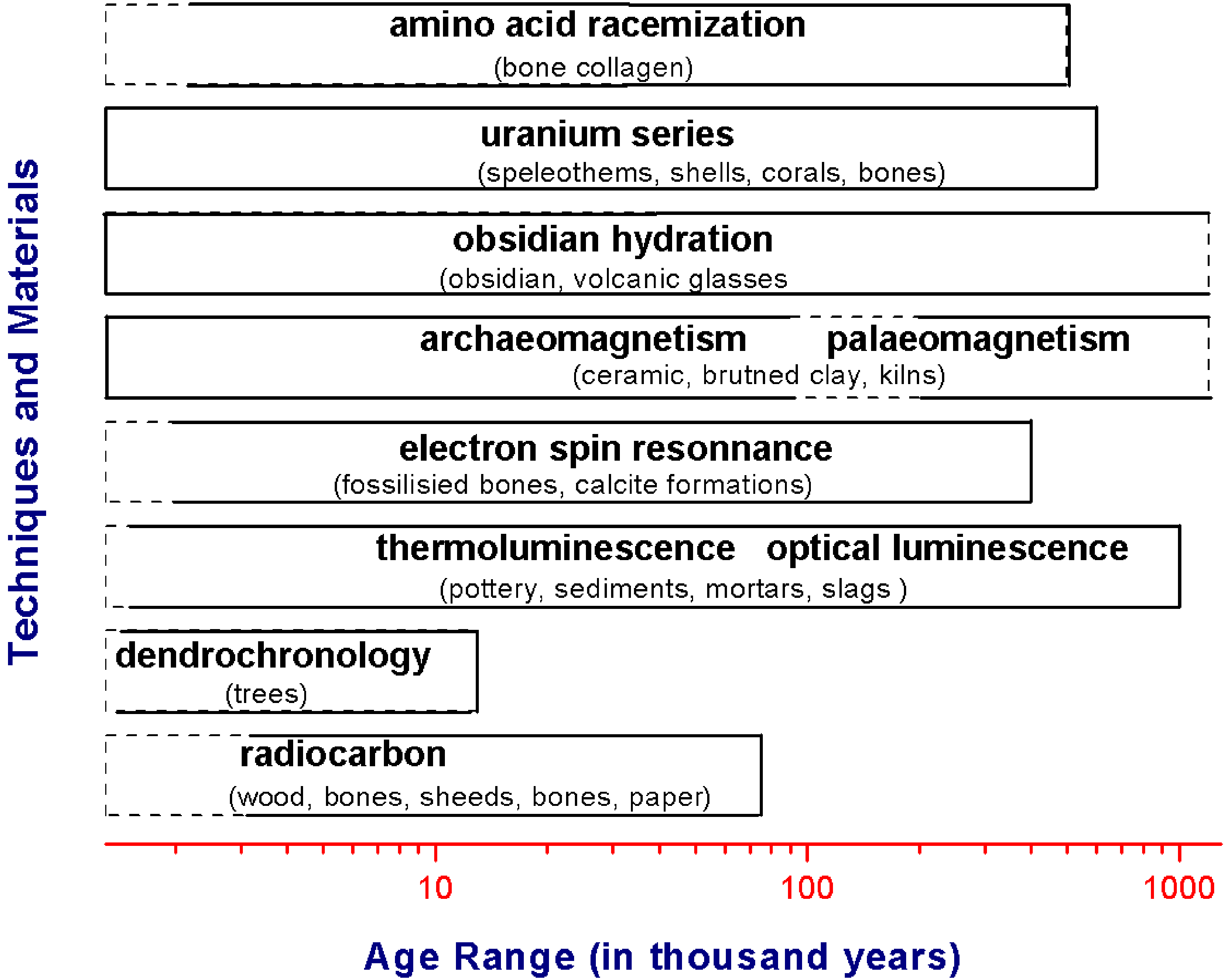
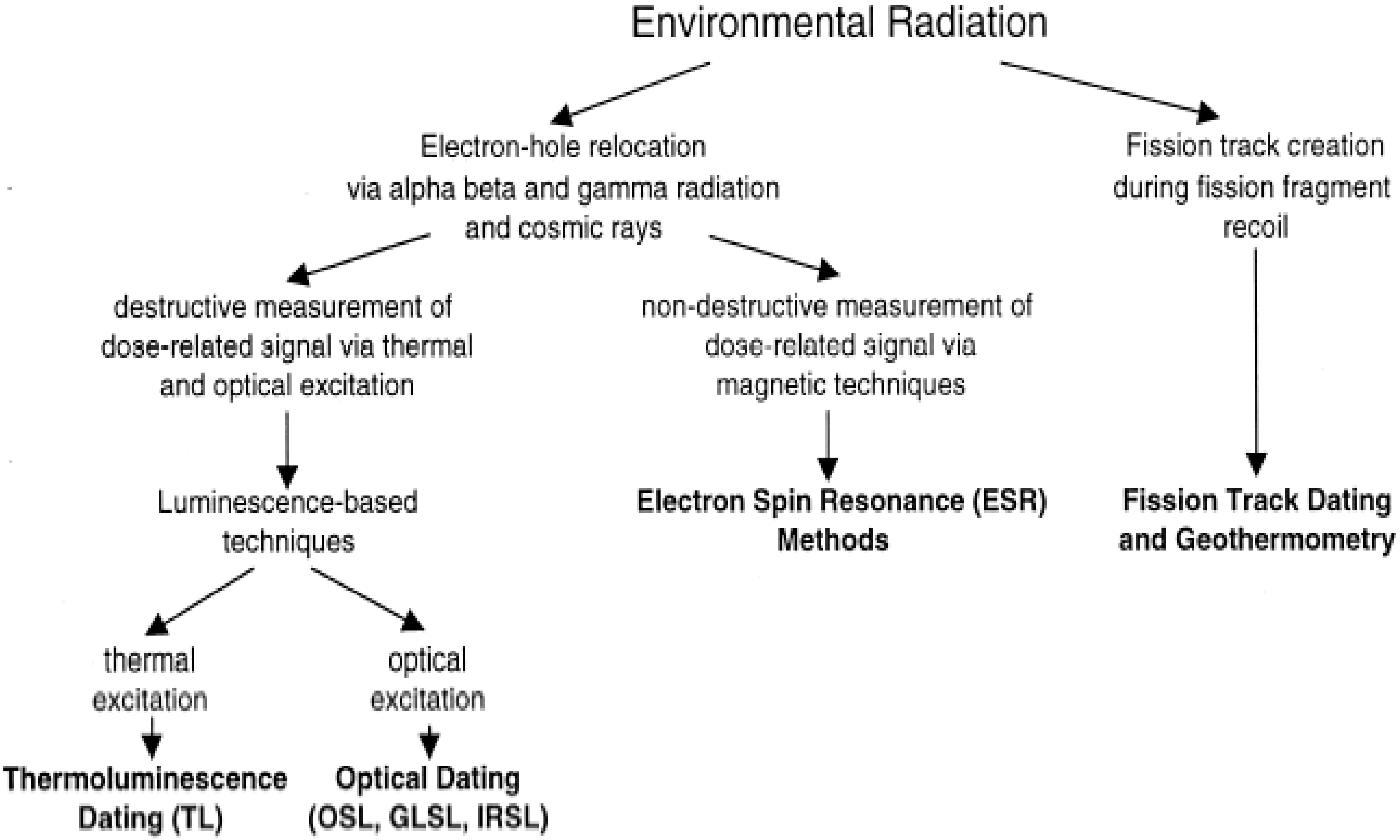

