Chapter 5
TIME-RESOLVED OSL EXPERIMENTS

Abstract In this chapter we discuss experimental data and models for time-resolved optically and infrared stimulated luminescence (TR-OSL, TR-IRSL).These techniques can help researchers understand the luminescence mechanisms involved in dosimetric materials. We show how to use R in order to extract the luminescence lifetimes from TR experimental data, and show how to analyze the temperature dependence of luminescence lifetimes and luminescence intensity. Specific R codes are provided for TR experiments in quartz and how they can be analyzed with R to obtain the thermal quenching parameters W and C, based on the Mott-Seitz competition mechanism. We show how to analyze TR-OSL signals from *delocalized* transitions and also TR-IRSL signals involving *localized* transitions in feldspars involving quantum tunneling. This chapter concludes with the presentation of a TR-photoluminescence model (TR-PL) for the important dosimetric material Al_2O_3:C.

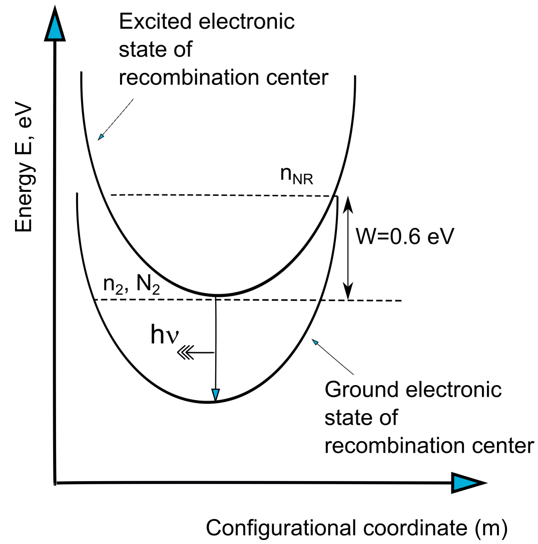

Fig. 5.1: The configurational diagram for quartz, based on the Mott-Seitz mechanism of thermal quenching. From Pagonis et al. [30].

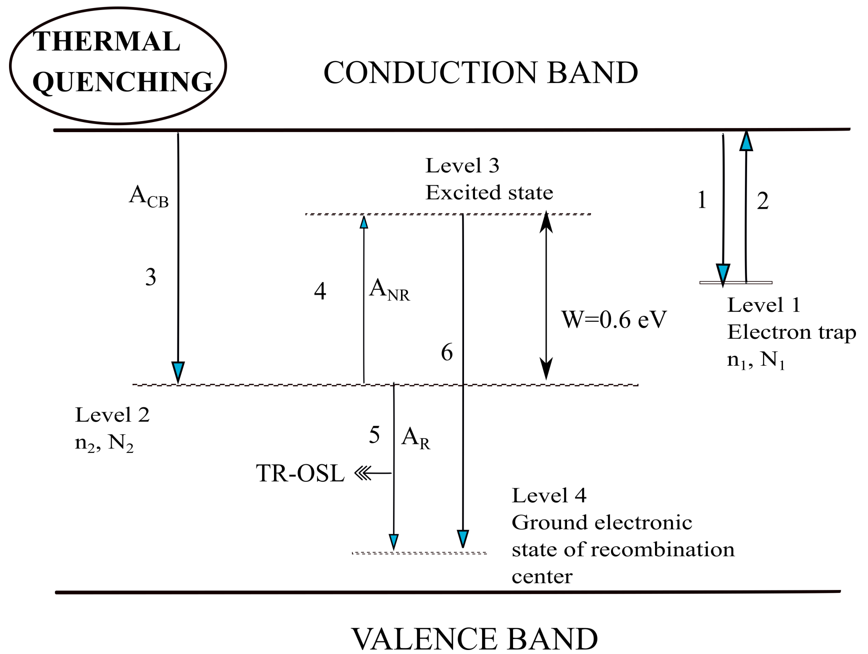

Fig. 5.2: The kinetic model of Pagonis et al. [30] for thermal quenching in quartz, based on the Mott-Seitz mechanism.

