Testing a simplified SAR TT-OSL protocol for loess deposits in the midcontinental United States

BY
NATHAN D. BROWN
B.S., Wheaton College, 2009

THESIS
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Defense committee:

Steven Forman, Chair and Advisor
Kathryn Nagy
Andrew Dombard
ACKNOWLEDGEMENTS

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NDB
This thesis is dedicated to my lovely Alexa. Thank you for putting up with a thesis in year one.
TABLE OF CONTENTS

1  SIGNIFICANT PRIOR RESEARCH .............................................................................. 1
  1.1  INTRODUCTION ................................................................................................. 1
  1.2  MIDCONTINENTAL LOESS STRATIGRAPHY ...................................................... 4
  1.3  LUMINESCENCE DATING .................................................................................... 8
    1.3.1  Pre-single aliquot regeneration (SAR) dosimetric dating methods .......... 8
    1.3.2  SAR dating method ..................................................................................... 10
    1.3.3  Testing SAR Dσ determinations ................................................................. 13
    1.3.4  OSL signal components ............................................................................. 14
    1.3.5  Thermally transferred SAR protocol ......................................................... 16

2  REFINING THE TT-OSL SAR PROTOCOL .......................................................... 22
  2.1  METHODS ......................................................................................................... 22
    2.1.1  Samples ....................................................................................................... 22
    2.1.2  Measurements .............................................................................................. 23
    2.1.3  Dose-rate determination ............................................................................ 24
  2.2  TESTING TT-OSL SAR PROTOCOLS ............................................................. 26
    2.2.1  Selection of preheat conditions ................................................................. 26
    2.2.2  Test dose evaluation .................................................................................. 33
    2.2.3  Dose recovery test ..................................................................................... 36

3  RESULTS .................................................................................................................... 42
  3.1  DOSE RESPONSE ............................................................................................... 42
  3.2  COMPARISON OF TL, IRSL, AND TT-OSL Dσ VALUES .................................. 45

4  DISCUSSION ............................................................................................................. 51
  4.1  THERMAL STABILITY OF THE REOSL TRAP ............................................. 51
    4.1.1  Isothermal decay analysis ......................................................................... 52
    4.1.2  Burial temperature ..................................................................................... 56
  4.2  PROTOCOL LIMITATIONS ................................................................................ 58
    4.2.1  Signal strength at low equivalent doses ................................................... 58
    4.2.2  Solar resetting ............................................................................................ 59
    4.2.3  Fast component separation ...................................................................... 60
  4.3  TIMING OF DEPOSITION FOR THE CROWLEY’S RIDGE SILT .................... 67

5  CONCLUSIONS ......................................................................................................... 68
  5.1  SUMMARY ......................................................................................................... 68
  5.2  FUTURE WORK .................................................................................................. 70

CITED LITERATURE .................................................................................................... 73

VITA ............................................................................................................................... 86
LIST OF TABLES

I  GENERALIZED SAR PROTOCOL .................................................................................. 3
II  VARIOUS TT-OSL PROTOCOLS ........................................................................... 19
III DOSE-RATE DATA FOR SAMPLES ........................................................................ 26
IV  TT-OSL PROTOCOLS TESTED IN THIS STUDY ..................................................... 29
V   TL, IRSL, AND TT-OSL EQUIVALENT DOSES AND AGES ............................... 49
VI  HEAT TREATMENTS USED IN ISOTHERMAL DECAY ANALYSIS .......................... 53
LIST OF FIGURES

1  Stratigraphic sequence and associated TL, IRSL, and radiocarbon ages ............... 7
2  Equivalent dose as a function of first and second preheat temperatures .......... 32
3  TT-OSL signal as a function of the subsequent test dose OSL signal ............... 36
4  TT-OSL remaining after various sunlamp exposure times ........................... 39
5  Dose recovery test ......................................................................................... 42
6  OSL and TT-OSL dose response curves ......................................................... 45
7  SAR protocol internal errors ........................................................................... 47
8  OSL and TT-OSL signal size comparison ......................................................... 48
9  TT-OSL, IRSL, and TL equivalent dose comparisons ....................................... 50
10 Arrhenius plot for ReOSL trap ....................................................................... 56
11 TT-OSL signal components and $De(t)$-plot explanation ............................... 63
12 Natural-to-regenerative TT-OSL ratios and $De(t)$-plot .................................. 66
NOMENCLATURE

Terms

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hole</td>
<td>Vacancy left by electron</td>
</tr>
<tr>
<td>Charge</td>
<td>Electron or hole</td>
</tr>
<tr>
<td>Trap</td>
<td>Impurity atom with affinity for charge</td>
</tr>
<tr>
<td>(Radiative) recombination center</td>
<td>Trap where opposite charges recombine and emit a photon (luminescence)</td>
</tr>
<tr>
<td>Paleodose or burial dose</td>
<td>Total radiation experienced by the sediment</td>
</tr>
<tr>
<td>Equivalent dose</td>
<td>Laboratory dose which causes the same luminescence as caused by the paleodose</td>
</tr>
<tr>
<td>Component</td>
<td>Portion of total luminescence sourced by specific trap type</td>
</tr>
<tr>
<td>Aliquot</td>
<td>Small (~1 cm diameter) aluminum disc holding many quartz grains</td>
</tr>
</tbody>
</table>

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>TL</td>
<td>Thermoluminescence</td>
</tr>
<tr>
<td>IRSL</td>
<td>Infrared stimulated luminescence</td>
</tr>
<tr>
<td>OSL</td>
<td>Optically stimulated luminescence</td>
</tr>
<tr>
<td>TT-OSL</td>
<td>Thermally transferred OSL; subdivided into ReOSL and BT-OSL</td>
</tr>
<tr>
<td>ReOSL</td>
<td>Recuperated OSL; geochronologically significant portion of TT-OSL</td>
</tr>
<tr>
<td>BT-OSL</td>
<td>Basic transferred OSL; thermally and optically stable portion of TT-OSL</td>
</tr>
<tr>
<td>CW-OSL</td>
<td>Continuous-wave OSL; stimulation power is constant (standard)</td>
</tr>
<tr>
<td>LM-OSL</td>
<td>Linearly modulated OSL; stimulation power is linearly increased to resolve signal components</td>
</tr>
<tr>
<td>SAR</td>
<td>Single aliquot regenerative method</td>
</tr>
<tr>
<td>$D_e$</td>
<td>Equivalent dose (Gy)</td>
</tr>
<tr>
<td>$L$</td>
<td>Luminescence due to natural or regenerative dose (counts per second)</td>
</tr>
<tr>
<td>$T$</td>
<td>Luminescence due to test dose (cps)</td>
</tr>
<tr>
<td>$E$</td>
<td>Trap depth (eV)</td>
</tr>
<tr>
<td>$s$</td>
<td>Trap frequency factor ($s^{-1}$)</td>
</tr>
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</table>
SUMMARY

The Mississippi and Missouri river valleys in the midcontinental United States contain extensive loess-paleosol sequences that are used to constrain glacial-interglacial transition times. Previous studies have been unsuccessful in producing finite ages for sediments older than ~200 ka due to saturation of luminescence emissions. Since the thermally transferred optically stimulated luminescence (TT-OSL) signal has been shown to grow with high (kGy) radiation doses, the TT-OSL dating technique is tested on the fine-grained (4-11 μm) quartz fraction of these loess deposits. The TT-OSL continued to increase with radiation dose > 900 Gy. Equivalent dose values are highly sensitive to preheat temperatures. Recycling ratios, zero-dose response values, and dose recovery tests all perform well for samples with burial doses > ~200 Gy. TT-OSL ages compare well with most thermoluminescence (TL) and infrared stimulated luminescence (IRSL) ages; all samples from the Peoria Loess, Roxana Silt, Teneriffe Silt, and Loveland Silt agree with both TL and IRSL ages within 1σ. For the oldest unit, the Crowley’s Ridge Silt, TT-OSL ages are younger than IRSL or TL ages by ~20%. This is interpreted as underestimation related to TT-OSL signal contamination, which can be avoided by isolating the fast component of the TT-OSL. Preliminary fast component TT-OSL ages for the Crowley’s Ridge Silt favor deposition during Marine Isotope Stage (MIS) 7 or 8, contrary to a previous inference of a MIS 12 deposition.
1 SIGNIFICANT PRIOR RESEARCH

1.1 Introduction

The preserved record of Quaternary climatic change is often fragmentary (Williams et al., 1993). Centennial-to-millennial scale climate change is well-documented, but there are fewer records with less resolution on multi-millennial to million-year timescales. Instrumental records yield hemispheric climate data spanning the past 150 years, and some regions have time series for the past few centuries (Mann, 2007). Tree rings, corals, ice cores, speleothems, laminated lake sediments, and marine sediments can provide continuous, high (annual to decadal) resolution climate data during the past two millennia (Mann, 2007). These archives, with sufficient age control (e.g., U/Th dating), often yield near-continuous, high-resolution records of climate variability for the Late Pleistocene (Jones et al., 2009; Dorale et al., 2010). Palaeoclimatic time series with centennial-scale resolution include non-laminated lake and marine sediments, fossil corals with floating chronologies, moraines, and ice and terrestrial borehole temperature measurements (Mann, 2007; Jones et al., 2009).

However, few records provide continuous climatic data at a scale necessary to observe the glacial-interglacial cycles (10^4 - 10^5 years), and most of the data come from two sources: marine sediment records and terrestrial ice cores (Ruddiman, 2001). Marine sediment records are comprised primarily of δ^{18}O and abundance measurements of foraminifera (Shackleton, 1967; Bond et al., 1993), although other marine core proxy climatic measurements such as
multi-elemental analyses (e.g., core-scanning X-ray fluorescence) are becoming more prominent (Peck et al., 2007; Nürnberg et al., 2008). These data provide information on sea surface and bottom water temperatures, sea-level histories, and elemental concentrations, which can be variously interpreted as climatic indicators (e.g., Shackleton, 1967; Bond et al., 1993; Pälike et al., 2001; Peck et al., 2007). Ice core data from Greenland and Antarctica provide long time series of greenhouse gas concentrations, isotopic variations (both $\delta^{18}$O and $\delta$D), and elemental concentrations (Jouzel et al., 2007; Masson-Delmotte et al., 2010).

Whereas the Greenland ice core records extend to the penultimate glacial period, the Antarctic ice core records have recently been extended to 800 ka (Jouzel et al., 2007; Masson-Delmotte et al., 2010). Ice core data reflect global-to-regional climate variations and can be generalized to other regions with variable confidence. For example, non-sea-salt calcium is inferred to represent dust production on southern mid-latitude continents (Masson-Delmotte et al., 2010).

Marine sediment and ice core data are frequently compared to assess ice volume and paleotemperatures (e.g., Bond et al., 1993).

In mid- to high- longitude regions, another important palaeoclimate record is wind-blown dust (loess) modified by pedogenic processes (Catt, 1991; Beget, 2001). Often referred to as the terrestrial equivalent of marine-sediment records, the more complete glacigenic loess-palaeosol sequences reflect a changing balance between pedogenesis and loess accumulation, which, in turn, reflects variable moisture conditions and sediment supply within a glaciofluvial environment (Kemp, 2001). In a palaeoclimatic context, loess-palaeosol sequences are of critical importance as quasi- to fully-continuous long-term evidence of terrestrial climate change in the Late Pleistocene, and provide climate information (e.g., local terrestrial moisture
conditions) beyond what is known from polar ice-core and marine-sediment records (Begét, 2001). Chronologic controls on loess deposition and palaeosol formation are therefore needed for two reasons. First, determining ages within a stratigraphic sequence quantifies the durations of glacial periods and ensuing interglacial or interstadial periods (Wang et al., 2009). Chronologic control can elucidate lead or lag times between, for example, ice sheet advance and loess deposition. Second, age-constrained loess-palaeosol records can be compared with marine- and ice-core isotopic records to gain a better understanding of climate dynamics on a global or hemispheric scale (Kemp, 2001; Nürnberg et al., 2008). Evaluating the ages of loess units within loess-palaeosol sequences from the midcontinental United States is therefore useful for assessing the timing and durations of glacial and interglacial maxima during the Late Pleistocene.

This chapter has two objectives. First, the context will be presented for the associated loess stratigraphy. Second, luminescence dating will be summarized, from its inception to the current status of thermally transferred optically stimulated luminescence (TT-OSL), the technique here examined. Chapter Two will then describe the TT-OSL protocol developed for this study. The results of applying this protocol to the samples will be given in Chapter Three. Chapter Four will discuss the limitations and implications of the results, and Chapter Five will summarize the major findings and offer suggestions for future midcontinental US loess or TT-OSL studies. The aim of this study is primarily to obtain finite ages for the oldest loess units, ages that have been unobtainable with traditional luminescence methods; the TT-OSL method is chosen as a chronometer appropriate for quartz deposited prior to the Illinoian glacial period. Secondly, this study characterizes the TT-OSL signal within midcontinental loess.
1.2  **Midcontinental loess stratigraphy**

In the major river valleys of the midcontinental United States (i.e., Missouri, Mississippi, Wabash, and Ohio), there are at least four (Blum et al., 2000) and possibly up to seven (Follmer, 1996) major loess sheets that are thickest near the river valleys and thin eastward, downwind (Ruhe, 1983). These loess sheets represent influxes of glacial meltwater and entrained sediment from the Laurentide ice sheet or proglacial lakes (Forman and Pierson, 2002). Specifically, braided streams aggrade with abundant sand and silt, which become available for aeolian transport (Forman and Pierson, 2002). Loess deposition usually spans all or part of a glacial-deglacial cycle; thus midcontinental loess represents an important proxy for North American Pleistocene glaciation history, with greatest thickness of loess (i.e., most complete record) near the source rivers (Ruhe, 1983). An understanding of glacial and nonglacial processes (i.e., erosion, deposition, weathering, and pedogenesis) is critical for a meaningful reconstruction of the glaciation history from loess sequences (Ruhe, 1983). Traditionally, palaeosol-loess sequences have been interpreted using the ‘static’ model: A break in loess deposition is followed by surface stabilization and vegetation growth that initiates pedogenesis (Gerasimov, 1973). Pedogenesis is interpreted to occur during interglacial and interstadial periods (Gerasimov, 1973). Currently, the ‘dynamic’ model is favored, which assumes an ever-changing balance between pedogenesis and loess accumulation (Kemp, 2001). This balance may be controlled primarily by sediment supply that is not necessarily in phase with glacial-interglacial intensities, thus confounding the static model (McDonald and Busacca, 1998; Kemp, 2001). Still, sediment supply and transport are typically limited, and the climate is warmer
and/or wetter during interglacials and interstadials such that most major palaeosol units are formed during interglacials and interstadials (Kemp, 2001).

