# Thesis Abstracts

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***Weili Bi***


**Electron spin resonance dating of germanium center in quartz in glacial tills**


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Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing, China

*Degree: Ph.D.*

*Supervisors: Chaolu Yi, Haijun Yang*



Electron spin resonance (ESR), provides a technique that plays an irreplaceable role in dating of quartz extracted from Quaternary deposits due to its wide dating time range. However, this technique used for dating of glacial till is limited due to lack of fundamental research in mechanisms of ESR signal depletion and test of independent dating. By using laboratory sunlight-grinding bleaching and field testing, this dissertation presents the results and conclusions of signal resetting of the germanium (Ge) center, correction of residual dose for moraine dating, and technical improvements in signal identification and measurement.

ESR dating of moraines is based on the supposition that either subglacial comminution or exposure to sunlight resets the signal. However, actual dating suggests that a signal that is initially present cannot be bleached to zero by grinding alone. We found that grinding coarse samples to fine sand reduced the signal intensity to 53-69 % of its original value. Exposure to sunlight for several days can reduce the signal intensity to 7-8 % of its original value within 1–2 mm depth of the polymineral sediment surface. However, within 5–8 mm of the sediment surface, exposure to sunlight for over one week only reduced the signal intensity to mean plateau values of 42–50 % of the initial value. The Ge signal in a modern till sample produced at 5400 m in the margin of an icecap in central Tibet is completely bleached. And the Ge signal in a modern sample in a basal moraine of a valley glacier in the Tianger Peak of the Tien Shan Mountain is partially bleached. It suggests that the level of bleaching varies spatially. Material which moraines initially deposited and which was subsequently overridden by sediments at the margins of ice caps or ice sheets may have been sufficiently exposed to sunlight to reset the clock to allow ESR dating of moraines.

The ESR signals in many sediments are not fully bleached before deposition and thus their ESR ages are overvalued. To solve this problem in fluvial and eolian sediments, residual signal intensity is reduced from the total signal intensity to correct ESR ages. However, it is not easy to determine the residual signal in glacial moraine. Here we propose that the residual dose in a modern moraine is subtracted from the total dose of a dated sample so as to correct ESR ages. The example shows that the ESR ages of tills without residual dose correction were 37.3-112.8 ka in the Tianger Peak area of the Tien Shan Mountains. After residual dose correction, the ages dropped and the corrected ESR ages are consistent with the results of 10Be surface exposure dating.

The signals in the Ge center in feldspar, mica, magnetic minerals and other heavy minerals occur in the same magnetic position as that in quartz. These signals from non-quartz minerals will interfere with the signal in quartz and therefore influence the quantification in ESR dating. Especially, feldspar has a significant impact on the signal of the Ge center in quartz due to its strong signal. In addition, the Ge signal in feldspar does not display the same decreasing trend as that in quartz when they are exposed to sunlight. The Ge signal of quartz decreases as exposure time increases. In contrast, the Ge signal of feldspar increases in the first four hours of exposure to sunlight and then decreases as the exposure time increases. After 34 to 62.5 hours of sunlight exposure, the EPR signal in feldspar reduced to 41.5-86.3 % of its original signal intensity. The procedure of heavy mineral separation and HF solution etching will greatly improve the purity of quartz.

Signal intensities in Ge and E centers in additionally irradiated samples is significantly and linearly correlated with quartz mass. Signal intensity for the Ge center is correlated with mass only if the mass is $> 0.3$ g for the sample without irradiation, and it is correlated with E center as the mass is reduced to $< 0.45$ g. The results provide a reference to general characteristics of some color centers in quartz responsive to mass increase, and also provide a solution of correction of signal intensity for the samples without sufficient mass.

We find that the smaller the microwave power, the higher the signal intensity of Ge center with the power between 0.02 to 5 mW. This abnormal phenomenon needs further study. We here suggest that small microwave power be used so as to increase ESR signal intensity to identify the weak signal in the Ge center.