amino acid racemization
(bone collagen)
uranium series
(speleothems, shells, corals, bones)
obsidian hydration
(obsidian, volcanic glasses
archaeomagnetism
palaeomagnetism
(ceramic, brutned clay, kilns)
electron spin resonnance
(fossilisied bones, calcite formations)
thermoluminescence
optical luminescence
(pottery, sediments, mortars, slags)
dendrochronology
(trees)
radiocarbon
(wood, bones, sheeds, bones, paper)
10
100
1000
Age Range (in thousand years)
Techniques and Materials

volcanic	coral	obsidian	unburnt sediment	burnt flint & stone	slag	pottery, baked earth	stalag. calcite	shells	tooth enamel	bone, antler, ivory, teeth	wood, plant, seeds etc.	
											●	dendrochronology
	◕		◑		◕	◑	◑	◕	◔	●	●	radiocarbon
●												potassium-argon
●	●		◔				●	◔	◑	◔		uranium-series
●		●			◕							fission tracks
◑			●	●	○	●	◕					luminescence
◔	●			◔		○	◕	◑	◕	○		ESR
								◑	◔	◔		amino acid
		◕										hydration
◑			◑			◑	○					magnetism



Environmental Radiation

Electron-hole relocation
via alpha beta and gamma radiation
and cosmic rays

Fission track creation
during fission fragment
recoil

destructive measurement of
dose-related signal via thermal
and optical excitation

non-destructive measurement of
dose-related signal via
magnetic techniques

Luminescence-based
techniques

Electron Spin Resonance (ESR)
Methods

Fission Track Dating
and Geothermometry

thermal
excitation

optical
excitation

Thermoluminescence
Dating (TL)

Optical Dating
(OSL, GLSL, IRSL)

Annual Dose Rate Estimation

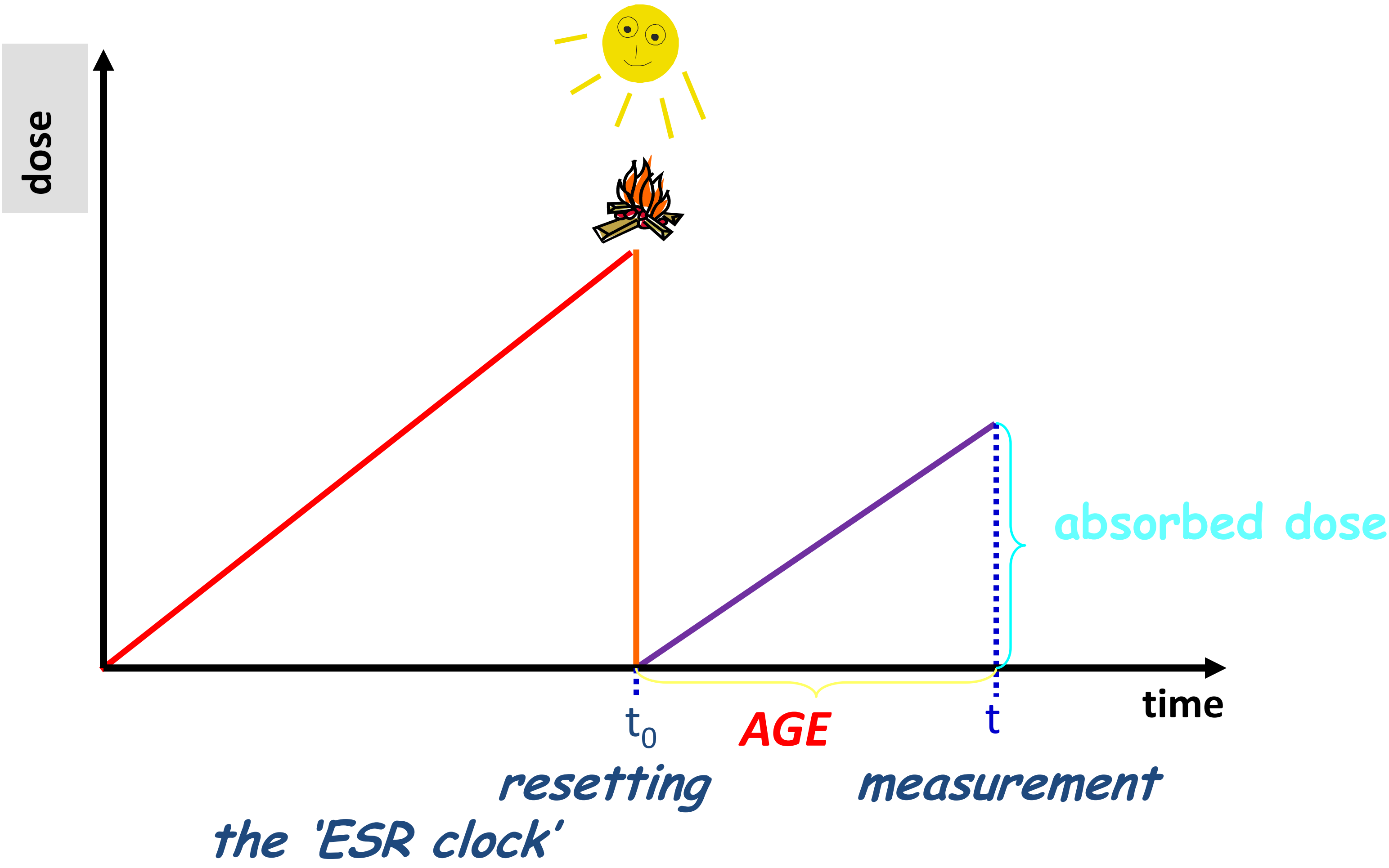
Natural U = ***^{235}U*** **AND** ***^{238}U*** ***^{232}Th***

