test dose,’ administered after the measurement of variable-dose response (Wintle and Murray, 2006). Implicit in this approach is the notion that changes in luminescence sensitivity can be corrected for by normalization. In other words, if the OSL decay shape were to change, or if the kinetic pathways involved were modified, this approach would be inappropriate. For optical dating (of quartz, especially), this is generally considered a valid assumption, as workers suspect that sensitivity changes (usually) involve the changes in relative accessibility of a single type of luminescence center (e.g., the L-center of Bailey, 2001).

For TL measurements where the initial heating measurement alters the shape of subsequent regenerative glow curves, this approach of ‘stripping out’ sensitivity change by monitoring test dose responses is inadequate, as only certain regions within the curve will become more or less sensitive to irradiation (in some cases, this is overcome by monitoring the changes in peak heights through measurement cycles, although this incorporates further assumptions; Adamiec et al., 2006). In this case, the MAAD approach is ideal for constructing dose-response curves, as all of the dose responses should exhibit natural luminescence efficiency (an exception would be a radiation-induced change in sensitivity; Zimmerman, 1971).

A major disadvantage of the MAAD approach to determining $D_e$ values is the nonlinearity encountered at higher doses. Backcasting a saturating exponential or the presence of supralinearity at low doses lead to much greater uncertainty than the uncertainty of interpolating between dose points involved in SAR protocols. For our purposes, however, we are primarily interested in how close the TL is to dose saturation, not the $D_e$ value, and the MAAD approach is well suited for this task. (The ‘cooling age’ should also carry impor-
tant information, but its utility is much more limited; fractional saturation, especially as a function of measurement temperature, \( n/N(T) \), can also be used to evaluate \( T - t \) history.

This will be the approach explored in this chapter, a TL MAAD protocol. First, I will describe the details of this measurement protocol. Next, I will offer an approach for interpreting the measured signals, including the choice of reaction pathways and kinetic parameters. This method will then be applied to the drill core samples in an effort to calibrate the kinetic model to known thermal conditions. Once calibrated, this model will be employed to estimate the recent cooling history of the Yucaipa Ridge tectonic block.

### 7.2 Protocol description

The measurement steps for the MAAD TL protocol are listed in Table 7.1. Several features of this protocol deserve comment. First, as has already been described in the previous section, this approach avoids the uncertainty and error associated with sensitivity changes resulting from heating to 500 °C. A similar SAR approach would be subject to these inaccuracies.

Second, this protocol allows the TL signals from several aliquots to be directly compared in absolute units after test-dose normalization (\( L/T \)). While the shape of the glow curves will be undisturbed by heating, the differences in intensity from one disc to the next makes the construction of a dose-response curve problematic. One approach would be to standardize the number of crystals added to each aliquot so that the intensities from one disc to the next should be quite similar. Aside from being time-consuming, this approach neglects the influence of abnormally bright crystals, which may overwhelm the brightness of discs at random. Our approach allows more confident and precise comparison between samples. (At present, we consider the total integrated counts for these glow curves. One could just as easily choose different integration limits; this deserves some attention.)

Third, the question of whether or not to preheat these TL signals should be addressed. Often in luminescence studies, preheats are necessary. For example, the 110 °C TL peak grows significantly during laboratory irradiation but is not stable enough to be present in the natural signal. As this peak would otherwise contribute to the regenerated OSL signal
Table 7.1: Protocol for MAAD TL thermochronology.

<table>
<thead>
<tr>
<th>Step</th>
<th>Treatment</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Additive dose, $D$ ($D \geq 0$ Gy)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Preheat ($T = 150 , ^\circ\text{C}$, 10 s)</td>
<td>Remove excess signal</td>
</tr>
<tr>
<td>3</td>
<td>TL ($\beta , ^\circ\text{C/s}$)</td>
<td>MAAD signal, $L$</td>
</tr>
<tr>
<td>4</td>
<td>TL ($\beta , ^\circ\text{C/s}$)</td>
<td>Black-body radiation</td>
</tr>
<tr>
<td>5</td>
<td>Test dose, $D_T$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Preheat ($T = 150 , ^\circ\text{C}$, 10 s)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>TL ($\beta , ^\circ\text{C/s}$)</td>
<td>Test dose signal, $T$</td>
</tr>
<tr>
<td>8</td>
<td>TL ($\beta , ^\circ\text{C/s}$)</td>
<td>Black-body radiation</td>
</tr>
</tbody>
</table>
(but not to the natural), the estimated geologic dose for a sample would be underestimated if the peak were not removed. Therefore a preheat is inserted after irradiation and before OSL measurement for quartz dating protocols.

In the case of these TL signals, it is true that some parts of the glow curve which are filled during lab irradiation would be unstable at geologic conditions; however, these would not necessarily obscure those regions which are stable, given that stability is a function of measurement temperature. Theoretically then, a preheat may not be necessary. Nevertheless, I incorporate a preheat of 150°C for 10 s for two reasons. The first is that many of the measured samples are very bright, to the point that our photomultiplier tube became saturated. If the brightness is too great, the PMT can be damaged. A preheat serves to empty the excess sites which contribute nothing to the interpretation of thermal history, but which contribute to this brightness (the unstable sites contribute by far the most TL in discs which have not been preheated). Another remedy was suggested to me by Georgina King: to add a cardboard circle with a hole punched out between the filter and the PMT. The size of the hole would then control the amount of light received by the PMT. The second reason to preheat is to offer better resolution when constructing the MAAD dose-response curves. This point is best understood by considering the regions of the TL curve lost during isothermal holding, as discussed in Chapter 4. The slight overlap in regions depleted by different treatments implies that a given measurement temperature comprises sites of multiple stabilities; a preheat offers a means to remove only those unstable sites so that the dose-response curve monitors the growth of stable sites only.

If a preheat is used, it should be chosen to not deplete the natural TL signal. The simplest way to directly determine this would be to measure the TL responses of an aliquot: first the natural signal, and then the regenerated signals following different preheats, i.e., the post-isothermal TL approach described in Chapter 4. Any heat treatment which would not significantly reduce the natural TL signal would be appropriate. The problem with depleting the natural TL signal during the preheat is that the apparent $n/N$ value that would eventually be measured would be artificially lowered, which would result in a mistaken interpretation of the most recent geothermal history.
The final point about the preheat is that, similar to optical dating routines, analysis of the \( n/N \) signal must begin at a temperature greater than the preheat temperature, for the same reason that the preheat must not deplete the natural signal. The precise temperature difference between the preheat and the beginning of TL curve analysis depends on the result from the pI-TL experiment; the approximate upper-bound of the region depleted by preheat conditions marks the lowest possible temperature which may be analyzed for thermal history. A faster, less precise approach would be to examine the natural TL signal, determine the initial rise temperature and choose a preheat temperature some tens of degrees below this for a short duration (e.g., initial rise at 220 °C would be unaffected by a preheat at 180 °C for 10 s).

### 7.3 Interpreting measured signals

Once the measurements are made with the MAAD TL protocol (Table 7.1), several additional steps must be taken to interpret \( T - t \) history. First, the user must choose which kinetic pathways are active; this will dictate the governing differential equations. Second, the parameter values used within these equations must be determined. Third, the model should be calibrated to experimental results. Fourth, the sensitivity of the forward model should be evaluated. Finally, natural TL signals can be used to estimate the \( T - t \) history of a sample.

#### 7.3.1 Choosing kinetic pathways

The pathways hypothesized for the feldspar luminescence system (optical and thermal) are detailed in Jain and Ankjaergaard (2011). Excluding optical transitions, electrons can detrap by the following means: i) ground-state tunneling; ii) excited-state tunneling; iii) phonon-assisted diffusion via the band-tail states (recombination from such a state can be direct or can involve tunneling); or iv) thermal excitation into the conduction band. For our purposes, pathways (iii) and (iv) can be lumped together, as the density of band-tail states increases continuously into the conduction band. What follows are the basic expressions that
capture these pathways. Note that I do not consider the defect pair model for luminescence production (Itoh et al., 2002), though it may also prove to be useful.

**Quantum mechanical tunneling** Tunneling from the ground or excited state (P5 and P6 in Fig. 7.2) is approximated as

\[ P_i(r) = P_0 \exp(-\alpha_i r), \]  

(7.1)

where \( \alpha_i \) is the potential barrier penetration constant as described in (Chen and McKeever, 1997, pp. 60-66):

\[ \alpha_i = \frac{2\sqrt{2m^* E_i}}{\hbar}. \]  

(7.2)

The potential barrier height, \( E_i \), is the thermal trap depth beneath the conduction band, either the ground state, \( E_g \), or an excited state, \( E_e \). The effective electron mass, \( m^* \), has been determined by Poolton et al. (2001) to be 0.79\( m_e \) for Na-feldspar. The pre-exponential term of equation 7.1 is discussed in Section 7.3.2. The Dirac constant, \( \hbar \), has a value of 6.582 \( \times 10^{-16} \) eV·s (1.055 \( \times 10^{-34} \) J·s). A thorough description of this treatment of tunneling for the feldspar luminescence system can be found in Poolton et al. (2002b).

Notice that this expression requires recombination distance \( r \) as an input. This is usually handled by imposing a density of randomly-distributed recombination centers to which trapped electrons can tunnel (Huntley, 2006; Jain et al., 2012). By assuming that tunneling only occurs between electron traps and nearest-neighbor centers, the probability of finding the nearest center between some distance \( r' \) and \( r' + dr' \) is

\[ p(r')dr' = 3(r')^2 \exp[-(r')^3]dr' \]  

(7.3)

where \( r' \) is the dimensionless distance defined as

\[ r' = \left( \frac{4\pi \rho}{3} \right)^{1/3} r \]  

(7.4)

This probability multiplied by the concentration of trapping sites dictates the total number of sites at every distance. If detrapping proceeds via tunneling, therefore, trap populations are monitored as a function of recombination density. For the full development of the resulting rate equation, see Section 5.3.1.
Figure 7.2: The hypothesized kinetic pathways for feldspar TL. The shown pathways are, in order: (P1) ionization by radiation and subsequent trapping; (P2) relaxation; (P3) thermal excitation; (P4) phonon-assisted diffusion and recombination; (P5) quantum mechanical tunneling from the excited state; and (P6) tunneling from the ground state. This figure is modified after Fig. 3 of Jain and Ankjaergaard (2011).
Phonon-assisted diffusion  Trapped electrons can couple with lattice vibrations and thereby gain enough thermal energy to hop from one lattice site to another (Poolton et al., 1995, 2002a; Jain and Ankjaergaard, 2011, P4 in Fig. 7.2). Several authors have offered expressions for this process. Li and Li (2013), for example, offer an expression involving a single transition from the trap to a localized state (with a density of states function decreasing exponentially from the conduction band towards the band gap) and from that site into a recombination center. For reasons discussed below, this expression neglects the diffusive nature of this process. Morthekai et al. (2012) developed a different expression to fit their time-resolved IRSL data, but their derivation is predicated on zero separation between electron-hole pairs at the start of stimulation (Murayama and Ninomiya, 1985)–an assumption well suited to geminate recombination in high-purity amorphous semiconductors (Hong et al., 1981), but inappropriate for natural feldspars (Poolton et al., 2009). Here, I develop an expression for this pathway.

