Two different groups of info

➤Quantitative information: Intensity of luminescence signal, signal integrals, sensitization **(quantifying TL)**

➤Qualitative information = **Characteristics of the TL peak for understanding the mechanism as well as for assessing the lifetime of each trap** Activation energy, frequency factor, order of kinetics → towards estimating the life time of each trap

Activation energy: definition

Activation energy (definition and properties)

It is the energy, E, expressed in eV, assigned to a **metastable state** or level within the forbidden band gap between the **conduction band** (CB) and the **valence band** (VB) of a crystal. This energy is also called trap depth. The metastable level can be an electron trap, near to the CB, or a hole trap, near the VB, or a **luminescence centre**, more or less in the middle of the band gap. The metastable levels are originated from **defects** of the crystal structure. A crystal can contain several kinds of traps and luminescence centers. If E is such that $E >$ several kT, where k is the Boltzmann's constant, then the trapped charge can remain in the trap for a long period. For an electron trap, E is measured, in eV, from the trap level to the bottom of the CB. For a hole trap, it is measured from the trap to the top of the VB.

Handbook of thermoluminescence, C. Furetta

Frequency Factor: definition

The frequency factor, s, is known as the attempt-to-escape frequency and is interpreted as the number of times per second, ν, that an electron interacts with the crystal lattice of a solid, multiplied by a transition probability κ, multiplied by a term which accounts for the change in entropy ΔS associated with the transition from a trap to the delocalized band. s may be written as

$$s = \nu \cdot \kappa \cdot \exp\left(\frac{\Delta S}{k}\right)$$

where k is the Boltzmann constant [1,2].

The expected maximum value of s should be similar to the lattice vibrational frequency (Debye frequency), i.e. $10^{12} - 10^{14}$ s^{-1}. According to Chen, the possible range for s is from 10^5 to 10^{13} s^{-1} [3].

Handbook of thermoluminescence, C. Furetta

Methods for determining E

More in detail, it is possible to group these methods in main sections:

a) Methods based upon maximum temperatures,
b) Methods based upon low temperatures side analysis,
c) Variable heating rates methods,
d) Area measurements methods,
e) Isothermal decay method,
f) Inflection points method,
g) Peak shape geometrical methods.

a)The simplest procedure is that searching for a linear relationship between glow temperature and activation energy. → First order of kinetics→ Requires knowledge of s.