Code 5.1: Analysis of TR-OSL experimental data in quartz

```
rm(list=ls())
library("minpack.lm")
mydata <- read.table("chithamboTROSLqzdata.txt")
plot(mydata,pch=2,col="red",  ylab="TR-OSL [a.u.]",
     xlab=expression(paste("Time [",mu,"s]")))
legend("topright",bty="n",legend=c("Sedimentary","quartz"," ",
"470 nm","LEDs"))
# fit ON data
t<-mydata[,1][1:20]
y<-mydata[,2][1:20]
fit_data <-data.frame(t ,y)
fit <- minpack.lm::nlsLM(
```

```
formula = y ~ N * (1-exp(- t/b))+abs(bgd), data = fit_data,
  start = list(N= max(y),b = 40,bgd=10))
t1<-0:55
lines(x = t1,  y = coef(fit)[1]  *
(1-exp(- t1/coef(fit)[2]))+abs(coef(fit)[3]),col = "blue")
coef(fit)
# fit OFF data
t<-mydata[,1][21:length(mydata[,1])]-51.27
y<-mydata[,2][21:length(mydata[,1])]
fit_data <-data.frame(t ,y)
fit <- minpack.lm::nlsLM(
  formula = y ~ N * (exp(- t/b))+abs(bgd),data = fit_data,
  start = list(N= max(y),b = 40,bgd=10))
t1<-5:300
lines(x=t1+51.2,y=coef(fit)[1]*(exp(-(t1)/coef(fit)[2]))+
abs(coef(fit)[3]),col = "blue")
coef(fit)
```

```
##           N           b         bgd
## 254.2423690  38.0707228   0.8669149
##         N         b       bgd
## 221.49526  38.47338   2.67049
```

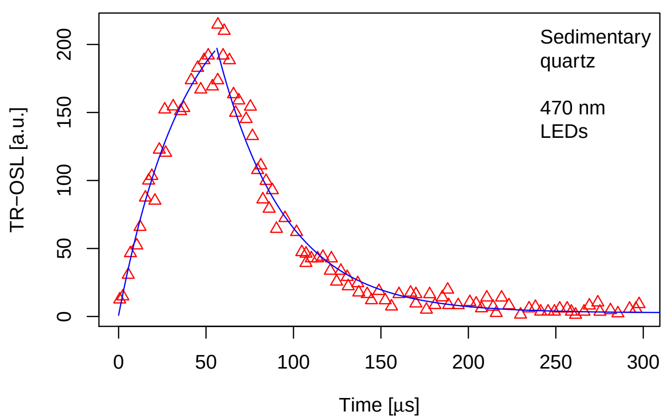

Fig. 5.3: Examples of TR-OSL curves for sedimentary quarts with 60 μs pulse. For more details see Chithambo et al. [8].

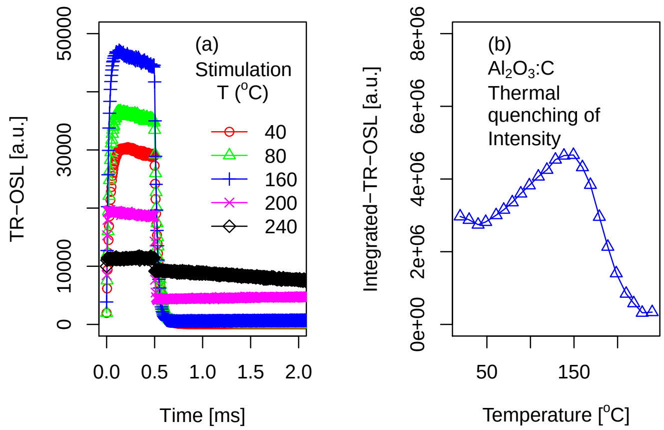

Fig. 5.4: Experimental dependence of (a) the TR-OSL luminescence signals, and (b) of the integrated TR-OSL intensity, on the stimulation temperature for Al_2O_3:C sample. For more details see Pagonis et al. [28].