***Michael Kenzler***

**Ice-sheet dynamics and climate fluctuations during the Weichselian glaciation along the southwestern Baltic Sea coast**

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*Degree: Dr. rer. nat.*
*Supervisors: PD Dr Heiko Hüneke, Prof. Dr. Manfred Frechen*

This thesis aims to develop a palaeogeographic and chronostratigraphic model of the southwestern Baltic Sea area, to improve our understanding of the depositional history of the Late Pleistocene on both a local and a transregional scale. New sedimentological, palaeontological and numerical age data are presented from three reference sites located at the coast of NE Germany. So far, the chronostratigraphic assignment of Saalian and Weichselian sediments of NE Germany has been based mainly on lithostratigraphic methods and on sparse numerical age data, resulting in a fragmentary age database. Modern sedimentological approaches, such as facies analyses, have been applied only at a few isolated profiles. Thus, a reliable reconstruction of the depositional environments and their stratigraphic positions is still missing for the study area, which makes the correlation between Pleistocene successions from NE Germany and other circum-Baltic regions problematic. To address these lithostratigraphic and geochronologic issues, three crucial profiles were re-investigated using a multiproxy approach, including sedimentological, geochronological, and palaeontological techniques. The Glowe and Kluckow sites are located on the peninsula of Jasmund (Rügen Island), whereas the Klein Klütz Höved (KKH) section is situated between Wismar and Travemünde at the coast of the Mecklenburg Bay. The age-constraining of critical horizons was conducted by luminescence dating of feldspar and quartz grain minerals. Together, these successions represent the Late Saalian to Late Weichselian period and give rise to the following picture.

The Glowe and Kluckow sections reveal that ice-free conditions dominated the study site between 47 and 42 ka. Deposition occurred in a steppe-like environment with moderate summers and cool winters. Meandering and braided river systems inhabited by various freshwater species, such as *Anodonta cygnea*, *Pisidium amnicum* and *Perca fluviatilis*, shaped the landscape. A subsequent cooling phase resulted in the establishment of a periglacial landscape and the formation of ice-wedges. This phase is shown in this thesis to be connected to the Klintholm advance documented at 34 $\pm$ 4 ka in Denmark. Furthermore, the data indicate the formation of a lacustrine basin during the transition of MIS 3 to MIS 2 under sub-arctic climate conditions. A potential link to the Kattegat ice advance (29–26 ka) will be proposed. At 23 $\pm$ 2 ka, the study area was characterised by proglacial and ice-contact lakes related to the Last Glacial Maximum ice advance of the Scandinavian Ice Sheet (SIS). This is the first documented SIS advance of Weichselian age, which reached Jasmund at 22 $\pm$ 2 ka.

The KKH sedimentary succession comprises deposits of Late Saalian to Late Weichselian age: after a period of deglaciation between ~139–134 ka (Termination II; MIS 6), which is preserved in a glaciofluvial sequence deposited in a braided river system, a lacustrine environment was established in an arctic to subarctic climate. During this time, the landscape was vegetated by typical Late Saalian flora communities. The Eemian interglacial is represented by lacustrine to brackish deposits covering the reference pollen zones 1 to 3. During this initial part of the Eemian, thermophile forest elements spread (*Quercus*, *Ulmus*), indicating a deciduous forest. The presence of brackish ostracods represents the influence of a marine transgression between 300 and 750 years after the beginning of the Eemian period. A hiatus of more than 90,000 years separates the Eemian from the overlying Late Weichselian sediments. During the Late Weichselian period, the deposition at KKH was dominated by glaciolacustrine and subglacial facies, where the first Weichselian ice advance occurred at 20 $\pm$ 2 ka.

The sedimentological and geochronological findings in this thesis provide valuable information for the reconstruction of the palaeoenvironmental history from the Late Saalian to Late Weichselian period. The Late Saalian palaeoenvironmental setting is reconstructed, including Termination II and the initial phase of the Eemian interglacial. Furthermore, the Eemian marine transgression is shown to have occurred 300 to 750 years after the beginning of this interglacial. The first proven Weichselian advance of the SIS approached NE Germany between ~23 and ~20 ka. In contrast, there is no evidence to support a pre-LGM advance of Weichselian age to the study area, as proposed by several authors, neither at Glowe and Kluckow, nor at the KKH site. Based on the presented results, and contra what was previously assumed, the MIS 3 Ristinge and Klintholm advance of the SIS, documented in Denmark, did not reach NE Germany.