Phonon-assisted diffusion (PAD) can be approximated as \( n \) hops, each with a probability dependent on the hop length, \( r \), and the difference in energies between the two states, \( W \) (Ambegaokar et al., 1971):

\[
\nu(r) = \nu_0 \exp(-\alpha r - W/k_B T).
\]  
(7.5)

The factor \( \nu_0 \) depends on phonon properties. For this study I approximated it as the Debye frequency for K-feldspar, \( 4.2 \times 10^{12} \text{s}^{-1} \) (Anderson and Liebermann, 1966; Anderson, 1995). The probability of a multi-hop transition can be expressed as

\[
\nu(r) = \prod_{i=1}^{n} \nu_0 \exp(-\alpha r_i - W_i/k_B T).
\]  
(7.6)

Unlike with tunneling, however, the electron travel from trap to recombination center via PAD will not be direct if the number of hops is greater than one. Instead, the direction of motion will be random, towards whichever site is nearest. Moreover, the energy difference between sites should by related to the density of band-tail states beneath the conduction band.

Therefore, a more sophisticated approach is warranted. Although much of the following was originally developed by Sir Nevill Mott (e.g., Mott and Twose, 1961; Mott, 1968), a
concise, useful, and clearly derived expression for thermally-activated hopping via band-tail states is found in Baranovskii et al. (1996). The following description of diffusion via band-tail hopping derives from that work, although nomenclature has been changed for consistency and a factor of 2 is removed from certain expressions because of how I have defined $\alpha$ (equation 7.2).

First, an exponential decrease in the density of localized states is assumed, described as

$$g(E_i) = \frac{N_0}{E_0} \exp\left(-\frac{E_i}{E_0}\right)$$

where $g(E_i)$ is the density of states at energy $E_i$ (the value of $E$ increases towards the valence band), $N_0$ is the total concentration of localized states (this may be different than the concentration of trapping sites, $N$), and $E_0$ is the tailing parameter. This has the consequence that the distance $r$ to the nearest localized state of equal or greater depth is defined as

$$r(E_i) = \left(\frac{4\pi}{3} \int_{E=E_i}^{\infty} g(E) dE\right)^{-1/3}$$

Next, it is observed (Monroe, 1985) that at for a given set of conditions, there will exist a characteristic transport energy, $E_t$, defined by Baranovskii et al. (1996) as

$$E_t = 3E_0 \ln \frac{3E_0(4\pi N_0/3)^{1/3}}{\alpha k_B T}$$

Electrons located in states deeper than $E_t$ can thermally activate up to $E_t$ and those in shallower sites shallower will spontaneously hop down to $E_t$. The diffusion coefficient associated with deeper states ($E_i \geq E_t$) is

$$D(E_i) = \frac{1}{6} r^2(E_t) \cdot \nu(E_i, E_t)$$

where

$$\nu(E_i, E_t) = \nu_0 \exp\left(-\alpha r(E_t) - \frac{E_i - E_t}{k_B T}\right)$$

Now that we have an expression for how electrons should diffuse throughout the crystal, the next question is how often do these wandering electrons recombine with a luminescence
center. The phenomenon of diffusion-controlled recombination is categorized as either Onsager or Langevin [Silver and Jarnagin, 1968]. Onsager recombination (also known as geminate recombination) occurs when a generated pair immediately recombines; their separation is not great enough to overcome their Coulomb interaction. For Langevin recombination, the pair is dissociated and one or both of the charge carriers (free electron or free hole) must drift to find the other. This is the process we are interested in describing.

Following [Butler, 1977], the Langevin recombination rate is given as

\[
\frac{1}{\tau_e} = \frac{4\pi q}{\epsilon} (\mu_p + \mu_e) \rho
\]

(7.12)

where \(\tau_e\) is the electron lifetime, \(q\) is the charge of the electron \((1.602 \times 10^{-19} \text{ C})\), \(\epsilon\) is the permittivity of the material, \(\mu_p\) and \(\mu_e\) are the hole and electron mobilities, and \(\rho\) is the carrier concentration (because \(\rho\) functions as the concentration of recombination ‘targets,’ I will redefine this term as the concentration of recombination centers.) The relative permittivity \((\epsilon_r;\) also known as the dielectric constant) of orthoclase is 4.34, which gives an absolute permittivity of \(\epsilon_r \times \epsilon_0 = 4.34 \times (8.85 \times 10^{-12}) = 3.84 \times 10^{-11} \text{ F/m}\) [Church et al., 1988].

Electron mobility is related to the diffusion constant (determined using equation 7.10) by the Einstein relationship:

\[
D = \frac{\mu_e k_B^* T}{q}
\]

(7.13)

which is rearranged as

\[
\mu_e = \frac{Dq}{k_B^* T}
\]

(7.14)

Note that \(k_B^*\) is the Boltzmann constant in SI units: \(1.381 \times 10^{-23} \text{ J/K}\) (not \(8.617 \times 10^{-5} \text{ eV/K}\) as is used in most luminescence contexts).

By setting the hole mobility to zero (immobile luminescence centers as are often assumed), and with substitution we get an expression for mean electron recombination probability expressed as a function of diffusivity (which depends on the depth of the localized state, \(E\), according to equation 7.10):

\[
p(E) = \frac{4\pi \rho q^2 D(E)}{\epsilon k_B^* T}
\]

(7.15)
This expression involves diffusivity which must be integrated for every band-tail state with a depth greater than \( E_t \) (equation 7.10). For simplicity I create the variable \( \phi \), where

\[
\phi = \frac{4 \pi \rho q^2}{\epsilon k_B T}
\]  

(7.16)

which allows us to rewrite equation 7.15 as

\[
p(E) = \phi D(E)
\]  

(7.17)

One additional step is necessary to describe the recombination rate of a trap population via phonon-assisted diffusion. We have quantified the density of states available (equation 7.7) and the diffusion coefficient for electrons found in any of those states (equation 7.10), but we must also know the concentration of electrons present in each of these available states. To do so, we must introduce the Fermi distribution which defines the probability of finding an electron at a given depth at thermodynamic equilibrium (pp. 12-14, Chen and Pagonis, 2011). The Fermi distribution, defined relative to state depth beneath the conduction band, is written as

\[
f(E) = \frac{1}{1 + \exp(-(E - E_g))/k_B T}
\]  

(7.18)

where \( E_g \) is the Fermi energy plus any potential energy of the electron, which for a trapped electron reduces to the ground-state energy level of the trap.

At thermodynamic equilibrium, the concentration of occupied localized sites found between energy \( E \) and \( E + dE \) is defined as the density of states within that energy level \( g(E)dE \) multiplied by the probability of an electron existing at that energy \( f(E) \) given the temperature of the system, so that if all traps were filled \( (n = N) \) and the concentration of localized sites \( N_0 \) were equal to the number of trap sites \( N \), the concentration of electrons found at any depth between \( E_g \) and the conduction band \( (E = 0) \) would be the following integral

\[
N(E) = \int_{E=0}^{E_g} g(E)f(E)dE
\]  

(7.19)

Of course, in most cases not all traps will be occupied, and it is unlikely that the concentration of trapping sites is equal to the concentration of band-tail states, so the above expression
would need to be rescaled to estimate the concentration of trapped electrons in the localized states

\[
\frac{n(E)}{n} = \int_{E=0}^{E_g} \frac{g(E)}{N_0} f(E) dE
\]  (7.20)

which can be rewritten to

\[
n(E) = \int_{E=0}^{E_g} \frac{n}{N_0} g(E) f(E) dE
\]  (7.21)

The final detrapping rate for a trapped population recombining via phonon-assisted diffusion is therefore the concentration of electrons in localized states (equation 7.21) scaled by the recombination probabilities of those states (equation 7.17). Because sites shallower than \( E_t \) are assumed to spontaneously jump down to \( E_t \) (equation 7.9), I integrate not from the conduction band down, but from \( E_t \) to \( E_g \):

\[
-\frac{dn}{dt} = \int_{E=E_t}^{E_g} n(E) \cdot p(E)
\]  (7.22)

\[
= \int_{E=E_t}^{E_g} \frac{n}{N_0} g(E) \cdot f(E) \cdot p(E) \cdot dE
\]  (7.23)

\[
= \int_{E=E_t}^{E_g} \frac{n}{N_0} \frac{N_0}{E_0} \exp\left(-\frac{E}{E_0}\right) \cdot \frac{\phi D(E)}{1 + \exp\left(-\frac{E - E_g}{k_B T}\right)} \cdot dE
\]  (7.24)

\[
= \frac{n \phi}{E_0} \int_{E=E_t}^{E_g} D(E) \exp\left(-\frac{E}{E_0}\right) \frac{\exp\left(-\frac{E - E_g}{k_B T}\right)}{1 + \exp\left(-\frac{E - E_g}{k_B T}\right)} \cdot dE
\]  (7.25)

To the author’s knowledge, this is an original result.

### 7.3.2 Quantifying parameter values

All of the 10 parameters necessary to incorporate all of the kinetic pathways are listed in Table 7.2. Constraining the values for these parameters may pose the single most significant challenge for workers hoping to employ luminescence for thermochronology purposes. Given that a) the governing equations which incorporate these parameters are often nonlinear, and b) these equations must be solved simultaneously, the \( T - t \) evolution of a set of traps is sensitive to the chosen values.
With the exception of the dose-rate, $\dot{D}$, which can be quantified in a straightforward manner for both geologic and laboratory dose-rates, the determination of each parameter requires certain assumptions. This section will summarize the measurements that can be made as well as the expected range of values according to current understanding. The intention is to provide a basic schema for a worker hoping to parameterize his or her samples, who has access to a luminescence reader but no more advanced capabilities. (For example, a sensitive EMCCD emission spectrometer could be useful in determining absolute or relative trap depths, and aliquots monitored at liquid N$_2$ temperatures provide information about recombination center density, but many luminescence workers in the geology community do not have access to such facilities).

7.3.2.1 Geologic dose-rate, $\dot{D}_G$

A comprehensive explanation of the factors controlling the geologic dose-rate received by a sample can be found in Aitken (1985), as well as a concise summary in Duller (2008). While this calculation is complex, it is well-defined. Online software has recently been produced which provides an intuitive interface for performing this calculation (Durcan et al., 2015), similar to the CRONUS program available to the cosmogenic nuclide dating community (Balco et al., 2008).

