4. Thermochronology – Techniques and Methods

4.1 Introduction to thermochronology

Thermochronology is the study of dating the cooling of rocks through exhumation. In its simplest form, thermochronology can be considered to date the moment when a mineral passes through a specific closure temperature ($T_c$) (Dodson, 1973). Minerals have different closure temperatures and so by using a suite of thermochronometers on a single sample, its cooling path through the crust can be reconstructed. The minerals and closure temperatures available for use are illustrated in figure 4.1. The highest temperature chronometers have closure temperatures in excess of 750°C (U-Pb in zircon). These higher temperature chronometers such as the U-Pb system in zircon are used to date, for example, Archean gneiss terrains, due to the unlikely nature of them having been reset, with depths required for reset at ~30 km (assuming a 25°Ckm$^{-1}$ geothermal gradient). This study focuses on the low temperature thermochronometers which may allow the geomorphic signature of the landscape to become etched into the thermochronometric record. Two principal low temperature thermochronometers are used in this study, apatite fission track analysis (AFT) and apatite (U-Th)/He analysis (AHe). These are the lowest temperature chronometers that are known about in sufficient detail and calibrated well enough to make them usable.

The low temperature thermochronometers may be used in a variety of ways, but one of their principal uses and that used in this study is to determine the temperature-time history of samples. As an extension to this they may also be used to determine exhumation rates by making some assumptions and for the higher temperature chronometers, to date the timing of formation of the rock/mineral in question.

This chapter discusses the principles behind the AFT and AHe, two low temperature thermochronometers, the development of sampling strategies and the important considerations to be aware of regarding their use in regions of high relief, i.e. the deformation of isotherms by topography.
4.2 (U-Th)/He thermochronometry

The decay of uranium and thorium to produce helium has been recognised since the discovery of radiation and the subsequent birth of geochronology. By measuring concentrations of uranium and helium, ages were calculated giving rise to the development of an absolute geological time scale (e.g. Rutherford, 1905; Strutt, 1905). Following these initial studies it was realised that measuring helium concentrations often led to unreasonably young ages (Hurley, 1954). The probable cause of these young ages was recognised early (Rutherford, 1905) and attributed to helium loss, implying that these He ages only provided a minimum estimate of the time elapsed since their formation (Reiners, 2002). Later developments in K-Ar and other geochronological techniques led to (U-Th)/He dating being regarded as suspect and relegated it to obscurity (Zeitler et al., 1987). Renewed interest was developed when Zeitler et al. (1987) proposed that for apatite, helium ages could be interpreted as those cooling through very low temperatures, with a closure temperature of ~100°C. It was shown that rapidly cooled apatites from the Durango fluorapatite (Cerro de Mercado, Mexico) (Young et al., 1969) had helium ages that matched those derived by other techniques (K-Ar and apatite fission track analysis, Zeitler et al., 1987). From this point onwards, an interest was rekindled in the use of (U-Th)/He dating of apatite as a potential low temperature thermochronometer, with a lower temperature sensitivity than that of the already established apatite fission track analysis. Subsequent studies have confirmed this low closure temperature (Lippolt et al., 1994; Wolf et al., 1996; Warnock et al., 1997) and step wise heating diffusion experiments show that monotonically cooled samples record the time when a sample passed through ~68±5°C (Farley, 2000). Natural calibration studies (e.g. House et al., 1999; Warnock, et al., 1997; Wolf et al., 1996) and laboratory studies (e.g. Farley, 2000) have confirmed the sensitivity of the apatite system to these low temperatures. This has provided a powerful tool for investigating, for example, the interactions between topography and exhumation (e.g. House et al., 1998) by allowing the movement of samples in the upper few kilometres of crust to be documented. This brief history has described the use of (U-Th)/He dating in apatites as a relative dating technique, recording the time when a sample has passed through a particular closure temperature. However, its use as an absolute dating technique has been applied in Quaternary volcanic rocks (Farley et al., 2002). This section discusses the background and the principles behind the use of (U-Th)/He dating of apatites as low temperature thermochronometers.
4.2.1 Production of helium

Nuclei of $^4$He ($\alpha$ particles) are produced during the radioactive series decay of $^{238}$U, $^{235}$U and $^{232}$Th (Farley, 2002), that ultimately results in the production of stable $^{206}$Pb, $^{207}$Pb and $^{208}$Pb. This forms the basis for U/Pb and Th/Pb dating. A generally insignificant amount is also produced by the decay of $^{147}$Sm to $^{143}$Nd (Reiners, 2002). The fundamental ingrowth equation for this system is:

$$ ^4 He = 8^{238} U \left[ \exp(\lambda_{238} t) - 1 \right] + 7^{235} U \left[ \exp(\lambda_{235} t) - 1 \right] + 6^{232} Th \left[ \exp(\lambda_{232} t) - 1 \right] $$

(1)

where $^4$He, $^{238}$U, $^{235}$U and $^{232}$Th are the present day atoms, $\lambda$s are their relevant decay constants and $t$ is the accumulation time or helium age (Farley, 2002; Reiners, 2002). The coefficients preceding the uranium and thorium abundances account for the multiple $\alpha$ particles emitted within each decay series (i.e. for $^{238}$U, 8 $\alpha$ particles are ejected, for $^{235}$U, 7 $\alpha$ particles are ejected etc.) (Farley, 2002). This equation assumes that no initial $^4$He is present in the sample, which is generally a valid assumption. In K/Ar or Ar/Ar dating atmospheric argon may frequently account for a substantial fraction of Ar being measured, but the concentration of He in the atmosphere is so low (5 ppm vs. 1% for $^{40}$Ar) that atmospheric helium is unlikely to be important (Farley, 2002). Fluid or mineral inclusions hosting $^4$He in crystals may invalidate this assumption and crystals containing these should not be selected during the picking/screening stage (section 4.2.3).

4.2.2 $\alpha$ ejection

A complication that exists with the use of (U-Th)/He dating is that, during radioactive decay, the $\alpha$ particles produced by the decay of U and Th are emitted with sufficient kinetic energy to travel many microns through solid matter before coming to rest (Farley et al., 1996). A consequence of this is that a spatial segregation between parent and daughter is introduced, which on a whole rock scale is negligible, yet in small crystals may be substantial (Farley et al., 1996). This can lead to areas of crystals displaying ages that are too old or too young. It is obvious that the distribution of parent isotopes is one of the strong controls on where the $\alpha$ particles will end up, and so zoning within crystals may exert an important control on helium distribution. Every $\alpha$ decay within the U and Th series has a characteristic energy and hence a characteristic stopping distance (Ziegler, 1977), within a specific material. This varies
from a minimum of ~11μm to a maximum of ~34μm (Farley et al., 1996). The mean stopping distance is shortest for the $^{238}\text{U}$ decay chain followed by $^{235}\text{U}$ and $^{232}\text{Th}$. Density of material is the strongest control on the $\alpha$ stopping distance for a given energy. So for the common datable minerals, as the density increases, apatite (3.2 g cm$^{-3}$), to titanite (3.6 g cm$^{-3}$) to zircon (4.4 g cm$^{-3}$), the average $\alpha$ stopping distance in the $^{238}\text{U}$ chain drop from 19.7 to 17.8 to 16.6μm respectively (Farley et al., 1996). For apatites the approximate stopping distance is taken as ~20μm. As a consequence of this an $\alpha$ particle will come to rest on the surface of a sphere of radius 20μm centred around the site of the parent nucleus (Farley, 2002). Figure 4.2a illustrates this effect and displays the three possible outcomes that can occur. If a parent nucleus is in a position, greater than the stopping distance in from the edge of the crystal, then no matter what vector the $\alpha$ particle takes away from the parent it will always be retained within the crystal. If a parent nucleus lies within one stopping distance of the crystal edge, then there is a possibility that the $\alpha$ particle may be ejected from the crystal. This rises to a 50% probability when the parent nuclide is found on the crystal edge assuming that all vectors have a similar chance of use. The third outcome is that a parent nucleus may lie outside the crystal and may therefore potentially add $\alpha$ particles to the crystal through implantation (Farley, 2002).