A PDF of this thesis can be downloaded from: http://ub-ed.ub.uni-greifswald.de/opus/volltexte/2017/2848/pdf/diss_Kenzler_Michael.pdf

***Anil Kumar***

**Late Quaternary landscape evolution along the Indus River: responses to climate and tectonics of Ladakh Himalaya**

*October 2016*

Wadia Institute of Himalayan Geology, Dehradun, India

*Degree: Ph.D.*
*Supervisor: Pradeep Srivastava*

The upper Indus River flowing NW in a longitudinal valley along the SW edge of Tibet, Karakoram fault zone, Indus Tsangpo Suture Zone, Ladakh Batholith, and Zanskar ranges, represents a first order geomorphological feature

of Ladakh Himalaya. The Indus River, which arises from Mount Kailas and sinks into the Arabian Sea via the plains of Punjab (Pakistan), has a very large ($1\times10^6$ $km^2$) catchment area.

Based on the longitudinal river profile and the stream length gradient index (SL index), ∼350 km stretch, the Indus River is divided into four segments. There are valley fill terraces in Segment I to III and one to two levels of strath terraces (T-2) with one cut-filled terrace (T-1) in Segment IV, which were used to calculate the aggradation and incision rates, respectively. The chronology of the channel bound and fan aggradation in Segment I to III, suggests that there are three pulses of wet phases at ∼16 ka, ∼28 ka and ∼52 ka, which facilitated fluvial aggradation. Hence aggradation was climatically controlled that occurred during the wetter phases in MIS-1 and MIS-3.

The SL index quantifies the variation in the bedrock erosion along a channel and any changes in this index indicate, (1) lithological contacts with varied erodibility, and/or (2) differential uplift along an active fault. In Segment-I, where, the Indus flows through the Indus Molasse, the SL index is low, whereas in Segment-II, between Kiari and Tirido, it attains higher values with batholith as bedrock. In the Segment-III, where channel follows the molasse-batholith contact, the SL values are again low. In Segment-IV, downstream of Spituk to Skyurbuchan, river cuts through the Indus Molasse, where the SL index increases and attains high values where the channel cutting into the Ladakh Batholith. SL index in Segment-IV exhibits an overall increasing trend. Ks for the Indus also shows a similar trend, which imply that the channel steepness is controlled by the active tectonic uplift and not by the bedrock erodibility. The chronology of the alluvial cover preserved over the strath terraces indicates incision of the order of 1.1–2.8 mm/a. The average incision rate from Nimu to Nurla is 1.8 mm/a and it increases downstream to 2.3 mm/a.

Putting together the height and chronology data of terraces helped in reconstructing the levels of paleo-riverbed profiles of Indus. The upper profile running at an average elevation of $134 \pm 24$ m arl has a central age of $62 \pm 15$ ka and an average incision rate of $2.2 \pm 0.6$ mm/a, whereas the lower profile at $45 \pm 5$ m arl has an age of $44 \pm 8$ ka and average erosion rate of $1.0 \pm 0.2$ mm/a. If we interpolate these reconstructed profiles upstream in the present river profile, then (i) the lower profile truncates upstream into the fill sequences preserved in the Segment-III (Leh valley) as both bear the same ages, (ii) the upper profile is older and the sediment of equivalent age might be present in the subsurface in Segment-III and upstream. This suggests that both lower and upper profiles are divergent downstream implying a base level fall in the downstream region.

Sand ramps of Ladakh provide composite records of wet and dry climate, e.g., the aeolian facies are represented relatively arid conditions while the fluvial facies and sedimentary hiatus (hard crust) and intra-dunal lakes facies are indicative of wetter climatic conditions. The deposition of hillslope debris also suggests the dominance of wetter conditions in the region. The OSL chronology on the studied sand ramps suggests that the ramp accumulation started prior to 44 ka and continued till ∼8 ka. The period between 25-17 ka and <12–8 ka was dominated by the aeolian activities in the Leh valley. At ∼12 ka, the formation of the intra-dunal lake and at 7 ka fluvial gullying suggest wetter climate. These subsequent dry and wet phases can be linked to variations in the ISM. The clay mineralogy from the Saboo sand ramp shows illite and chlorite throughout the profile, which supports physical weathering. Here one important inference is made that although climate fluctuated between wet and dry, a signal captured by iron mineralogy, the climatic fluctuations were limited to the threshold of alteration of clay mineralogy during the late Pleistocene in the Leh valley.