b)E value independent on s. Thermal quenching and temperature lag could result in underestimation→ *Low β*
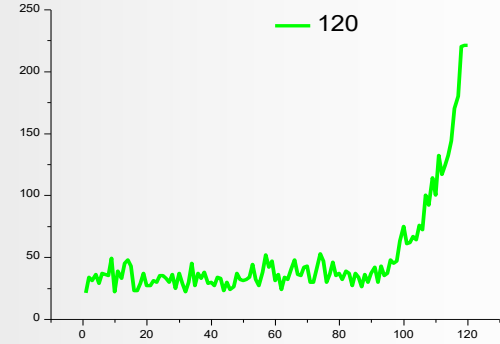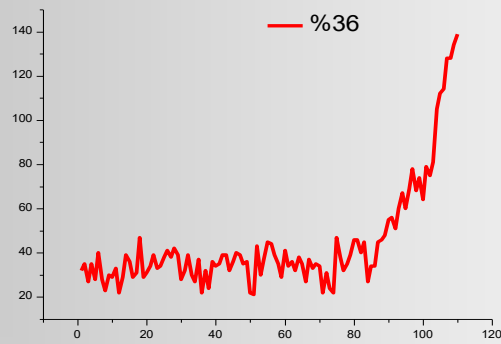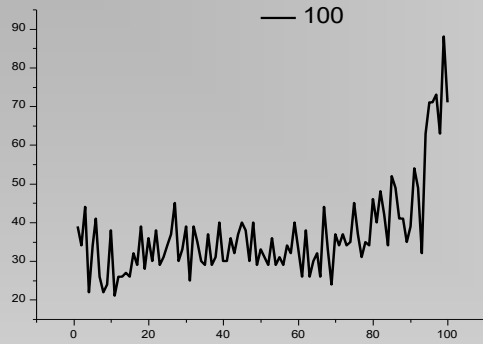
c)E value not affected by thermal quenching but s value is some affected → *Low β is suggested*
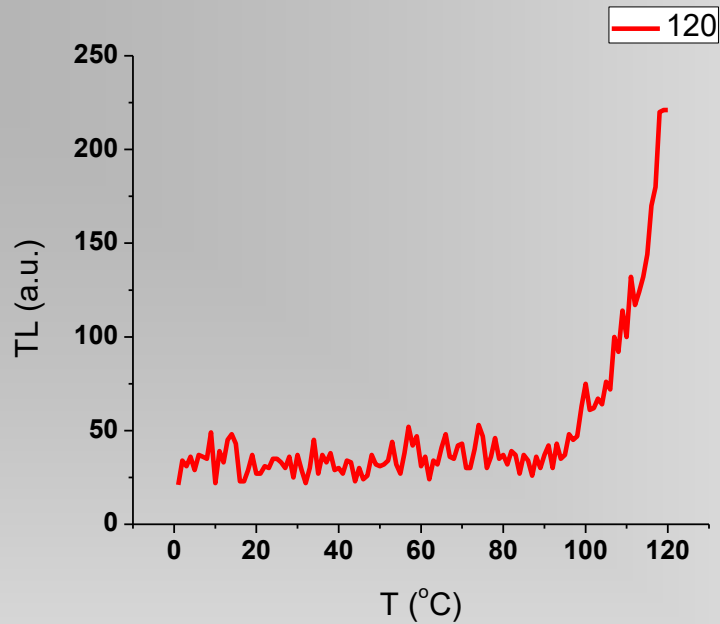
5 different methods for E

➤ De-convolution (*both quantitative and qualitative info*)