The third of these possible outcomes is often ignored related to the fact the spacing between parent-rich accessory crystals is large in most rocks and so can be discounted (Farley et al., 1996). However this may be violated in very U-Th poor apatites (Farley, 2002) or in rocks with large quantities of monazite present (Farley, 2003). If this last outcome is disregarded then the distribution of $\alpha$ particles within a crystal is given in figure 4.2b, where full retention is recorded in the core of the crystal, decreasing to 50% retention at the edge of the crystal. This observation suggests that in apatite only the outer 20μm of a crystal is affected. From this a simple solution to the problem can be proposed, the dissolution of the outer surface of crystals to be dated (Farley et al., 1996; Farley, 2002). However in some minerals (specifically apatite) the grain itself provides the helium diffusion domain (Farley, 2000), and as the crystal edge is the site of diffusional helium loss then it will have a lower concentration of helium than the grain interior (Farley, 2002). Removal of this outer skin will therefore bias the crystal towards erroneously high values as the magnitude of the gradient in helium concentration in the crystal is a sensitive function of the crystals thermal history (Reiners and Farley, 1999; Farley, 2002). This removal may be appropriate for rapidly cooled crystals, but will in general, result in erroneous ages where the diffusion and $\alpha$ ejection boundaries coincide (Farley, 2002). Similarly if a crystal shows strong zoning in
parent isotopes, then removal of the outer skin, may again lead to erroneous ages (Farley et al., 1996).

Therefore a correction factor must be calculated in order to account for the effects of $\alpha$ ejection. A quantitative model along these lines has been developed by Farley et al., (1996) to correct helium ages for effects of long $\alpha$ stopping distances, based on measured grain geometries and sizes. One of the important assumptions associated with the correction is that the distribution of U and Th is not zoned and is assumed to be homogeneous. This is considered in greater detail in section 4.2.4.

The $F_T$ parameter, the factor by which a measured age must be divided by to obtain an $\alpha$ corrected age, is based on the surface to volume ratio ($\beta$) of the crystal, and the $\alpha$ stopping distance of the crystal in question. Consequently, the larger the crystal the smaller $\beta$ will be and the smaller the correction required. In contrast, a small crystal with a large $\beta$ will have a greater surface area affected by $\alpha$ ejection and so will require a larger correction. As discussed above, each parent isotope has a different stopping distance for a particular medium, but calculating the mean $F_T$ separately for each parent does not differ substantially from using a single mean stopping distance for each parent (Farley et al., 1996).

In order to calculate a $F_T$ correction for each sample, the width and length of an apatite crystal must be measured. The shapes of the terminations are also noted (flat/parallel, good pyramidal or irregular). The crystals are then treated as prisms due to a relative insensitivity of $F_T$ to original length (Farley et al., 1996). As single crystal samples are not routinely analysed, a bulk $F_T$ correction is then calculated based on taking an average of all of the measured crystals weighted by their mass contribution to the fraction (Farley et al., 1996). Each aliquot contains crystals of a homogeneous size. If crystals of different sizes are used, that unknowingly have different U-Th contents, then the weighting will be incorrect as the weighting implicitly implies that grains contribute helium in proportion to their mass (Farley, 2002).

Figure 4.3 illustrates a graph showing the variation of $F_T$ with crystal size, showing the fact that the smaller the crystal the larger the required correction.

$F_T$ correction is also known as recoil correction or $\alpha$ correction.
4.2.3 Crystal selection

One of the single greatest problems/difficulties that exists in the (U-Th)/He dating of apatite is the presence of uranium- and thorium-rich inclusions within the crystals to be dated (Farley, 2002). These inclusions tend to be composed of zircon, monazite, xenotime or fluid inclusions (Ehlers and Farley, 2003). If these inclusions are small (<15μm) then all α particles are ejected into the host apatite. However, zircon is often not dissolved by the standard dissolution techniques used on apatite. Consequently parentless or excess helium may be measured as the parental uranium and thorium is not measured, leading to erroneously old ages. Therefore, when selecting crystals for analysis, effort must be made to ensure that they are inclusion free. Crystals are picked for analysis using a binocular microscope at magnifications up to ~150x. They are selected on the basis of good crystal morphology (necessary for F_T correction) and on being inclusion free. The majority of inclusions may be seen using a normal binocular microscope, showing up as bright areas under cross polars. Unfortunately, if quantities of monazite are present then they may escape detection, due to their small size and acicular habit. All efforts are made to ensure crystals are inclusion free and a double checking system is used, with another experienced person checking crystals before loading for analysis.

Crystals used in each individual aliquot are of a homogeneous size, and prior to loading are measured for use with the F_T correction using a calibrated graticule in the binocular microscope. A minimum grain size of 50μm diameter is used as smaller than this the errors associated with measuring and subsequent F_T corrections increase dramatically. Crystals are loaded into a small, degassed stainless steel capsule and then wrapped in degassed copper foil ready for analysis. The amount of uranium and thorium in a crystal and its age will determine the amount of material required, that is the number of crystals. Prior to loading, photographs of the grains are taken as an extra step to note morphologies before analysis. Examples of such grains are shown in figure 4.4.

If grains with inclusions do get through the picking screening, then if they contain excess helium, then this will be discovered during the re-heat (section 4.2.9) or by poor age reproducibility.
4.2.4 Zoning effects

Zoning of U and Th in apatite crystals can have a major influence on the final corrected age of a sample. One of the key assumptions of the \( F_T \) correction technique is that uranium and thorium are uniformly distributed in the host grain, yet this is not always the case. It can be that the distribution of U and Th is zoned, usually either by rim or core enrichment, which will have strong implications for \( \alpha \) ejection. Examples of zoned crystals are given by Meesters and Dunai, (2002b), where strong zoning is shown by the distribution of fission tracks, both spontaneous and induced. The consequence of such zoning is that the technique of using \( F_T \) to correct for \( \alpha \) ejection could be incorrect for zoned samples. For example, core enriched samples with >20\( \mu \)m of crystal around the core will not require an \( F_T \) correction as all helium will be retained within the crystal, while rim enriched crystals will require a different correction to a standard \( F_T \) correction. The result of this is that some characterisation of crystal zoning is required in order to decide whether a standard \( F_T \) correction should be applied or not. The effects of heterogeneity can be accounted for using numerical solutions provided through modelling in the program DECOMP (section 4.8.4) (Meesters and Dunai, 2002b).