***Amit Kumar Prasad***

## Understanding defect related luminescence processes in wide bandgap materials using low temperature multi-spectroscopic techniques

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*Degree: Ph.D.*
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Feldspar is a dominant, naturally occurring mineral that comprises about 60 % of the Earths crust. It is widely used in optically stimulated luminescence (OSL) dating of sediments to obtain chronologies of past events as old as ∼0.5 Ma, and thus, plays a crucial role in understanding Quaternary climate changes, landscape development and human evolution and dispersal. Optical properties of feldspar originate from a) a wide band gap (∼7.7 eV), b) crystal defects (impurity atoms and distortions) that create localized energy states within the bandgap, and c) conduction band and the low-mobility band tail states, which play a role in charge transport.

Despite a rapid progress in the infra-red stimulated luminescence (IRSL) dating technique using feldspar, a clear understanding of luminescence process is still lacking. A better understanding of feldspar as a physical system is expected to lead to its improved exploitation as a luminescence chronometer. My Ph.D. investigates the nature of luminescence generating defects and processes in feldspar, and tests whether the intra-defect relaxation transitions may be successfully used to improve the dating technique. It includes mapping the energy states of defects individually and characterizing their emission process, understanding the dynamics of the excited-state relaxation and tunneling, and defect interactions with the crystal lattice and the band tail states. The experiments were carried out using the Risø station for CryOgenic LUminescence Research (COLUR) and a high sensitive spectrometer attached to the Risø TL/OSL reader. The key findings of my Ph.D. research are summarize as follows:

1. I discovered the excitation-energy dependent emission (a red edge effect) in the green-orange emission in feldspar, and demonstrated that this effect arises from interaction of a deep lying defect with the band tail states. This effect can be used to measure the band-tail width through relatively simple spectroscopic (photoluminescence) measurements.

2. My studies on $Fe^{3+}$ show that its deep red emission varies with site dependence of $Fe^{3+}$ even within a single sample. Furthermore, it is observed that there exists an excitation-energy dependence of the main radiative transition ($^4T_1 \rightarrow {}^6A_1$) in $Fe^{3+}$; this is possibly related to spin-lattice interaction.

3. I explored a model analogue system for feldspar called $YPO_4$: Ce, Sm, in order to understand OSL produced by excited-state tunneling. For the first time, a precise mapping of the energy levels of the metastable $Sm^{2+}$ was carried out, and the temperature-dependent relaxation lifetime of $Sm^{2+}$ excited state was determined using the defects internal radiative-transition. It was then demonstrated that OSL decay curves resulting from optically induced, sub-conduction band electron transfer ($Sm^{2+} \rightarrow Ce^{4+}$ ) can be adequately described using the prevalent mathematical model of excited-state tunneling.

4. Finally, inspired by the results of $YPO_4$: Ce, Sm, I discovered a Stokes-shifted, infra-red photoluminescence (IRPL) signal arising from the principal trap in feldspar (excitation $\sim$ 1.4 eV (885 nm), emission: $\sim$ 1.3 eV (950 nm)). Current methods of OSL rely on transfer of electrons from the principal trap to holes located elsewhere in the lattice; this is by default a destructive readout of dosimetric information. Furthermore, OSL (or IRSL) suffer from sensitivity changes because of competition in the recombination process, leading to possible uncertainties in the dose measurement. In contrast to IRSL, the IRPL signal arises from intra-defect excitation and the subsequent radiative relaxation within the principle trap (i.e. the trap giving rise to IRSL). IRPL is a non-destructive readout technique and the lifetime of the excited state relaxation is estimated to be $\sim$40 s at 7K and $\sim$29 s at 295 K. The IRPL signal increases with dose and the preliminary dating investigations indicate that this signal contains an athermal non-fading component, likely arising from the trapped electrons that do not have a nearby hole center.

There are two important technique developments in my thesis. Firstly, based on the model of the red edge effect, a simple method is proposed for estimation of the width of the band tail states in feldspar. Secondly, it is shown that the new IRPL signal can be used for non-destructive probing of dosimetric information in the IR trap. The IRPL technique is likely to provide a) a robust understanding of the behavior of electron trapping centers in feldspar, b) a possibility of selective probe of non-fading electrons without using any thermal assistance, and c) precise measurements of luminescence from very small volumes by repeated readout. These possibilities open new windows for development of robust dating methods as well as advanced imaging techniques. I envision that the IRPL signal will significantly impact the field of optical dating.

A PDF of this thesis can be downloaded from: https://www.researchgate.net/profile/Amit_Prasad10 or http://orbit.dtu.dk