In short, the dose received by a crystal of feldspar within bedrock will be the sum of contributions from alpha, beta, and gamma radiation fields from natural radionuclides as well as any contribution from cosmic rays. The most conventional way estimate the radiation coming from nearby minerals is to measure the abundances of radionuclides (mostly U, Th, and K) by send off a representative subsample of the bedrock for mass spectrometry or neutron activation analysis and convert those abundances into their constituent dose-rates under the infinite matrix assumption (e.g., Adamiec and Aiken 1998, Guérin et al. 2012). Other approaches include emission counting (or spectrometry for alpha particles and gamma rays), or the in situ measurement of gamma ray contribution with NaI scintillation counters.

The determination of the cosmic dose-rate depends on the overburden depth (and de-
Table 7.2: Sample parameters controlling kinetics. The pathways affected by each parameter are shown in Fig. 7.2.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
<th>Pathways involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>Dose rate</td>
<td>(Gy/s)</td>
<td>P1</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Characteristic dose</td>
<td>(Gy)</td>
<td>P1</td>
</tr>
<tr>
<td>$N$</td>
<td>Trap concentration</td>
<td>(m$^{-3}$)</td>
<td>P1,P4</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Recombination center concentration</td>
<td>(m$^{-3}$)</td>
<td>P1,P4,P5,P6</td>
</tr>
<tr>
<td>$s$</td>
<td>Attempt-to-escape frequency factor</td>
<td>(s$^{-1}$)</td>
<td>P2,P3</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>Attempt-to-hop frequency factor</td>
<td>(s$^{-1}$)</td>
<td>P4</td>
</tr>
<tr>
<td>$P_0$</td>
<td>Attempt-to-tunnel frequency factor</td>
<td>(s$^{-1}$)</td>
<td>P5,P6</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Tailing parameter</td>
<td>(eV)</td>
<td>P4</td>
</tr>
<tr>
<td>$E_e$</td>
<td>Excited-state trap depth</td>
<td>(eV)</td>
<td>P3,P5</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Ground-state trap depth</td>
<td>(eV)</td>
<td>P3,P6</td>
</tr>
</tbody>
</table>
sity), elevation and the geomagnetic latitude (Prescott and Hutton, 1994). The internal water content will contribute to dose-rate attenuation, though a standardized approach to measuring this quantity has not been put forward, though typically workers estimate a on the order of 2 - 4 wt.% water content (e.g., Herman et al., 2010; King et al., 2016a).

7.3.2.2 Laboratory dose-rate, $\dot{D}_L$

Most luminescence workers today use a Risø automated luminescence reader equipped with a $^{90}\text{Sr}/^{90}\text{Y}$ beta source delivering approximately 0.1 Gy/s (Bøtter-Jensen et al., 2003). An exact determination of the dose-rate is typically performed using a calibration quartz sample irradiated with a $^{137}\text{Cs}$ gamma source, which delivers a uniform dose to all grains (Göksu et al., 1995; Hansen et al., 2015). This calibration quartz is then measured using a standard SAR protocol to determine the apparent equivalent dose (Murray and Wintle, 2000). Because exposure time is known to within one second, the dose-rate can then be determined with a standard deviation of about 2% (Hansen et al., 2015) (using Fricke dosimetry instead of aliquot-mounted grains, Bos et al., 2006 were able to reduce this uncertainty to < 1%). This approach could also be used with other luminescence reader systems (e.g., lexsyg; Richter et al., 2013).

(This calibrated dose-rate applies only to grains of similar size to the calibration quartz, which is available in 4 - 11 $\mu$m or 180 - 250 $\mu$m grain sizes. Armitage and Bailey (2005) found that grain sizes between 55 and 250 $\mu$m (uppermost tested limit) showed no dependence of beta dose-rate on grain size, but that below 40 $\mu$m a clear relationship is found due to the sample-to-source spacing.)

7.3.2.3 Trap concentration, $N$

The total concentration of trapping sites is treated as a scaling factor. The dynamics of trapping and detrapping are independent of this parameter; only brightness is affected by changing the value. If there were multiple (electron or hole) trap sites (e.g., quartz luminescence), then their relative concentrations would influence kinetics, but in the case of feldspar
luminescence, one trap and one recombination center are regularly assumed (Andersen et al., 2012; Pagonis et al., 2016). Another condition which would make this parameter influential is if the density of recombination centers were of similar magnitude (Chen and Pagonis, 2013). Contemporary models for feldspar luminescence assume that the density of recombination centers is much higher than that of trapping sites, so that the recombination center density is effectively constant (Huntley, 2006). Because this factor serves only to scale the total luminescence signal, it is often therefore set at some arbitrary value of the order $10^{20} \text{m}^{-3}$.

### 7.3.2.4 Recombination center concentration, $\rho$

Unlike the density of trapping sites, the density of recombination centers greatly controls the behavior of the feldspar luminescence system (Sfampa et al., 2015). As the concentration of recombination centers increases, the distribution of nearest neighbor distances will bias towards lower values, which will make recombination by tunneling more likely (Jain et al., 2012).

The difficulty with evaluating $\rho$ is that, under room temperature conditions, recombination is thought to be some combination of thermally-activated tunneling (from the original trap site or from sites accessed via phonon-assisted diffusion) and ground-state tunneling. Because of this, the value of $\rho$ is tied to both the expression and the values used to describe detrapping.

(This would not be a problem if the luminescence following irradiation were monitored at liquid nitrogen temperature, which has been done but requires an elaborate experimental arrangement (Visocekas, 1985, 1993; Visocekas et al., 1994, 2014; Guérin and Visocekas, 2015). Unfortunately, these measurements at LNT have not been used to constrain $\rho$.)

Curve-fitting is therefore the optimal approach for determining $\rho$. Often workers will instead report the dimensionless parameter, $\rho' = \frac{4\pi \alpha^{-3}}{3} \rho$. This simplification has the effect of incorporating the trap depth ($E_e$ or $E_g$) within the $\alpha$ parameter. The most straightforward method to determine $\rho'$ is fit either isothermal TL or TL-lost using the model of Jain et al.
as simplified by Sfampa et al. (2015):

\[ I(t) = n_0 \left( 1 - \exp \left[ -\rho' \left( \ln[1 + zs \exp(-\Delta E/k_B T) \cdot t] \right)^3 \right] \right) \] (7.26)

where \( n_0 \) is the concentration of trapped electrons at \( t = 0 \), \( z \) is the time differential of the critical lifetime (typically 1.8, but fitted to be as high as about 5), and \( \Delta E \) is the energy difference between the ground and excited state.

### 7.3.2.5 Frequency factors: \( s, P_0, \text{ and } \nu_0 \)

The frequency factors, which all function as pre-exponentials in detrapping expressions, each have different physical meanings but are all expressed in units of frequency \( (s^{-1}) \) and represent an upper limit to the number of times per second that a transition is attempted by a localized electron.

**Attempt-to-escape factor, \( s \)**  

The frequency factor \( s \) found within the traditional Arrhenius (1889) expression \( (p = s \exp[-E/k_B T]) \); cf. Eq. (1.4) is, in the case of thermoluminescence, normally defined as the number of times per second that a trapped electron interacts with a lattice phonon, \( v \), scaled by some transition probability, \( K \), and exponentially dependent upon the entropy change during detrapping, \( S \), resulting in the following expression (pp. 48–49 McKeever, 1985):

\[ s = vK \exp \left( S/k_B \right) \] (7.27)

This \( s \) value, often called the attempt-to-escape frequency factor, is typically assumed to be of the order \( 10^{12} \) s\(^{-1} \), similar to the lattice vibration frequency; the Debye frequency for K-feldspar is \( 4.2 \times 10^{12} \) s\(^{-1} \) (Anderson and Liebermann 1966, Anderson 1995). Many experimental methods allow for the determination of this factor under first-order kinetics (Chen and Kirsh 1981, Chen and Pagonis 2011). In the case of feldspar TL, first-order kinetics do not apply and the available analytical methods are few. While methods have been developed to estimate frequency factors from TL curves (e.g., Brown and Rhodes 2017), these values almost certainly conflate \( s \) and tunneling probability.
Attempt-to-tunnel factor, $P_0$  Unlike the $s$-value, the attempt-to-tunnel frequency factor, $P_0$, does not depend upon interactions with lattice phonons, which allows for quantum mechanical tunneling even at temperatures of absolute zero. Instead, under the 1-D square quantum well approximation (Poolton et al., 2002a) this factor should represent the number of times per second that a localized electron collides with the potential barrier, which would simply be the speed of the electron normalized by the well width (Tsuchiya et al., 1987).

Given the formula for the mean thermal speed of an electron

$$\bar{v} = \sqrt{\frac{8k_BT}{\pi m^*}} \quad (7.28)$$

where $m^*$ is the effective mass of the electron within the lattice ($0.79m_e$ Poolton et al., 2001); and given that the width of the quantum well is probably similar to the length of the Si - Si atomic separation, 2.6 Å (Poolton et al., 2002a), I can calculate a reasonable value for $P_0$ at room temperature:

$$P_0 = \frac{\bar{v}}{w} \quad (7.29)$$

$$= \sqrt{\frac{8k_BT}{\pi m^*}} \cdot \frac{1}{w} \quad (7.30)$$

$$= \sqrt{\frac{8}{\pi} \left(\frac{1.381 \times 10^{-23} \text{ J/K}}{293.15 \text{ K}}\right) \frac{1}{3.142 (0.79 \cdot 9.109 \times 10^{-31} \text{ kg})} \cdot \frac{1}{2.6 \times 10^{-10} \text{ m}}} \quad (7.31)$$

$$= 4.603 \times 10^{14} \text{ s}^{-1} \quad (7.32)$$

Attempt-to-hop factor, $\nu_0$  Lastly, the attempt-to-hop frequency factor, $\nu_0$, represents an intermediate case: the electron will require thermal assistance to hop into higher-energy states, but not to hop into lower-energy states. The factor depends on electron-phonon coupling strength, the phonon density of states, other material properties and weakly on the energy differences between states, though its exact definition is unclear (Ambegaokar et al., 1971). Like the $s$ value, $\nu_0$ is expected to be of the order of $10^{12} \text{ s}^{-1}$ (Monroe, 1985).
7.3.2.6 Activation energies: $E_g$, $E_e$, and $E_0$

Activation energies can be thought of as the minimum thermal assistance needed to enable a reaction, in our case de-trapping\(^1\). Usually, in the context of luminescence, an activation energy is defined as the depth beneath the conduction band. In other words, an electron receiving that amount of thermal energy (by coupling to one or multiple phonons) may escape its trap, freely travel through the conduction band and then recombine. For the main dosimetric trap within feldspar the activation energy of a particular recombination route may be more complicated. A ground-state electron may thermally-excite but remain localized before recombining via tunnelling. That route would have an activation energy of $\Delta E = E_g - E_e$. Or, instead of tunneling directly to a recombination center, the electron may hop to several neighboring sites before recombination, requiring still more thermal energy. I will restrict myself here to describing the depth beneath the conduction band of the ground- and excited-states as well as the tailing parameter, which describes the extent of the band-tail states.