Multiple loess units from the Mississippi and Missouri river basins are well-expressed at the Bonfils Quarry section, located just south of the confluence of the Mississippi and Missouri rivers in Missouri (Forman and Pierson, 2002). Four representative loess sheets are exposed at Bonfils Quarry: the Peoria Loess, the Roxana Silt, the Loveland Silt, and the Crowley’s Ridge Silt (Figure 1) (Forman and Pierson, 2002). The ages of deposition for these midcontinental loess sheets and their associated palaeosols have been studied extensively (Frye et al., 1974; McKay, 1979; Follmer, 1983; Ruhe, 1983; Forman et al., 1992; Forman and Pierson, 2002), although with increasing stratigraphic depth comes decreasing chronologic control. The Peoria Loess is a common surficial deposit in the midcontinent and is confidently assigned to the Wisconsinan glacial period (Frye et al., 1974). Radiocarbon ages from included organic matter and optical ages from mineral grains within the Peoria Loess have returned dates from ca. 25 to 10 ka (Snowden and Priddy, 1968; McKay, 1979; Leigh and Knox, 1992; Follmer, 1983; Forman and Pierson, 2002), with some loess in Iowa dated as early as 29 ka (Ruhe, 1983). The Peoria Loess occurs above the Farmdale Geosol, the most prominent interstadial soil of the Wisconsinan period (Follmer, 1983). Organic matter from the Farmdale Geosol A-horizon has yielded radiocarbon ($^{14}$C) ages of 30 to 16 ka, thus providing an age constraint on the burial of the Farmdale Geosol by the Peoria Loess (Follmer, 1983; Ruhe, 1983). The Farmdale Geosol developed in the Roxana Silt, and the deposition of the Roxana Silt marked the beginning of the Wisconsinan glacial period (Frye et al., 1974). Radiocarbon ages throughout the Roxana Silt range from $>47.7$ $^{14}$C ka B.P. to 28 ka (McKay, 1979; Follmer, 1983; Leigh and Knox, 1992;
Figure 1. Stratigraphic sequence and associated TL, IRSL, and radiocarbon ages for study sites. Radiocarbon ages are calibrated to calendar years before present by using the calibration curve described in Fairbanks et al. (2005). Samples are identified adjacent to their location in the profile. Figure modified from Forman and Pierson (2002).
Wang et al., 2009), and thermoluminescence (TL) ages range from 53 to 30 ka (Forman et al., 1992; Rodbell et al., 1997; Markewich et al., 1998). Infrared stimulated luminescence (IRSL) ages from this unit range from 34.5 ± 3.0 to 82.5 ± 6.8 (Forman and Pierson, 2002), although the upper age-limit may reflect pedologic mixing with the subjacent Sangamon Geosol (Forman and Pierson, 2002), or may represent a separate stratigraphic unit (Wang et al., 2009).

Radiocarbon and IRSL ages of ca. 50 to 40 ka from the base of the Roxana Silt date the initial deposition of this loess (McKay, 1979; Follmer, 1983; Follmer et al., 1986; Forman and Pierson, 2002). Other studies place the base of the Roxana Silt at ca. 75 ka based on linear extrapolation of radiocarbon ages (Frye et al., 1974). The Roxana Silt buries the Sangamon Geosol, the last interglacial soil of the Illinoian Stage (Frye et al., 1974). U-series isochron ages for carbonate nodules in the basal Sangamon Bt-horizons range from 80 ± 8 (2σ) to 104 ± 26 (2σ) (Wang et al., 2009). The Sangamon Geosol developed in the Loveland Silt (or the presumed correlative Teneriffe Silt), which was inferred to be from the Illinoian Stage (Frye et al., 1974; Forman and Pierson, 2002). Thermoluminescence ages from the Loveland Silt ranged from 181 to 110 ka (Forman et al., 1992; Forman and Pierson, 2002), and IRSL ages ranged from 182 to 126 ka (Forman and Pierson, 2002). The Loveland Silt overlies the Yarmouth Geosol (Forman and Pierson, 2002). Though there are no reliable radiometric ages for the Yarmouth, it could be correlated with Marine Isotope Stage (MIS) 7 (based on absolute ages) or MIS 11 (based on mineralogy) and is therefore generally assigned to MIS 7-11 (Wang et al., 2009), i.e., ~191-478 ka (Lisiecki and Raymo, 2005). It is also unclear if it represents an interstadial or an interglacial period (Forman and Pierson, 2002). The Yarmouth Geosol developed in the Crowley’s Ridge Silt, which was dated in Arkansas by TL at 250 to 200 ka (Markewich et al., 1998) and was dated
in Missouri with TL and IRSL at ≥ 274 to ≥ 159 ka (Forman and Pierson, 2002). The Crowley’s Ridge Silt has been estimated to be as young as MIS 8 (Markewich et al., 1998) or as old as MIS 11 (Grimely et al., 2003).

1.3 Luminescence dating

To understand the TT-OSL protocol described in Chapter Two and the results presented in Chapter Three, it will be helpful to consider the progression of quartz luminescence dating protocols over the past 25 years. First, dosimetric methods generally will be described. Next, the single aliquot regenerative (SAR) optical dating method will be outlined, including the basic physics of the luminescence signal and the tests used to internally verify age estimates. Finally, the development of the TT-OSL protocol will be presented along with the benefits of TT-OSL as a long-range chronometer and the difficulties inherent in isolating a thermally transferred signal.

1.3.1 Pre-single aliquot regeneration (SAR) dosimetric dating methods

Luminescence dating is a dosimetric dating technique that measures the photons emitted from defects in the crystal lattice structure (traps) of minerals, such as quartz and feldspar, when these lattices are excited by imparting heat or light energy (Duller, 2008). This technique is based on the principle that, given a known accumulated radiation dose from nearby thorium, uranium, and potassium as well as cosmic rays and small amounts of rubidium
(paleodose) and a known rate at which the dose has been delivered, it is possible to calculate the time since burial by dividing the paleodose by the dose rate (Aitken, 1998, p. 7). Implied in this method is the assumption that the total energy stored within the grains was first reset by exposure to sunlight and that the grains were subsequently sequestered from sunlight upon deposition (Duller, 2008). Upon light or heat exposure, the emitted photon flux is assumed to be proportional to the paleodose, although further measurements are required to determine the dose response of geologic materials (Murray and Roberts, 1998) - a process explored in this study. Early luminescence dating studies (Morozov, 1968; Wintle and Huntley, 1979; Wintle and Huntley, 1980) used heat as the excitation energy-an approach encompassed by thermoluminescence (TL) dating. However, a problem inherent to TL is that associated traps take hours to days to reset with sunlight exposure. Therefore, the signal generated by excitation is often dominated by a residual (i.e., predepositional) luminescence signal instead of the desired postdepositional signal, thus leading to burial-event age overestimates (Aitken, 1998, p. 20). That is, TL cannot be used when the sediment is exposed to light briefly. As an alternative, researchers turned to optically stimulated luminescence (OSL), as the OSL signal derives from traps that are solar reset in seconds to minutes, therefore yielding a high signal-to-noise ratio (Duller, 2008). Ugumori and Ikeya (1980) suggested using laser-induced luminescence, and Huntley et al. (1985) outlined the first successful use of a green light laser for dating of quartz.

Optically stimulated luminescence can be subdivided into additive- and regenerative-dose approaches (Duller, 2008). Additive multiple-aliquot methods irradiate (e.g., exposure to $^{90}\text{Sr}/^{90}\text{Y}$ beta radiation source), all but the natural ‘aliquot,’ or subsample, and extrapolate the
additive-dose function to find the paleodose. A persistent challenge associated with the additive OSL method is a nonlinear signal growth with dose, leading to large uncertainty with extrapolation of the paleodose (Aitken, 1998, p. 12). The regenerative multiple-aliquot method optically resets all aliquots except the natural and then progressively irradiates the reset aliquots. The luminescence signals from these aliquots are then plotted as a function of dose (i.e., dose-response curve) from which the paleodose can be interpolated, as the natural luminescence is known. This method avoids the pitfalls of nonlinear growth and the related uncertainty, but it must deal with changes in sensitivity between natural and regenerated dose measurements because the luminescence efficiency of the traps may change between measurements (Murray and Wintle, 2000) because of intervening heat (Bøtter-Jensen et al., 1995; Poolton et al., 2000) or radiation treatments (Murray and Roberts, 1998; Murray and Mejdahl, 1999).

1.3.2 SAR dating method

In their landmark optical dating study, Huntley et al. (1985) reported that equivalent dose measurement with a single aliquot was possible, using an additive-dose protocol. They argued that a brief light exposure should not significantly deplete the OSL traps, thus enabling multiple measurements on a single aliquot (Huntley et al., 1985). Murray et al. (1997) developed the first single-aliquot additive protocol for quartz grains, using a 10 second heat treatment (ranging from 160 to 300 °C) followed by a 0.1 s stimulation with blue/green light at 110 °C. The purpose of this pre-stimulation heat treatment (commonly referred to as a
‘preheat’) is to isolate the chronologically significant signal as described in Section 1.3.2. After measuring the natural OSL, a laboratory dose \(D_i\) is administered to the aliquot (e.g., exposure to a radioactive \(^{90}\text{Sr}/^{90}\text{Y}\) beta source), and the measurement procedure (10 s preheat followed by a 0.1 s stimulation) is repeated (Murray et al., 1997). Finally, a preheat/stimulation cycle is repeated without irradiation to monitor the decay rate of the OSL to correct earlier measurements for stimulation- and preheat-related signal decay (Murray et al., 1997; Murray and Roberts, 1998). This shift from multiple- to single-aliquot protocols allowed for the use of a smaller sample size, reduced the time needed to derive an equivalent dose, and eliminated some problems associated with intra-aliquot mineralogical heterogeneity (Murray and Roberts, 1998).

The additive-dose single-aliquot protocol may be inappropriate for some quartz, because the optical decay rate is not always exponential (Bailey et al., 1997; Murray et al., 1997; Murray and Roberts, 1998). This deficiency in the additive-dose protocol led Murray and Roberts (1998) to develop a single-aliquot regenerative-dose (SAR) protocol. A generalized SAR procedure is shown in Table I. The critical advantage of regenerative- over additive-dose single-aliquot protocol is the ability to monitor sensitivity change per cycle through the use of a test dose \(D_t\), a small \((D_t \approx 0.1 D_i)\) beta dose that is followed by heating and stimulation; this test dose is kept constant throughout all stimulations (Murray and Roberts, 1998). Murray and Roberts (1998) monitored the test dose 110 °C TL peak as a proxy for sensitivity change. The test dose OSL signal alone was explored as a proxy (Strickertsson and Murray, 1999), as were the OSL and 110 °C TL measurements together (Roberts et al., 1998; Murray and Mejdahl,
1999). Murray and Wintle (2000) demonstrated that the test dose emission accurately reflected the sensitivity change by testing six quartz samples from glaciofluvial, loess-like, and water-lain sediments, as well as ceramics. A linear relationship was found between the natural and regeneration luminescence emissions plotted against the test dose emissions, with the best-fit line intercepting close to the origin (a condition not met by the $D_110^\circ C$ TL peak [Murray and Roberts, 1998; Murray and Wintle, 2000]). This showed the suitability of the $D_1$ OSL signal as a measure of sensitivity change (Murray and Wintle, 2000). So, a sensitivity-corrected OSL signal is defined as the natural or regenerative luminescence ($L_i$) divided by the test dose luminescence ($T_i$) (Murray and Wintle, 2000; Wintle and Murray, 2006). A dose-response curve can then be generated by plotting the corrected OSL signal ($L_i/T_i$) against the corresponding dose (Wintle and Murray, 2006). Using the dose-response curve, an equivalent

\[ TABLE I \]

**GENERALIZED SAR PROTOCOL**

<table>
<thead>
<tr>
<th>Step</th>
<th>Treatment</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Give dose, $D_i$</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Preheat (160-300 °C, 10 s)</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Stimulate for 100 s at 125 °C</td>
<td>$L_i$</td>
</tr>
<tr>
<td>4</td>
<td>Give test dose, $D_T$</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Heat to 160 °C</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Stimulate for 100 s at 125 °C</td>
<td>$T_i$</td>
</tr>
<tr>
<td>7</td>
<td>Return to 1</td>
<td>-</td>
</tr>
</tbody>
</table>

*a Adapted from Murray and Wintle (2000).
dose ($D_e$) is derived by interpolating the corrected natural luminescence ($L_n/T_n$) onto the dose-response curve (Wintle and Murray, 2006).

1.3.3 Testing SAR $D_e$ determinations

Three tests are typically used to verify SAR equivalent dose measurements: the recycling ratio test, the recuperation test, and the dose recovery test (Wintle and Murray, 2006). Murray and Wintle (2000) first described the recycling ratio as the ratio of the final regeneration dose response to the first regeneration dose response ($L_i/T_i$) / ($L_1/T_1$). For this test to be meaningful, the final regeneration dose must equal the first regeneration dose (Wintle and Murray, 2006). Theoretically, if sensitivity change is fully accounted for the ratio should equal unity because the same radiation dose, administered at different stages of the protocol should yield the same (corrected) OSL signal. A range from 0.90 to 1.10 is considered acceptable for the recycling ratio (Murray and Wintle, 2000). Murray and Wintle (2000) also outlined the recuperation test. This test is administered during the construction of the dose-response curve and uses 0 gray (Gy) as a regeneration dose; ideally, this dose will result in luminescence at or near background levels (<70 photon counts per second). The presence of a luminescence signal implies charge transfer from traps that are more thermally stable than the primary OSL traps; this charge transfer is caused by previous irradiation, optical stimulation, and/or preheating (Murray and Wintle, 2003; Wintle and Murray, 2006). This residual signal is termed ‘recuperation’ (Aitken and Smith, 1988), and the maximum acceptable recuperation is 5% of the equivalent dose (Murray and Wintle, 2000). The final test, the dose recovery test, measures the luminescence
from an optically zeroed, then irradiated aliquot (Roberts et al., 1999; Wallinga et al., 2000). When the dosed aliquot is analyzed as an ‘unknown’ age sample, the ratio of the recovered dose to the administered (known) dose should be unity, or the histogram of aliquot ratios should be centered on unity with a normal distribution (Wintle and Murray, 2006); if not, the first sensitivity measurement is not applicable to the natural signal because of preheat-related sensitivity change (Wintle and Murray, 2006).

