Course of Geothermics

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Course Outline:

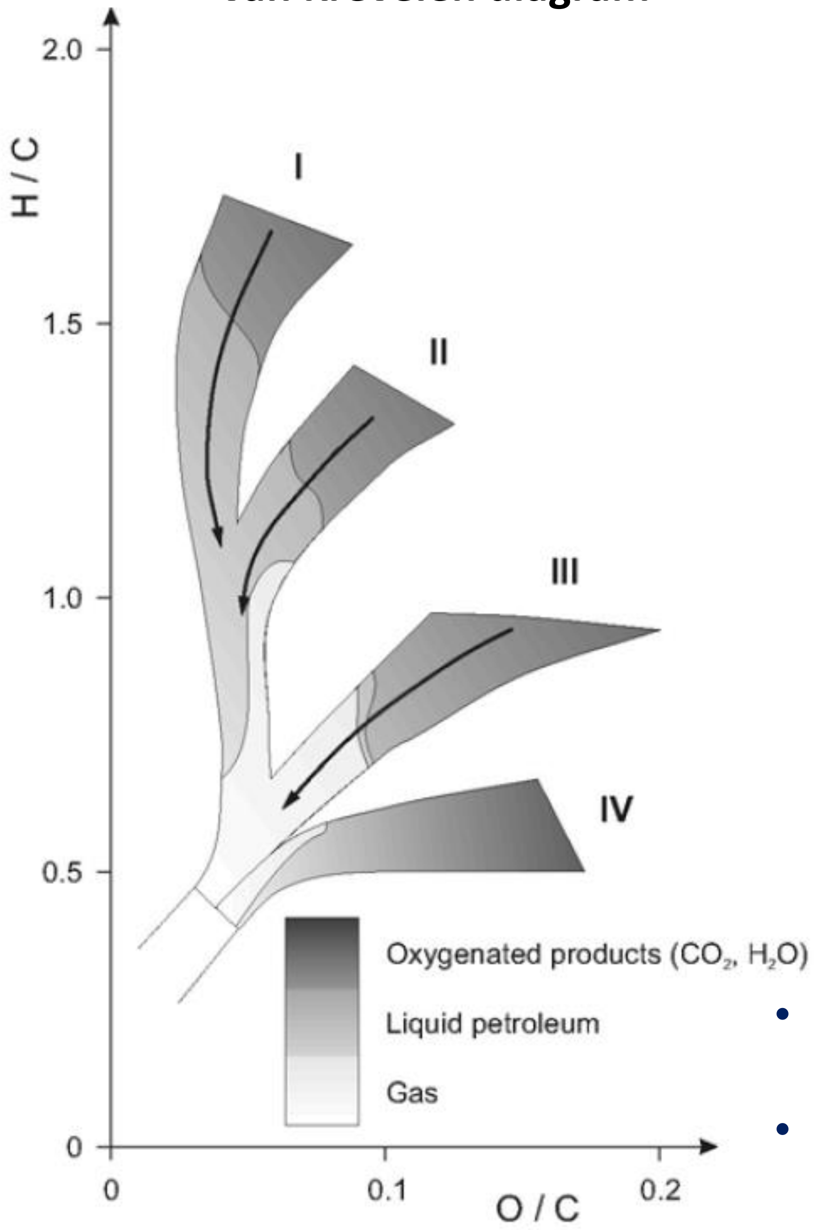
1. Thermal conditions of the early Earth and present-day Earth’s structure
2. Thermal parameters of the rocks
3. Thermal structure of the lithospheric continental areas (steady state)
4. Thermal structure of the lithospheric oceanic areas
5. Thermal structure of the lithosphere for transient conditions in various tectonic settings
6. Heat balance of the Earth
7. Thermal structure of the sedimentary basins
8. **Thermal maturity of sediments**
9. Mantle convection and hot spots
10. Magmatic processes and volcanoes
11. Heat transfer in hydrogeological settings

Thermal evolution of sedimentary basins

- **Hydrocarbons** are derived from the metamorphism of organic material, OM (everything from woody cell walls, spore cases, leaf cuticles, pollen, resins, algae, bacteria and plankton), a process involving the expulsion of volatiles, gas, liquids, and oil.
- The **thermal maturity** of a rock is a measure of the degree to which this metamorphism has progressed (or degree of thermal degradation of the OM).
- Sedimentary OM can be divided into **bitumen:** the fraction of sedimentary OM soluble in typical organic solvents (e.g., chloroform, benzene) and **kerogen:** the fraction of sedimentary OM insoluble, left in the rocks after washing with solvents.
- The type and maturity of kerogen depends on the content of carbon (C), hydrogen (H), and oxygen (O).
- The temperature limits of the **oil window** are within the range of about 50-150 °C (323–423 K) and they depend on the age of source rocks with significant decrease in T with increase in age.
- For deposits of ~300 Myr, the formation of oil starts at T <50°C and continues up to T ≥100°C and gas is formed above this limit up to T ~215°C. Above that T both oil and gas are destroyed. For rocks ~10 Myr, the oil generation starts at T of ~83°C and continues to about 170°C, above which gas is usually formed to T of ~300°C.
- Within the oil window increasingly more oil is generated with increase in T until maximal production is reached, at which point the quantity of oil decreases and increasingly more gas is formed.

Thermal evolution of sedimentary basins
van Krevelen diagram

van Krevelen diagram



I Hydrogen-rich, oxygen-poor: they derive from the deposition in lakes as bacterial and vegetable waxes or algae.

II Intermediate H:C and O:C ratios: they derive from bacterially altered marine organic matter. With some terrigenous material (e.g., leaf cuticles and spores).

III Hydrogen-poor, oxygen rich: they derive from terrigenous woody OM and cuticular waxes, associated with near-shore deltaic environments.

IV very low H:C, high O:C: they consist of highly reworked OM with no hydrocarbon generative potential.

- **The kerogens trace characteristic path through the van Krevelen diagram during the gradual maturation (alteration of atomic ratios).**
- **The amount of petroleum generated and expelled increases with the increase of H/C.**

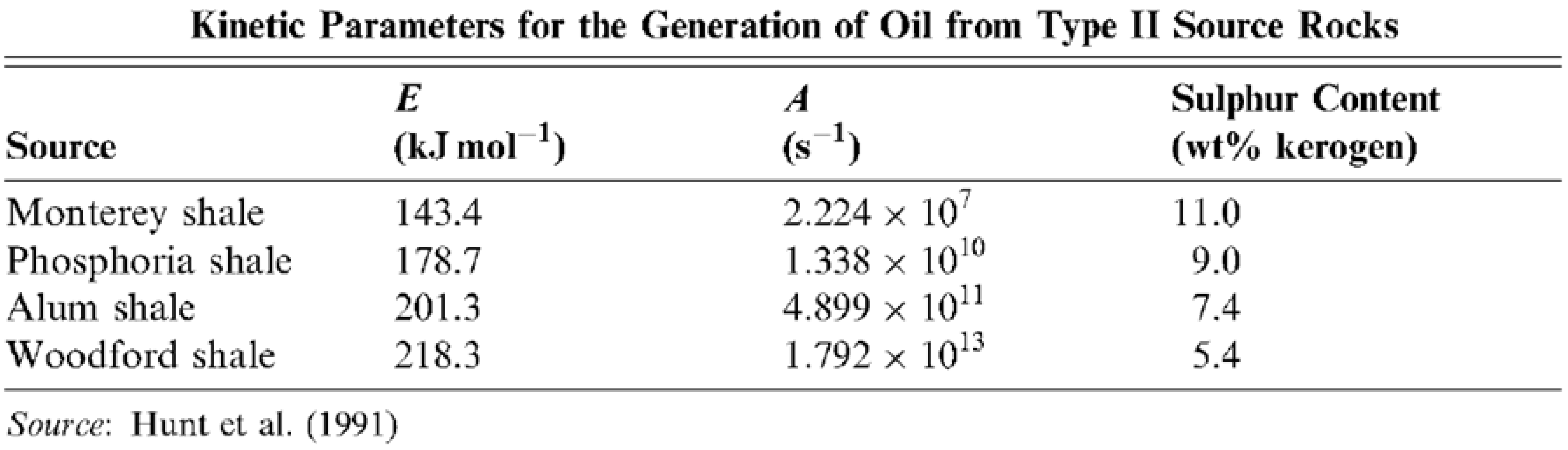
Thermal evolution of sedimentary basins (chemical kinetics)

- Temperature (exponential dependence) and time (linear dependence) are the main factors influencing OM maturation.
- Arrhenius equation, expressing the relationship between temperature and rate of chemical reactions, suggests that reaction rates (*k*) increases exponentially with *T*, but the rate of increase in reaction rate slows down with increasing *T*:

$$k(T) = A \times \exp(-E/RT)$$

A=frequency factor (10^{13}-10^{16} s^{-1}), it is possibly related to the vibrational frequency of the reacting moleculas
E=Activation energy, 160-340 kJ mol^{-1} (energy barrier that must be overcome before the reaction can proceed)
R=universal gas constant (8.314 JK^{-1} mol^{-1})

E has been determined using **pyrolysis**, which artificially forces a source rock to release all of its potential hydrocarbon product, by increasing *T* at constant heating rate, *r*.

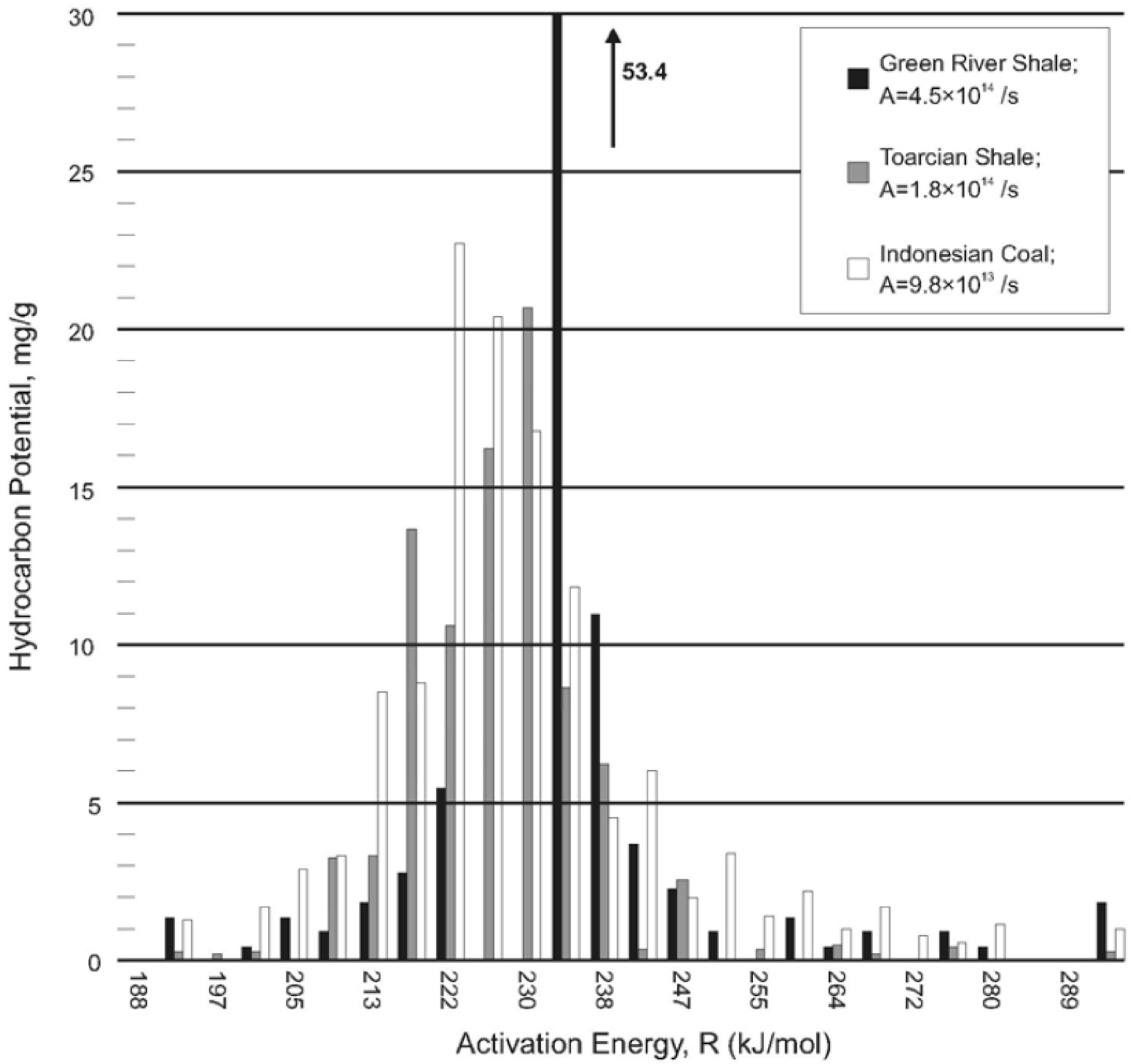


Kinetic Parameters for the Generation of Oil from Type II Source Rocks

Source	*E* (kJ mol^{-1})	*A* (s^{-1})	Sulphur Content (wt% kerogen)
Monterey shale	143.4	2.224×10^{7}	11.0
Phosphoria shale	178.7	1.338×10^{10}	9.0
Alum shale	201.3	4.899×10^{11}	7.4
Woodford shale	218.3	1.792×10^{13}	5.4

Source: Hunt et al. (1991)

Thermal evolution of sedimentary basins
(chemical kinetics)



Kinetic data derived for the generation of hydrocarbon for Type I and Type II kerogens

Thermal evolution of sedimentary basins (chemical kinetics)

We can represent the kerogen as initially having a certain potential to produce hydrocarbons, ***M_0***, which decreases as the hydrocarbon yield, ***m***, increases:

$$-(\partial M/\partial t) = (\partial m/\partial t) = k \times (\mathbf{M}_0 - \mathbf{m})$$

k=reaction rate

The rate at which hydrocarbons are released from samples is *T* dependent:

$$\frac{\partial \mathbf{m}}{\partial T} = \sum_{i=1}^{n} \mathbf{M}_{i0} \frac{A}{r} \left(-\frac{E_i}{RT} - \frac{A}{r} \mathbf{J}_i \right) \qquad \mathbf{J}_i = \int_0^T \exp\left(-\frac{E_i}{RT} \right) dT$$

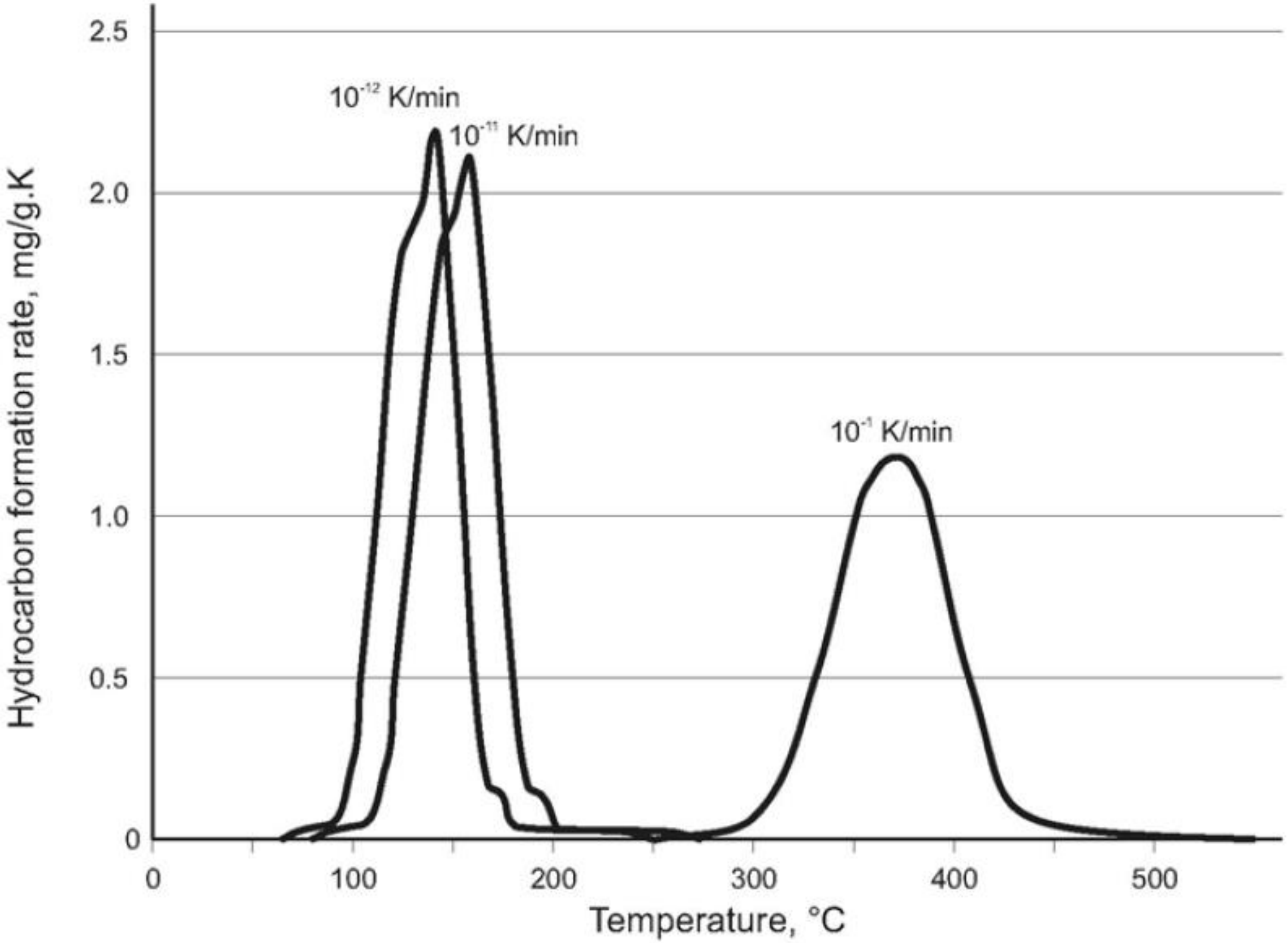
r=heating rate

- According to Connan (1974), the threshold of the principal zone of oil generation is related to the logarithm of the age of the formation.
- The cumulative effect of increasing *T* can be evaluated from the maturation integral (the reaction rate integrated over time), estimated if decompacted burial history, heat flow through time, and thermal conductivity of sedimentary basin is known:

$$C = A \int_0^t \exp(-E_a/RT) + C_0$$

C_0=original level of maturation of the organic material at *t*=0 (depositional time)

