Figure 1.7 Radiation effects produced by radiation of α-particles and fission tracks. Point defects (vacancy and interstitial) and tracks are formed along the path of the charged particles. β- and γ-rays can produce point defects and trapped electrons (holes) in insulating (ceramic) materials.

Materials	Chemical Form	Applications
Carbonates	$CaCO_3$	stalactite, travertine spring deposit, etc.
Biocarbonates	$CaCO_3$	coral, shell, foraminifera egg shell, calcrete
Sulfates	$CaSO_4$ $CaSO_4 \cdot 2H_2O$	anhydrite gypsum (desert deposit, cave deposit)
Bicarbonates	$NaHCO_3$	saline lake deposit
Phosphates	$Ca_5(PO_4)_3X$ $CaHPO_4$	hydroxyapatite, tooth, bone phosphate nodule
Silica	SiO_2	geological fault volcanic rock, altered rock
Silicates	$ZrSiO_4$	zircon feldspars, clay minerals
Ice & Dry Ice	H_2O, CO_2	comet, solid H_2O and CO_2
Organics	radicals * radicals metal ions *	food, crop, leather, paper alanine, sugar mummy, blood

3.8.1 *Sampling and Preparation*

(a) *Sampling* : Samples which have been *recrystallized* should be avoided unless you are interested in the age of recrystallization. Recrystallization always produces a younger age than expected. Note that brown iron minerals included in crystalline materials give signals which interfere with ESR signals of radiation–induced defects.

If possible, avoid samples whose *radiation environment* might have changed during the burial time, for example, by groundwater radioactivity. Samples close to wind–blown or water–deposited soils make the dose rate assessment difficult due to non–uniform radiation both in space and time.

Avoid samples which have been exposed to *light* and wrap them with aluminum foil to avoid excessive sunlight. Avoid samples previously examined by *X–rays* or *electron microscopy* since these processes produce defects. Even the light intensity of a surface microscope is high enough to destroy some defects. Avoid samples that might have been *heated* unless you are interested in the time after the heating event.

(b)   *Sample preparation* :   First, <u>wash off</u> any attached dirt with water in an ultrasonic bath. A slight acid treatment may be necessary to remove all the dirt and surface carbonate deposits.   A magnetic separator should be used to remove ferromagnetic minerals. Etch the sample with weak acid to remove the surface material of grains or small particles attached to large grains. Do not heat the sample or grind it into a fine powder. Use water cooled saws for cutting to avoid heating. Note that grinding reduces the content of unpaired electron spins and creates defects which trap electrons produced by irradiation.   An early interlaboratory comparison project for carbonate speleothems milled into fine powder failed because of the selection of inappropriate samples and the grinding effect (Hennig *et al*. 1983).

A sample <u>grain size</u> of 100 ~ 250 μm is preferable for an ordinary experiment. Grains of 40 ~ 80 μm are used for fault dating. Small grains of less than 100 μm have a tendency to stick to the quartz sample holder. Samples of large size crystalline materials show angular–dependent signals and may vary in density due to the degree of packing.

Use a <u>fixed amount</u> of the sample, for example, 200 or 300 mg for carbonate if available.

Table 3.2   Conditions for ESR measurements

Microwave
  Frequency υ X–band (9.5 GHz)
  Power   P   Appropriate power from the power dependence.
                     (Simply 1 mW if the signal is not saturated)

Modulation field
  Frequency f_m 100 kHz (commercial apparatus), not 80 Hz.
  Width ΔH_m 0.05 ~ 0.5 mT (or close to the peak to peak
                     if no signal overlaps)

Amplifier
  Gain   G $1 \sim 10{,}000 \times 10$,
                     Confirm the intensity at two gain setting.
  Time constant τ 0.1 or 0.3 s
                     (If noisy, 1 or 3 s with slow field sweep)

Magnetic field H
  Center field H_o 340 or 345 (335) mT at $g = 2.0$.
                     Calibrate with DPPH ($g = 2.0036$) or Mn^{2+}.
  Sweep width ΔH ± 5 mT or appropriate

Recorder & Computer
  Time constant τ Shorter than τ of the amplifier.
  Data acquisition   If the signal intensity is accurately determined,
                     any software is all right.