➤ Initial rise technique

➤ Fractional glow technique

➤ Various heating rates method *(Check for thermal quenching first)*

➤ *Isothermal decay*

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

Fractional glow
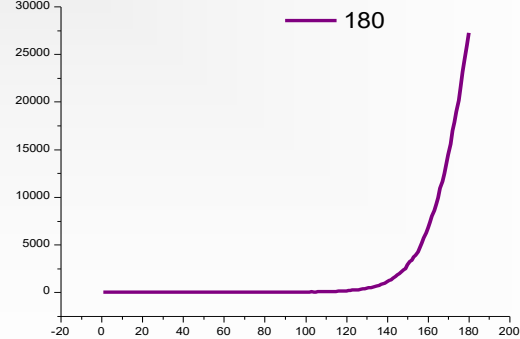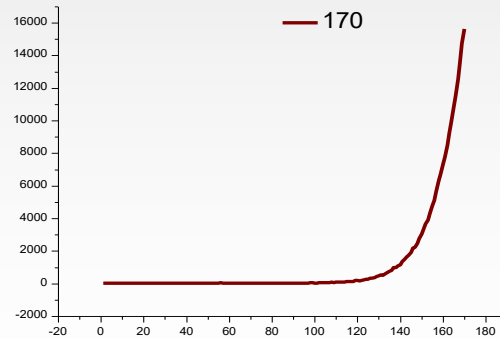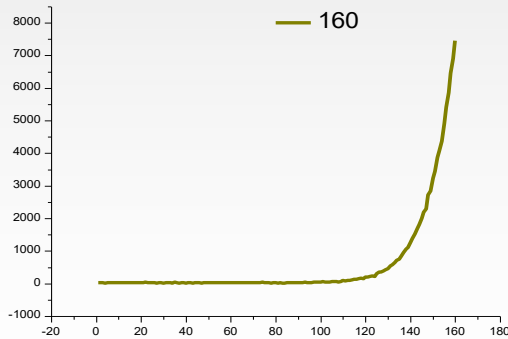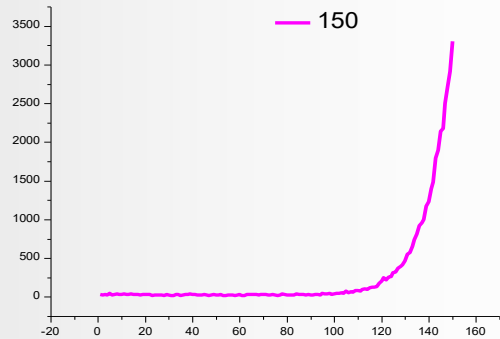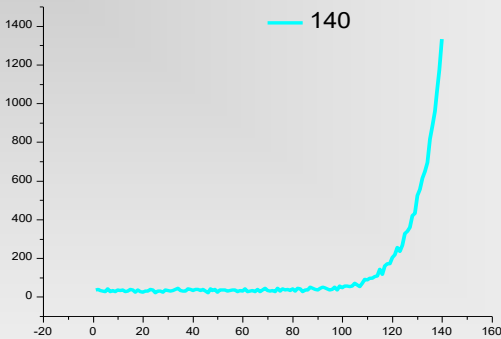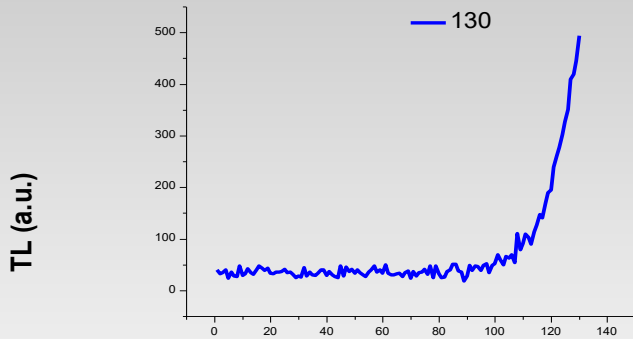
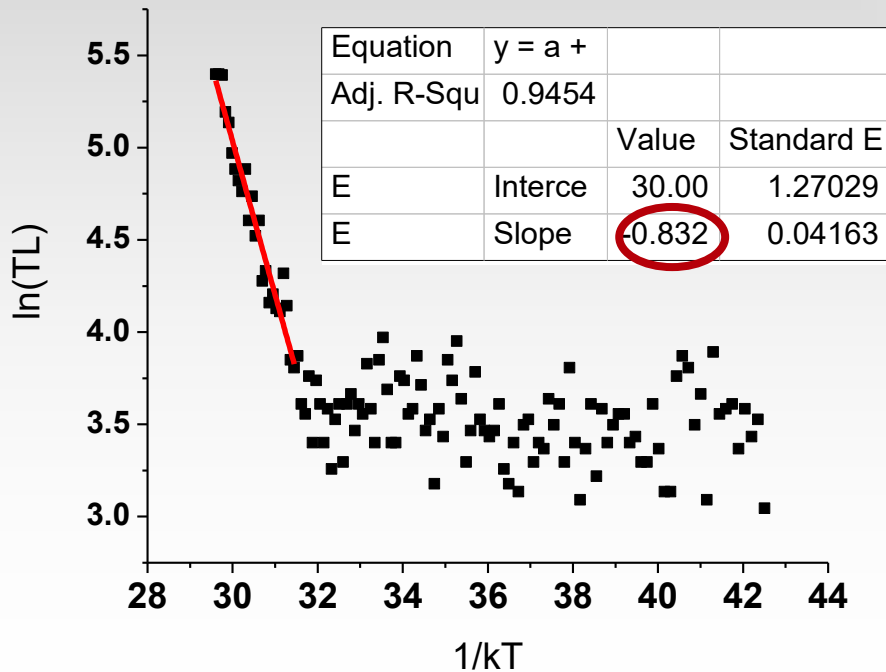**Initial part:**

