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Chilisa Marie Shorten
Syracuse University

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General Abstract

Since the early development of the fission-track dating method by Price, Walker and Fleischer in the 1960's and 1970's, the method has evolved into a robust tool for constraining thermal histories and determining exhumation rates within the upper continental crust. Low-temperature thermochronology, notably apatite fission-track thermochronology because it has a kinetic parameter (i.e. track lengths), is commonly used to constrain the tectonic history of orogenic belts and the thermal history within sedimentary basins for hydrocarbon resource assessment. Collisional tectonics in the Paleozoic which formed of the Appalachian Orogen and the foreland basin has been a subject of considerable study. The objective of this dissertation is to apply low-temperature thermochronology to constrain the post-orogenic thermal history and exhumation of the Northern Appalachian Basin. Previous work has identified that the post-rifting evolution of eastern North America involves a number of periods of rapid cooling and/or exhumation, yet significant debate remains on the temporal and spatial resolution of the periods of rapid cooling within the Mesozoic and Cenozoic, and hence their significance. Chapters one and two of this dissertation are focused on constraining the post-orogenic thermal history and exhumation of the Northern Appalachian Basin, within New York and Pennsylvania. Chapter three is a comprehensive analysis of the thermal history trends and variations synthesized from published low-temperature thermochronology studies across the Appalachian orogen in eastern North America.

Chapter one constrains the post-orogenic thermal history and exhumation of the Northern Appalachian Basin utilizing apatite fission-track (AFT) thermochronology and (U-Th)/He dating integrated with paleothermometers and geologic constraints. Samples were collected from

Devonian-aged Catskill delta wedge formations across New York and Pennsylvania (USA). The AFT age of samples decreases from west to east across the Northern Appalachian Basin (~180-120 Ma) a result of synchronous onset of exhumation, with greater amounts of burial and exhumation in the east. Apatite fission-track thermochronology data, apatite (U-Th)/He ages, and vitrinite reflectance maximum paleotemperature information provide inputs for inverse thermal models, which constrain a multi-stage post-orogenic history. Overall cooling rates documented in the Northern Appalachian Basin are slow, however we constrain two periods of “rapid” cooling separated by a long period of slower cooling: (1) Late Triassic to Early Jurassic onset of rapid cooling (1-3 °C/Myr) from maximum temperatures, generally higher than the retentivity of fission-tracks in apatite (i.e. >~110-120 °C); (2) Slow cooling (0.1-0.3 °C/Myr), which is referred to as a period of stabilization within the Northern Appalachian Basin, from the Cretaceous to Late Cenozoic; (3) Rapid cooling (1-2 °C/Myr) from the Mid-Miocene to present. Low-temperature thermochronology, combined with paleothermometers, constrains the thermal and exhumation history of Devonian strata and relates episodes of cooling to contemporaneous tectonic events occurring along the northeastern North American margin.

Chapter two focuses on the thermal history and exhumation of the Catskill Mountains, New York. A ~1 km age-elevation profile of samples collected from Catskill delta wedge units of Slide Mountain were analyzed with apatite fission-track thermochronology and apatite (U-Th)/He dating. The Catskill Mountains formed via exhumation and erosion of the Appalachian Plateau. The slope of the AFT age-elevation profile constrains an apparent exhumation rate of ~50 m/Myr in the Early Cretaceous. Multi-kinetic inverse thermal models reveal “rapid” cooling episodes from the Early Jurassic to the late Early Cretaceous and from the Mid-Miocene to recent. As documented in the Northern Appalachian Basin, these episodes of rapid cooling in the

Catskills are separated by a period where samples experienced stabilization and much slower cooling for ~100 Myr. This chapter discusses the debate surrounding the resolution and existence of a Miocene cooling event along eastern North America, which because of its low magnitude makes it challenging to document with low-temperature thermochronology. Miocene cooling constrained in modeling of the Catskills age-elevation profile samples is compared to previous low-temperature thermochronology studies that either rejected or confirmed this cooling. Studies rejecting Miocene cooling used mono-kinetic annealing algorithms in early generation AFT modeling programs, which often produced a spurious late-stage rapid cooling event. However, other low-temperature thermochronology and geomorphological studies in the central and southern Appalachians and a rapid Miocene increase offshore sedimentation rates suggest exhumation and erosion of Appalachian strata was necessary in the Miocene.

Chapter three collates low-temperature thermochronology data and thermal histories from 26 studies utilizing apatite fission-track thermochronology and/or apatite (U-Th)/He dating within the Appalachian physiographic provinces (the Appalachian low-temperature thermochronology database). While there is an abundance of thermochronology data from many studies scattered over the eastern U.S., an orogen-scale synthesis of the low-temperature thermal and exhumation history has not been undertaken. The objective is to determine temporal and spatial trends in the post-orogenic thermal histories, through identifying events which occurred throughout the Appalachian provinces, as well as province-specific events. Challenges exist in interpreting the thermal history trends given that the studies range in publication from the 1980's to present day and hence vary in style of analysis and objectives, contain synthesis of results from different methods, and utilize different data interpretation and modeling approaches with several generations of modeling programs. Many of the low-temperature thermochronology

studies undertaken along the eastern U.S. lie within present day catchments that drain into Mid-Atlantic offshore basins. We examine the onshore record and conclude episodes of rapid cooling and exhumation documented within these catchments correlate well with periods of increased sediment flux into offshore Mid-Atlantic basins. Synthesizing the temporal correlation between onshore exhumation and offshore sediment flux and the provinces' thermal histories, the post-orogenic low-temperature thermal history across the eastern U.S. passive margin is divided into three extended periods of cooling and exhumation. These periods are related to regional effects of Early Mesozoic continental rifting and post-rift crustal extension, Late Mesozoic variable cooling due to the development of the passive margin and to exogenic mechanisms, and Late Cenozoic (i.e. Miocene) rapid cooling related to the establishment of dynamic topography and drainage reorganization.

**POST-OROGENIC THERMAL HISTORY AND EXHUMATION OF
THE NORTHERN APPALACHIAN BASIN:
LOW-TEMPERATURE THERMOCHRONOLOGIC CONSTRAINTS**

by

Chilisa M. Shorten

B.S., University of Pittsburgh, 2010

Dissertation

Submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in Earth Sciences.

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Chapter One

Post-Orogenic Thermal History and Exhumation of the Northern Appalachian Basin: Low-Temperature Thermochronologic Constraints

Abstract

The Appalachian Foreland Basin extends from New York to Alabama in the eastern United States and contains sediment derived from the Appalachian Orogen. The post-orogenic thermal history and exhumation of the Northern Appalachian Basin in New York and Pennsylvania is constrained with apatite fission-track (AFT) thermochronology and (U-Th)/He dating, also incorporating other paleothermometers and geologic constraints. Thirty-eight samples were collected across twelve formations from the Devonian-aged Catskill delta wedge, which is positioned stratigraphically above the hydrocarbon-rich Marcellus Shale. AFT ages range from ca. 185-120 Ma, with a younging trend from west to east. Mean track lengths range from 10.6 to 13 μm , with unimodal, slightly negatively skewed distributions. Except for samples from the westernmost region, all samples reached temperatures higher than the retentivity of fission-tracks in apatite (i.e. $>\sim 110\text{-}120\text{ }^{\circ}\text{C}$). Inverse thermal models constrain a multi-stage post-orogenic evolution: (1) Late Triassic to Early Jurassic onset of cooling from maximum temperatures. Cooling at rates of $\sim 1\text{-}2\text{ }^{\circ}\text{C}/\text{Myr}$ is likely due to erosion of the orogenic overburden, contemporaneous with extension and rifting along the eastern United States. Paleothermometers and AFT age trends indicate that eastern samples reached higher maximum temperatures and experienced greater erosion than western and central samples. (2) From the Early Cretaceous to the Late Cenozoic, cooling rates slow significantly as the basin stabilizes after the removal of most of the orogenic overburden and the transition to a passive margin. Western and west-central samples cooled more slowly ($<0.5\text{ }^{\circ}\text{C}/\text{Myr}$) with longer residence times within the partial annealing zone than eastern samples (cooling rates $<\sim 1\text{ }^{\circ}\text{C}/\text{Myr}$). (3) Inverse models of western and central samples, including a drill core sample, indicate the onset of more rapid cooling ($\sim 1\text{-}2\text{ }^{\circ}\text{C}/\text{Myr}$) in the Late Cenozoic, continuing to present. This Late Cenozoic event is highly debated

but thermochronology results from this study indicate it is real and significant and most likely associated with landscape rejuvenation in Miocene to recent times. Low-temperature thermochronology, combined with paleothermometers, constrains the thermal history of Devonian strata, exhumation rates, and contemporaneous tectonic events occurring along the Eastern U.S. margin.

Introduction

Low-temperature thermochronology, paleothermometers and geologic constraints provide a valuable integrative approach to constrain upper crustal thermal histories (e.g. Naeser et al., 1989). Paleothermometers such as vitrinite reflectance (e.g. Zhang & Davis, 1993; Weary et al., 2000), fluid inclusion microthermometry and overpressure history (e.g. Wojcik et al., 1994; Lash & Blood, 2007; Wilkins et al., 2014) or a combination of those methods (e.g. Tobin & Claxton, 2000; Reed et al., 2005) are traditionally used to constrain thermal maximums and burial histories of sedimentary basins. Apatite fission-track (AFT) thermochronology applied to sedimentary basin strata can constrain maximum temperatures (T_{\max}) up to ~100-120 °C, as well as assess the timing and rates of cooling (e.g. Gleadow et al., 1983; Bray et al., 1992; Green et al., 1995; Green & Duddy, 2012). AFT is also well-suited for characterizing potential hydrocarbon generation zones due to the overlap between the partial annealing zone (PAZ) temperature range and temperatures of initial source rock maturity (Figure 1). For sedimentary basins, combining thermochronology and paleotemperature methods, is often used to establish T_{\max} , thermal cooling rates, exhumation histories, and provide insight into hydrocarbon source rock maturation levels (e.g. Green et al., 1989; Gallagher et al., 1998; Green & Duddy, 2012; Ketcham, 2012).

This study utilizes low-temperature AFT thermochronology, combined with apatite (U-Th)/He (AHe) dating and maximum paleotemperature indicators (i.e. vitrinite reflectance and conodont alteration indices), to constrain the thermal and exhumation history of the Northern Appalachian Foreland Basin (NAB), in the states of Pennsylvania (PA) and New York (NY; Figure 2). Previous work, which used AFT analysis to constrain the thermal history of the NAB in NY (Miller and Duddy, 1989), and this study observe similar AFT age trends but different thermal histories. Without inverse thermal modeling, Miller and Duddy (1989) schematically determined a thermal history based on spatial trends of AFT ages and the relationships between AFT age, mean track length and standard deviations (i.e. “boomerang plots”, Figure 3 & 6 of Miller & Duddy, 1989). They hypothesized that all samples across the basin were exhumed to the near present surface within the Early Cretaceous (ca.120-140 Ma). In this paper precise measurements of confined fission track lengths and composition proxies are input into inverse thermal modeling, utilizing a multi-kinetic annealing algorithm (e.g. Ketcham et al., 2007), an approach not typically undertaken until the 1990’s. With these advances, this study builds on previous work while revealing a more complex, multi-stage cooling history.

Geologic Setting

The formation of the Appalachian Mountains of eastern North America and the adjacent foreland basin is a result of the Taconic, Acadian and Alleghanian orogenies in the Paleozoic (e.g. Hatcher, 2010). Tectonic deformation and loading close to the orogenic front controlled the extent and shape of the basin, generating an asymmetrical accommodation space (Figure 3; e.g. Beaumont et al., 1987; Ver Straeten, 2010). The Devonian sedimentary units preserved in the NAB, referred to as the Catskill delta wedge, were deposited during the Acadian Orogeny in a series of westward-migrating depositional episodes (Faill, 1985; Ver Straeten, 2010). The

provenance of the Catskill delta wedge includes mainly sedimentary and low-grade metamorphic rocks from predominantly Acadian sources with lesser contributions of sediment from Taconic- (~30%) and Grenville-age (~5%) sources (Ver Straeten, 2009).

The total preserved Paleozoic sedimentary section in the NAB is estimated at 6-8 km thick in the west and 10-16 km thick in the east (Lindberg, 1985; Ver Straeten, 2010) as shown in a diagrammatic cross section (Figure 3). Paleocurrent analyses indicate detritus was carried westward from the mountains formed during the Acadian orogeny, resulting in a general fining of the grain-size from east to west (Faill, 1985; Ver Straeten, 2010). Basin units dip gently $\sim 1\text{-}2^\circ$ to the southwest, due to post-depositional tectonics associated with basin inversion and/or regional uplift (e.g. Johnsson, 1986; Isachsen et al., 1991; Eaton & Frederiksen, 2007). Thus, outcropping units are stratigraphically younger to the south.

A significant amount of sediment was deposited on top of the Catskill delta wedge during the Acadian and Alleghanian Orogenies and is reflected in maximum burial depths from T_{\max} indicators (e.g. Johnsson, 1986; Levine, 1986; Beaumont et al., 1987; Reed et al., 2005; Lash & Blood, 2007). Estimates of the amount of sediment (i.e. “overburden”) which has been removed from above the Catskill wedge range from $\sim 2\text{-}4$ km (Johnsson, 1986; Faill, 1998), with some estimates as high as 7 km (Friedman, 1987). The duration of T_{\max} due to burial and the timing of temperatures within the hydrocarbon generation window is more elusive, since common indicators such as vitrinite reflectance and conodont alteration indices only constrain T_{\max} and are dependent on heating rate and residence time (e.g. Green & Duddy, 2012). In the Late Triassic (ca. 237 Ma), after syn- and post-Alleghanian deposition westward into the NAB, Pangea began to break apart and a passive margin developed along the eastern North American continent (Withjack et al., 1998; Withjack & Schlische, 2005). As the Atlantic Ocean expanded,

drainage patterns shifted, and sediment was transported eastward across much of the NAB (Judson, 1975).

Methods

Sampling Strategy

Devonian sandstones from the Catskill delta wedge were collected in a broad swath along the NY-PA border (Figure 2). Samples were collected from Devonian Catskill delta wedge units, including several depositional groups (i.e. Conewango, Conneaut, Canadaway, West Falls and Hamilton) and 12 different formations (see supplementary file A). Sample locations were influenced by the availability of suitable sedimentary outcrops (i.e. medium sandstone or coarser, as immature as possible). Suitable outcrops are less abundant in the west, as this region was distal from the source region lying to the east (Figure 3). Fifty-four outcrop samples were collected and eight core samples were obtained from the PA Department of Conservation and Natural Resources Topographic and Geologic Survey. Thirty-seven outcrop samples and one core sample yielded sufficient apatite fractions for AFT analysis using conventional heavy liquid and magnetic separation techniques (Table 1).

Analytical Techniques

Apatite Fission-track Thermochronology is commonly applied to constrain the thermal and exhumation history within the upper ~4-5 km of the Earth's crust (e.g. Gallagher et al., 1998). This technique is a powerful tool for basin analysis (e.g. Gleadow et al., 1983; Naeser et al., 1989; Bray et al., 1992; Green et al., 1995; Green & Duddy, 2012), notably due to the kinetic parameter provided by measuring confined track lengths. Fission-track thermochronology is based on measuring the density and length distribution of fission tracks formed in a crystal as a result of the spontaneous fission of ^{238}U . In the external detector method, the density of tracks in

the apatite grain is determined along with the density of induced ^{235}U tracks for the same area within a mica external detector (e.g. Hurford & Green, 1983). This, in conjunction with the density of induced tracks in a mica over a standard glass of known [U], allows an age determination for each grain (e.g. Green et al., 1989). The length of a fission track is proportional to the maximum temperature experienced and thus the confined track length distribution (CTLD) within a sample can be used to constrain the thermal history of the sample (e.g. Gleadow et al., 1986; Green et al., 1986; Ketcham et al., 1999). A narrow distribution of long tracks indicates rapid cooling of the sample while a broad distribution of shorter and longer tracks indicates partial annealing and/or a more complex thermal history (e.g. Gleadow et al., 1986). AFT low-temperature thermochronology was undertaken at Syracuse University following standard procedures summarized in Table 1 as summarized in Riccio et al. (2014).

For samples with similar compositions to the Durango apatite standard, the AFT system has a closure temperature of $120\text{ }^{\circ}\text{C}$ for cooling rates of $\sim 10\text{ }^{\circ}\text{C}/\text{Myr}$ (Gleadow & Duddy, 1981) over long-term durations of 10^8 years (Naeser, 1981). At temperatures higher than $120\text{ }^{\circ}\text{C}$ all fission tracks are typically completely annealed, between $\sim 110\text{-}60\text{ }^{\circ}\text{C}$ fission track length is reduced in the partial annealing zone (PAZ), and at temperatures lower than $60\text{ }^{\circ}\text{C}$ most tracks are retained (e.g. Gleadow & Duddy, 1981; Gleadow et al., 1986; Gleadow & Fitzgerald, 1987; Laslett et al., 1987; Gallagher et al., 1998). Closure temperature varies with chemical composition ($\sim 120\text{-}100\text{ }^{\circ}\text{C}$; Green et al., 1986; Barbarand et al., 2003) and D_{par} , the diameter of etch pits parallel to the c-axis, is a simple and efficient measurement of an apatite's resistance to annealing (e.g. Burtner et al., 1994; Carlson et al., 1999; Donelick et al., 1999; Ketcham et al., 1999; Donelick et al., 2005). D_{par} was measured on each apatite grain used for AFT analysis.

grains which are more resistant to annealing than standard fluoroapatites (e.g. Donelick et al., 2005) and the base of the PAZ is extended to ~120 °C for those samples.

(U-Th)/He Dating is a low-temperature thermochronometric method that is used to calculate an age from the concentrations of the daughter product (^4He) and the parent isotopes (^{238}U , ^{235}U , ^{232}Th , and ^{147}Sm). Retention of the daughter product depends on the temperatures experienced and He diffusivity of the mineral (e.g. Zeitler et al., 1987; Farley, 2002; Harrison & Zeitler, 2005). The closure temperature for the AHe dating method is ~65-70 °C and the partial retention zone (PRZ), the temperature range over which radiogenic He is partially lost due to diffusion out of the crystal, is typically ~30-90 °C (e.g. Flowers et al., 2009). Single-grain ages can vary considerably as a result of a number of factors including the presence of [U]-rich inclusions, effective uranium (i.e. [eU], a parameter that weights the decay of the parent isotopes, calculated as $[\text{U}] + 0.235 \times [\text{Th}]$), grain size and/or zonation, plus cooling rate and residence time in the PRZ which tends to magnify any single-grain age variation (e.g. Wolf et al., 1996; 1998; Reiners & Farley, 2001; Farley, 2002; Meesters & Dunai, 2002; Fitzgerald et al., 2006; Flowers et al., 2009). The variation of single-grain ages, the cause of this dispersion, the significance, and how to interpret the data has been a topic of continued discussion for >10 years (e.g. Fitzgerald et al. 2006; Flowers & Kelley, 2011; Brown et al., 2013; Wildman et al., 2016; Green & Duddy, 2018).

Two of the ten samples screened for apatite quality (i.e. crystal size, shape, and inclusion presence) yielded suitable grains for AHe dating (Table 2). Five grains were analyzed per sample to reveal possible single-grain age dispersion, common in AHe dating, especially in detrital samples (e.g. House et al., 1999; Armstrong, 2005). In this study, as reference, mean AHe ages are reported with 1σ error and variation of the single-grain ages from the mean age. Similar to

other low-temperature techniques, ages do not necessarily correlate to specific geological events. AHe analyses were performed by the University of Colorado, Boulder, Thermochronology Research and Instrumentation Lab (CU TRaIL) and the methods, summarized in Table 2, are detailed in Weisberg et al. (2018).

Maximum Paleotemperature Indicators included in this study are published vitrinite reflectance (%R_o) values and measured conodont alteration index (CAI) values (Table 1). The percentage of light reflected off vitrinite, an organic substance naturally occurring in rocks, is a proxy for thermal maturity primarily controlled by temperature and time (Burnham & Sweeny, 1990). Published maps of %R_o values from Devonian shale drill core and cuttings samples (East et al., 2012; Ryder et al., 2013) were used to estimate %R_o values for this study's samples. Values for individual samples were estimated based on their proximity to %R_o isograds or, if they were within <15 km of a drill core location, values were estimated directly from measured values (Table 1). %R_o values were used to estimate maximum paleotemperatures experienced by this study's samples using the Easy%R_o model (Burnham & Sweeny, 1990). Given that the Devonian shales measured by East et al. (2012) and Ryder et al. (2013) are stratigraphically below this study's samples (Figure 3), %R_o values were interpreted as an absolute maximum bound for potential T_{max} experienced by this study's samples.

Conodont alteration index (CAI) values were measured on the four samples which contained conodonts in their >200 μm apatite separates (Table 1). Conodonts are an index microfossil (0.1-1 mm in size) found in Cambrian to Triassic aged marine rocks (Epstein et al., 1977). During burial and resultant temperature increase, conodonts irreversibly change color from pale yellow (unaltered) to dark brown then black (Epstein et al., 1977). CAI is the systematic measurement of the color of the basal portion of the conodonts, which is a proxy for maximum temperature

experienced. Variation in color within a sample may be due to the dimensions or maturity of the individual pieces, as larger, thicker, and/or adult elements are darker in color (Epstein et al., 1977; Repetski et al., 2008). CAI determines a range of T_{\max} possible for durations between 1-500 Myr (Figure 1), however the low end of the range is commonly used to estimate T_{\max} of the sample since the higher end of the range indicates extreme conditions (Epstein et al., 1977). Conodonts were examined under binocular microscope using unfiltered reflected light and matched to Munsell soil color chips to determine CAI values, following the procedures of Epstein et al. (1977).

Inverse Thermal Modeling

Inverse thermal modeling was undertaken using the modeling program HeFTy (Ketcham, 2005). HeFTy uses a Monte Carlo approach to evaluate the time-temperature (T-t) space by modeling many mutually independent trials. Modeled thermal histories are compared to measured data and evaluated using “goodness of fit” tests, specifically equations 31-34 in Ketcham (2005) for age and the Kolmogorov-Smirnov (K-S) test for CTLD. Both tests determine the probability of a modeled T-t path to recreate the data (age or CTLD) and are weighted equally in a combined merit function, which evaluates if a T-t path is supported by the data (good fit at a significance level of 0.5) or is not ruled out by the data (acceptable fit at a significance level of 0.05; Ketcham, 2005).

AFT thermochronology data (i.e. AFT single-grain ages, confined track lengths, their angle to the c-axis, and D_{par} for each grain used in determining age or measuring track lengths; Table 1) were the primary inputs into inverse thermal models (Ketcham, 2005). Models were run using c-axis projection which has been demonstrated to fix user bias (Ketcham et al., 2007). The Ketcham et al. (2007) multi-kinetic annealing algorithm was used. As proposed by Sobel and

Seward (2010), I applied a user specific calibration factor (0.96) to this study's D_{par} measurements to convert measurements to an equivalent D_{par} value measured by Raymond A. Donelick (reported in Carlson et al., 1999). Calibration of D_{par} is recommended in the HeFTy manual (Donelick et al., 2005; Ketcham, 2005) and accounts for the influence of etching conditions and user error on measuring apatite fission-track etch pit diameter (Sobel & Seward, 2010). In modeling, the calibration affects the kinetic behavior estimate of the grains, but there is very little difference between calibrated and uncalibrated models.