Thermal evolution of sedimentary basins (chemical kinetics)

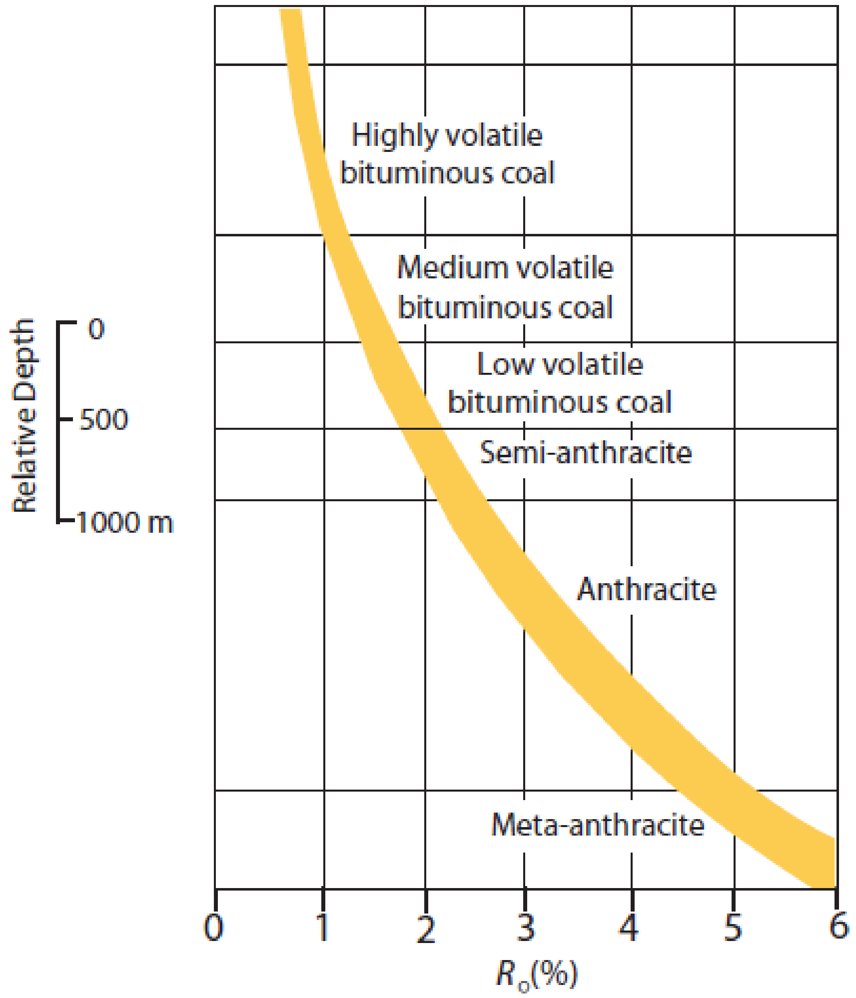


- Petroleum forms at a lower and narrower *T* range at geological heating rates than during pyrolysis.
- *T* of the sediments should be in the range 70-120°C for significant period of time, at cooler *T* the reaction rate is too slow to produce hydrocarbons, while at higher *T*, the rate is too rapid to allow expulsion before the oil degrades.

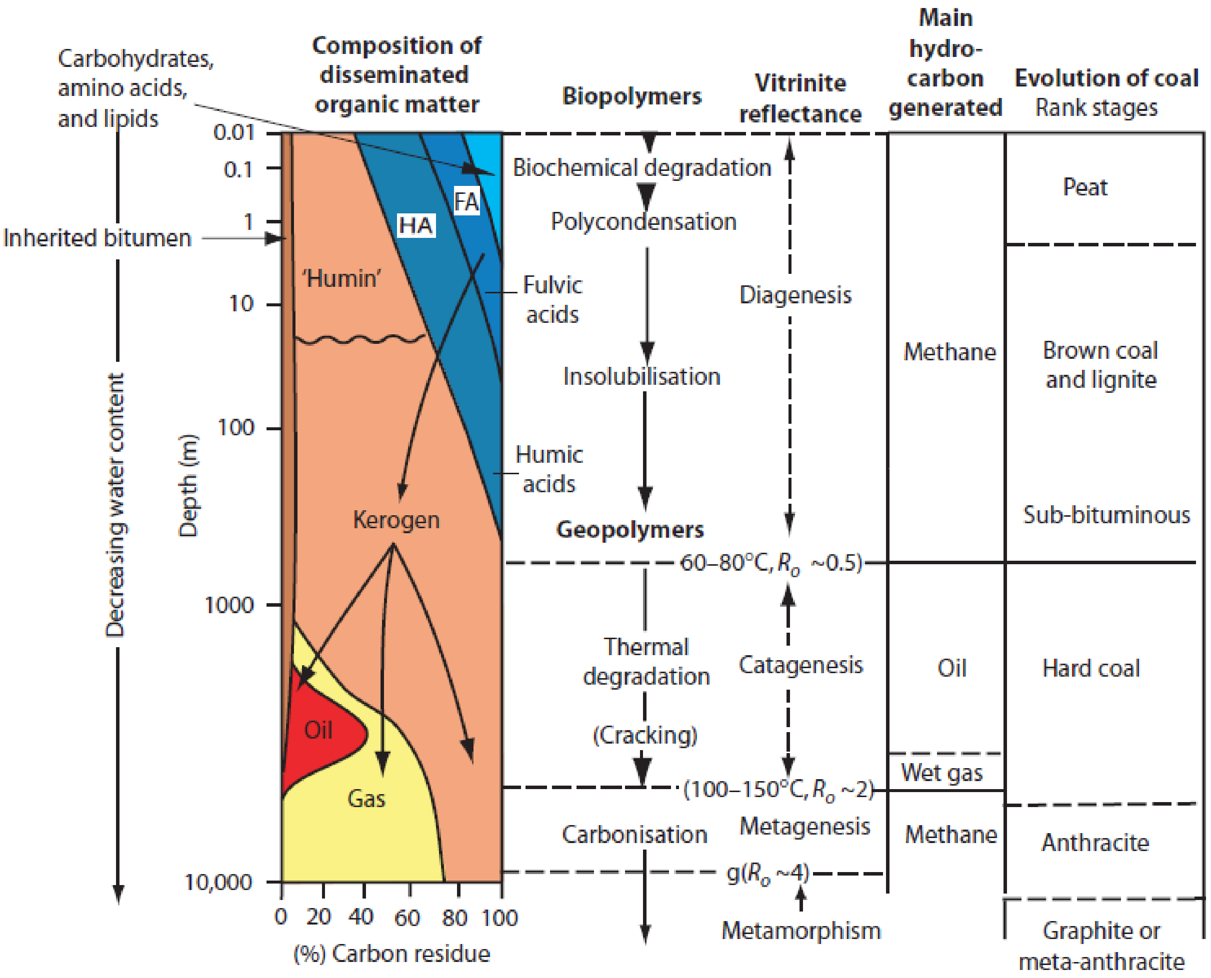
Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

- **Vitrinite is a detrital plant material**, transported with other sediments to the final deposition zone. It is a class of maceral, one of the microscopic constituents of coal and dispersed OM.
- Macerals can be broadly divided into three classes on the basis of morphology, reflectance in white light, and fluorescence:
- **Liptinite**: It is derived from the waxy, lipid-rich and resinous art of plants (e.g., leaf cuticles, algae). Liptinite is the least reflective among the macerals and fluoresces under ultraviolet light.
- **Vitrinite**: It is derived from plant cell walls, cell contents or precipitated gels. The reflectance of vitrinite lies somewhere between that of liptinite and inertinite, and increases with the rank of coal. It may show a weak brownish fluorescence.
- **Inertinite**: It has the same derivation of vitrinite, but has been oxidised, altered or degraded in early stage of coal formation. Inertinites are the most reflective, but do not fluorescence.
- The percentage of carbon increases with increase of burial time and *T*. A higher **reflectance** implies that the coal is of a higher rank (percentage) and has been raised to a higher *T* or buried for long time.
- **Reflectance (R_0) or Vitrinite Reflectance (VR)** is a measure of the percentage of an incident beam of polarized white light that is reflected off a polished surface (optical parameter) and gives an indication of the geothermal gradients in the history of the basins.
- Estimates of paleo-*T* based on the analysis of VR relies on the **property of vitrinite to undergo increasing reflectance with increasing *T***. The amount of light reflected by vitrinite particles (R_0) is affected by time and *T* of burial and irreversibly changes with increases in *T*.
- **Vitrinite is an anisotropic, bireflectant substance**: There are two identical reflectance maxima at 180° separation, with minima mid-way between the maxima. The magnitude of anisotropy is related to sediment compaction and increases with increasing rank.

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

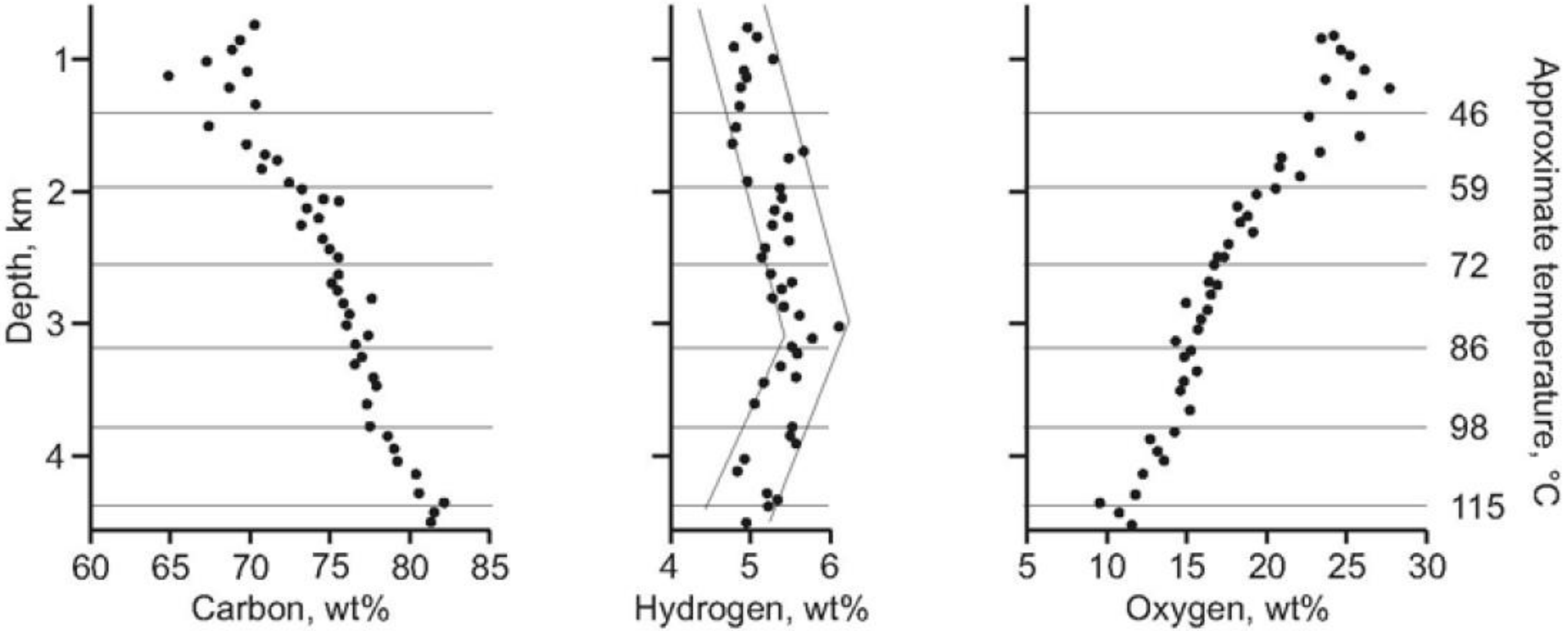


Evolution of organic matter and coal



- **VR is the most widely used indicator of maturity of OM. R_0< 0.5-0.7% indicates that the source rocks are immature.**
- **Progressive maturation of OM causes a coalification process, which changes peat to anthracite through brown coal and bituminous coal.**

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)



Changing atomic composition of coal with *P* and *T*

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

Since vitrinite is an anisotropic substance, there are two methods to estimate the reflectance:

(1) It records the maximum reflectance (**R_{vMAX}**) for each vitrinite grain. It is more precise, but it requires rotation of the microscope through 360° to detect the maxima.

(2) It records only a single randomly oriented reflectance for each grain (**R_0,R_0%,R_v%**). It is faster, but less precise.

$$R_{v\,\max}(\%) = R_o(\%)\ \times 1.066$$

The thermal history of a rock can be broken down into a number of discrete *T* intervals (Lopatin, 1976), so that the thermal maturity or time-temperature index (*TTI*) of a kerogen is:

$$\mathrm{TTI} = \Sigma(\Delta t_i)(2^{n_i})$$

Δt_i=time(Myr) spent by the kerogen in the *i*th *T* interval
n_i=integer weighting factor for the *i*th interval

Each *T* interval covers 10°C and is assigned a weighting factor n_i (which changes by 1 for each 10°C). The reference interval for which n=0 corresponds to 100-110°C.

According to McKenzie (1981), the TTI function is a continuous integral: $\mathrm{TTI} = \int_{t_s}^{t_f} 2^{[(T_t-105)/10]}dt$

T_t=time-dependent temperature (C°), t_s and t_f =start and finish times (Myr)

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

Question*:* Organic matter is deposited within sediment at a surface temperature of 20°C. It is buried to a temperature of 100°C at a constant rate over a period of 40 Ma. Sedimentation then slows, and after another 30 Ma the temperature has increased to 130°C. How mature is the sediment, expressed in terms of TTI?