1.3.4 OSL signal components

Smith and Rhodes (1994) developed the first holistic charge-transfer model to deconvolute the possible subcomponents of the OSL signal. This analysis underscored that the OSL signal decay is not a simple exponential but is typically best fit by three exponential components: a long-term component, which contributes little to the OSL and can usually be treated as a background constant, and the fast and medium components, which explain the majority of the OSL (Smith and Rhodes, 1994). The fast and medium components differ in mean lives by a factor of four and show extreme thermal quenching of luminescence efficiency, i.e., the luminescence measured decreases at higher temperatures (Wintle, 1975; Smith and Rhodes, 1994). To account for the nature of the decay of the multiple components, Smith and Rhodes (1994) used thermoluminescence measurements immediately after optical stimulations to monitor charge movement. According to their model, charge moves through the conduction band, and is captured by a luminescence center, a shallow (<280 °C) trap, or a deep (280-400 °C) trap (Smith and Rhodes, 1994). During optical stimulation, most of the charge is removed
from the thermally stable, optically sensitive 325 °C trap. However, if measurements are made at room temperature (17 °C), a substantial amount of charge is retrapped in the 100 °C optically stable trap during stimulation (Smith and Rhodes, 1994). OSL signal recuperation during heating or delay following prolonged stimulation implies retrapping in deep traps, and thus OSL components represent different trapping sites with different mean lives (Smith et al., 1986; Smith and Rhodes, 1994). Heating an irradiated sample prior to OSL measurement is thus advised to redistribute the charge from thermally unstable traps (Smith and Rhodes, 1994; Murray and Wintle, 1998). This preheat also acts to isolate a thermally stable and geochronologically significant OSL emission (Wintle and Murray, 2006). Bailey et al. (1997) extended the work of Smith and Rhodes (1994), and identified the fast and medium components as the charge population of the 325 °C TL region, and observed that the fast component comprises a majority of the fast and medium total signal due to recuperation during the preheat. The slow component was identified as fundamentally different in emitted wavelength and thermal stability (>650 °C) and was therefore attributed to different luminescence centers (Bailey et al., 1997). Fast, medium, and 110 °C TL charge populations share a common luminescence center, separate from the slow component luminescence center (Bailey et al., 1997). The slow component, with a high dose saturation level and thermal stability, is therefore a potential long range (~1 Ma) chronometer, though long solar-reset times (hours) may preclude its usefulness for some sedimentary environments (Bailey et al., 1997).

All three components, with light excitation, decay at a temperature-dependant rate. The mean lifetimes for the fast, medium, and slow components, with optical stimulation at room temperature (~20 °C) are 6.2, 25, and 4300 seconds, respectively (Bailey et al., 1997). Jain et al.
(2003) identified a total of seven components by linearly modulating stimulation power (e.g., 0-100%) with time (‘LM-OSL’): ultrafast, fast, medium, slow 1, slow 2, slow 3, and slow 4, in order of optical depletion rate. These components are thermally distinct, with luminescence intensity reduced by 50% when temperatures are held at 160 °C (ultrafast), 310 °C (fast), 400 °C (medium), 400 °C (S2), and 260 °C (S3); the slow 4 component remains present even above 600 °C (Jain et al., 2003). The slow 4 component was also found to recuperate to about 80%, compared with the other slow components which recuperated to 10% (S1) and 5% (S3) (Jain et al., 2003).

1.3.5 Thermally transferred SAR protocol

Wang et al. (2006a,b) developed the first multiple-aliquot regenerative-dose protocol that used the thermally transferred OSL (TT-OSL) signal and they concluded that the derived signal is useful in dating quartz deposited in the past 130 ka to 0.8 Ma (Wang et al., 2006a). The thermally transferred signal was well documented prior to the development of TT-OSL dosimetric protocols, but the trap responsible for the thermally transferred charge was unidentified and the dosimetric properties of the source trap(s) remained unexplored (Huntley et al., 1985; Aitken and Smith, 1988; Aitken, 1998; Rhodes, 2000). Thus, the use of the recuperated OSL signal as a long-range chronometer was groundbreaking.

To measure the TT-OSL signal, Wang et al. (2006a) followed a laboratory treatment sequence of regenerative-dose irradiation, preheat, and blue-light stimulation, but then added a second preheat and blue-light stimulation followed by a test dose measurement (Table IIA).
The second preheat/stimulation measures the charge that is thermally transferred to the main OSL trap (Wang et al., 2006a). The protocol rests on the assumption that the thermally transferred OSL signal is a composite of two signals: the recuperated signal and the basic transferred signal (Aitken, 1998, p. 176; Adamiec et al., 2010). According to the single charge transfer model of Pagonis et al. (2008), the recuperated signal (ReOSL) is derived from a trap with thermal stability at 260 °C that allows for some charge to be transferred to the OSL fast component trap. This component has less solar sensitivity compared to the main OSL traps, but is solar-reset during prolonged subaerial light exposure (Pagonis et al., 2008), characteristic of loess deposition (hours to days); it has been suggested that the slow 4 trap of Jain et al. (2003) is this source trap (Wang et al., 2007). The ReOSL signal increases with dose > 3.78 kGy, as compared with the standard OSL signal that has either non-linear growth or saturation at regenerative doses > ~ 500 Gy (Wang et al., 2006a). In contrast, the basic transferred signal (BT-OSL) is derived from light-insensitive traps and is therefore unsuitable for dating, as it may contain charge that accumulated prior to the solar resetting event (Wang et al., 2006; Pagonis et al., 2008). Thus, a successful sensitivity-corrected TT-OSL protocol should remove the contribution of the BT-OSL signal to isolate the datable ReOSL signal (Wang et al., 2006a,b):

\[
\text{Corrected } L(\text{ReOSL}) = \frac{L(\text{TTOSL})}{T(\text{TTOSL})} - \frac{L(\text{BTOSL})}{T(\text{BTOSL})} \quad (1.1)
\]

Repeated preheat and stimulation cycles (Steps 4 and 5 repeated after Step 8; see Table IIA) on a single aliquot can identify accurately the BT-OSL signal as the background value remaining after the ReOSL signal is depleted (Wang et al., 2006a,b). Unfortunately, this method is too
TABLE II
VARIOUS TT-OSL PROTOCOLS

<table>
<thead>
<tr>
<th>Step</th>
<th>Protocol&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Protocol&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Protocol&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dose, $D_i$</td>
<td>Dose, $D_i$</td>
<td>Dose, $D_i$</td>
</tr>
<tr>
<td>2</td>
<td>Preheat (260 °C, 10 s)</td>
<td>Preheat (200-260 °C, 10 s)</td>
<td>Preheat (260 °C, 10 s)</td>
</tr>
<tr>
<td>3</td>
<td>OSL (125 °C, 270 s)</td>
<td>OSL (125 °C, 300 s)</td>
<td>OSL (125 °C, 60 s)</td>
</tr>
<tr>
<td>4</td>
<td>Preheat (260 °C, 10 s)</td>
<td>Preheat (260 °C, 10 s)</td>
<td>Preheat (260 °C, 10 s)</td>
</tr>
<tr>
<td>5</td>
<td>TT-OSL (125 °C, 90 s)</td>
<td>TT-OSL (125 °C, 100 s)</td>
<td>TT-OSL (125 °C, 60 s)</td>
</tr>
<tr>
<td>6</td>
<td>Test dose, $D_t$</td>
<td>Test dose, $D_t$</td>
<td>OSL (280 °C, 400 s)</td>
</tr>
<tr>
<td>7</td>
<td>Preheat (220 °C, 20 s)</td>
<td>Preheat (220 °C, 10 s)</td>
<td>Test dose, $D_t$</td>
</tr>
<tr>
<td>8</td>
<td>OSL (125 °C, 90 s)</td>
<td>OSL (125 °C, 100 s)</td>
<td>Preheat (260 °C, 10 s)</td>
</tr>
<tr>
<td>9</td>
<td>Preheat (300 °C, 10 s)</td>
<td>Heat (300 °C, 100 s)</td>
<td>OSL (125 °C, 60 s)</td>
</tr>
<tr>
<td>10</td>
<td>OSL (125 °C, 90 s)</td>
<td>Heat (300 °C, 100 s)</td>
<td>OSL (290 °C, 400 s)</td>
</tr>
<tr>
<td>11</td>
<td>Preheat (260 °C, 10 s)</td>
<td>Preheat (125 °C, 60 s)</td>
<td>TT-OSL (125 °C, 60 s)</td>
</tr>
<tr>
<td>12</td>
<td>OSL (125 °C, 100 s)</td>
<td>TT-OSL (125 °C, 60 s)</td>
<td>OSL (290 °C, 400 s)</td>
</tr>
<tr>
<td>13</td>
<td>Test dose, $D_t$</td>
<td>Test dose, $D_t$</td>
<td>OSL (290 °C, 400 s)</td>
</tr>
<tr>
<td>14</td>
<td>Preheat (220 °C, 20 s)</td>
<td>Preheat (260 °C, 10 s)</td>
<td>OSL (290 °C, 400 s)</td>
</tr>
<tr>
<td>15</td>
<td>OSL (125 °C, 90 s)</td>
<td>OSL (125 °C, 90 s)</td>
<td>OSL (290 °C, 400 s)</td>
</tr>
</tbody>
</table>

<sup>a</sup>MAR protocol defined by Wang et al. (2006a).

<sup>b</sup>SAR sequence defined by Porat et al. (2009).

<sup>c</sup>SAR sequence from Stevens et al. (2009).
time-consuming as a practical protocol (Wang et al., 2006a,b). Instead, Wang et al. (2006a)
experimentally determined the thermal treatment that reduces the TT-OSL signal to the
previously determined BT-OSL value and used this thermal treatment (300 °C for 10 s) in a
modified MAR protocol.

A significant advance in TT-OSL dosimetry was the development of a SAR protocol
(Wang et al., 2007). The first SAR TT-OSL protocol used a slightly shorter preheat to avoid
depletion of the BT-OSL signal, and repeated the measurement cycle (Steps 1-15, Table IIA)
multiple times per aliquot to derive a sensitivity-corrected ReOSL dose-response curve (i.e.,
equation 1.1) for each aliquot (Wang et al., 2007). Unfortunately, this shorter preheat does not
completely remove the ReOSL signal, and, for this reason, a final 0 Gy regeneration dose
measurement (Step 1, Table IIA) must be made to account for charge build-up during the
administration of previous regeneration and test doses (Wang et al., 2007). Despite the time-
consuming nature of the new recuperated SAR protocol, the sensitivity changes in both the TT-
OSL and the BT-OSL signals--about a 50% decrease in sensitivity--were successfully monitored
with the test dose (Wang et al., 2007). Comparisons with both ReSAR and MAR $D_e$
determinations from the same section agreed within the 95% confidence interval; use of the
ReSAR protocol also avoided the MAR protocol $D_e$ overestimation by accounting for the charge
accumulation (Wang et al., 2007). Tsukamoto et al. (2008) modified this ReSAR protocol by
adding a blue light stimulation (280 °C for 100 s) at the end of each cycle to remove charge
carry-over from the final test dose to the regeneration dose.

Porat et al. (2009) developed a protocol that did not make a separate BT-OSL
measurement, arguing that the BT-OSL is dose dependent and behaves similarly to the TT-OSL
and the ReOSL. This revised protocol removed the BT-OSL signal as completely as possible at
the end of each cycle using a high temperature treatment (300 °C for 100 s) to minimize BT-OSL
build-up during repeated SAR cycling (Table IIB). This protocol yielded recycling ratios near
unity (i.e., there was no charge build-up), gave a linear L/T relationship, and recovered doses up
to 700 Gy (Porat et al., 2009).

Stevens et al. (2009), however, found difficulties with the protocol developed by Wang
et al. (2007) when applied to Chinese loess, including poor recycling ratios, negative intercepts
on the sensitivity-corrected TT-OSL axis, and non-linear relationships between regeneration
dose TT-OSL and test dose OSL. To explain these difficulties, Stevens et al. (2009) argued for a
single transfer model (Adamiec et al., 2008; Pagonis et al., 2008) where the source traps for the
TT-OSL signal are different from the source traps for the fast component OSL signal. Wang et
al. (2007) had assumed a double transfer model in which the TT-OSL signal arose from electrons
retrapped in the main OSL trap during heating. If the source of the fast component charge
differs from the source for the TT-OSL charge, a TT-OSL response to a test dose may be needed
to adequately normalize the TT-OSL signal (Stevens et al., 2009). Notably, Porat et al. (2009)
observed a sensitivity change in the TT-OSL signal not properly monitored by the OSL test dose
response; this would corroborate the single transfer model and further demand a TT-OSL
specific test dose response. Finally, charge was found to carry-over from the regeneration dose
to the test dose, such that the test dose L/T was elevated, impacting the veracity of the dose-
response function. To prevent this problem, a high-temperature treatment at 350 °C for 100 s
was added immediately following the $L_{TT-OSL}$ measurement (Stevens et al., 2009). A high
temperature treatment was also added to the end of each regenerative-dose measurement
cycle (i.e., $L_{TOSL}$ and $T_{TOSL}$ for a given dose, $D_i$) to eliminate charge from carrying over from the test dose to the regeneration dose. This heat treatment was later increased to 350 °C for at least 100 s to completely reset the ReOSL signal (Adamiec et al., 2010). The improved protocol (Table IIIC) showed signal growth to at least 1.2 kGy, though not all samples showed enough sensitivity to be accurately dated (Stevens et al., 2009). Trap characterization later identified the thermal stability of the ReOSL signal to be high enough to warrant a heat treatment of 350 °C for at least 100 s to completely reset the signal (Adamiec et al., 2010).
This chapter will first describe the methods used to isolate the silt size fraction of quartz from the bulk samples, the instrumentation and techniques used for luminescence measurements, and the determination of dose rates. Secondly, the SAR TT-OSL protocol will be outlined. Specifically, this chapter will discuss the determination of preheat temperatures, the appropriateness of the test dose size, and the accuracy and precision of the dose recovery tests.

2.1 Methods

2.1.1 Samples

Six samples from the Bonfils Quarry site, Missouri; three samples from the Loveland Loess type locality, Loveland, Iowa; and three samples from the Pleasant Grove School section, Illinois were analyzed (OTL 405, OTL 407, OTL 454, OTL 406, OTL 391, OTL 456, ITL 207, ITL 197, ITL 208, ITL 216, ITL 215, ITL 217; see Figure 1) (Forman and Pierson, 2002). Additionally, two samples (UIC 2745, UIC 2746) were taken from the Lake El’gygytgyn, a meteorite impact crater north of the Arctic Circle in northeast Siberia (see Forman et al. [2007] for depositional context); these samples were used only to refine the TT-OSL SAR protocol. Fine-grained (4-11 µm) quartz was extracted from all samples under subdued yellow light conditions. Samples were pretreated for 24 hours with 11.1% HCl and then 30% H₂O₂ to remove carbonates and
organic material, respectively. Using physical separation methods based on Stokes’ Law, the fine silt fraction (4-11 µm) was isolated. Finally, broken glass was placed in H₂SiF₆ (i.e., hexafluorosilicic acid) for six days to saturate the acid with respect to SiO₂. The polymineral sediment was then bathed in silicon-saturated H₂SiF₆ for six days to isolate the quartz component (Berger, 1980; Roberts, 2007). To ensure the purity of the quartz separate, the IR-OSL depletion ratio (Duller, 2003) was examined after the hexafluorosilicic acid treatment; if the ratio was > 0.1, samples underwent a second H₂SiF₆ treatment.