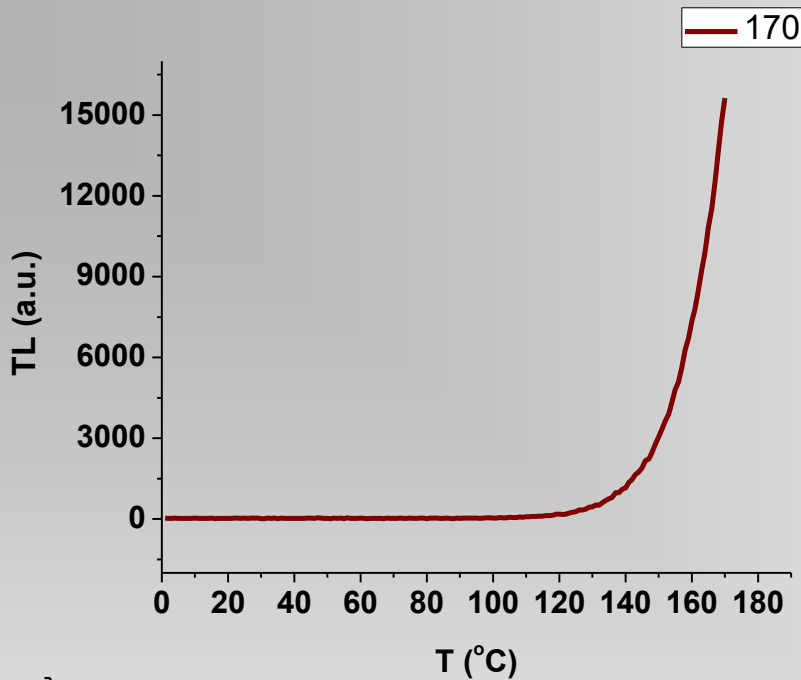**Boltzmann factor**

→Initial Rise Technique

$$I \propto T^{\alpha} \exp\left(-\frac{E}{kT}\right)$$

$$\ln I = \alpha \ln T - \frac{E}{kT}$$

Arrhenius plot

Initial part:
Boltzmann factor
→Initial Rise Technique

$$I \propto T^{\alpha} \exp\left(-\frac{E}{kT}\right)$$
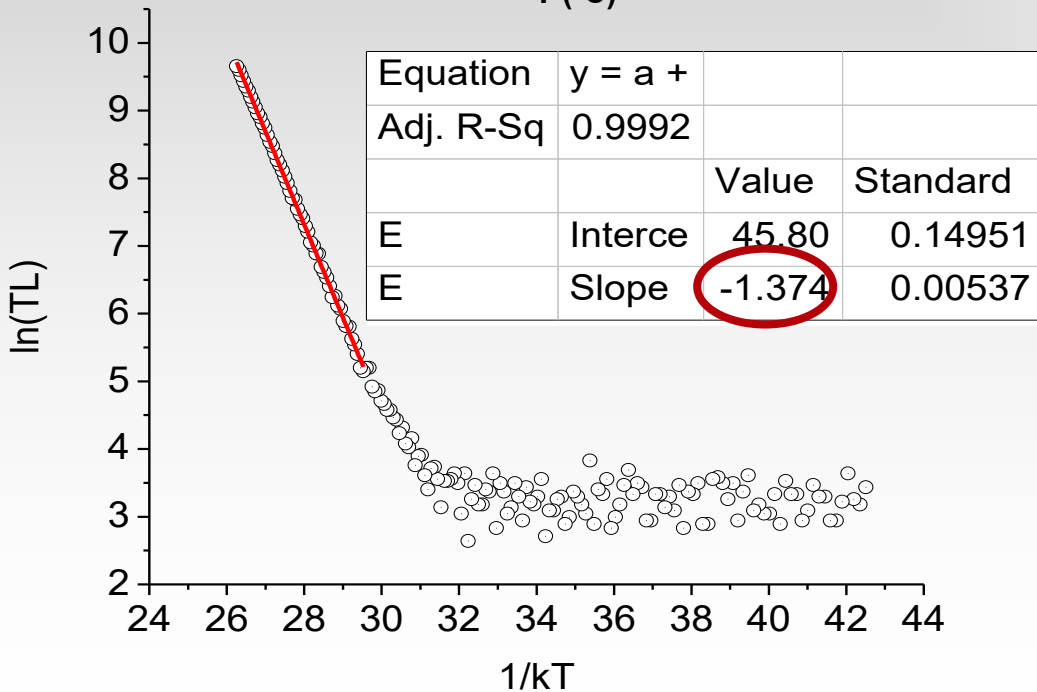
$$\ln I = \alpha \ln T - \frac{E}{kT}$$