(1) $$\mathrm{TTI} = \Sigma(\Delta t_i)(2^{n_i})$$

(2) $$\mathrm{TTI} = \int_{t_s}^{t_f} 2^{[(T_t - 105)/10]} dt$$

1st Answer*:* In the first period of burial, the sediment passes through eight temperature intervals in 40 Ma, spending 5 Ma in each. The initial interval (20-30°C) has a weighting factor n^{-8}.

$$\mathrm{TTI} = \Sigma(\Delta t_i)(2^{n_i}) = (\Delta t_i)\Sigma(2^{n_i}) = 5 \times (2^{-8} + 2^{-7} + 2^{-6} + 2^{-5} + 2^{-4} + 2^{-3} + 2^{-2} + 2^{-1}) = 4.98$$

The sediment then spends 10 Myr in each of the next three temperature intervals, *n* = 0, 1 and 2. The total maturity is then:

$$\mathrm{TTI} = 4.98 + 10 \times (2^0 + 2^1 + 2^2) = 74.98$$

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

2nd Answer*:* The thermal history should be broken into two segments:
The first:

$T_t = 20 + 2t,$ $\quad 0 < t < 40$ Ma

$$\mathrm{TTI} = \int_{t_s}^{t_f} 2^{[(T_t-105)/10]}dt$$

the second:

$T_t = 60 + t,$ $\quad 40 < t < 70$ Ma

$$\mathrm{TTI} = \int[2^{(-8.5+0.2t)}dt = 2^{-8.5}\int[2^{0.2t}]dt = 2^{-8.5} \times [1/(0.2 \times \ln 2)] \times [2^8 - 2^0] = 5.08$$

$$\mathrm{TTI} = \int[2^{(-4.5+0.1t)}dt = 2^{-4.5}\int[2^{0.1t}]dt = 2^{-4.5} \times [1/(0.1 \times \ln 2)] \times [2^7 - 2^4] = 71.41$$

$$\mathrm{TTI} = 5.08 + 71.41 = 76.49$$

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

Waples (1980) presented a calibration between *TTI* (using discrete *T* intervals) and the reflectance of vitrinite:

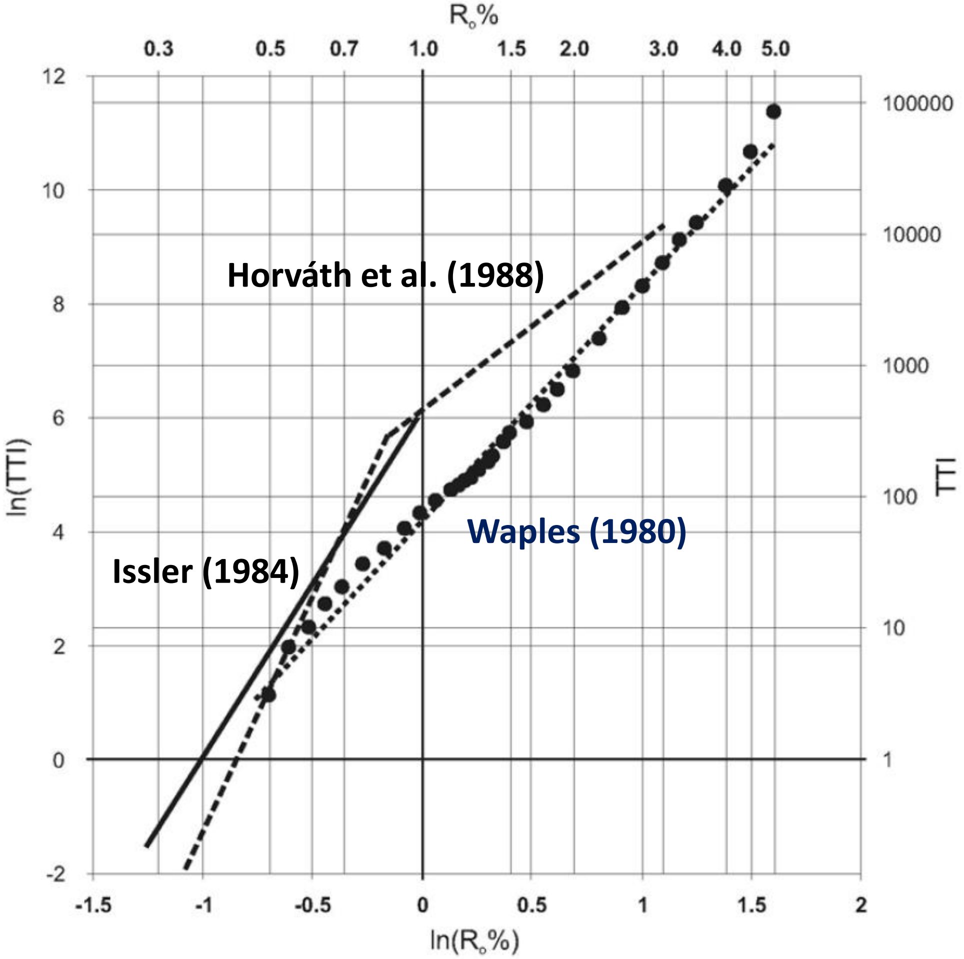
$$\ln(\mathrm{TTI}) = A \times \ln(R_o) + B$$

A=4.144 B=4.168
(over the range $0.5 \leq R \leq 5.0\%$)

The estimates of vitrinite reflectance are used to estimate the thermal maturity of a kerogen in terms of *TTI* (forward modelling).

According to **Issler (1984):**
A= 6.184 and B=6.115
(over the range $0.29 \leq R_0 \leq 0.98\%$).

According to **Horváth et al. (1988)**:
A=8.278, B=6.992 for *TTI* <292 (for $R_0 < 0.853\%$)
A=2.936 B=6.143 for *TTI* > 292 (for $R_0 > 0.853\%$)



Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

what VR value should we expect?
According to Waples' (1980) calibration:

$$\ln(\mathrm{TTI}) = A \times \ln(R_o) + B$$

$$\ln(74.98) = 4.144 \times \ln(R_o) + 4.168$$

$$\ln(R_o) = [\ln(74.98) - 4.168]/4.144 = 0.036$$
$$R_o = 1.04\%$$

According to Issler (1984) calibration:

$A = 6.184$ and $B = 6.115$: $\ln(76.49) = 6.184 \times \ln(R_o) + 6.115$ R_0=0.75%

According to Horvàth et al. (1988) calibration:

$A = 8.278$ and $B = 6.992$: $\ln(76.49) = 8.278 \times \ln(R_o) + 6.992$ R_0=0.73%

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

It is possible to estimate the max paleo *T* (T_{max}) experienced by a sample of vitrinite from its reflectance (from a compilation of > 600 R_0-T_{MAX} (°C) data pairs):

$$\ln(R_o) = 0.0078 \times T_{\max} - 1.2$$

Burial *T* increases linearly with time, considering burial depth proportional to $\sqrt{t}$ and thermal gradient proportional to: $1\sqrt{t}$

For t_s=0 $$T_t = T_s + (T_f - T_s)t/t_f \longrightarrow \mathrm{TTI} = \int_{t_s}^{t_f} 2^{[(T_t-105)/10]}dt$$

$$\mathrm{TTI} = 2^{[(T_s-105)/10]} \times [2^{[(T_f-T_s)/10]} - 1] \times 10t_f/[(T_f - T_s) \times \ln(2)]$$

Since “-1” is negligible:

$$T_f = P \times \ln(Q \times (T_f - T_s)) \qquad P = [10/\ln(2)] = 14.427$$

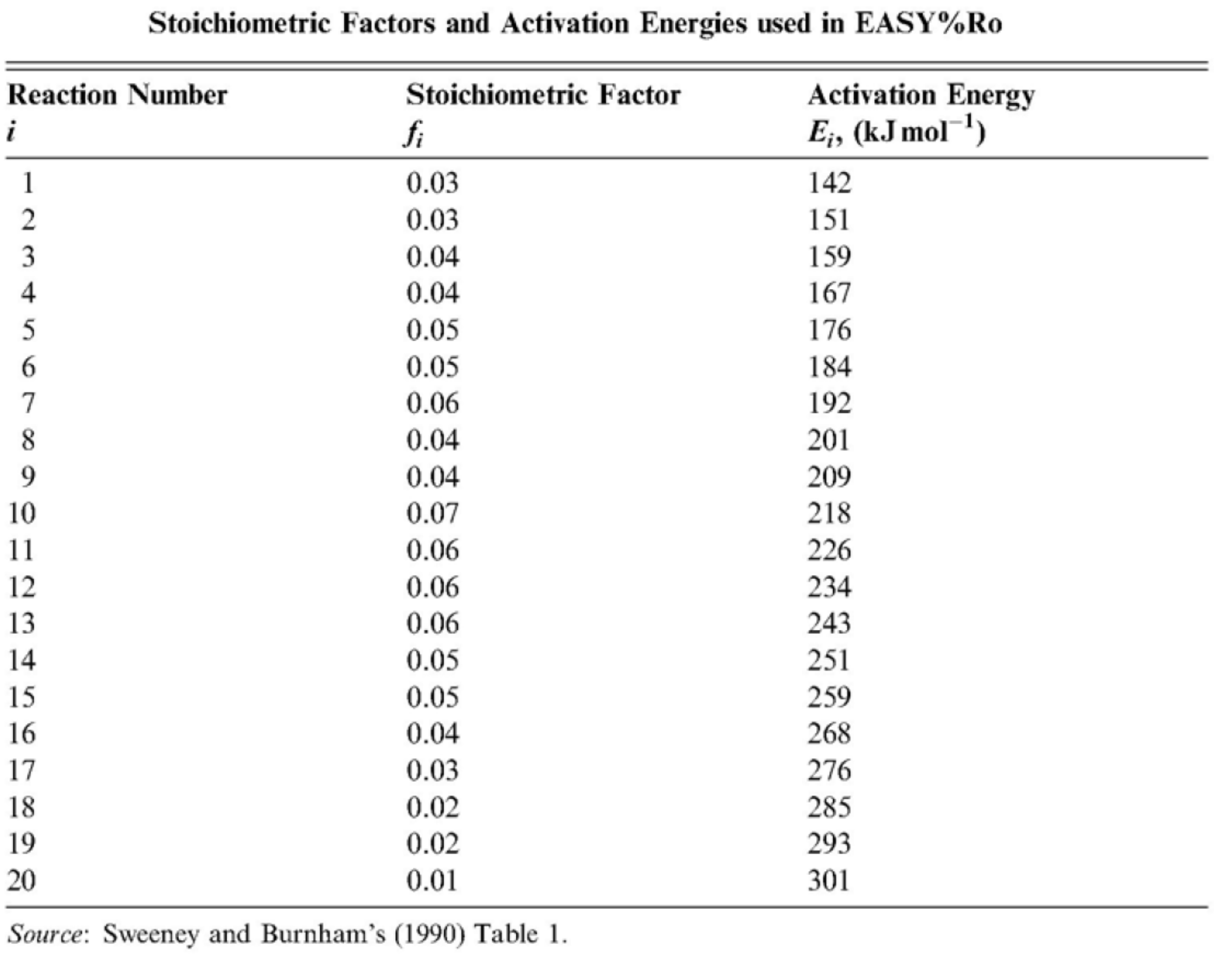
$$Q = \mathrm{TTI} \times 2^{(105/10)}/(P \times t_f)$$

for $T_f > [T_s + 2\exp(T_s/P)/Q]^\circ\mathrm{C}$. We can rapidly find T_f value

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

To model VR, EASY%R_O uses a set of 20 reactions with a common pre-exponential factor A=1.0x10^{13} s^{-1} and is calibrated in the range 0.3% < *Ro* < 4.5%, and for heating rates in the range of of ~ 10^{-15}-10^{-5} K s^{-1}.

EASY%R_O breaks the thermal history of a sedimentary basin into segments of constant heating rate



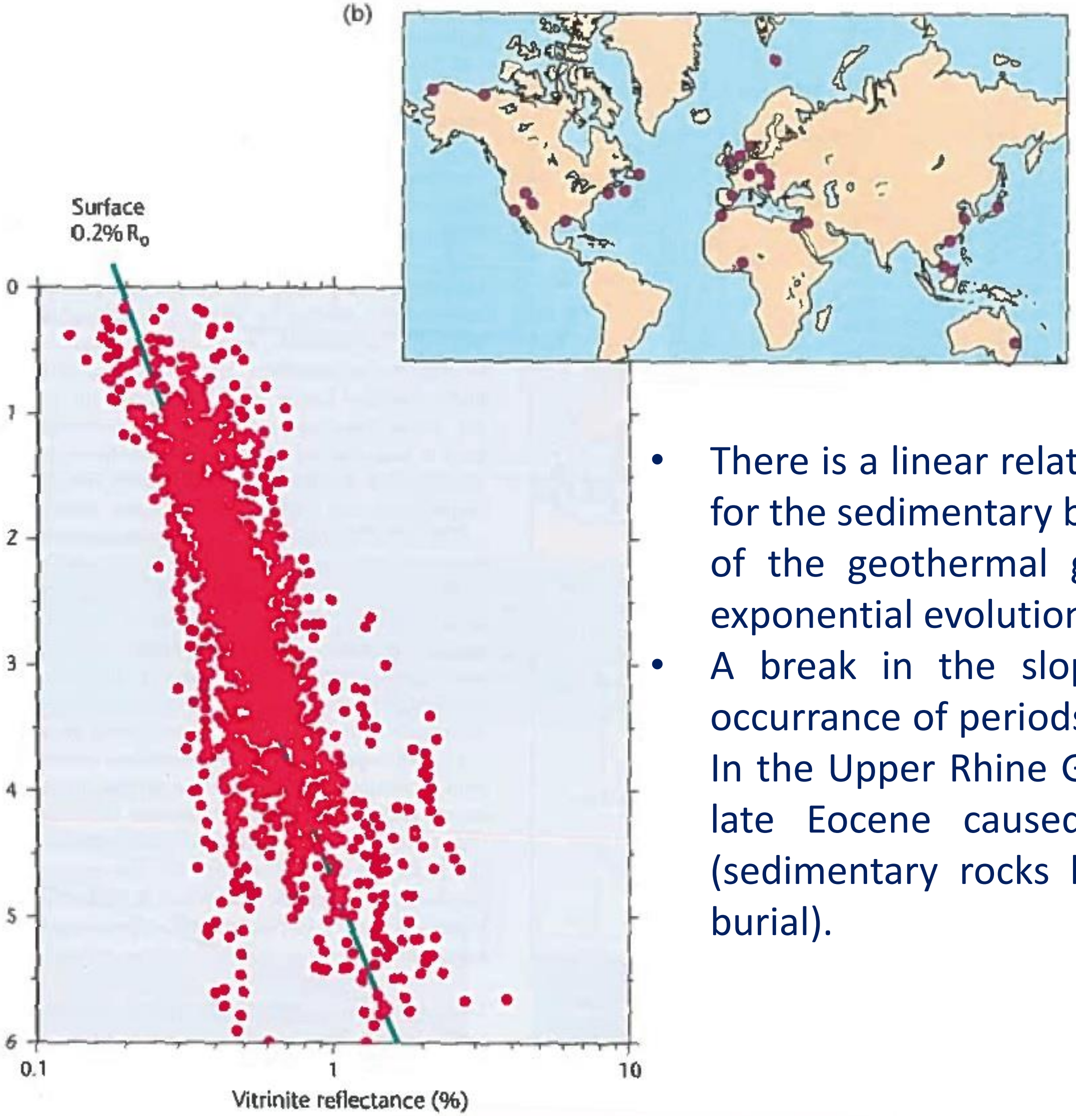
Stoichiometric Factors and Activation Energies used in EASY%Ro

Reaction Number i	Stoichiometric Factor f_i	Activation Energy E_i, (kJ mol^{-1})
1	0.03	142
2	0.03	151
3	0.04	159
4	0.04	167
5	0.05	176
6	0.05	184
7	0.06	192
8	0.04	201
9	0.04	209
10	0.07	218
11	0.06	226
12	0.06	234
13	0.06	243
14	0.05	251
15	0.05	259
16	0.04	268
17	0.03	276
18	0.02	285
19	0.02	293
20	0.01	301

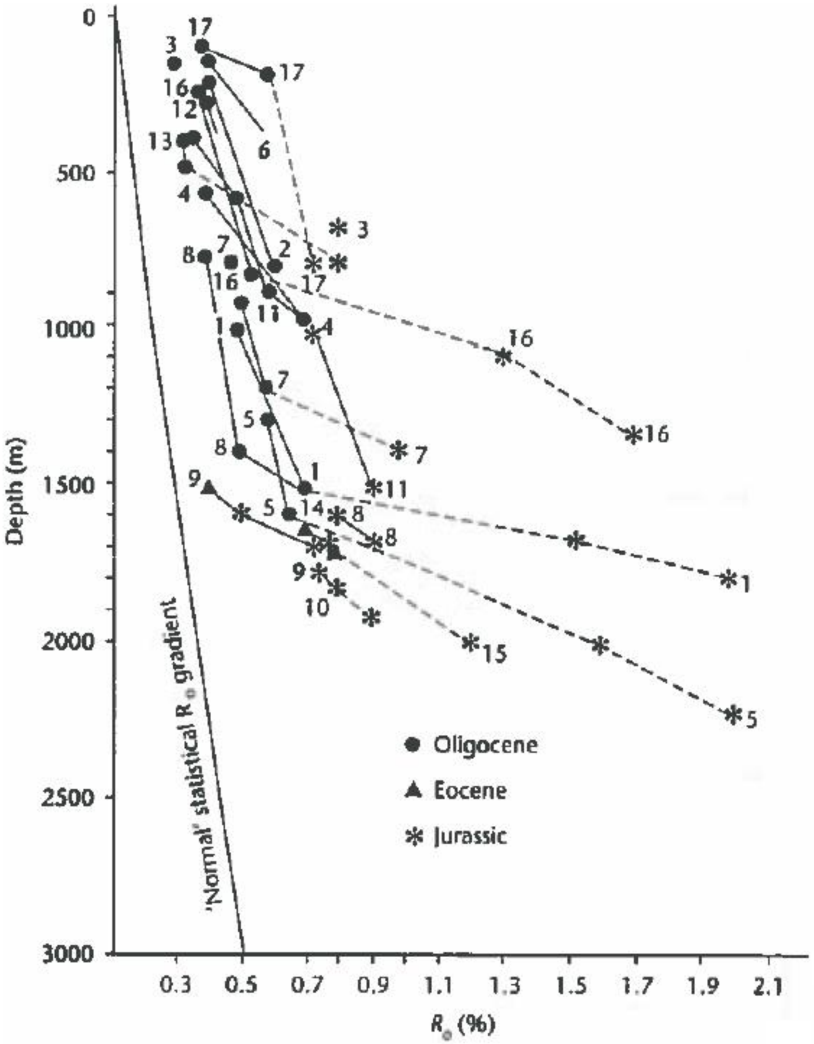
Source: Sweeney and Burnham's (1990) Table 1.