2.1.2 Measurements

An automated Risø TL/OSL-DA-20 system was used for all OSL analyses (Bøtter-Jensen, 1997; Bøtter-Jensen et al., 2003). This system utilizes 28 blue (470 ± 20 nm) light-emitting diodes; samples were stimulated at 80% power, which is approximately 40 mW/cm². Photon emissions are measured using a Thorn EMI 9235 QA photomultiplier coupled with three Hoya U-340 detection filters that transmit wavelengths between 290 and 370 nm. A ⁹⁰Sr/⁹⁰Y beta source is used to irradiate samples. Heating for all preheat steps and OSL measurements proceeded at a rate of 5 °C s⁻¹. Unless otherwise noted, all luminescence signals were detected for 60 s in 150 channels (bin width of 0.4 s), and the first 0.4 s integral minus the mean signal from the last 20 s was used for all luminescence measurements. Equivalent doses were estimated with the assistance of Risø Luminescence Analyst (v. 3.24) software (Duller, 1997).
2.1.3 *Dose-rate determination*

The environmental dose rate measures the exposure of mineral grains to ionizing radiation during the burial period (Section 1.3.1). The majority of ionizing radiation within sediments results from the decay of isotopes within the U and Th series and $^{40}$K (Aitken, 1998, p. 38; Forman and Pierson, 2002), and the dose-rate value is inferred from elemental concentration measurements of these three species. U and Th contents are determined using thick-source alpha counting, assuming secular equilibrium (Sjostrand and Prescott, 2002). $^{40}$K contents are determined using inductively coupled plasma mass spectrometry measurements of K$_2$O; analyses were performed by Activation Laboratories LTD, Ontario, Canada. U, Th, and K, concentrations are then converted to dose rates using standard conversion factors (Adamiec and Aitken, 1998). The $\alpha$-values for samples are found to range from 0.8 to 0.4 (J. Pierson, pers. comm.). Also included in the dose-rate measurement is a small (0.12 ± 0.02 Gy/ka) cosmic ray component (Prescott and Hutton, 1994). A moisture content of 15 ± 5% (by weight) is assumed for dose-rate calculations (Forman and Pierson, 2002). The dose-rate equation for fine silt-sized grains is thus

\[
\text{Dose rate} = D'_\alpha + D_\beta + D_\gamma + D_c \quad (2.1)
\]

where $D'_\alpha$, $D_\beta$, $D_\gamma$, and $D_c$ are respectively the effective alpha contribution (dose rate multiplied by efficiency), beta, gamma, and cosmic dose rates (Aitken, 1998, p. 41). Dose-rate estimates are shown in Table III.
<table>
<thead>
<tr>
<th>Laboratory number</th>
<th>α count rate (ks/cm²)</th>
<th>Th (ppm)</th>
<th>U (ppm)</th>
<th>Unsealed/sealed</th>
<th>K₂O (%)</th>
<th>Dose rate (mGy/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITL 197</td>
<td>0.53 ± 0.01</td>
<td>7.08 ± 0.97</td>
<td>2.37 ± 0.30</td>
<td>0.99</td>
<td>2.22 ± 0.05</td>
<td>3.19 ± 0.14</td>
</tr>
<tr>
<td>ITL 207</td>
<td>0.63 ± 0.01</td>
<td>6.74 ± 0.97</td>
<td>3.32 ± 0.30</td>
<td>0.98</td>
<td>2.25 ± 0.04</td>
<td>3.89 ± 0.14</td>
</tr>
<tr>
<td>ITL 208</td>
<td>0.54 ± 0.01</td>
<td>6.94 ± 0.96</td>
<td>2.51 ± 0.30</td>
<td>1.00</td>
<td>2.18 ± 0.04</td>
<td>3.20 ± 0.14</td>
</tr>
<tr>
<td>ITL 215</td>
<td>0.46 ± 0.01</td>
<td>5.83 ± 0.85</td>
<td>2.09 ± 0.26</td>
<td>0.98</td>
<td>2.27 ± 0.04</td>
<td>3.02 ± 0.12</td>
</tr>
<tr>
<td>ITL 216</td>
<td>0.44 ± 0.01</td>
<td>4.48 ± 0.75</td>
<td>2.22 ± 0.24</td>
<td>1.01</td>
<td>1.89 ± 0.04</td>
<td>2.65 ± 0.11</td>
</tr>
<tr>
<td>ITL 217</td>
<td>0.44 ± 0.01</td>
<td>5.32 ± 0.64</td>
<td>2.08 ± 0.20</td>
<td>0.96</td>
<td>1.84 ± 0.04</td>
<td>2.65 ± 0.09</td>
</tr>
<tr>
<td>OTL 391</td>
<td>0.61 ± 0.01</td>
<td>9.20 ± 1.25</td>
<td>2.33 ± 0.37</td>
<td>1.01</td>
<td>1.95 ± 0.02</td>
<td>3.19 ± 0.19</td>
</tr>
<tr>
<td>OTL 405</td>
<td>0.59 ± 0.03</td>
<td>6.51 ± 0.91</td>
<td>2.88 ± 0.36</td>
<td>0.96</td>
<td>2.24 ± 0.02</td>
<td>3.32 ± 0.15</td>
</tr>
<tr>
<td>OTL 406</td>
<td>0.62 ± 0.03</td>
<td>8.28 ± 1.14</td>
<td>2.58 ± 0.42</td>
<td>0.96</td>
<td>1.90 ± 0.02</td>
<td>3.15 ± 0.18</td>
</tr>
<tr>
<td>OTL 407</td>
<td>0.62 ± 0.03</td>
<td>7.90 ± 1.19</td>
<td>2.70 ± 0.43</td>
<td>0.96</td>
<td>2.12 ± 0.02</td>
<td>3.31 ± 0.18</td>
</tr>
<tr>
<td>OTL 454</td>
<td>0.66 ± 0.03</td>
<td>7.29 ± 1.11</td>
<td>3.19 ± 0.42</td>
<td>1.02</td>
<td>1.99 ± 0.02</td>
<td>3.32 ± 0.17</td>
</tr>
<tr>
<td>OTL 456</td>
<td>0.58 ± 0.03</td>
<td>8.66 ± 1.18</td>
<td>2.11 ± 0.42</td>
<td>0.98</td>
<td>1.90 ± 0.02</td>
<td>3.03 ± 0.18</td>
</tr>
</tbody>
</table>


*U and Th ppm levels calculated from α count rate, assuming secular equilibrium.

*The ratio of bulk α count rate under sealed and unsealed counting conditions. A ratio of >0.94 indicates little to none radon loss.

*Percent potassium determined by ICP-MS on a homogenized 50-g aliquot by Activation Laboratories LTD, Ontario, Canada.

*Alpha dose rates are calculated using an α-value of 0.06 ± 0.02 (J. Pierson, pers. comm.)

*Dose-rate value includes a contribution from cosmic radiation of 0.12 ± 0.02 mGy/yr (Prescott and Hutton, 1994) and assuming a moisture content of 15 ± 5%. All errors are at one σ.
2.2 Testing TT-OSL SAR protocols

Aliquots were initially tested with the simplified TT-OSL protocol of Stevens et al. (2009) (Table IIC) instead of the protocol of Porat et al. (2009) (Table IIB). The reason for this preference is the predictive power of the single transfer model (Section 1.3.5) for TT-OSL protocols applied to samples from the Chinese Loess Plateau (e.g., Wang et al., 2006a,b; Wang et al., 2007; Lu et al., 2007; Stevens et al., 2009). Furthermore, it has been suggested that the single transfer model implies the need for a ‘TT-OSL-specific’ test dose response, and thus the Stevens et al. (2009) protocol includes a second preheat and stimulation after the test dose is administered (Table IIC, Steps 10-11; Stevens et al., 2009). Additionally, the protocol incorporates a high temperature treatment (280 °C for 400 s) immediately following the $L_{TTOSL}$ measurement (Table IIC, Step 6) to prevent charge carry-over from the $L_{TTOSL}$ measurement to the $T_{TTOSL}$ measurement (Stevens et al., 2009).

2.2.1 Selection of preheat conditions

The heat treatment immediately prior to luminescence measurements (preheat) can significantly affect the magnitude of the luminescence due to various effects (e.g., thermal transfer of charge, thermal erosion of charge) (cf. Porat et al., 2009). This section outlines the effects experienced with different preheat temperatures, and prescribes temperatures for the first and second preheats. These temperatures are meant to provide the maximum intensity TT-OSL signal, while avoiding distortion in $D_e$ estimation.
Samples OTL 391, OTL 208, UIC 2745 were tested with the Stevens et al. (2009) protocol (Table IVA) and exhibited very poor recycling ratios (e.g., 1.77), significant equivalent dose ($D_e$) underestimates, and consistently low $L_{TTOSL}$ signal-to-noise ratios. The temperature of the preheats immediately preceding the measurements of $L_{OSL}$, $L_{TTOSL}$, $T_{OSL}$, and $T_{TTOSL}$ (Table IVA, Steps 2, 4, 8, 10) were thus tested at 180, 240, 260, 280, and 300 °C to identify the temperature that would thermally transfer the most charge into the main OSL trap, while minimizing thermal charge-eviction prior to optical stimulation (Porat et al., 2009; Stevens et al., 2009). Preheats were varied concurrently (i.e., all four preheats were tested at 180 °C, then all four were tested at 240 °C, etc.). Despite various preheat temperatures, the protocol yielded poor recycling ratios, suggesting that changes in trap sensitivities were not monitored adequately by test dose measurements (Murray and Wintle, 2000). Moreover, the $L_{TTOSL}/T_{TTOSL}$ values measured after a regenerative dose of 0 Gy were >5% of the $L_{TTOSL}/T_{TTOSL}$ values measured for the natural dose, which indicates a build-up in charge with SAR cycling (Murray and Wintle, 2000; Murray and Wintle, 2003). Finally, both $L_{TTOSL}$ and $T_{TTOSL}$ signals were small (e.g., ~750 photon counts per second (cps) before background subtraction, compared with a ‘dark’ count of ~70 cps and typical OSL counts of ~10,000-500,000), confounding precise $D_e$ measurements.

To enhance the $T_{TTOSL}$ signal, the protocol was modified by decreasing the temperature of the $T_{TTOSL}$ preheat (i.e., cutheat). Additionally, the final heat treatment (Table IVB, Step 12) was elevated to 350 °C for 200 s to minimize charge build-up with SAR cycling (Adamiec et al., 2010). Tested on sample UIC 2746, this modified protocol (Table IVB) yielded recycling ratios near unity, but the zero dose regeneration cycle had a substantial (> 5% $L_N/T_N$) signal. The final heat treatment (Table IVB, Step 12) was thus increased to 390 °C for 200 s to minimize charge
## Table IV

**TT-OSL Protocols Tested in This Study**

<table>
<thead>
<tr>
<th>Step</th>
<th>Protocol&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Protocol&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Protocol&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Protocol&lt;sup&gt;d&lt;/sup&gt;</th>
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<td>Dose, Di</td>
<td>Dose, Di</td>
<td>Dose, Di</td>
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<td>2</td>
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<td>Preheat (180 °C, 10 s)</td>
<td>Preheat (160 °C, 10 s)</td>
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<td>OSL (125 °C, 60 s)</td>
<td>OSL (125 °C, 60 s)</td>
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<tr>
<td>4</td>
<td>Preheat (260 °C, 10 s)</td>
<td>Preheat (260 °C, 10 s)</td>
<td>Preheat (260 °C, 10 s)</td>
<td>Preheat (290 °C, 10 s)</td>
</tr>
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<td>TT-OSL (125 °C, 60 s)</td>
<td>TT-OSL (125 °C, 60 s)</td>
<td>TT-OSL (125 °C, 60 s)</td>
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<tr>
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<td>Test dose, Dt</td>
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<td>8</td>
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<td>Preheat (260 °C, 10 s)</td>
<td>OSL (350 °C, 200 s)</td>
<td>OSL (350 °C, 200 s)</td>
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<tr>
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<td>TT-OSL (125 °C, 60 s)</td>
<td>TT-OSL (125 °C, 60 s)</td>
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<td>12</td>
<td>OSL (290 °C, 400 s)</td>
<td>OSL (350 °C, 200 s)</td>
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</table>

<sup>a</sup>SAR protocol defined by Stevens et al. (2009).

<sup>b</sup>With modified final heat treatment and lower cutheat temperature.

<sup>c</sup>With lower first preheat temperature and OSL response to a test dose.

<sup>d</sup>With optimized preheat values.
build-up with SAR cycling, but the zero dose TT-OSL signal did not diminish. Equivalent dose values were also significantly lower than expected.

It has been demonstrated that lowering the first preheat temperature (i.e., preheat following the first OSL measurement) can increase the magnitude of the TT-OSL signal (Porat et al., 2009). This is because the relatively small charge population that gives rise to the ReOSL signal can be thermally depleted by the first preheat—a preheat intended to move thermally unstable charge into the main OSL trap for optical eviction (Porat et al., 2009; Section 1.3.5). For example, a temperature of 180 °C for 10 s for the first preheat preserves a ReOSL signal that is nearly three times larger than a ReOSL signal measured after a 260 °C preheat, and yields the same equivalent dose (Porat et al., 2009). Porat et al. (2009) advocated a temperature < 260 °C for the first preheat. To remove thermally unstable charge without thermally degrading the ReOSL source trap, a first preheat temperature of 180 °C was tested. Additionally, instead of a thermally transferred test dose response, a test dose response was measured after a single preheat of 220 °C for 10 s (Table IV C). This simplified test dose measurement is still consistent with the single transfer model (Adamiec et al., 2008; Pagonis et al., 2008; Stevens et al., 2009) because it is assumed that charge is transferred from TT-OSL source traps. However, luminescence sensitization should occur at the luminescence centers of the main OSL trap; therefore a simple test dose measurement should accurately monitor sensitization with SAR cycling and a TT-OSL-specific test dose response may be both redundant and imprecise (E. Rhodes, pers. comm., 2010).