**Ground-state depth, $E_g$** The difficulty of constraining the thermal depth of the ground-state in feldspar, $E_g$, is best understood by contrast. The depth of the 325 °C TL trap within quartz can readily be determined because recombination must proceed via the conduction band, so that TL glow curve near 325 °C is dominated by electrons moving directly from the ground-state up into the conduction band (Spooner and Questiaux, 2000). The primary difficulty in measuring the thermal depth of the ground-state is the existence of alternate recombination pathways which are more probable than activation into the conduction band. This difficulty prompted the work of Brown and Rhodes (2017).

As developed in Chapter 4 (published as Brown and Rhodes 2017), one strategy is to use progressive thermal treatments to observe the lost-TL at different $T - t$ conditions. These post-isothermal TL measurements can be compared and the lost-TL can be fitted to reveal the gradual increase in apparent thermal activation energies associated with recombination.

\(^1\)Interestingly, trapping processes can also exhibit activation energies embedded within trapping cross-sections (p. 16; Chen and Pagonis 2011).
In this way, an $E$-value plateau may be observed which is hypothesized to correspond to the maximum apparent activation energy (i.e., $E_g$).

**Excited-state depth, $E_e$** The indirect evaluation of $E_e$ by first estimating $E_g$ and then $\Delta E$ may be required for three reasons. First, the time spent in the excited state is irresolvably small with standard instrumentation, as an excited electron will return to the ground state with a frequency $s \sim 10^{12}$ s$^{-1}$ (temporal resolution is increasing, but as of yet even the most advanced commercially-available photon timers only allow microsecond resolution; [Denby et al., 2006; Pagonis et al., 2016]). This has the limitation that even if electrons were first elevated to the excited-state, they would not remain long enough to be excited further into the conduction band. A potential way around this difficulty would be to involve infrared stimulation. The energy of infrared light happens to be similar to the optical transition energy from ground-to-excited state ([Poolton et al., 1995]), such that thermo-optical luminescence (heating constantly while turning the IR diodes on and off regularly) may contain information about the thermal depth of the excited state (cf. [Hütt et al., 1988]).

Second, in the absence of IR stimulation, heating is necessary to excite charge, thus making it impossible to monitor only the single transition from excited-state to conduction band.

Third, the excited state is thought to lie within the band-tail states, which would result in a more continuous transition into the conduction band instead of a discrete energy barrier ([Poolton et al., 2009]).

How to determine $\Delta E$ in the feldspar system is an open problem. By stimulating with different wavelengths, one can readily determine the optical energy needed to tunnel from the excited state. [Poolton et al., 2009] for example observed a resonant peak in luminescence intensity at 1.44 and 1.46 eV for Na- and K-feldspar samples, respectively, which they interpreted as the optical $\Delta E$ values. The ratio of optical-to-thermal activation energies should equal the dielectric constant of a crystal at static frequency, $k$, divided by the dielectric constant at high frequency, $k_0$ (p. 36; [Chen and Pagonis, 2011]). For potassium feldspar, this ratio is approximately 2.2 (p. 25; [Baril, 1997]), which would yield a $\Delta E$ value of 0.65 eV.

Interestingly, the regenerative pI-TL apparent $E$ values measured by [Brown and Rhodes]
increase progressively up to about 1.86 eV, but start around 0.73 eV, just slightly above the value of 0.65 that would be gotten from a simple conversion of the optical $\Delta E$ value. Given that some of the least stable sites will empty prior to pI-TL measurements, a value of 0.65 eV seems plausible.

**Tailing factor**, $E_0$  
The tailing factor, $E_0$, defines the extent of the band-tail states beneath the conduction band as defined in Equation 7.7. It is analogous to the concept of the Urbach band-tail width, $E_U$ (Poolton et al. 2002a). Poolton et al. (2009) compared their OSL excitation spectroscopy work to the measurements of Strickertsson (1985) to estimate a band-tail width of about 0.4 eV for sodic and potassic feldspsars. Li and Li (2013) fitted experimental isothermal decay results of IRSL signals to obtain similar values for $E_U$.

### 7.3.3 Calibrating the model to results

Having chosen the pathways that will describe trapping and detrapping as well as the values of the relevant parameters, the user should then check the model against samples of known $T - t$ history, if possible. For this section, I will use the drill core samples discussed in Chapter 5, specifically samples J1012 ($T_{SS} = -4.1^\circ$C; E802), J1026 ($T_{SS} = 19.8^\circ$C; R716), and J1030 ($T_{SS} = 55.1^\circ$C; R716), chosen to represent a wide range of ambient temperatures.

#### 7.3.3.1 MAAD TL to $n/N(T)$ values

Before the results from these samples can be compared with model results, I must convert the measured MAAD TL data into $n/N$ ratios. Operating on the assumption that each measurement channel (in our case, with 250 channels, a channel represents $dt = 0.4$ s and $dT = 2^\circ$C) should probe one trap type, one should be able to approximate MAAD TL dose growth with a single saturating exponential function.

Here, we should be explicit in our meaning. Below about 400 $^\circ$C (Murray et al. 2009), I will assume that we are dealing with a single defect type, probably the 390 - 440 nm emission band of Krbetschek et al. (1997) (note however, that they caution that two peaks
of different type may comprise this emission: one at 260 - 280 °C, the other at 320 - 340 °C). Even though I assume one defect type, each recombination distance will dictate a different recombination probability, so there will be a continuum of trap behaviors. Therefore, the assumption is that each channel represents a sufficiently narrow range of recombination distances (i.e., probabilities) that it can be approximated as deriving from a singular trap. If this holds (and setting aside more complex phenomena such as retrapping or trapping competition), then we should expect dose response at room temperature to follow a single saturating exponential function.

For samples J1012, J1026, and J1030 the following procedure was followed. A total of 10 stainless steel discs were prepared per sample (~2 mm diameter spot adhered to the disc with silicon oil). In pairs, discs were given an additional dose of 0, 60.1, 120.1, 240.2, or 480.5 Gy. The samples were then measured following the procedure described in Table 7.1 (preheats were omitted for these samples, as the signals were not overly bright). The results are shown in Fig. 7.3.

For all samples, the TL intensity grows the most at lower temperatures and the temperature at which the natural signals approach the high-dose signals shifts to higher temperatures as the natural burial temperatures of the samples increase (J1012 $T_{SS} = -4.1^\circ$C; J1026 $T_{SS} = 19.8^\circ$C; J1030 $T_{SS} = 55.1^\circ$C). As the measurement temperature nears about 300 °C ($\beta = 5^\circ$C/s), there seems to be no systematic growth for sample J1012, suggesting that the sample is in full saturation, even at laboratory dose-rates. Sample J1026 does grow, but grows less at 300 °C than it does at 250 °C. By 350 °C the TL responses following all doses are mostly indistinguishable. The interpretation here would be that the MAAD TL from this sample saturates, but at higher temperatures. Finally, at 300 °C sample J1030 grows substantially with dose and does not reach saturation until about 375 °C.

This trend of decreasing growth (i.e., increasing degree of saturation) is detailed for sample J1026 in Fig. 7.4. This figure illustrates how the sensitivity-corrected, background-subtracted TL curves from the MAAD protocol shown in Table 7.1 can be converted to fractional saturation values at every TL measurement channel (e.g., 2 °C). The dose-response
Figure 7.3: The sensitivity-corrected TL responses (5 °C/s) of the drill core samples J1012 (linear y-axis in (a), logarithmic y-axis in (b)), J1026 (c, d), and J1030 (e, f) are shown following additive doses of 0, 60.1, 120.1, 240.2, and 480.5 Gy.
Figure 7.4: The sensitivity-corrected TL responses (5 °C/s) of J1026 are shown at three different measurement temperatures: 250, 276, and 300 °C. The dose-response points for each temperature ‘slice’ are fitted to a single saturating exponential function to determine the intensity at the upper asymptote (full saturation, $N$). The natural intensity can then be normalized by this upper limit to describe the fractional saturation at that temperature, $n/N$. As the measurement temperature increases (and sites of greater stability are measured), the measured $n/N$ values increase.
points are fitted to a single saturating exponential function:

\[ TL = a \left( 1 - \exp \left[ - \left( D + b \right)/D_0 \right] \right) \]  \hspace{1cm} (7.33)

where \( a \) adjusts the intensity of the TL, \( b \) offsets the x-axis intercept (in the case of MAAD experiments, \( b = D_e \)), \( D_0 \) defines the dose at which saturation effects begin, and \( D \) is the dose given. Other dose-response functions are available (e.g., Guralnik et al., 2015b), though a single saturating exponential is the simplest explanation for a one-trap system. The upper asymptote of this function is considered to be the brightness resulting when the trapping sites are fully saturated, this is designated as \( N \). The natural brightness \( n \), normalized by this maximum brightness \( N \), gives the fractional saturation at that measurement temperature \( n/N(T) \). To be precise, \( n \) and \( N \) actually represent site concentration in the crystal rather than emitted luminescence, but since I assume that brightness is proportional to the number of occupied sites, the ratio of naturally-occupied to total available sites should be approximately the same as the ratio of naturally-produced to maximum measurable luminescence.

This approach was taken to determine the \( n/N(T) \) values for drill core samples J1012, J1026, and J1030, and for Yucaipa Ridge Block samples J0165, J0172, J0214, J0216, and J0218. The results are shown in Fig. 7.5. When the natural TL response nears the responses of the high-dose points (i.e., when the natural signal is near saturation), the best-fit functions become poorly-constrained. For example, it becomes difficult to distinguish between a saturating exponential which is fully saturated and one which grows to extremely high doses and therefore has a very small local slope at the dose-response points. Therefore, the allowed (or prescribed) values for \( D_0 \) influence the resulting \( n/N \) values. To illustrate this effect, two sets of results are shown. On the left-hand side of Fig. 7.5 the dose-response points are fitted to a single saturating exponential where the \( D_0 \) value is allowed to range between 500 Gy and 2 kGy, a range estimated from SAR TL results (e.g., Fig. 5.8). On the right-hand side, the \( D_0 \) value is held constant at 1.6 kGy, the \( D_0 \) value measured for sample J1012 in the region of the natural \( T_{1/2} \) value, also shown in Fig. 5.8.