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

28 World extensional basins

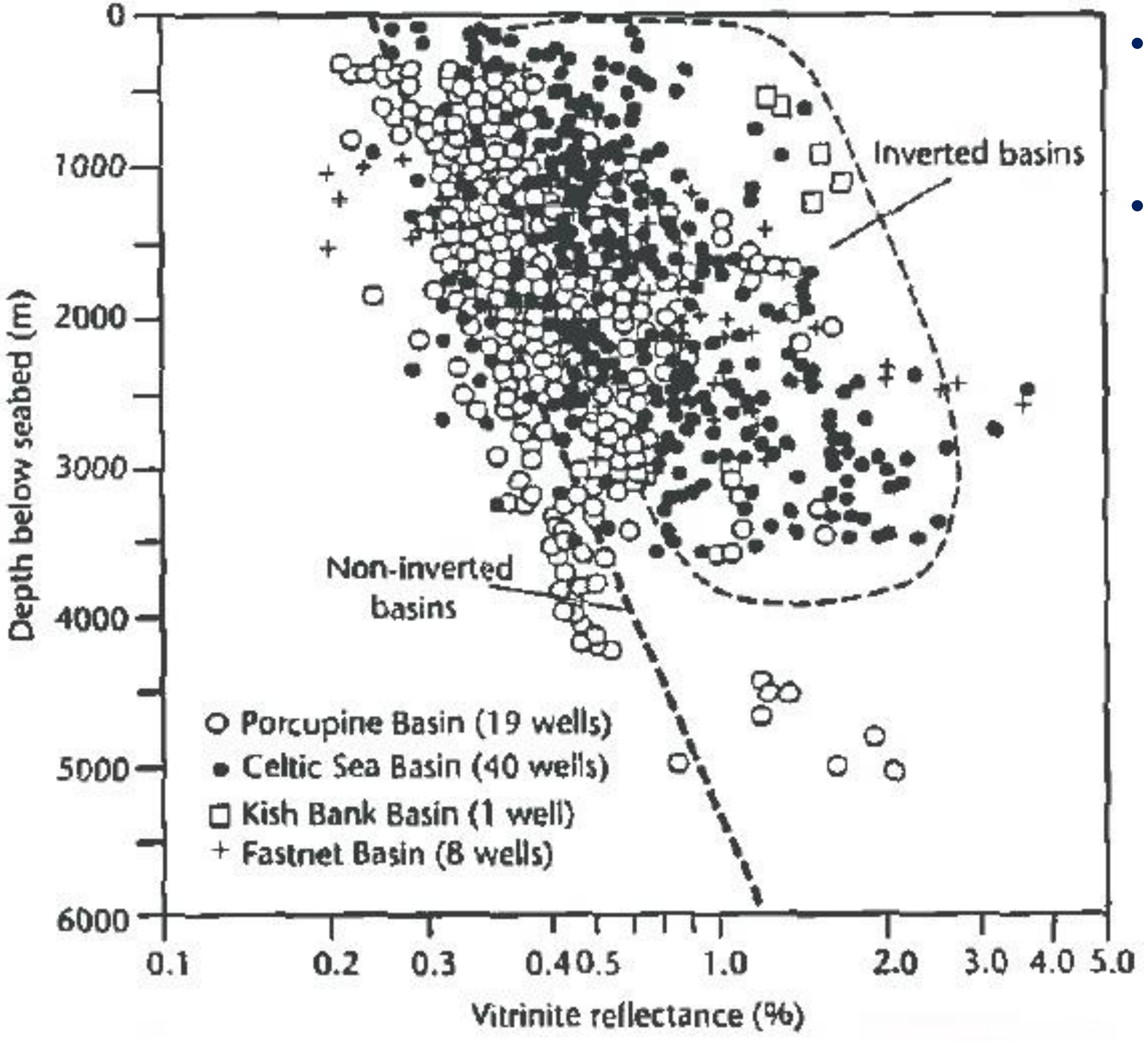


Upper Rhine Graben



- There is a linear relationship between depth and log R_0 for the sedimentary basins, charcterized by no variation of the geothermal gradients with time (due to the exponential evolution of *OM* with *T*).
- A break in the slope of these curves identify the occurrance of periods of different geothermal gradient: In the Upper Rhine Graben, the rifting occurred in the late Eocene caused higher than normal maturity (sedimentary rocks have high R_0 in relation to their burial).

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)



- Basins that experienced tectonic uplift and exhumation show R_0 profiles indicating higher thermal maturity than expected from their depth of burial.
- Maximum depths of burial can be estimated from R_0 values:

$$\ln R_0 = 0.00096T - 1.4$$ (Barker and Pawlewicz, 1986)

where *T* must be converted to depth using geothermal gradient (high uncertainty)

Paleotemperature Indicators
Vitrinite Reflectance (*VR*)

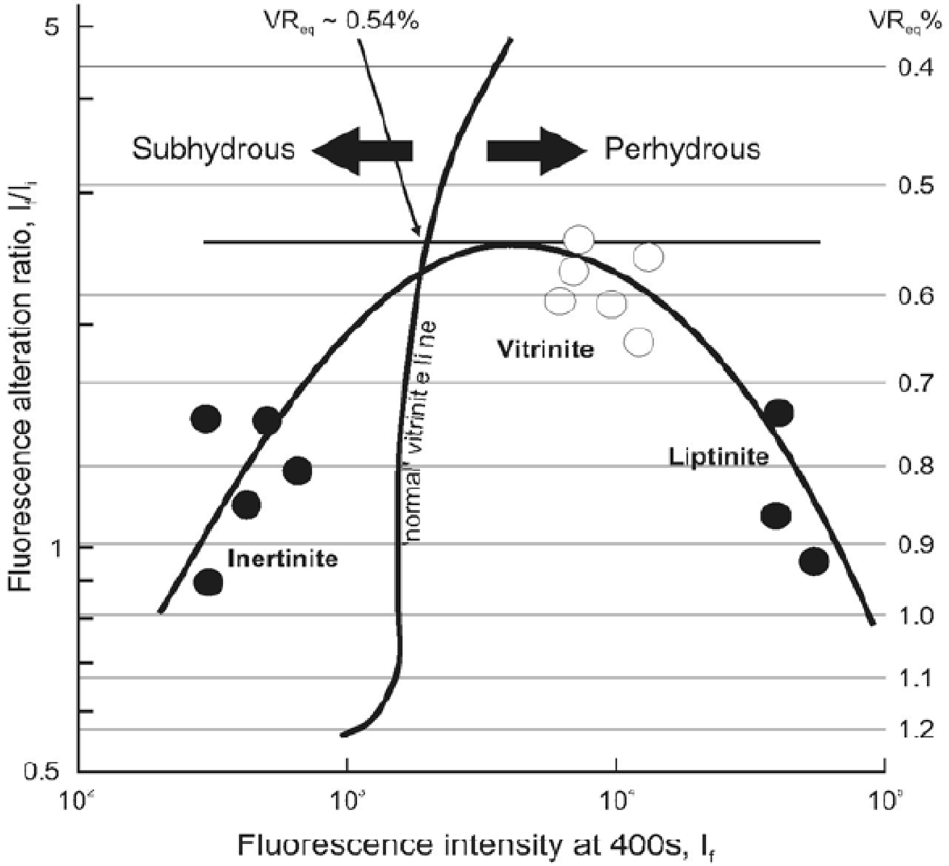
Drawbacks of VR measurements arise from:

- R_0 measurements from different maceral types (within or outside the vitrinite group) may be significant different.
- *OM* may have been reworked.
- Lack of of plants having vitrinite before Devonian age.
- R_0 tend to be unreliable at low level of maturity (R_0<0.7-0.8).
- At high T corresponding to a depth > 4 km the vitrinite maceral is highly anisotropic (accurate measurements are difficult).
- Uncertatinty in the knowledge of parameters in Arrhenius equation:
  (E_a= 200-300 kJmol^{-1} A= 2.5x10^{10} – 7.48x 10^{18} s^{-1})

Paleotemperature Indicators
Fluorescence Alteration of Multiple Macerals (FAMM)

- This method involves measuring the flourescence emission from polished maceral samples in response to a laser beam focused to ~ 1-2μm diameter.
- The intensity of the emitted red (625 nm) fluorescence varies with time and the effect is quantified by measuring the intensity at the beginning (I_i) and end (I_f) of a specified period (400 s).

Fluorescence alteration diagram



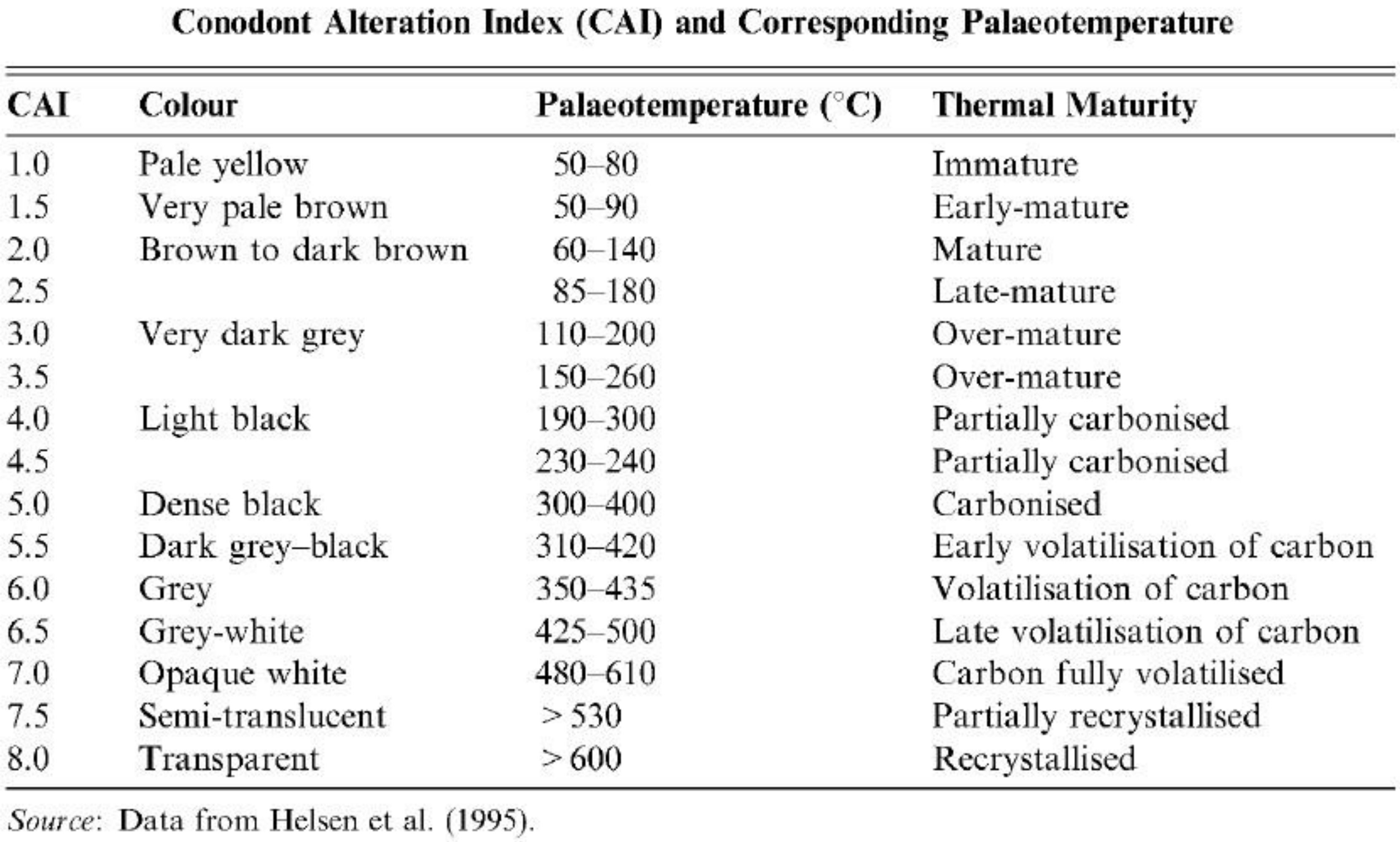
- The abscissa I_f is controlled by maceral types (Inertite the lowest values and liptinite the highest).
- The ordinate I_s/I_f is mainly controlled by the thermal maturity, decreasing as maturity increases.
- To determine the equivalent vitrinite reflectance (VR_{eq}) of the sample, a best-fit second-order polynomial curve is placed through the complete data set.
- This technique has been calibrated such that the curve maximum indicates Vr_{eq} for samples with Vr_{eq} <0.9.

Paleotemperature Indicators
Thermal Alteration Index (*TAI*)

- The ***TAI*** index is an arbitrary scale (from 1 to 4) that ranks the gradual change in colour and opacity of liptinite (spore, pollen, and leaf cuticle material) with *T*.
- ***TAI*** 1 is equivalent to the lowest levels of organic maturity and is assigned to liptinite particles showing a greenish-yellow color.
- ***TAI*** and maturity increase as the colour of liptinite progresses through pale yellow, yellow amber, deep red-brown, and opaque black at ***TAI*** 4.
- The entire oil generation window falls within a narrow range of **TAI** values (~ 2.0-2.7). Below **TAI** 2 no oil can be expected, while above **TAI** 3.5, *T* is too high (gas zone).
- Paleo*T* are measured with a precision of ±20°C.

Paleotemperature indicators
Conodont Alteration Index (*CAI*)

- The ***CAI*** index refers to the coloration of conodont fossils that reflects the max paleo*T.*
- It has eight levels, from the lowest to the highest *T*, related to the gradual change in colour and opacity of conodonts with *T*.



Conodont Alteration Index (CAI) and Corresponding Palaeotemperature

CAI	Colour	Palaeotemperature (°C)	Thermal Maturity
1.0	Pale yellow	50–80	Immature
1.5	Very pale brown	50–90	Early-mature
2.0	Brown to dark brown	60–140	Mature
2.5		85–180	Late-mature
3.0	Very dark grey	110–200	Over-mature
3.5		150–260	Over-mature
4.0	Light black	190–300	Partially carbonised
4.5		230–240	Partially carbonised
5.0	Dense black	300–400	Carbonised
5.5	Dark grey–black	310–420	Early volatilisation of carbon
6.0	Grey	350–435	Volatilisation of carbon
6.5	Grey-white	425–500	Late volatilisation of carbon
7.0	Opaque white	480–610	Carbon fully volatilised
7.5	Semi-translucent	> 530	Partially recrystallised
8.0	Transparent	> 600	Recrystallised

Source: Data from Helsen et al. (1995).