Samples UIC 2746, ITL 197, and ITL 208 showed an enhanced $L_N/T_N$ signal when tested with the low (180 °C for 10 s) first preheat protocol (Table IVC), which corroborates previous
results (Porat et al., 2009). Whereas the sample from Lake El’gygytgyn had an apparent non-zero response to a 0 Gy regeneration dose (likely an artifact of the extremely weak $L_N/T_N$ signal), the samples from the United States loess exhibited a more robust natural TT-OSL signal (~1000 cps above background) and the dose-response curve intercepted at the origin (i.e., no sensitivity-corrected TT-OSL signal with a dose of 0 Gy). Equivalent dose values, however, were underestimated by a maximum of 52% and an average of 37% (Forman and Pierson, 2002).

To optimize both the first and second preheat temperatures (Table IV, Steps 2 and 4) for maximum TT-OSL signal, a single sample (ITL 197) was tested using the protocol outlined in Table IV C, but with various and independent temperatures for steps 2 and 4. To isolate the effects of each preheat, the first preheat was held constant while the second preheat was varied and then the first preheat was varied while the second preheat was held constant. Several combinations of first/second preheats (°C) were tested: 180/260, 180/280, 180/290, 180/300, 180/310; and 160/290, 180/290, 200/290, 220/290, 240/290. The first preheat temperature was held constant at 180 °C, being < 260 °C, to avoid thermal depletion of ReOSL source trap (Porat et al., 2009), and > 140 °C to evict thermally unstable charge (Smith and Rhodes, 1994; Murray et al., 1997; Murray and Wintle, 2000). The plateau in equivalent dose values with second preheat temperatures ranging from 290 °C to 310 °C (Figure 2b) prompted the choice of 290 °C as the constant second preheat temperature. The increase in $D_e$ with the second preheat implies that more charge is transferred from naturally filled, thermally shallow but optically insensitive traps (Murray and Wintle, 2000; Bailey et al., 2001), and a plateau in $D_e$ values indicates that the majority of the charge has been transferred (i.e., maximum TT-OSL signal). Given that second preheat temperatures of 290, 300, and 310 °C all result in similar $D_e$
Figure 2. (a) Variations in equivalent dose as a function of first preheat temperature for sample ITL 197. The second preheat temperature is kept constant at 290 °C. The regeneration doses are 0, 151, 302, 605, and 151 Gy, and the test dose is 67 Gy. Three discs are tested at each preheat temperature combination and the mean and standard error are displayed. The solid line marks the average $D_e$ for first preheat temperatures 160-200 °C, which is 502.3 ± 17.9 Gy. (b) Same as in (a) for variations in second preheat temperatures with first preheat temperature constant at 180 °C. The average $D_e$ for preheat temperatures 290-310 °C is 501.39 ± 37.44 Gy. Note the similarity in the two plateau $D_e$ values.
values, and that any preheat temperature within a preheat plateau can be selected for use in a protocol (Wintle and Murray, 2006), 290 °C is selected because it is furthest from 325 °C, the temperature of thermal eviction from the main OSL trap (Smith and Rhodes, 1994; Bailey et al., 1997).

A plateau in $D_e$ values is also observed with various first preheat temperatures (Figure 2a), although this plateau and subsequent increase in $D_e$ with higher temperatures probably does not reflect thermally assisted charge transfer. Consider again the single transfer model (Adamiec et al., 2008): A sample is preheated to thermally excite charge from thermally shallow traps; this charge moves via the conduction band to the main OSL luminescence center from where it recombines and produces luminescence. The fast component OSL trap is likewise emptied during optical stimulation. The second preheat then thermally elevates charge from the ReOSL and BT-OSL traps to the conduction band. Assuming this model, increasing the second preheat temperature should, as is observed, increase the natural TT-OSL signal by thermally transferring more charge into the fast component OSL trap that contributes to the main luminescence center during stimulation. Increasing the first preheat temperature should not, however, increase the equivalent dose, as is observed, since all additional charge that is thermally transferred to the main OSL luminescence centers will recombine prior to the measurement of the TT-OSL signal. Therefore, the mechanism of charge transfer cannot explain the observed increase in $D_e$ with increasing first-preheat temperature.

The increase in equivalent dose with an increase in first preheat temperature may instead be an expression of thermal sensitization of the main OSL luminescence centers (Bailey et al., 1997). When sensitized, quartz will produce a higher luminescence response per
radiation dose because of increased efficiency of charge recombination at luminescence centers (Aitken, 1998, p. 195). Sensitization is a widely recognized phenomenon that occurs primarily due to heat treatment (Bøtter-Jensen et al., 1995; Poolton et al., 2000), although to a lesser degree sensitization depends on dose (Murray and Roberts, 1998; Murray and Mejdahl, 1999). Sensitization may represent the creation of donor centers caused by annealing (Jain et al., 2003), or changes in competing non-luminescent centers (i.e., stable point defects [Jain et al., 2003]) caused by heating (Poolton et al., 2000). Whereas test dose measurements are intended to monitor sensitivity changes in SAR protocols (Murray and Wintle, 2000), sensitivity changes occurring prior to the test dose measurement can give rise to inaccurate $D_e$ estimates (Jain et al., 2003), and it is important to monitor the relationship between $L_i$ and $T_i$ with repeated SAR cycling (Section 2.2.2) (Wintle and Murray, 2006).

### 2.2.2 Test dose evaluation

The magnitude of the sensitivity-corrected TT-OSL signal is dependent on the size of the test dose for two reasons (Wang et al., 2007). First, a larger test dose emission ($T_{TTOSL}$) results in a smaller normalized TT-OSL value ($L_{TTOSL}/T_{TTOSL}$) (Wang et al., 2007). Second, charge trapped during the administration of the test dose (Table IVD, Step 7) is liable to remain trapped until the measurement of the subsequent $L_{TTOSL}$ measurement (Table IVD, Step 5) (Wang et al., 2007). Whereas the effects associated with charge build-up will be minimized by the high temperature heating (350 °C for 200 s) and stimulation used in the final step of the protocol (Adamiec et al., 2010), it is still advisable to apply a small $D_t$ to preserve a high $L_{TTOSL}$ signal-to-
background ratio (Wang et al., 2007; Porat et al., 2009). Therefore, for all samples the administered test dose was chosen to be ~ 10% of the expected equivalent dose (Wang et al., 2007).

For conventional SAR protocols $L$ and $T$ should relate linearly, and when plotted as a function of cycle ($L$-$T$ graph), the regression line should pass through the origin (Murray and Mejdahl, 1999; Wintle and Murray, 2006), although this requirement may be too restrictive for TT-OSL SAR protocols (Athanassas and Zacharias, 2010; Pagonis et al., 2011). Therefore, the relationship between $L_{\text{TTOSL}}$ and $T_{\text{OSL}}$ is monitored through repeated TT-OSL SAR measurement cycles (Table IVD) for samples OTL 405 and OTL 454, with constant regeneration doses of 442 and 208 Gy and constant test doses of 44.2 and 20.8 Gy, respectively (Figure 3).

Two conclusions are drawn from the results shown in Figure 3. First, the relation between $L_{\text{TTOSL}}$ and $T_{\text{OSL}}$ is linear ($R^2 > 0.95$ for both samples), which implies that increases in $L_{\text{TTOSL}}$ sensitivity are accompanied by proportional increases in $T_{\text{OSL}}$ sensitivity; this corroborates the idea that a common luminescence center is accessed and that the $T_{\text{OSL}}$ signal is an appropriate measure of sensitivity change with TT-OSL SAR cycling (Porat et al., 2009). Second, the regression lines do not intercept the origin. A corollary of this lack of direct proportionality at low $L_{\text{TTOSL}}$ values is a ‘lower limit’ to TT-OSL accuracy; Figure 3 implies that sensitivity changes cannot be monitored at very low $L_{\text{TTOSL}}$ signals. This illustrates a critical limit to TT-OSL protocols: low thermally transferred signal magnitude (Stevens et al., 2009; Porat et al., 2009). These limitations should be considered when interpreting $D_e$ estimates, particularly for samples with low equivalent doses (e.g., <200 Gy; see Section 3.1.1). However, many TT-OSL SAR
Figure 3. TT-OSL signal ($L_{\text{TT-OSL}}$) as a function of the subsequent test dose OSL signal ($T_{\text{OSL}}$) with repeated TT-OSL SAR cycling for samples OTL 405 and OTL 454. The regenerative doses are similar to the previously estimated equivalent dose values (442 and 208 Gy for OTL 405 and 454, respectively) and the test doses are 10% of the regenerative doses. The arrow shows the direction of sensitivity change. Note the negative $T$-axis intercept.

Studies report non-zero intercepts on $L$-$T$ graphs as well as successful dose recovery tests and favorable $D_e$ comparisons with independent age estimates (Tsukamoto et al., 2008; Athanassas and Zacharias, 2010; Rosenberg et al., 2011). Moreover, recent numerical simulations of ReSAR protocols informed by a kinetic model of quartz (Bailey, 2001; Pagonis et al., 2008) produce $L$-$T$ graphs wherein data points are linear but have significant non-zero $T$-axis intercepts (Pagonis et
al., 2011). Importantly, the accuracy and precision of the protocols are not adversely affected (Pagonis et al., 2011). Therefore, the test dose magnitude (10% expected $D_e$) appears to be an appropriate measure of sensitivity changes occurring during application of the TT-OSL SAR protocol.

2.2.3 Dose recovery test

The dose recovery test is of paramount importance in evaluating the effectiveness of SAR protocols, because the successful recovery of an administered dose is a direct test of the dosimetric accuracy of a SAR protocol (Section 1.3.2). To simulate natural conditions, naturally trapped charge is removed (usually with exposure to a solar simulator or a UV lamp) and then a known laboratory dose is administered (Wintle and Murray, 2006). The known laboratory dose is treated as the natural dose to be measured with the TT-OSL SAR protocol (Table IVD) (Wallinga et al., 2000); the natural irradiation is thereby replicated, although at a dose rate $\sim 10^9$ times higher than in situ (Murray and Wintle, 2003). Investigations have revealed that the discrepancy between natural and laboratory dose rates may have an adverse effect on OSL $D_e$ estimates (Bailey, 2004). Because thermally unstable traps fill more quickly during laboratory irradiation, charge competition is greater in the laboratory than in nature, which will differentially affect the dose response of the OSL traps and thus the $D_e$ estimates (Bailey, 2004; Bailey et al., 2005). When this effect is prominent, laboratory doses are administered incrementally with intervening heat treatments; the effect of this ‘pulsed-irradiation’ is to reduce trap competition during irradiation, simulating a more natural dose rate (Bailey et al,
To test for the presence of this effect, two aliquots of sample OTL 454 were given doses in addition to the natural dose (TL and IRSL $D_e$ values of 215 ± 2.9 and 242 ± 1.9 Gy, respectively; Forman and Pierson, 2002). The first aliquot received 450 Gy without any heat treatment (i.e., single-irradiation), and the second aliquot received three doses of 150 Gy, with intervening preheats of 240 °C for 10 s (i.e., pulsed-irradiation; cf. Bailey et al., 2005). The sensitivity-corrected natural signal was measured for both aliquots (Table IVD, Steps 2-10). The resulting TT-OSL $L/T$ ratio of pulsed-irradiation to single-irradiation is 0.9831 ± 0.0164, which suggests that both methods populate traps similarly. However, it cannot be assumed that pulsed-irradiation is thus analogous to natural irradiation, or that laboratory irradiation mimics trap filling experienced in nature. Accurate laboratory dose recovery cannot ensure accurate natural dose recovery (Pagonis et al., 2011), and the shape of the natural TT-OSL signal should be compared with the regenerative TT-OSL signal to monitor individual component growth with dose (Section 4.2.3).

Studies have also reported difficulties in optically resetting the ReOSL signal, a necessary step in dose recovery tests (Li et al., 2006; Tsukamoto et al., 2008; Kim et al., 2009). One study measured 10-18% of the original ReOSL signal after a 7-day exposure to a SOL2 solar simulator (Tsukamoto et al., 2008), whereas another experiment demonstrated a similar signal reduction after only one half hour exposure to direct sunlight (Athanassas and Zacharias, 2010). A third study estimates a sunlight exposure time of 26 weeks for the ReOSL signal to deplete to 1% (Jacobs et al., 2011). To investigate the optical sensitivity of the thermally transferred signal, sensitivity-corrected TT-OSL measurements (i.e., $L'_N/T'_N$; Steps 1-9, Table IV) were taken of
Figure 4. Sensitivity-corrected TT-OSL intensity remaining after various sunlamp exposure times for sample OTL 391. Each point represents the average measurement from three aliquots and the associated 1σ error, normalized to the pre-exposure luminescence intensity. The inset shows the same data with time on a logarithmic axis.

samples OTL 391, OTL 454, and OTL 405 after various times of exposure to a General Electric 275-watt RSM sunlamp. These samples vary significantly in IRSL $D_e$, with values of $695.7 \pm 9.2$ Gy (OTL 391), $241.8 \pm 1.9$ Gy (OTL 454), and $82.7 \pm 2.9$ Gy (OTL 405). TT-OSL intensities were measured after 0, 0.01, 0.1, 1, 8, 48, and 95 hours of exposure to the sunlamp. Three aliquots per sample were measured for each exposure time. Figure 4 shows the sensitivity-corrected TT-OSL intensity for sample OTL 391, normalized to the unexposed aliquots. All three samples exhibited a logarithmic decay in TT-OSL with exposure time; however, none of the samples
were optically reset to a negligible level. After 1 hour of sunlamp exposure, samples retained 86.1 ± 8.4% (OTL 391), 75.8 ± 58.8% (OTL 405), and 91.1 ± 9.5% (OTL 454) of the initial, natural TT-OSL intensity, and even after 95 hours of sunlamp exposure, 40.2 ± 4.3% (OTL 391), 27.1 ± 12.8% (OTL 405), and 49.8 ± 34.4% (OTL 454) of the natural signal remained. For this reason, young-to-modern samples should be used for TT-OSL dose recovery tests to ensure that the ReOSL traps are completely emptied prior to laboratory irradiation (Adamiec et al., 2010).

Alternately, the natural (Tsukamoto et al., 2008) or post-bleach (Kim et al., 2009) \(D_e\) value may be subtracted from the recovered dose when evaluating TT-OSL dose recovery tests.