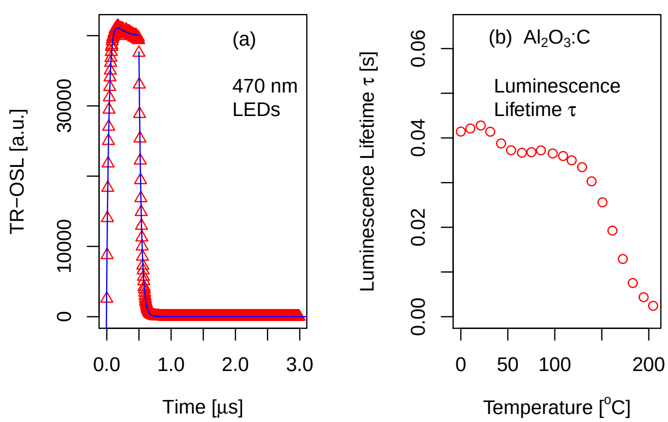

Fig. 5.5: (a) Analysis of the TR-OSL signal measured at a stimulation temperature of 100°C for an Al_2O_3:C sample, using exponential functions shown as solid lines. The signal contains a slower temperature-dependent phosphorescence signal, sometimes referred to as the “delayed-OSL” signal. (b) Experimental dependence of the luminescence lifetime τ on the stimulation temperature for the same sample. For more details see Pagonis et al. [28].

Code 5.2: Analysis of TR-OSL experimental data in alumina

```
rm(list=ls())
library("minpack.lm")
par(mfrow=c(1,2))
aluminatau470nmx<-unlist(read.table("aluminax1.txt"))
aluminatau470nmy<-unlist(read.table("aluminay1.txt"))
x<-aluminatau470nmx[8:20]+273
y<-aluminatau470nmy[8:20]
kB<-8.617*1e-5 # Boltzmann constant in eV/K
fit_data <-data.frame(x ,y)
plot(aluminatau470nmx+273,aluminatau470nmy,
xlab=expression("Temperature [K]"),
ylab="Integrated-TR-OSL [a.u.]")
legend("topright",bty="n","(a)")
legend("bottomleft",bty = "n", legend =
c(expression('Al'[2]*'O'[3]*':C',' ',
 'Thermal','quenching',' ','Fit to find C,W')))
fit <- minpack.lm::nlsLM(
  formula = y ~ N /(1+c*exp(-W/(kB*x))),data = fit_data,
  start = list(N= max(y),c=1e6, W =1))
x1<-seq(from=350,to=500,by=1)
lines(x=x1,y=coef(fit)[1]/(1+coef(fit)[2]*
exp(-coef(fit)[3]/(kB*x1))),      col = "blue")
coef(fit)
al2o3risoOSLvsTempx<-unlist(read.table("aluminax2.txt"))
al2o3risoOSLvsTempy<-unlist(read.table("aluminay2.txt"))
x<-al2o3risoOSLvsTempx[4:10]
y<-al2o3risoOSLvsTempy[4:10]
y<-log(y)
x<-1/(kB*(x+273.15))
bestfit<-lm(y~x)
coefficients(bestfit)
plot(x, y, xlab = "1/(kT)  [1/eV]",ylab = "ln(TR-OSL)")
legend("topright",bty = "n", legend =c('(b)',expression(' ',
```

```
'Fit to find E'[th]*' ')))
abline(lm(y~x))
```

```
##            N            c            W
## 3.698208e-02 5.659581e+11 1.014901e+00
## (Intercept)           x
## 17.19471165 -0.06542585
```

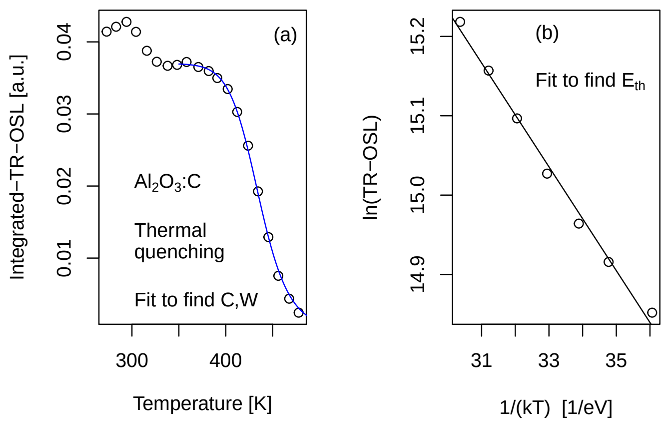

Fig. 5.6: Experimental determination of the thermal quenching parameters C, W, E_{th}. (a) The values of C, W are obtained by fitting the *decreasing* part of the data. The best fit is shown by the solid line. (b) The thermal activation energy E_{th} is obtained with an Arrhenius analysis of the *increasing* part of the data in (a). For more details see Pagonis et al. [28].