SPECTROSCOPY, THICK SOURCE ALPHA COUNTING

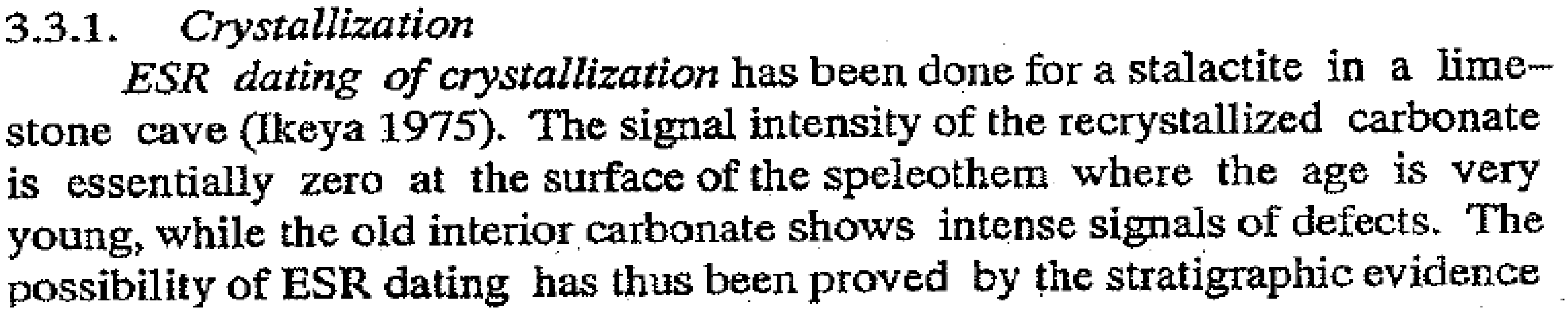
^{40}K

XRF, Flame Photometry, Scanning Electron Microscopy

Growth and Resetting of the ESR Signal

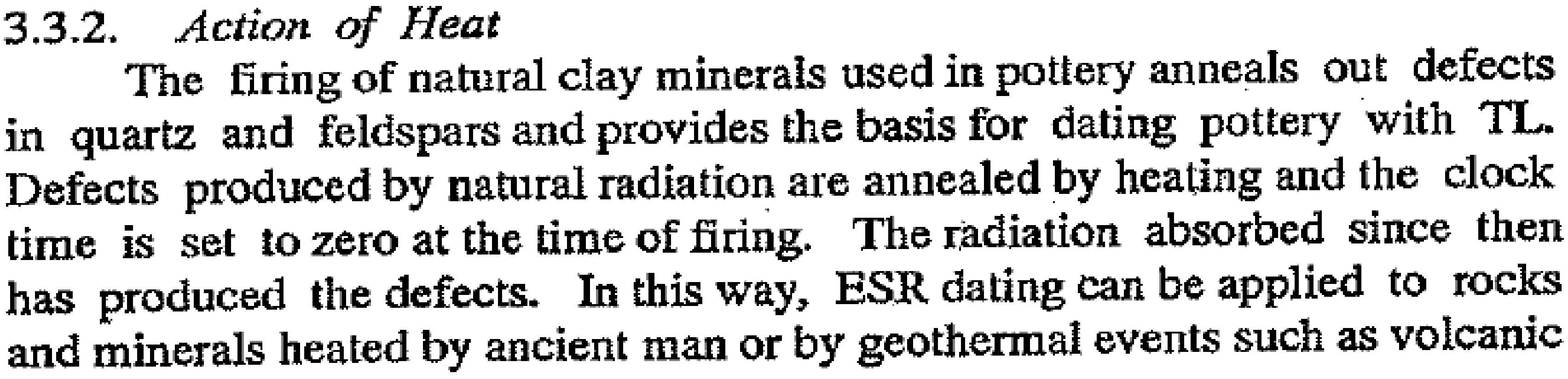


Zeroing effects – dating effect 1



3.3.1. *Crystallization*

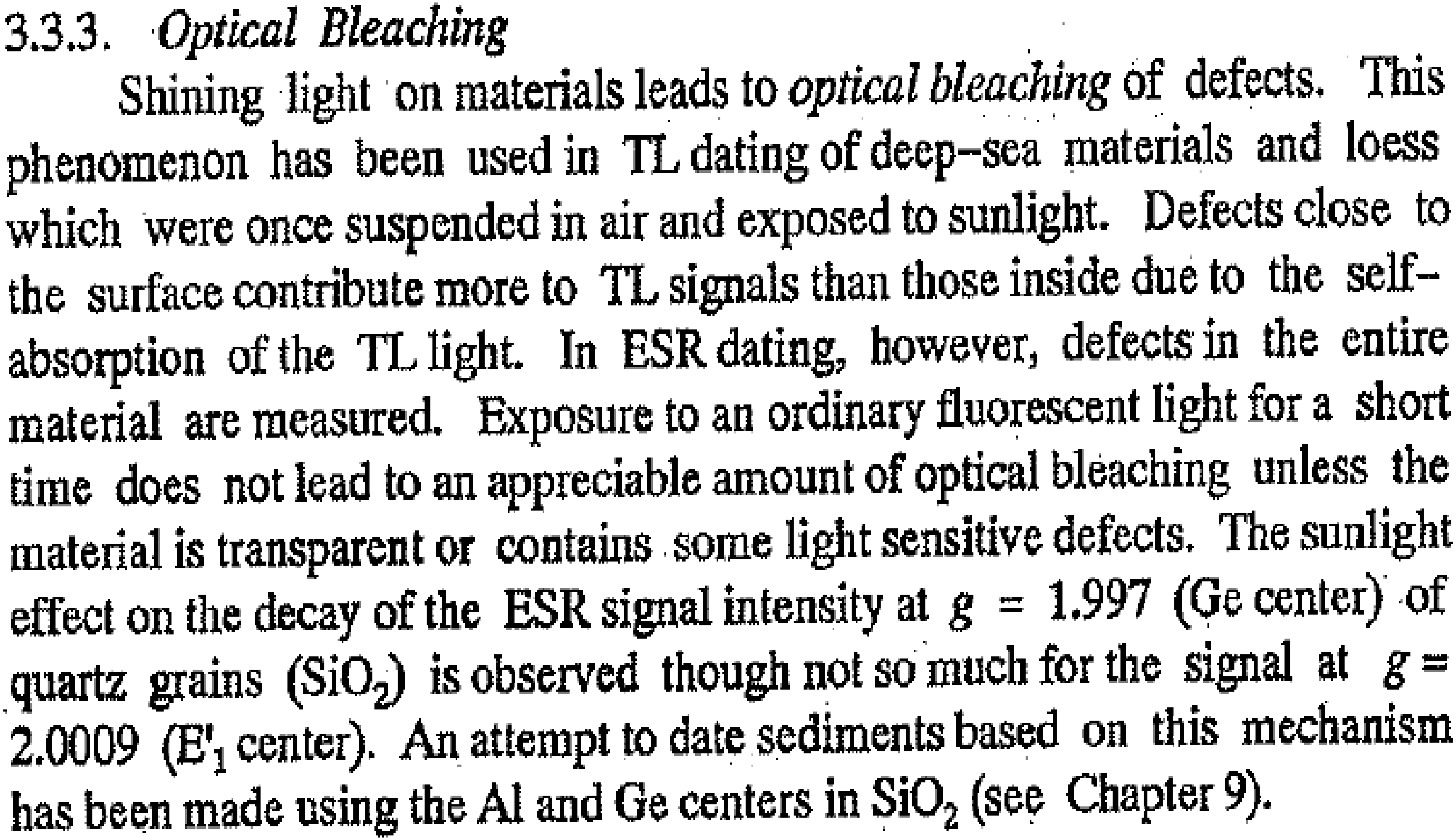
ESR dating of crystallization has been done for a stalactite in a limestone cave (Ikeya 1975). The signal intensity of the recrystallized carbonate is essentially zero at the surface of the speleothem where the age is very young, while the old interior carbonate shows intense signals of defects. The possibility of ESR dating has thus been proved by the stratigraphic evidence