Unsurprisingly, more continuity is observed at higher temperatures when the \( D_0 \) value
Figure 7.5: The fractional saturation \((n/N)\) values are shown as a function of measurement temperature for both the drill core samples (a, b), the Yucaipa Ridge Block samples (c, d), and both together (e, f). The left-hand side shows the values resulting from best-fit functions where the \(D_0\) value (characteristic dose of saturation) is allowed to range between 0.5 and 2.0 kGy, while the right-hand panels result from fittings with \(D_0 = 1.6\) kGy, based on SAR measurements.
is fixed. For example, with sample J0172, the jump to lower \( n/N \) values around 320 °C in Fig. 7.5c (variable \( D_0 \)) is absent when \( D_0 \) is fixed (Fig. 7.5d). For tracking the relative changes in \( \frac{n}{N}(T) \), a fixed \( D_0 \) value may be preferable. Which approach better approximates the true degree of saturation remains to be seen.

7.3.3.2 Comparison of measured and modelled \( \frac{n}{N}(T) \) values

Given our measured \( \frac{n}{N}(T) \) values from stable drill core samples and the rate equations necessary to approximate the natural evolution of these values, the sensible next step is a comparison of predicted and observed \( \frac{n}{N}(T) \) values for these ‘known-history’ drill core samples. This is shown in Fig. 7.6 for three sets of kinetic parameters used within the excited-state tunneling model (the same as used in modelling \( T_{1/2} \) values in Chapter 5).

In each case, 5 Ma of burial was simulated at \( T = -4.1 \) (left-hand column), 19.8 (center column), and 55.1 (right-hand column) to represent samples J1012, J1026, and J1030. The TL curves simulated at the end of 5 Ma are shown in black next to the TL curves resulting from full saturation (\( n/N = 1 \)). Below these simulations in blue are the resulting \( \frac{n}{N}(T) \) values (geologic signal divided by saturation signal). These simulation results can then be compared to the measured MAAD TL \( \frac{n}{N}(T) \) values for these three samples shown with green circles.

Notice how small changes to kinetic parameters strongly influence trapping accumulation. For example, moving from parameter set A to B (top to middle), the only change is that the excited-state is shallower by 0.1 eV (which makes tunneling more likely but requires more heat for thermal activation). This has the effect of lowering the stability of sites, such that the signals resulting from long-term burial at low temperatures have lower intensity than those at saturation (unlike with parameter set A). By further increasing the activation energy (\( E_g - E_e \)) in parameter set C, I increase site stability at lower measurement temperatures so that the saturation signal is brighter and becomes significant at lower temperatures, which results in a high-temperature shift of the simulated \( n/N \) values.

Of the physically reasonable parameter space explored, none of the parameter sets yielded
Parameter set A:

- $E_a = 0.8$ eV
- $E_g = 2.1$ eV
- $s = 1\times10^{15}$ s$^{-1}$
- $P_0 = 5\times10^{16}$ s$^{-1}$
- $\rho = 5\times10^{25}$ m$^{-3}$
- $D_0 = 1.6$ kGy

Parameter set B:

- $E_a = 0.7$ eV
- $E_g = 2.1$ eV
- $s = 1\times10^{15}$ s$^{-1}$
- $P_0 = 5\times10^{16}$ s$^{-1}$
- $\rho = 5\times10^{25}$ m$^{-3}$
- $D_0 = 1.6$ kGy

Parameter set C:

- $E_a = 0.7$ eV
- $E_g = 2.3$ eV
- $s = 1\times10^{15}$ s$^{-1}$
- $P_0 = 5\times10^{16}$ s$^{-1}$
- $\rho = 5\times10^{25}$ m$^{-3}$
- $D_0 = 1.6$ kGy
Figure 7.6: Three sets of model runs are shown to illustrate sensitivity of model output to parameter choice. Each set of 3 red/black and 3 blue/green panels represents a common parameter set shown on the far right. The red and black curves are the modelled TL when all traps are full and after 5 Ma at $T\,^\circ\text{C}$, respectively. By dividing the simulated geologic TL response by the simulated saturated TL response, I can predict $\frac{n}{N}(T)$ values, which are shown as blue dots (only simulated above measurement temperatures of 200 °C). Shown along with the simulated $n/N$ values are the measured MAAD TL $n/N$ values from samples J1012 (left-hand column), J1026 (middle column), and J1030 (right-hand column).
perfect comparison to drill core signals. In the end, the parameter set B shown in Fig. 7.6 was used for the inversions found in the following section. The $n/N$ values are likely to be the most informative below the influence of high-temperature peaks (e.g., 410 °C TL peak of Murray et al., 2009), so the divergence of observations and predictions at high temperatures is not surprising. That said, the trends in $n/N$ values agree reasonably well at $T = -4.1$ and 19.8 °C, but predicted $n/N$ values are too low for the simulated burial temperature of 55.1 °C compared with MAAD results from J1030. If these results from J1030 are reproducible and representative, the model can be expected to underestimate actual burial temperatures starting somewhere between $T = 19.8$ and 55.1 °C. More results are needed to explore this discrepancy.

(At this stage only the excited-state tunneling model is numerically stable enough to be useful. The phonon-assisted diffusion model was initially added as an additional pathway, but the stiffness of the resulting equations prevented its incorporation into the inversion results (the stiff ODE solvers available in MATLAB regularly diverged or gave unstable, ‘spikey’ solutions). Future work could focus on making the PAD pathway more tractable in this context.)

7.4 Interpreting the recent exhumation history of the Yucaipa Ridge block

At this point, I have developed a MAAD TL measurement protocol that yields natural fractional saturation values ($\frac{n}{N}(T)$; Section 7.2). I have also outlined a physically-based framework for understanding and numerically reproducing these values (Section 7.3). This final section will feature an application of this method for bedrock samples taken from the Yucaipa Ridge block (YRB). After a brief introduction to the geologic context and existing constraints on the exhumational history of the YRB during the Quaternary, I will use the TL $\frac{n}{N}(T)$ values from several bedrock samples to elucidate recent cooling rates. Although the initial condition of the cooling history is fixed to be in agreement with the apatite (U-Th)/He results of Spotila et al. (2001), the probable cooling scenario that emerges from our
TL results is corroborated by recent $^{10}$Be erosion-rate data (Binnie et al., 2008).

### 7.4.1 Tectonic setting and constraints on Quaternary cooling history

As the San Andreas fault (SAF) enters Southern California it forms a restraining bend, the ‘southern big bend’ (Fig. 7.7). Plate motion at this bend is no longer parallel to the fault trace and the resulting transpressional force has led to a complex network of faults to accommodate vertical and lateral displacement. This fault network, which can be broadly described as the San Andreas and San Jacinto fault systems, has reorganized several times during the Quaternary period, activating and abandoning different strands such that slip histories for a given strand or tectonic block are often irregular and uncertain (Yule and Sieh, 2003).

The San Bernardino Mountains ($\sim 80 \times 100$ km$^2$) can be divided into four major tectonic blocks (from north-to-south: Big Bear, San Gorgonio, Yucaipa Ridge, and Morongo blocks) which have uplifted in the past $\sim$2.5 Myr in response to this transpressive force, with uplift increasing as one approaches the SAF from the north (Spotila et al., 1998; Spotila and Sieh, 2000). The highest rate of uplift within the San Bernardino Mountains is found in the YRB, bounded to the north and southwest by the Mill Creek and San Bernardino strands of the SAF, respectively, and to the southeast (direction of plate motion) by the Mission Creek strand of the SAF, which in this locality is dominated by reverse slip motion (e.g., Cooke and Dair, 2011).

The Quaternary uplift history of the YRB is constrained by geologic observations, apatite (U - Th)/He (AHe) cooling ages, and basin-averaged $^{10}$Be erosion-rate results. As reasoned by Spotila et al. (1998), the Mill Creek fault must have accommodated vertical motion for the differential uplift between the YRB and the San Gorgonio block to the north. While this fault strand displaces Pleistocene gravel deposits dated around 0.5 Ma, it is also covered by Holocene and latest Pleistocene alluvial deposits along its length (Matti et al., 1992). Based on these observations, most workers interpret the Mill Creek as having been active from 0.5 - 0.1 Ma (Cooke and Dair, 2011; Fattaruso et al., 2016).
Figure 7.7: The locations of collected samples from the Yucaipa Ridge tectonic block near Yucaipa, CA. The major regional tectonic structures are shown as an inset (modified from Fig. 1 of Spotila et al. 1998).
Binnie et al. (2008) collected alluvial sediments from 22 small (0.3 - 8.4 km$^2$) basins which together constitute a north-south transect crossing all major tectonic blocks of the San Bernardino Mountains. Five of these basins are within the YRB (regions outlined in fuschia in Fig. 7.9). The concentration of cosmogenic $^{10}$Be was measured for these sediments to determine the basin-averaged denudation rates, the principle behind the technique being that the longer that quartz sits near the ground surface before eroding out and washing away, the lower the erosion rate must be (Brown et al., 1995). Of these five basins, one gave an anomalously low erosion rate of 0.2 m/Ma. The authors noticed that the mean hillslope gradients were lower in this basin. The other basins exhibited steeper hillslopes, steep enough to categorize the terrain as threshold topography, meaning that channel incision and slope failure dictate the rate of denudation (Binnie et al., 2007). Considering the other four catchments, a mean denudation rate of 1.5±0.29 m/Ma was measured, with individual basins ranging from 1.1±0.2 to 2.7±0.5 m/Ma.

Spotila et al. (1998, 2001) collected 22 samples for AHe thermochronometry, 8 of which were from a vertical transect of the YRB with a relief of ∼1 km. Titanite (U - Th)/He ages were also measured for 4 of the YRB samples to constrain cooling at higher temperatures ($T_C = 200$ °C; Reiners and Farley, 1999). The primary observations were old titanite helium ages (57.1 - 81.8 Ma), young AHe ages (1.4 - 1.6 Ma), and little change in AHe ages with increasing elevation. Combined with the local geothermal gradient of 30 °C/km, these observations imply the following history for the YRB. The top of the modern YRB must have been buried by no more than 5.7 km for at least 57 Ma to accumulate the amount of radiogenic helium in the titanite samples. The numerical solutions of helium production and diffusion equations best fit the apatite results when the YRB cooled at a rate of 210 °C/km between 1.65 and 1.25 Mya. Within that time the YRB must have been exhuming at 7 m/ka, which also explains the trend in AHe ages with elevation (see their Fig. 3). After passing through the AHe partial retention zone (PRZ), the history of the samples is unknown. That is, two boundary conditions are well known: the mean annual surface temperature of about 10 °C at

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2Mean hillslope gradient has since been shown to be less informative for oversteepened catchments in active tectonic settings than catchment-mean channel steepness, $k_m$ (Wobus et al., 2006), but the two tend to covary (Ouimet et al., 2009; DiBiase et al., 2010; Kirby and Whipple, 2012).
present, and (for the base of the YRB) the temperature 1.25 Ma, about 50 °C. Spotila et al. (2001) suggest that the exhumation rate could have remained at 7 m/ka and then ceased when the block reached the surface or the rate could have decreased after the YRB passed through the AHe PRZ (see their Fig. 4). This is the region of interest that I will solve for in the following sections.