Code 5.3: Fit microcline TR-IRSL data with analytical equation

```
#Fit FL1 TR-IRSL data with analytical equation
rm(list = ls(all=T))
options(warn=-1)
library("minpack.lm")
```

```
par(mfrow=c(1,2))
## fit ON data to analytical TR-IRSL equation ----
mydata <- read.table("FL1ONdata.txt")
t<-1e-6*mydata[,1]
y<-mydata[,2]
mydata<-data.frame(t,y)
plot(t*1e6,y,xlab="Time [s]",ylab="TR-IRSL [Normalized]",
col="black",pch=1)
fit_data <-mydata
fit <- minpack.lm::nlsLM(
  formula=y~ imax*(1-exp (-rho*(log(1 + A*t)) ** 3.0))+bgd,
  data = fit_data,
  start = list(imax=3,A=1e6,rho=0.001,bgd=min(y)))
imax_fit <- coef(fit)[1]
A_fit <- coef(fit)[2]
rho_fit <- coef(fit)[3]
bgd_fit <- coef(fit)[4]
## plot analytical solution
t1<-seq(from=1e-7,to=5e-5,by=1e-7)
lines(
  x = t1*1e6,
  y =imax_fit*(1-exp (-rho_fit*(log(1 + A_fit*
t1)) ** 3.0))+bgd_fit,   col = "red",lwd=2)
legend("topleft",bty="n","(a)")
legend("right",bty="n", pch=c(NA,NA,NA,1,NA),lwd=2,
       lty=c(NA,NA,NA,NA,"solid"),
       c(expression('TR-IRSL','Microcline',' ',
                    'Experiment','Analytical')),
col=c(NA,NA,NA,"black","red"))
## print results
cat("\nParameters from Least squares fit")
cat("\nImax=",formatC(imax_fit,format="e",digits=2)," cts/s",
       sep="    ","A=",round(A_fit,digits=2)," (s^-1)")
cat("\nrho=",round(rho_fit,digits=4),sep=" ",
       "  bgd=",round(bgd_fit,digits=2)," cts/s")
## Use same parameters to fit the OFF data
mydata <- read.table("FL1OFFdata.txt")
t<-1e-6*mydata[,1]
y<-mydata[,2]
mydata<-data.frame(t,y)
plot(t*1e6,y,xlab="Time [s]",ylab="TR-IRSL [Normalized]",
col="black",pch=1)
## plot analytical solution
t1<-seq(from=5e-7,to=1e-4,by=1e-7)
```

```
lines(
  x = t1*1e6,
  y =.06+ imax_fit*(exp (-rho_fit*(log(1 + A_fit*t1)) ** 3.0)-
exp (-rho_fit*(log(1 + A_fit*(t1+5e-5))) ** 3.0))+bgd_fit,
  col = "red",lwd=2)
legend("topleft",bty="n","(b)")
legend("right",bty="n", pch=c(NA,NA,NA,1,NA),lwd=2,
       lty=c(NA,NA,NA,NA,"solid"),
       c(expression('TR-IRSL','OFF data',' ',
'Experiment','Analytical')),col=c(NA,NA,NA,"black","red"))
```

```
##
## Parameters from Least squares fit
## Imax=    1.03e+00      cts/s    A=    6592795     (s^-1)
## rho= 0.0212   bgd= -0.04  cts/s
```