3.3.2. *Action of Heat*

The firing of natural clay minerals used in pottery anneals out defects in quartz and feldspars and provides the basis for dating pottery with TL. Defects produced by natural radiation are annealed by heating and the clock time is set to zero at the time of firing. The radiation absorbed since then has produced the defects. In this way, ESR dating can be applied to rocks and minerals heated by ancient man or by geothermal events such as volcanic

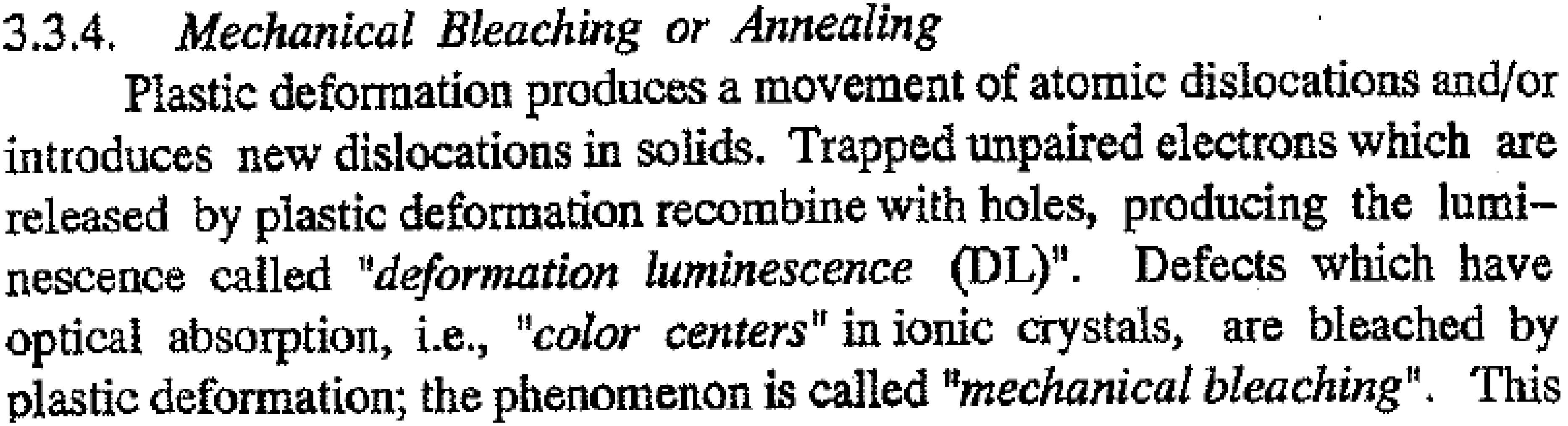
Zeroing effects – dating effect 1



3.3.3. *Optical Bleaching*

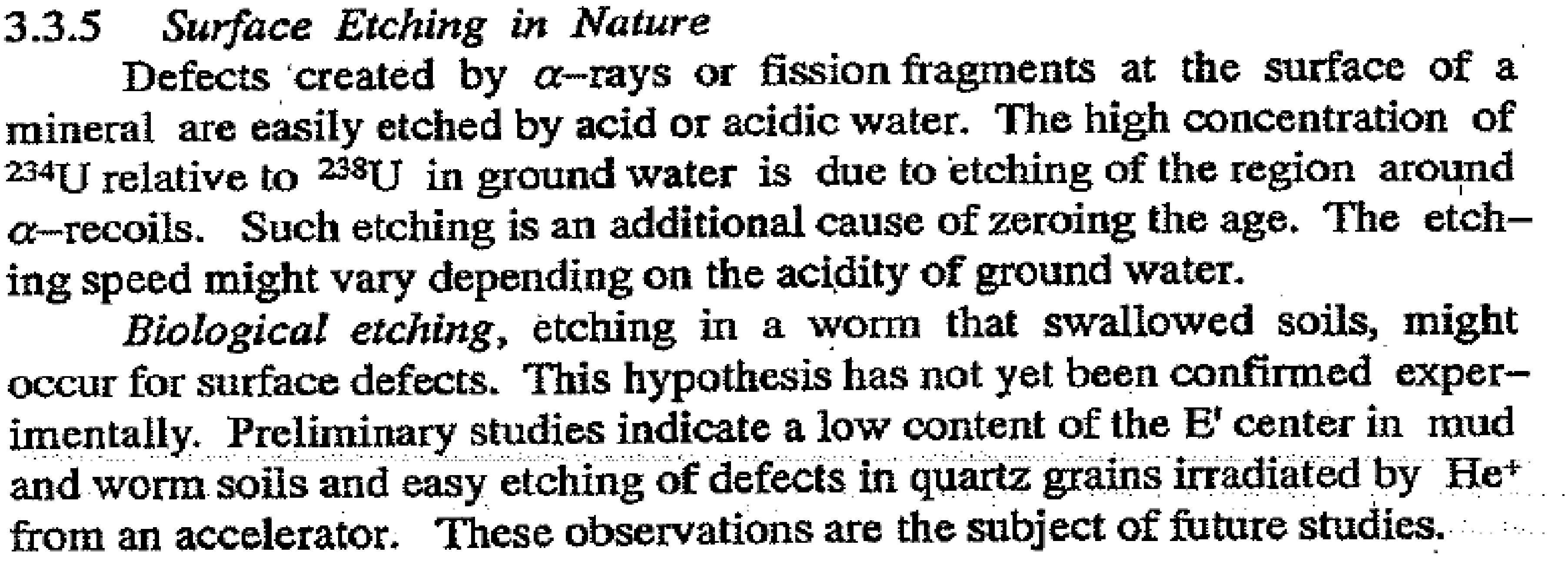
Shining light on materials leads to *optical bleaching* of defects. This phenomenon has been used in TL dating of deep–sea materials and loess which were once suspended in air and exposed to sunlight. Defects close to the surface contribute more to TL signals than those inside due to the self–absorption of the TL light. In ESR dating, however, defects in the entire material are measured. Exposure to an ordinary fluorescent light for a short time does not lead to an appreciable amount of optical bleaching unless the material is transparent or contains some light sensitive defects. The sunlight effect on the decay of the ESR signal intensity at $g = 1.997$ (Ge center) of quartz grains (SiO_2) is observed though not so much for the signal at $g = 2.0009$ (E'_1 center). An attempt to date sediments based on this mechanism has been made using the Al and Ge centers in SiO_2 (see Chapter 9).