4.2.5 Diffusion behaviour of helium in apatite

One of the bounding principles in geochronology as a whole is the requirement to be measuring a closed system, where no parent or daughter has been gained or lost since the time of formation (Reiners, 2002). This is often violated to some degree, particularly with \((U-\text{Th})/\text{He}\) dating, where the transition from loss to retention occurs over a range of temperatures. This transitional region is known as the Partial Retention Zone or PRZ and can be defined as the range of temperatures where the ages fall between 90% to 10% of the holding time, i.e. the temperature range where the helium age changes most rapidly with temperature (Wolf et al., 1998). The measured age will reflect a balance between production of radiogenic \(^4\text{He}\) and its diffusion out of the crystal. In the case of apatite at high temperatures (~265-300\( ^\circ \text{C} \)), no helium is retained within the lattice of the mineral and all is diffused out over geological timescales (Wolf et al., 1996; Farley, 2000). In order to use a dating technique such as \((U-\text{Th})/\text{He}\), the diffusion behaviour of helium must be understood in order to establish the temperature ranges over which it is sensitive. The simplest case for loss of helium from an apatite crystal is that it is lost via a single, thermally-activated process (Farley, 2000). Under these conditions the temperature dependence of diffusivity is defined.
by the activation energy ($E_a$) and the diffusivity at infinite temperature ($D_0$) giving the following relationship:

$$D/a^2 = D_0/a^2 \exp(-E_a/RT)$$  \hspace{1cm} (2)$$

where $R$ is the gas constant, $T$ is the temperature and $a$ is the diffusion domain radius, the characteristic length scale over which diffusion occurs (Farley, 2000). Results from this relationship will yield a line on an Arrhenius plot with the slope proportional to the activation energy ($E_a$) and a y-intercept of $\ln(D_0/a^2)$. The diffusion domain in for helium in apatite is suggested as being the grain itself (Farley, 2000). Laboratory experiments involving the Durango fluorapatite show that an extremely linear Arrhenius plot is produced, with an activation energy of ~33 kcalmol$^{-1}$ (Farley, 2000). The closure temperature of a system may be calculated from the above results (Dodson, 1973) and for a crystal of ~90µm radius of Durango fluorapatite is 68°C (assuming a cooling rate of 10°CMyr$^{-1}$). This varies by ±5°C with varying grain radius (50-150µm) (Farley, 2000). These experiments also established the approximate boundaries of the helium PRZ in Durango fluorapatite to be 45-75°C (Wolf et al., 1998; Farley, 2000). The laboratory measurements involving stepwise degassing of Durango fluorapatite, set a basis for testing the system in a more geologically realistic setting and applying the theory. Calibration studies were performed, for example in the Otway Basin, Australia using borehole samples (House et al., 1999) and in the White Mountains, California (Stockli et al., 2000). In borehole samples it was successfully shown, that at low temperatures, helium is retained within the crystal lattice, whilst at high temperatures, >100°C, little is retained (House et al., 1999). Borehole studies make possible the detection of the modern PRZ, whilst surface sampling enables the identification of a palaeo-PRZ that has been exhumed (Stockli et al., 2000). Here a similar pattern in the apatite ages is observed over the exhumed rock column, with older ages near the top of the rock column and younger ages near the base. These studies have helped confirm and define the temperature range over which the (U-Th)/He system is sensitive in apatite and so how it may be applied to geological problems. They also note the importance of crystal size on the capacity of diffusion in apatites as the following section discusses.
4.2.6 Crystal size effects

One of the controls on the diffusive loss of helium is crystal size. This is due in part to the effect of size on α ejection and also as the grain is itself the diffusion domain (a in equation 2 and section 4.2.5), such that larger crystals retain a larger fraction of helium than smaller crystals (Reiners and Farley, 2001). This effect is most apparent when crystals have spent long periods of residence in the PRZ (>10^7 years). In the Bighorn Mountains (Wyoming), it has been shown that in crystals varying in size from 30-90μm radii, ages vary from ~100-350 Ma (Reiners and Farley, 2001). These samples have spent time at temperatures less than 70-90°C for long periods (possibly as early as the Precambrian) at very low geothermal gradients. The effects of crystal size will also influence all chronometers to some degree particularly where the grain itself is the diffusion domain.

4.2.7 Sampling considerations

Fresh rocks are the best to sample for use in (U-Th)/He dating, but they may not always provide apatites suitable for use. Although the rock may be fresh and have undergone little weathering, it is not known until it has been separated whether the apatites are inclusion free. This cannot be seen whilst collecting samples and so consequently poor samples are sometimes collected having either poor yields of apatites or inclusion rich apatites.

Proximity to faults and other potential fluid pathways can affect the measured AHe ages by providing excess helium from outside the apatite crystal or late stage heating resetting ages and as such should be avoided when sampling.

It has also been suggested (Mitchell and Reiners, 2003) that samples that have been subject to wildfires may lead to 10-90% loss of helium in apatite in the upper few centimetres of exposed bedrock. This is of concern if sampling in regions where wildfires are relatively common, but can be avoided by removing the outer few centimetres of rock before performing separation. This is not considered to be a major concern in the Pyrenees.

4.2.8 Other minerals suitable for (U-Th)/He dating

Minerals other than apatite have been developed for use as (U-Th)/He thermochronometers. Zircon (Reiners et al., 2002b) has a closure temperature of around 200°C, whilst titanite
(sphene) has a closure temperature in the range of 191–218°C (Reiners and Farley, 1999). The addition of further minerals suitable for use is still growing with others (e.g. haematite) also partially calibrated for use (Farley, 2002). As a result an entire suite of chronometers may be used to track the path a sample took to get to the surface today just by using the (U-Th)/He system.

### 4.2.9 Apparatus and protocol for measuring ages

AHe ages were measured at the Scottish Universities Environmental Research Centre (SUERC), East Kilbride.

After selection of crystals described in section 4.2.3 and loading in a stainless steel capsule wrapped in degassed copper foil, a two stage process is followed. The first stage involves measuring the helium concentration in the sample. The loaded capsule is heated in a double walled resistance furnace at 950°C for 35 minutes. The liberated gas is then purified on hot and cold TiZr getters and a liquid nitrogen cooled charcoal trap for 10 minutes after heating. $^4$He abundance is then measured relative to a 99.9% pure $^3$He spike in a quadrupole mass spectrometer (Hiden HAL3F) equipped with a Faraday detector. Following measurement the sample is re-heated for a further 35 minutes to ensure complete extraction of helium. Helium blank levels throughout the period of analysis are kept at less than 0.1% of the total $^4$He released by the sample. If the blank exceeds this value, another reheat is performed until this value is achieved. The reproducibility of the $^3$He spike is determined from twice daily measurements against an accurately known standard $^4$He (Persano et al., 2002).

The second stage involves measuring the uranium and thorium in the apatites. Following retrieval of the capsule from the furnace, the samples are dissolved in 5% nitric acid and spiked with approximately 3 ng $^{230}$Th and 1.3 ng $^{235}$U. Uranium and thorium were then purified using conventional cation exchange chemistry. Uranium and thorium concentrations are then measured by VG PlasmaQuad 2 ICP-MS.

An uncorrected AHe age can then be calculated on the basis of the relative amounts of helium versus uranium and thorium. Analytical errors by this technique are ±8% due to measuring uncertainties developed on both mass spectrometers.
Repeated analysis by the above technique of Durango fluorapatite at SUERC typically gives an age of 32.1±1.4 Ma (Persano et al., 2002) which is in good agreement with that measured at the California Institute of Technology laboratory of 32.0±1.0 Ma (Farley, 2002).