Temperature   Room temperature for ordinary signals.
                     Low temperature (77 K) for particular signals.

The appropriate condition depends on materials as will be mentioned in each chapter. Conditions used for measurement should be described in ESR papers for reproduction by other researchers.

3.8.3 *Artificial Irradiation*

(a) *Albedo effect* : Irradiate samples sandwiched between PMMA plates or placed in a thick glass holder (about 1 mm). The surface of the sample must be subjected to secondary electrons to the same extent as the inside, and to do this the sample should be covered with another material of the same density. Otherwise, the dose is generally lower at the surface than inside. This can be the cause of an inaccurate absorption dose and results in a fluctuation of the intensity – dose response curve. *X–rays should not be used* because the energy dependence is appreciable in the tens of kV region.

(b) *High dose rate effect* : Avoid a higher dose rate than 100 Gy/h (Ikeya 1985). A higher dose rate creates fewer electron centers as is known from TL dating studies (Groom *et al*. 1978). This *"high dose rate effect"* leads to an erroneously high *ED*. The effect is not due to the temperature rise by γ–ray heating but presumably due to the interaction among electrons and holes during irradiation. The sample holder should never be irradiated.

4.2 Dosimetric Quantities and Units

The most important dosimetric quantity is the "**absorbed dose**", which is defined as the mean energy imparted by an ionizing radiation to a material of unit mass (ICRP 1983, Brodsky 1976). The special name for the unit of Joule/kg, [J/kg], for the absorbed dose is "**gray [Gy]**". The Gy should not be confused with Giga (10^9) years in earth science. Radiation energy is usually expressed in MeV. The conversion of MeV per kg of material to Joule/kg and Gy is: 1 MeV/kg $= 1.6 \times 10^{-19} \times 10^6$ J/kg $= 1.6 \times 10^{-13}$ Gy. The TD or ED referred to in the previous chapter should be in Gy. The special old unit, rad, in erg/g (1 rad $= 10^{-2}$ Gy) will not be used here (Brodsky 1978).

The radiation quantity for an additive artificial irradiation of γ–rays should be expressed strictly as absorbed dose in Gy. Another quantity conventionally used is the "**exposure**". The exposure is defined as the absolute value of the total charge of ions (of one sign) produced in air of the unit mass when all the secondary electrons are liberated by the γ–ray photons. The unit of exposure is "**Coulomb/kg [C/kg]**". The conventional unit, roentgen [R], corresponds to 2.58×10^{-4} C/kg. One may say that an additive artificial irradiation was made in a photon field of an exposure in C/kg.

The exposure can be converted into the absorbed dose in a medium using a **conversion factor** f when electronic equilibrium exists (Attix *et al.* 1986). The conversion factor is expressed as

$$f = 33.7 \, (\mu_{en}/\rho)_{med} / (\mu_{en}/\rho)_{air} \qquad [\text{Gy/(C/kg))}] \quad , \qquad (4.1)$$

where μ is the *mass absorption coefficient* and ρ is the *density*. $(\mu_{en}/\rho)_{med}$ and $(\mu_{en}/\rho)_{air}$ are the *mass energy absorption coefficients* for the electro–magnetic radiation (photons) in the medium and air, respectively and depend on the energy of photons. Tables 4.1 and Table 4.2 show (μ_{en}/ρ) and f, respectively for various media.

Table 4.3 Disintegration, average energies of α-, β- and γ-rays and half-lives ($T_{1/2}$) of isotopes in ^{238}U-series.