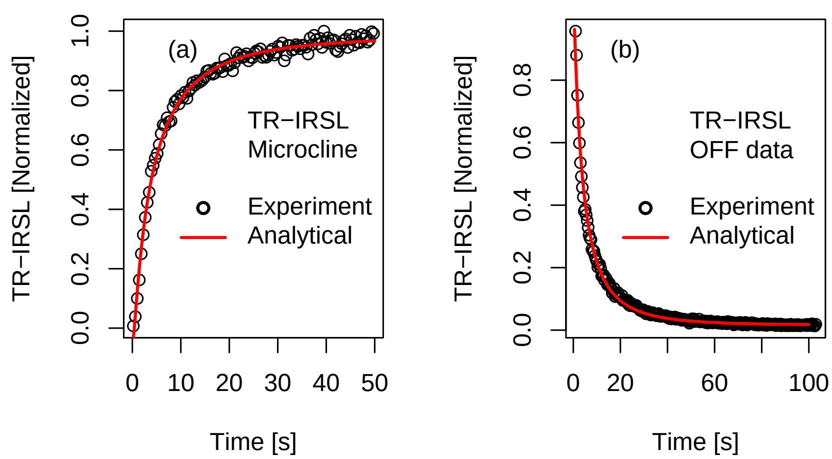

Fig. 5.7: Fit TR-IRSL data for microcline sample FL1, with the analytical Eqs.(**??**) and (**??**). (a) The IR excitation is ON (b) The excitation is OFF. For more details see Pagonis et al. [29].

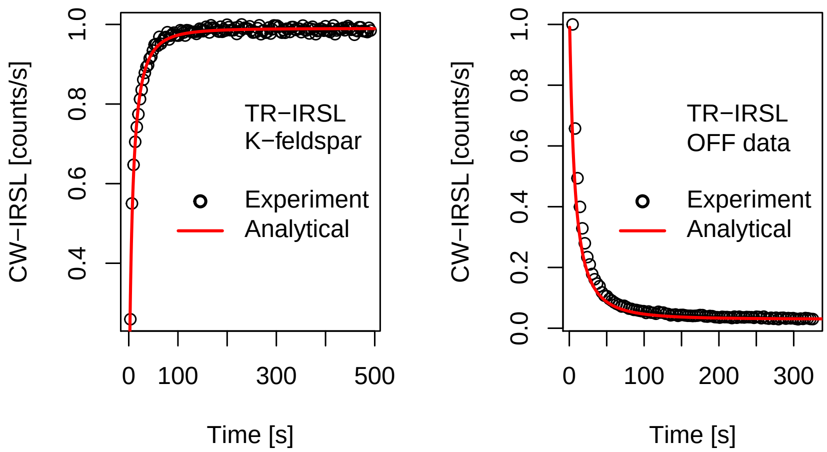

Fig. 5.8: Fit of K-rich feldspar TR-IRSL data with analytical Eqs.(**??**) and (**??**). (a) The IR excitation is ON (b) The excitation is OFF. For more details see Pagonis et al. [29].

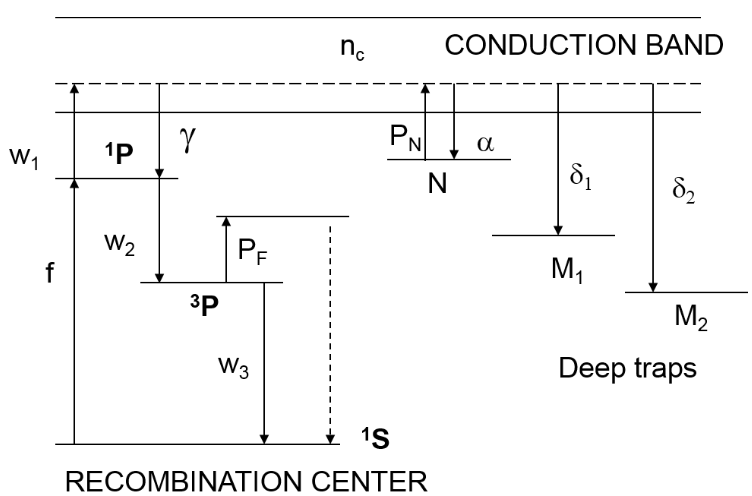

Fig. 5.9: The TR-PL model for time-resolved photoluminescence (TR-PL) experiments in α-Al_2O_3:C by Pagonis et al. [34], based on an earlier version of the model by Nikiforov et al. [27].