AHe data included in modeling used the radiation damage accumulation and annealing model RDAAM (Flowers et al., 2009) and the alpha ejection correction for age (Farley et al., 1996). AHe data provides a lower temperature constraint to inverse models. Fixed constraints were specified for the stratigraphic (depositional) age range with paleo-mean annual temperature (MAT) (25 ± 10 °C; Woodrow et al., 1973) and present-day MAT (5 ± 5 °C; Hijmans et al., 2005). Post-depositional time-temperature constraint boxes are broad, which allows the model paths full latitude to explore T-t space (see supplementary file B1). $\%R_o$ values, estimated from published isograd maps (East et al., 2012; Ryder et al., 2013), were included in models using the Easy $\%R_o$ method of Sweeney and Burnham (1990). In models, $\%R_o$ values were calculated in passive mode, which allows AFT data full latitude to constrain thermal histories with $\%R_o$ values functioning as a confirmation point (Ketcham, 2005).

Results

AFT Data

AFT ages from 37 outcrop samples, and 1 core sample, range from 115 ± 6 Ma to 185 ± 11 Ma ($\pm 1\sigma$) (Table 1, Figure 2). Mean track lengths vary from 10.6 to 13.2 μm (Table 1). CTLDs have a weak negative skewness, which indicates that the NAB experienced a protracted cooling

history (e.g. Corrigan et al., 1998). Twenty-one samples pass the chi-square probability test (χ^2) while 17 samples fail. The χ^2 test determines the probability that the grains are from a single age population given the single-grain age variation (e.g., Galbraith and Laslett, 1993). Since these samples are sandstones, with grains likely sourced from multiple provenances that have experienced long-term residence within the PAZ, magnification of single-grain age dispersion between multiple kinetic populations is to be expected. Samples were examined for D_{par} variation and RadialPlotter (Vermeesch, 2008) was used to determine multiple kinetic populations, which were input as guides for inverse thermal modeling (see supplementary file C).

AHe Data

The central region contained two samples (3P and 43P) which yielded apatites of sufficient size (radius > 60 μm) for (U-Th)/He dating (e.g. Flowers et al., 2009). There was significant variation of AHe single-grain ages (~16-17%) with single-grain ages ranging from 188 to 116 Ma (Table 2). Including outliers, mean ages of 154 and 134 Ma were calculated for 3P and 43P respectively using the methods of Ault et al. (2013). Most of the AHe single-grain ages from samples 3P and 43P are younger than the sample's AFT central age but there are older ages, especially for sample 3P. Single-grain age variation is likely due to residence time within the PRZ which magnifies age differences due to varying [eU], zonation and/or grain size (e.g. Reiners & Farley, 2001; Meesters & Dunai, 2002; Fitzgerald et al., 2006). Age variation may also be affected by the poor quality of the detrital apatites (Ehlers & Farley, 2003). Grains analyzed were sub-rounded with surface pits and striations indicative of transportation, and as such were difficult to evaluate for the presence of inclusions.

AHe single-grain ages plotted against [eU] and grain size display weak or no trends (see supplementary file D). Thus it is not recommended to use AHe as the only data to constrain the thermal history (e.g. Green and Duddy, 2018). F_T measures of the amount of He ejected from the crystal with lower values (i.e. <0.65) indicating greater loss (e.g. Farley et al., 1996; Ketcham et al., 2011). Grain sizes are small (33-61 μm), which means the alpha ejection correction (F_T) values are low and hence the correction of a raw age for alpha-particle ejection is high (up to ~60-70%), with larger non-analytical uncertainties. These non-analytical uncertainties can affect the thermal history and its precision (e.g. Ketcham et al., 2011). AHe single-grain ages are shown overlain along inverse thermal model output as reference points in Figure 5. Where appropriate, AHe data was used as another constraint in HeFTy inverse thermal models, in all cases, providing verification of AFT constrained thermal histories.

Regional Trends

There is a younging trend of AFT ages from west to east across the NAB (Figure 4). Samples were divided into the same three regions as did Miller and Duddy (1989). The oldest AFT ages (>160 Ma) generally lie in the western region (west of 78 °W) and the youngest ages (<140 Ma) occur in the eastern region (east of 75.5 °W; Figure 2 & 3). The central region contains the greatest range of AFT ages (115-159 Ma), a core sample (28Pc), and two samples with AHe data (3P and 43P). Depositional age of samples ranges from Early Devonian to Early Mississippian which may cause some variation between samples' AFT ages (Table 1). Published % R_o and measured CAI data also indicate a trend of increasing maximum paleotemperatures from west to east, ~100 °C to >200 °C (Repetski et al., 2008; East et al., 2012; Ryder et al., 2013).

Western Region: Sampled lithologies (sandstones) in the western region are finer-grained than those preserved closer to the orogenic front in the east. AFT ages from 8 samples yield ages

from 185 ± 11 to 146 ± 8 Ma (Table 1). Four samples fail the χ^2 test, while single-grain age variance ranges from 0-37%. Mean track lengths are 11.9 to 12.5 μm with standard deviations of 1.3 to 1.9 μm (Table 1). Several samples retain single AFT grain ages between ca. 385-250 Ma, which are older than the depositional age (383-359 Ma), indicating that the samples were not fully reset after deposition and burial temperatures did not exceed ~ 120 °C. Three samples in this region contained conodonts that yielded CAI values between 2-2.5, which agree with published values (Repetski et al., 2008; Weary et al., 2000). Vitrinite reflectance (VR) isograds range from 0.6-1.5 % R_o (East et al., 2012; Ryder et al., 2013).

Central Region: AFT ages range from 159 ± 10 to 118 ± 6 Ma for the 22 outcrop samples (Table 1). The core sample (28Pc at 1048-1051 m depth) is the youngest at 115 ± 7 Ma, which is expected since it is stratigraphically below the central region outcrop samples and passed through the PAZ more recently. The outcrop sample closest to the core (55P) has an AFT age of 150 ± 8 Ma. Ten samples fail the χ^2 test, while single-grain age variance ranges from 0-29%. This region contains the largest AFT age range and variability, possibly because it incorporates more samples and/or that samples are from a greater number of depositional groups/formations. Mean track lengths range from 10.9 to 13.2 μm with standard deviations of 1.5 to 2.5 μm (Table 1). Sample 35N contains conodonts that yielded a range of CAI values between 2.5-3 and VR isograds range from 0.77-3 % R_o (Table 1). As discussed above, sample 3P and 43P yielded mean AHe ages of 154 and 134 Ma respectively with ~ 16 -17% variation of AHe single-grain ages (Table 2).

Eastern Region: Seven samples yielded AFT ages ranging from 141 ± 7 to 120 ± 9 Ma (Table 1). Three samples fail the χ^2 test, while single-grain age variation ranges from 9-27%. Mean track lengths vary from 12.7 to 13.1 μm with standard deviations of 1.3 to 1.6 μm . VR

isograds range from 2.45-3 %R_o (Table 1) and no samples contained conodonts. Given %R_o values estimate temperatures between ~215-230 °C (using Easy%R_o model; Sweeny & Burnham, 1990), AFT ages likely represent cooling from temperatures greater than the base of the PAZ.

Thermal History Interpretation

The initial part of the samples' thermal histories, representing Taconic and Acadian uplift/erosion, is unconstrained by AFT and AHe data. The complete thermal history is included in model output to provide geologic context and to prevent introduction of bias, such as operator-imposed T-t constraints. Due to the geologic history of the samples, all models were started between 500 to 375 Ma at temperatures >140 °C (e.g. Ver Straeten, 2009). In Figure 5, the parts of the model that are not directly constrained have been made semi-opaque (i.e. temperatures higher than the base of the PAZ and times before the oldest modeled track).

AFT ages are relatively “old” (Jurassic to Cretaceous) and have experienced a protracted history with significant time spent in the PAZ. Thus, only significant cooling events are distinguishable. Cooling rates constrained in the thermal models, and throughout the Appalachian Basin (e.g. Blackmer et al., 1994; Boettcher & Milliken, 1994; Reed et al., 2005), are slow (<2.75 °C/Myr) in comparison to other tectonic settings, such as young, active collisional orogens (~40-50 °C/Myr; e.g. Thiede et al., 2004). In this study, Early Jurassic cooling and Late Cenozoic cooling is referred to as “rapid” in comparison to the Cretaceous period of slower cooling.

Six representative inverse thermal models are presented which demonstrate the T-t history trends while also capturing variability within, and between the regions (Figure 5). From the central region the core sample (28Pc) and near-by surface sample (55P) are also included, as they

add a vertical element to the data. However, trends are based on the models from all included samples (HeFTy output for all samples is included in supplementary file B2). Across the NAB, inverse models exhibit multi-stage post-orogenic cooling patterns with similar timing of events: (1) Onset of cooling from maximum temperatures began in the Late Triassic to Early Jurassic; (2) Cooling rates slow significantly in the western and west-central NAB from the Early Cretaceous to Late Cenozoic while the eastern and east-central NAB cooling rates only slow slightly within the Cenozoic; (3) Western and west-central models suggest a rapid cooling event initiated in Late Cenozoic times. In context with these events, the differences across the NAB (i.e. T_{\max} , rate of cooling, and resolution of a Late Cenozoic rapid cooling event) are discussed below.

(1) Early Jurassic to Cretaceous Cooling: Thermal models from sample results across the NAB indicate initial cooling rates of 1-2 °C/Myr, from the Late Triassic to Early Jurassic (Figure 5). Faster initial cooling is recorded in eastern samples. For example, the weighted mean path of 3P (east-central) indicates a cooling rate of ~1.7 °C/Myr while 51N (western) cooling rate is ~0.9 °C/Myr. That the oldest modeled track in the western most sample (51N) is 256 Ma and a 0.6 % R_0 value (Table 1) suggests the sample did not exceed ~125 °C. Thus, this sample has fission tracks that formed prior to T_{\max} and the timing of T_{\max} is constrained to ca. 187 Ma. Most of the samples reached temperatures greater than the PAZ, annealing all pre-existing tracks.

In the central region, samples 3P and 43P AHe ages were incorporated as inputs for inverse thermal modeling (Figure 5). These models constrain cooling to ~70 °C by the end of the Early Cretaceous, placing samples within the upper part (lower temperatures) of the PAZ and the lower part (higher temperatures) of the PRZ. Models that do not utilize AHe ages (because there were

none for those samples) also constrain that samples were at temperatures lower than 90 °C by the end of the Early Cretaceous.

(2) Cretaceous to Late Cenozoic Stabilization: Thermal histories from western and central samples constrain that initial rapid cooling was followed by extended residence time in the PAZ and slow cooling ($\sim 0.15\text{-}0.25$ °C/Myr) during the Cretaceous to Late Cenozoic (i.e. “stabilization period”). In the east and east-central region, the best-fit T-t paths for samples 3P and P12 constrain periods of slower cooling during the Cretaceous, at rates of ~ 0.13 °C/Myr and ~ 0.20 °C/Myr respectively. However, overall the thermal histories of the eastern and east-central samples suggest only slightly reduced cooling, at average rates of ~ 0.8 °C/Myr beginning in Cretaceous times to present. AHe single-grain ages for sample 43P lie within the modeled T-t envelopes during this period of slow cooling while AHe ages from sample 3P do not (Figure 5). Based on these results, the interpretation is that eastern samples spent less time resident in the PAZ than western and central samples.

(3) Late Cenozoic Cooling: Models from western and central samples show an increase in cooling rates to $\sim 1\text{-}2$ °C/Myr from the Late Cenozoic to present (Figure 5). The core sample (28Pc) constrains the onset of Late Cenozoic cooling in the Miocene (ca. 23 Ma), with the model paths cooling from within the PAZ. Inverse thermal models from the east-central (3P) and eastern samples (P12) do not clearly reveal the Late Cenozoic “rapid” cooling event. This can be explained as follows: As eastern samples cooled more rapidly through the PAZ, the proportion of tracks that were shortened by residence within the PAZ is not significant, and this relative lack of shorter tracks from the stabilization period means that inverse modeling does not detect this Late Cenozoic accelerated cooling. Therefore, although multi-stage cooling may have occurred, the eastern models cannot resolve between initial stabilization and the later rapid cooling.

Given the importance of identifying Late Cenozoic cooling, CTLD of western and central samples were measured multiple times to verify data. Note that modeling using early apatite mono-kinetic annealing algorithms (e.g. Laslett et al., 1987; Crowley et al., 1991) often produced a spurious late stage cooling event (e.g. De Bruijne & Andriessen, 2002). Early algorithms were based on annealing experiments on Durango apatite and these models ran on the assumption that all apatite's had the same annealing characteristics as Durango. However, annealing is variable, depending on the composition of the apatite. Thus, multi-kinetic models used since ca. 1999 measure kinetic parameters for each grain (e.g. Ketcham et al. 1999; Ketcham et al., 2007). This later generation models do not produce an apparent late-stage cooling artifact. In other words, the Late Cenozoic initiation of rapid cooling in these western and central samples is regarded as significant and real.

Discussion

AFT Age Trends

A younging trend in AFT ages from west to east is clearly documented in this study (Figure 4). Miller and Duddy's (1989) data also shows this trend in the NAB but contains more scatter due to greater N-S distribution of their sampling and the inclusion of more northerly samples from older stratigraphic units that yielded older AFT ages (Figure 4). Blackmer et al. (1994) noticed AFT ages are generally older in the NAB in western PA than eastern PA but determined that the intervening ages did not define an eastward decreasing trend. Roden & Miller (1989) identify tectonic provinces with different thermal regimes but state that their AFT ages do not exhibit a clear trend of eastward younging across the basin in Pennsylvania.

The pattern of younging AFT ages from west to east across the NAB may reflect either diachronous onset of exhumation across the NAB or differential amounts of burial. Most studies

that present maximum temperatures, burial curves and/or regional thermal history trends in the Appalachian region conclude that the primary control on trends in thermal proxies is the varying magnitude of burial across the foreland basin (e.g. Friedman & Sanders, 1982; Gerlach & Cercone, 1993; Lakatos & Miller, 1983; Blackmer et al., 1994; Johnsson, 1986; Gurney & Friedman, 1986; Miller & Duddy, 1989; Roden & Miller, 1989). Data from this study also supports this interpretation. AFT samples in the east are younger since they reached greater temperatures due to greater burial (documented with %R_o and CAI values; e.g. East et al., 2012; Ryder et al., 2013), and thus cooled through the base of the PAZ more recently than shallower western samples, some of which have not exceeded temperatures at the base of the PAZ.

Paleogeothermal Gradient in the NAB

To convert cooling rates to exhumation rates in the NAB, a paleogeothermal gradient must be assumed. This can be estimated based on reasonable geologic assumptions for similar situations (i.e. 20-30 °C/km is common for sedimentary basins), through independent means, or from modeling programs that provide thermal gradients as an output. Several low-temperature thermochronology studies in the Appalachian Basin and New England assumed a steady state paleogeothermal gradient between 25-30 °C/km throughout the thermal history considered (e.g. Roden & Miller, 1989; Roden, 1991; Roden-Tice & Tice, 2005; Lash & Blood, 2007; Roden-Tice et al., 2009). However, other studies utilizing heat flow models, T_{max}, and/or subsidence histories have estimated an elevated paleogeothermal gradient of ~30-45 °C/km during and directly after the Alleghanian Orogeny (Vitarello & Pollack, 1980; Chyi et al., 1987; Weary et al., 2000), with some estimates as high as 50 °C/km (Hulver, 1997).

Studies based on the presence of authigenic clay minerals (Daniels et al., 1990), coal rank patterns (Hower and Gayer, 2002), heat-flow calculations based on fluid-inclusions (Harrison et

al., 2004), and % R_o trends (Ruppert et al., 2010) determined that an elevated paleogeothermal gradient during the Alleghanian Orogeny was produced as overthrust terranes forced migration of hot fluids through the newly formed basin sedimentary package. An increased geothermal gradient (~ 35 °C/km) due to regional fluid flow would not continue long after the end of the Alleghanian Orogeny, as it requires thrusting to force fluid migration, and estimated rates of hot fluid flow are high and short-lived (Oliver, 1986; Dorobek, 1989). There is significant evidence to indicate that the geothermal gradient has varied over time in the Appalachian Basin (e.g. Weary et al., 2000; Ruppert et al., 2010) but has decreased to average estimates (~ 20 - 30 °C/km) since the Alleghanian Orogeny (e.g. Reed et al., 2005). AFT data and thermal models in this study do not constrain the part of the thermal history that may have experienced an elevated geothermal gradient (i.e. the Alleghenian Orogeny until the Late Permian) since samples were still being buried and had not reached T_{max} , which reset most samples.

It is evident, given the overall slow cooling rates documented in this study, that the samples experienced a relatively stable, post-orogenic thermal regime without much advection or significant changes in the paleogeothermal gradient, such as may be caused by rapid cooling due to fault movement (e.g. Ehlers & Farley, 2003). Small, local kimberlite intrusions (ca. 146-110 Ma; Heaman & Kjarsgaard, 2000; Bailey & Lupulescu, 2015) occur in the central region of the NAB in NY, but there is no evidence that they have regionally influenced the paleogeothermal gradient (e.g. Johnsson, 1986), such as would be caused by a large magmatic intrusion (e.g. Gleadow & Duddy, 1984; Gleadow & Fitzgerald, 1987). Core sample 28Pc was collected from an exploration drill hole with a present-day maximum downhole temperature of ~ 48 °C at ~ 2 km depth, indicating a present-day geothermal gradient of 24 °C/km. Also, the offset between the T-t paths for the core sample in the central region and the closest surface sample (55P) is on the

order of ~ 25 °C during the Cretaceous to Late Cenozoic stabilization (Figure 5). Therefore, assuming a relatively stable, unperturbed geothermal gradient during the post-orogenic history of the NAB, cooling rates are converted to exhumation rates using a geothermal gradient of 25 °C/km (Figure 6).

Post-Orogenic Exhumation

This section discusses the exhumation history, constrained by inverse thermal modeling and converted to exhumation rates using the assumptions discussed above. The exhumation history is divided into the same three stages as the cooling history: (1) Early Jurassic to Cretaceous initial onset of exhumation; (2) Cretaceous to Late Cenozoic stabilization in the west with continuous and slower exhumation documented in the east; (3) a Late Cenozoic increase in exhumation rates (Figure 6).

(1) Early Jurassic to Cretaceous Exhumation: All models suggest the onset of exhumation in the Late Triassic to Early Jurassic with the western sample (51N) constraining onset of exhumation to the Early Jurassic, ca. 187 Ma (Figure 6). This initial exhumation event continued until the Early Cretaceous, at rates of 40-50 m/Myr in western samples and slightly higher rates of 50-70 m/Myr in eastern samples (Figure 5 & 6). The differences in exhumation rates across the NAB further support the conclusion regarding the west to east younging AFT age trend. That is, the AFT age trend is due to differential burial, and thus the region experiences differential amounts/rates of exhumation which was initiated at about the same time across the NAB.

Concurrent with the onset of exhumation, was the rift initiation and the formation of the Northern Atlantic Ocean in the Late Triassic (ca. 237 Ma; Withjack et al., 1998; Withjack & Schlische, 2005). This provided accommodation space for sediment eroded from the Appalachian Highlands and NAB basin. As the eastern U.S. margin underwent rifting and the

lowering of regional base levels, river incision, backwearing and valley widening may have allowed the re-excavation and erosion of the NAB, similar in style to Late Neogene re-excavation of the Ebro Basin, Spain (e.g. Coney et al., 1996; Babault et al., 2006; Beamud et al., 2010). Initial exhumation of the NAB correlates well with rapid unroofing rates estimated by Blackmer et al. (1994) in the western Appalachian basin of Pennsylvania during the Late Permian through the Early Jurassic. They suggested that this event may be due to flexural rebound of the lithosphere related to the erosion of the Alleghenian overburden. The variation in exhumation rates from west to east constrained in this current study further supports this mechanism, as samples were buried more deeply in the east and thus the flexural response was greater, recorded as higher exhumation rates.

The timing of initial exhumation within the NAB (this study) generally agrees with low-temperature thermochronology studies across the Appalachian Basin and New England, which constrain exhumation beginning in the Triassic to Late Jurassic (Roden & Miller, 1989; Roden, 1991; Roden & Miller, 1991; Blackmer et al., 1994; Roden-Tice & Wintsch, 2002; Reed et al., 2005). Other low-temperature thermochronology studies constrain the onset of rapid exhumation in the Early Cretaceous, referring to it as the “Early Cretaceous rapid cooling event” (e.g. Miller & Duddy, 1989; Boettcher & Milliken, 1994; Roden-Tice et al., 2000; Spotila et al., 2004; Roden-Tice & Tice, 2005; Roden-Tice et al., 2009; Taylor & Fitzgerald, 2010; McKeon et al., 2014). However, most of the studies reporting rapid cooling and exhumation onset in the Early Cretaceous are based on samples that reached temperatures greater than the PAZ and, though they document timing of rapid cooling through the PAZ, they do not constrain when cooling was initiated from T_{\max} .

(2) *Cretaceous to Late Cenozoic Stabilization:* From the Cretaceous until the Late Cenozoic, significantly slower rates of exhumation are documented in the NAB (Figure 6). Western and west-central thermal models indicate relatively slow cooling and exhumation at rates of 6-9 m/Myr. These rates are the slowest rates in their post-orogenic exhumation histories, which indicate a period of basin stability. The central model (55P) and corresponding core sample (28Pc) indicate slow exhumation rates of 8-11 m/Myr. However, models within the central region show the greatest variation in exhumation rates during this time (i.e. 3P; Figure 6). Eastern models suggest exhumation at rates of 25-30 m/Myr, which is approximately half the rate of initial exhumation but is still more rapid than western and central samples during this period. Also, the easternmost sample (P12) records a short period (ca. 35 Myr) of slower exhumation (~10 m/Myr) in the Cretaceous (Figure 5). Other studies throughout the Appalachian Basin also document variable exhumation rates similar to these during the Cretaceous to Late Cenozoic (i.e. Blackmer et al., 1994; Reed et al., 2005; McKeon et al., 2014).

During the early Middle Jurassic, the east coast of North America transitioned from an active continental rift zone into a passive continental margin (e.g. Klitgord et al., 1988; Etensohn, 2008) and flexural rebound due to erosion no longer contributed to exhumation (Blackmer et al., 1994). Most models in the NAB constrain significantly reduced exhumation rates, implying relative stability, during the Cretaceous to Late Cenozoic (Figure 6). Stability during the Late Cretaceous to Late Cenozoic is also observed in models from the Appalachian Basin in PA (Blackmer et al., 1994) and Kentucky (KY; Boettcher & Milliken, 1994). Models for the eastern samples tend to indicate continuous exhumation during this period – albeit slightly slower than initial rates – as this region continued to erode, likely a result of additional flexural rebound. However, the eastern region may have also experienced relative stability but the AFT data (i.e.

relative components of confined tracks) are not sensitive enough to constrain variations in exhumation rate. Western and central region samples are more sensitive to changes in exhumation rates due to slower exhumation rates throughout their post-orogenic history and longer residence in the PAZ, and these changes are discussed below.

(3) ***Late Cenozoic Exhumation:*** Beginning in the Late Cenozoic, rapid exhumation is well constrained in models for western and central samples (Figure 5 & 6). As discussed above, this event is real and significant. Since the core sample cooled from within the PAZ, its thermal model best constrains the onset of Late Cenozoic exhumation as Miocene (ca. 23 Ma). Western and west-central samples (i.e. 51N and 43P) record exhumation rates of 40-50 m/Myr and central samples record rates of 50-65 m/Myr, beginning in the Oligocene to Miocene (ca. 30-20 Ma).