For this study, a total of 17 bedrock samples were collected, by removal using a chisel and hammer, from two vertical transects, each ascending from the range-bounding fault up towards the ridge (Fig. 7.7). Transects were hiked from the valley bottom (accessible by Valley of the Falls Drive near the town of Forest Falls, CA), which is roughly defined by the trace of the Mill Creek fault, up towards the ridge via two different draws about 4 km apart. Both paths were steep, the first (samples J0165 - J0173) covering 391 m of vertical relief over 1.4 km, and the second (sample J0211 - J0218) gaining 273 m over 1.3 km. These samples were collected by David Sammeth, Natalia Solomatova, Andreas Lang, and Ed Rhodes before my arrival at UCLA.

7.4.2 Evaluating model sensitivity to probable cooling histories

In the following sections, I follow the approach to numerical inversion of luminescence results previously developed by King et al. (2016a,b). This approach involves first forward modelling to test the sensitivity of luminescence signals to plausible cooling histories, and then inverse modelling to estimate the actual cooling history given the measured luminescence signal.

The forward modelling steps are as follows. First, the kinetic parameters are defined. For the remainder of the chapter, the parameters used in figures and analyses are listed as parameter set B from Fig. 7.6. Second, a cooling path is prescribed. Both paths suggested by Spotila et al. (2001) were used (shown as fuschia functions in Fig. 7.8). Third, for the prescribed path the chosen trapping and detrapping rate equation is solved for the specified

3While they used this approach to interpret SAR multiple-elevated-temperature (MET) IRSL signals, I will consider MAAD TL signals. In both cases, fractional saturation is the target measurement.
times. In our case I use the following equation, developed in Section 5.3.1:

$$\frac{dn(r)}{dt} = \frac{\dot{D}}{D_0} \left( N(r) - n(r) \right) - n(r) \exp \left( -\frac{\Delta E}{k_B T} \right) \frac{P(r)s}{P(r) + s}$$

(7.34)

and I solve for a total time of 1.2 Ma, with temperature varying as shown in in Fig. 7.8. The end result after 1.2 Ma of cooling (present time) is an array containing the concentration of trapped electrons at every considered recombination distance, or $n(r)$ (I simulated distances of 0 to 50 Å with an increment of 0.5 Å). In the fourth step, this array, $n(r)$ after geologic cooling, is then used as the input for a simulated TL curve (Eq. 7.34 solved for 100 s with $dT/dt = 5 {}^\circ\text{C/s}$). Fifth, the TL that would result from entirely full traps at every $r$ value is simulated. By dividing the geologic TL simulation by the saturated TL simulation, the fractional saturation values at every TL measurement temperature ($\frac{n}{N}(T)$) are gotten. In other words, we have predicted the level of fractional saturation that we should measure with the TL signal after the prescribed paths.

The central question addressed by the forward modelling approach is whether this $\frac{n}{N}(T)$ signal can be used to discriminate between cooling scenarios. To answer this question, we must now generate $n$ paths at random. In this example, the number of inner nodes was limited to one, so that there will be at most two line segments defining cooling (since the known forward model paths are both one-node cooling histories, I am biasing the paths towards accuracy in an artificial way; any predictive success should be qualified with this caveat). I simulated 1000 paths per forward model path. Equation 7.34 was then evaluated for every path. Most paths took about 2 seconds to solve using MATLAB’s ode15tb solver. The resulting $n(r)$ arrays were used to generate TL curves which were divided by the saturated TL curve to give us 1000 sets of $\frac{n}{N}(T)$ measurements. (Because the solver generates uneven time steps, these TL curve solutions must be fitted before they can be compared at equal temperature intervals. Polynomial fitting over defined temperature intervals seems to be a relatively fast solution to this problem).

At this point I have the prescribed path $\frac{n}{N}(T)$ values and the random path $\frac{n}{N}(T)$ values. I use a modified version of the likelihood function used by [King et al. (2016a)], as our $\frac{n}{N}(T)$ values do not yet have formally defined measurement uncertainties and I compare for each
Figure 7.8: The two cooling scenarios suggested by Spotila et al. (2001) were: a) a slower rate of cooling up to the present (upper panel), or b) a continued rapid cooling and then a steady temperature until the present (lower panel). Both scenarios are bound by the well-constrained rapid cooling through the partial retention zone of the apatite (U - Th)/He technique, but at temperatures lower than about 50 °C the cooling history is not constrained by thermochronology. The fuschia function illustrates the prescribed cooling paths that were modelled. For both scenarios, 1000 paths were simulated and the resulting numerical TL results were compared to the forward model TL results. The pixelated background is a type of histogram: warm colors indicate that a greater number of likely paths are found in that cell. Notice that both histories are better resolved recently, but in the case of continued rapid cooling followed by stasis I am able to show preference for an accurate cooling timing, even at times >1 Ma.
temperature measurement instead of for each MET trap.

\[ L = \exp \left( -\chi \sum_{T=T_0}^{T_F} \left[ \left( \frac{n}{N} \right)_F - \left( \frac{n}{N} \right)_R \right]^2 \right) \] (7.35)

where \( \chi \) is a scaling factor, \( \left( \frac{n}{N} \right)_F \) are the forward model fractional saturation values, and \( \left( \frac{n}{N} \right)_R \) are the random path values. Using this function, each set of \( \frac{n}{N}(T) \) values resulting from a randomly generated cooling path can be compared against the \( \frac{n}{N}(T) \) values after the prescribed cooling path to get a likelihood score, \( L \), which represents the likelihood that the random cooling path is the same as the prescribed cooling path. I then set some arbitrary likelihood threshold: if a random path scores higher than the threshold value, it is considered a likely path. In this way, the 1000 paths can be reduced to a smaller number of likely paths (of course the ratio of likely-to-unlikely paths can be tuned by adjusting this threshold value).

To summarize these likely paths I chose to use a 2-D histogram instead of showing individual paths. The approach is quite simple. First, create a grid of the \( T - t \) space explored (e.g., \( T = 10 - 50 \, ^\circ C \) and \( t = 1.2 - 0.0 \, Ma \)). Then, count the number of paths found in every cell within that grid. The results are shown in Fig. 7.8.

We can see from Fig. 7.8 that both scenarios suggested by Spotila et al. (2001) are well resolved, especially for the past several hundred thousand years. The lower panel shows that the model seems able to distinguish between very rapid and more gradual cooling prior to 0.6 Ma, though this effect is enhanced by the fixed \( T - t \) node at 1.2 Ma. The interpretation is that, if the model is a good approximation to the actual feldspar TL system, then we can confidently discriminate between these two scenarios.

7.4.3 Inverting TL signals to estimate cooling paths

The process for inversion of measured \( \frac{n}{N}(T) \) values is exactly the same as described in the previous section, with the only difference being that the actual geologic history replaces the prescribed cooling path of the forward model. For the five YRB samples analyzed using the MAAD TL protocol (J0165, J0172, J0214, J0216, J0218) 1000 randomly-generated, monotonic cooling paths were simulated with the same boundary conditions described previously.
Up to three internal nodes were possible for each cooling path, meaning that each path could be composed of up to four linear segments. The evaluation of these paths took about an hour per sample. The simulated $\frac{\Delta N}{N}(T)$ values were then compared with the measured values (see Fig. 7.5) and the underlying cooling path was scored as likely or unlikely. The density plots for cooling histories over the past 1.2 Ma are shown for each sample on the right-hand side of Fig. 7.9. The number of paths included for each sample ($n/1000$) is shown. The probability threshold for which paths were counted as probable was adjusted for visual clarity.

7.4.4 Interpreting the thermal history implied by TL signals

The fundamental qualitative observation from these predicted cooling histories is their coherent pattern with elevation. Those samples collected from the lowest reaches of the drainages, nearest to Mill Creek (J0165 and J0218), seem to have experienced rapid cooling throughout the Late Pleistocene continuing into the present. Moving up the drainages, the samples exhibit decreasing cooling rates. This trend holds both for the individual catchments but also holds as a function of elevation above sea level, or, more to the point, local base-level.

Before moving further, two concerns should be addressed. First, the similarity between $\frac{\Delta N}{N}(T)$ results from sample J1030 ($T_{SS} = 55.1 \, ^\circ C$) and modelled values was low (Fig. 7.6), suggesting that at temperatures near 50 $^\circ C$ (the initial condition for these simulations), the model performance may suffer. The error that would result from the mismatch shown in Fig. 7.6 would be an underestimation of high temperatures. If that were a problem here, the corrected cooling rates would increase.

Second, the thermal gradient that would need to be sustained over a total elevation difference of about 400 m would be quite high. At 0.1 Ma, for example, the gradient would be about 60 $^\circ C$/km. This is twice the value of 30 $^\circ C$/km used by Spotila et al. (2001) who used a mean value for southern California adjacent to the San Andreas fault zone after Lachenbruch et al. (1985) (though they do acknowledge that advection during exhumation and near-surface topography may both perturb this gradient).

To examine whether such a high gradient is feasible, I calculate the depths of isotherms
Figure 7.9: The top panels show the location context. The tectonic evolution of the San Bernardino Mountain region is adapted from Cooke and Dair (2011) (notice the Yucaipa Ridge block highlighted in yellow). The main panel is a colored elevation model (see ‘detail’ box in >0.5 Ma panel above for context). Outlined in fuschia are basins sampled by Binnie et al. (2008) for $^{10}$Be erosion-rate determination. The black crosshair symbols are AHe samples from Spotila et al. (2001) and the blue squares are the samples collected in this study. The fault locations shown in yellow are taken from Kendrick et al. (2015). The right-hand panels are the inversion results for the MAAD TL signals, increasing in elevation from J0165 to J0214.
under steady-state conditions given the maximum exhumation rate and regional geothermal
gradient used by Spotila et al. (2001): 7 m/ka and 30 ◦C/km. To represent surface topog-
raphy, I used QGIS (an open source geographical information system application) to draw
a transect across the YRB, which was used to extract the elevation values from a digital
elevation model with 1/3 arc second (∼10 m) resolution. Given these inputs along with an
average thermal diffusivity value for granodiorite (1.6 × 10−6m2/s), I then use the equations
of Stüve et al. (1994) which provide a semi-analytical solution for this problem. The results
are shown in Fig. 7.10. The initial condition of the solution is an isotherm of 0 ◦C at the
lowest surficial elevation, so the absolute values of the isotherms are uninformative, but their
spacing adequately addresses our question. Notice the compression of isotherms at higher
rates of exhumation (exhumation being the rate of overburden removal, not to be confused
with uplift, which is a change in elevation; England and Molnar, 1990). While the underly-
ing, regional geothermal gradient of 30 ◦C/km was prescribed, the gradient in the vicinity of
the river valley during rapid exhumation is nearly 60 ◦C/km due to the upward advection of
heat (Braun, 2002a). (Although there is some upwarping of isotherms internal to the block,
near the location of the samples this gradient is nearly vertical.)