Paleotemperature Indicators
Conodont Alteration Index (*CAI*)

- The disadvantages of the ***CAI*** index are due to: (1) the broad T range associated to the index, (2) the large uncertainty (±20-50 °C), since the colour is subjective, (3) the large number of pristine conodonts required for statistical accuracy (30-100).
- The computer analysis observed that the intensity of the RGB components decreases almost linearly with the increase of ***CAI*** up to 5.0, and increases rapidly in the range ***CAI*** 5.0-8.0.
- Nestell and Balsam (1996) found that the reflectance of white light off conodonts increases almost linearly with wavelength in the range of 550-800 nm and that the slope of the reflectance vs wavelength varies with CAI:

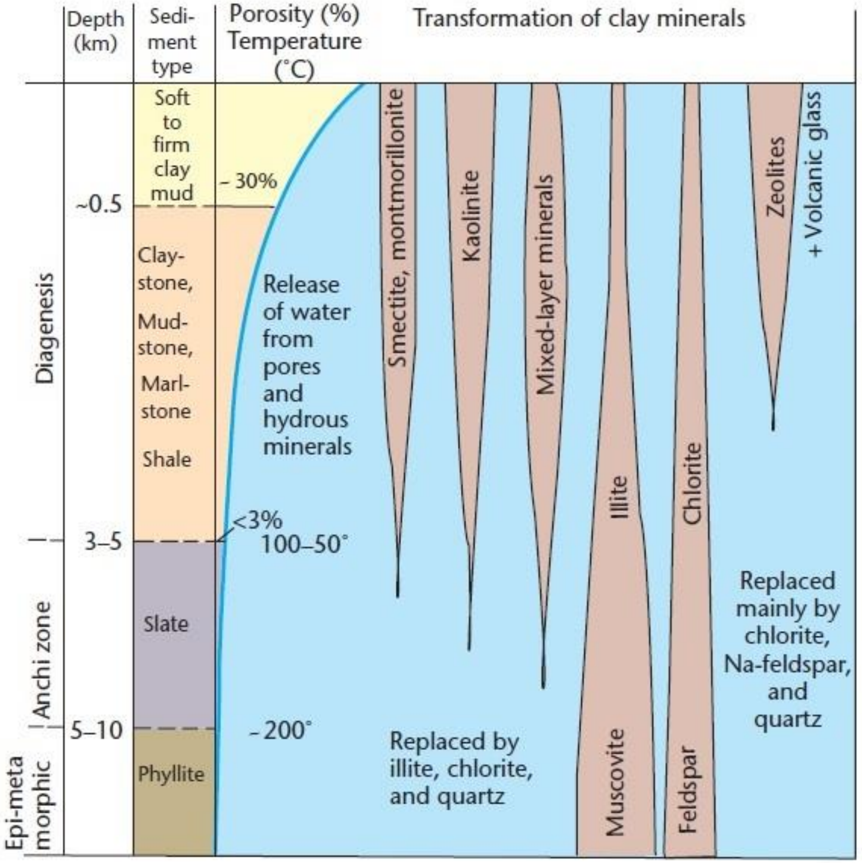
$$\mathrm{CAI} = -95.818(\mathit{slope}) + 623.996(\mathit{slope})^2 + 4.558$$

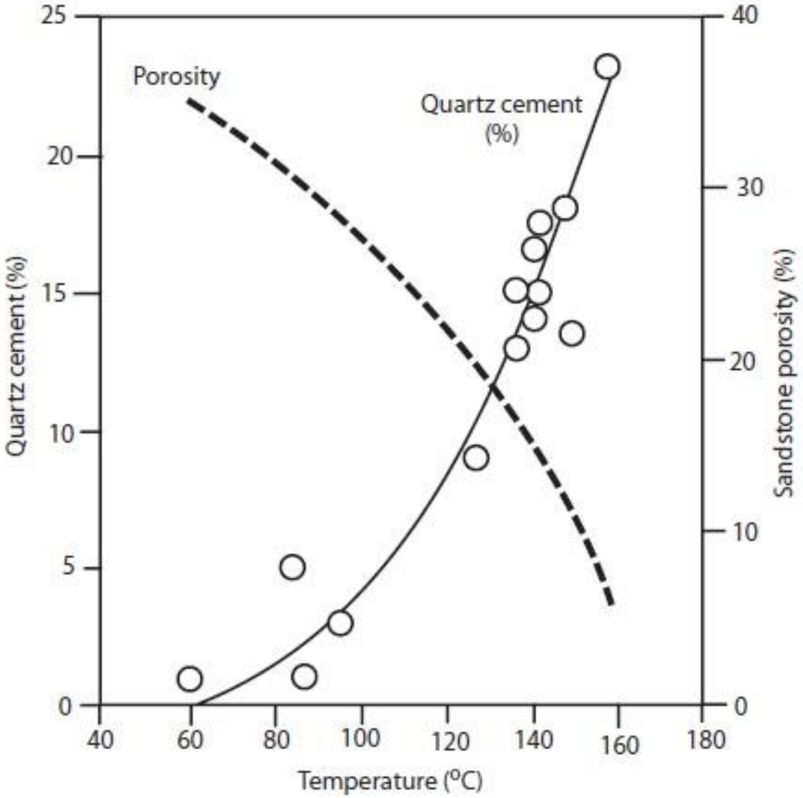
Slope = %/nm

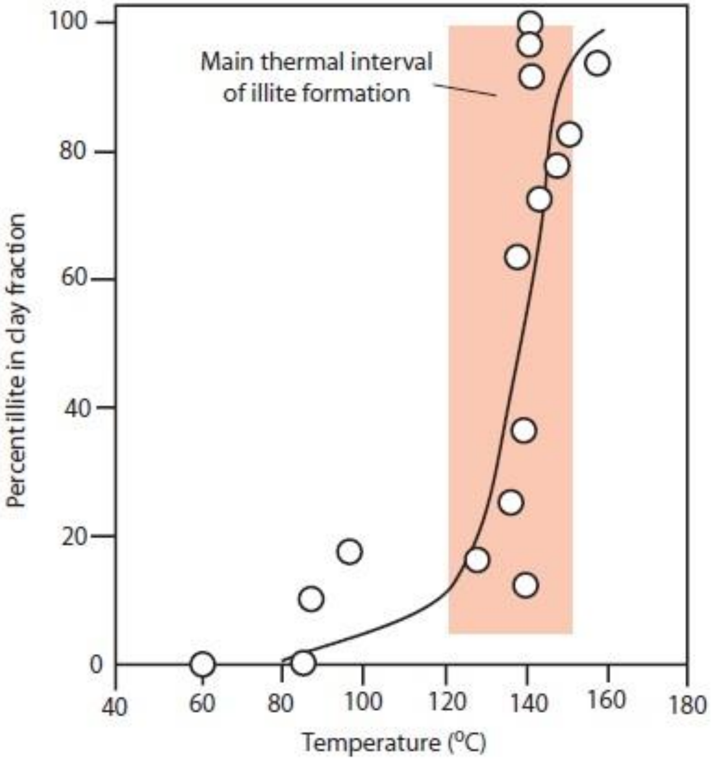
Uncertainty: ±0.2% with 95% confidence

Paleotemperature Indicators
Mineralogical Indices

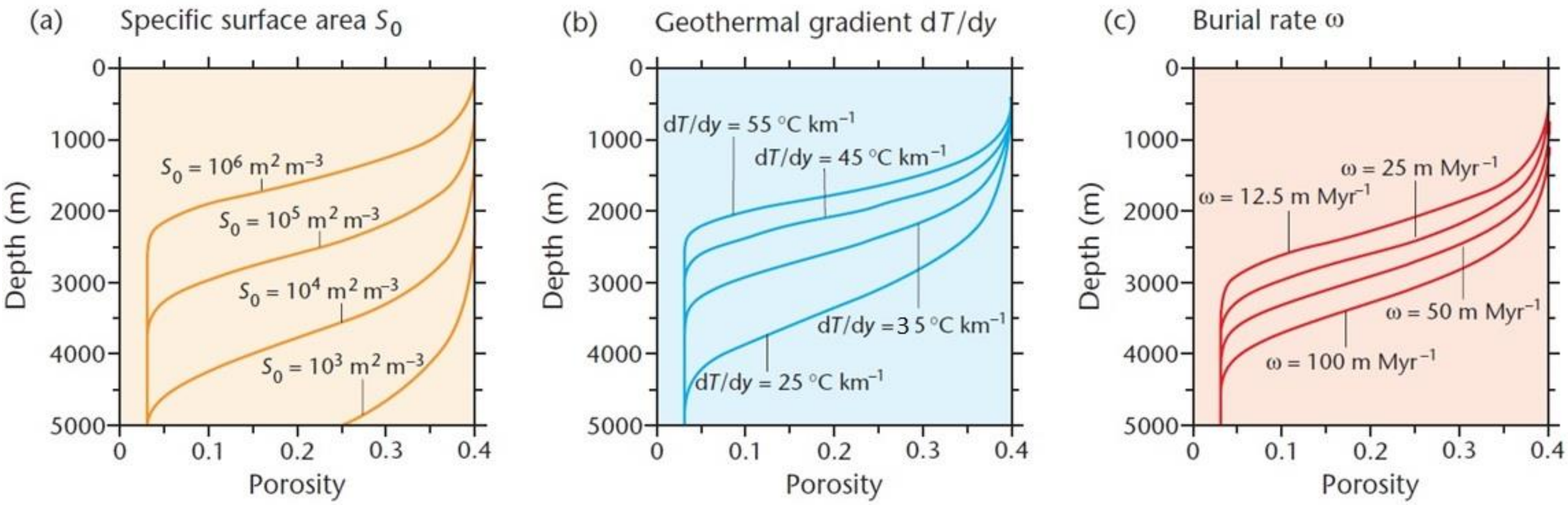
- The beginning of oil generation is correlated with the disappearance of smectite in favour of illite.
- Quartz cementation act in sandstones buried to T > 60 °C (90°-120°C) and is mainly due to dissolution in pressure solution seams (stylolites), where silica solubility is enhanced by the presence of clay minerals and micas.







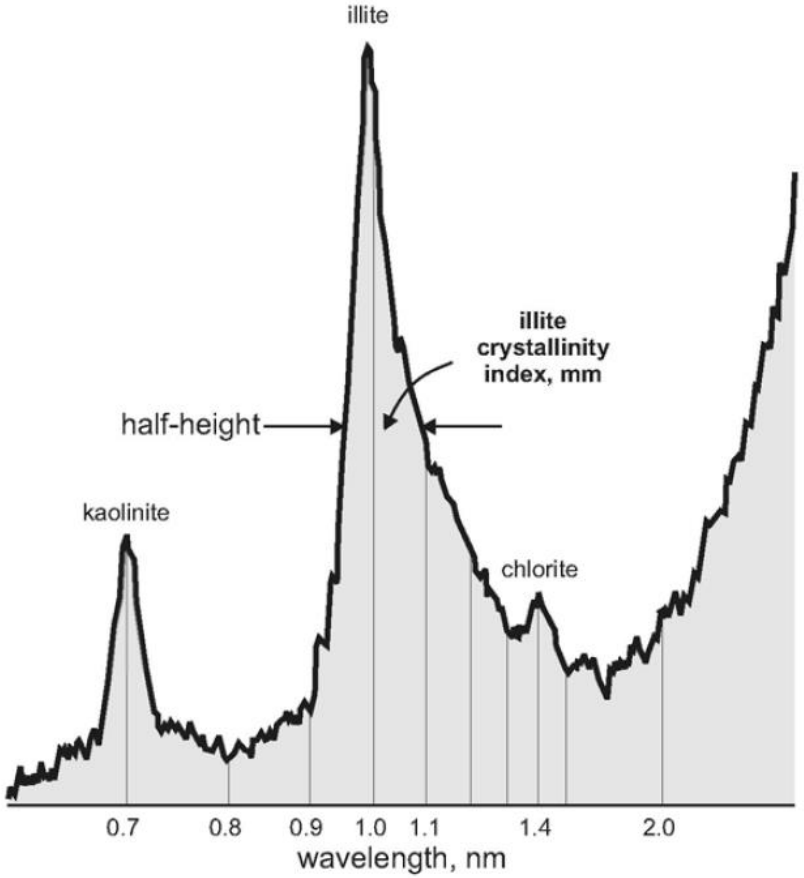
Paleotemperature Indicators
Mineralogical Indices



- Porosity-depth curve assuming quartz cementation during a constant burial rate depends on (a) the initial specific surface S_0 (a), (b) the geothermal gradient dT/dy , and (c) the deposition (burial) rate ω.

Paleotemperature Indicators
Mineralogical Indices

- As diagenetic processes increase clay minerals (kaolinite, smectite, illite and chlorite) enrich in illite and chlorite at the expense of smectite (typically disappears at a depth of 1-2.5 km) and kaolinite.
- The abundance of illite in a material is measured using x-ray diffraction: illite shows on an x-ray spectrum as a characteristic peak at wavelength ~ 1 nm. As *T* increases the *index of crystallinity*, defined as the width of the 1 nm illite peak (at half-height) decreases (progressive narrowing of the 1nm illite peak).
- This method works at high maturity level and identifies the transition between diagenesis and metamorphism occurs between indices 4.0-2.5, which is equivalent of vitrinite reflectance of R_{vmax}=2.3-3.3%.



Paleotemperature Indicators
Mineralogical Indices

Other methods using clay minerals are based on the relative proportion of smectite with respect to illite with increasing time and *T*, considering that the ratio of the chemical activities potassium/sodium (K/Na) in the clay exerts some control on the reaction rate.

Pytte and Reynolds, 1989

$$-\partial S/\partial t = S^5 \times (\mathrm{K/Na}) \times A \exp(-E/RT)$$

$S =$ mole fraction of smectite in illite–smectite mixed
$(\mathrm{K/Na}) = 74.2 \times \exp(-2490/T)$
$A = 5.2 \times 10^7\ \mathrm{s}^{-1}$
$E = 138\ \mathrm{kJ\,mol}^{-1}$
$R =$ the gas constant $= 8.314472\ \mathrm{J\,K}^{-1}\ \mathrm{mol}^{-1}$
$T =$ temperature (K)

$$S^4 = \frac{S_0^4}{1 + (1.543 \times 10^{10}) \times t \times S_0^4 \exp(-19{,}110/T)}$$

S_0=mole fraction of smectite in the initial mixed-layer clay
t-=time (s) spent by the clay at more than 90% of peak *T*

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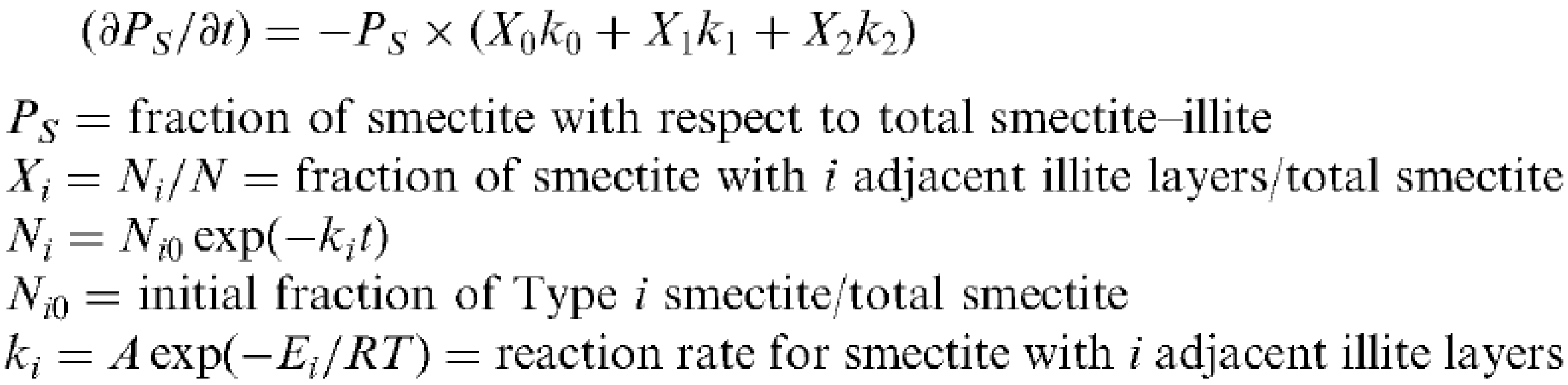
Bethke and Altaner (1986) found that a smectite layer adjacent to a single illite layer converts to illite at lower energy than smectite layer totally surrounded by either smectite or illite.

They derived a weighted kinetic relationship for the reactions of the three different smectite types:



$$(\partial P_S/\partial t) = -P_S \times (X_0k_0 + X_1k_1 + X_2k_2)$$

P_S = fraction of smectite with respect to total smectite–illite
$X_i = N_i/N$ = fraction of smectite with i adjacent illite layers/total smectite
$N_i = N_{i0}\exp(-k_it)$
N_{i0} = initial fraction of Type i smectite/total smectite
$k_i = A\exp(-E_i/RT)$ = reaction rate for smectite with i adjacent illite layers

They assumed: A=10^{-3} s^{-}1

E_0=77.5kJmol-1 (Type 0)
E_1-75.5 kJmol-1 (Type 1)
E_2=100.5 kJmol-1 (Type II)

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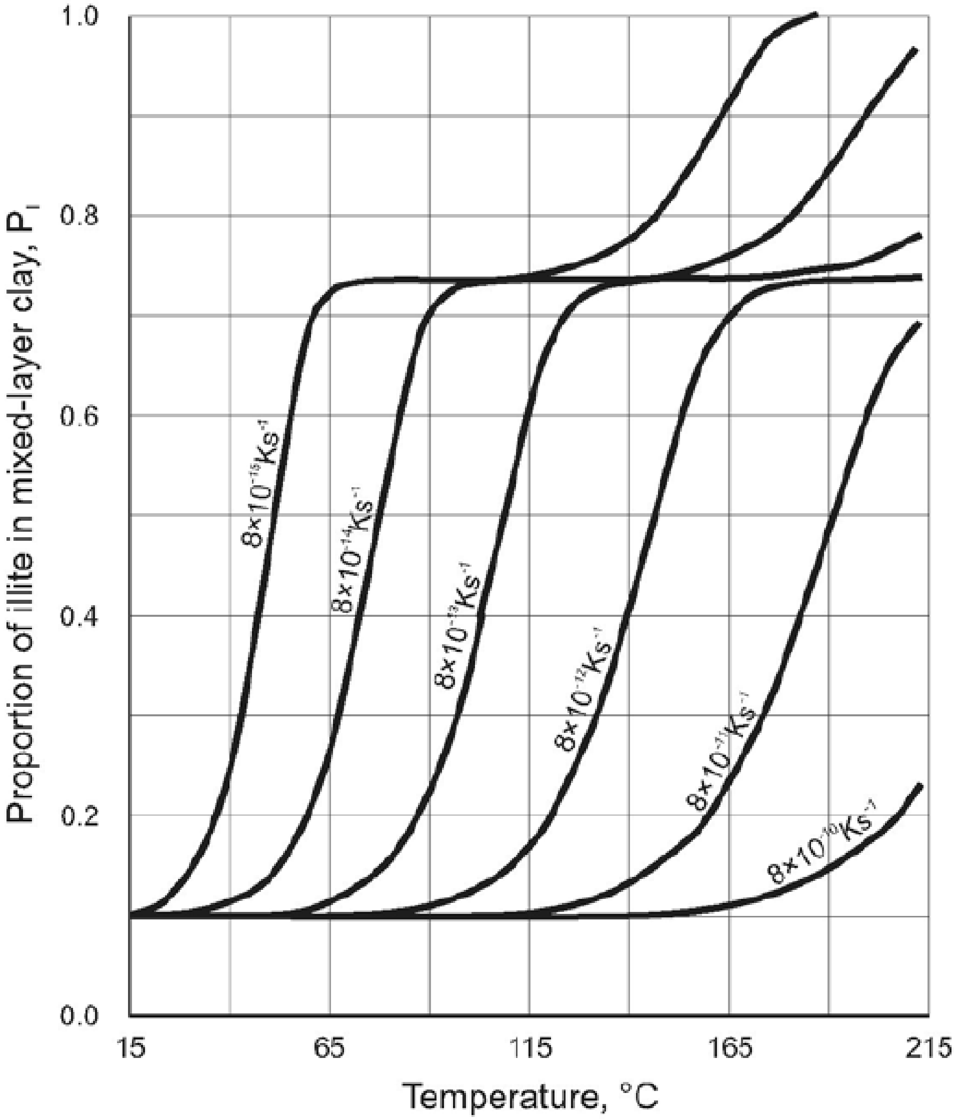


Question: A particular clay sample is exhumed from a formation that was deposited 25 Myr ago. The present temperature of the formation is 80°C. Assuming an average surface temperature of 15°C, what is the expected illite content in relation to the total smectite-illite?