Code 5.4: Simulation of TR-PL experiments in Al2O3:C

```
#Simulate TR-PL experiments with Nikiforov/Pagonis model
rm(list = ls(all=T))
library("deSolve")
PagonisAlumina <- function(t, x, parms) {
  with(as.list(c(parms, x)), {
    dn<- -s*exp(-E/(kb*(273+T)))*n+alpha*(N-n)*nc
    dm1<- delta1*(M1-m1)*nc
    dm2<- delta2*(M2-m2)*nc
    dnc<- s*n*exp(-E/(kb*(273+T)))-delta1*(M1-m1)*nc-
    delta2*(M2-m2)*nc-Gamma*nF*nc-alpha*(N-n)*nc+w1*n1P
    dnF<- -Gamma*nF*nc+w1*n1P
    dn3P<-w2*n1P-C*exp(-W/(kb*(273+T)))*n3P-w3*n3P
    dn1P<-f+Gamma*nF*nc-w1*n1P-w2*n1P
    res <- c(dn,dm1,dm2,dnc,dnF,dn3P,dn1P)
    list(res)  })}

TempVar<-function(T){
parms<- c(E=1.3, s=1e13,alpha=1e-14, delta1=1e-12, delta2=1e-14,
  Gamma=1e-11,N=1e13,M1=1e15,T=T,M2=1e14,C=1e13,W=1,w1=1,w2=3e3,
  w3=w3,f=1e10,kb=8.617e-5)
  y <- xstart <- c(n = 0, m1=1e14,m2=0,nc=0,nF=1e14,n3P=0,n1P=0)
  out <-  ode(xstart, times, PagonisAlumina, parms)  }
w3<-29
times  <- seq(0, .2,by=.005)
Temps<-seq(70,220,10)
Lc<-temps<-matrix(NA,nrow=length(times),ncol=length(Temps))
areaLc<-vector(length=length(Temps))
for (i in 1:length(Temps)){
  T<-Temps[i]
  a<-TempVar(T)
  Lc[,i]<- w3*a[,"n3P"]
  areaLc[i]<-sum(Lc[,i],rm.NA=TRUE)}
par(mfrow=c(1,2))
plot(times,Lc[,6],typ="o",col="black",xlim=c(0,.2),
ylim=c(0,1.7e10),pch=1, xlab="Time [s]",
ylab="TR-OSL Intensity [a.u.]")
lines(times,Lc[,12],typ="o",col="red",pch=2)
```

```
lines(times,Lc[,15],typ="o",col="blue",pch=3)
legend("topleft",bty="n",pch=c(NA,1,2,3),
lty=c(NA,rep("solid",3)),col=c(NA,"black",
"red","blue"),legend=c(expression("(a)  Al"[2]*"O"[3]*":C",
"120"^o*"C","180"^o*"C","210"^o*"C")))
plot(Temps,areaLc,typ="o",col="blue",lwd=2,pch=1,ylim=c(0,6e11),
xlab=expression("Stimulation Temperature"^o*"C"),
ylab="TR-OSL Areas [a.u.]")
legend("topleft",bty="n",legend=c("(b)"," ","Thermal quenching",
  "TR-OSL Areas"))
```

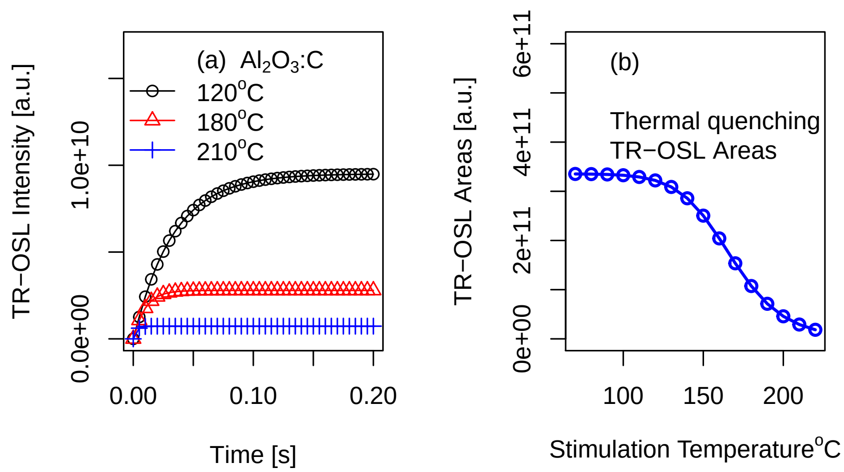

Fig. 5.10: Simulation of TR-PL experiments for Al_2O_3:C while the light excitation is ON. (a) The TR-OSL intensity at three different stimulation temperatures T =120, 180, 210°C; (b) The area under the TR-OSL curves in (a), is plotted as a function of the stimulation temperature and shows the effect of thermal quenching. For more details see Pagonis et al. [34].