The Late Cenozoic history of the Appalachian basin is enigmatic. Several thermochronology studies suggest rapid exhumation in the Cenozoic (i.e. Roden, 1991; Blackmer et al., 1994; Boettcher & Milliken, 1994; Roden-tice & Wintsch, 2002; Reed et al., 2005), but some of these studies used mono-kinetic annealing algorithms which produce spurious late-stage cooling, as discussed above. Also, there are no direct AFT or AHe (i.e. Late Miocene ages) to document rapid cooling at that time (e.g. Spotila et al., 2004; McKeon et al., 2014). Thus, the identification of this Late Cenozoic cooling event in these previously published models should be regarded as suspect until confirmed. However, there are other lines of evidence which support the identification of a Late Cenozoic pulse of rapid exhumation, such as evidence of uplift from knickpoint migration in stream profiles (Miller et al., 2013) or the increase in sediment flux to mid-Atlantic basins during the Miocene (Pazzaglia & Brandon, 1996). Sediment flux is reportedly too rapid to be primarily driven by decreasing sea level or climate change (Poag &

Sevon, 1989) and it has been suggested that it was controlled by uplift and erosion of the Appalachian source terrane (Poag & Sevon, 1989; Pazzaglia & Brandon, 1996).

Studies constraining rapid exhumation within the Miocene (ca. 15 Ma) attribute exhumation as an isostatic flexural response (Pazzaglia & Gardner, 1994; Blackmer et al., 1994) or to landscape rejuvenation caused by dynamic topography (e.g. Pazzaglia & Brandon, 1996; Miller et al., 2013). Isostatic flexure is estimated to produce 35-130 m of rock uplift of the Appalachian terrane (Pazzaglia & Gardner, 1994) and dynamic topography induces long-wavelength, low amplitude uplift of ~100 m over the last 30 Ma (Moucha et al., 2008). This study constrains an increase in exhumation rates (~30-65 m/Myr) across the NAB beginning in the Late Cenozoic (30-20 Ma), which accounts for the removal of ~1 km of sediment since then (Figure 6). Isostatic flexure or dynamic topography alone does not induce enough exhumation to explain the Late Cenozoic exhumation constrained in models from this study. Instead, the documented exhumation is likely due to a complex combination of drivers causing landscape rejuvenation, including dynamic topography (e.g. Pazzaglia & Brandon, 1996; Gallen et al., 2013; Miller et al., 2013), climatic changes causing increased mechanical erosion within the Appalachian Basin (e.g. Poag & Sevon, 1989; Boettcher & Milliken, 1994), and flexural response of the continental crust to sediment deposition offshore (Pazzaglia & Gardner, 1994; Blackmer et al., 1994).

Conclusions

This study constrains the post-orogenic history of the Northern Appalachian Basin, adding insight into the timing and rates of cooling, thermal regimes, and exhumation events. AFT thermochronology, AHe dating, T_{\max} indicators, and stratigraphic constraints are integrated to constrain the cooling and exhumation history of the NAB as occurring in 3 stages:

(1) A Late Triassic to Early Jurassic onset of cooling from T_{\max} with the first event extending to the Early Cretaceous (1-2 °C/Myr cooling rate; ~40-70 m/Myr exhumation rate). The younging trend of AFT ages from west to east across the NAB is due to differential amounts of burial and subsequent unroofing, which causes the difference in exhumation rates as the lithosphere experiences flexural rebound related to overburden removal. This event is contemporaneous with rifting (Withjack & Schlische, 2005) and includes the “Early Cretaceous” rapid cooling documented by other studies, since most studies document the passage of samples through the base of the PAZ and not onset from T_{\max} (e.g. Miller & Duddy, 1989; Roden, 1991; Boettcher & Milliken, 1994; Roden-Tice et al., 2000; Spotila et al., 2004; Roden-Tice & Tice, 2005; Roden-Tice et al., 2009; McKeon et al., 2014).

(2) The Cretaceous to Late Cenozoic event is a period of stabilization within the NAB. Slow cooling and exhumation are documented in the western and central regions of the NAB (0.15-0.25 °C/Myr; ~6-9 m/Myr) while inverse models in the eastern region constrain cooling and exhumation at rates of 0.5-1 °C/Myr and ~25-30 m/Myr, which are slightly slower than initial cooling rates. Although it is undocumented in thermal models, eastern region samples may have experienced relative stability at this time. The slow exhumation experienced in the NAB is related to the stabilization of the interior of the craton, which is contemporaneous with the transition of the east coast of North America to a passive continental margin (e.g. Klitgord et al., 1988; Ettensohn, 2008).

(3) Rapid exhumation is documented from the Late Cenozoic (30-25 Ma) to present (1-2 °C/Myr; ~30-65 m/Myr) and accounts for the removal of ~1 km of sediment. This event was not constrained in all samples across the NAB, likely due to the relative sensitivity of the AFT and AHe systems. The cause of increased exhumation during this time is highly debated and

often beyond the resolution of low-temperature thermochronology datasets, especially those techniques that lack a kinetic parameter (e.g. McKeon et al., 2014). However, there is other evidence, such as sediment flux to mid-Atlantic basins and knickpoint migration in stream profiles, which indicates that there were increased exhumation rates during the Late Cenozoic along the eastern U.S. (e.g. Blackmer et al., 1994; Boettcher & Milliken, 1994; Pazzaglia & Brandon, 1996; Miller et al., 2013). Neither dynamic topography or isostatic flexural response can be attributed as the primary cause of the increase in exhumation rates. This Late Cenozoic cooling is a real and significant event, likely due to combination of drivers causing landscape rejuvenation.

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Figures and Tables

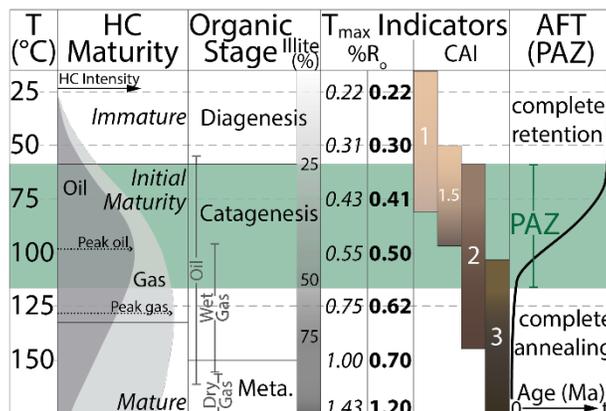


Figure 1. Comparison of hydrocarbon (HC) maturity, organic diagenetic stages, maximum paleotemperature (T_{max}) indicators (i.e. vitrinite reflectance ($\%R_o$) and conodont alteration index (CAI)), and the apatite fission track (AFT) partial annealing zone (PAZ) (modified from: Tissot & Welte, 1978; Gleadow et al., 1983). Organic diagenetic stages (meta. for metagenesis) and illite percentage in the illite/smectite mixed layer included as reference for hydrocarbon generation zone identification (modified from Foscolos et al., 1976; Tissot & Welte, 1978; Jiang, 2012). Generation windows for oil and gas included within the organic stage column (Tissot & Welte, 1978). $\%R_o$ values based on a heating rate of 2.8 °C/Myr from 10 °C (Nielsen et al., 2017), with the easy $\%R_o$ model in italics (Sweeny & Burnham, 1990) and the basin $\%R_o$ model in bold (Nielsen et al., 2017). CAI values characterizes a maximum temperature range and the coloration of the conodont fossils (Epstein et al., 1977). The AFT PAZ (shaded green) the age profile is included (black line) is from ~60 to 110-120 °C, depending on composition, and closely overlaps with the hydrocarbon generation window (e.g., Gleadow et al., 1983; Green et al., 1989).

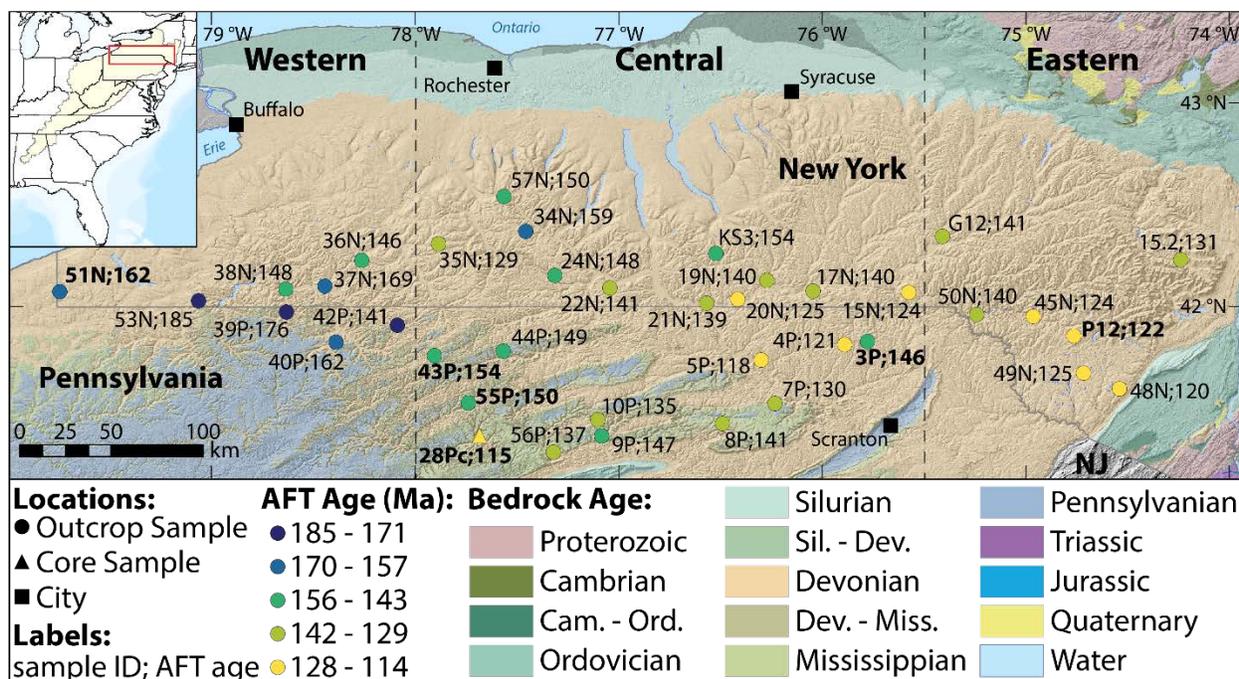


Figure 2. Map of the Northern Appalachian Basin showing 37 Devonian sedimentary outcrop samples (circles) and a core sample (triangle) with AFT ages (sample ID; AFT age (Ma)). Sample colors highlight the AFT age trend. Insert shows study location (red) and extent of the Appalachian Basin (yellow). Included are regional divides and the six representative samples used in the results and discussion section are bolded. Base map generated in ArcGIS using STRM 90m DEM relief shaping overlain by bedrock geologic ages for NY and PA (Dicken et al., 2005; Jarvis et al., 2008).

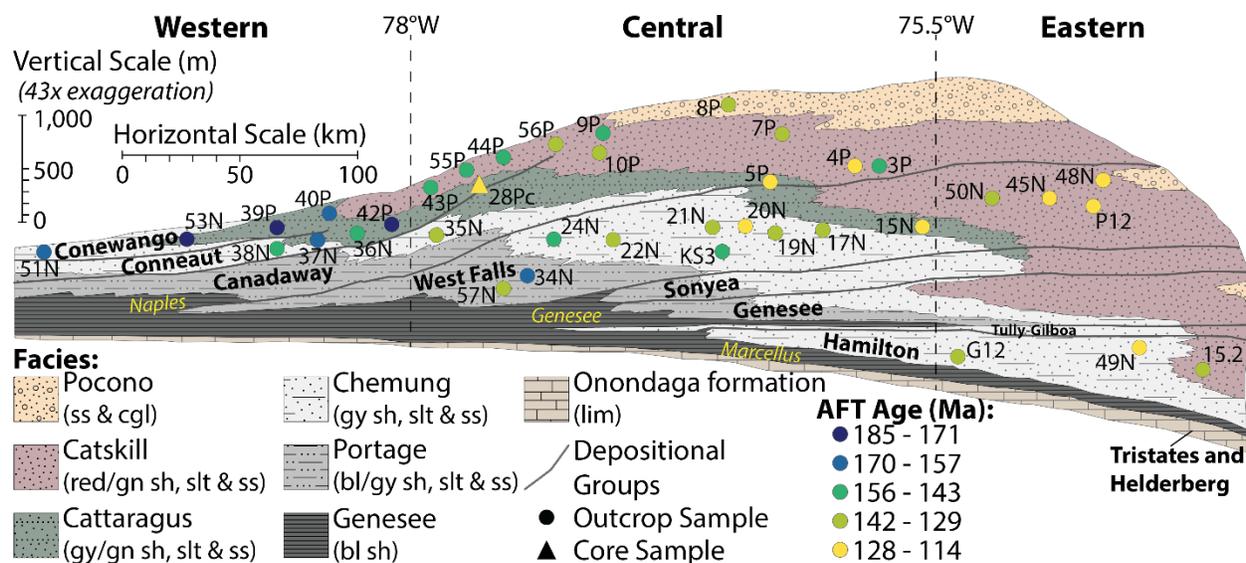


Figure 3. Diagrammatic cross section of the outcropping Catskill Delta strata in the NAB (modified from Isachsen et al., 1991) with stratigraphic locations of the samples, labeled and colorized by AFT age. The section is flattened on the Genesee Formation, with thickness of units exaggerated 43x width of the units to show details (Isachsen et al., 1991). Given that the sedimentary Paleozoic rocks of the Appalachian Basin gently dip ($\sim 1-2^\circ$) to the southwest (e.g. Johnsson, 1985; Isachsen et al., 1991; Eaton and Frederiksen, 2007), the facies at the base of the cross section (i.e. the Onondaga Formation) outcrop in the northern most parts of the basin (e.g. Buffalo, NY). The Catskill Delta strata are divided into groups based on episodes of deposition (in bold) and the facies indicate the depositional environment (detailed in Isachsen et al., 1991). Abbreviations: cgl – conglomerate; ss – sandstone; sh – shale; lim – limestone; bl – black; gy – grey; gn – green.

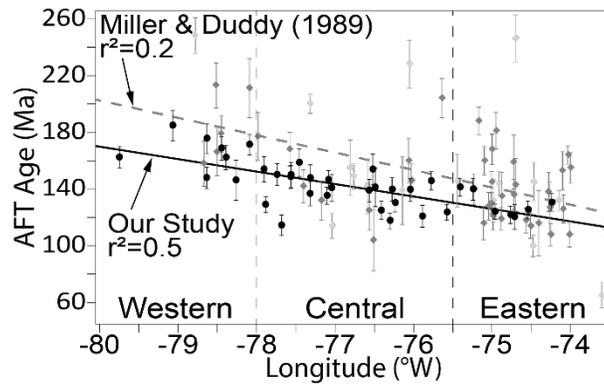
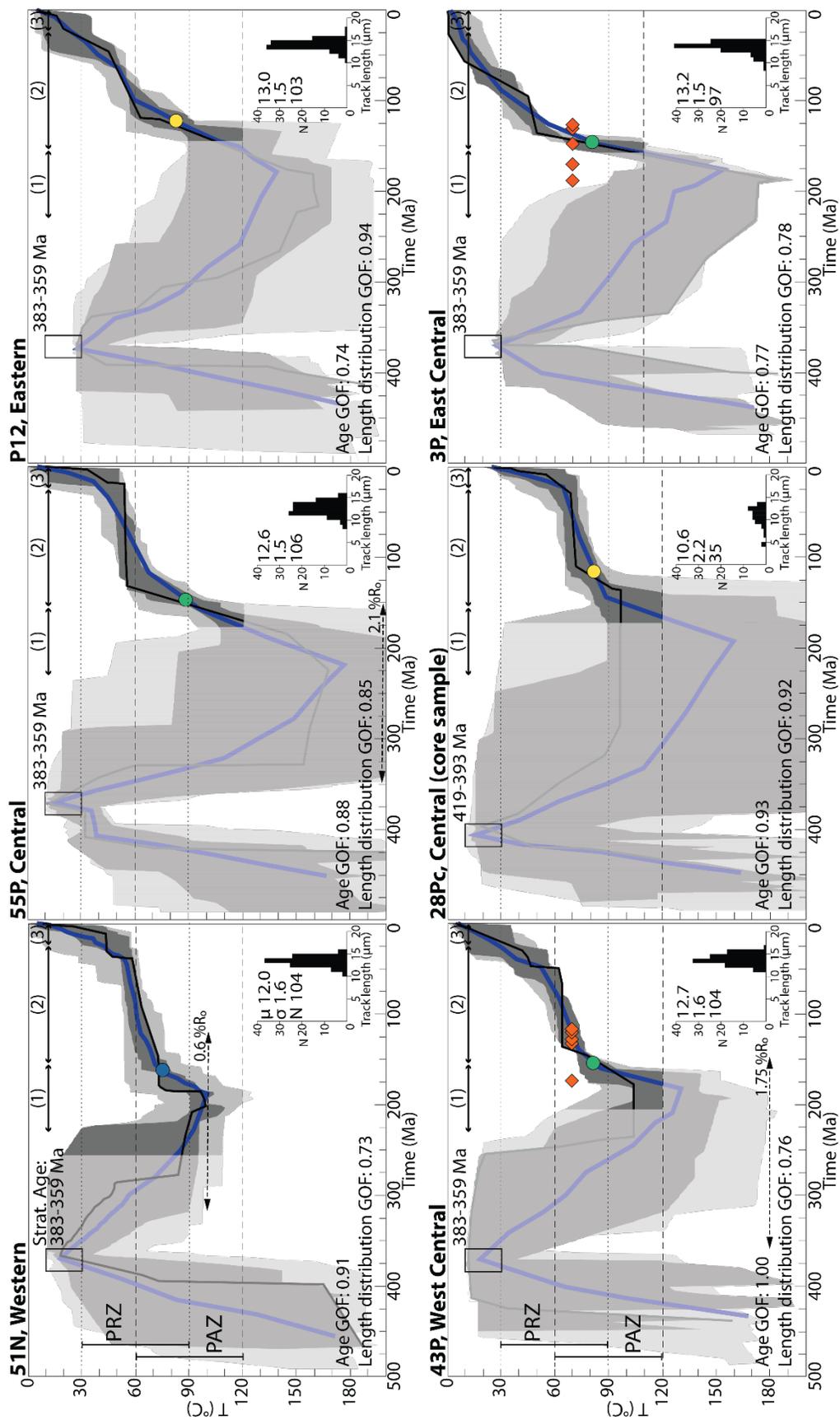


Figure 4. AFT ages ($\pm 1\sigma$) from this study (black points, solid best-fit trend line) and Miller and Duddy's (1989; grey diamonds, dashed best-fit trend line) plotted against longitude. Miller and Duddy's samples are further divided by distance from this study's samples (i.e. samples >15 km north of this study's samples are light grey).

Figure 5. Inverse thermal (time-temperature) models undertaken using HeFTy v1.9.1 (Ketchum, 2005) arranged from west to east, with regional divides. Dark grey envelope indicates the good paths, light grey envelope are the acceptable paths, thick blue path is the weighted mean, and the thin black line is the best-fit path. The timing and duration of the thermal/exhumation events (1, 2, 3) is included for reference. Constraints used include: stratigraphic age (Late Devonian, 383-359 Ma), paleo-surface temperature (25 ± 10 °C; Woodrow et al., 1973), present-day surface temperature (7 ± 5 °C; Hijmans et al., 2005), and present-day core sample temperature (25 ± 5 °C). PAZ (~60-120 °C, depending on composition) and PRZ (~30-90 °C) are marked with dashed lines. Semi-opaque white shading over the models masks parts unconstrained by AFT data (i.e. older than the oldest modeled track and/or at temperatures greater than the base of the PAZ). AFT central age (circles colorized same as Figure 2 and 3) is included on weighted mean path and AHe single-grain ages (orange diamonds) are included in the PRZ, when measured. Published % R_0 values (East et al., 2012; Ryder et al., 2013) used passively in inverse thermal modeling are included when they are within bounds of figure (i.e. <200 °C). Goodness-of-fit (GOF) statistics for model age and track length distributions in bottom left corner of models. Track length distributions with mean track length (μ), standard deviation (σ), and number of tracks measured (N) in bottom right.