As no modern (i.e., naturally zeroed) samples exist within the suite of samples, the dose recovery test was performed using both suggested methods: a) optically zero, then irradiate a sample (OTL 405), and b) (additively) irradiate a sample with a well-known age (ITL 207). For sample OTL 405, \(D_e\) is estimated at 75 ± 8 Gy (TL) and 83 ± 3 Gy (IRSL) (Forman and Pierson, 2002); it is therefore the youngest sample available and will have the least residual burial dose when bleached. After 48 hours of exposure to a sunlamp, three aliquots of sample OTL 405 were given a beta dose of 500 Gy, and the average recovered dose was 485 ± 34 Gy (Fig 2.5).

Consideration of residual TT-OSL signal is appropriate given the long sunlamp exposures needed for signal resetting (Figure 4). The natural TT-OSL \(L/T\) ratio remaining for OTL 405 after 48 hours exposure to the sunlamp was measured to be 0.0023 ± 0.0017, compared with the pseudo-natural ratio of 0.033 ± 0.001. A comparison between these values implies that the error associated with remaining charge is <10%. The average recycling ratio for these aliquots was 0.87 ± 0.07, which falls slightly outside of the optimal range of 1.0 ± 0.1; the effect appears to be minimal with regard to \(D_e\) estimation and may reflect minor BT-OSL charge build-up or a
differential sensitivity change between $L_{TTOSL}$ and $T_{OSL}$ measurements (Wintle and Murray, 2006; Stevens et al., 2009).

Sample ITL 207 was not optically reset before beta irradiation. The burial dose is well-known, however (IRSL $D_e = 81.9 \pm 0.3$ Gy), and dose recovery can be monitored by accounting for both burial dose and beta dose administered. In this case, three aliquots of ITL 207 were exposed to 800 Gy of beta irradiation, which is added to the inherent $\sim$82 Gy to give a total expected dose of 881.9 ± 0.3 Gy. This method circumvents uncertainty associated with incomplete resetting of the TT-OSL signal. The recovered dose for these three aliquots was 875 ± 41 Gy, a 1σ correspondence with the expected dose. All three discs showed a zero-dose response of nearly 10% of the natural signal, though this is attributed to the low magnitude of the TT-OSL regenerative signal rather than charge build-up.

Taken as a whole, the accurate and precise dose recoveries (Figure 5), the linear relationship between $L_{TTOSL}$ and $T_{OSL}$ with cycling (Figure 3), and the nearly identical $D_e$ values of both preheat plateaux (Figure 2) are indicators of an internally consistent TT-OSL SAR protocol (Table IVD). The following chapter will examine the degree of external consistency when applied to estimate depositional ages.
Figure 5. The dose recovery test for sample OTL 405 measured with the protocol shown in Table IVd. The closed triangle is the ‘natural’ signal, the closed diamond is the corresponding equivalent dose of 485 ± 34 Gy, and the open diamond is the given dose of 500 Gy. Data are averaged from three aliquots and a saturating exponential is fitted to the regenerative dose response points.
3 RESULTS

This chapter will briefly outline the construction of the dose-response curves used in this study, the rejection criteria for individual aliquots, problems encountered with young samples, and the general correspondence between previously published ages and TT-OSL ages.

3.1 Dose response

The TT-OSL SAR protocol was applied to 12 samples (114 aliquots). Dose-response curves were constructed for each aliquot using five regeneration-dose responses. After measurement of the natural signal and subsequent test-dose response, the response to a zero dose was measured to monitor recuperation (Section 1.3.2). The sensitivity-corrected response to a zero dose should be negligible, and aliquots were rejected if the zero-dose response was >5% of the corrected natural signal (Murray and Wintle, 2000). Following the zero dose, three successively larger beta doses were administered; the magnitude of these were chosen to bracket the Forman and Pierson (2002) $D_e$ values estimated by IRSL and TL methods (Murray and Wintle, 2000; Wintle and Murray, 2006). Finally, a fifth regeneration dose was given that was identical to the first non-zero regeneration dose. The ratio of the sensitivity-corrected luminescence resulting from these two identical beta doses (i.e., recycling ratio) should be unity, and aliquots with a ratio outside 10% of unity were rejected (Murray and Wintle, 2000). It should be noted that this protocol is time-consuming. For example, to produce $D_e$ values for
sample OTL 456 (regenerative doses of 0, 229, 458, 917, and 229 Gy), each aliquot requires 8 hours using an automated Risø TL/OSL-DA-20 system equipped with a $^{90}\text{Sr}/^{90}\text{Y}$ beta source ($\sim0.112$ Gy s$^{-1}$). For future work and when possible, it may be advisable to construct a standardized growth curve with a few aliquots and measure only the natural signal for remaining aliquots to reduce measurement time (Roberts and Duller, 2004; Kim et al., 2009; Kim et al., 2010).

The TT-OSL signal exhibits higher dose saturation properties than the fast OSL component, a phenomenon reported elsewhere (Wang et al., 2006a,b; Rosenberg, 2011). For example, Figure 6 shows the dose-response curves constructed for sample OTL 456 using both OSL and TT-OSL SAR protocols. The OSL dose-response curve is fitted to a saturating exponential function

$$I = I_0 \left(1 - \exp\left[-D/D_0\right]\right)$$  \hspace{1cm} (3.1)

where $I$ is OSL intensity, $D$ is the administered dose, $I_0$ is the saturation intensity, and $D_0$ is the dose characteristic of saturation. Wintle and Murray (2006) advise $2D_0$ as the upper limit for $D_e$ calculations. By this criterion, the OSL signal for OTL 456 is only valid to calculate $D_e$ values $< 465.6$ Gy ($D_0 = 232.8$ Gy), and the expected $D_e$ for OTL 456 is $> 862$ Gy (Forman and Pierson, 2002). Hence, for OTL 456 conventional OSL measurements are inappropriate for $D_e$ evaluation whereas the TT-OSL dose-recovery curve is predicted to saturate at $D = \sim 2100$ Gy, which validates the use of TT-OSL as a means to evaluate $D_e$ for OTL 456, the oldest sample tested.

Problems are encountered when young ($D_e < 200$ Gy) samples are evaluated. Figure 7
Figure 6. Sensitivity-corrected luminescence response to laboratory dose for sample OTL 456. The (a) OSL response to dose begins to saturate at higher doses and is unusable beyond ~466 Gy \((n = 2)\), whereas the (b) TT-OSL signal is far from saturation with beta irradiation doses up to 917 Gy \((n = 4)\); the predicted upper limit for the TT-OSL best fit line is ~2100 Gy.
shows the zero-dose responses and recycling ratios for all 114 aliquots, plotted as a function of IRSL $D_e$ values from Forman and Pierson (2002). For samples with IRSL $D_e < 200$ Gy (i.e., samples ITL 207, ITL 215, ITL 216, OTL 405, and OTL 407), both recycling ratios and recuperation levels are very poor. The mean recycling ratios and recuperation values (given as percent of corrected natural signal) for all aliquots with IRSL $D_e < 200$ Gy are $0.96 \pm 0.32$ and $11.7 \pm 13.3\%$, respectively ($n = 34$). By comparison, aliquots with IRSL $D_e > 200$ Gy have values of $0.95 \pm 0.10$ and $1.2 \pm 1.7\%$ ($n = 80$). This suggests that $\sim 200$ Gy may be the lower limit of recoverable $D_e$ values using TT-OSL on quartz from the midcontinental United States loess sheets. This is likely the result of low signal intensity (Figure 8), an effect that is prevalent in young samples.

### 3.2 Comparison of TL, IRSL, and TT-OSL $D_e$ values

All TT-OSL equivalent doses and ages calculated using the protocol found in Table IVD and the dose-rate data found in Table III are shown in Table V, along with the previously calculated IRSL and TL values (Forman et al., 1992; Forman and Pierson, 2002). Equivalent dose values are calculated using all aliquots with acceptable recycling ratios (0.9-1.10) and zero-dose responses ($<5\% L_N/T_N$); only $\sim 40\%$ of aliquots were usable by these criteria. The central age model is used to estimate $D_e$ standard errors for samples (Galbraith et al., 1999). Age uncertainties are calculated by incorporating uncertainties associated with dose rate and equivalent dose estimates into a variance-covariance matrix within custom-written software. All errors are reported at $1\sigma$. 
Figure 7. SAR protocol internal errors as a function of IRSL $D_e$ values. Both the zero-dose response values (top), and the recycling ratios (bottom) indicate very poor protocol performance at $D_e < \sim 200$ Gy, suggesting a lower limit to paleodose recovery.
Figure 8. A typical sample (OTL 454) luminescence response: the initial (a) OSL signal is usually ~100 times larger than the preheat-induced (b) TT-OSL signal. Signals are displayed as photon counts per second (cps) with blue light stimulation time (s).
### TABLE V
TL, IRSL, AND TT-OSL EQUIVALENT DOSES AND AGES

<table>
<thead>
<tr>
<th>Sample number</th>
<th>IRSL $D_e$ (Gy)</th>
<th>IRSL age (ka)</th>
<th>TL $D_e$ (Gy)</th>
<th>TL age (ka)</th>
<th>TT-OSL $D_e$ (Gy)</th>
<th>TT-OSL age (ka)</th>
<th>No. of aliquots used</th>
<th>No. of aliquots tested</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Peoria Loess</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>ITL 207</td>
<td>81.9±0.3</td>
<td>24.4±1.9</td>
<td>88.0±11.7</td>
<td>22±3</td>
<td>N/A</td>
<td>N/A</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>OTL 405</td>
<td>82.7±2.9</td>
<td>24.2±2.1</td>
<td>74.9±7.6</td>
<td>22.2±2.7</td>
<td>N/A</td>
<td>N/A</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td><strong>Roxana Silt</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ITL 215</td>
<td>82.2±3.5</td>
<td>30.4±2.8</td>
<td>101.2±15.4</td>
<td>31±4</td>
<td>N/A</td>
<td>N/A</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>ITL 216</td>
<td>86.5±2.7</td>
<td>28.6±2.5</td>
<td>82.2±15.7</td>
<td>27±5</td>
<td>N/A</td>
<td>N/A</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>OTL 407</td>
<td>182.6±3.5</td>
<td>54.9±4.6</td>
<td>199.3±11.3</td>
<td>45.3±3.9</td>
<td>172.6±6.1</td>
<td>52.1±5.7</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>OTL 454</td>
<td>241.8±1.9</td>
<td>73.4±6.0</td>
<td>214.6±2.9</td>
<td>62.2±6.0</td>
<td>208.3±8.0</td>
<td>62.8±6.9</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td><strong>Teneriffe Silt</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>ITL 217</td>
<td>245.4±1.9</td>
<td>89.1±7.7</td>
<td>202.3±19.6</td>
<td>77±8</td>
<td>173.9±24.8</td>
<td>65.6±10.0</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td><strong>Loveland Silt</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ITL 197</td>
<td>511.6±2.9</td>
<td>161.5±13.4</td>
<td>644.0±69.3</td>
<td>140±15</td>
<td>429.0±80.2</td>
<td>134.3±24.8</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>ITL 208</td>
<td>512.5±3.9</td>
<td>165.0±14.5</td>
<td>389±47.8</td>
<td>110±15</td>
<td>425.3±54.7</td>
<td>132.9±19.3</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>OTL 406</td>
<td>599.1±6.2</td>
<td>182.0±14.6</td>
<td>643.5±19.6</td>
<td>181.5±15.1</td>
<td>605.2±71.0</td>
<td>192.2±27.4</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td><strong>Crowley’s Ridge Silt</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OTL 391</td>
<td>695.7±9.2</td>
<td>≥ 218.5±17.9</td>
<td>581.6±8.5</td>
<td>≥ 183.8±15.0</td>
<td>532.0±18.8</td>
<td>≥ 166.6±18.1</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>OTL 456</td>
<td>861.3±9.1</td>
<td>≥ 264.5±21.1</td>
<td>877±7±12.1</td>
<td>≥ 274.4±22.2</td>
<td>607.1±58.7</td>
<td>≥ 200.3±26.7</td>
<td>6</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^a\)From Forman and Pierson (2002).
\(^b\)From Forman et al. (1992).
\(^c\)Central age model (G. Bailey et al., 1999); All data are shown with 1σ error.
Importantly, there is $1\sigma$ agreement between every (calculable) TT-OSL age and published TL and IRSL ages, with the notable exception of the Crowley’s Ridge Silt, for which there is $2\sigma$ agreement between TT-OSL and TL or IRSL ages. The TT-OSL ages (which are reported as minimum and nonfinite as explained in the following chapter) both underestimate the previously published ages.

To facilitate comparison among methods, TT-OSL $D_e$ values are plotted against IRSL (Figure 9a) and TL (Figure 9b) $D_e$ values. TT-OSL $D_e$ values underestimate both IRSL and TL $D_e$ values. Best-fit lines have slopes of $0.804 \pm 0.04$ and $0.807 \pm 0.05$ for IRSL and TL comparison plots, respectively. Caution should be exercised when interpreting comparisons between TL, IRSL, and TT-OSL $D_e$ estimates, however, as the ages for the Crowley’s Ridge Silt samples (OTL 456 and OTL 391) are neither finite nor reliable (Forman and Pierson, 2002). The reason for this uncertainty is saturating signal growth with irradiation, which leads to large uncertainties when extrapolating to find the equivalent dose (Wintle and Huntley, 1982). Therefore, for the Crowley’s Ridge Silt, discrepancies between TT-OSL $D_e$ values and IRSL and TL $D_e$ values should not preclude TT-OSL age estimates.
Compiled TT-OSL $D_e$ values compared with (a) IRSL and (b) TL $D_e$ values from Forman and Pierson (2002) along with best-fit (dashed) and 1:1 (solid) lines ($m = 0.804 \pm 0.04$ and $0.807 \pm 0.05$ for IRSL and TL plots, respectively).
This chapter will examine potential limitations to accuracy, including the thermal stability of the ReOSL trap, the signal strength at low doses, exposure to sunlight, and separation of the fast component from the bulk TT-OSL signal. Assuming these limits the depositional ages of the loess units will be considered, with special attention given to the oldest unit: the Crowley’s Ridge Silt.