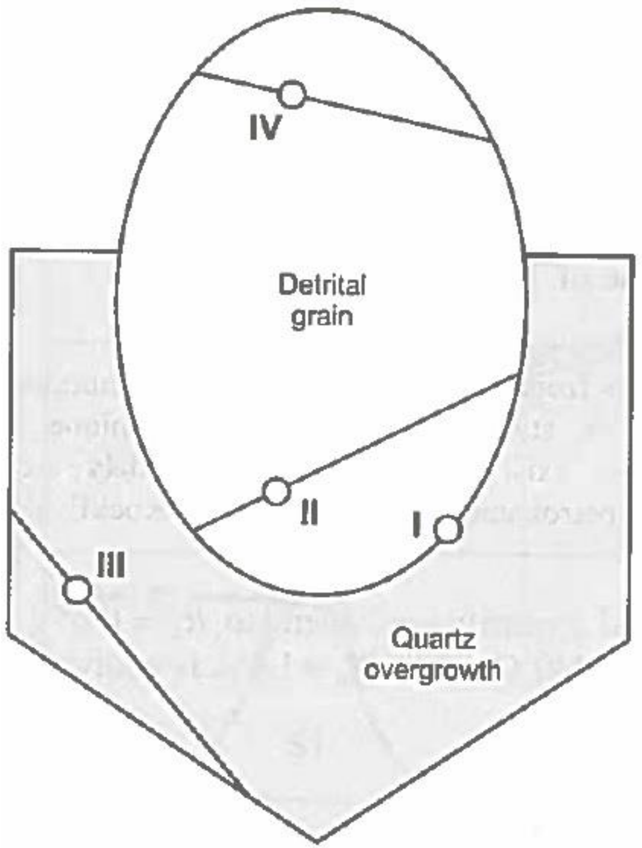
***Answer**:* We need to determine the average heating rate:
average heating rate = change in temperature / change in time

$$dT/dt = (80^\circ\mathrm{C} - 15^\circ\mathrm{C})/25\ \mathrm{Ma} = 65\ \mathrm{K}/(25 \times 3.1557 \times 10^{13}\ \mathrm{s}) = 8.24 \times 10^{-14}\ \mathrm{K\,s^{-1}}$$

Assuming a heating rate of 8.24×10^{-14} Ks^{-1} and a present T of 80°C:
P_I~ 0.55

Paleotemperature Indicators
Fluid Inclusion Microthermometry (FIM)

- Fluid inclusions between crystals can be used to constrain the timing of oil migration in relation to mineral diagenesis and give some indications about *P*-*T* conditions at the time of entrapment.
- The fluid (trapped as a single phase) separates into a liquid and vapour components upon reduction to surface conditions. Upon reheating the inclusion, the fluid reverts to a single phase at T_h (homogenization temperature), the minimum T_h recorded for a given population of fluid inclusion is likely the actual *T* at which the inclusion was originally trapped.

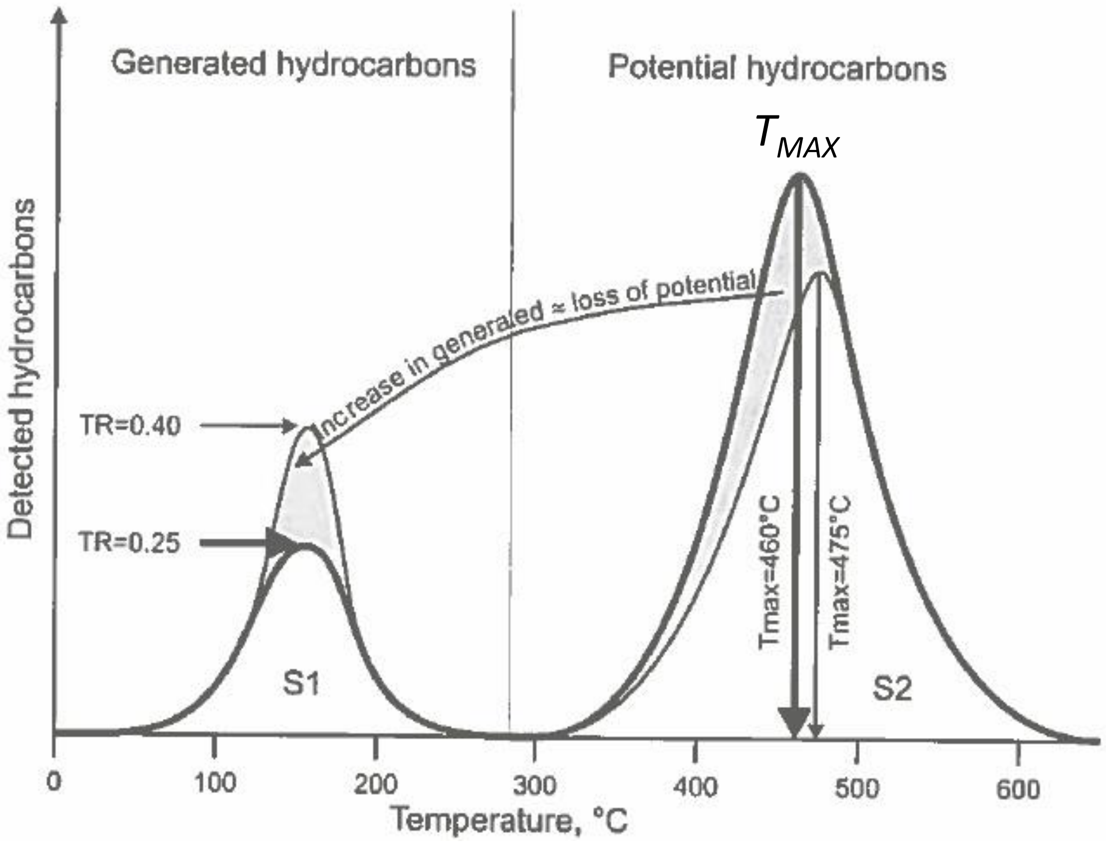


I: Fluid trapped during crystallization of quartz overgrowth.
II: Fluid trapped during healing of fractures prior to quartz overgrowth.
III: Fluid trapped during healing of fractures during or after quartz overgrowth.
IV: It cannot be used for timing in detrital quartz.

Paleotemperature indicators
Pyrolysis (Rock-Eval)

- **Pyrolysis** (annihilation by fire), in the petroleum industry, describes a procedure whereby a rock's sample is heated in an inert gas (e.g., argon).
- Heating rate is kept constant while hydrocarbons boiled from the rock are carried with the inert gas to a chromotograph, which records the volume of hydrocarbons through time.

- The hydrocarbons present in the pores of the rock sample are expelled and detected by the pyrolysis instrument at $T < 200$ °C. Then, a distinct peak of detected hydrocarbons occurs at 100-200 °C (S1).
- The kerogen material left in the sample reaches maturation if the *T* is raised at sufficient level (reactions generating hydrocarbons occur in a hour) and thus a second distinct peak of detected hydrocarbons occurs at 400-500 °C (S2).
- The higher is the thermal maturity, the lower the volume of potential hydrocarbons and the higher is the *T* required to mobilize it during pyrolysis.

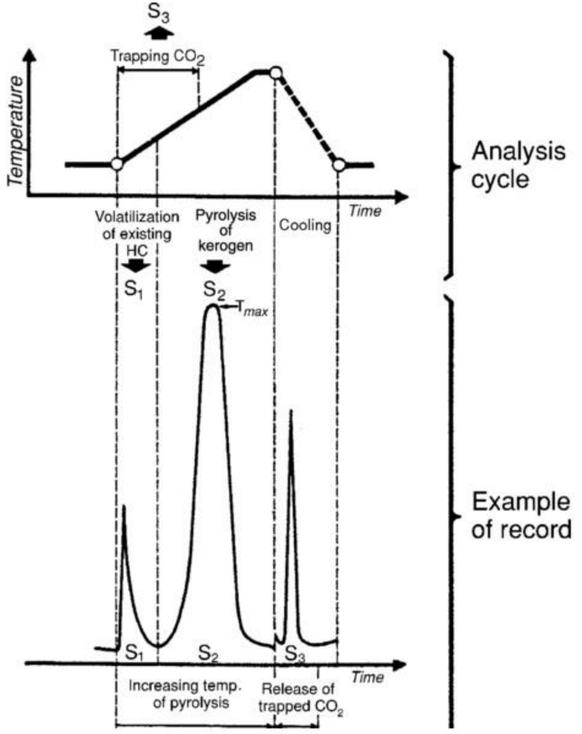


A higher heating rate results in a higher value of T_{MAX}

Transformation rate (TR)=S1/(S1+S2)

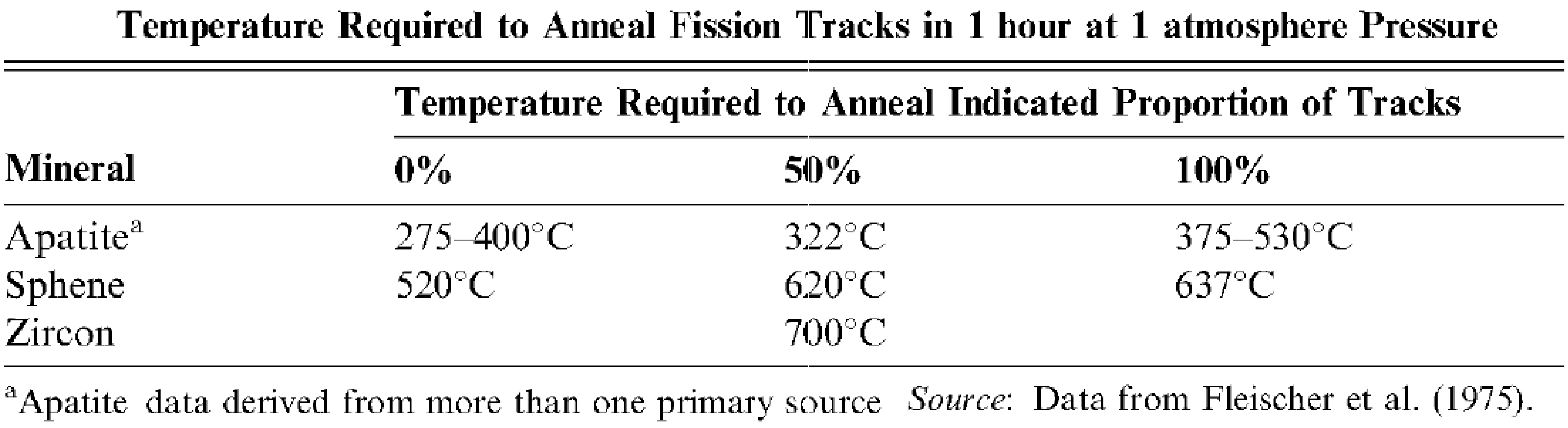
Paleotemperature Indicators
Pyrolysis (Rock-Eval)

- Pyrolysis method is based on determination and analysis of a number of parameters such as the Total Organic Carbon (**TOC**), **S_1**, **S_2**, **S_3**, **T_{max}** range, hydrogen index (***HI***), oxygen index (***OI***), production index (***PI***), pyrolyzable carbon (***PC***).
- **S_1** = amount of free hydrocarbons in the sample (in milligrams of hydrocarbon per gram of rock) volatilized at a temperature of <300 °C. S_1 normally increases with depth
- **S_2** = amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter by heating in temperature intervals from 300 to 550 °C (~650 °C at the start and upwards to 800 /850 °C). S_2 normally decreases with burial depths >1 km.
- **S_3** = amount of CO_2 (in milligrams CO_2 per gram of rock) produced during pyrolysis of kerogen within the 300–400 °C range.
- **T_{max}** = T at which the maximum release of hydrocarbons from cracking of kerogen occurs during pyrolysis (top of S_2 peak). T_{max}= 400–430 °C represents immature organic matter; T_{max} = 435–450 °C indicates a mature or oil zone; T_{max} > 450 °C represents an over-mature zone.
- **TOC** (expressed as weight percentage) = weight percentage of carbon in CO_2 formed during pyrolysis below 400 °C, and in CO formed below 500 °C, and in the hydrocarbon peaks, S_1 and S_2;
- **HI** = $(100 \text{ x} S_2)/TOC$;
- **OI** = $(100 \text{ x} S_3)/TOC$;
- **PI** = $S_1/(S_1 + S_2)$;
- **PC** = $0.083 \text{ x } (S_1 + S_2)$.



Paleotemperature Indicators
Fission Track Thermochronology (*FFT*)

- **Fission track analysis** is based on the observation that the crystal lattices of some minerals preserve the scars of spontaneous nuclear fission event (^{238}U). Apatite, zircon and shene contain uranium a are commonly used for this analysis.
- The initial length of a fission track is relatively constant for a given mineral (~ 16 μm) for apatite, but gradually anneals starting at each end of the fission track and moving inwards, decreasing the track length at a rate dependent on *T*, mineral composition and the angle between the fission track and the c-axis of the crystal.
- Temperature of annealing is different for each mineral (e.g., apatite starts to anneal at T >50° C). Zircons retain tracks for much longer at higher *T* than sphene and apatite.



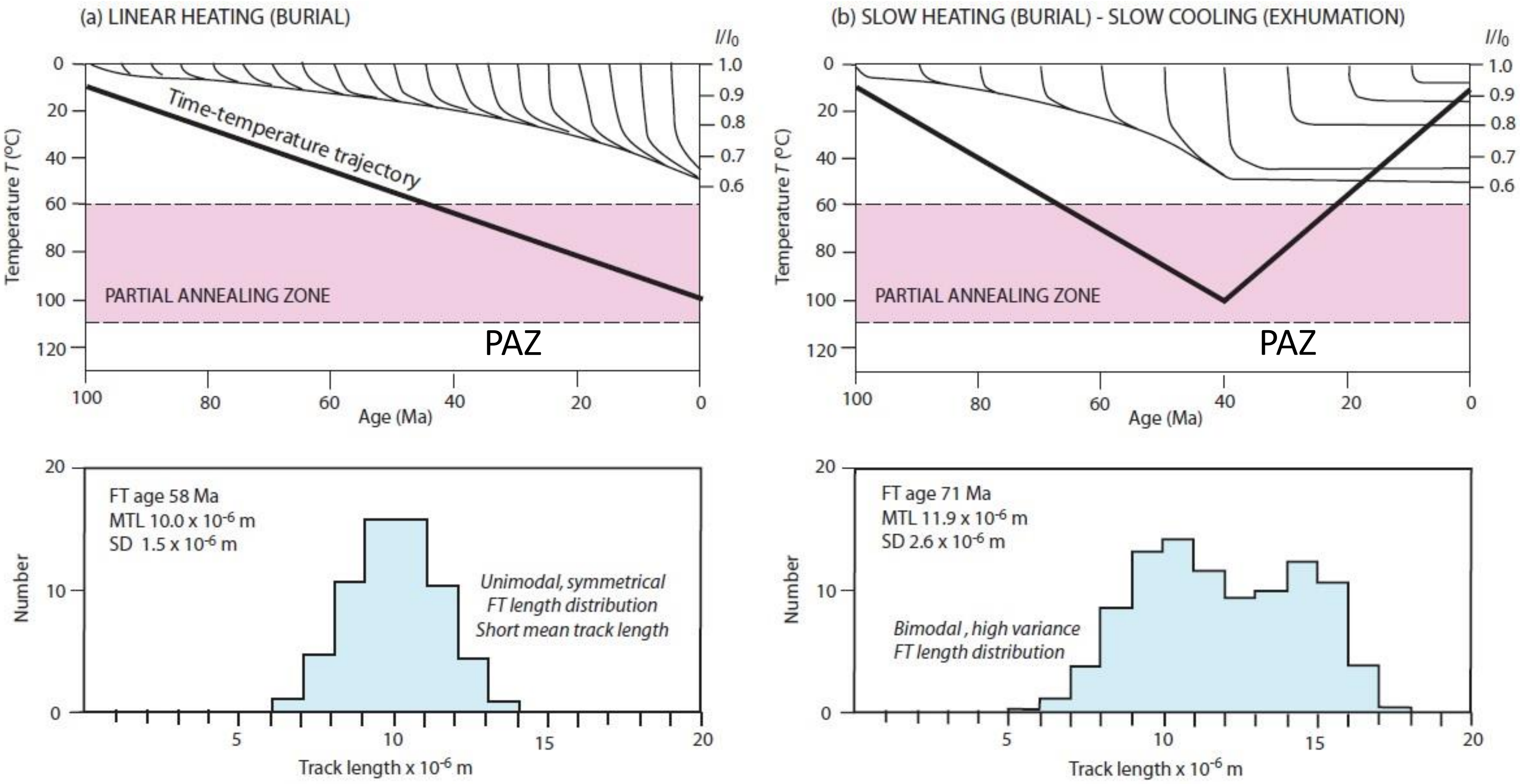
Temperature Required to Anneal Fission Tracks in 1 hour at 1 atmosphere Pressure

	Temperature Required to Anneal Indicated Proportion of Tracks		
Mineral	**0%**	**50%**	**100%**
Apatite[a]	275–400°C	322°C	375–530°C
Sphene	520°C	620°C	637°C
Zircon		700°C	

[a] Apatite data derived from more than one primary source *Source*: Data from Fleischer et al. (1975).