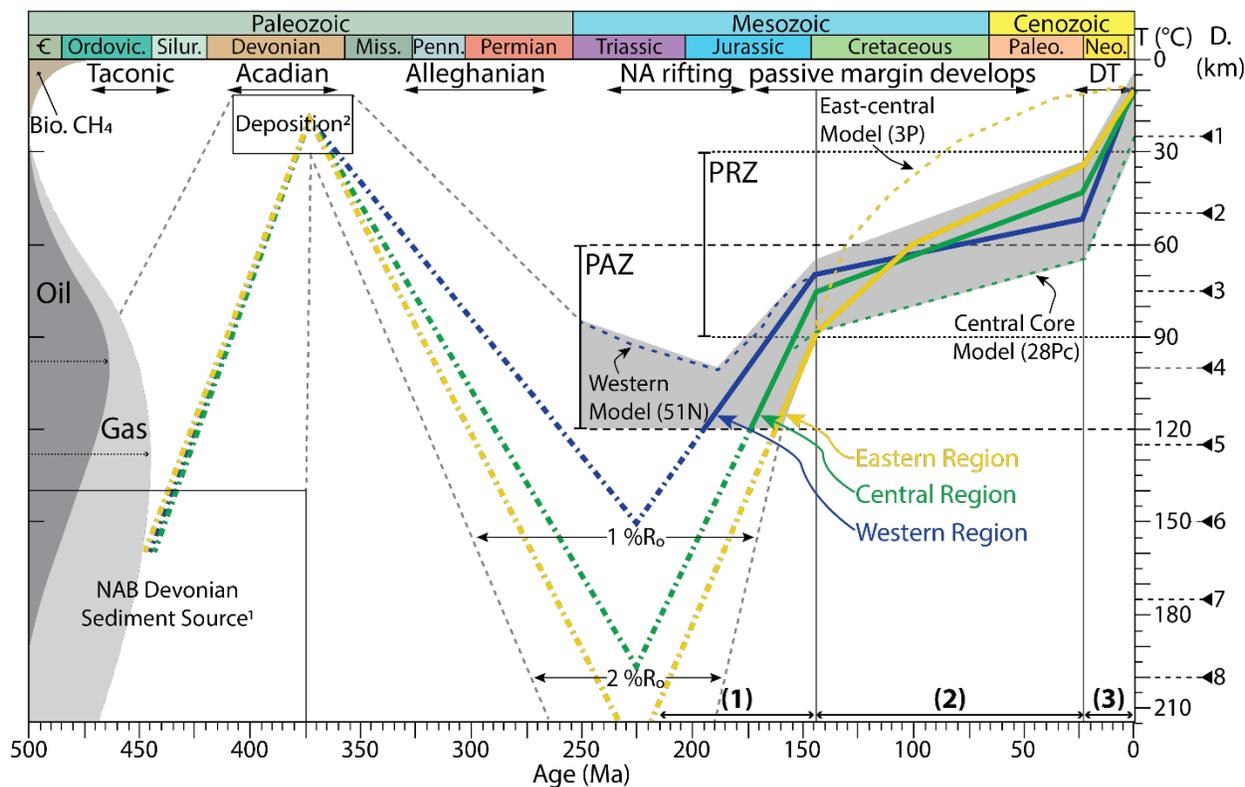


Figure 6. Schematic time-temperature histories of the eastern (yellow), central (green), and western (blue) region – based on AFT ages and CTLD, AHe ages, T_{max} indicators (CAI and $\%R_o$), and geologic constraints (¹Ver Straeten, 2009; ²Woodrow et al., 1973) – with portions unconstrained by AFT data dashed. The grey envelope indicates the temporal trends across the NAB, solid grey where constrained by thermal modeling and dashed extent where unconstrained. Temperature converted to depth using a geothermal gradient of 25 °C/km, as discussed. Hydrocarbon maturity window and peak oil and gas generation temperatures included (modified from: Tissot and Welte, 1978; Gleadow et al., 1983). Appalachian orogenies and geologic events occurring along the eastern USA included along the top (summarized from: Klitgord et al., 1988; Poag and Sevon, 1989; Pazzaglia and Brandon, 1996; Withjack et al., 1998; Withjack and Schlische, 2005; Ettensohn, 2008; Hatcher, 2010; Miller et al., 2013). Along the bottom are the three cooling/exhumation events identified in this paper with vertical reference lines. Table 1 page 1

Table 1. Summary of apatite fission-track thermochronology results.

| Sample (Strat. Age) | Lat., Long. (°) Elev. (m) | No. of Grains | Standard Track Density ($\times 10^6 \text{cm}^{-2}$) | Spontaneous Track Density ($\times 10^6 \text{cm}^{-2}$) | Induced Track Density ($\times 10^6 \text{cm}^{-2}$) | χ^2 prob. (%) | Var. (%) | Age (Ma) ($\pm 1\sigma$) | Mean Track Length (μm) | Std. Dev. (μm) | D_{par} (μm) | % R_o {CAI} |
|------------------------|--------------------------------------|------------------|--|---|---|--------------------------|-------------|-------------------------------|--|-----------------------------------|--------------------------------|----------------------|
| Western Region | | | | | | | | | | | | |
| 36N (LD) | 42.226, -78.2598 504 | 23 | 1.124 (6976) | 1.7081 (568) | 2.574 (856) | 0.0 | 37 | 146 \pm 14 | 11.9 \pm 0.2 (41) | 1.5 | 2.13 (0.3) | 0.8 |
| 37N (LD) | 42.1001, -78.4433 441 | 25 | 1.027 (6589) | 2.2654 (934) | 2.433 (1003) | 41.4 | 7 | 169 \pm 8 | 12.4 \pm 0.2 (93) | 1.8 | 1.83 (0.3) | 1.2 |
| 38N (LD) | 42.0835, -78.6338 447 | 25 | 1.13 (6976) | 1.8752 (667) | 2.522 (897) | 76.7 | 0 | 148 \pm 8 | 12.5 \pm 0.1 (101) | 1.4 | 2.28 (0.4) | 1.2 {2} |
| 39P (LD) | 41.9713, -78.6302 403 | 25 | 0.993 (6679) | 2.116 (950) | 2.156 (968) | 5.0 | 18 | 176 \pm 11 | 12.5 \pm 0.2 (100) | 1.8 | 2.43 (0.4) | 1.3 {2- 2.5} |
| 40P (LD) | 41.824, -78.3859 618 | 25 | 1.001 (6679) | 2.0179 (1638) | 2.269 (1842) | 0.0 | 20 | 162 \pm 9 | 12.4 \pm 0.1 (101) | 1.3 | 2.37 (0.3) | 1.5 |
| 42P (LD) | 41.9045, -78.087 495 | 25 | 1.029 (6589) | 2.4414 (2412) | 2.63 (2598) | 0.1 | 15 | 171 \pm 8 | 12.2 \pm 0.2 (101) | 1.9 | 1.56 (0.2) | 1.4 |
| 51N (LD) | 42.0731, -79.7453 443 | 25 | 1.04 (6679) | 2.3798 (848) | 2.68 (955) | 58.8 | 0 | 162 \pm 8 | 12.0 \pm 0.2 (104) | 1.6 | 2.08 (0.2) | 0.6 |
| 53N (LD) | 42.0265, -79.0644 618 | 25 | 1.049 (6679) | 2.9793 (1236) | 3.093 (1283) | 0.1 | 20 | 185 \pm 11 | 12.0 \pm 0.2 (101) | 1.5 | 2.15 (0.3) | 1.2 {2} |
| Central Region | | | | | | | | | | | | |
| 3P (LD) | 41.8265, -75.7744 326 | 25 | 1.083 (6881) | 1.5306 (1335) | 1.992 (1737) | 13.5 | 11 | 146 \pm 7 | 13.2 \pm 0.2 (97) | 1.5 | 1.64 (0.2) | 2.75 |
| 4P (LD) | 41.8116, -75.8852 491 | 19 | 1.086 (6881) | 1.8536 (831) | 2.969 (1331) | 0.1 | 22 | 121 \pm 8 | 12.4 \pm 0.2 (97) | 2.0 | 1.62 (0.2) | 2.75 |
| 5P (ED) | 41.7358, -76.2975 323 | 25 | 1.092 (6881) | 1.8362 (1207) | 3.123 (2053) | 5.9 | 12 | 118 \pm 6 | 13.1 \pm 0.2 (101) | 1.6 | 1.65 (0.3) | 2.5 |
| 7P (LD) | 41.5206, -76.2312 377 | 20 | 1.098 (6881) | 1.7436 (683) | 2.591 (1015) | 92.2 | 0 | 130 \pm 7 | 12.5 \pm 0.2 (93) | 1.9 | 1.62 (0.3) | 3* |
| 8P (EM) | 41.4228, -76.4886 570 | 17 | 1.048 (6976) | 0.8979 (514) | 1.246 (713) | 0.0 | 29 | 141 \pm 14 | 10.9 \pm 0.4 (53) | 2.5 | 1.88 (0.5) | 3 |
| 9P (LD) | 41.363, -77.082 242 | 25 | 1.008 (6589) | 1.2861 (1671) | 1.572 (2043) | 4.9 | 13 | 147 \pm 7 | 13.2 \pm 0.2 (102) | 1.6 | 1.67 (0.2) | 2.54* |
| 10P (LD) | 41.4414, -77.1006 389 | 25 | 1.010 (6589) | 2.6588 (1705) | 3.482 (2233) | 0.8 | 14 | 135 \pm 6 | 12.8 \pm 0.2 (103) | 2.0 | 1.85 (0.3) | 2.54* |
| 15N (LD) | 42.0681, -75.5716 464 | 22 | 1.017 (6589) | 1.228 (851) | 1.772 (1233) | 97.9 | 0 | 124 \pm 6 | 13.1 \pm 0.2 (98) | 1.6 | 1.81 (0.3) | 2.45 |
| 17N (LD) | 42.0751, -76.0418 328 | 25 | 1.054 (6976) | 1.7958 (514) | 2.39 (684) | 54.1 | 4 | 140 \pm 8 | 12.2 \pm 0.2 (47) | 1.6 | 1.93 (0.3) | 2.12* |
| 19N (LD) | 42.1258, -76.2702 233 | 25 | 1.066 (6976) | 1.7639 (506) | 2.37 (680) | 65.1 | 0 | 140 \pm 8 | 12.2 \pm 0.3 (65) | 2.1 | 1.98 (0.3) | 1.9 |
| 20N (LD) | 42.0333, -76.4116 242 | 25 | 1.022 (6589) | 1.793 (602) | 2.886 (969) | 91.0 | 0 | 125 \pm 7 | 12.6 \pm 0.2 (99) | 1.9 | 1.79 (0.3) | 1.75 |
| 21N (LD) | 42.014, -76.5657 396 | 25 | 1.072 (6976) | 1.5341 (594) | 2.102 (814) | 35.3 | 9 | 139 \pm 8 | 12.1 \pm 0.2 (102) | 1.7 | 2.03 (0.3) | 1.75 |
| 22N (LD) | 42.0904, -77.0414 359 | 25 | 1.083 (6976) | 1.8573 (620) | 2.549 (851) | 2.6 | 20 | 141 \pm 10 | 12.7 \pm 0.2 (102) | 1.9 | 2.00 (0.3) | 1.4 |
| 24N (LD) | 42.1515, -77.3132 315 | 25 | 1.095 (6976) | 2.0116 (546) | 2.649 (719) | 15.3 | 14 | 148 \pm 10 | 12.5 \pm 0.2 (103) | 1.5 | 2.20 (0.3) | 1.2 |
| 28Pc (ED) | 41.3649, -77.6804 1048-1051 depth | 23 | 1.107 (6976) | 2.495 (620) | 1.4113 (1096) | 17.0 | 7 | 115 \pm 7 | 10.6 \pm 0.4 (35) | 2.2 | 2.08 (0.4) | 2.22* |
| 34N (LD) | 42.3659, -77.4529 446 | 25 | 1.024 (6589) | 2.5243 (729) | 2.926 (845) | 14.9 | 15 | 159 \pm 10 | 12.2 \pm 0.2 (96) | 1.9 | 1.75 (0.3) | 0.77* |
| 35N (LD) | 42.3053, -77.8841 592 | 25 | 1.113 (6976) | 2.4506 (848) | 3.725 (1289) | 92.9 | 0 | 129 \pm 6 | 12.6 \pm 0.1 (101) | 1.3 | 2.12 (0.2) | 1.05* {2.5- 3} |
| 43P (LD) | 41.7573, -77.9034 621 | 25 | 1.142 (6976) | 1.7604 (1044) | 2.342 (1389) | 0.4 | 19 | 154 \pm 9 | 12.7 \pm 0.2 (104) | 1.6 | 2.32 (0.2) | 1.75 |
| 44P (EM) | 41.7785, -77.5638 427 | 25 | 1.01 (6679) | 1.454 (1892) | 1.826 (2376) | 0.0 | 21 | 149 \pm 8 | 13.0 \pm 0.1 (105) | 1.5 | 2.54 (0.4) | 1.75 |

Table 1. Summary of apatite fission-track thermochronology results.

| Sample (Strat. Age) | Lat., Long. (°) Elev. (m) | No. of Grains | Standard Track Density (x 10 ⁶ cm ⁻²) | Spontaneous Track Density (x 10 ⁶ cm ⁻²) | Induced Track Density (x 10 ⁶ cm ⁻²) | χ^2 prob. (%) | Var. (%) | Age (Ma) ($\pm 1\sigma$) | Mean Track Length (μ m) | Std. Dev. (μ m) | D_{par} (μ m) | %R _o {CAI} |
|------------------------|------------------------------|------------------|---|--|--|--------------------------|-------------|-------------------------------|---------------------------------------|----------------------------|-------------------------|--------------------------|
| 55P (LD) | 41.5253, -77.7366 373 | 25 | 1.058 (6679) | 1.7099 (2006) | 2.214 (2597) | 0.0 | 20 | 150 \pm 8 | 12.6 \pm 0.1 (106) | 1.5 | 2.51 (0.4) | 2.1 |
| 56P (LD) | 41.2836, -77.3185 180 | 24 | 1.067 (6679) | 1.7536 (829) | 2.454 (1160) | 0.9 | 20 | 137 \pm 9 | 13.0 \pm 0.1 (103) | 1.5 | 2.21 (0.3) | 2.29* |
| 57N (LD) | 42.5379, -77.5593 453 | 25 | 1.075 (6679) | 1.663 (722) | 2.124 (922) | 10.2 | 15 | 150 \pm 9 | 12.8 \pm 0.1 (106) | 1.4 | 2.24 (0.3) | 0.77* |
| KS3 (LD) | 42.2585, -76.5184 337 | 22 | 1.084 (6679) | 1.4717 (1400) | 1.917 (1824) | 0.0 | 26 | 154 \pm 11 | 12.9 \pm 0.2 (94) | 1.6 | 2.48 (0.5) | 1.5* |
| Eastern Region | | | | | | | | | | | | |
| 45N (LD) | 41.9492, -74.9608 390 | 25 | 1.019 (6679) | 0.881 (1148) | 1.279 (1667) | 12.6 | 9 | 124 \pm 6 | 13.0 \pm 0.1 (105) | 1.3 | 2.15 (0.3) | 3 |
| 48N (LD) | 41.6726, -74.7131 442 | 25 | 1.027 (6679) | 0.7998 (749) | 1.24 (1161) | 0.0 | 27 | 120 \pm 9 | 12.9 \pm 0.1 (107) | 1.4 | 2.34 (0.3) | 3 |
| 49N (MD) | 41.5954, -74.5389 457 | 25 | 1.031 (6589) | 1.1589 (1212) | 1.7 (1778) | 0.7 | 16 | 125 \pm 7 | 12.8 \pm 0.1 (146) | 1.6 | 1.61 (0.3) | 3 |
| 50N (LD) | 41.957, -75.2388 341 | 25 | 1.036 (6679) | 1.1867 (932) | 1.548 (1216) | 3.2 | 16 | 140 \pm 8 | 13.0 \pm 0.1 (100) | 1.3 | 2.31 (0.2) | 2.75 |
| G12 (MD) | 42.3423, -75.4055 339 | 24 | 0.983 (6671) | 1.6355 (1113) | 2.006 (1365) | 15.2 | 9 | 141 \pm 7 | 13.1 \pm 0.2 (100) | 1.5 | 1.87 (0.2) | 2.45 |
| P12 (LD) | 41.8541, -74.7617 552 | 25 | 0.993 (6671) | 1.0465 (867) | 1.51 (1251) | 8.8 | 11 | 122 \pm 6 | 13.0 \pm 0.2 (103) | 1.5 | 1.84 (0.2) | 3 |
| 15.2 (MD) | 42.2281, -74.2372 595 | 25 | 1.014 (6671) | 1.659 (1001) | 2.269 (1369) | 19.1 | 11 | 131 \pm 6 | 12.7 \pm 0.1 (100) | 1.4 | 1.94 (0.2) | 3 |

Samples listed numerically within regions, with stratigraphic age: EM – Early Mississippian (359-345 Ma); LD – Late Devonian (383-359 Ma); MD – Middle Devonian (393-383 Ma); ED – Early Devonian (419-393 Ma). All samples were crushed and apatites were separated using conventional heavy liquid and magnetic separation techniques. Apatites were mounted and prepared for AFT thermochronology using standard methods (e.g. Kohn et al., 2018). As is preferred, 25 grains (no. of grains) were counted to determine AFT ages when possible. Standard and induced track densities were counted on mica external detectors and spontaneous track densities were counted on internal apatite mineral surfaces, with the track count in parentheses. Chi-square probability (χ^2 prob.) determines if grains are from a single age population; if the χ^2 value is $>5\%$, it is likely that there is a single age population. Age variation (Var.) is the relative standard deviation of the central age and when variation is low ($<15\%$) the data are consistent with a single population. The external detector method (e.g. Gleadow, 1981) and zeta calibration approach (Hurford and Green, 1983) was used with a zeta of 353 ± 13 ($\pm 1\sigma$) for Shorten (Supplementary File E). Central ages are reported (Galbraith and Laslett, 1993). When possible and as is preferred, at least 100 horizontal confined fission track lengths per sample were measured using a projection tube and a digitizing tablet (number of tracks measured in parentheses) and standard deviation of fission-track lengths (Std. Dev.) is reported. Mean D_{par} calculated from D_{par} measurements on grains used for AFT age, with std. dev. in parentheses. Vitrinite reflectance (%R_o) is estimated from Devonian %R_o isograds (Ryder et al., 2013 and East et al., 2012) or nearest (<15 km) measured reading (*; Ryder et al., 2013). Conodont alteration index values (in { }) were measured following the procedures of Epstein et al. (1977) and, when a range of CAI values were present, the range was reported as is common practice (e.g. Repetski et al., 2008).

Table 2. Summary of (U-Th)/He results.

| Grain # | Dim. Mass (mg) | r (μm) | l (μm) | U (ppm) | Th (ppm) | Sm (ppm) | eU | ^4He (nmol/g) | F_T | Raw Age (Ma) | Corr. Age (Ma) | Error (Ma) |
|---|-------------------|------------------------|------------------------|------------|-------------|-------------|-------|---------------------------|-------------|-----------------|-------------------|---------------|
| 3P , Catskills facies (Late Devonian), East-Central Region, 41.8265°, -75.7744° | | | | | | | | | | | | |
| a1 | 5.1 | 61 | 204 | 38.1 | 62.9 | 41.4 | 52.8 | 29.1 | 0.76 | 101 | 131 | 1.0 |
| a2 | 2.8 | 50 | 217 | 17.1 | 56.4 | 54.9 | 30.4 | 22.3 | 0.70 | 133 | 188 | 1.3 |
| a3 | 1.1 | 37 | 153 | 27.7 | 101.0 | 81.4 | 51.4 | 25.6 | <i>0.61</i> | 90 | 148 | 1.2 |
| a5 | 1.7 | 44 | 162 | 94.7 | 117.3 | 81.0 | 122.3 | 77.7 | 0.67 | 116 | 171 | 1.2 |
| a6 | 4.5 | 60 | 168 | 36.9 | 63.6 | 36.9 | 51.8 | 28.3 | 0.76 | 100 | 130 | 1.0 |
| <i>Mean age $\pm 1\sigma$ (% std. dev.): 154 \pm 25 (16 %)</i> | | | | | | | | | | | | |
| 43P , Catskills facies (Late Devonian), West-Central Region, 41.7573°, -77.9034° | | | | | | | | | | | | |
| a1 | 1.1 | 35 | 106 | 75.7 | 216.6 | 71.0 | 126.6 | 72.3 | <i>0.59</i> | 104 | 175 | 0.7 |
| a2 | 1.3 | 34 | 149 | 37.7 | 272.5 | 50.0 | 101.7 | 36.9 | <i>0.57</i> | 66 | 116 | 0.8 |
| a3 | 1.1 | 33 | 130 | 22.9 | 161.1 | 30.5 | 60.8 | 22.3 | <i>0.55</i> | 67 | 120 | 0.7 |
| a4 | 1.1 | 34 | 123 | 16.6 | 311.2 | 34.7 | 89.7 | 36.4 | <i>0.56</i> | 74 | 133 | 1.3 |
| a6 | 1.2 | 33 | 149 | 68.9 | 564.0 | 72.2 | 201.5 | 78.0 | <i>0.55</i> | 71 | 128 | 0.6 |
| <i>Mean age $\pm 1\sigma$ (% std. dev.): 134 \pm 24 (17 %)</i> | | | | | | | | | | | | |

Analyses were completed by CU TRaIL. Dim. Mass = dimensional mass of grain calculated from crystal volume and average apatite density; r = radius of a sphere with equivalent surface area to volume ratio as the grain; l = longest dimension of the grain. Concentrations of U, Th and Sm measured via isotope dilution on an ICP-MS. eU is the effective Uranium, calculated as $[\text{U}] + 0.235[\text{Th}]$ (e.g. Flowers et al., 2009). Grains were degassed by heating with a laser to determine the amount of ^4He (nmol/g) in the grain. Alpha ejection correction (F_T) is a measure of the amount of He ejected from the crystal, values <0.65 (italicized, grey) indicate that a significant amount of He was ejected (Farley et al., 1996). Ages and F_T were calculated using methods described in Ketcham et al. (2011). Raw Age = age calculated from isotope concentrations, without F_T correction; Corr. Age = age calculated from isotope concentrations, with F_T correction; Error = 2σ analytical uncertainty (not incorporating F_T uncertainty). Summarized in bold italics, is the mean age of the single-grain corr. ages with 1σ error on the ages (1 standard deviation). In parenthesis is the coefficient of variation (% std. dev.), calculated from the ratio of the standard deviation to the mean. Coefficient of variation is used to show the variation of single-grain ages from the mean age.

Chapter Two

Episodic Exhumation of the Appalachian Orogen in the Catskill Mountains

Abstract

An increasing abundance of evidence documenting episodic post-rift exhumation indicates eastern North America is not a tectonically quiescent passive margin. The timing, resolution and significance of post-orogenic exhumation events are debated, notably an enigmatic Miocene event. We add insight to this post-orogenic exhumation history by constraining the thermal history of the Catskill Mountains of New York (USA) utilizing apatite fission-track (AFT) thermochronology and apatite (U-Th)/He (AHe) ages from a 1 km age-elevation profile collected from Slide Mountain. While the overall cooling rates are slow, multi-kinetic inverse thermal models reveal relatively rapid cooling at rates of $\sim 1\text{-}3$ °C/Myr from the Early Jurassic to Early Cretaceous and rates of $\sim 1\text{-}2$ °C/Myr from the Miocene to Recent. These “rapid” episodes are separated by much slower cooling at rates $< \sim 0.5$ °C/Myr, during which samples resided for ca. 100 Myr in the partial annealing zone (for AFT) and partial retention zone (for AHe). Cooling was due to erosional exhumation and cooling episodes can be correlated with Early Jurassic rifting of the Atlantic margin, development of the passive margin, and a period of landscape rejuvenation likely associated with dynamic topography in the Miocene. The relatively low magnitude of the Miocene event means that documentation using low-temperature thermochronology constraints has been elusive. However, onshore thermochronology correlates with the sedimentation record in offshore Mid-Atlantic basins that indicate an increase in Miocene sedimentation rates, while geomorphologic studies in the southern Appalachians document accelerated erosion in the Miocene due to landscape rejuvenation. Our findings contrast with previous thermochronologic studies that were unable to verify the existence of Miocene exhumation and those that rejected the Miocene cooling as a spurious artifact of an early generation of thermal models.

Introduction

Post-orogenic development of topography along the Eastern North American passive margin and persistence of mountainous topography in the Appalachian Mountains has been a source of debate over the past 50 years (e.g. Hack, 1960, 1982; Miller and Duddy, 1989; Pazzaglia and Brandon, 1996; Roden-Tice et al., 2009; Miller et al., 2013; McKeon et al., 2014; Amidon et al., 2016). Conventionally, after initial rifting, passive margins were considered tectonically quiescent regions with decreasing topographic relief attributed to exponentially-decaying relict topography (Davis, 1899). Since the 1990's there has been a renewed interest in exploring the correlation between tectonics and topography and demonstrating a more dynamic post-rift history along passive margins (c.f. Bishop, 2007). Pulses of accelerated sediment flux into offshore Mid-Atlantic basins, such as in the Baltimore Canyon Trough, since the Late Jurassic – including a strong Miocene pulse – suggests renewed periods of tectonic uplift and/or erosion along the Appalachian orogen and eastern North America (e.g. Poag, 1985; 1992; Poag and Ward, 1993; Pazzaglia and Brandon, 1996). There is also onshore geomorphologic evidence of Miocene surface uplift of ~100-200 m, documented in the central and southern Appalachians (e.g. Miller et al., 2013; Gallen et al., 2013).