4.1 Thermal stability of the ReOSL trap

A recent set of numerical simulations suggest a possible reason for this apparent TT-OSL $D_e$ underestimation. Pagonis et al. (2011) use a comprehensive kinetic model of quartz (Bailey, 2001; Pagonis et al., 2008) to define charge movement parameters. Natural sample variability is simulated by assuming fixed empirical parameters (e.g., electron trap depth and conduction band to electron trap transition probability) and random charge distribution (i.e., trap concentrations). Various ReSAR protocols were then simulated. Simulation results showed burial dose underestimates when $D > 400$ Gy, and these underestimations increased with burial dose (Pagonis et al., 2011). The physical parameter responsible for this ReSAR dose underestimation appears to be the thermal stability of the ReOSL trap (Pagonis et al., 2011). This would explain the degree of discrepancy present in Figure 9, and would limit paleodose recovery by TT-OSL for burial doses $> 400$ Gy. However, a more direct test of ReOSL trap thermal stability is attempted in the following section.
4.1.1 Isothermal decay analysis

To investigate the thermal stability of the ReOSL trap, isothermal decay analysis was performed (cf., Spooner and Questiaux, 2000), using the LM-OSL signal isolation method described fully in Singarayer (2002). An aliquot of OTL 391 was first heated (350 °C, 200 s) under blue light stimulation to clear all TT-OSL signal. Next, the sample received a beta irradiation of ~329 Gy. The sample then experienced the first three steps of the TT-OSL protocol (preheat: 160 °C for 10 s; OSL: 125 °C for 60 s; preheat: 290 °C for 10 s). At this stage in a typical TT-OSL protocol, the TT-OSL signal would be measured; instead, the sample was held at temperature $T$ °C for $t$ seconds. Temperature and hold-time values are shown in Table VI. Following the respective heat treatments, the thermally transferred LM-OSL signals were measured for 400 s at 160 °C. The LM-OSL response to a test dose of 110 Gy (followed by a cutheat of 220 °C for 10 s) was measured at the end of each sequence. This sequence was repeated for every combination of time and temperature shown in Table VI.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>270</th>
<th>290</th>
<th>310</th>
<th>330</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time held at temperature (s)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>0</td>
<td>40</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>250</td>
<td>0</td>
<td>80</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>600</td>
<td>0</td>
<td>150</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
The LM-OSL signals measured were then analytically separated into three components of the form:

\[ I(t) = n_o \sigma P t \exp\left(\frac{\sigma P t^2}{T}\right) \]  \hspace{1cm} (4.1)

where \( I(t) \) is the LM-OSL intensity (cps) at time \( t \) (s), \( n_o \) is proportional to the initial trapped charge concentration, \( \sigma \) is the photoionization cross-section (cm\(^2\)), \( P \) is the maximum stimulation intensity (mW cm\(^2\)), and \( T \) is the total stimulation time (s) (Singarayer and Bailey, 2003). Each of the three LM-OSL components represent the contribution of charge from an individual trap (fast, medium, slow); the fast trap component is identified by rapid optical depletion (i.e., greatest value of \( \sigma \)) (Jain et al., 2003). The ReOSL and BT-OSL traps both empty into the fast component trap during thermal transfer (Pagonis et al., 2008), and assuming the majority of the transferred charge is from the ReOSL trap,\(^1\) the isothermal decay of the fast component of the TT-LM-OSL signal should represent the isothermal decay of the ReOSL traps. Therefore, the \( n_o \) best-fit parameter (proportional to trapped charge) from equation 4.1 was found for every post-heat treatment LM-OSL measurement using least-squares analysis within LAB Fit Curve Fitting Software, version 7.2.43 (http://www.labfit.net). For each heat temperature, \( n_o \) values were plotted according to the time held at that temperature to find the isothermal decay constant, \( \tau \). Finally, an Arrhenius plot was constructed by plotting \( \ln(t) \) (s) on the y-axis and \( 1/T \) (°K) on the x-axis (Figure 10). From the Arrhenius plot, the ReOSL trap

\(^1\) A recent study indicates that \(~97\% \) of the total TT-OSL signal is derived from ReOSL traps (Kim et al., 2009).
parameters: trap depth, $E$ (eV), and trap frequency factor, $s$ ($s^{-1}$), can be extracted by assuming that a best-fit line describes the following relationship:

$$\ln(\tau) = \ln(s^{-1}) + \frac{E}{k_B} \cdot \frac{1}{T} \quad (4.2)$$

where $\tau$ is the isothermal decay constant at temperature $T$ (°K), $s$ is the frequency factor ($s^{-1}$), $E$ is the trap depth (eV), and $k_B$ is Boltzmann’s constant (~8.615 x 10^{-5} eV K^{-1})(Singarayer, 2002). This method yields ReOSL trap parameter values of $E = 1.57$ eV and $s = 3.1 \times 10^{11}$ $s^{-1}$. These values compare to previously published values. Pagonis et al. (2008) used $E$ and $s$ values of 1.65 eV and $6.5 \times 10^{13}$ $s^{-1}$ for numerical simulations of the ReOSL trap based on observations of the 325 °C TL peak in Spooner and Questiaux (2000). These parameter values simulated the ReOSL signal well, but the authors were careful to note that a robust simulation of empirical data does not preclude different trap parameter values. Adamiec et al. (2010) investigated ReOSL trap parameters by measuring TL glow curves before and after various stimulation and heat routines; 1.46 eV and $7.60 \times 10^{11}$ $s^{-1}$ were estimated as the ReOSL trap $E$ and $s$ values based upon the TL peak positions. Whereas the isothermal decay $E$ value (this study) compares similarly with both previous studies, the isothermal decay $s$ value appears to favor the Adamiec et al. (2010) empirical TL peak $s$ value instead of the inferred value used in the Pagonis et al. (2008) numerical simulations.
Figure 10. Arrhenius plot of the natural log of the isothermal decay constant (y-axis) plotted against the inverse of the hold temperature. ReOSL trap depth ($E$) is derived from the slope of the best-fit line and the ReOSL trap frequency factor ($s$) is derived from the y-intercept value (cf. Singarayer, 2002).
It should be noted that errors are introduced into $E$ and $s$ value calculations during all three data fitting steps, and the degree of final error is uncertain (Singarayer, 2002). Trap lifetime estimations using isothermal decay analysis also assumes that the eviction processes are simple (i.e., first order) and that it is valid to extrapolate from laboratory- to actual-decay times (Aitken, 1998).

### 4.1.2 Burial temperature

From these two ReOSL trap parameters, $E$ and $s$, the thermal lifetime of trapped charge can be estimated. However, the burial temperature history of a sample must be estimated for this calculation, and trap thermal stability has a strong dependence on burial temperature (Aitken, 1998). For example, according to the calculated $E$ and $s$ values, the ReOSL trap has a lifetime of 9065, 861, or 96 Ma at burial temperatures of 0, 10, or 20 °C, respectively. Thus, it is critical to quantify the burial temperature history to accurately assess the ReOSL trap lifetime.

As the oldest samples would experience the most thermal decay with time, the thermal history of the Crowley’s Ridge Silt at the Bonfils Quarry location was investigated (e.g., OTL 391, OTL 456). Epimerization of amino acids in fossil gastropod shells from the Peoria Loess unit of the Mississippi Valley imply a mean annual ground temperature of ~8 °C at the latitude and depths of interest for the past 20 ka (Oches et al., 1996). $\delta^{18}$O speleothem data from Missouri give a variable mean annual temperature history between ca. 25-75 ka with range of ~4 °C (Dorale et al., 1998). An energy balance climate model simulation offers insight into MIS Stage 5e, the last full interglacial, which appears to have been ~4 °C warmer than present during maximum
intensity (Crowley and Kim, 1994). Finally, ostracod assemblages and pollen records from glacial lake sediments in western Tennessee suggest that the regional temperature regime during MIS 6 was comparable to that of the Wisconsinan glacial period (Grimley et al., 2009). As a time-weighted average, these data suggest a mean burial history temperature of about \(~10 \, ^\circ C\), assuming a modern mean annual air temperature of \(~14 \, ^\circ C\) for the Bonfils Quarry region (Oches et al., 1996).

Assuming a mean burial temperature of \(~10 \, ^\circ C\), the ReOSL trap is expected to have a lifetime of 943 Ma. Aitken (1998) advises using traps with lifetimes ten times larger than the expected burial dose to avoid systematic underestimation of more than 5%. By this criterion the ReOSL trap appears stable enough to date samples from the Late Pleistocene. However, the error associated with the Arrhenius plot best-fit line should be considered. For example, the slope of the best-fit line in Figure 10 is \((1.57 \pm 0.14)/k_B\), which means that the 1σ lower limit for the trap depth, \(E\), results in a trap lifetime of 3 Ma. Likewise, the 1σ upper limit for the frequency factor, \(s\), yields a trap lifetime of 57 Ma. A combination of both the lower-limit \(E\) and the upper-limit \(s\) gives a trap lifetime of 162 ka. As the final case is unlikely, let us assume a lower limit stability of \(~3\) Ma. If the Crowley’s Ridge samples are 300 ka and a systematic error of 5% can be expected (assuming a thermal stability lifetime of 3 Ma), the apparent sample age should be \(~285\) ka. Therefore, an age underestimation of \(~20\)% cannot be attributed to the thermal stability of the ReOSL traps, assuming experimental \(E\) and \(s\) values.
4.2 Protocol limitations

This modified SAR TT-OSL protocol should be applied to quartz from the midcontinental United States loess with careful consideration of the observed limits for precision and accuracy. Specifically, low signal-to-noise ratios in young samples obscure accurate dose recovery, long solar-reset times limit the depositional environments that may be dated with TT-OSL, and the separation of the fast component from the total TT-OSL signal appears necessary to avoid $D_e$ contamination from the medium and slow components. The following section will expand on these limitations.

4.2.1 Signal strength at low equivalent doses

Consistent with previous findings (Wang et al., 2006; Kim et al., 2009), the TT-OSL signal is about two orders-of-magnitude smaller than the preceding OSL signal (Figure 3.3), impeding precise equivalent dose calculations. It follows that the signal-to-noise difficulty increases as paleodose decreases. The TT-OSL signals, and especially the regenerated signals, from samples with low equivalent doses (IRSL $D_e < \sim 200$ Gy) have consistently low signal-to-noise ratios. Paleodose recovery is thus highly variable and imprecise. Recycling ratios ranging from 0.2 to 1.8, and zero-dose response values up to 55% of the natural signal indicate that at IRSL $D_e$ values $< \sim 200$ Gy, the protocol yields irreproducible and unreliable $D_e$ results. This appears to be the lower limit to this protocol.
4.2.2 Solar resetting

The extensive solar exposure necessary to reset the ReOSL signal (Section 2.2.3) limits the depositional environments that may be studied using this TT-OSL protocol. This study suggests that ~40% of the burial dose TT-OSL remains after 95 hours of exposure to a sunlamp (Figure 4a). Another study placed 180-212 μm sand grains in direct sunlight for 8 hours per day and reported a 50% and 90% ReOSL signal reduction after 3.9 and 12.9 weeks, respectively (Jacobs et al., 2011). If the slow 3 electron trap is the ReOSL source trap (Wang et al., 2007), aeolian transport may indeed reset the ReOSL signal, given that the slow components appear to reset to ~ 0.2 Gy during typical aeolian sunlight exposure (Singarayer et al., 2005). Additionally, modern deposition processes for fine-grained loess involve long-term, high-altitude suspension (Crouvi et al., 2010) and accumulation rates <2 mm yr⁻¹ (Enzel et al., 2010). Therefore, residual ReOSL signal is likely negligible, even considering the long solar-reset times. Quartz grains are much less likely to be solar reset during fluvial transport due to the reduction of sunlight intensity and the attenuation of shorter wavelengths, which are more efficient at resetting the OSL signal (Berger, 1990; Bailey et al., 2003). Given the prevalence of partial bleaching of the fast and medium OSL components in subaqueous systems (Singarayer et al., 2005), the difficult-to-reset ReOSL signal is almost certainly not reset in fluvial environments. Therefore, extensive sunlight exposure is mandatory for TT-OSL studies and care must be taken when optically resetting samples (e.g., dose recovery test).
4.2.3 Fast component separation

Tsukamoto et al. (2008) observed a trend of increasing TT-OSL $D_e$ underestimation with larger doses when performing dose recovery tests. To overcome this effect, the empirical TT-OSL signal was mathematically separated into fast and constant components. The equivalent dose was then calculated using only the fast component of the TT-OSL signal. In their study, the ratio of recovered-to-given laboratory doses were near unity for all doses when the fast component TT-OSL signal was analyzed, suggesting that such a separation may be necessary for accurate dose recovery (Tsukamoto et al., 2008). Therefore, for this study, equivalent dose values were evaluated at various integration times and for the fast component individually.

Equivalent dose by integration time

As a weak fast component within the TT-OSL signal would produce age underestimations (the ReOSL charge is thermally transferred into the fast component trap), a $D_e(t)$-plot was constructed for sample OTL 391 ($n = 11$) to check for variations in $D_e$ by signal components (Figure 11a). The $D_e(t)$-plot shows the $D_e$ calculated by integrating the natural and regeneration curves at a time, $t$ (time bin width = 0.4 s). For example, the $D_e$ value at $t = 1.2$ s represents the $D_e$ calculated using the photon count measured from 0.8 to 1.2 seconds. $D_e(t)$-plots can show, in a single OSL signal, contributions from multiple traps with different thermal stabilities and dose response characteristics (Huntley et al., 1985; Bailey, 2000). Variations in $D_e(t)$-plots can thereby yield information about the importance of separating the fast component...
for \( D_e \) calculations. \( D_e(t) \)-plots were examined for three samples: OTL 391 \((n = 11)\) (Figure 11a), OTL 454 \((n = 4)\), and OTL 456 \((n = 6)\). Samples show a plateau in \( D_e \) values when integrated at \( t > \sim 2-3 \) s, but decrease supralinearly from 0.4 to 2 s. This suggests that using the first 0.4 s of TT-OSL signals to calculate \( D_e \) values (i.e., the \( D_e \) values here reported) is a composite of multiple components with different dose response characteristics and therefore provides only a minimum age.