Nucleus Z		Decay	$T_{1/2}$	Energy (MeV)					
				E_α [a]	(b_α)	E_β [a]	(b_β)	E_γ [a]	(b_γ)
92	^{238}U	α	4.468×10^9 a	4.198	(77)	0.00815		0.00136	
				4.149	(23)				
90	^{234}Th	β	24.10 d			0.0506	(73)	0.00935	
						0.0249	(19)		
91	^{234}Pa	β	1.17 min			0.8253	(98)	0.01880	
92	^{234}U	α	2.45×10^5 a	4.773	(72)	0.0110		0.00172	
				4.721	(28)				
90	^{230}Th	α	7.70×10^4 a	4.688	(76)	0.0127		0.00154	
				4.621	(23)				
88	^{226}Ra	α	1,602 a	4.785	(94.4)	0.0034		0.00674	
				4.602	(5.6)				
86	^{222}Rn	α	3.8235 d	5.490	(99.9)			0.5100	(0.00078)
84	^{218}Po	α, β	3.05 min	6.003	(100)	0.0705	(0.0002)	0.0000	
82	^{214}Pb	β	26.8 min			0.2072	(48)	0.2486	
						0.2274	(42)		
83	^{214}Bi	α, β	19.9 min			0.6482		0.6093	(46)
84	^{214}Po	α	1.64×10^{-4} s	7.685	(100)			0.00008	
82	^{210}Pb	β	22.3 a			0.0042	(80)	0.0130	(11)
						0.0161	(20)		
83	^{210}Bi	α, β	5.01 d			0.3889	(100)		
84	^{210}Po	α	138.4 d	5.297	(100)				
82	^{206}Pb		stable						

Table 4.4 Disintegration, average energies of α–, β– and γ–rays and half–lives ($T_{1/2}$) for isotopes in ^{232}Th–series.

Nucleus		Decay	$T_{1/2}$	Energy (MeV)			
Z	^{A}Element			E_α [a]	(b_α)	E_β	E_γ
90	^{232}Th	α	1.41×10^{10} a	4.010	(77)	0.0104	0.00130
				3.952	(23)		
88	^{228}Ra	β	5.75 a	–		0.0144	
89	^{228}Ac	β	6.31 h	–		0.4516	0.92870
90	^{228}Th	α	1.913 a	5.396		0.0184	0.00322
88	^{224}Ra	α	3.66 d	5.674		0.0021	0.00989
86	^{220}Rn	α	55.6 s	6.282			0.54970 [b]
84	^{216}Po	α	0.15 s	6.779			0.80600 [b]
82	^{212}Pb	β	10.64 h	–		0.1702	0.14810
83	^{212}Bi	α, β	60.6 min	2.172		0.4667	0.18460
84	^{212}Po (64.07%)	α	0.307 μs	5.633		–	–
81	^{208}Tl (35.93%)	β	3.07 min			0.2147	1.20589
82	^{208}Pb		stable				

4.3.2 Annual Dose Rate

The annual dose rate D is calculated using the radiation energy of the i–th disintegration element, E_i in MeV, the decay rate, λ_i in a^{-1} and the number of element, N_i, per kg of the material as

$$D = (1.60218 \times 10^{-19} \text{ J/eV})(10^6 \text{ eV})(\Sigma\, \lambda_i N_i E_i) \times 10^3 \quad [\text{mGy/a}]$$

$$= 1.60218 \times 10^{-10} (\Sigma\, \lambda_i N_i E_i) \quad [\text{mGy/a}] \quad . \tag{4.2}$$

The number of disintegration per year, $\lambda_i N_i$, is calculated using the half–life $T_{1/2}$ as $\lambda_i N_i = (\ln 2/T_{1/2\,i})N_i = (0.69315/T_{1/2\,i})N_i$ ($T_{1/2}$ of each nuclide is shown in Tables 4.3 and 4.4). For the **radioactive equilibrium** of ^{238}U, $\lambda_i N_i = \lambda_{i+1} N_{i+1} = \cdots = \lambda_{38} N_{38}$, where λ_{38} is the decay rate and N_{38} is the number of ^{238}U per kg of the material. Hence the dose rate is written as

$$D = 1.60218 \times 10^{-10} \lambda_{38} N_{38} \Sigma\, E_i \quad [\text{mGy/a}] \quad . \tag{4.3}$$

For example, for 1 ppm ^{238}U, i.e., 1 mg per kg of the material,
1) $N_{38} = 6.02214 \times 10^{23} \times (10^{-3}/238.05) = 2.5300 \times 10^{18}$ and
     $\lambda_{38} = 0.69315/(4.468 \times 10^9 \text{ a}) = 1.55136 \times 10^{-10}\ a^{-1}$ are obtained.
2)   Then, $\underline{D = 0.062879 \times \Sigma\, E_i}$ is used to calculate the dose rate.