4.2.10 Examples of uses

Examples of the use of (U-Th)/He dating have been given throughout this section, but some additional studies require highlighting. Due to the low closure temperatures of the (U-Th)/He system in apatite, in regions of high relief, some deformation of the isotherms will take place (section 4.7). This effect has been used as a tool for palaeogeomorphology in the Sierra Nevada where the 60-80 Ma antiquity of valleys and ridges was demonstrated (House et al., 1998). Other palaeo-geomorphic studies have been performed such as in the Cascade Mountains (Washington State, NW USA), where attempts have been made to show the coupling of orographic precipitation with erosion rates again making use of the low temperature nature of this system (Reiners et al., 2002a; 2003a). Other palaeo-geomorphic studies (House et al., 2001; Pik et al., 2003; Spotila et al., 2004) have highlighted the use of such a thermochronometer for use in geomorphology. (U-Th)/He dating has also been used in a more traditional way with studies such as Reiners et al. (2003b) in the Dabie Shan, eastern China, using the (U-Th)/He system in apatite and zircon amongst other chronometers to document the cooling paths of samples to the surface.

4.3 Apatite fission track thermochronology

Like (U-Th)/He thermochronology, apatite fission track analysis (AFT) is a relative, not an absolute dating technique (Gleadow et al., 1986). It records the time at which a rock passed through a closure temperature of roughly 110°C (Wagner, 1968; Wagner and Reimer, 1972; Haack, 1977; Gleadow and Lovering, 1978; Gunnell, 2000). It is often used in conjunction with other radiometric systems to define the cooling path that a sample has undertaken (Gallagher, 1995). It has been used predominantly with higher temperature systems but with the advent of the lower temperature (U-Th)/He system it has been utilised as an upper boundary constraint on the exhumation of rocks in the top few kilometres of the Earth’s crust. Fission track ages do not generally represent discrete events in the cooling of a rock and one of the advantages of fission track analysis is that information other than cooling age
is contained within the data (Wagner and Storzer, 1972; Gallagher, 1995). This additional information is based on how a fission track age is obtained.

The principal of fission track dating is the presence of tracks within a crystal. Fission is defined as the process by which a heavy nucleus breaks down into two daughter nuclides of roughly similar size. This may occur by the impact of a neutron from an external source such as a nuclear reactor or spontaneously because of inherent nuclear instability. When fission occurs by either of the above processes it is accompanied by the emission of neutrons and gamma radiation. When fission occurs within a crystal lattice (e.g. the breakdown of $^{238}$U in apatites) this emission of neutrons and energy results in a damage track appearing in it as the energy is dissipated (Wagner, 1968). The size and length of the tracks produced are dependent on the material properties of the crystal host, but are usually 10-20 µm long and 10 nm wide. They occur principally in inorganic isolating materials such as crystals, glasses and plastics (Green et al., 1986). In any given mineral all newly formed tracks have approximately the same etchable lengths. The lengths of these tracks are dependent on temperature, with the etchable length decreasing as temperature increases (Green et al., 1986; Laslett et al., 1987; Duddy et al., 1988; Green et al., 1989; Gallagher, 1995). This shortening of track length is known as annealing. In apatites at temperatures below ~80°C all tracks formed will be retained and are not appreciably annealed over geological time periods (Wagner, 1968; Naeser and Faul, 1969; Naeser, 1981; Burbank and Anderson, 2001). Similarly above ~110°C all newly formed tracks are rapidly annealed and will disappear, with the crystal effectively healing the damage tracks. Between ~80-110°C a continuum exists with comparatively more annealing taking place closer to 110°C than 80°C. This zone of variable annealing is termed the Partial Annealing Zone or PAZ (Gleadow and Fitzgerald, 1987). These temperatures are for the apatite system, but fission track analysis is also performed on other minerals such as zircon with closure temperatures of 250±25°C (Yameda et al., 1995).

The principal technique by which fission track ages are calculated is known as the ‘External Detector Method’ (Gleadow, 1981; Hurford and Green, 1982; 1983; Green, 1985; Gleadow et al., 1986; Hurford, 1990). Natural fission tracks observed in apatites are formed as a result of spontaneous fission of $^{238}$U. The fission track age is calculated using the ratio of fission tracks present in a sample to the amount of $^{238}$U present in a crystal. It is difficult to measure the amount of $^{238}$U in a small crystal (<150 µm diameter), but comparatively easy to measure the amount of $^{235}$U using thermal-neutron activation analysis. Once this has been
measured the \(^{238}\text{U}\) concentration may be calculated using the constant \(^{238}\text{U}/^{235}\text{U}\) ratio of 137.88 observed in natural systems (Donelick, 2004). Thermal-neutron activation analysis relies on the fact that \(^{235}\text{U}\) rarely undergoes spontaneous fission and therefore requires that fission be induced via irradiation in a nuclear reactor. In this process, samples are irradiated and bombarded with neutrons which induce fission tracks that can be measured. In order to produce a surface to observe the induced fission tracks, each grain mount (technique for creation of mounts described in section 4.3.3) is covered by a thin, low-uranium muscovite mica sheet placed in intimate contact with the polished and etched apatite crystals. Following irradiation and subsequent cooling down, the mica sheets are etched to reveal the induced tracks resulting from the induced fission of the \(^{235}\text{U}\) in the sample. For standardisation a similar mica sheet is also placed in contact with a small chip of \(^{235}\text{U}\) doped glass. This is dealt with similarly and the results from the induced track densities for the apatite grains and the doped glass allow the \(^{238}\text{U}\) concentration in the apatite grain to be calculated (Donelick, 2004).

The fission track age for each crystal is then calculated using a modified form of the radioactive decay equation

\[
FTAge \approx \frac{1}{\lambda_D} \ln \left[ 1 + \lambda_D \zeta \frac{\rho_s}{\rho_i} \rho_d \right]
\]

(3)

where \(\lambda_D\) is the total decay constant for \(^{238}\text{U}\), \(\rho_s\) is the spontaneous track density in the sample, \(\rho_i\) is the induced track density within the sample, \(\rho_d\) is the induced track density of the doped glass and \(\zeta\) is a calibration factor personal to each analyst (Hurford and Green, 1982; 1983). The calibration factor \(\zeta\) is also dependent on the doped glass used, its position in and the reactor used. If any of these differs it should be re-measured.

The calculated age assumes that all crystals are from a single age population and thus all their track density counts can be pooled, the Pooled Fission Track Age. However, in certain scenarios this interpretation is invalid and a better estimate to use is the central age, which is effectively the mean of the log distribution of single grain ages, weighted by individual measurement precision (Galbraith and Laslett, 1993; Gallagher, 1995). The type of samples dictates which of these ages it is better to use considering whether they are rapidly exhumed.
samples or that they are detrital samples from a sedimentary basin, where each grain may have undergone a different exhumational history.

4.3.1 Confined track-length distributions

The total etched length of a natural fission track provides a strong indicator of the thermal history it has experienced (Ketcham et al., 2000; Donelick, 2004). The distribution of fission track lengths therefore provides information on the cooling history subsequent to the time of peak temperature. When track lengths are discussed, the tracks described are confined as opposed to projected (Laslett et al., 1982; Gleadow et al., 1986). Confined tracks are those that are found entirely within the crystal and do not intersect the surface, allowing the entire track to be accurately measured. Projected tracks are those that do intersect the surface of the polished grain mount, only showing part of the original track and consequently their lengths cannot be accurately determined (Gleadow et al., 1986). Only horizontal tracks with clearly visible ends that are confined within the crystal are measured, when the grain is mounted approximately parallel to the c crystallographic axis. This is related to the strong anisotropy of annealing in apatite, where tracks perpendicular to the c-axis are shortened more rapidly than those parallel to it (Gleadow et al., 1986). The length and crystallographic orientation of each fission track is determined at high magnification and using a digitising tablet. Measurement precision is approximately ±0.20 μm, with the precision of each track angle to the c-axis approximately ±2 degrees (Donelick, 2004). In order to enhance the measurability of the natural fission-track length distributions a duplicate grain mount is irradiated with ~10^7 tracks/cm² fission fragments from a 50 μCi ^252^Cf source in a vacuum chamber (Donelick, 2004). This is used in order to yield a greater number (20x) of fission-tracks available for length measurement (Donelick and Miller, 1991).