Arrhenius plot
Intercept~ln(s)

Arrhenius equation

The Arrhenius equation gives the mean time, τ, that an electron spends in a trap at a given temperature T. It is

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

where s is the frequency factor (in the case of thermoluminescence the frequency factor is also called attempt-to-escape frequency), E is the energy difference between the bottom of the CB and the trap position in the band gap, also called trap depth or activation energy, k is the Boltzmann's constant.

Equation (1) can be rewritten as

$$p = \tau^{-1} \tag{2}$$

which gives the probability p, per unit of time, of the release of an electron from the trap.

$$s = \frac{\beta \cdot E}{k \cdot T_M^2} \exp\left(\frac{E}{kT_M}\right) \quad [\text{sec}^{-1}]$$

First order

$$s = \frac{\beta E \exp\left(\dfrac{E}{kT_M}\right)}{kT_M^2}\left[1 + \frac{2kT_M}{E}\right]^{-1}$$

Second order

$$s = \left[\frac{kT_M^2 \exp\left(-\dfrac{E}{kT_M}\right)}{\beta E}\left(1 + \frac{2kT_M(b-1)}{E}\right)\right]^{-1}$$
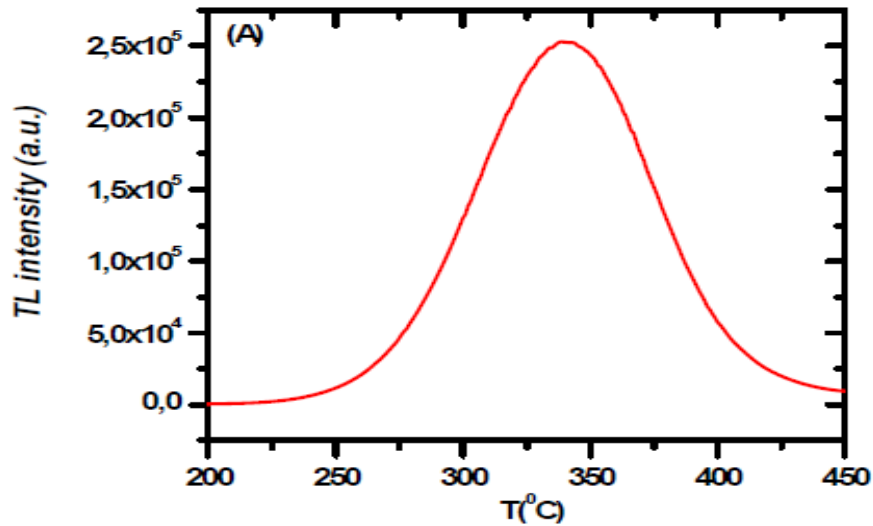
General order
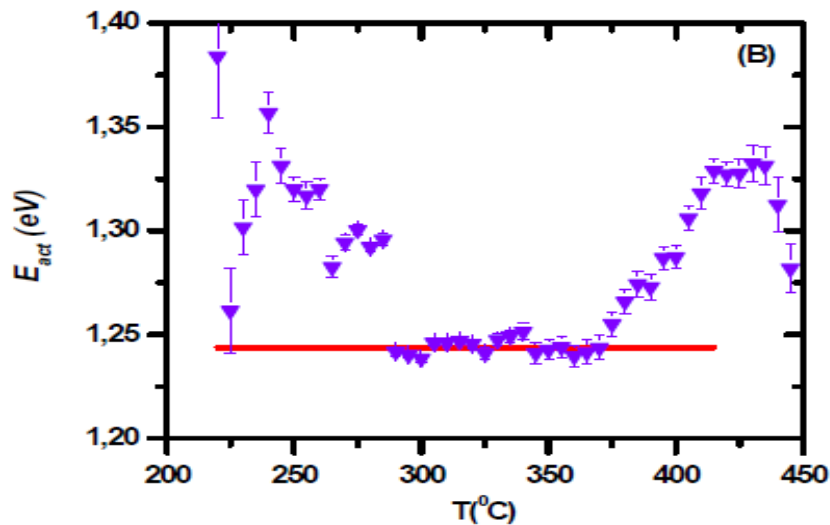
Fig. 1A: Natural TL (NTL) glow curve signal of obsidian