Paleotemperature Indicators
Fission Track Thermochronology (*FFT*)

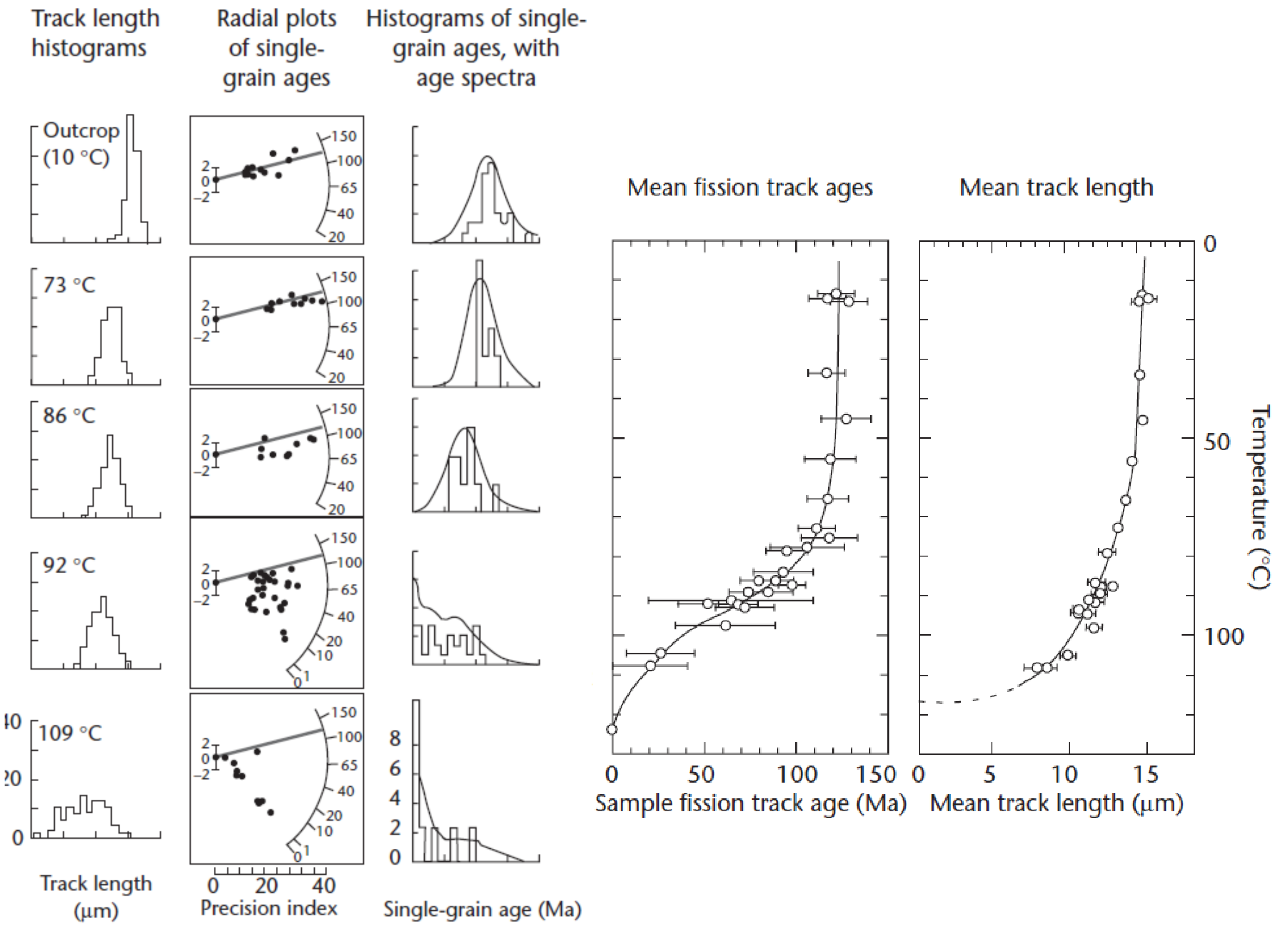
- Above the PAZ, the fission track lengths are tithly clustered and long (14μm), indicating minimal annealing.
- Newer tracks experience different maximum *T* during the cooling phase (sedimentary basin inversion), causing a bimodal histogram, with a high STD.



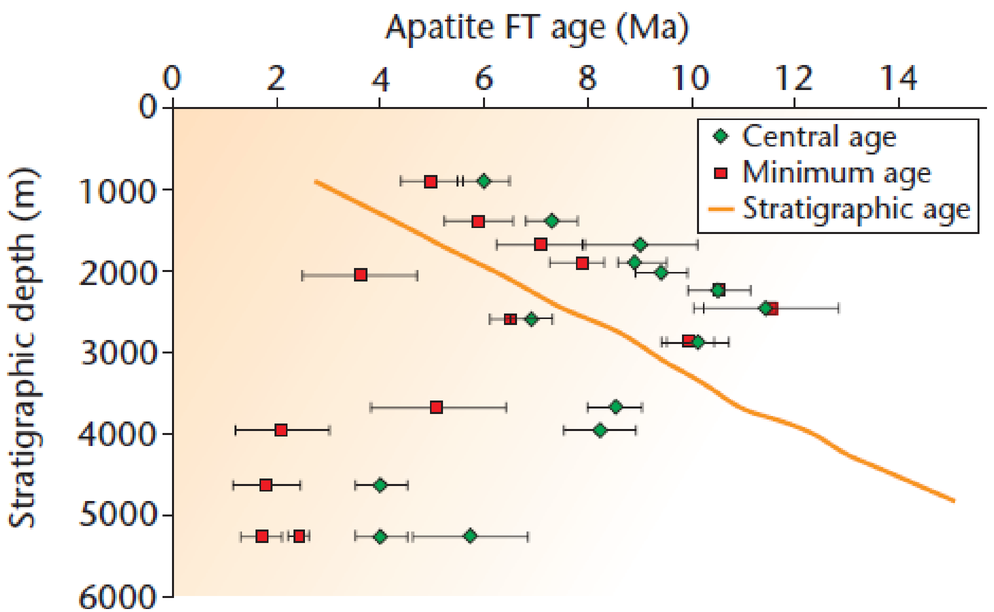
MTL=Medium Track length *l*=track length l_0=Initial track length

Paleotemperature Indicators
Fission Track Thermochronology (*FFT*)

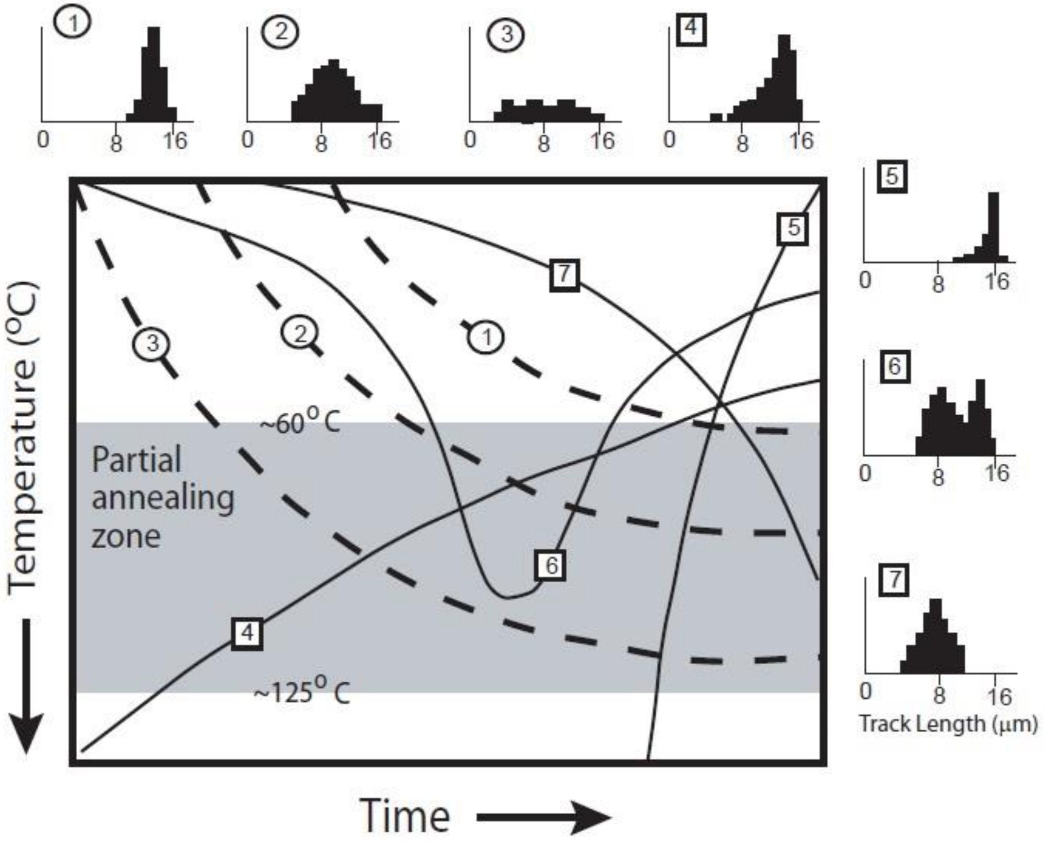
- With greater depth, fission track length histograms show a wider distribution and a shorter MTL.
- The fission track ages decrease due to the greater amount of annealing at eleveted *T*, reaching 0 Myr at *T* of 120°C.
- Annealing during burial (e.g., at a depth > 2.5 km) causes a decrease of the age of samples (< of the stratigraphic age).
- Samples above the line of stratigraphyic age indicate rapid exhumation, transport, and burial without annealing.



Western Nepal



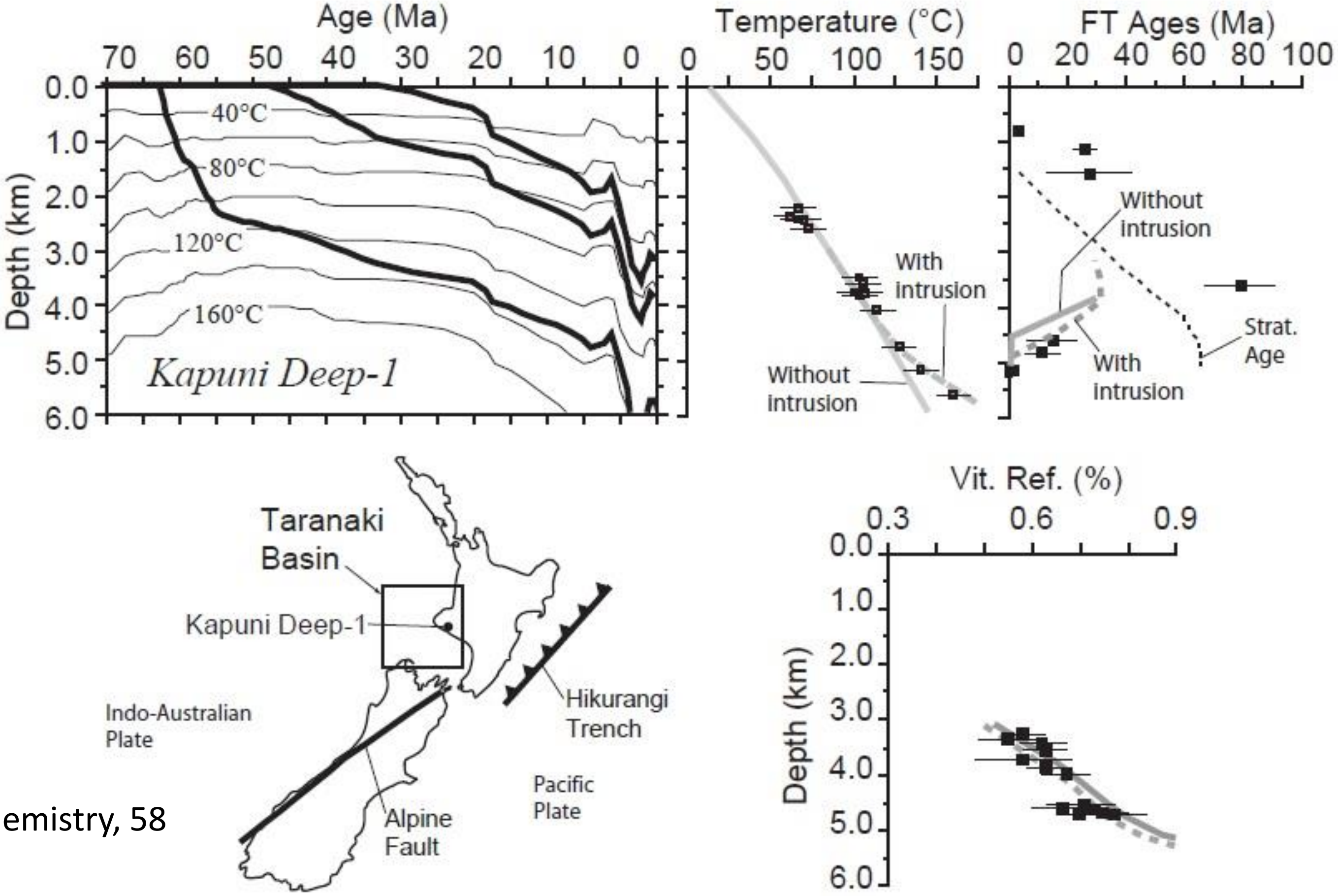
Paleotemperature Indicators
Fission Track Thermochronology (*FFT*)



Armstrong, 2005, Rev. Min. & Geochemistry

- Paths 1–3 show progressive burial to maximum depths below the top of the PAZ followed by near isothermal conditions: long track lengths with narrow distributions indicative of that sample's grains not being annealed after deposition. With greater depth (and temperature) the average track lengths progressively get shorter and the distribution of tracks spreads out reflecting the partial annealing.
- Paths 4 and 5 show cooling from depths within or below the PAZ. With cooling from temperatures above the base of the PAZ for this apatite species, average track lengths tend to be long but with negative skewness and the distribution gets narrower with more rapid cooling through the PAZ—compare path 4 with 5.
- Path 6 shows heating into the partial annealing zone followed by cooling out of it. For a sample that is heated to PAZ temperatures and then cooled, a bimodal distribution can be expected because tracks that were shortened while the sample was in the PAZ are mixed with longer tracks that formed after cooling out of the PAZ.
- Path 7 shows rapid heating to temperatures in the partial annealing zone. In thsi case average track lengths will be relatively short but not as spread out as in the case of longer periods of time in the PAZ (paths 2 and 3).

Paleotemperature Indicators
Fission Track Thermochronology (*FFT*)



Armstrong, 2005, Rev. Min. & Geochemistry, 58

Burial/thermal history and output parameters temperature, apatite fission-track, and vitrinite reflectance data for well Kapuni Deep-1 in Taranaki Basin.

Solid curves in the temperature, fission track, and vitrinite reflectance plots are model values for case of tracking thermal history with burial and erosion only. Thick dashed curves are for case of including sill intrusion below the sediments in the last <1 M.y.

- Vitrinite reflectance data show essentially the same fit with both the intrusion and non-intrusion model, indicating that the vitrinite reflectance data are less sensitive to the short-term transient thermal effects than are the AFT data.