4.3.1.1 Track-length distributions

The amount of annealing and the distribution of track-length data can yield important information about the thermal history a sample has experienced. Examples of different confined track-length distributions are given in figure 4.5. The undisturbed volcanic distributions are what is observed if rapid cooling through the PAZ has taken place, with no
prolonged residence at these temperatures (~110-80°C), and have subsequently not been appreciably heated (Gleadow et al., 1986). This distribution may also be found in rocks of a non-volcanic origin and is diagnostic of a rapid cooling, following by residence at lower temperatures (Gleadow et al., 1986; Green, 1986). Mean track length indicative of this history would be between 14.5 to 15 μm with a standard deviation of 1.0 μm. Induced \(^{235}\text{U}\) tracks show a similar distribution related to instantaneous formation and no annealing with a longer mean track length of the order of ~16.3 μm and a standard deviation of 0.9 μm. The undisturbed basement distribution with shorter track lengths and larger standard deviations would suggest a monotonic cooling from high temperatures, where tracks are not retained, to surface temperatures where tracks are retained (Gleadow et al., 1986; Hurford, 1986). This distribution has shorter mean track lengths than that of undisturbed volcanic rocks due to the duration spent in the PAZ, with a mean track length of 12-13 μm and a standard deviation of 1.2-2 μm. The third type of distribution is that of mixed track lengths, where bimodal is a special case of this distribution. It is produced in samples that have undergone at least a two stage thermal history, where some tracks have been partially thermally annealed, whilst others have formed subsequent to the later cooling. The shorter track lengths represent those tracks from the first cooling event that have been subsequently returned to the PAZ and partially annealed, whilst the longer tracks represent those that have formed after later cooling to lower temperatures. Mean track lengths tend to be less than ~11.5 μm, with high standard deviations of greater than ~2.0 μm. The bimodal distribution is a special case of the mixed distribution, where both new and old tracks can be distinctly resolved (Gleadow et al., 1986; Moore et al., 1986). In summary, if samples have short mean track lengths and have large standard deviations then the samples have spent prolonged periods of time within the PAZ, either by monotonic cooling or by later reburial and consequent exposure to higher temperatures.

By modelling the resultant track length distributions in software such as AFTSolve (section 4.8.3), or other software potential thermal histories may be derived (Gallagher, 1995; Willett, 1997; Ketcham et al., 2000).
4.3.2 Kinetic classification of apatite grains

The chemical composition of the measured apatite grains is an important factor governing the kinetics of fission track annealing behaviour (Gleadow and Duddy, 1981; Burtner et al., 1994). The apatite can accommodate a variety of anions in its crystalline structure, with fluorine (F), chlorine (Cl) or a hydroxyl (OH) anion present in varying quantities (Deer et al., 1992). The majority of apatite grains are dominant in fluorine as opposed to chlorine. An increase in Cl content relative to F is accompanied by an increasing resistance to fission-track annealing (Green et al., 1985). This also has an effect on the closure temperature, such that Cl rich grains have closure temperatures up to 150°C (Burtner et al., 1994). However it is a less simple relationship between Cl content and resistance to annealing, with Mn- or Sr-bearing fluorapatites showing a similar annealing behaviour to that of chlorapatite (Burtner et al., 1994). In order to quantify this effect a parameter known as Dpar is used. Dpar refers to the maximum diameter of fission-track etch pits parallel to the crystallographic c-axis at their intersection with the polished and etched apatite surface (Donelick, 2004). Dpar less than 2.0 μm are considered to be relatively fluorine rich, whilst those greater than 2.0 μm are considered more relatively less fluorine rich and more chlorine rich (Burtner et al., 1994).

For example, for apatite from Durango, Mexico (F = 3.33 wt%; Cl = 0.43 wt%), has a Dpar = 1.83 μm; while for apatite from Bamble, Norway (F = 0.08 wt%; Cl = 6.37 wt%), has a Dpar = 4.99 μm (Donelick, 2004). This technique appears to be more robust than simply using chlorine wt % if Mn or rare earth element concentrations are anomalous, but fails if significant amounts of hydroxyl ions are present in an apatite (Burtner et al., 1994). Dpar is a patented measurement (US Patent Number 5,267,274; Australian Patent Number 658,800 to Donelick, R.A).

Some measurement of the kinetics of apatite grains is required in order to consider the effects of apatite grain chemistry on the fission-track age and susceptibility to annealing.

4.3.3 Sample preparation for AFT analysis

Apatites are separated from the host rock as described in section 4.5. Following separation of approximately pure apatite, two or more grain mounts per sample are prepared by immersing a quantity of apatite grains in epoxy resin and curing on a hotplate. Following curing, each mount is polished to a glass like finish to expose the internal surfaces of the
apatite grains within it. Then the grain mount is then immersed in concentrated (5M) nitric acid (HNO$_3$) for about 20±0.5 seconds at 21±1°C to reveal the natural spontaneously produced fission tracks that intersect the polished apatite grain surfaces (Donelick, 2004).

4.4 Overlap between FT and (U-Th)/He dating in apatite

The relative positions of both the Partial Annealing Zone (PAZ) and the Partial Retention Zone (PRZ) in apatite vary with a number of factors. In AFT, the temperatures of annealing vary with respect to the kinetics of the grains being measured such that the amount of chlorine or high REE concentrations can lead to higher temperatures at which annealing can take place (Burtner et al., 1994). In (U-Th)/He dating of apatites, factors such as grain size and also chemistry can have effects on closure temperatures and the position of the PRZ (Farley, 2002). Different authors tend to place the boundaries of these zones at different temperatures, with some proposing that the PAZ extends down to temperature of 60-70°C (Gleadow and Fitzgerald, 1987; Stockli et al., 2000). These temperature variations suggest that the PAZ and PRZ may overlap, abut or have a gap between each another. This observation allows for a more detailed position of a sample at different points in time to be calculated. Such that a sample may have cleared the top of the PAZ and record an AFT age with a specific track length history and then may pass through the PRZ later whilst still retaining the previous record of its history in the fission tracks. These features and the presence of kinks in PAZs and PRZs allow for pulses of exhumation to be picked out in the history of a rock column (section 4.6).

4.5 Mineral separation

In order to perform the thermochronometric procedures described, separates of approximately pure apatite are required. The first steps of this procedure required crushing of the rock samples to sand-sized grains (<355 μm) using both coarse and fine jaw crushers using facilities at the Scottish Universities Environmental Research Centre (SUERC) in East Kilbride and at the Department of Geology at the University of Glasgow. These separates were then washed to remove dust/clay-sized particles and dried at room temperature. At this point the treatment of different samples varied. A vertical transect was initially sampled (section 4.6) and the samples prepared to this stage. At this point it was considered that a
froth flotation mechanism would be the best technique to get maximum rapid apatite yields from the sample. The agent used was Sodium Oleate \( (C_{18}H_{33}NaO_2) \) This or a very similar compound is used in the mining industry to separate apatite on a large scale in phosphate mines. It works by preferentially clinging/coating the apatite grains related to their calcium contents. It causes these grains to float and so in theory relatively pure apatites may then be skimmed off the surface, after agitating the liquid to generate a froth. Initial viewing of these separates under the picking microscope revealed that the required yields of apatites were not being achieved and further refining of the separates was required. In order to do this, samples were passed through the Franz isodynamic magnetic separator to remove many mafic grains, particularly micas, that appeared to float in the oleate mixture. Then heavy liquid separation was used to separate the apatites from the remaining minerals (LST – lithium heteropolytungstates, with density of 2.95 g/ml at 25°C). However following these separations it was found that poor separates were still being obtained. The problem was that following the use of the oleate, it was very difficult to clean all of the oleate off the grains. As a consequence, the heavy liquids did not perform to maximum efficiency and yields of heavy minerals were poor. Intensive attempts to clean the separates followed, using repeated rinsing in water, acetone and detergents such as Decon, whilst agitating the grains in an ultrasonic bath. Some progress was made using Decon, but many grains still floated in pure water leading to density contrasts used in heavy liquid separation to be impossible. An additional problem with using oleate was that since it is a hydrocarbon, it must be fully cleaned off the grains before analysis, as the noble gas mass spectrometer is sensitive to any hydrocarbons present on the grains to be analysed.