Zeroing effects – dating effect 3



3.3.4. *Mechanical Bleaching or Annealing*

Plastic deformation produces a movement of atomic dislocations and/or introduces new dislocations in solids. Trapped unpaired electrons which are released by plastic deformation recombine with holes, producing the luminescence called "*deformation luminescence* (DL)". Defects which have optical absorption, i.e., "*color centers*" in ionic crystals, are bleached by plastic deformation; the phenomenon is called "*mechanical bleaching*". This

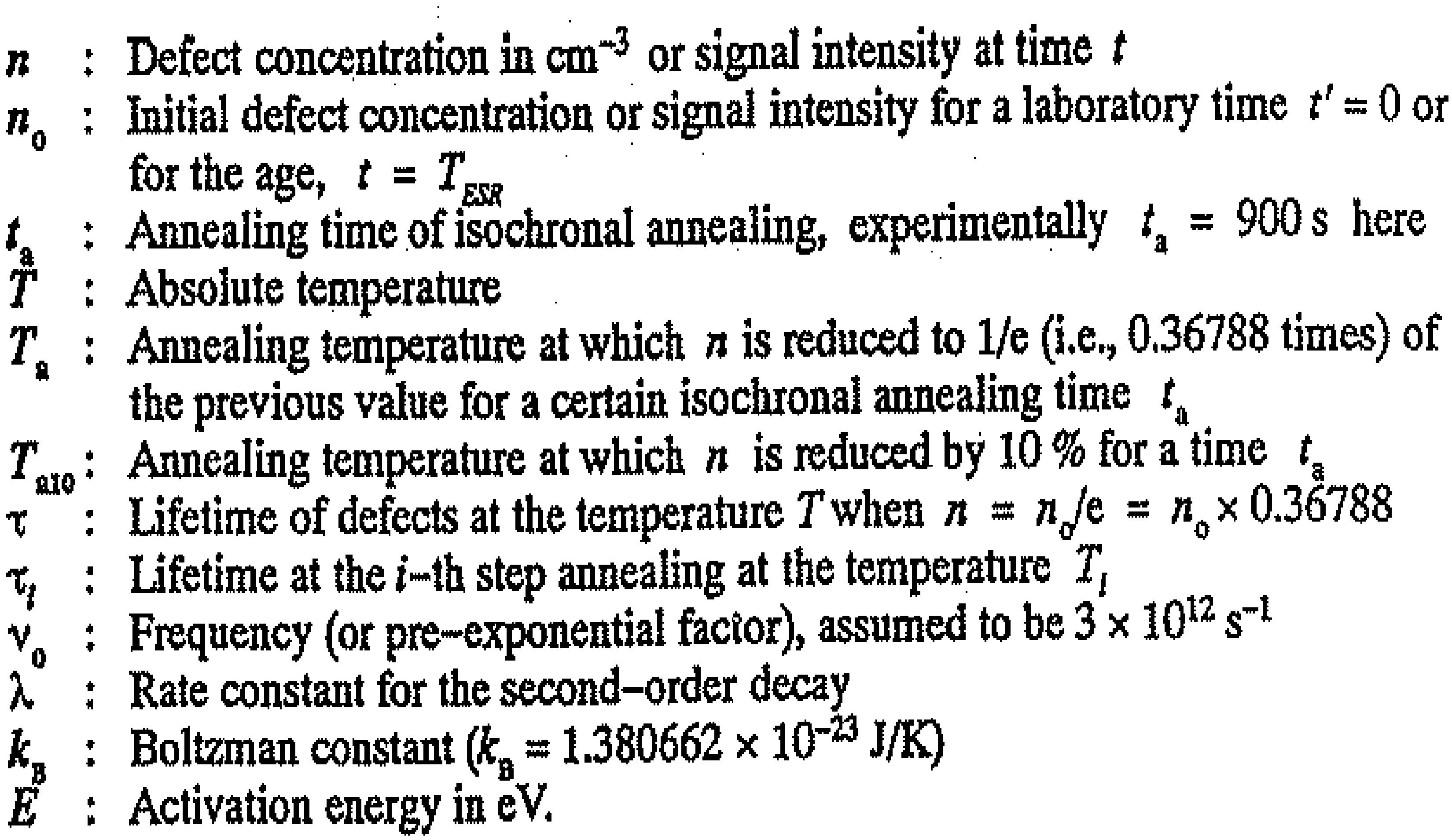


3.3.5 *Surface Etching in Nature*

Defects created by α–rays or fission fragments at the surface of a mineral are easily etched by acid or acidic water. The high concentration of ^{234}U relative to ^{238}U in ground water is due to etching of the region around α–recoils. Such etching is an additional cause of zeroing the age. The etching speed might vary depending on the acidity of ground water.

Biological etching, etching in a worm that swallowed soils, might occur for surface defects. This hypothesis has not yet been confirmed experimentally. Preliminary studies indicate a low content of the E' center in mud and worm soils and easy etching of defects in quartz grains irradiated by He^+ from an accelerator. These observations are the subject of future studies.

Stability of EPR signal: parameters



n : Defect concentration in cm^{-3} or signal intensity at time t

n_0 : Initial defect concentration or signal intensity for a laboratory time $t' = 0$ or for the age, $t = T_{ESR}$

t_a : Annealing time of isochronal annealing, experimentally $t_a = 900$ s here

T : Absolute temperature

T_a : Annealing temperature at which n is reduced to 1/e (i.e., 0.36788 times) of the previous value for a certain isochronal annealing time t_a

T_{a10} : Annealing temperature at which n is reduced by 10 % for a time t_a

τ : Lifetime of defects at the temperature T when $n = n_0/e = n_0 \times 0.36788$

τ_i : Lifetime at the i-th step annealing at the temperature T_i

ν_0 : Frequency (or pre-exponential factor), assumed to be $3 \times 10^{12}\ \text{s}^{-1}$

λ : Rate constant for the second-order decay

k_B : Boltzman constant ($k_B = 1.380662 \times 10^{-23}$ J/K)

E : Activation energy in eV.