Paleotemperature Indicators
Fission Track Thermochronology (*FFT*)

- Annealing results in shorter spontaneous tracks, reduced spontaneous track density and a reduction in the apparent fission track age (t_a).
- Above a critical T, fission tracks anneal instantaneously and t_a is reduced to zero, resetting the fission track clock.

$$t_a = \frac{1}{\psi_D} \ln\left[1 + \frac{\psi_D \phi \sigma I \rho_s}{\psi_f \rho_i}\right]$$

ψ_D = total decay constant of $^{238}\mathrm{U} = 1.55125 \times 10^{-4}$ (Ma^{-1})
ψ_f = spontaneous fission decay constant of $^{238}\mathrm{U}$ (Ma^{-1})
I = isotopic ratio of $^{235}\mathrm{U}/^{238}\mathrm{U} = 7.2527 \times 10^{-3}$
σ = thermal neutron fission cross section for $^{235}\mathrm{U} = 580.2 \times 10^{-24}$ (cm^2)
ϕ = thermal neutron fluence (cm^{-2})
ρ_s/ρ_i = spontaneous/induced track density ratio

A glass standard of known uranium concentration is included with each batch of apatite grain mounts sent for irradiation and is mounted with a muscovite detector.

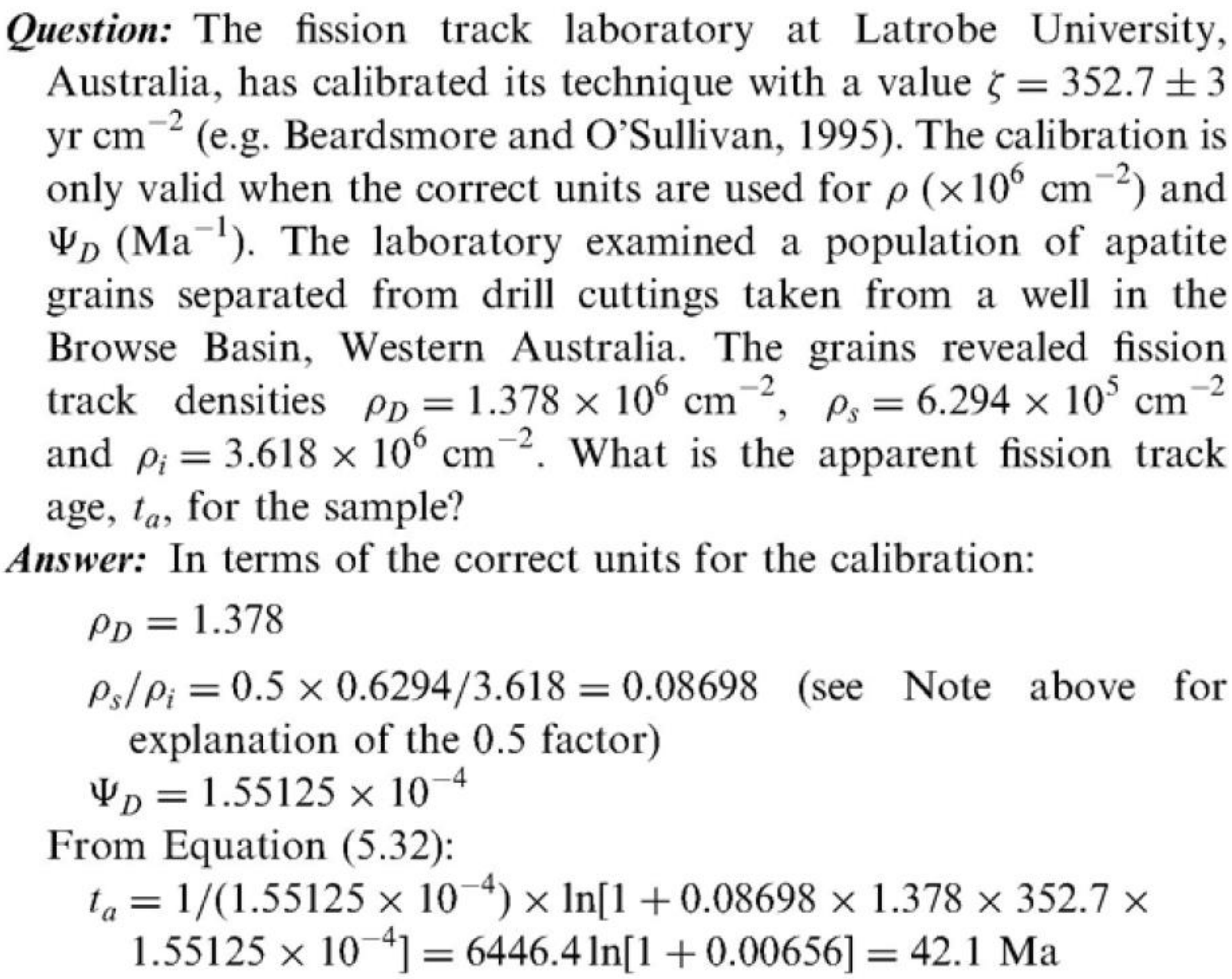
$$\Phi = B \times \rho_D$$

ρ_D=density of fission tracks revealed on the muscovite detector
B=calibration factor characteristic of the glass

$$t_a = \frac{1}{\psi_D} \ln\left[1 + \frac{\rho_s \rho_D}{\rho_i} \zeta \psi_D\right]$$

ζ=calibration constant

Paleotemperature Indicators
Fission Track Thermochronology (*FFT*)



Question: The fission track laboratory at Latrobe University, Australia, has calibrated its technique with a value $\zeta = 352.7 \pm 3$ yr cm^{-2} (e.g. Beardsmore and O'Sullivan, 1995). The calibration is only valid when the correct units are used for ρ ($\times 10^6$ cm^{-2}) and Ψ_D (Ma^{-1}). The laboratory examined a population of apatite grains separated from drill cuttings taken from a well in the Browse Basin, Western Australia. The grains revealed fission track densities $\rho_D = 1.378 \times 10^6$ cm^{-2}, $\rho_s = 6.294 \times 10^5$ cm^{-2} and $\rho_i = 3.618 \times 10^6$ cm^{-2}. What is the apparent fission track age, t_a, for the sample?

Answer: In terms of the correct units for the calibration:

$$\rho_D = 1.378$$

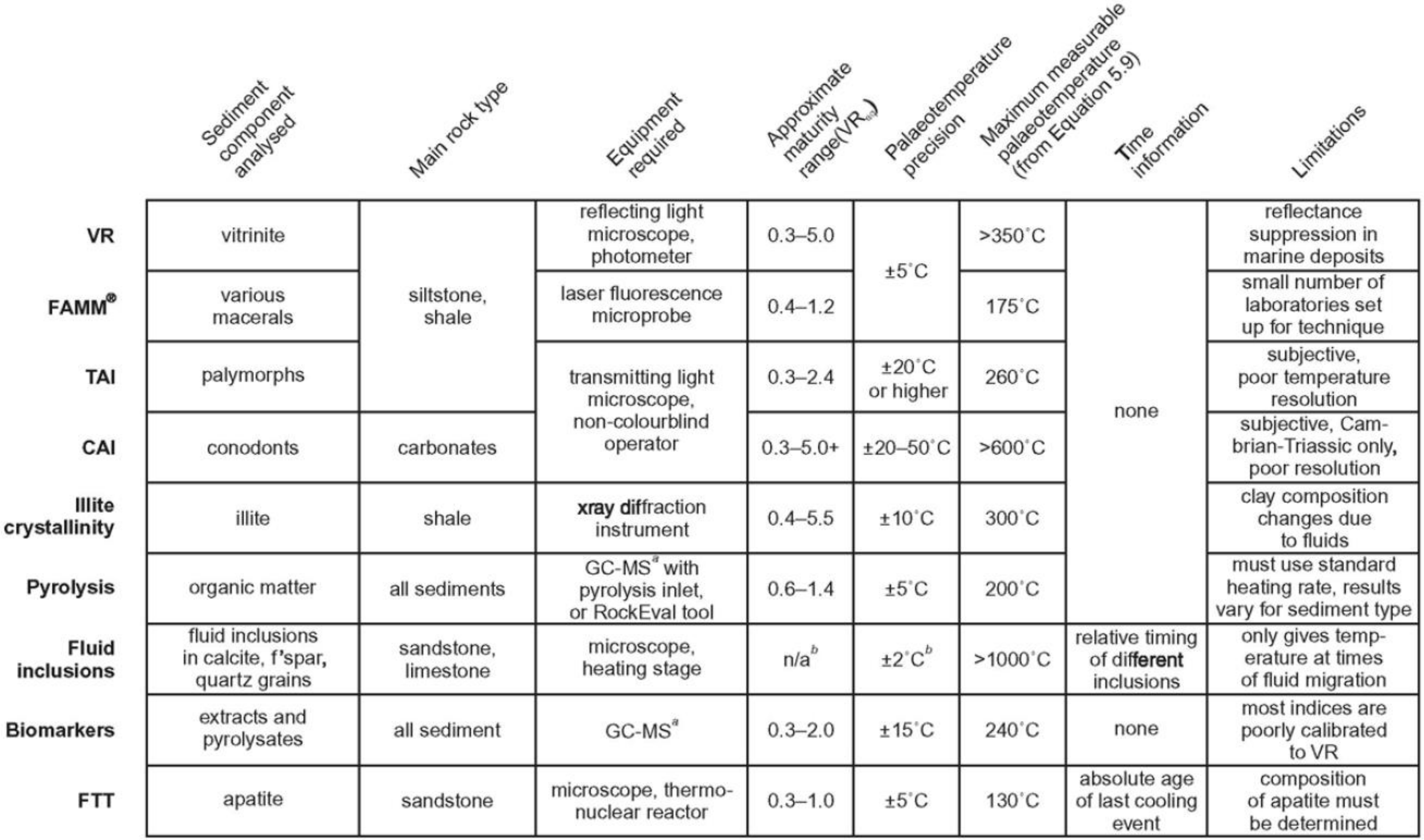
$\rho_s/\rho_i = 0.5 \times 0.6294/3.618 = 0.08698$ (see Note above for explanation of the 0.5 factor)

$$\Psi_D = 1.55125 \times 10^{-4}$$

From Equation (5.32):

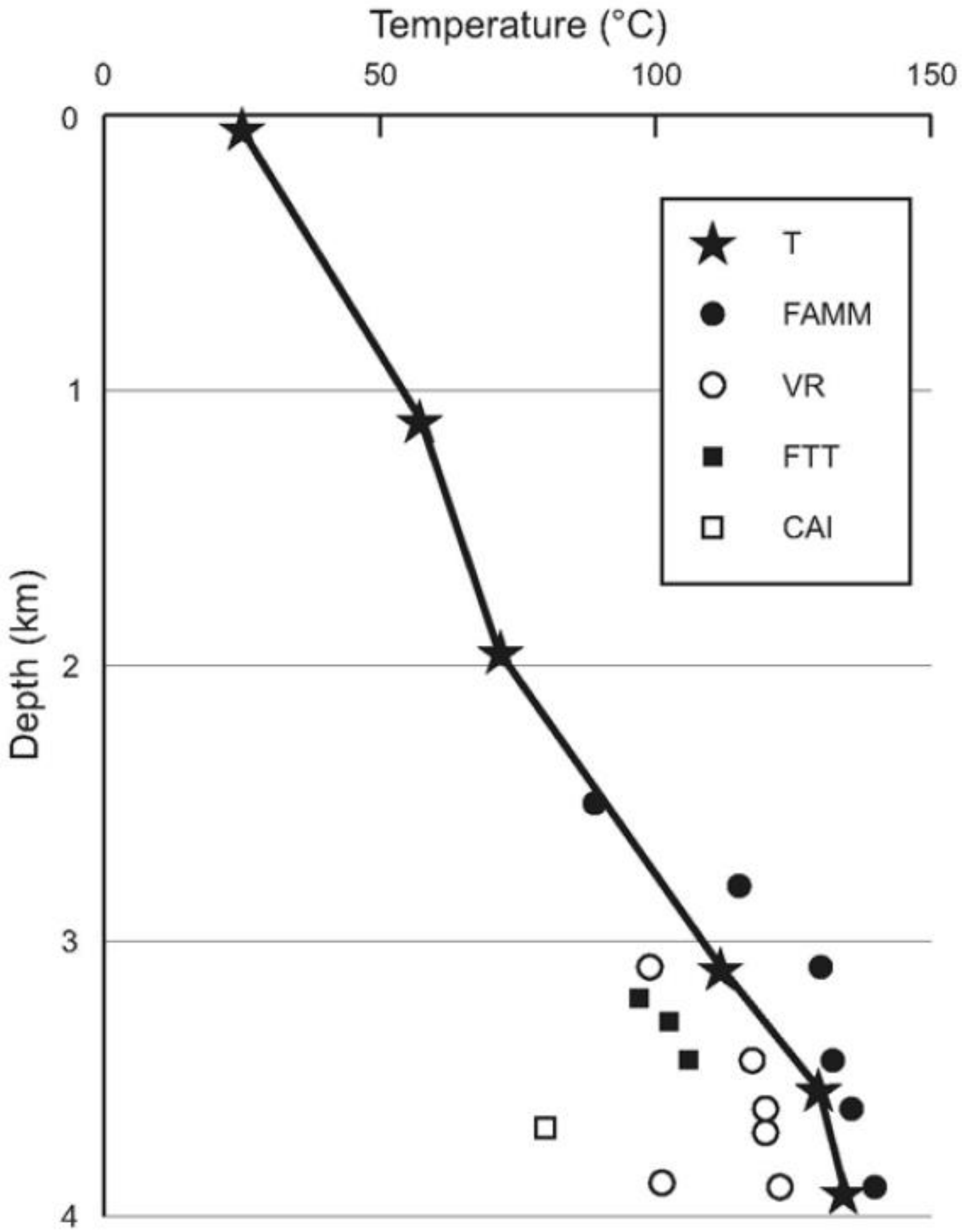
$$t_a = 1/(1.55125 \times 10^{-4}) \times \ln[1 + 0.08698 \times 1.378 \times 352.7 \times 1.55125 \times 10^{-4}] = 6446.4 \ln[1 + 0.00656] = 42.1 \text{ Ma}$$

Thermal maturity Indicators



	Sediment component analysed	Main rock type	Equipment required	Approximate maturity range(VR_{eq})	Palaeotemperature precision	Maximum measurable palaeotemperature (from Equation 5.9)	Time information	Limitations
VR	vitrinite	siltstone, shale	reflecting light microscope, photometer	0.3–5.0	±5°C	>350°C	none	reflectance suppression in marine deposits
FAMM®	various macerals		laser fluorescence microprobe	0.4–1.2		175°C		small number of laboratories set up for technique
TAI	palymorphs		transmitting light microscope, non-colourblind operator	0.3–2.4	±20°C or higher	260°C		subjective, poor temperature resolution
CAI	conodonts	carbonates		0.3–5.0+	±20–50°C	>600°C		subjective, Cambrian-Triassic only, poor resolution
Illite crystallinity	illite	shale	xray diffraction instrument	0.4–5.5	±10°C	300°C		clay composition changes due to fluids
Pyrolysis	organic matter	all sediments	GC-MS[a] with pyrolysis inlet, or RockEval tool	0.6–1.4	±5°C	200°C		must use standard heating rate, results vary for sediment type
Fluid inclusions	fluid inclusions in calcite, f'spar, quartz grains	sandstone, limestone	microscope, heating stage	n/a[b]	±2°C[b]	>1000°C	relative timing of different inclusions	only gives temperature at times of fluid migration
Biomarkers	extracts and pyrolysates	all sediment	GC-MS[a]	0.3–2.0	±15°C	240°C	none	most indices are poorly calibrated to VR
FTT	apatite	sandstone	microscope, thermonuclear reactor	0.3–1.0	±5°C	130°C	absolute age of last cooling event	composition of apatite must be determined

Paleo-temperature Indicators



VR		TTI (Horváth et al., 1988)	TAI (Staplin, 1969)	CAI	TMAX (Tissot and Welte, 1984)
0.2	**immature**				
			1.0 green-yellow	1.0 pale yellow	
0.5		3	1.5 pale yellow		
0.7	**oil**	50	2.0 yellow	1.5 pale brown	440
1.0		500			
			2.5 amber	2.0 brown-dark brown	460
1.3		1000	2.7		
	condensates				
1.5			3.0 brown		480
		2000			
				3.0 very dark grey	
2.0	**gas**		3.5 deep red-brown		500
		5000			
2.5		8000			
		10000			
3.0			4.0 black	4.0 light black	>550

References

Main Readings:

Books:

- Beardsmore and Cull, 2001, Crustal Heat Flow A Guide to Measurement and Modelling, Chapter 5: Thermal Maturity, 146-200.
- Allen and Allen, Basin Analysis, Chapter 10: Thermal history, 343-367.
- Eppelbaum Interpretation of Thermal Measurements, 393-475.

Further readings:

Armstrong, 2005, Thermochronometers in Sedimentary Basins, Reviews in Mineralogy & Geochemistry, 58, 1-29.