As a consequence of the failure of the oleate method, the entire vertical transect was abandoned and a new set of samples collected from the Pyrenees. The subsequent samples were separated by more conventional means and due to time pressures and the requirement to create some fission track slides the separation was undertaken by Apatite to Zircon, Inc. in Idaho, USA. Here, separation was performed in the standard way as described above, except omitting the oleate steps (Donelick, 2004). The result of separation was a small separate of roughly pure apatite (and zircon and sphene) suitable for picking for \((U-\text{Th})/\text{He}\) thermochronology.
4.6 **Sampling strategies for low temperature thermochronology**

When sampling rocks for use with low temperature thermochronology, certain factors must be considered. In order to obtain a section through the crust a vertical or pseudo-vertical sampling section must be taken. This may be simply achieved through a borehole, giving a perfectly vertical section. However as distance down the borehole increases, so correspondingly does the temperature. At certain depths (chronometer specific) the sensitive temperatures may be reached and so possibly, if the borehole goes deep enough, showing the reset of ages down to zero (House et al., 1999). If a cheaper strategy is used by using the natural relief of the landscape sampling up the side of a valley or mountain, a corresponding amount of vertical section may be obtained. That will allow a pseudo-vertical profile through the crust to be developed assuming that the closure temperature isotherm is flat with respect to the geoid (section 4.7). This enables a vertical section of crust to be analysed, which allows determination of the exhumation rate using differences between valley and ridgetop samples (e.g. Fitzgerald and Gleadow, 1988; Mancktelow and Grasemann, 1997; Safran, 2003) and the presence of any kinks in the age elevation relationship profiles, permits the interpretation of periods of stasis/stop-starting of exhumation in the crust (e.g. Fitzgerald et al., 1999). Kinks or breaks in slope in age-elevation relationships imply that the rock column has remained at a constant depth with respect to the surface, long enough to allow a PAZ or PRZ to develop. This period is then followed by relatively rapid exhumation which preserves this pattern of ages, allowing interpretation of changing rates and timing of exhumation. This pattern has been observed and interpreted in many different tectonic regions around the world (e.g. Fitzgerald et al., 1995; Stockli et al., 2000).

It should also be noted that vertical profiles from boreholes and those using natural relief will complement one another, each providing a different section of the rock column, with the borehole providing a thermochronologically younger section of crust compared to that at the surface.

The prerequisites therefore for sampling the relief of a landscape for thermochronology are to achieve the maximum amount of relief over as short a horizontal distance as possible in order to maintain a close to vertical profile.
4.7 Topography and isotherms

Topography and relief structure play an important part in the use of thermochronology as a means of deducing amounts, timings and rates of denudation. Without the presence of relief, more costly sampling strategies such as by drilling and coring boreholes are required to achieve vertical or pseudo-vertical transects. Relief permits the sampling of surface exposed bedrock from elevations up a valley or mountain side to obtain a pseudo-vertical transect. The resultant suite of data allows a different, thermochronologically older section of rock to be observed compared to a thermochronologically younger one from a borehole. Using data from a variety of elevations gives the potential to calculate features such as exhumation rate and the identification of palaeo-PAZs and -PRZs.

Assumptions on the interpretation of thermochronologic data are made, often ignoring the effects of topography/relief that made the sampling possible in the first place. Many of the assumptions were initially used for AFT analysis and then presumed valid for lower temperature chronometers such as the (U-Th)/He system. Here, the common assumptions for thermochronometry are examined and then discussed in the context of topographic relief considering whether they require revision in the light of isotherm deformation and the effects of heat advection.

4.7.1 Common thermochronometric assumptions

Several assumptions are made in the interpretation of thermochronometric data when calculating factors such as exhumation rate by techniques such as the mineral pair method (e.g. Zeitler et al., 1982) or by the elevation dependence method (e.g. Fitzgerald and Gleadow, 1988; Mancktelow and Grasemann, 1997; Safran, 2003). One of the key assumptions made, particularly by the mineral pair method, is that the palaeo-geothermal gradient must be known or at least a value assumed during cooling (Mancktelow and Grasemann, 1997; Safran, 2003). By using a uniform, unchanging geothermal gradient the effects of heat advection are then neglected, assuming that isotherms remain at a constant depth with respect to the surface (Brown and Summerfield, 1997; Moore and England, 2001).
Another common assumption is that the closure temperature isotherms of the system in question are flat with respect to the surface and consequently undeformed by the topography (Parrish, 1983; Stüwe et al., 1994; Brown and Summerfield, 1997).

When sampling up a mountain side, the resultant data suite is plotted on an age elevation diagram and from this plot interpretations are made. This presumes that the horizontal locations of the sample sites can be ignored and that the profile may be approximated to that of a vertical borehole.

A final assumption is that the surface does not change in amount of relief, e.g. more deeply incising valleys or lowering of ridgelines (Parrish, 1983; Braun, 2002; Safran, 2003).

The following discussion considers each of these assumptions and how they are required to be refined in the treatment and interpretation of thermochronometric data.

### 4.7.2 Geothermal gradients and the effects of heat advection

One of the required assumptions of using the mineral pair method for calculating exhumation rate is that the average geothermal gradient between the two closure temperatures of the systems of interest is known and remains constant throughout exhumation (Safran, 2003).

The calculation of the palaeo-geothermal gradient is a challenge in itself (Brown and Summerfield, 1997; Howard and Foster, 1996; Bray et al., 1992), and large uncertainties may exist, which can be passed on and often magnified by possible future uses of the data. Calculating modern geothermal gradients over regions is often difficult because of anomalies in heat flow measurements as a result of local fluid flow and heterogeneous heat production (Pollack et al., 1993; Morris, 1999). This may be hard to reconcile so as to achieve a meaningful average geothermal gradient for a region. All of these potential errors occur without even considering the effects of heat advection during exhumation and consequently whether geothermal gradients remain constant at all. If heat advection is neglected during exhumation, then cooling curves will simply follow straight lines in T-t space (figure 4.6a) assuming constant continuous exhumation (Mancktelow and Grasemann, 1997). In a similar scenario allowing for heat advection, cooling curves in T-t space begin to become curved (figure 4.6b and 4.6c). These curves have slower cooling initially becoming faster towards the end related to an elevated geothermal gradient near the surface (Mancktelow and Grasemann, 1997; Moore and England, 2001), with the isotherms migrating towards the
surface during periods of exhumation (Brown and Summerfield, 1997). Both of these model runs (figure 4.6b and 4.6c) start with a constant geothermal gradient and are later modified if heat advection occurs. Figure 4.6 illustrates how the cooling curves may be modified by allowing for heat advection, whilst also demonstrating that one of the principal controls on this process is the magnitude of the exhumation rate. The faster the exhumation rate the greater the effect of heat advection plays on the higher temperature isotherms (figures 4.6c, 4.6d). This migration of isotherms towards the surface has implications not only for calculating exhumation rates but also for the actual age a thermochronometer records. With the effects of heat advection, if a sample is forced to cross a particular isotherm at a shallower depth than it would have done if the isotherms had remained static, a younger age is recorded. Consequently if heat advection is ignored, the depth of any critical isotherm will always be overestimated leading to an overestimation in the magnitude of the exhumation rate (Brown and Summerfield, 1997).