How do our results compare with the cosmogenic 10Be denudation rates of Binnie et al.
(2008)? Answering this question is difficult for several reasons, the first of which has been
discussed already: the dynamic nature of near-surface isotherms in regions of changing
uplift rates complicates the assignment of a geothermal gradient (Glotzbach et al., 2015).
Moreover, the denudation rates gotten from catchment-averaged 10Be production are liable
to be underestimates if deep-seated landsliding, rock falls, or debris flows are significant
(Yanites et al., 2009; Scherler et al., 2014). The samples are also taken from draws which
experience seasonal flow, and fluvial incision rates in rapidly-uplifting regions are observed
to outpace mean catchment denudation (e.g., Fuchs et al., 2015). Basin-wide denudation
rates also conflate different erosional processes (e.g., hillslope diffusion, landslides Mudd
2017), whereas I consider only tributaries (ridgeline sampling would be a logical next step
on our part). All of this to say that even if I were able to assign an exhumation rate to the
luminescence results, it may actually be higher than the basin-wide denudation rates from
Figure 7.10: (a) The topography of the Yucaipa Ridge block on the ridge adjacent to bedrock samples J0214 - J0218 (see transect location in panel b) is shown as a solid black line. Predicted isotherms during the period of rapid tectonic uplift implied by the AHe results of Spotila et al. (2001) are shown in dashed green (assuming that erosion balanced uplift). Also shown are isotherms with a $10 \times$ slower exhumation rate. The downwarping of isotherms adjacent to the Mill Creek fault is not reproduced with this solution.
alluvial samples. Perhaps the most conservative approach at this stage is to simply observe that the nearby $^{10}$Be erosion rates from Binnie et al. (2008), which range from 1.1 - 2.7 m/ka and have averaging times of a few thousand years, require significant ongoing erosion in the catchments adjacent to Mill Creek.

Topographic analysis offers yet another perspective on the recent exhumational history of these samples. In regions of rapid tectonic uplift such as this, channelized erosion—both fluvial and colluvial (DiBiase et al., 2012)—is thought to dictate km-scale denudation (Lavé and Avouac, 2001; Ouimet et al., 2009). More specifically, with differential uplift rates, the longitudinal profiles of bedrock rivers often contain stretches where the channel steepness is higher than predicted by the stream-power law (Whipple and Tucker, 1999). I therefore use TopoToolbox (Schwanghart and Kuhn, 2010; Schwanghart and Scherler, 2014), a set of MATLAB functions that allow the user to quantify the normalized steepness index of Wobus et al. (2006). The results are shown in Fig. 7.11.

Within the two drainage basins that were sampled, the western catchment only determines steepness for the lower reaches (this is a consequence of the assigned critical drainage size; any cell which is not fed by a minimum number of surrounding cells is not considered, even if it is part of a flow path). In this catchment, J0165 is not located within a zone of high relative steepness. The eastern catchment is more revealing. On the flow path just higher than J0214 (on the neighboring tributary) is a segment of abnormal steepness. The simple interpretation is that an erosional front has recently propagated up this drainage, likely in response to rapid uplift relative to stream base level (Whipple, 2004). Notice that the difference in basin-averaged denudation rates in the two nearby basins measured by Binnie et al. (2008) track well with this interpretation: the catchment with a segment of continuous high steepness exhibits erosion at a rate 10× greater than the adjacent catchment to the west, which shows no clear erosion front. (The $\chi$ plot of Perron and Royden (2013) was poorly suited to this setting as the northern block has had a different recent uplift history, so any defined stream network would include two different erosional and uplift histories). Our conclusion is that after the Mill Creek fault deactivated some time around 0.1 Ma, a transient erosional response may have initiated, propagating up through the network. The
Figure 7.11: The normalized channel steepness $k_{sn}$ values adjacent to the Yucaipa Ridge block (the YRB is south of the main drainage channel, which would represent Mill Creek). Also shown are two catchments for which $^{10}$Be denudation rates were measured.
travel speed of knickpoint migration (i.e., celerity) has been demonstrated to be on the order of 40 km/Ma along the Yarlung river at the base of the Tibetan plateau (Schmidt et al., 2015), a value broadly consistent with this interpretation.

Although the overall interpretation of the thermal history for these samples is still uncertain, the available constraints provide a coherent possibility. The Mill Creek fault activated around 0.5 Ma and drainage reconstruction implies a total uplift of $\sim 975 \pm 70$ m along this fault, before its deactivation around 0.1 Ma (Kendrick et al., 2015). This uplift (and accompanying erosion) could have brought the highest sample, J0214, close to its current temperature. The shutdown of this fault at 0.1 Ma would have been followed by a pulse of fluvial downcutting (e.g., Zhang et al., 2017), ongoing at present. The change in cooling rates with elevation could then be attributed to both the relaxation of isotherms as well as the fluvial incision.

## 7.5 Conclusions

In this chapter, I have developed a MAAD TL protocol that can be used for bedrock feldspar samples to evaluate the level of fractional saturation as a function of measurement temperature, $\frac{n}{N}(T)$ (Table 7.1). This $\frac{n}{N}(T)$ array is a record of electron trapping according to site stability: at higher measurement temperatures ($T \lesssim 350$ °C at $\beta = 5$ °C/s), trap populations of greater thermal stability are measured.

Different hypothesized kinetic pathways for feldspar TL production have been summarized and I developed a novel expression for phonon-assisted diffusion throughout the band-tail states. The different physical parameters that control the rates of these pathways were also summarized. I chose to quantify the detrapping rate as excited-state tunneling to the nearest neighboring recombination center (Jain et al., 2015; Pagonis et al., 2016), and I used the same rate equations as were used to explain the TL signals from drill core samples in Chapter 5.

After comparing the $\frac{n}{N}(T)$ values measured from three drill core samples ($T_{SS} = -4.1, 19.8, 55.1$ °C) to modelled $\frac{n}{N}(T)$ values, I introduced a scheme for interpreting samples
of unknown thermal history, based on the approach taken by King et al. (2016a). This involved the simulation of trapping for a couple known cooling paths to produce $\frac{dN}{dN}(T)$ values. These ‘forward models’ represent different signals that would be measured after realistic geothermal histories. Next, I simulated 1000 random cooling paths and the resulting $\frac{dN}{dN}(T)$ values were quantitatively compared to each of the forward model results. I found that by only considering the random-path $\frac{dN}{dN}(T)$ results most similar to the forward model results, I could accurately predict the cooling histories. This process was then repeated, but instead of forward model results, I set the measured $\frac{dN}{dN}(T)$ values as the comparison targets. In this way, I inverted for the $T - t$ conditions experienced by bedrock samples taken from the Yucaipa Ridge tectonic block.

The cooling histories from the Yucaipa Ridge block samples suggest that samples closer to the ridge have been at present temperatures for the longest time. Moving down the two sampled drainages, the cooling rates of samples increase. I interpret this to reflect the compounding effects of isotherm relaxation back to steady-state and a lagged erosional response to a changing uplift rate. I hope to gain further insight into this scenario in the future by sampling: a) topographic spurs coming down from the ridgetop, b) ridgetop samples, and c) samples from the San Gorgonio block to the north. Additionally, the incorporation of landscape evolution modelling would improve our ability to resolve the complex interactions between tectonic uplift, a changing near-surface geothermal gradient, and fluvial erosion.

Lastly, I look forward to the further application of this MAAD TL protocol to areas of rapid Quaternary exhumation. While numerical results (e.g., sections 3.4.2 and section:coolingSensitivity) suggest that feldspar TL may be useful in resolving cooling rates as low as several °C/Ma, measuring bedrock feldspar $\frac{dN}{dN}(T)$ values in regions of known cooling rates will be necessary to define the utility of feldspar TL as a thermochronometer.
APPENDIX A

TL measurements from Rock Creek glacial valley

The natural TL measurements discussed in Chapter 6 are presented here. For each sample, the natural TL signal is compared to regenerated TL signals (single-aliquot regenerative measurement, or ‘SAR’). Also shown are the TL responses when laboratory dose is added to the natural dose (‘multiple-aliquot additive-dose, or ‘MAAD’). All MAAD signals have been normalized to a test dose response from each disc. All heatings done at 5 °C/s.
Figure A.1: The natural TL signals are shown for samples J0994 and J0995 (top row), along with the single-aliquot regenerative (SAR) TL signals (middle row) and the multiple-aliquot additive-dose (MAAD) TL signals (bottom row).
Figure A.2: The natural TL signals are shown for samples J0996 and J0997 (top row), along with the single-aliquot regenerative (SAR) TL signals (middle row) and the multiple-aliquot additive-dose (MAAD) TL signals (bottom row).
Figure A.3: The natural TL signals are shown for samples J0999 and J1000 (top row), along with the single-aliquot regenerative (SAR) TL signals (middle row) and the multiple-aliquot additive-dose (MAAD) TL signals (bottom row).
Figure A.4: The natural TL signals are shown for samples J1001 and J1002 (top row), along with the single-aliquot regenerative (SAR) TL signals (middle row) and the multiple-aliquot additive-dose (MAAD) TL signals (bottom row).
Figure A.5: The natural TL signals are shown for samples J1003 and J1004 (top row), along with the single-aliquot regenerative (SAR) TL signals (middle row) and the multiple-aliquot additive-dose (MAAD) TL signals (bottom row).
Figure A.6: The natural TL signals are shown for samples J1006 and J1008 (top row), along with the single-aliquot regenerative (SAR) TL signals (middle row) and the multiple-aliquot additive-dose (MAAD) TL signals (bottom row).
Figure A.7: The natural TL signal is shown for sample J1009 (top), along with the single-aliquot regenerative (SAR) TL signals (middle) and the multiple-aliquot additive-dose (MAAD) TL signals (bottom).
APPENDIX B

Sample preparation, instrumentation, and dosimetry measurements

B.1 Sample collection

Bedrock samples were detached by sledge and chisel from rock outcrops that seemed to be in place (i.e., not ‘float’). As discussed in Chapter 6, at least one sample was inadvertently taken from a detached block within a larger rockfall. The latitude, longitude, and elevations of sample collection locations were measured with a handheld GPS system.