For 1 ppm ^{232}Th, $\underline{D = 0.020514 \times \Sigma\, E_i}$ is used.

$$D_\alpha = C_U D_{U-\alpha} + C_{Th} D_{Th-\alpha} \quad , \qquad\qquad (4.4)$$

$$D_\beta = C_U D_{U-\beta} + C_{Th} D_{Th-\beta} + C_{K,Rb} D_{K,Rb-\beta} \quad , \qquad (4.5)$$

$$D_\gamma = C_U D_{U-\gamma} + C_{Th} D_{Th-\gamma} + C_K D_{K-\gamma} \quad , \qquad\qquad (4.6)$$

Table 4.5 The annual dose rates for $\alpha-$, $\beta-$ and $\gamma-$rays for radioactive equilibrium of $^{238}U-$ and $^{232}Th-$series disintegration and for natural potassium and rubidium [a].

Disintegration	D_α [b]	D_β [b]	D_γ [b] (mGy/a)
U (1 ppm)	2.3195 (1.0006)	0.12181 (0.04909)	0.09259 (0.00324)
^{238}U (1 ppm)	2.6916 (1.1528)	0.14273 (0.05739)	0.10207 (0.00248)
^{232}Th (1 ppm)	0.7371 (0.3091)	0.02762 (0.01019)	0.05092 (0.01935)
K_2O (1%)	--	0.67805	0.20287
Rb_2O (1 ppm)	--	0.00047	--
K_2O (1%) & Rb_2O (50 ppm)	--	0.70170	0.20287
$^{238}U \longrightarrow {}^{234}Pa$	0.26321	0.05568	0.001856
^{234}U	0.29899	0.00069	0.000108
$^{230}Th \longrightarrow {}^{206}Pb$	2.1294 (0.5906)	0.08636 (0.0010)	0.10824 (0.00052)
$^{226}Ra \longrightarrow {}^{206}Pb$	1.8388 (0.3001)	0.08556 (0.0002)	0.10815 (0.00042)
$^{222}Rn \longrightarrow {}^{206}Pb$	1.5387 (--)	0.08534 (--)	0.10772 (--)
$^{235}U \longrightarrow {}^{207}Pb$	0.11518 (0.05786)	0.00468 (0.00202)	0.001857 (0.001429)

a) The dose rates are based on the data presented by Liritzis and Kokkoris (1992) and revised by Ogoh *et al.* (1993). Further revision made the table closer to that by Nambi and Aitken (1986) against the reported discrepancy of $2 \sim 3\%$.

b) Numbers in parentheses are the dose rates for 100% loss of ^{222}Rn or ^{220}Rn. The factors of 0.8322 and 0.8788 are multiplied for the dose rate of 1 ppm of UO_3 and ThO_2, and the dose rates are divided by 0.8301 and 0.9158 for 1% of K and Rb, respectively.

4.4.2 *Quality Effect : k-values for α-Rays*

Considering the efficiencies of stable defect production by α-, β- and γ-rays, the effective annual dose rate may be written as

$$D = k_\alpha D_\alpha + k_\beta D_\beta + k_\gamma D_\gamma \; , \qquad (4.8)$$

where k_α, k_β and k_γ are defect production efficiencies relative to those of the artificial irradiation. We usually disregard the k-value for β- and γ-rays ($k_\beta = k_\gamma = 1$) and leave only k_α as the k-value. Then, Eq. (4.8) becomes
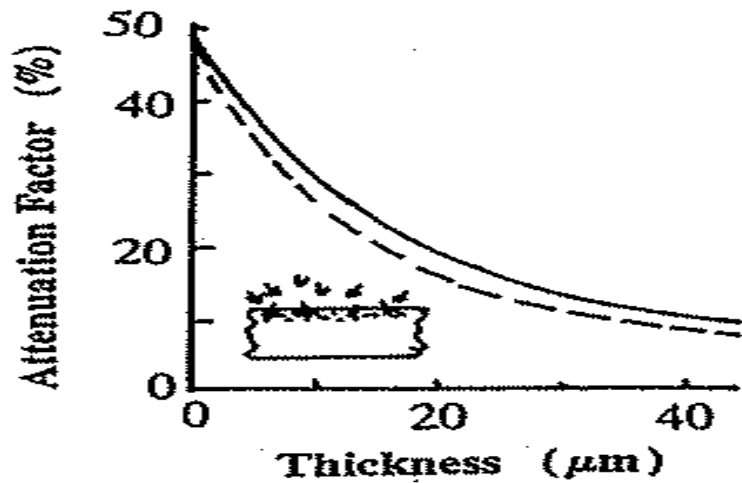
$$D = k D_\alpha + D_\beta + D_\gamma \; . \qquad (4.9)$$