The interpretation of Miocene exhumation based on low-temperature thermochronology in the Appalachian highlands has not yielded definitive results where this approach has been applied, for example in the Blue Ridge Mountains, New England, and central Appalachians in New Jersey (e.g. Spotila et al., 2004; Roden-Tice et al., 2009; McKeon et al., 2014; Amidon et al., 2016). No Miocene ages have been documented, even with low-temperature techniques such as apatite (U-Th)/He (AHe) dating. There are 3 AFT Paleogene ages (48-33 Ma) recorded in the Appalachian Basin and Ridge and Valley provinces of southwestern Pennsylvania and West

Virginia, however these ages are considered anomalous and related to thermal resetting, possibly due to decreasing temperatures of thermal springs in the Cenozoic which were at temperatures >100 °C in Mesozoic (Roden, 1991). The absence of younger ages, associated with Miocene exhumation, suggests that erosion since the Miocene must be less than ~ 2 km (e.g. McKeon et al. 2014). Interpretation of thermochronologic data from studies utilizing inverse thermal modeling is mixed, for a variety of reasons. Two studies have constrained accelerated Miocene cooling in their thermal history interpretations of data from the central and southern Appalachian basin (Blackmer et al., 1994; Boettcher and Milliken, 1994). However, these studies employed modelling that used mono-kinetic annealing algorithms (e.g. Laslett et al., 1987; Crowley et al., 1991) that often produced a late-stage cooling artifact (i.e. Miocene cooling) which, without supporting geologic evidence makes the interpretation of modeling results unreliable and lacking confidence (e.g. De Bruijne and Andriessen, 2002; Ketcham et al., 1999). Miocene cooling was modeled in other thermochronologic studies within the Blue Ridge Mountains and New England, also using mono-kinetic annealing algorithms of Laslett et al. (1987) and Crowley et al., (1991), but in contrast these studies rejected Miocene cooling revealed in their thermal models as a spurious artifact because of these issues with modeling programs at that time (Spotila et al., 2004; West et al., 2008; Roden-Tice et al., 2009).

In this study low-temperature thermochronologic results are presented for a suite of samples collected over short-wavelength topography and significant relief (~ 1 km) from Slide Mountain, near West Shokan, New York (Figure 1). The AFT age-elevation profile and multi-kinetic inverse thermal modeling of AFT data, AHe ages, and maximum paleotemperature (T_{\max}) indicators constrains the episodic cooling and exhumation history of the Catskill Mountains (Catskills) during the Mesozoic and Cenozoic. AFT thermochronology utilizes confined track

lengths as a kinetic parameter (e.g. Gleadow et al., 1986). Multi-kinetic models characterize individual apatite grains' variability to annealing within a sample and does not produce a spurious late-stage cooling artifact (Ketcham et al., 1999). From the Slide Mountain data it is possible to document two episodes of accelerated cooling: Late Jurassic to Early Cretaceous; and Miocene to present, separated by a period from the Cretaceous to Miocene of much slower cooling ("stabilization"). Results are discussed in context of previous studies and correlate events with regional tectonics and proposed Cenozoic mantle upwelling along eastern North America (NA).

Geologic Setting

The Catskill Mountains are comprised of Devonian, near-horizontal, undeformed sedimentary strata of the Catskill delta wedge (Figure 1; Faill, 1985; Ver Straeten, 2013). The Catskill wedge consists of a series of delta-alluvial wedges and submarine facies that coarsen up-section as the delta front prograded cratonward (Ettensohn, 1985; Ver Straeten, 2013). Sediments reflect a dominant Acadian provenance with lesser contributions from Taconic and Grenville sources (Ver Straeten, 2009). The preserved sediments (~2.7 km in thickness) were deposited during the Acadian orogeny (ca. 419-365 Ma; Ver Straeten, 2013). Younger sedimentary packages were deposited on top of the currently preserved sediments in the Catskill region during the Acadian and the Alleghenian orogeny (ca. 330-265 Ma, Ettensohn, 2008) are missing as they have since been eroded. The thickness of eroded sediments in the Catskills is estimated as ~5 km (e.g. Friedman and Sanders, 1982; Lakatos and Miller, 1983; Miller and Duddy, 1989).

Thrusting during the Alleghenian orogeny led to over-pressurization of sediments, and formation of joints in the Catskill wedge strata (Lash and Engelder, 2009; Ver Straeten, 2013). However, there is no other deformation of the Middle to Late Devonian strata in the Catskills

(Ver Straeten, 2013). Alleghenian thrusting also resulted in regional hot fluid-flow within the Catskill wedge, which elevated the geothermal gradient, but not after the Alleghenian Orogeny (Dorobek, 1989). At the end of the Alleghenian Orogeny the Catskill Delta wedge and overlying Early Pennsylvanian to Permian units comprised the expansive, flat-lying Alleghenian Plateau (Ver Straeten, 2013). The Catskill Mountains' peaks all have similar elevations (summit-height concordance), indicating that they were formed from the erosional incision and exhumation of the Alleghenian plateau (e.g. Ettensohn, 2008; Ver Straeten, 2013). The timing of this post-orogenic exhumation, documented throughout the Appalachian Basin in various thermochronology studies, is episodic but variable (e.g. Blackmer et al., 1994; Reed et al., 2005; Amidon et al., 2016) and does not occur as one rapid pulse (e.g. Miller and Duddy, 1989) or as a result of slowly decaying topography due to erosion (Davis, 1889).

Methods, Results, and Geothermal Gradient

Five samples of Middle to Late Devonian sandstones were collected at elevations ranging from 281 to 1,272 m to generate an age-elevation profile (Figure 1, Supplementary Table 1). Samples were collected along the shortest, most direct trail to the peak of Slide Mountain and in the surrounding valleys, within ~8 km of the peak. The vertical profile was collected over short wavelength topography to minimize modification of the slope due to topographic effects on subsurface isotherms (e.g. Reiners et al., 2003; Fitzgerald and Malusà, 2018). AFT low-temperature thermochronology (Supplementary Table 1) was undertaken at Syracuse University following standard procedures (e.g. Riccio et al., 2014) and AHe dating (Supplementary Table 2) at CU TRaIL (Colorado Thermochronology Research and Instrumentation Laboratory, University of Colorado, Boulder, e.g. Weisberg et al., 2018). T_{\max} information is from published Vitrinite reflectance (% R_o) isograd maps of Devonian shales (Ryder et al., 2013). Apatite grains from

these samples are well-rounded, often pitted and semi-opaque (stained) likely due to transportation prior to burial and diagenesis since, making the selection of appropriate grains for AHe difficult (Supplementary Table 3).

AFT central ages range from 133 ± 7 to 114 ± 8 Ma ($\pm 1\sigma$). For all samples, the variation of single-grain AFT ages is low (0-16%) and all pass the χ^2 test, indicating that grains for each sample define a single age population (Supplementary Table 1). AFT ages increase with increasing elevation, with the slope representing an apparent exhumation rate of ~ 50 m/Myr during the Early Cretaceous (Figure 2). Mean track lengths vary from 13.1 to 12.8 μm with standard deviations of 1.6 to 1.1 μm . Confined track length distributions (CTLDs) exhibit a weak negative skewness (Figure 2). Track length data thus indicates a complex thermal history involving partial annealing and/or an episodic cooling (e.g. Gleadow et al., 1986, Green et al., 1986). D_{par} values range from 2.15 to 2.39 μm , which indicate that the apatite grains are more resistant to annealing than standard fluorapatites (i.e. $D_{\text{par}} > 1.75$ μm ; e.g. Donelick et al., 2005). This means that the partial annealing zone (PAZ), the temperature range in which fission-tracks are annealed, is ~ 120 -60 $^{\circ}\text{C}$.

AHe single-grain ages on samples C1, C3, and C5 range from $1,850 \pm 69$ to 83 ± 1 Ma with significant variation about the mean (e.g. 52-125%; Supplementary Table 2). There are obvious outliers, potentially due to the influence of one or more well documented factors such as poor grain quality or inclusions with high uranium content (Supplementary File A; e.g. Ehlers and Farley, 2003; Fitzgerald et al., 2006; Wildman et al., 2016). Green and Duddy (2018) summarize problems of “excessive dispersion” of single-grain ages, use of mean AHe ages for interpretation, and He retentivity due to radiation damage. They also discuss that models (i.e. RDAAM; Flowers et al., 2009) cannot yet accurately replicate single-grain age dispersion. There

is no clear age-elevation trend in the AHe ages from Slide Mountain. Overall challenges remain for the interpretation of AHe data (e.g. Green and Duddy, 2018), however the interpretation of such data, including that from Slide Mountain are fortified by the use of inverse thermal models that rely dominantly on AFT data (see below). Mean AHe ages calculated from AHe single-grain ages without obvious outliers (e.g. Ault et al., 2013) decreases variation to 27-31 %. Mean AHe ages for samples C1 (highest elevation), C3, and C5 are 159 ± 49 Ma ($\pm 1\sigma$), 111 ± 3 Ma, and 128 ± 34 Ma respectively.

Samples are estimated to have reached maximum temperatures of ~ 215 - 235 °C, estimated from % R_o values (Ryder et al., 2013; Supplementary Table 1) using the Basin % R_o model (Nielsen et al., 2017). Fission tracks in apatite grains have therefore been reset and thermochronology data does not constrain the timing of T_{max} but does constrain the post-orogenic thermal history. Inverse thermal modeling of AFT and AHe data, using the modeling program HeFTy v1.9.1 (Ketcham, 2005), constrains cooling since the Late Jurassic (Figure 3; Supplementary File B). Overall, cooling rates are low enough that effects of advection due to rapid exhumation or distortion of the geothermal gradient are likely to be insignificant (e.g. Braun, 2002). Fluid-flow influenced the geothermal gradient during the Alleghenian orogeny, but it did not continue after thrusting ceased (Dorobek, 1989). The cooling history is therefore converted to exhumation rates using a relatively stable, modern geothermal gradient of 25 °C/km, similar to other studies in eastern North America using this approach (e.g. Reed et al., 2005; Amidon et al., 2016; Shorten and Fitzgerald, in review).

Episodic Cooling and Exhumation History

The age-elevation profile combined with track length information and inverse modeling (Figure 3) indicates episodic cooling (Figure 4). Initial, relatively rapid cooling from T_{max} is

model constrained to begin in the Early Jurassic and samples pass into the PAZ by the Late Jurassic (event 1-1a). Between the Early Cretaceous and Miocene, thermal models constrain a time of slower cooling (“stabilization”) when samples are resident in the upper crust (event 2). Beginning in the Miocene models constrain an acceleration in cooling to present day (event 3).

Event 1-1a: Initial cooling from T_{\max} and exhumation of Appalachian basin strata began in the Early Jurassic. This timing is not revealed clearly in Slide Mountain inverse models (Figure 3) but is revealed in AFT data from the northern Appalachian Basin lying to the west of Slide Mountain (Shorten and Fitzgerald, in review). The Catskill samples cooled into the PAZ in the Late Jurassic. Thus, we break this initial exhumation event into (1 – northern Appalachian Basin samples) and (1a – Catskills samples). Estimated cooling rates between the start of rapid cooling and ca. 120 Ma (end of event 1a) are 0.6-2.4 °C/Myr (weighted mean paths), with rates up to 2.1-9.6 °C/Myr constrained in individual best-fit model paths. Assuming a geothermal gradient of 25 °C/Myr for the weighted mean paths, suggests the removal of ~3-6 km of overburden at rates of 24-95 m/Myr during this event (Figure 4). These rates correlate well with the apparent exhumation rate derived from the slope of the age-elevation profile (~50 m/Myr).

We relate initial rapid cooling (events 1 and 1a) to rift flank uplift, extension and subsequent rifting that led to the formation of the North Atlantic Ocean (Figure 4). This period of rapid cooling and exhumation in the Catskills correlates well with an increase in sediment flux into the Baltimore Canyon Trough, starting in the Late Jurassic (Pazzaglia and Brandon, 1996). Lowering of regional base levels due to the extension and rifting, and formation of the Atlantic passive margin likely increased river incision and backwearing resulting in re-excavation and increased erosion rates of the onshore Appalachian orogen and sedimentary strata in the Catskills (c.f. Wildman et al., 2018). In the Appalachian Basin in Pennsylvania, Blackmer et al. (1994)

state that initial exhumation at this time is likely due to erosion of the sedimentary overburden in response to flexural rebound of the lithosphere after the cessation of deposition. Our timing of initial cooling also overlaps with Miller and Duddy's (1989) estimate of 140-120 Ma for the Catskills. However, our estimates of the amount of exhumation differ from Miller and Duddy (1989), who suggested this event accounted for the removal of almost all the orogenic overburden.

Event 2: Inverse thermal models clearly indicate residence of samples in the PAZ and AHe partial retention zone (PRZ, ~30-90 °C; Flowers et al., 2009) from the Early Cretaceous to Miocene. Cooling is very slow, with rates of 0.2-0.5 °C/Myr. Event 2 accounts for <1 km of exhumation over ca. 100 Ma at rates of ~9-21 m/Myr. AHe Single-grain age variations often result from variations in grain size, zonation patterns, and/or effective uranium (eU) concentrations (e.g. Fitzgerald et al., 2006; Flowers et al., 2009). Long-term residence within the PRZ is also well-known for magnifying the effect of these factors, causing significant single-grain age dispersion (e.g. Reiners et al., 2003; Fitzgerald et al., 2006). Offshore sedimentation rates decrease significantly during this time (Pazzaglia and Brandon, 1996). Thus, we propose that event 2 is associated with stabilization with decreasing relief within the Catskills as eastern North America transitioned into a passive continental margin (Figure 4; e.g. Withjack and Schlische, 2005; Ettensohn, 2008).

Event 3: Following long-term residence within the PAZ and PRZ, thermal models constrain an increase in cooling rates, to 0.9-1.9 °C/Myr (based on weighted mean paths), with best-fit model rates ranging from 1.2-3.2 °C/km (Figure 3). The timing of this increase in cooling rate occurs at ca. 23 Ma (Miocene), but the timing is variable between models for samples from different elevations (ca. 30 to 20 Ma). Since higher elevation samples pass into the PAZ earlier

than those at lower elevations, models from higher elevation samples suggest onset of rapid cooling earlier, as to be expected. Exhumation rates are between 34-75 m/Myr on average, with peak best-fit estimates up to 128 m/Myr. This period of relatively rapid exhumation accounts for the removal of the final 1-2 km of overburden and the exposure of the Devonian strata to the surface (Figure 4).

The increase in exhumation in the Miocene documented for samples in this study and the offshore sedimentation record have a positive correlation (Pazzaglia and Brandon, 1996). The mechanisms responsible for this increase in Miocene exhumation and sedimentation are highly debated. Initially, studies hypothesized that the Miocene increase in offshore sedimentation rates resulted from a change to a cool/dry climate in the Miocene, causing increased mechanical weathering and exhumation of the onshore Appalachian region (e.g. Poag and Sevon, 1989; Boettcher and Milliken, 1994). However, given the timing and amount of exhumation documented in the Appalachian Basin, most studies now agree that tectonic processes must be the driving factor in the Appalachian Basin thermal history trends and pulses of offshore sedimentation (e.g. Pazzaglia and Gardner, 1994; Blackmer et al., 1994; Pazzaglia and Brandon, 1996; Miller et al., 2013; Gallen et al., 2013). Both geomorphologic and low-temperature thermochronology studies that constrain Miocene cooling conclude the mechanism was either due to interaction of isostatic forces on the ancient foreland and flexural response due to sedimentation along the margin (Pazzaglia and Gardner, 1994; Blackmer et al., 1994) or a result of dynamic topography (e.g. Pazzaglia and Brandon, 1996; Miller et al., 2013; Gallen et al., 2013). Given that our models constrain 1-2 km of exhumation, we conclude that there must have been a complex combination of factors causing broad, regional landscape rejuvenation.

Eastern US Context for Miocene Exhumation

Offshore Mid-Atlantic basins (e.g. Salisbury Embayment, Baltimore Canyon Trough, and the Hatteras Basin) record pluses of increased sediment flux rates during the Jurassic, Late Cretaceous, and Miocene, suggested as due to tectonic uplift and erosion of Appalachian terranes (e.g. Poag and Sevon, 1989; Pazzaglia and Brandon, 1996; Amidon et al., 2016). Sediment flux into the basins and erosion rate in the Appalachian hinterland is greatest in the Miocene, requiring >1.1 km of rock to be removed from catchments across the central Appalachians to New England (Braun, 1989). Zircon fission track analysis conducted on Atlantic Coastal Plain sediments and in Blue Ridge Mountains of Virginia and North Carolina suggest that headwaters of catchment basins incised westward and began to transport western Appalachian detritus eastward beginning in the late early Oligocene to middle early Miocene (Naeser et al., 2016). Naeser et al. (2016) suggested that the increase in offshore sedimentation is partially due to rivers gaining access to easily eroded Paleozoic sedimentary rocks of the western Appalachians. Geomorphological evidence also constrains an onshore increase in erosion rates in the Miocene. Stream profile analysis and ^{10}Be erosion rates of the Susquehanna River catchment basin in PA indicates ~100-150 m of river incision propagating upstream in the Miocene due to rock uplift (Miller et al., 2013). Also, generation of knickpoints and preservation of relict landscape in North Carolina (NC) is interpreted as surface response to broad, regional uplift of the Appalachians by dynamic mantle forcing during the mid-Miocene (Gallen et al., 2013).

Thermochronology studies have struggled to confidentially verify this Miocene exhumation signal. There are no recorded Miocene AFT or AHe ages (e.g. Spotila et al., 2004; McKeon et al., 2014), and there is contradictory information from thermal models. As discussed above, early studies utilizing mono-kinetic annealing algorithms either concluded that there was

real Miocene cooling (e.g. Blackmer et al., 1994; Boettcher and Milliken, 1994) or that it has not occurred and is a model artifact (e.g. Spotila et al., 2004; West et al., 2008; Roden-Tice et al., 2009). The reason why mono-kinetic models often indicated spurious late-stage cooling was because these models used annealing algorithms based on annealing experiments undertaken on Durango apatite (e.g. Laslett et al., 1987). Fission-tracks in Durango tend to be more resistant to annealing than the average fluorapatite, thus using Durango kinetics during modeling of a fluorapatite would cause tracks to not be annealed early in the model, which would then produce a late-stage rapid cooling as the model sought to end at present day temperatures. Late-stage cooling (often Miocene) documented with mono-kinetic algorithms are therefore questionable given the input assumption of uniform apatite composition and annealing characteristics (e.g. De Bruijne and Andriessen, 2002; Roden-Tice et al., 2009).

Documentation of Early Cretaceous AHe ages in several studies from New England, was also cited as a reason against Miocene cooling, since samples would have to be within the PRZ during the Mesozoic (e.g. West et al., 2008; Roden-Tice et al., 2009). Our AHe ages in the Catskills are also, generally Cretaceous in age but, as discussed above, samples also contain outliers of Paleozoic and Precambrian AHe single-grain ages (Supplementary Table 2). West et al. (2008) comment on the discordance of several of their AHe ages and corresponding AFT ages, such as AHe ages significantly older or within standard error of AFT ages. They state that it is possible that single-grain age dispersion is caused by retention of He in apatite due to radiation damage and/or high eU concentrations. Further south in the Blue Ridge Mountains, McKeon et al. (2014) used the lack of Miocene ages as evidence that any Miocene exhumation was <2 km in magnitude. Otherwise, reset AHe ages would have been present at the surface, assuming a typical continental geotherm (e.g. 20-30 °C/km). Mesozoic (and older) AHe ages do

not preclude Miocene cooling, as documented in the multi-kinetic thermal models, they simply constrain the amount of Miocene cooling and hence estimates on exhumation.

It is important to note that offshore sedimentation flux is calculated for the ten major catchments, spanning from New Hampshire to northern Virginia, which feed sediment to the Mid-Atlantic margin (Pazzaglia and Brandon, 1996). Thus, onshore exhumation and erosion required to account for a Miocene plus in offshore Mid-Atlantic basin sedimentation should be focused on that region, which includes the Catskills. Also, there is an inherent assumption in this study and Pazzaglia and Brandon's (1996) work that the catchment basins have not greatly changed extent through geologic time. Some of the studies which do not constrain Miocene cooling (e.g. Spotila et al., 2004; West et al., 2008; Roden-Tice et al., 2009; McKeon et al., 2014) either completely or partially lie within catchments (i.e. Mississippian or St. Lawrence catchments) which drain into the North Atlantic or Gulf of Mexico, something that was also commented on by McKeon et al. (2014). Given that our study area is in the Hudson river catchment, which directly drains into the Baltimore Canyon Trough, it is plausible that Miocene exhumation of the relatively high-standing Catskills region is more closely correlated with documented offshore sedimentation.

Conclusions

Our results show that the Catskills experienced an episodic cooling history since the end of the Alleghenian orogeny. Initial cooling and exhumation from the Late Triassic to Early Cretaceous is contemporaneous with rifting (events 1-1a), followed by a long period of stabilization as eastern North America drifted and developed into a passive margin (event 2), then a final period of rapid cooling and exhumation in the Miocene (event 3), due to landscape rejuvenation. Triassic to Cretaceous and Miocene exhumation correlates with increases in

offshore sedimentation rates (e.g. Pazzaglia and Brandon, 1996). Significant Miocene to present rapid cooling due to erosional exhumation is revealed in multi-kinetic inverse thermal models. Miocene cooling has previously been regarded as controversial and highly debated due to the late-stage rapid cooling artifact of first-generation inverse thermal models that used mono-kinetic annealing algorithms, as well as the lack of Miocene AFT and AHe ages (e.g. Spotila et al., 2004; Roden-Tice et al., 2009). Miocene-Recent exhumation in the Catskills is constrained as 1-2 km, most likely resulting from a combination of mechanisms, each of which produce relatively small magnitude effects. These include isostatic flexural response to offshore sedimentation and dynamic topography causing landscape rejuvenation. We note that the detection of this Miocene event is often near the resolution of the methods employed, and that the causes of this Miocene-recent exhumation remain enigmatic and offer future avenues for research and greater understanding.

Acknowledgments

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Figures

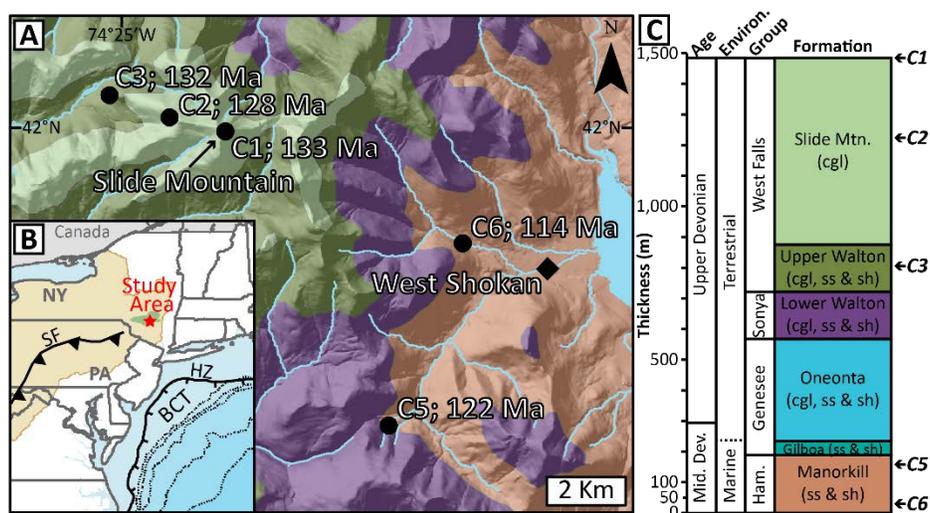


Figure 1. (A) Geologic map with samples and AFT ages. (B) Insert of study area (red star), Catskill state park (green), Appalachian Basin (tan), Appalachian structural front (SF), North American passive margin hinge zone (HZ), Baltimore Canyon Trough (BCT), and bathymetry (dashed lines represent 200, 1000, 2000, 3000 and 4000 m depth, from west to east). (C) Stratigraphic column of Catskill Delta Wedge units from Slide Mountain to West Shokan, NY (modified from Ver Straeten, 2013) with estimated stratigraphic sample locations. Mid. Dev. – Middle Devonian; Environ. – environment; Ham. – Hamilton; cgl – conglomerate; ss – sandstone; sh – shale.