Fig. 1B: Initial rise (I.r.) plot for the NTL signal of obsidian. For both figures, the heating rate applied was 1 °C/s.

Initial part:
Boltzmann factor
→Initial Rise Technique

$$I \propto T^{\alpha} \exp\left(-\frac{E}{kT}\right)$$
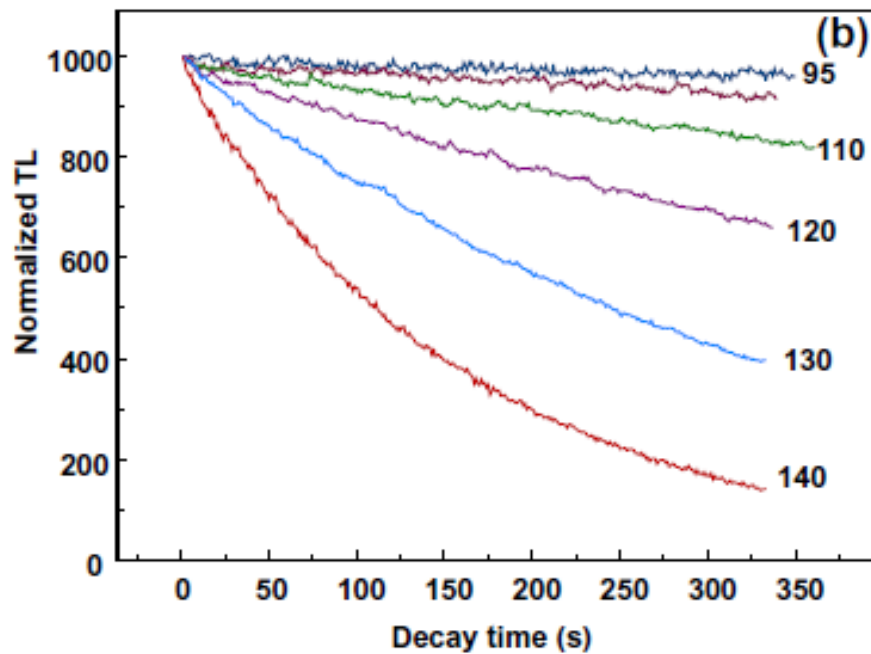
$$\ln I = \alpha \ln T - \frac{E}{kT}$$

T in units of Kelvin

Isothermal decay

$$I(t) = I_0 \exp(-tp),$$

First order

Measurements in various Temperatures

$$\ln\left(\frac{S_{t_1}}{S_0}\right) = -pt_1$$

$$m_i = -s \exp\left(-\frac{E}{kT_i}\right)$$

$$\ln(m_i) = \ln(-s) - \frac{E}{kT_i}$$