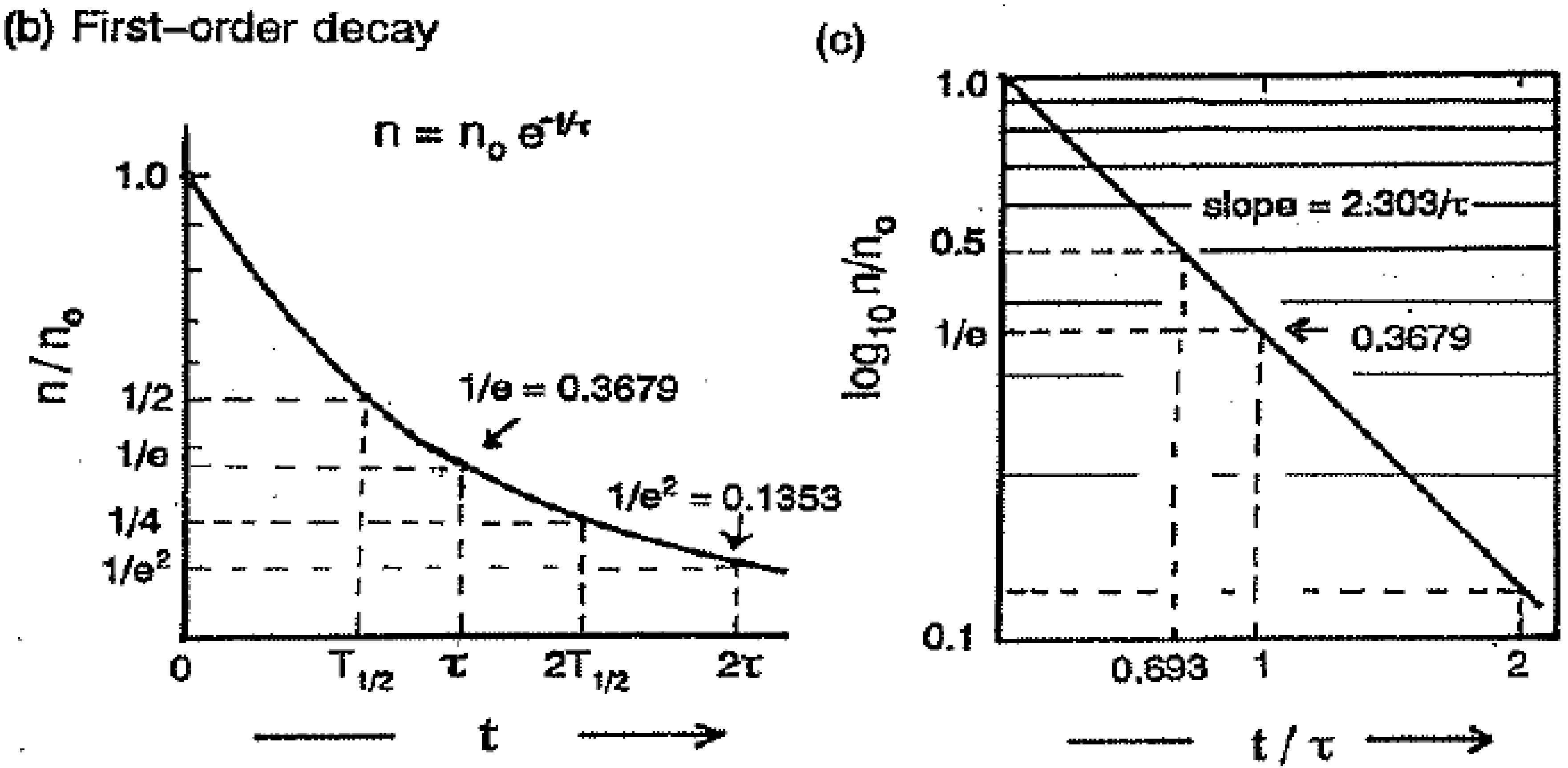


Figure 3.6 (a) Recombination of a correlated pair of an electron and a hole (vacancy and interstitial) leading to first–order annealing. (b) The exponential decay of the defect concentration n as a function of time t. (c) A semilogarithmic plot of first–order decay gives a straight line with a slope of 2.303/τ.

$$dn/dt = -n/\tau \ .$$

$$n = n_0 \exp(-t/\tau) \ .$$

$$\tau = (1/\nu_0)\exp(E/k_B T) \ ,$$

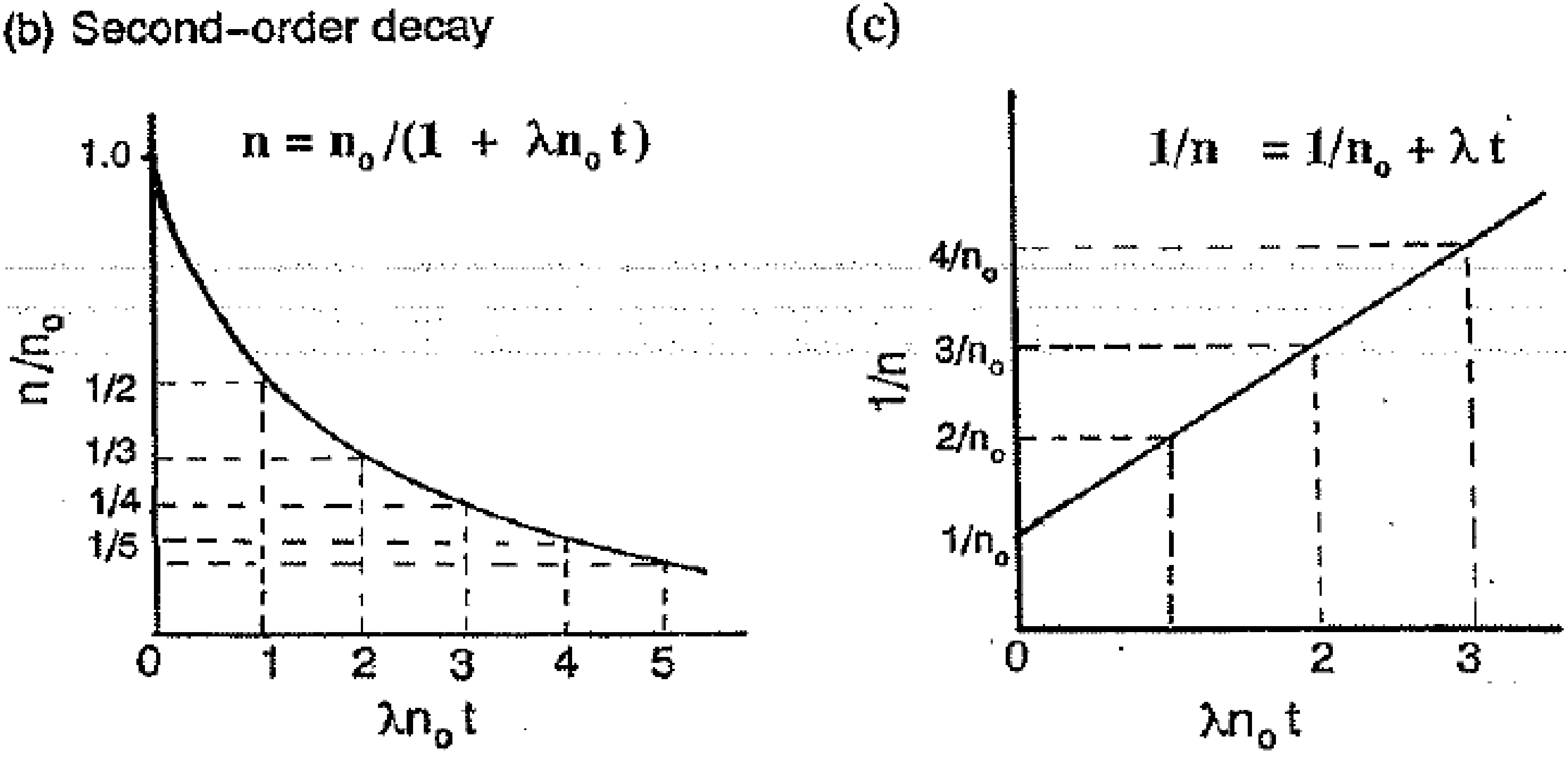
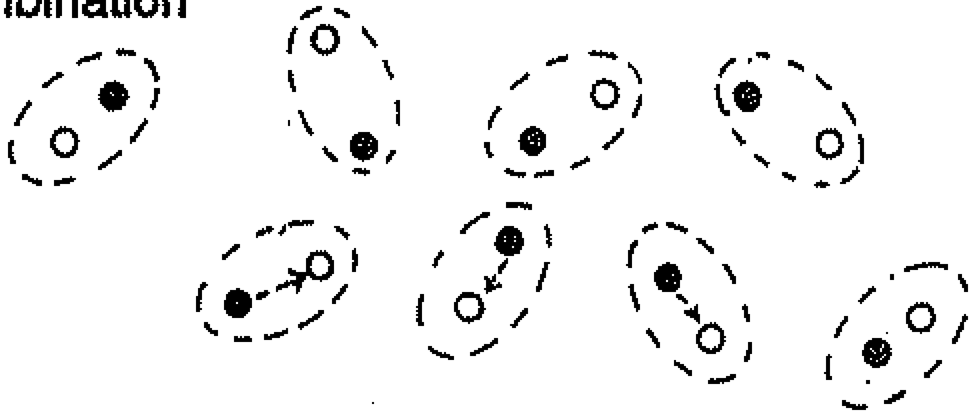