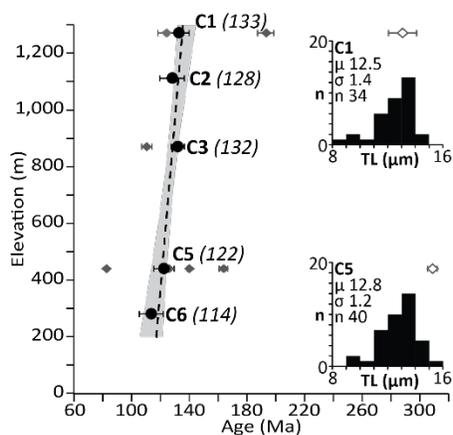


Figure 2. Age vs. elevation profile. AFT central ages ($\pm 1\sigma$, black), with sample ID and AFT age. AHe single-grain ages ($\pm 2\sigma$, dark grey), with outliers made hollow. Trendline of AFT ages (dashed) and 1σ error envelope (light grey). CTLD of C1 and C5 include: track lengths (TL), mean track length (μ), standard deviation (σ) and number of tracks measured (n).

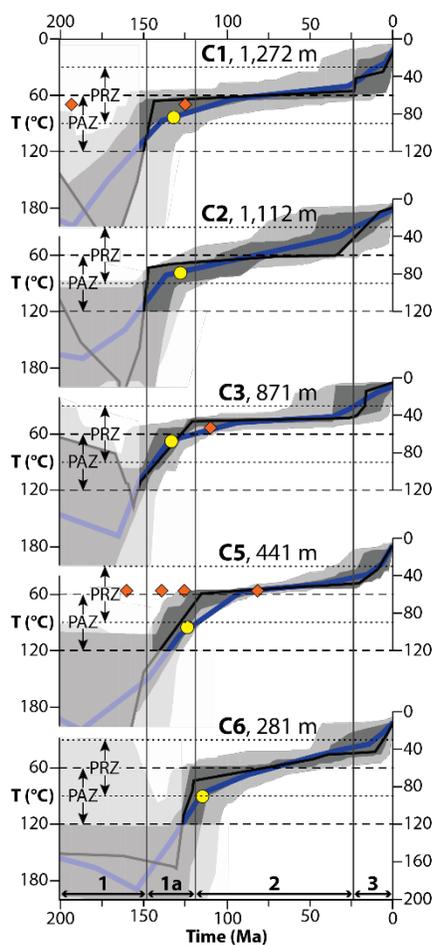


Figure 3. Inverse thermal models from HeFTy (Ketcham, 2005) arranged according to elevation. AFT central ages (yellow circles) and single-grain AHe ages (orange diamonds). Black line is the “best fit”, thick blue line is the weighted mean, dark gray envelopes are “good fit” paths (i.e. T-t paths supported by the data) and light gray envelopes are “acceptable fit” paths (i.e. T-t paths not ruled out by the data). Areas unconstrained by AFT data are semi-transparent. Vertical lines (numbered 1, 1a, 2, 3) highlight thermal history trends. PAZ – partial annealing zone; PRZ – partial retention zone; T – temperature.

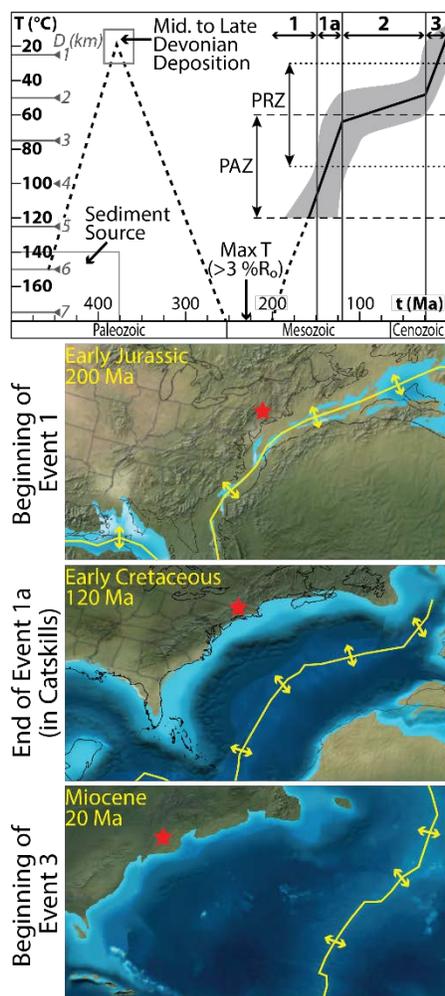


Figure 4. Schematic T-t history of the Catskills. Dashed line is the history constrained by geologic information, sediment source (Ver Straeten, 2009), deposition time/paleo-surface temperature (25 ± 10 °C; Woodrow et al., 1973), and T_{\max} % R_o data (Ryder et al., 2013). Solid line and grey envelope is the average history and range constrained with low-temperature thermochronology data. Present-day surface temperature is 7 ± 5 °C (Hijmans et al., 2005). Temperature (T) and estimated depth (D), using geothermal gradient of 25 °C/km, are along the left side and cooling/exhumation events (1, 1a, 2, 3) with vertical reference lines are listed along the top. Paleogeographic maps (Blakey, 2013) include the study location (red star) and divergent boundary (yellow), illustrating the rifting of Pangea and transition to drift and passive margin development (e.g. Withjack and Schlische, 2005).

Chapter Three

Synthesis of Post-Orogenic Low-Temperature Thermal Histories along the eastern United States

Abstract

Following the Appalachian orogeny, the eastern United States (U.S.) has experienced a complex, episodic cooling and exhumation history. To constrain major orogen-wide thermal and tectonic events as well as distinguish those events that are localized or only occur within a small region, we undertake a comprehensive synthesis of data from 26 low-temperature thermochronology studies along the eastern U.S. Challenges exist in comparing thermal histories from studies which are spread across the entire Appalachian orogen, have different sampling strategies and objectives, apply different methods and span in publication from the early 80's to today. There are also variations in timing, duration, rates and resolution of the different events across the various physiographic provinces of the eastern U.S. (i.e. the Taconic and Acadian province in New England, the Adirondacks, the Appalachian Basin, and the Ridge and Valley province).

Many of the low-temperature thermochronology studies undertaken along the eastern U.S. lie within present day catchments that drain into Mid-Atlantic offshore basins. We examine the onshore record and conclude episodes of rapid cooling and exhumation documented within these catchments correlate well with periods of increased sediment flux into offshore Mid-Atlantic basins. Synthesizing the temporal correlation between onshore exhumation and offshore sediment flux and the provinces' thermal histories, the post-orogenic low-temperature thermal history across the eastern U.S. passive margin is divided into three extended periods of cooling and exhumation. These periods are related to regional effects of Early Mesozoic continental rifting and post-rift crustal extension, Late Mesozoic variable cooling due to the development of the passive margin and to exogenic mechanisms, and Late Cenozoic (i.e. Miocene) rapid cooling related to the establishment of dynamic topography and drainage reorganization.

Introduction

The Paleozoic collisional and other tectonic events that formed the Appalachian Mountains, followed by the Mesozoic to Cenozoic evolution of the passive margin of the eastern United States (U.S.) are the subject of considerable study (e.g. Hatcher et al., 1989; Miller and Duddy, 1989; Poag and Sevon, 1989; Faill, 1997a; Roden-Tice and Tice, 2005; Ettensohn, 2008; Moodie et al., 2018). The geologic processes controlling post-orogenic passive margin development are complex (e.g. Green et al., 2018) and often involve episodic syn- and post-rift magmatic and thermal events (e.g. de Boer et al., 1988). Low-temperature thermochronology is a method often applied to constraining the post-orogenic thermal history and exhumation rates of passive margins such as the eastern U.S. (Table 1). While there is an abundance of thermochronology data from many studies scattered over the eastern U.S., an orogen-scale synthesis of the low-temperature thermal and exhumation history has not been undertaken. This comprehensive, thermal and exhumation history synthesis of available data provides insight into the exogenic forces (i.e. tectonics, dynamic topography or climate change) which are responsible for the larger, orogen-scale cooling and exhumation events as well as the more localized events.

To undertake this synthesis, apatite fission-track (AFT) thermochronology and (U-Th)/He (AHe) data was collated from 26 low-temperature thermochronology studies located throughout eastern U.S. (24 published studies and Chapters 1 and 2; Figure 1 and 2). In regions where the rate of cooling is overall very slow, such as the post-orogenic history of the eastern U.S., AFT and AHe ages can be meaningless when taken out of context with the thermal history that the sample has experienced (e.g. Gleadow and Brown, 2000). In other words, AFT and AHe ages cannot be simply interpreted as closure temperature ages. AFT ages are a function of time and temperature, that when combined with the measurement of fission-track lengths (as a kinetic

parameter) and D_{par} (as a compositional proxy) allows for inverse thermal modeling of the time-temperature paths at temperatures $<120\text{-}100\text{ }^{\circ}\text{C}$ (e.g. Gleadow et al., 1986; Gallagher et al., 1998). The distribution of fission-track lengths constrains the thermal history that a rock has experienced, with broad distributions and mean fission-track lengths (MTL) $< 14\text{ }\mu\text{m}$ indicative of complex or slow cooling while narrow distributions with $\text{MTL} \geq 14\text{ }\mu\text{m}$ are indicative of rapid cooling (e.g. Gleadow et al., 1986; Green et al., 1989). AHe ages reflect the interaction of in-situ radiogenic He production and diffusive loss at temperatures $< \sim 70\text{ }^{\circ}\text{C}$ that can help constrain the lower-temperature thermal history (e.g. Reiners and Farley, 2001). Trends identified and discussed in the paper are thus mainly based on model-constrained cooling histories with the aid of data-driven interpretations (i.e. AFT ages of samples with $\text{MTL} \geq 14\text{ }\mu\text{m}$).

Thermal histories from different studies, both within and across physiographic provinces of the Appalachian orogen (i.e. Taconic and Acadian province, Adirondacks, Appalachian Basin, Ridge and Valley province, Blue Ridge Mountains, Piedmont, Mesozoic rift basins), often constrain differential rates of cooling with variation in resolution, duration and significance of cooling events. The episodicity of cooling events and variation of such across the provinces reveal which events occur throughout the entire orogen as compared to those events which are more localized (i.e. province-specific and more likely to originate from a localized geologic event) during the post-orogenic history. There are challenges in comparing thermal histories from studies published over the last 40 years. Different studies focused on constraining different specific geologic events, may incorporate a range of thermal and geologic constraints, and utilize several generations of thermal models (i.e. mono-kinetic (e.g. Laslett et al., 1987; Crowley et al., 1991) versus multi-kinetic annealing algorithms (e.g. Ketcham et al., 1999; 2007)). However, commonality and differences between thermal histories at different scales can be determined.

After providing an overview of the geologic history of the eastern U.S. for context, this chapter discusses the database created from the 26 low-temperature thermochronology studies and the challenges of interpreting thermal histories. The synthesis is undertaken in 2 stages. (1) Comparing thermal histories from samples that lie within catchment basins which drain into Mid-Atlantic offshore basins (i.e. Salisbury Embayment, Baltimore Canyon Trough and Hatteras Basin; Poag and Sevon, 1989). The onshore thermal record from these samples record cooling and exhumation related to North American rifting and 4 periods of increased sediment flux to offshore Mid-Atlantic basins, calculated by Pazzaglia and Brandon (1996). (2) Determining major thermal trends documented within individual provinces and across the eastern U.S. These are analyzed to determine which events are orogen-wide in scale and which are more localized and hence what exogenic events are responsible. Despite the challenges in comparing the different generations of studies, we provide new insight into the temporal and spatial patterns of the post-orogenic exhumation history and landscape evolution of the passive margin of the eastern U.S.

Geologic overview

Eastern U.S. is geologically complex, containing several provinces that formed from collision and terrane accretion along the eastern Laurentian margin during different orogenic and exhumation events since the beginning of a Wilson cycle in the Neoproterozoic (Rast, 1989; Hatcher, 2010). Figure 1A shows the main physiographic provinces, including the Adirondack mountains (Grenville), accreted island arcs and terranes (i.e. Taconic and Acadian provinces), preserved structural features (i.e. Blue Ridge Mountains, Alleghenian structural front and Paleozoic contractional structures), and thick sedimentary packages of both deformed (i.e. Ridge and Valley province) and flat lying strata (i.e. Appalachian Basin). The present drainage divide

between the Atlantic Ocean and Gulf of Mexico is thought to have been relatively steady since the early-Mid Mesozoic (Hack, 1982), with local westward migration in the southern Blue Ridge province since Oligocene (e.g. Spotila et al., 2004; Naeser et al., 2016). Modern catchment basins are used in this study to approximate areas which drain into the Northern, Middle and Southern North Atlantic Ocean and the Gulf of Mexico (Figure 1B).

Paleozoic Era: The Appalachian Mountains stretch from Alabama, U.S. to Newfoundland, Canada (Hatcher et al., 1989; Hatcher, 2010). The development of the Appalachian Mountains and resulting foreland basin are well-documented (e.g. Hatcher et al., 1989; Rast, 1989; Faill, 1997a; Faill, 1997b; Faill, 1998; Ettensohn, 2008; Hatcher, 2010). To briefly summarize, the Appalachian orogen was formed from 3 diachronous orogenic events: (i) the Taconic orogeny, in the Middle Ordovician to Early Silurian (ca. 472 – 436 Ma; Ettensohn, 2008), during which the eastern margin of Laurentia collided with volcanic island arc terranes (Hatcher, 2010); (ii) the Acadian orogeny, in the Early Devonian–earliest Mississippian (ca. 410 – 360 Ma; Rast and Skehan, 1993), marking the transpressional accretion of terranes to the Laurentian proto-North American craton (Ettensohn, 2008); and (iii) the Alleghanian orogeny, Early Pennsylvanian–Permian (ca. 330-265 Ma; Hatcher, 2002), which closed the Iapetus ocean from north-to-south as Gondwana rotated and collided against the southeastern margin of Laurentia to form supercontinent Pangea.

Mesozoic Era: A massive rift zone developed within Pangea during the early Mesozoic time (ca. 237 Ma), separating North America from Gondwana, beginning with the north-central Atlantic basin and progressing southward (Withjack et al., 1998; Withjack and Schlische, 2005). Rifting occurred along the entire boundary of North America and Gondwana by the Late Triassic (Withjack et al., 2012). Crustal extension produced asymmetric rift basins, bounded to the west

by extensional faults (Figure 1; Faill, 1997). During continental rifting and before development of oceanic crust, the Central Atlantic Magmatic Province (CAMP), one of the largest igneous provinces on Earth, was emplaced ca. 200 ± 4 Ma (Marzoli et al., 1999; Hames et al., 2003; Nomade et al., 2007). Igneous intrusions (e.g. basaltic lava flows and diabase sheets) in the Mesozoic rift basins are associated with the CAMP (e.g. Hames et al., 2003; Withjack et al., 2012).

As the Atlantic basin continued to open in the Early Jurassic, the margin experienced vertical crustal rebound (e.g. Faill, 1997a). This resulted in tilting of the Mesozoic rift basins and of crustal blocks in New England (Faill, 1973; Withjack et al., 2012) as well as the formation of a prominent topographic ridge along the eastern edge of the Piedmont (e.g. Hack, 1982; Faill, 1997a). Onset of seafloor spreading and the cessation of rifting along the North American margin occurred first in southeastern North America (latest Triassic) and progressed to northeastern North America by Early Jurassic and into Newfoundland by the Early Cretaceous (Schettino and Turco, 2009; Withjack et al., 2012).

Post-rift exhumation eroded the Appalachian highlands and greatly modified the Appalachian landscape (e.g. Etensohn, 2008). Sediment was transported eastward to the newly formed Atlantic basin, extending the coastal plain, covering Mesozoic rift basins and filling offshore basins (e.g. Poag, 1992; Steckler et al., 1993). There are several generations of syn- and post-rift magmatic/thermal events recorded along the Appalachian orogen (de Boer et al., 1988). In the Early Cretaceous (ca. 120-100 Ma), the regions of northern New York (Adirondacks) and New England translated to the northwest over the Great Meteor hotspot (GMHS; Figure 1). Timing of this event and the trace of the hotspot trail NW to SE across northern North America is constrained through U-Pb dating on progressively younger kimberlitic intrusions (Heaman and

Kjarsgaard, 2000). In the Late Cretaceous, ca. 85 to 65 Ma, there was a change in the Atlantic stress regime from due to a temporary 45° shift in seafloor spreading direction from NW-SE to W-E (Klitgord and Schouten, 1986; Fairhead and Binks, 1991).

Cenozoic Era: The Early Cenozoic history is tectonically quiescent, exhibiting background erosion rates of 20-30 m/Myr (e.g. Boettcher and Milliken, 1994; Blackmer et al., 1994; Roden-Tice et al., 2009; McKeon et al., 2014; Amidon et al., 2016 Shorten and Fitzgerald, in review). The Late Cenozoic history, Oligocene to present, contains evidence to support the development of long-wavelength, low-amplitude dynamic topography due to mantle flow (e.g. Moucha et al., 2008; Miller et al., 2013; Gallen et al., 2013). Geomorphology studies in the central and southern Appalachian regions have documented Miocene (ca. 15 Ma) rock uplift and erosion of ~100-200 m (e.g. Miller et al., 2013; Gallen et al., 2013). There is also zircon fission-tracks (ZFT) and lithic detritus data to indicate that the drainage divide in the southern Appalachian migrated westward in the Oligocene and Miocene (Naeser et al., 2016). Offshore sediment flux records a 5x increase in sedimentation rates in the mid-Miocene, decreasing slightly at ca. 8 Ma (Pazzaglia and Brandon, 1996).

Database and Thermal History Interpretation Challenges

Thermal history trends were determined based on 24 published studies, Chapter 1 and Chapter 2 (Table 1 and Figure 2). Studies range across 23 catchments, drain to 4 different offshore oceanic basins, and are in 7 different physiographic provinces of the Appalachian orogen (Figure 1). The collection of data and the challenges of the thermal history trend analysis will be discussed in this section.

Database: There are 26 low-temperature thermochronology studies along the Appalachian orogen in eastern U.S. from which we collated AFT and AHe data, creating the

“Appalachian low-temperature thermochronology database” (AppLTDB; Appendix C). The AppLTDB consists of the following information for each datapoint: location, elevation, AFT age data and chi-squared values (when reported), AHe ages and single-grain age variation (when reported), tectonic provinces (Hack, 1989; Soeder et al., 2014), Mesozoic rift basins (Withjack et al., 2012), lithology (Horton, 2017), catchment area (Lehner et al., 2008) and drainage outlets. Location and thermochronology data were collated directly from published tables and/or georeferenced figures in ArcGIS. GoogleEarth was used to determine approximate elevation when it was not reported. Drainage outlets (i.e. which offshore basin/ocean does the catchment ultimately lead to) were determined from the following sources: Pazzaglia and Brandon (1996); the HydroSHEDS database (i.e. hydrological data and maps based on shuttle elevation derivatives at multiple scales; Lehner et al., 2008); and Hack (1989). Additional information on source material and the AppLTDB can be found in Appendix C.

Study focus and scale: Studies from different provinces, as well as when they were published which is important with respect to how evolved thermal modeling was at the time, focus their analysis on constraining different regional thermal or tectonic processes. For example, the determination of the development of relief in the Appalachian Mountains of New Hampshire during the Cretaceous (Roden-Tice et al., 2012) or the origin and evolution of the Blue Ridge escarpment in Virginia and North Carolina since the Mesozoic era (Spotila et al., 2004). There are also differences in the scale of the studies. The analysis includes smaller and/or more focused studies which constrained thermal histories and trends based on <10 samples (e.g. Doherty and Lyons, 1980) and/or age-elevation or age-depth profiles (e.g. Reed et al., 2005; Taylor and Fitzgerald, 2010; Amidon et al., 2016; Shorten and Fitzgerald, in prep. Chapter 2) as well as large regional studies which include up to ~100 samples (e.g. Miller and Duddy, 1989;

Roden-Tice and Tice, 2005; Shorten and Fitzgerald, in review). Smaller and/or more focused studies can provide precise, well constrained thermal histories and exhumation through time but are limited in geographical coverage (e.g. Taylor and Fitzgerald, 2010) while regional studies provide information on the generalized thermal history over a larger area but can result in imprecise thermal histories, which may combine smaller events so that only an average cooling histories are revealed (e.g. Roden-Tice et al., 2000; Roden-Tice and Tice, 2005).

“Rapid” Cooling: Within all the studies, differential cooling rates constrained by thermal modeling are all relatively slow (i.e. <12 °C/Myr) in comparison to other tectonic settings such as young, active collisional orogens (on the order of ~ 40 - 50 °C/Myr; e.g. Thiede et al., 2004). For this paper, slow cooling is defined as cooling at rates <1 °C/Myr (e.g. Amidon et al., 2016). Slow cooling and long residence in the partial annealing zone (PAZ; ~ 110 - 60 °C), referred to as “stabilization”, is due to low rates of erosion, isostatic flexure, and/or post-rift decay of the passive margin interior (e.g. Boettcher and Milliken, 1994). “Rapid” cooling is defined as cooling at rates >1 °C, usually relative to preceding or subsequent slow cooling rates constrained in thermal modeling (i.e. changing from 0.2 to 1 °C/Myr; Shorten and Fitzgerald, in review). Relatively rapid cooling may be due to several different mechanisms, such as: rock uplift caused by a combination of surface uplift and exhumation of strata; erosion due to lowering of base level bringing strata closer to surface; or geothermal gradient decreases causing strata to cool in place, also referred to as relaxation of isotherms (e.g. Malusà and Fitzgerald, 2018).

Most studies identify periods of rapid cooling through forward or inverse thermal modeling, however there are 30 AFT samples from 7 studies which record mean fission-track lengths (MTL) and distributions indicative of rapid cooling through the PAZ (Supplementary Table 2). Samples with MTL >14 μm and narrow standard distributions ($<\sim 1.5$ μm) did not

reside for a significant amount of time in the PAZ and thus retain longer fission-tracks with less variation (e.g. Gleadow and Brown, 2000; Hurford, 2018). These samples are used as reference points for rapid cooling events while constraining and analyzing thermal history trends (e.g. Gleadow et al., 1986; Green et al., 1989).

Data Interpretation: Studies range in publication date, from the early 1980's to today, and contain various methods of data interpretation (i.e. schematic data-driven thermal histories, forward and inverse modeling, age-elevation profiles to estimate exhumation timing and rates). Also, AHe dating which is now a commonly applied method was not applied until the 2000's. The 26 studies all include at least AFT and/or AHe data, while some also included other geochronometers or maximum paleotemperature indicators such as ZFT or vitrinite reflectance (Table 1). Given that AFT and AHe ages are a function of their thermal history and may or may not represent a real cooling event, thermal histories cannot necessarily be interpreted simply using the closure temperature principle (c.f. Gleadow and Brown, 2000; Malusà and Fitzgerald, 2018). There are 3 included studies which interpret thermal events via closure temperatures of AFT and ZFT ages (Lakatos and Miller, 1983; Roden and Miller, 1989; Steckler et al., 1993).