The drill cores were sampled according to the policies of the USGS Core Research Center located within the Denver Federal Center in Colorado. Each sample was a half-cylinder with a radius of about 1 inch and a height of about 1.5 inches. The sampled drill cores are referenced by their CRC library numbers: E802, W219, and R716. In all three cases, the sampled core was chosen to have maximal depth range within a uniform lithology and intact core material (i.e., slabbed, whole, or split cores, not cuttings, to ensure that the luminescence signals have not been bleached by exposure to light).

B.2 Sample preparation

B.2.1 Preparation for luminescence analysis

After sample collection, the bedrock samples were spray-painted with a contrasting color and then broken into smaller pieces under dim amber LED lighting. The sunlight-exposed, outer-surface portions of the bedrock samples were separated from the inner portions. To
isolate the inner portion of the split drill cores, the samples were spray-painted and then the outer surfaces were removed using a rotary tool fitted with a tile-cutting bit.

The unexposed inner portions from the bedrock and drill core samples were then ground with a pestle and mortar and sieved to isolate the 175 - 400 µm size fraction. These separates were then treated with 3% hydrochloric acid and separated by density using lithium metatungstate heavy liquid (ρ < 2.565 g/cm³; Rhodes 2015) in order to isolate the most potassic feldspar grains. Grains were mounted on stainless steel discs in a small-diameter (3 - 5 mm) monolayer using silicon oil. No hydrofluoric acid was used to etch these crystals.

B.2.2 Dose-rate determination

The outer portions of each sample were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS) to estimate the U and Th contents, and with inductively-coupled optical emission spectrometry (ICP-OES) to measure the K content. These values were converted into an annual dose-rate using the factors of Adamiec and Aiken (1998). We estimate an internal dose-rate assuming a feldspar potassium content of 12.5 ± 0.12 wt% (Huntley and Barill 1997). Beta attenuation is calculated assuming a water content of 0.01 ± 0.01 (water weight divided by wet sediment weight). Cosmic dose-rates were estimated using the geomagnetic latitude along with a shielding depth. For the drill core samples, the modern depths are used (and are large enough that differences through burial history would have a negligible effect). For detached bedrock samples, a shielding depth of 5 ± 5 cm was used, as this represents the typical radius of collected specimens (a shielding density of 2.65 g/cm³ was used). The resulting annual dose-rate values are listed in Tables B.1, B.2, B.3, and B.4.

B.2.3 Preparation for electron-probe microanalysis (EPMA)

Several separated grains of each sample were prepared for electron-probe microanalysis (EPMA) to determine their chemical compositions. These grains were mounted within epoxy, the surface of which was then progressively polished to expose the internal surfaces of grains. Prior to analysis, this mount was coated with a surficial layer of carbon to avoid electrical
charging during electron bombardment.

B.3 Instrumentation

All luminescence measurements were performed at the UCLA luminescence laboratory using a TL-DA-20 Risø automated reader equipped with a $^{90}\text{Sr}/^{90}\text{Y}$ beta source which delivers 0.1 Gy/s at the sample location [Bøtter-Jensen et al., 2003]. Unless otherwise noted, emissions were detected through a Schott BG3-BG39 filter combination (transmitting between $\sim$325 - 475 nm), thermoluminescence measurements were performed in a nitrogen atmosphere and glow curves were measured at a heating rate of 5 °C/s.

For EPMA measurements, the mounted and polished grains were measured with a JEOL JXA-8200 electron-probe microanalyzer at UCLA. First, backscattered electron (BSE) images were acquired to assess the compositional structure of grains, and then spot analyses with wavelength-dispersive spectroscopy (WDS) were used to quantitatively determine the K, Na, and Ca abundances of each grain [Huot and Lamotte, 2012]. Grains with more heterogeneous compositions (i.e., phases of disparate average Z-values) were measured multiple times to quantify each phase. Duplicate measurements were performed to assess reproducibility. Spot analyses were performed using a defocused electron beam of diameter 10 µm, an accelerating voltage of 15 keV, and a beam current of 15 nA. Immediately prior to measurement, spectrometer calibration was performed with anorthite, albite, and K-feldspar standards. Spot analyses were rejected when the interpreted total mass was outside the range of 98 - 102% (Table 4.1).
Table B.1: Dosimetry information for drill cores E802 and W219. See Section B.2.2 for details.

<table>
<thead>
<tr>
<th>Core</th>
<th>Sample</th>
<th>Depth (m)</th>
<th>$T_{SS}$ (°C)</th>
<th>K (%)</th>
<th>Th (ppm)</th>
<th>U (ppm)</th>
<th>Total dose-rate (Gy/ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E802</td>
<td>J1012</td>
<td>159</td>
<td>-4.1</td>
<td>1.1</td>
<td>5.2</td>
<td>2.04</td>
<td>2.85 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>J1013</td>
<td>303</td>
<td>0.8</td>
<td>0.9</td>
<td>3.5</td>
<td>1.39</td>
<td>2.39 ± 0.10</td>
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<tr>
<td></td>
<td>J1014</td>
<td>367</td>
<td>3.0</td>
<td>1.1</td>
<td>4.9</td>
<td>1.77</td>
<td>2.76 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>J1015</td>
<td>496</td>
<td>7.4</td>
<td>1.3</td>
<td>5.5</td>
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<tr>
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<td>J1016</td>
<td>656</td>
<td>12.8</td>
<td>0.9</td>
<td>6.1</td>
<td>2.09</td>
<td>2.73 ± 0.10</td>
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<td>J1017</td>
<td>7</td>
<td>6.4</td>
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<td>9.7</td>
<td>2.39</td>
<td>5.72 ± 0.27</td>
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<td>J1018</td>
<td>72</td>
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<td>1.87</td>
<td>4.36 ± 0.19</td>
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<td>J1019</td>
<td>150</td>
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<tr>
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<td>J1020</td>
<td>240</td>
<td>18.7</td>
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<td>4.6</td>
<td>4.21</td>
<td>3.49 ± 0.13</td>
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<tr>
<td></td>
<td>J1021*</td>
<td>321</td>
<td>23.0</td>
<td>1.6</td>
<td>3.5</td>
<td>2.34</td>
<td>3.27 ± 0.14</td>
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<td>418</td>
<td>28.2</td>
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<td>2.47</td>
<td>3.11 ± 0.12</td>
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<tr>
<td></td>
<td>J1023*</td>
<td>509</td>
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<td>12.1</td>
<td>3.55</td>
<td>4.70 ± 0.18</td>
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<td></td>
<td>J1024*</td>
<td>575</td>
<td>36.5</td>
<td>0.4</td>
<td>1.9</td>
<td>0.98</td>
<td>1.72 ± 0.08</td>
</tr>
</tbody>
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*The natural signals from these samples were conflated with black-body radiation emissions during measurement and are disregarded from further analysis.
Table B.2: Dosimetry information for drill core R716. See Section B.2.2 for details.

<table>
<thead>
<tr>
<th>Core</th>
<th>Sample</th>
<th>Depth (m)</th>
<th>$T_{SS}$ (°C)</th>
<th>K (%)</th>
<th>Th (ppm)</th>
<th>U (ppm)</th>
<th>Total dose-rate (Gy/ka)</th>
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<td>R716</td>
<td>J1025</td>
<td>307</td>
<td>15.1</td>
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<td>1.57</td>
<td>3.81 ± 0.17</td>
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<tr>
<td></td>
<td>J1026</td>
<td>445</td>
<td>19.8</td>
<td>2.5</td>
<td>17.1</td>
<td>4.81</td>
<td>5.61 ± 0.21</td>
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<td>J1027</td>
<td>606</td>
<td>25.4</td>
<td>2.4</td>
<td>16.4</td>
<td>3.59</td>
<td>5.19 ± 0.20</td>
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<td>881</td>
<td>35.0</td>
<td>2.1</td>
<td>23.8</td>
<td>5.43</td>
<td>5.83 ± 0.21</td>
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<td>J1029</td>
<td>1030</td>
<td>40.1</td>
<td>1.9</td>
<td>13.8</td>
<td>2.82</td>
<td>4.36 ± 0.17</td>
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<td>1462</td>
<td>55.1</td>
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<td>16.9</td>
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<td>4.77 ± 0.18</td>
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<td>1609</td>
<td>60.2</td>
<td>0.9</td>
<td>3.2</td>
<td>2.15</td>
<td>2.60 ± 0.10</td>
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Table B.3: Dosimetry information for Rock Creek glacial valley. See Section B.2.2 for details.

<table>
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<th>Sample</th>
<th>Lat. (°N)</th>
<th>Long. (°W)</th>
<th>Elev. (masl)</th>
<th>K (%)</th>
<th>Th (ppm)</th>
<th>U (ppm)</th>
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<td>109.483</td>
<td>3365</td>
<td>4.1</td>
<td>11.8</td>
<td>1.37</td>
<td>6.39 ± 0.51</td>
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<td>J0994</td>
<td>45.038</td>
<td>109.408</td>
<td>2940</td>
<td>7.0</td>
<td>4.5</td>
<td>0.57</td>
<td>8.41 ± 0.62</td>
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<tr>
<td>J0995</td>
<td>45.038</td>
<td>109.409</td>
<td>2895</td>
<td>0.7</td>
<td>11.8</td>
<td>0.76</td>
<td>3.00 ± 0.38</td>
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<td>1.34</td>
<td>3.98 ± 0.40</td>
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<td>2241</td>
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<td>109.439</td>
<td>2691</td>
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<td>109.446</td>
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</tr>
<tr>
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<td>109.517</td>
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<td>0.81</td>
<td>3.46 ± 0.34</td>
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Table B.4: Dosimetry information for Yucaipa Ridge tectonic block. See Section B.2.2 for details.

<table>
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<tr>
<th>Sample</th>
<th>Lat. (°N)</th>
<th>Long. (°W)</th>
<th>Elev. (masl)</th>
<th>K (%)</th>
<th>Th (ppm)</th>
<th>U (ppm)</th>
<th>Total dose-rate (Gy/ka)</th>
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<td>J0165</td>
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<td>1578</td>
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<td>3.11 ± 0.32</td>
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<td>0.72</td>
<td>4.09 ± 0.36</td>
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Bibliography


Harrison, T., 1981. Diffusion of $^{40}$Ar in hornblende. Contributions to Mineralogy and Petrology 78, 324–331.


Silver, M., Jarnagin, R.C., 1968. Carrier yield in molecular systems due to photo and high energy $\beta$ particle ionization. Molecular Crystals 3, 461–469.