A further complication is introduced if there has not been constant continuous exhumation through time. If exhumation is pulsed or has continually varied through time then the thermal relaxation of the isotherms must be considered. The relaxation of isotherms to resume to a steady state configuration may take a long time particularly at depths greater than 20 km (Mancktelow and Grasemann, 1997). This effect is particularly important in many mountain systems where an initially rapid exhumation rate that dies off exponentially is considered more realistic than a stop-starting of exhumation (Mancktelow and Grasemann, 1997).

This discussion has demonstrated that the effects of heat advection and subsequent relaxation have strong implications for the common assumptions made relating to geothermal gradients during exhumation.

### 4.7.3 Topographic effects on isotherms

The previous section has shown the importance of heat advection during exhumation assuming a flat upper boundary surface. This effect may be true if sampling took place by borehole (e.g. House et al., 1999; Cederbom et al., 2004), but what are the consequences of introducing relief onto the upper surface of such scenarios?
At crustal depths greater than 20 km, isotherms are considered to approximate a flat surface whatever the surface topography may be (Stüwe et al., 1994; Mancktelow and Grasemann, 1997). This assumes that there are no local additional heating sources such as magma chambers creating temperature heterogeneities. For simplicity, at the surface isotherms can be considered to approximate the topography, assuming that the effects of lapse rates are ignored. In mountainous regions, if a lapse rate such as the SALR is followed then in regions with 2 km of relief there may be a temperature difference of 13°C between valleys and mountain summits (section 3.2). The magnitude of this effect is minimal and serves to intensify the relationship described later between ridges and valleys. Thus from flat isotherms at depth to curved isotherms following the topographic relief at the surface, some continuum must exist. The critical questions are what is the magnitude of this continuum and how are the critical isotherms such as the 110, 80, 75 and 45°C affected? The perturbation of these low temperature isotherms is intrinsically linked to the exhumation rate and consequently the effects of heat advection. When considering a flat upper boundary, this surface would be cooled equally at all points by diffusion, but when considering an undulating upper boundary a different effect occurs. Ridges are more efficiently cooled by diffusion than valleys leading to isotherms becoming more compressed beneath valleys than ridges (Stüwe et al., 1994; Braun, 2002; Safran, 2003). Therefore, for isotherms above a critical depth, which varies with exhumation rate, a difference in spacing will exist between valleys and ridges (figure 4.7) (Stüwe et al., 1994).

This effect of topography on the distribution of isotherms is related to a number of factors. The magnitude of the exhumation rate will affect the degree of perturbation, but the wavelength and amplitude of the topography also play an important role. For short wavelength, low amplitude topography the effects are minimal, with increasing perturbations for larger wavelengths and amplitudes (Stüwe et al., 1994). To a first order approximation, the magnitude of the perturbation at depth will be directly proportional to the amplitude of the topography, whilst the wavelength and exhumation rate will determine the depth of penetration of the topographic effects (Mancktelow and Grasemann, 1997). At low erosion rates (<0.5 kmMyr⁻¹) the degree of perturbation of isotherms is minimal (100s of m), but for higher rates (>0.5-1 kmMyr⁻¹), this may be of the order of kilometres for wavelengths larger than 20 km (Stüwe et al., 1994). These rates are based on deformations of the 110°C isotherm (Stüwe et al., 1994) with a rate of only 0.3 kmMyr⁻¹ required to deform the 75°C isotherm (Braun, 2002). Therefore, when considering the effects for lower temperature isotherms such as 45°C, temperature perturbations may be highly significant.
The deformation of the isotherms with respect to topography also plays an important role when considering whether topographic sampling profiles (i.e. up the side of a valley/mountain) can truly be considered as proxies for vertical profiles (i.e. like a borehole). If the closure temperature isotherm of a thermochronometric system cannot be assumed to be flat then this assumption falls apart. If the closure temperature isotherms are significantly curved then the samples from the high points will appear relatively younger, due the elevated depth of the critical isotherms beneath ridges (Stüwe et al., 1994). This has consequences for estimating exhumations rates particularly by the elevation dependence method where the spacing between the closure temperature isotherms remains constant in time (problem relating to effects of heat advection) and space (difference between valleys and ridges) (Safran, 2003). This leads to an overestimation of the exhumation rate (Stüwe et al., 1994; Manktelow and Grasemann, 1997; Braun, 2002) and if interpreted on an age elevation plot it will lead to a steepening in the age elevation relationship (AER) (Braun, 2002).

These observations suggest caution in the description/interpretation of AERs, with the data distribution potentially being non-linear, merely being a function of the dampened shape of the critical isotherm with respect to the topography (Stüwe et al., 1994).

### 4.7.4 Effects of increasing or decreasing surface relief

Previous models considering the deformation of isotherms by topography have used a constant topographic surface, i.e. no changes in altitude or surface shape through time (e.g. Stüwe et al., 1994). However more recent work has considered the effects of changing the form of the topographic surface through time (Braun, 2002; Safran, 2003). The effects of both increasing and decreasing relief are considered.

#### 4.7.4.1 Increasing relief

For local relief to increase, valleys must erode more rapidly than ridges, so it would be expected that ridge and valley cooling ages would diverge through time as isotherms are advected closer to the surface beneath valleys than ridges (Safran, 2003). Additionally for a set wavelength, diffusive cooling will become more effective and the depth of a given low temperature isotherm will increase beneath ridges (Mancktelow and Grasemann, 1997;
Safran, 2003). The effect of this is demonstrated in figure 4.8, with older ages observed on the ridges and younger ages in the valleys. With a greater age divergence than in the constant relief case (Braun, 2002). This will still, however, overestimate the imposed exhumation rate. The behaviour for thermochronometers of differing temperatures is not identical with higher temperature chronometers such as the AFT system taking longer to respond to the effects of increasing relief. This is due to its depth and therefore being less susceptible to near-surface cooling effects than lower temperature systems such as the (U-Th)/He system (Safran, 2003).

4.7.4.2 Decreasing relief

For local relief to decrease, ridges must erode more rapidly than valleys. Closure temperature isotherms are advected more rapidly towards the surface beneath ridge tops than beneath valley bottoms, which causes ridge cooling ages to become younger. In contrast valley ages may become older compared to constant relief scenarios (Safran, 2003), as closure temperature depth increases beneath valleys. The effect of this in an endmember case is to produce an inverted age-elevation relationship with a negative slope (figure 4.8) (Braun, 2002). The results of these relief changes and temperature and topographic effects are summarised in figure 4.9.

As can be noted from the variability that increasing and decreasing relief may have on the AER, traditional methods for determining exhumation rates such as mineral pairs or elevation-dependence (slope of AER) fail in such scenarios for low temperature thermochronometers. This failure is usually characterised by overestimating exhumation rates (e.g. Stüwe et al., 1994; Braun, 2002; Safran, 2003) and in extreme scenarios of decreasing relief, they produce a negative answer (Braun, 2002)!