Collecting samples over significant relief (i.e. vertical profiles from steep terrane) or down boreholes and plotting age vs. elevation is a useful method for determining timing and rates of apparent exhumation, in which a break in slope may reveal the timing of transition from slow, tectonically stable cooling to rapid cooling and exhumation (e.g. Fitzgerald and Malusà, 2018). There are 2 studies which rely on age-elevation profiles and 7 more which combine age-elevation profile interpretations with inverse thermal modeling (Table 1).

Modeling Programs and their Influence on Interpretation: 17 studies constrained thermal histories with forward and/or inverse thermal modeling. The challenge with interpreting

model results is that due to the range in publication date, there are several different generations of annealing algorithms utilized in forward and inverse models (Table 1). First-generation models utilize mono-kinetic annealing algorithms (Laslett et al., 1987; Crowley et al., 1991) while second-generation models utilize multi-kinetic annealing algorithms (e.g. Ketcham et al., 1999; 2007). Mono-kinetic annealing models assume modeled apatite grains contain uniform apatite composition and identical annealing characteristics as the annealing algorithm experimental samples (i.e. Durango apatites used in Laslett et al. (1987) and Crowley et al. (1991)). Given this input assumption, first-generation models often produced spurious late-stage cooling (e.g. Ketcham et al., 1999). Thus, interpretations of Late Cenozoic cooling documented using first-generation models requires geologic constraints to confirm the cooling is real and not a model artifact (e.g. Ketcham et al., 1999; de Bruijne and Andriessen, 2002). More recently, second-generation multi-kinetic annealing models characterize individual apatite grains' variability to annealing within a sample and do not produce a spurious late-stage cooling artifact (e.g. Ketcham et al., 1999). In studies that utilize second-generation multi-kinetic modeling, Late Cenozoic rapid cooling, if present, is not a model artifact and thus can be determined to be a real event with more confidence than first-generation models.

The studies utilized the following modeling techniques (summarized in Table 1): 1 early study conducted forward modeling with time-temperature paths constrained based on geologic scenarios with model results then compared to measured data; 10 studies were conducted with first-generation mono-kinetic annealing modeling programs (i.e. AFTINV; Issler, 1996); 4 studies were conducted with second-generation multi-kinetic modeling programs (i.e. HeFTy; Ketcham, 2005); and 2 studies relied mostly on inverse modeling of AHe ages with the radiation damage accumulation and annealing model (RDAAM; Flowers et al., 2009). Amidon et al.

(2016) also employed HeFTy forward models (Ketcham, 2005), to test if AHe data best fit a linear, long-term cooling or an episodic cooling model.

Cooling History Interpretation: Most of the 26 studies indicate that samples cooled from temperatures greater than the retentivity of fission-tracks in apatite (i.e. $> \sim 110\text{-}120\text{ }^{\circ}\text{C}$). There are a few examples of western Appalachian Basin samples cooling from $< 120\text{ }^{\circ}\text{C}$ because of a shallower their burial depth prior to post-orogenic cooling (e.g. Blackmer et al., 1994; Shorten and Fitzgerald, in review). Five studies utilize ZFT, with a closure temperature $\sim 250\text{ }^{\circ}\text{C}$ for cooling rates of $1\text{-}15\text{ }^{\circ}\text{C}/\text{Myr}$ (Doherty and Lyons, 1980; Lakatos and Miller, 1983; Roden and Miller, 1991; Steckler et al., 1993; Roden-Tice and Wintsch, 2002). ZFT ages from those 5 studies suggest temperatures prior to the Middle Triassic were $> 250\text{ }^{\circ}\text{C}$ in the Taconic and Acadian province of New England and temperatures were $\sim 175\text{ }^{\circ}\text{C}$ from deposition (ca. 360 Ma) to 125 Ma in the Catskills of New York. We acknowledge that “onset” of cooling constrained in some studies, without the use of a higher temperature constraint, is not the onset of cooling and exhumation from maximum temperatures but rather documents when that sample cooled into the PAZ and began retaining fission-tracks ($\sim 110\text{ }^{\circ}\text{C}$ for AFT) (e.g. Steckler et al., 1993; West and Roden-Tice, 2003; Kunk et al., 2005; Shorten and Fitzgerald, in review).

Cooling rates documented in the various studies may also be an averaging of short-term, intermittent rapid and slow cooling events (e.g. McKeon et al., 2014). Averaging of differential rates, notably in modeled time-temperature paths, may be due to the resolution of the models or the brevity/magnitude of the rapid cooling episode(s). There are a few studies that model samples which constrain the onset of cooling in the Early Jurassic, followed by monotonic cooling (e.g. Roden-Tice and Wintsch, 2002; Roden-Tice and Tice, 2005). However, monotonic

cooling does not rule out episodic cooling as it may be due to averaging of more subtle peaks due to the sensitivity of the methods/models.

Onshore thermal histories related to Offshore Mid-Atlantic deposition

Pazzaglia and Brandon (1996) calculated sediment flux rates into Mid-Atlantic offshore basins (i.e. Salisbury Embayment, Baltimore Canyon Trough and Hatteras Basin; Figure 1), using estimates of siliciclastic sediment volumes from 23 stratigraphic time intervals (Poag, 1985; 1992; Poag and Sevon, 1989). Pazzaglia and Brandon (1996) determined 4 peaks in sediment flux, the volume delivered into the basins per million years (Figure 3). They suggested that the peaks are best explained by tectonic forcing causing episodic increase in onshore erosion. Thus, while they caution against the dogmatic use of their end-member tectonic model to explain increased sediment flux, they state that the model adds a quantitative prediction to the distribution, timing and magnitude of onshore erosional events in the Mesozoic and Cenozoic. Low-temperature thermochronology studies often correlate cooling and exhumation events recorded onshore to periods of increased offshore sediment flux (e.g. Reed et al., 2005; Miller et al., 2013; McKeon et al., 2014).

In similar fashion, while we acknowledge that there are variations in timing and duration seen within the studies, we use the timing of North American rifting and the four peaks in sedimentation flux to contextualize thermal history trends (Figure 3 and 4). Since Pazzaglia and Brandon's (1996) study constrained offshore sediment flux in Mid-Atlantic basins, this section only includes low-temperature thermochronology studies which currently drain into the Mid-Atlantic Ocean (Figure 3 and 4). Although there is evidence of westward shifting of drainage divides and catchment boundaries (e.g. Spotila et al., 2004; Naeser et al., 2016; Moodie et al., 2018), modern catchment basins were used as an (Figure 1B). 7 studies are located completely

outside of Mid-Atlantic drainage basin and drain into the North Atlantic (Miller and Lakatos, 1983; West and Roden-Tice, 2003; West et al., 2008; Roden-Tice et al., 2012; Amidon et al., 2016) or the South Atlantic and Gulf of Mexico (Boettcher and Milliken, 1994; Spotila et al., 2004).

Event 1. Middle Triassic to Early Jurassic (ca. 237-175 Ma)

The first event spans from the Middle Triassic to the Early Jurassic (ca. 237-175 Ma), representing cooling which is concurrent with rifting of North America from Gondwana (e.g. Withjack et al., 2012). Eleven studies located in catchments which drain to Mid-Atlantic basins identify rapid cooling beginning during event 1 (Figure 3B). These studies span across all the physiographic provinces except for the Adirondacks. Within the Adirondacks and parts of the Taconic and Acadian province, there are samples that were at temperatures greater than the PAZ during this time and thus do not record event 1 in their thermal histories (Figure 4.1).

The Taconic and Acadian province contains one study (Roden and Tice, 2005) which constrains the onset of cooling ca. 200-180 Ma, however most of the area is at temperatures greater than the PAZ. In the northern Appalachian Basin in New York and Pennsylvania, western samples from Devonian sedimentary strata were not completely reset and constrain onset of rapid cooling to ca. 187 Ma at rates of 1-3 °C/Myr (Shorten and Fitzgerald, in review). There are several northern Appalachian Basin samples with mean track lengths (MTL) >14 μm which also indicate rapid cooling between ca. 245-200 Ma (Figure 3B; Miller and Duddy, 1989). Further south in the Appalachian Basin and the Ridge and Valley province rapid cooling is constrained to begin ca. 250-245 Ma (according to one rapidly cooled sample) and continues until 180 Ma (e.g. Roden and Miller, 1989; Roden, 1991; Blackmer et al., 1994). Reed et al. (2005) also present a schematic thermal history based on VR and AFT data interpreted as closure

temperature ages in the southern Appalachian Basin which estimates slow cooling of $\sim 0.2\text{-}0.3$ °C/Myr between the late Permian to Early Cretaceous from ~ 145 °C to ~ 110 °C.

To the east, within Early Mesozoic rift basins, samples record onset of cooling from temperatures >175 °C between 225-200 Ma to temperatures near the base of the PAZ (~ 100 °C) by ca. 180 Ma (e.g. Roden and Miller, 1991; Steckler et al., 1999; Tseng et al., 1999). In North Carolina's Blue Ridge Mountains there is a suggestion of rapid cooling from the base of the zircon (U-Th)/He window ($\sim 160\text{-}200$ °C) at ca. 250-220 Ma (Triassic) to the upper part of the AHe partial retention zone (PRZ, $\sim 40\text{-}80$ °C) by ca. 170 Ma (McKeon et al., 2014). However, this event is only constrained in one (of two) presented thermal histories and their other model does not constrain the high-temperature cooling history prior to 120 Ma (McKeon et al., 2014).

In Summary, cooling begins in the region as early as the mid-Triassic, with most studies indicating temperatures within the PAZ by the Early Jurassic. In the rift basins along the U.S. east coast and in the Acadian and Taconic province, rapid cooling at this time is mainly attributed to crustal extension and an elevated geothermal gradient associated with rifting of North America (e.g. Roden and Miller, 1991; Steckler et al., 1999; Tseng et al., 1999). The thermal effect of lithospheric extension and hydrothermal fluid flow during the continental phase of rifting caused a higher geothermal gradient which reset AFT and ZFT ages (e.g. Roden and Miller, 1991; Tseng et al., 1999). Also during continental rifting, diabase sheets and dykes were intruded ca. 200 Ma (i.e. CAMP), which may have also contributed to resetting or partially-resetting ages (Marzoli et al., 1999; Olsen et al., 2003). To the west in the Appalachian Basin and Valley and Ridge provinces cooling during event 1 is attributed to far-field effects of rifting causing a regional lowering of base level and thus increasing erosion and exhumation (e.g. Blackmer et al., 1994; Shorten and Fitzgerald, in review). Overall, the timing of event 1 and the

proposed mechanisms relate to the geologic consequences of continental rifting of North America and formation of the North Atlantic Ocean.

Event 2. Middle Jurassic to Early Cretaceous (ca. 170-140 Ma)

The second event, during the Middle Jurassic to Early Cretaceous (170-130 Ma), correlates with the first peak of offshore sediment flux increase by ~2x followed by a ~3x decrease (Figure 3C). Rapid cooling at this time is identified in 13 studies during event 2, across all provinces except for the Blue Ridge Mountains (Figure 4.2). In the Taconic and Acadian province located in New England, cooling rates of ~0.5-1 °C/Myr are constrained in regional studies located along Paleozoic contractional faults in southern Maine, Massachusetts and Connecticut (e.g. Roden-Tice and Wintsh, 2002; West et al., 2008). Models of AFT data from south-central Maine indicate cooling to temperatures <120 °C did not occur until 140 Ma (West et al., 2008), which is also suggested by one sample from western CT with an AFT age of 143 Ma with MTL >14 μm (Roden-Tice and Wintsch, 2002).

Samples from the western side of the northern Appalachian Basin constrain rapid cooling beginning in event 1 and extending until ca. 145 Ma while eastern samples continue to cool until ca. 120 Ma. To the south, within the Ridge and Valley province of Pennsylvania, AFT and ZFT samples from the Alleghenian structural front indicate rapid cooling from ca. 150-105 Ma (Roden and Miller, 1989). Along the coastal piedmont and within the Newark and Taylorsville rift basins (New Jersey and Virginia), rapid cooling at rates between ~1-4 °C/Myr are documented to begin during event 1, and extend into event 2 (Steckler et al., 1993) or continue through event 3 (Tseng et al., 1999). There is evidence of rapid cooling during this time preserved in AFT ages from samples with MTL >14 μm as well (Figure 3, Supplementary Table

2). Along the coast of the eastern U.S., the Potomac terrane of the Piedmont province constrains rapid cooling at rates of 1-2 °C/Myr (Kunk et al., 2005).

In summary, no periods of modeled cooling are entirely contained in event 2 (Figure 3B). There are studies which show a continuation of rapid cooling which began in event 1 and other studies which document the onset of cooling during event 2 and extend into event 3. Pazzaglia and Brandon (1996) suggest the offshore sedimentation increase during event 2 was due to increased onshore erosion rates caused by surface uplift due to upwelling of hot mantle during rifting. Then, the subsequent decrease in sediment flux to lower rates is attributed to thermal relaxation and loss of thermal buoyancy (Pazzaglia and Brandon, 1996). In the Taconic and Acadian province, cooling is explained by either a change in the local stress field from extension to horizontal compression causing tilting of crustal blocks (Roden-Tice and Wintsch, 2002; Roden-Tice and Tice, 2005) or a discontinuous reactivation of major orogen-parallel faults (e.g. West et al., 2008). While variable cooling recorded in Appalachian Basin at this time is likely due to differential erosional exhumation caused by differential burial (e.g. Miller and Duddy, 1989; Roden and Miller, 1989). Rift basin and Piedmont cooling is suggested to be due to differential uplift in the Jurassic (Tseng et al., 1999) and thermal relaxation in the Late Jurassic to Early Cretaceous (Steckler et al., 1993; Tseng et al., 1999) or kilometer scale Early Cretaceous tilting of crustal blocks (Kunk et al., 2005). Cooling during event 2 cannot be attributed to a unique tectonic event occurring along eastern NA and instead is a continuation of cooling due to rifting, post-rift thermal relaxation and onset of seafloor spreading.

Event 3. Early Cretaceous (ca. 133-119 Ma)

Offshore, the third event is related to a small 1x increase in sediment flux during the Early Cretaceous (ca. 133-119 Ma; Figure 3C). This event is the smallest offshore sediment

pulse and onshore there is variation in the cooling rates (Figure 4.3). Rapid cooling is seen during event 3 in 4 studies in the Taconic and Acadian province, 1 study along the southeastern edge of the Adirondacks, 1 in the Ridge and Valley, and 2 in the Mesozoic Rifts and Piedmont. However, most studies document slow cooling ($< 1^{\circ}\text{C}/\text{Myr}$) and several studies contain both rapid and slowing cooling samples within their study area during event 3.

Within the Taconic and Acadian province, all studies constrain continuous rapid cooling since at least the Late Jurassic (Figure 3B). In the southeastern margin of the Adirondacks, at the boundary between the Adirondacks and the Taconic and Acadian province, Roden-Tice et al. (2000) suggest slightly faster cooling ($0.9\text{-}1.3^{\circ}\text{C}/\text{Myr}$) beginning in event 2 and continuing through event 3. However, overall rates in the Adirondacks during the Early Cretaceous are slow, $\leq 0.6^{\circ}\text{C}/\text{Myr}$ (e.g. Roden-Tice et al., 2000; Taylor and Fitzgerald, 2010).

In the northern Appalachian Basin, Miller and Duddy (1989) schematically determined that samples rapidly cooled to near surface temperatures between 140-120 Ma (red dots in Figure 4.3). They used closure temperature principles and AFT ages from samples with $\text{MTL} \geq 14 \mu\text{m}$, measured using binned track lengths, and my previous chapters further discuss this interpretation. Through using precise fission-track length measurements and second-generation inverse thermal modeling, Chapter 1 and 2 of this dissertation constrains cooling at rates of $\sim 1\text{-}2^{\circ}\text{C}/\text{Myr}$ began in the Early Jurassic (event 1) and continued into event 3. Samples from the eastern region of the Appalachian Basin and the Catskills record rapid cooling ($1\text{-}1.5^{\circ}\text{C}/\text{Myr}$) continuing from initial onset during event 1 until the end of event 3, ca. 120 Ma (Shorten and Fitzgerald, in review; Shorten and Fitzgerald, in prep. Chapter 2) while western samples constrain rapid cooling ending in event 3 and slow cooling ($< 0.5^{\circ}\text{C}$) during event 3.

In the Appalachian Basin and the Ridge and Valley there are 2 other studies which identify differential cooling during event 3 (e.g. Roden, 1991; Reed et al., 2005). In the Appalachian Basin and Ridge and Valley of West Virginia, Roden (1991) constrains onset of rapid cooling ($\sim 1\text{-}1.5$ °C/Myr) with northeastern samples while northwestern samples cooled earlier during events 1 and 2 (Figure 3B). In the same area, Reed et al. (2005) constrains rapid cooling (~ 1.5 °C/Myr) in Upper Pennsylvanian strata while Lower Pennsylvanian strata concurrently cool slowly (~ 0.8 °C/Myr). During event 3 in the Blue Ridge Mountains of Virginia and North Carolina, McKeon et al. (2014) constrains that valley bottoms cool at average rates of ~ 1 °C/Myr while summit ridges cool at ~ 0.5 °C/Myr (McKeon et al., 2014).

In summary, Event 3, in the Early Cretaceous, contains considerable variation in the documentation of rapid and slow cooling across the physiographic provinces. Event 3 is roughly coeval with when the GMHS was located to the northwest of Montreal, Canada (ca. 120 Ma) and with magmatic activity associated with GMHS in western New England and Quebec (e.g. Pazzaglia and Brandon, 1996; Heaman and Kjarsgaard, 2000). Pazzaglia and Brandon (1996) interpreted the short-term increase in sediment flux, followed by a decrease to lower rates, to support the idea that parts of northeastern U.S. were experiencing dynamically supported topography in the Early Cretaceous. This explanation accounts for the slow cooling and elevated geothermal gradient documented in the Adirondacks during event 3 (e.g. Taylor and Fitzgerald, 2010). While the Taconic and Acadian province document continuous cooling beginning in event 1 or 2 and continuing into event 3, which is most often attributed to continual cooling related to initial rifting and fault reactivation (e.g. Roden et al., 2009; 2012). To the south, in the Appalachian Basin, Ridge and Valley, and Blue Ridge Mountains, differential cooling is recorded and in previous chapters I have suggested that this difference is due to eastern samples,

buried to greater depths, experiencing greater post-orogenic exhumation (Shorten and Fitzgerald, in review; Shorten and Fitzgerald, in prep. Chapter 2). Other studies agree and relate differential cooling to landscape evolution and a more pronounced trend of stabilization in the Appalachian basin, concurrent with the development of the passive margin and possible drainage reorganization (e.g. Roden, 1991; Blackmer et al., 1994; Reed et al., 2005; McKeon et al., 2014).

Event 4. Late Cretaceous (ca. 100-65 Ma)

The fourth event occurs in the Late Cretaceous, constrained by a ~2x increase in offshore sediment flux (Figure 3C). Six studies in northeastern U.S. identify a rapid cooling event at this time (Figure 4.4). This event is the most province-specific event and is recorded onshore as two rapid cooling events, the first occurring between ca. 105-95 Ma in the Adirondacks and the second between ca. 85-65 Ma in the Taconic and Acadian province. The offshore sedimentary record records one pulse of sediment flux, which is the average of these two onshore events.

Large, regional studies in New England and the Adirondacks constrain Late Cretaceous (ca. 100-72 Ma) cooling at rates of ~0.7 -1.1 °C/Myr (Roden-Tice et al., 2009) and emphasize AFT age discontinuities and differential unroofing (e.g. Roden-Tice and Wintsch, 2002; Roden-Tice and Tice, 2005; Roden-Tice et al., 2009). An Adirondack regional study by Roden-Tice et al. (2000), identifies fault reactivation ca. 100 Ma and a period of rapid cooling ca. 110-80 Ma. Linked age-elevation profiles from Mt. Marcy in the High Peaks and Prospect Mountain provide the clearest constraints and resolve rapid cooling (~6 °C/Myr) ca. 105-95 Ma (Tayler and Fitzgerald, 2010).

Later during event 4, between 85-65 Ma there is documentation of rapid cooling at rates of 9-12 °C/Myr constrained in inverse thermal models and an age-elevation profile from the White Mountains of NH and coastal Maine (Amidon et al., 2016). AFT age discontinuities

across the Norumbega fault zone in Maine also constrain Late Cretaceous (ca. 80 Ma) rapid cooling (West and Roden-Tice, 2003). Throughout the Taconic and Acadian province, studies identify rapid cooling and fault reactivation during the Late Cretaceous (e.g. Roden et al., 2000; West and Roden-Tice, 2003; Roden et al., 2009).

In summary, studies in the Adirondacks constrain fault reactivation and movement ca. 105-95 Ma (Roden-Tice et al., 2000), which is contemporaneous with the transit of the GMHS from onshore to offshore (Figure 1 and 3B). It is suggested that this rapid cooling is due to the interplay of thermal doming causing surface uplift followed by thermal relaxation as the North American craton translated to the northwest over the hotspot until, the GMHS was located offshore ca. 100 Ma (Figure 1; Taylor and Fitzgerald, 2010). There is also regional evidence of the effects of the GMHS passage causing fault reactivation ca. 100 Ma along the eastern and southern edge of the Adirondacks (Roden-Tice et al., 2000).

Studies in the Taconic and Acadian province constrain rapid cooling and fault reactivation at the end of event 4, ca. 85-65 Ma (West and Roden-Tice, 2003; Roden-Tice et al., 2009; Amidon et al., 2016). Between ca. 85-65 Ma there was a 45° shift in Atlantic mid-oceanic ridge spreading direction from southeast-northwest to east-west (Klitgord and Schouten, 1986; Fairhead and Binks, 1991), which has been suggested as a far-field trigger for reactivation of faults and associated cooling at this time. This shift is suggested to have caused a change in the stress regime which reactivated the faults, which is a common mechanism to explain cooling documented during this event (e.g. Roden-Tice et al., 2000; Roden-Tice and Wintsch, 2002; Roden-Tice and Tice, 2005; Amidon et al., 2016). Age discontinuities across and rapid cooling documented in the Acadian and Taconic province may also be related to the effects of the

GMHS, as the thermal anomaly in the mantle may have caused NW-SE extension reactivating pre-existing orogen parallel faults (Roden-Tice et al., 2009).

As highlighted in Figure 4.4, there are a few studies in the Southern Appalachian Basin, Blue Ridge Mountains and Rift Basins which constrain differential or continuous cooling rates during event 4 (Tseng et al., 1999; Reed et al., 2005; McKeon et al., 2014). However, the cause of these events related to a continuation of mechanisms that began in events 2-3. It is likely that cooling constrained in these studies is due to localized differential erosion and valley incision (e.g. McKeon et al., 2014; Moodie et al., 2018).

Event 5. Miocene to present (ca. 25-0 Ma)

The fifth event, spanning 25 Ma to present, marks the largest increase in offshore sediment flux (~5x; Figure 3C and 4.5), but is also the most poorly understood and most debated. There are four studies, including our work in the Northern Appalachian Basin, which have modeled Miocene cooling and concluded it is a real, significant cooling event (Blackmer et al., 1994; Boettcher and Milliken, 1994; Shorten and Fitzgerald, in review; Shorten and Fitzgerald, in prep. Chapter 2). Four studies in the Adirondacks and Taconic and Acadian provinces model rapid cooling in the Cenozoic, but state that more work is required to validate this event (e.g. Roden-Tice and Wintsch, 2002; West et al., 2008; Taylor and Fitzgerald, 2010; Roden-Tice et al., 2012). However, three of the listed studies which contain a Miocene cooling event lie outside of Mid. Atlantic drainage and thus are unlikely to contribute to the large increase in offshore sediment flux (Boettcher and Milliken, 1994; West et al., 2008; Roden-Tice et al., 2012). The challenge in revealing this event is that identification of Late Cenozoic cooling relies on thermal modeling, since the exhumation was not great enough to bring Miocene aged samples to surface (e.g. McKeon et al., 2014).