To further investigate the importance of separating the fast component from the TT-OSL signal, the \( L_{TTOSL} \) and \( T_{OSL} \) signals (natural and regenerative) from a single aliquot of OTL 391 were fitted to a linear combination of three exponential functions

\[
I = a \cdot \exp(-b \cdot t) + c \cdot \exp(-d \cdot t) + e \cdot \exp(-f \cdot t) \quad (3.2)
\]

where \( I \) is TT-OSL intensity (cps), \( t \) is time (s), and \( a, b, c, d, e, \) and \( f \) are constants calculated using a Levenberg-Marquardt least-squares algorithm (Marquardt, 1963) within LAB Fit Curve Fitting Software. The results are shown in Figure 11b. The best-fit components are termed ‘fast,’ ‘medium,’ and ‘slow’ for discussion purposes; however, photoionization cross-sections were not calculated (e.g., Bailey et al., 1997; Jain et al., 2003). \( D_e \) values were then calculated using only fast, medium, or slow component growth with dose. Finally, the natural \( L_{TTOSL} \) signal was deconvoluted into the three exponential decay components (i.e., fast, medium, and slow) and a ‘pseudo-\( D_e(t) \)-plot’ was calculated as the linear combination of the component-specific \( D_e \) values weighted by the relative proportion of the components at time, \( t \).
Figure 11. (a) A linear combination of three exponential components fitted to the natural TT-OSL of a single aliquot of sample OTL 391. (b) Diamonds represent the average $D_e$ values for all aliquots of OTL 391 when integrated using the TT-OSL curves at time $t$ (i.e., $D_e(t)$-plot). To explain the significant drop in $D_e$ in the first three seconds, the natural and regenerative curves are fitted to a linear combination of three exponential decay functions (fast, medium, and slow), and $D_e$ is estimated using the dose-response curves from these individual components. The $D_e(t)$-plot is then recreated assuming the $D_e$ at any instant is the linear combination of all three component-specific $D_e$’s weighted by the relative proportion of signal contribution (solid black curve). That the relative component contribution calculation closely resembles the $D_e(t)$-plot within 1σ suggests need for signal deconvolution for TT-OSL $D_e$ recovery.
For example, if at \( t = 1.2 \text{ s} \) there is 75% fast component, 20% medium component, and 5% slow component contribution, and \( D_e \text{ (fast)} = 700 \text{ Gy} \), \( D_e \text{ (medium)} = 600 \text{ Gy} \), and \( D_e \text{ (slow)} = 500 \text{ Gy} \), then the pseudo-\( D_e(t) \) equation would be

\[
\text{pseudo-}D_e(1.2 \text{ s}) = (0.75 \cdot 700 \text{ Gy}) + (0.2 \cdot 600 \text{ Gy}) + (0.05 \cdot 500 \text{ Gy}) \quad (3.3).
\]

The pseudo-\( D_e(t) \) is shown in Figure 11a as a solid black curve. The 1σ correspondence between the pseudo- and empirical-\( D_e(t) \) data implies that the empirical \( D_e(t) \) represents a linear combination of component-specific \( D_e \) values and not a single TT-OSL source trap \( D_e \) value. This observation corroborates the mechanism of thermal transfer into the fast component OSL trap, i.e., only the fast component trap should donate TT-OSL charge to the luminescence center and therefore contribution from the medium and slow components should obscure the true TT-OSL equivalent dose. Therefore, the fast component \( D_e \) should be isolated for accurate paleodose recovery.

*Natural-to-regenerative TT-OSL ratio*

Further complications are encountered when the fast component is proportionally more dominant in the natural than the regenerative TT-OSL signals. Steffen et al. (2009) isolated this effect using the ratio of the natural to regenerative OSL signals according to integration time (i.e., an NR(t) plot). Ratios below 1 indicate that the fast component is present in a lesser proportion for regeneration dose TT-OSL signals and that the medium and slow components
are correspondently larger (Steffen et al., 2009). Interestingly, aliquots with a negative slope on NR(t) plots have also been observed to produce a negative slope on $D_e(t)$ plots (Steffen et al., 2009), a phenomenon also observed in the present study (Figure 2). The NR(t) and $D_e(t)$ plots for the same aliquot of sample OTL 456 are shown in Figure 2a and b, respectively. For reference, similar plots are given for the analysis of a conventional OSL signal (Steffen et al., 2009). For aliquots with decreasing values for both N/R and $D_e$ with integration time, Steffen et al. (2009) obtained higher $D_e$ values when the using only the fast component for $D_e$ calculation.

To estimate fast component $D_e$ values, CW-OSL curves were mathematically deconvoluted to isolate the fast component contribution for the conventional OSL signals. Unfortunately, the low magnitude of the TT-OSL signal makes such deconvolutions (e.g., Figure 11a) subjective and imprecise.

Furthermore, the NR(t) plot suggests a possible reason for the success of the dose recovery test despite age inaccuracies for the oldest samples. That the decay shape of the natural signal is steeper than the decay shape of the regenerative signals implies that traps fill differently in nature than in the laboratory. The fast component may be more dominant in the natural signal because irradiations taking place over geologic time allow for thermally unstable charge to transfer to the TT-OSL source traps. To test this hypothesis, the ratio of a sensitivity-corrected natural TT-OSL (OTL 456) to the sensitivity-corrected pseudo-natural TT-OSL (ITL 207 + 800 Gy) was plotted by integration time. The ratio was found to decrease with time, suggesting that even for comparable dose amounts (~880 Gy), the fast component traps for the TT-OSL natural and pseudo-natural are populated in different proportions.
Figure 2. (a) Natural-to-regenerative TT-OSL ratios (N/R) by integration time for sample OTL 456. The decreasing ratio with increasing time implies that the regenerative TT-OSL signal has proportionately less fast component contribution. (b) $D_e$ values by integration. The negative slope suggests that the fast component retains a higher $D_e$ value than the bulk (TT-) OSL signal.
Therefore, a dose recovery test may show a given/recovered dose ratio near unity because trap filling is similar in the pseudo-natural irradiation and the regenerative irradiations. However, the trap filling will be not be similar in nature, leading to inaccurate estimations of the natural dose if a simple integration technique is used instead of fast component separation.

These observations strongly imply the need to extract the fast component from the bulk TT-OSL signal, either by analytical separation or direct measurement. Unfortunately, it is difficult to directly measure the fast component. LM-OSL measurements provide more distinct component signals, but curve deconvolutions are still required and high signal intensity is prerequisite (cf. Jain et al., 2003). Similarly, IR stimulated at elevated temperature has been demonstrated to deplete the fast component only, allowing for a protocol based on the differential between pre- and post-IR OSL measurements (‘differential-OSL;’ Jain et al., 2005). However, this differential-OSL measurement is also useless with insufficient signal strength (Steffen et al., 2009). TT-OSL dose recovery tests have been conducted with improved accuracy by deconvoluting the fast component from CW-OSL measurements and estimating the $D_e$ values using only the fast component (Tsukamoto et al., 2008). Therefore, for this study $D_e$ values were estimated using the fast component deconvoluted from the total CW-OSL signal, and the fast component $D_e$ values were indeed higher than the bulk signal TT-OSL $D_e$ values. The preliminary ages based on fast component TT-OSL are $241 \pm 52$ ka for OTL 456 ($n = 1$) (TT-OSL age of $200.3 \pm 26.7$ ka), and $197 \pm 42$ ka for OTL 391 ($n = 1$) (TT-OSL age of $166.6 \pm 18.1$). The fast component TT-OSL ages should be more accurate (Tsukamoto et al., 2008), but given current analytical and instrumental component separation methods, an efficient and precise protocol remains elusive. The future development of an accurate TT-OSL chronology for the
midcontinental US loess sheets may therefore hinge on the ability to separate the fast component from the bulk TT-OSL signal.

4.3 Timing of deposition for the Crowley’s Ridge Silt

The Crowley’s Ridge Silt has been broadly assigned to MIS 8 (~243-300 ka; Lisiecki and Raymo, 2005) based on absolute ages (Markewich et al., 1998), and to MIS 12 (~424-478 ka; Lisiecki and Raymo, 2005) based on weathering intensities (Grimley et al., 2003). Initial attempts to measure the fast component TT-OSL \( D_e \) seem to favor a MIS 8 deposition for the Crowley’s Ridge Silt, though more work in fast component TT-OSL dating is warranted. Whereas the calculated thermal stability of the ReOSL trap does not permit the fading necessary to explain a MIS 12 age, uncertainties inherent to standard TT-OSL integration result in minimum rather than finite ages. The TT-OSL signal grows with dose, and the dose response curves used for \( D_e \) estimation show no sign of saturation (Figure 6). Therefore, if instrumental or analytical component separation methods are advanced, the ‘uncontaminated’ age probably lies within the bulk TT-OSL signal, but fast component isolation appears necessary.
CONCLUSIONS

5.1 Summary

Fine-grained quartz samples from the midcontinental United States loess sheets were submitted to various SAR TT-OSL protocols in an effort to refine the loess deposition chronology. Constraining loess deposition and soil formation during the Late Pleistocene clarifies regional moisture conditions changes in sediment supply driven by Laurentide Ice Sheet dynamics. However, previous depositional chronologies remain unclear for loess units of Illinoian age or older (i.e., Loveland Silt and Crowley’s Ridge Silt). The thermally transferred signal within quartz was therefore chosen as a suitable chronometer according to its capacity to accumulate charge at high doses and therefore long (~0.8 Ma) burial periods (Wang et al., 2006). The Stevens et al. (2009) SAR TT-OSL protocol was modified to achieve adequate recycling ratios, negligible zero-dose luminescence response, and dose recoveries near unity. When tested on samples, the modified protocol (Table IVD) produced TT-OSL signal growth at doses up to ~917 Gy (highest dose tested). The protocol was used to calculate equivalent doses and ages for 12 samples. Ages for young \( (D_e < \sim 400 \text{ Gy}) \) samples generally show good agreement with previously published TL and IRSL values. Discrepancies in TL and IRSL age estimates for older \( (D_e > \sim 400 \text{ Gy}) \) samples are interpreted as inconclusive and finite due to the nonlinear extrapolation methods used in determining \( D_e \) values. TT-OSL age values, however, are limited by the multiple traps contributing to the TT-OSL signal. The TT-OSL traps empty into the fast component trap, and therefore the fast component decay
reflects the TT-OSL charge present (Pagonis et al., 2008). However, the medium and slow components are also accessed during stimulation. If the fast component is not dominant during optical stimulation, then the ‘TT-OSL’ signal may be contaminated by the medium and slow components, which have different dose response characteristics. Unless these contaminating components are separated, either during the measurement sequence by differentially stimulating the fast component, or after the measurements by mathematically separating the respective curves, the purported ‘TT-OSL age’ will actually be the TT-OSL age mixed with the medium and slow component ages. Moreover, the decay shape of the natural signal is different than the regenerative signals even at similar doses, suggesting that trap filling in nature is different than trap filling in the laboratory. This would explain the accurate dose recovery tests, as there would be no discrepancy between the pseudo-natural and the regenerative trap filling.

Fast component separation was attempted analytically by curve deconvolution, assuming three components. Unfortunately, this method is time-consuming and subjective, i.e., the chosen initial conditions for least squares analyses bias the best-fit results when deconvoluting the TT-OSL signal. The preliminary fast component TT-OSL ages were older than the bulk signal TT-OSL ages and appear to support either an MIS 7 (~191-243 ka; Lisiecki and Raymo, 2005) or 8 (~243-300 ka) deposition (197 ± 42 and 241 ± 52 ka for samples OTL 391 and 456, respectively).
5.2 Future work

Several changes to the Stevens et al. (2009) protocol significantly enhanced performance and are therefore advisable for similar studies in the future. Equivalent dose values strongly depended on the first and second (Table IV, Steps 2 and 4) temperatures, and future studies should directly investigate the effect of varying each preheat independently to avoid substantial age underestimates (Figure 2). Recycling ratios improved with the addition of the final heat treatment of 350 °C for 10 s, a step recommended for future SAR TT-OSL protocols (Adamiec et al., 2010). The use of an OSL response to a test dose (instead of a TT-OSL response) improved $D_e$ precision by enhancing the signal strength, and the ReOSL source trap sensitivity changes appear to have been adequately monitored (Figure 3).

Care should be taken in applying TT-OSL protocols to sediments: to completely reset the ReOSL traps, sediments must be exposed to light for many hours (Figure 4). Therefore, depositional environments where long-term (days to weeks) light exposure is not guaranteed (e.g., subaqueous transportation) are inappropriate for TT-OSL dating. However, the transport and depositional processes typical of fine-grained loess offer substantial, direct sunlight exposure and are considered to reduce the ReOSL signal to negligible amounts.

The thermal stability of the ReOSL trap (e.g., $E$ and $s$ values) should also be explored in more detail. Current studies are limited to TL peak data (Adamiec et al., 2010) and values inferred from previous isothermal decay work on the 325 °C TL peak traps (Pagonis et al., 2008). Values reported in this study are subject to regression uncertainties during LM-OSL fitting, isothermal decay fitting, and Arrhenius plot fitting. More certain ReOSL trap parameters would
clarify the ReOSL trap lifetime, and thereby: a) define the upper age limit for TT-OSL chronologies, and b) determine errors inherent to TT-OSL ages that approach the upper age limit.

Isolating the fast component within the overall TT-OSL signal may significantly improve \( D_e \) estimates, as simple signal integration seems to inadvertently mix the relevant ReOSL signal with irrelevant medium and slow component signals. Whereas in conventional OSL measurements this effect is imperceptible due to the fast component’s initial dominance over the other components, the low magnitude of the TT-OSL signal makes the isolation of the fast component, into which the ReOSL traps empty, critical for equivalent dose evaluation. Similarly, this effect may not be evidenced by poor dose recovery, as laboratory irradiation may populate traps differently than natural irradiation. Unfortunately, analytical and instrumental component separation methods are most powerful given high signal-to-noise ratios (Steffen et al., 2009), which typically precludes their use in deconvoluting the characteristically weak TT-OSL signal. Current research is tending towards fast component isolation techniques (cf. Wintle, 2010), however, which may advance TT-OSL precision.

TL and IRSL ages have been generally corroborated by TT-OSL ages; there is 1σ correspondence between all Loveland Silt IRSL and TT-OSL ages and between all TL and TT-OSL ages (Forman and Pierson, 2002). Roxana Silt TT-OSL ages also have 1σ correspondence for IRSL and TL ages (Forman and Pierson, 2002). Peoria Loess ages were incalculable given low TT-OSL signal strength. Unfortunately, for the Crowley’s Ridge Silt samples ages remain vague; bulk signal TT-OSL offers minimum ages and fast component TT-OSL ages are imprecise. Deposition during MIS 7 or 8 appears likely given preliminary fast component TT-OSL ages,
contrary the MIS 12 interpretation (Grimley et al., 2003). However, more work is still needed to offer precise, finite ages.
CITED LITERATURE


VITA

NAME: Nathan David Brown

EDUCATION: M.S., Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, Illinois, 2011
-GPA: 4.0/4.0

B.S., Geology; minor in Mathematics, Wheaton College, Wheaton, Illinois, 2009
-GPA: 3.26/4.0

TEACHING ASSISTANTSHIPS: Department of Earth and Environmental Sciences, University of Illinois at Chicago; Exploring the Earth’s Interior and Hydrology courses, 2009-2010

Geology Department, Wheaton College; Hydrogeology and Geographical Information Systems (GIS) laboratory courses, 2008-2009

RESEARCH ASSISTANTSHIPS: Department of Earth and Environmental Sciences, University of Illinois at Chicago; Luminescence Dating Research Laboratory, 2010-2011

PROFESSIONAL MEMBERSHIP: Geological Society of America