If α-rays are used as an additive artificial dose to get the ED_α, the ratio of ED_α to that by γ-rays gives the k-value, i.e.,
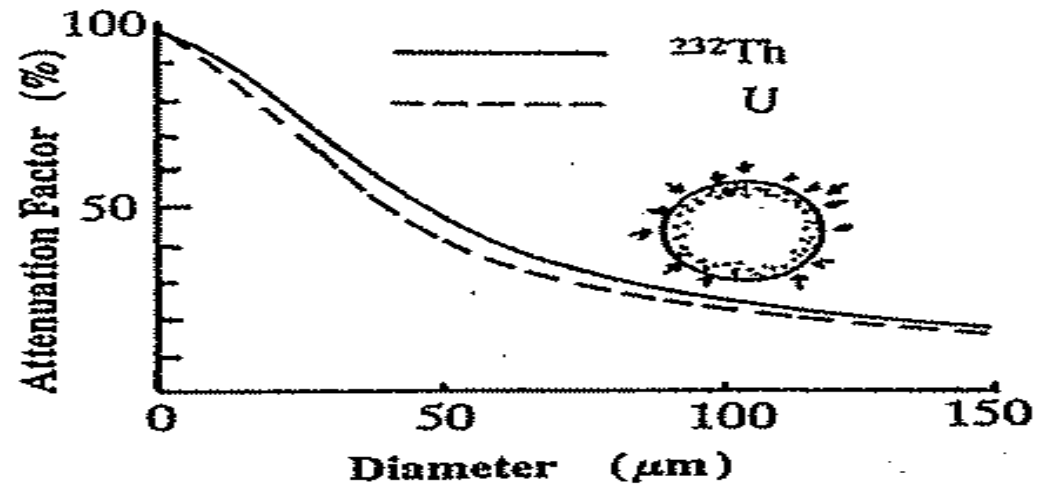
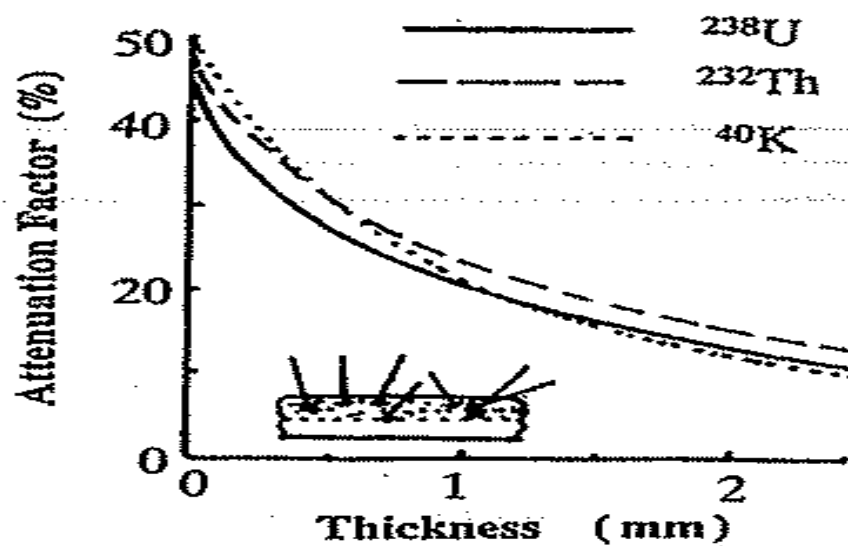$$k = ED_\gamma / ED_\alpha \; , \qquad (4.10)$$

Dose Attenuation Factor

(a) α-dose attenuation

(b) α-dose attenuation

(c) β-dose attenuation

(d) β-dose attenuation