Figure 3.10 (a) Recombination of uncorrelated pairs of defects (electron and hole or vacancy and interstitial). (b) Second–order decay as a function of time normalized by $1/\lambda n_o$. (c) Plot of $1/n$ versus t gives λ from the slope and $1/n_o$ at the abscissa.

$$dn/dt = -\lambda n^2 = -n/(1/\lambda n) \ , \qquad \tau = 1/\lambda n \ . \qquad n = n_o/(1 + \lambda n_o t) \ .$$

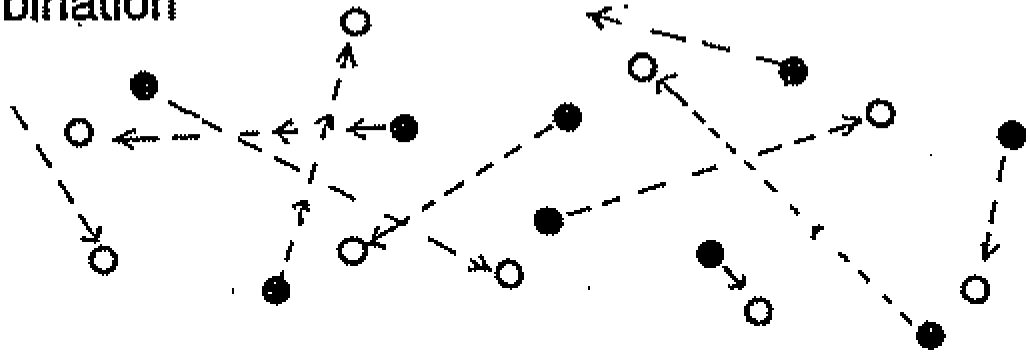
$$1/n = 1/n_o + \lambda t \ .$$

(a) Correlated recombination



First Order of kinetics

Uncorrelated recombination



Second Order of kinetics

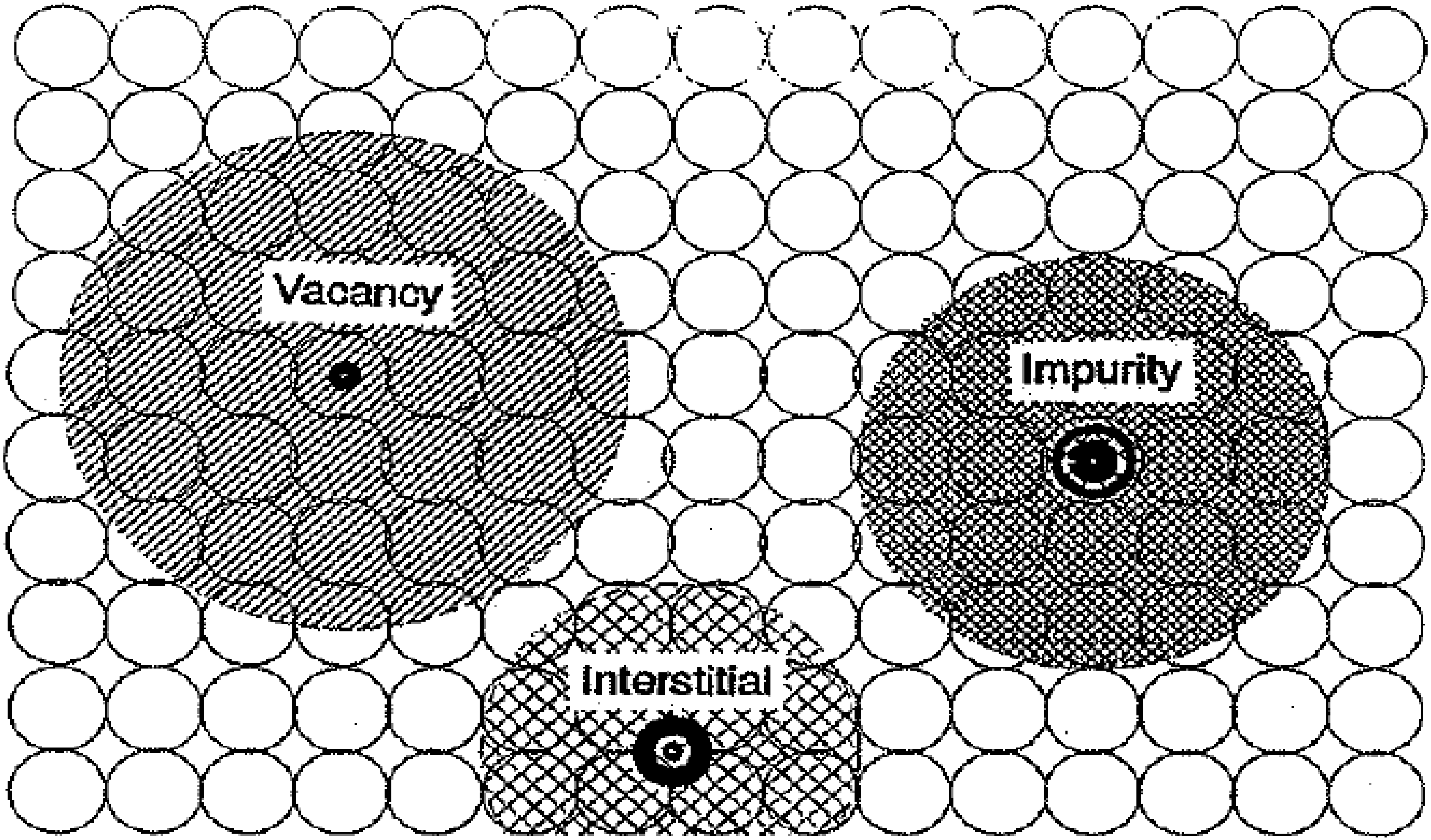


Figure 3.11 Saturation of the ESR signal intensity at a high dose region due to interaction among defects. The insensitive volumes around defects such as a vacancy, an interstitial and a substitutional impurity are indicated by shaded circles. Small open circles are atoms at the lattice site.

D, D' : Dose rate of natural radiation and artificial irradiation, respectively.

t, t' : Time in nature and in additive artificial irradiation, respectively.

I, I_0, I_s : Signal intensities at time t and time $t' = 0$ ($t = T_{ESR}$) and saturation intensity, respectively.

a : Defect creation efficiency [$\mathrm{cm}^{-3}\ \mathrm{Gy}^{-1}$] expressed in terms of G (the number of radicals formed per 100 eV) and the density of the material, ρ, as

$$a = 6.25 \times 10^{13} G \rho \tag{3.23}$$

$a = 1.7 \times 10^{13}\ \mathrm{cm}^{-3}\ \mathrm{Gy}^{-1}$ when $G = 0.1$ and $\rho = 2.6$.

b : Interaction volume defined as the number of lattice sites insensitive to radiation as schematically shown in Figure 3.11 (usually $b = 10^3 \sim 10^5$). Neither interstitials nor vacancies are stabilized since the lattice is distorted in this volume.

N_0 : The number of the available lattice site expressed as

$$N_0 = 6 \times 10^{23} \times \rho / MW \tag{3.24}$$

$N_0 = 2.6 \times 10^{22}/\mathrm{cm}^3$ for the *molecular weight*, $MW = 60$ and the density, $\rho = 2.6$.

τ_s, τ_s' : Saturation lifetime defined as the time required to fill all sites with the volume b at the natural dose rate D and the artificial one D', respectively.

τ_e : Effective lifetime, $1/\tau_e = 1/\tau + 1/\tau_s$.

The defect concentration n is described by a rate equation of the defect formation during additive irradiation at the dose rate D' as

$$\begin{aligned} \mathrm{d}n/\mathrm{d}t &= aD'(N_0 - bn)/N_0 \\ &= aD' - n/[N_0/(abD')] = aD' - n/\tau_s' \, . \end{aligned} \qquad (3.25)$$

$$n = (N_0/b)\left[1 - e^{-(ab/N_0)D't'}\right] \, .$$

$$\begin{aligned} n &= aD'\tau_s'(1 - e^{-t'/\tau_s'}) \\ &= aD\tau_s(1 - e^{-D't/D\tau_s}) \, . \end{aligned}$$