4.7.5 Summary

This summary has discussed the common assumptions that are used in some thermochronometry studies and shown that many are oversimplifications. In particular if AERs are used to calculate exhumation rates then these will always be a maximum rate and
consequently always provide an overestimation in regions with relief for low temperature thermochronometric systems. As a consequence, any interpretation of thermochronometric data from these systems, usually less than $200^\circ C$ except in very high wavelength and high exhumation rate terrains, requires that the topographic effects be taken into account. The result of this is that some degree of thermal modelling is required for interpretations of thermochronologic data in any region where significant relief exists. The challenge for interpreting thermochronology data is the ability to convert the variations of temperature with time to the variations of depth with time (Brown and Summerfield, 1997).

A final assumption that is sometimes made with regard to thermochronometers is that the recorded age represents the time at which a sample passed through its closure temperature. With rapid exhumation, this may be valid, but if slow exhumation occurs and significant periods are spent in either the PAZ for AFT or the PRZ for AHe then this is no longer the case. The potential cooling paths require consideration, along with observing the track length distributions for AFT analysis for evidence of extensive annealing. So potential cooling histories need to be considered before conclusions are drawn about the thermal histories.

### 4.8 Thermal modelling

In order to interpret the thermochronometric results for the Pyrenees in light of timings of exhumation and to give rough estimates on rates, a variety of techniques were used to simulate the exhumation of rocks in the study area. In the discussion of topography and isotherms, it was shown that isotherms can be strongly perturbed by the topography and large variations can occur relating to increasing or decreasing relief. The purpose of modelling the data was to test if:

a) Topography was important to the interpretations imposed on the data

b) Increasing or decreasing relief played an important role in modifying the interpretations

c) To observe how different tectonic scenarios fit the data and to find a preferred solution for the independent data sets.
4.8.1 Creating synthetic T-t histories

In order to perform these tests the Pecube code was used (Braun, 2002; 2003). Pecube is a finite element code that solves the transient heat equation in three dimensions (Braun, 2003) in a crustal block undergoing uplift and denudation. Major benefits of this code over previous attempts are that:

a) It works in three dimensions allowing the general shape of the topography to play a role and not simply two dimensional sections

b) It includes the effect of a time-varying surface topography – so increasing and decreasing relief scenarios may be modelled (Braun, 2003)

c) It allows for heat transport by conduction and advection and also allows for heat production, often ignored in other models (Mancktelow and Grasemann, 1997; Safran, 2003).

Topographic data to be modelled may be inputted from a DEM in GRID or TIN format such as output from the CASCADE landscape evolution model. This topography can be specified at various time steps throughout the model to allow for changes in relief and exhumation rate.

Output from the model is in the form of individual time-temperature-depth paths for individual nodes and some short additional code was written to extract specific nodes from this data. This allows for the locations where a sample was taken to be analysed for a particular set of parameters e.g. changing timing of relief development or amounts and timings of exhumation and from these a thermochronometric age may be calculated for the sample site. These ages were calculated by using thermochronometer specific software such as AFTSolve for AFT analysis (Ketcham et al., 2000) and DECOMP for AHe (Meesters and Dunai, 2002a; 2002b; Dunai et al., 2003).

4.8.2 Calculating synthetic thermochronometric ages

The simplest way to approach this problem is to use a fixed closure temperature for each thermochronometer with the time at which the sample crosses this isotherm as the thermochronometric age of the sample. This technique is fast and effective at achieving ballpark figures for rapidly exhuming samples as figure 4.10 illustrates. However if a
sample remains in the PAZ or PRZ for a significant period of time then this quick method becomes erroneous with younger ages fixed in the sample (figure 4.10). If varied exhumational histories are to be explored then the effects of annealing of fission tracks and diffusion of helium need to be accounted for. In order to achieve this thermochronometer specific software was employed.

4.8.2.1 Calculating apatite fission track ages

AFTSolve is a computer program for deriving thermal histories from AFT data (Ketcham et al., 2000) (figure 4.11a). It implements a variety of fission track annealing models that take into account the known kinetic variability among different apatite species. This aspect of the code is useful for inverse modelling i.e. deriving a T-t history from an AFT age and track length distribution. However, it also allows for forward modelling, by inputting a T-t history and deriving an AFT age and its respective track length distribution. This aspect of the code was used in the Pecube modelling to derive synthetic ages and track length distributions that could then be compared with the real data. As it incorporates annealing models it makes it ideal for use particularly with T-t histories that may have had a prolonged residence in the apatite PAZ.

4.8.2.2 Calculating AHe ages

DECOMP is a computer program that allows for synthetic AHe ages to be calculated based on a particular T-t history (Meesters and Dunai, 2002a, 2002b, Dunai et al., 2003) (figure 4.11b). It approximates the apatite crystal as a sphere whose size/volume/surface area can be easily converted to a real crystal. By allowing the size of the diffusion domain to be varied along with the distribution of U and Th it allows for the different crystal sizes used in the analysis to be accounted for. The results generated are uncorrected for recoil and therefore require correction before use (Farley et al., 1996; Farley, 2000). DECOMP provides a forward modelling package but its ability to account for periods in the PRZ create a powerful tool for use in accounting for slower periods of exhumation close to the Earth’s surface.
4.9 Summary

This chapter has explained the techniques and principals behind low temperature thermochronology. The following chapter considers the results from these thermochronometers and topographic considerations to the central Pyrenees.
Figure 4.1 - Closure temperatures of the different thermochronometers
(adapted after: http://su-thermochronology.syr.edu/)
Figure 4.2 - The effects of $\alpha$-ejection on helium retention.  
(A) shows the three possibilities within a schematic crystal, $\alpha$-retention, possible $\alpha$-ejection from crystal and possible $\alpha$-implantation. 
(B) shows how $\alpha$-retention changes from core to rim along A-A'.  
After Farley (2002).
Figure 4.3 - Variation of $F_T$ correction with crystal diameter
Figure 4.4 - Apatite crystals with good morphologies and inclusion free shown prior to loading
Figure 4.5 - Possible confined track length distributions and their associated thermal histories. Values in red on track length distribution graph are example mean track lengths and associated standard deviations.
Figure 4.6 - Calculated cooling curves for two rock samples, A and B initially at 12 km and 10 km depth respectively. Initial constant isotherm of 25°Ckm⁻¹ is assumed (no internal heat production). (A) shows effect of no heat advection whilst (B-D) allow heat advection with different applied exhumation rates. After Mancktelow and Grasemann (1997).
Figure 4.7 - Cartoon illustrating the distribution of isotherms beneath valleys and ridges for the AHe PRZ.
Figure 4.8 - Predicted (U-Th)/He AERs for a range of relief evolution scenarios. After Braun (2002).
(A) High Tc Thermochronometry

(B) Low Tc Thermochronometry

(C) Low Tc Thermochronometry and Relief Change

Figure 4.9 - Three scenarios in which exhumation rate can be estimated from the slope of an AER.

a) A flat $T_c$ isotherm where the slope of the AER equals the exhumation rate
b) Low temperature thermochronometers where the slope overestimates the exhumation rate
c) A decrease in relief can lead to a negative slope to the AER.

(Adapted from Braun, 2002)
Figure 4.10 - Two very different thermal histories, yet if age is taken as time when sample passes through $T_c$ then the same result is obtained for histories 1 and 2. However if annealing or diffusion are taken into consideration then history 2 will record a younger age.
Figure 4.11 - Screen dumps of (A) AFTSolve and (B) DECOMP showing technique for synthetic age calculation.