The saturation concentration : $N_0/b = aD't' = 8.5 \times 10^{18}\ \mathrm{cm}^{-3}$
The inactive volume : $b = 3 \times 10^3$
The saturation lifetime : $\tau_s = (N_0/b)/aD = D't'/D = 5 \times 10^8$ a

3.5.2 *Formation and First-Order Decay in Nature*

(a) *Analysis of growth curve* : Formation and decay of defects in nature are described using the lifetime τ as

$$dn/dt = aD(1 - bn/N_o) - n/\tau \ . \tag{3.29}$$

This indicates a saturation curve due to equilibrium between formation and decay if b is zero. If we use the relation $N_o = a\,b\,D\,\tau_s$, then

$$\begin{aligned} dn/dt &= aD - n(1/\tau_s + 1/\tau) \\ &= aD - n/\tau_e \ , \end{aligned} \tag{3.30}$$

where the *effective lifetime* τ_e is expressed as

$$1/\tau_e = 1/\tau + 1/\tau_s \ . \tag{3.31}$$

Then the solution of Eq. (3.29) is

$$n = aD\tau_e(1 - e^{-t/\tau_e}) \ . \tag{3.32}$$

If we substitute Eq. (3.31) into Eq. (3.32), then

$$n = [aD\tau\tau_s/(\tau + \tau_s)][1 - e^{-t/\tau}\, e^{-t/\tau_s}] \ . \tag{3.33}$$

If we normalize the defect concentration with the saturation concentration obtained by artificial irradiation and express it as the signal intensity ratio, then

$$I/I_s = [(\tau/\tau_s)/(1 + \tau/\tau_s)][1 - e^{-t/\tau}\, e^{-t/\tau_s}] \ . \tag{3.34}$$

3.7.1 *Time Range : Upper and Lower Limits*

An *upper limit* of billions of years for quartz grains has been proposed based on the correlation between geological ages and the signal intensity for the E′ center (an electron at an oxygen vacancy) created by α–recoils in quartz grains (Odom and Rink 1988, Grün 1989a). Similar trials have been made by correlating TL intensity to geologic age of minerals. If the defects have been formed by α–rays or α–recoil atoms, the growth should be logarithmic and not saturated as described in Appendix A1.4. Quartz grains contain only a few ppb of uranium in the SiO_2 lattice and the γ–rays from the external environment have been simply assumed not to create oxygen

The *lower limit* of the age range in ESR dating depends on the signal to noise (*S/N*) ratio and interfering impurity signals. Impurity signals may overlap and mask the signal associated with radiation–induced defects. If one improves the *S/N* ratio by a signal–averaging technique and subtraction of an impurity signal, the lower limit is reduced to about 10 years (*TD* = 10 mGy) for carbonate fossils. Thus, it is possible to extend ESR dating to quite recent events. The general limit using commercially available spectrometers (sensitivity : 10^{10} spins/0.1 mT) without signal averaging is about a thousand years (*TD* = 1 Gy) for ordinary materials or a few hundred years