Using second-generation multi-kinetic annealing algorithms (Ketcham et al., 2007) and inverse thermal modeling (Ketcham, 2005), we have constrained Miocene rapid cooling at rates of 1-3 °C/Myr in the western/central Northern Appalachian Basin and in the Catskills (Shorten and Fitzgerald, in review; Shorten and Fitzgerald, in prep. Chapter 2). The two other studies which have modeled and accepted Miocene cooling as a real event are also within the Appalachian Basin and Ridge and Valley (e.g. Boettcher and Milliken, 1994; Blackmer et al., 1994). They constrain cooling rates of 1-2.75 °C/Myr beginning in the Late Oligocene to Early Miocene (ca. 25-20 Ma), using forward models (Blackmer et al., 1994) and first-generation inverse modeling (Boettcher and Milliken, 1994).

In Summary, there must have been no more than 2 km of Miocene exhumation within any one location, or else there would be Miocene AHe ages and possibly AFT ages (e.g. McKeon et al., 2014). A recent paper (Moodie et al., 2018) proposed that exogenic forces, such as flexural isostatic crustal response (Blackmer et al., 1994) and the development of dynamic topography (e.g. Pazzaglia and Brandon, 1996; Moucha et al., 2008), caused the westward migration of the eastern U.S. drainage divide. Thus, it is possible that cooling/exhumation is localized to the Appalachian Basin and Ridge and Valley provinces due to the westward shift of the continental divide in the Oligocene-Miocene which caused eastward flowing rivers to access the easily erodible strata of these areas (e.g. Naeser et al., 2016; Moodie et al., 2018). The mechanism controlling this cooling/exhumation remains enigmatic and, given the magnitude of cooling, there are most likely a combination of mechanisms driving cooling and causing landscape rejuvenation (c.f. Shorten and Fitzgerald, in prep. Chapter 2).

Province Thermal History Trends

To further analyze thermal history trends and expand the study to incorporate all available low-temperature thermochronology data in the eastern U.S., this section synthesizes major thermal history trends documented within individual physiographic provinces. There are challenges in comparing thermal models from different studies, as even models created from the same area may vary on details due to including different data, methods of data entry, model constraints, modeling program, and generation of annealing algorithm (Ketcham et al., 2018). However, despite the variation of details, models from the same area agree on major features and reveal key thermal history trends within provinces related to geologically relevant events. Synthesized thermal histories discussed in this section (Figure 5) include the full range of potential time-temperature paths presented in published modeled thermal histories for each province as well as a best-fit thermal history constrained by the major trends.

Taconic and Acadian

In the Taconic and Acadian province, regional studies constrain cooling at rates of $\sim 0.6\text{-}2$ °C/Myr, on average ~ 1 °C/Myr, beginning ca. 200 Ma and continuing until ca. 100 Ma (Figure 5A). There is documentation of differential cooling related to structural depth/elevation, resulting in the range of cooling contained in figure 5A (e.g. Roden-Tice and Tice, 2005; Roden-Tice et al., 2009; Roden-Tice et al., 2012; West et al., 2008). For example, along an age-elevation profile of Mt. Washington in New Hampshire, high elevation samples document cooling at ~ 1 °C/Myr during the Late Jurassic (160-140 Ma) while low elevation samples document cooling at ~ 2 °C/Myr during the Early Cretaceous (ca. 110-90 Ma; Roden-Tice et al., 2012).

While some regional studies constrain slow cooling in the Late Cretaceous, there is evidence in the White Mountains in New Hampshire of rapid cooling ($9\text{-}12$ °C/Myr) occurring

between ca. 85-65 Ma (e.g. Amidon et al., 2016). Several other studies in the Taconic and Acadian province also document Late Cretaceous cooling related to compressive fault reactivation causing as much as ~2 km of west-side-up vertical movement (e.g. Roden et al., 2000; West and Roden-Tice, 2003; Roden et al., 2009). As discussed in event 4, this cooling event may be related to a change in the stress regime due to a 20 Myr shift in seafloor spreading direction to more east-west direction (Klitgord and Schouten, 1986; Fairhead and Binks, 1991).

Since ca. 65 Ma, cooling histories across the Taconic and Acadian province converge with slow cooling to present day conditions (Figure 5). There is Miocene cooling event recorded in first-generation models, but most studies indicated that this event is an artifact of the annealing algorithm and/or that more research is needed to determine if it is a real event (e.g. Roden-Tice and Wintsch, 2002; West et al., 2008; Roden-Tice et al., 2012) The prevailing explanation for the Cenozoic cooling history of the region is that by the end of the Cretaceous the relief was established across New England and steady-state topography has persisted through the Cenozoic to the present (e.g. Roden-Tice et al., 2012).

Adirondacks

In the Adirondacks, the thermal history is the most different from the surrounding provinces and begins with slow cooling (≤ 0.5 °C/Myr) from the Middle Jurassic to Early Cretaceous (Figure 5B; Miller and Lakatos, 1983; Roden-Tice et al., 2000; Taylor and Fitzgerald, 2010). The slow cooling documented throughout the High Peaks suggests the Adirondacks were experiencing a relatively stable thermal and tectonic regime with samples resident at temperatures at or above the PAZ for long periods during the Middle Jurassic through Early Cretaceous (ca. 175-110 Ma; Roden-Tice et al., 2000; Taylor and Fitzgerald, 2010). Within the end of the Early Cretaceous (ca. 120-100 Ma), northeastern U.S. passed over the GMHS

(Figure 1) and, due to the proximity to the Adirondacks, there was an elevated geothermal gradient estimated at $\sim 60\text{-}38$ °C/Km (e.g. Taylor and Fitzgerald, 2010).

In the Late Cretaceous, ca. 105-95 Ma, the Adirondacks clearly resolves rapid cooling (~ 6 °C/Myr; Figure 5B). As previously discussed in event 4, it is suggested that rapid cooling is due to the interplay of thermal doming causing surface uplift followed by thermal relaxation as the North American craton translated to the northwest over the hotspot until, the GMHS was located offshore ca. 100 Ma (Figure 1; Taylor and Fitzgerald, 2010). There is also regional evidence of the effects of the GMHS passage causing fault reactivation ca. 100 Ma along the eastern and southern edge of the Adirondacks (Roden-Tice et al., 2000; Figure 5). Since the late Cretaceous rapid cooling event, the Adirondacks have slowly cooled to present day conditions (e.g. Roden-Tice et al., 2000; Taylor and Fitzgerald, 2010). There is some indication for an increase in cooling rates during the Miocene to present however resolution of this event is questioned and needs closer examination (e.g. Taylor and Fitzgerald, 2010).

Appalachian Basin/ Ridge and Valley

In the Appalachian Basin and Valley and Ridge province, rapid cooling ($\sim 1\text{-}2$ °C/Myr) from temperatures above the PAZ began in the Early Jurassic and continued until the mid-Early Cretaceous (Figure 5C; e.g. Boettcher and Milliken, 1994; Shorten and Fitzgerald, in review). There is a general trend of AFT ages decreasing from west to east (e.g. Roden, 1991; Blackmer et al., 1994; Shorten and Fitzgerald, in review) and a range of AFT ages with MTL >14 μm , ranging from 246-114 Ma (Supplementary Table 2), measured using binned track lengths by Miller and Duddy (1989). Younger ages in the east are due to greater burial, resulting in samples passing through the PAZ at later times and cooling faster (~ 2 °C/Myr) than western samples (~ 1 °C/Myr). Cooling and exhumation in the Appalachian Basin and Ridge and Valley

are suggested to be due to lowering of regional base levels as the Atlantic Ocean opened causing higher rates of incision and erosion of the landscape, as well as a flexural feedback response as material is removed (e.g. Roden, 1991; Blackmer et al., 1994; Shorten and Fitzgerald, in review).

Beginning in the Early Cretaceous and extending until the Oligocene to Miocene, there is no record of rapidly cooled AFT ages and most thermal histories constrain slow cooling ($\sim 0.2\text{-}0.6$ °C/Myr; e.g. Roden, 1991; Reed et al., 2005; Shorten and Fitzgerald, in review). This period marks a stabilization of terrain in the Appalachian Basin and Ridge and Valley province (e.g. Blackmer et al., 1994; Shorten and Fitzgerald, in review). Most of the orogenic overburden was removed during rifting and post-rift erosional exhumation, and the stabilization is likely a result of no additional overburden to be removed and the transition of the eastern U.S. to a passive margin.

Inverse thermal modeling of the Appalachian Basin and Ridge and Valley strata reveals rapid cooling from ca. 25 Ma to recent (e.g. Blackmer et al., 1994; Boettcher and Milliken, 1994; Shorten and Fitzgerald, in review). Miocene offshore sediment flux estimates require an average of >1.1 km of rock to be removed across the region that drains into the Middle Atlantic Basin (Figure 1 and 3C), but it does not indicate that erosion was uniform across the catchments (e.g. Braun, 1989; McKeon et al., 2014). Two recent studies in the central and southern Ridge and Valley and Blue Ridge Mountain provinces suggested a westward migration of the drainage divide in the Oligocene and Miocene, which gave catchments access to more easily erodible Valley and Ridge and Appalachian Basin detritus (Naeser et al., 2016; Moodie et al., 2018). Offshore sedimentation flux, geomorphologic studies and mantle flow simulations indicate that rapid cooling documented in event 5 may be due to the development of dynamic topography causing landscape rejuvenation (e.g. Pazzaglia and Brandon, 1996; Moucha et al., 2008; Miller et

al., 2013; Gallen et al., 2013). Although this event results in the largest increase in offshore sediment flux, the resolution of an onshore signature and determining the mechanisms are the most enigmatic of all the events.

Blue Ridge Mountains

The Triassic to Jurassic thermal history of the Blue Ridge Mountains is not well constrained, since the low-temperature thermochronology studies conducted in the region primarily utilized AHe dating (e.g. Spotila et al., 2004; McKeon et al., 2014). ZFT ages (Naeser et al., 2016) and available inverse models based on AHe data (McKeon et al., 2014) indicates that the area cooled between ca. 250-170 Ma at rates of ~1-1.5 °C/Myr from temperatures >150 °C to within temperatures of the AHe PRZ (~30-90 °C; Figure 5D). In the Cretaceous, from ca. 120-80 Ma, McKeon et al. (2014) constrain differential cooling in the Blue Ridge Mountains, with samples from the valley bottoms cooling approximately twice as rapidly as nearby ridge tops. This differential cooling is suggested to be due to short, episodic periods of valley incision and drainage reorganization (McKeon et al., 2014). Since ca. 80 Ma, the Blue Ridge Mountains may have slowly cooled to present day (Figure 5). However, there is ZFT data (e.g. Naeser et al., 2016) and drainage divide discrepancies with topography (e.g. Moodie et al., 2018) which indicate that that drainage divide moved westward past the Blue Ridge Mountains into the Appalachian Basin in the Oligocene-Miocene. This migration may have caused an Oligocene-Miocene cooling event in the Blue Ridge Mountains, but if there was a cooling event it must account for ≤ 2 km of sediment removal via exhumation since there are no Miocene AHe ages (e.g. Spotila et al., 2004; McKeon et al., 2014).

Mesozoic Rift Basins

Mesozoic rift basins (i.e. Hartford, Deerfield, Newark and Taylorsville basins) along the east coast of the U.S. record cooling at rates of $\sim 1\text{-}2$ °C/Myr from the Late Triassic through the Late Jurassic (e.g. Roden and Miller, 1991; Steckler et al., 1999; Tseng et al., 1999). There is a range of AFT ages which indicate rapid cooling (196-136 Ma; Figure 5E and Supplementary Table 2), which may extend initial cooling into the earliest Early Cretaceous. There are also differences in the onset of cooling recorded across basins (e.g. Roden and Miller, 1991; Tseng et al., 1999). For example, samples in the eastern part of the Taylorsville basin (Virginia) began to cool ca. 30 Myr earlier than western samples (Tseng et al., 1999). This difference in timing may be related to the westward tilt of the rift basins (e.g. Withjack et al., 2012) and/or hydrothermal fluid flow along the western boarder fault during rifting (e.g. Steckler et al., 1999). Overall, rates indicate rapid cooling from the Late Triassic to Late Jurassic, which is likely due to rifting, compression of isotherms, and the subsequent post-rift the relaxation of the isotherms (e.g. Roden and Miller, 1991; Steckler et al., 1999; Tseng et al., 1999). Coastal-plain sediments were deposited over top of the rift basins in the Early Cretaceous, marking the end of rapid cooling related to exhumation (Steckler et al., 1999; Figure 5E). Since the Early Cretaceous, the Mesozoic rift basins cooled slowly to present day conditions and the coastal-plain sediments were removed by slow but steady erosion associated with Late Cretaceous sea-level fall and glaciation (e.g. Steckler et al., 1999).

Piedmont

The low-temperature thermal history of the piedmont, outside of the Mesozoic rift basins, is discussed only in Kunk et al. (2005) and contains similar temporal trends as the Mesozoic rift basins with differences in cooling rate. The coastal piedmont rapid cools at rates of $3\text{-}4$ °C/Myr,

cooling to temperatures within the PAZ beginning in the Early Jurassic with rapid cooling continuing into the earliest Early Cretaceous (Figure 5F). There are two rapidly cooled AFT ages, 131 Ma in the western region of their study and 179 Ma in the east (Kunk et al., 2005; Supplementary Table 2). Kunk et al. (2005) note that AFT ages become older from west to east, spanning ca. 70 Myr, and attribute this pattern to differential amounts of cooling in the Cretaceous due to westward tilting of the Potomac terrane in the piedmont. Basin tilting and older ages in the east compared to the west was also noted in Mesozoic rift basins (Tseng et al., 1999). Tilting is related to the rifting and onset of seafloor spreading and rapid cooling ceases at ca. 150 Ma in the Piedmont. Since initial rapid cooling, the area has likely slowly cooled to present day at rates $\sim 0.1\text{-}0.5$ °C/Myr (Figure 5E).

Conclusions

This study presents a comprehensive synthesis of low-temperature data from 26 studies scattered across the Appalachian orogen of the eastern U.S. to constrain the cooling and exhumation history at a variety of scales (i.e. across catchments which drain into the Mid-Atlantic, within physiographic provinces, and across the orogen as a whole). The cooling and exhumation history of onshore regions that drain into Mid-Atlantic basins correlates well with rifting of the eastern U.S. and periods of increased sediment flux into offshore Mid-Atlantic basins. Province thermal histories, composed through synthesizing the available low-temperature thermochronology data and thermal models, identify major orogen-scale trends and localized, province-specific trends (figure 5).

1. Across the orogen, except for the Adirondacks, relatively rapid cooling is constrained from temperatures above the PAZ beginning in the Late Triassic to Early Jurassic (ca. 237-175 Ma). This orogen-wide, rapid cooling and exhumation event is contemporaneous with

rifting of the eastern U.S. and the formation of the Atlantic Ocean (i.e. event 1, rifting). Within the Appalachian Basin and Ridge and Valley province, western samples cool to temperatures within the PAZ earlier than eastern samples. This is due to differential burial and hence differential exhumation during the initial unroofing phase (e.g. Roden, 1991; Blackmer et al., 1994; Shorten and Fitzgerald, in review). Often, due to differential burial, AFT-constrained cooling will not be recorded until the Middle Jurassic to Early Cretaceous (ca. 170-140 Ma). The Middle Jurassic to Early Cretaceous also includes the first pulse in offshore sediment flux calculated by Pazzaglia and Brandon (1996), referred to in the chapter as event 2 (Figure 3). There is also variation in the timing of cooling closer to the coast as recorded in Mesozoic rift basins and Piedmont, likely a result of westward block rotation during rifting and extension (e.g. Steckler et al., 1993; Kunk et al., 2005). While the variable rapid cooling and exhumation history suggests different mechanisms are operating at a smaller scale or within a localized region, these mechanisms are likely all related to rifting and erosional exhumation occurring at the orogen-scale through the eastern U.S. during the Late Triassic to Cretaceous.

2. Within the Cretaceous, there is greater variation between province cooling histories. In the Early Cretaceous (ca. 133-119 Ma; i.e. event 3), it appears that the eastern U.S. experienced a period of tectonic quiescence and slow cooling with the continued evolution of the passive margin. In comparison, in the Late Cretaceous (ca. 100-65 Ma; i.e. event 4), there are two province-specific onshore events which resulted in an increase of sediment in the offshore Mid-Atlantic basins. In the Adirondacks there is rapid cooling ca. 105-95 Ma. This has been related to the passage of the GMHS (e.g. Taylor and Fitzgerald, 2010). In the Taconic and Acadian province there is rapid cooling along normal faults ca. 85-65 Ma, which has been

related to compressional reactivation of faults during a ~20 Myr shift in the direction of seafloor spreading along the Mid-Atlantic ridge (e.g. Amidon et al., 2016). During the Cretaceous, the Appalachian Basin, Ridge and Valley and Blue Ridge Mountains also record differential cooling, albeit at slower than initial rates, likely due to continuing erosional exhumation (e.g. Roden, 1991; Blackmer et al., 1994; Reed et al., 2005) and/or episodic periods of valley incision and drainage reorganization (e.g. McKeon et al., 2014). In general, the eastern U.S. continues to cool through the Cretaceous with variations related to differential mechanisms influencing different regions.

3. The Cenozoic history for the eastern U.S. on the orogen-scale consists mainly of slow cooling to present day. However, from the Miocene to present (ca. 25-0 Ma), studies in the Appalachian Basin and Valley and Ridge province constrain relatively rapid cooling (e.g. Blackmer et al., 1994; Boettcher and Milliken, 1994; Shorten and Fitzgerald, in review; Shorten and Fitzgerald, in press). The ability to distinguish this period of cooling in low-temperature thermochronology data is often beyond the sensitivity of the method (e.g. Spotila et al., 2004; McKeon et al., 2014; Shorten and Fitzgerald, in review). However, with the use of AFT's kinetic parameter, several studies have concluded that Miocene cooling is real and significant (e.g. Blackmer et al., 1994; Boettcher and Milliken, 1994; Shorten and Fitzgerald, in review; Shorten and Fitzgerald, in press). So far, Miocene cooling and exhumation appears to be localized within catchments that drain into the Mid-Atlantic basins and relates to the largest offshore sediment pulse (event 5). It is likely that Miocene cooling is due to drainage reorganization and the westward migration of the continental drainage divide during the Oligocene-Miocene, allowing for increase erosional exhumation of Appalachian and Ridge and Valley provinces (e.g. Naeser et al., 2016; Moodie et al., 2018).

Figures and Tables

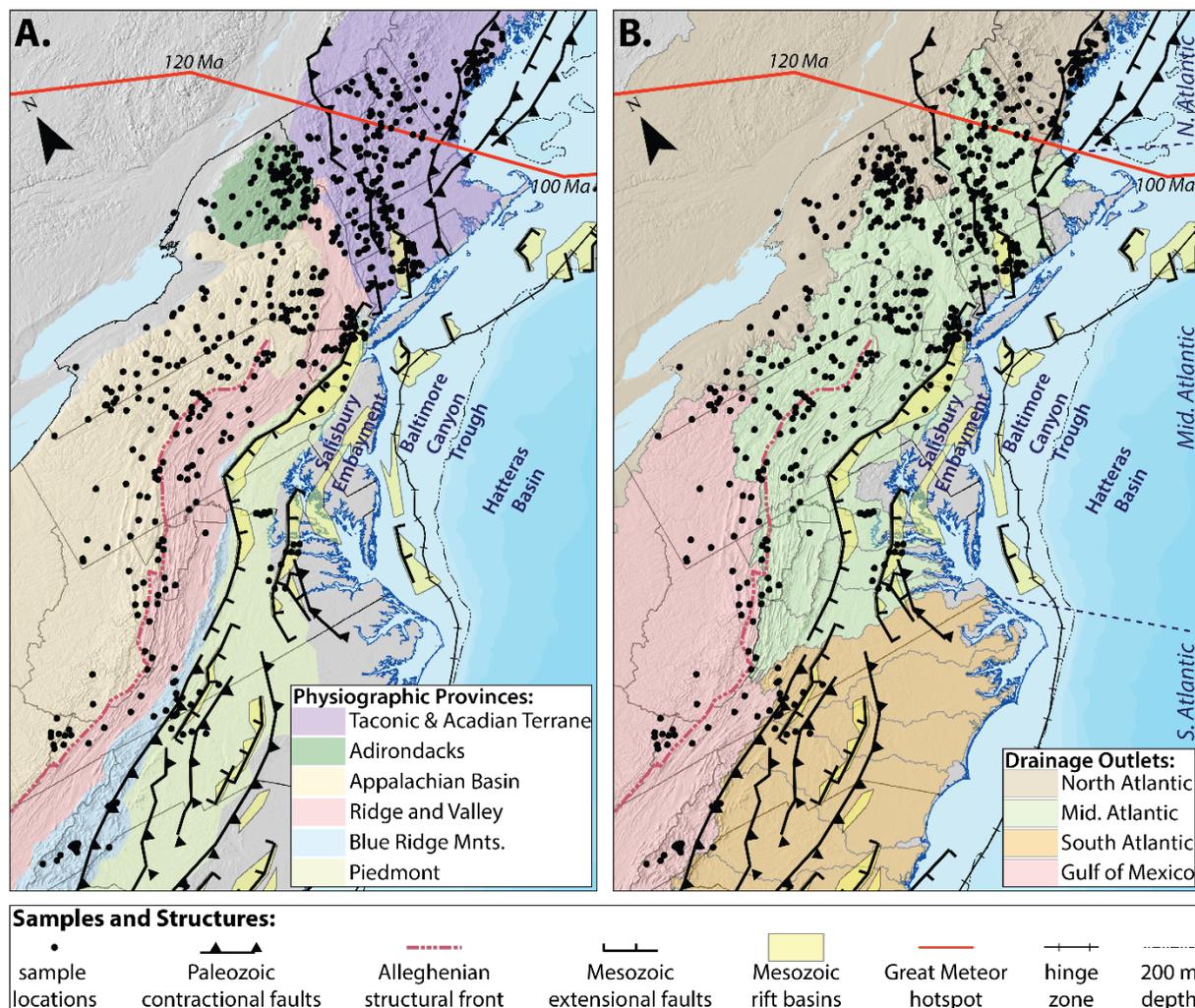


Figure 1. Map of eastern U.S. illustrating the sample locations from the 26 low-temperature thermochronology studies, structural features and rift basins (Withjack et al., 2012), path of the Great Meteor Hotspot (Heaman and Kjarsgaard, 2000), continental hinge zone, bathymetry (200 m depth and 1000 m shading), and the Middle (Mid.) Atlantic offshore basins (i.e. Salisbury embayment, Baltimore Canyon trough, Hatteras basin; Pazzaglia and Brandon, 1996) as well as the northern (N.) and southern (S.) Atlantic offshore basins. (A) General physiographic provinces (Hack, 1989; Soeder et al., 2014) and (B) catchments (Lehner et al., 2008) and drainage outlets (Hack, 1989; Pazzaglia and Brandon, 1996). Maps rotated 30° counterclockwise.

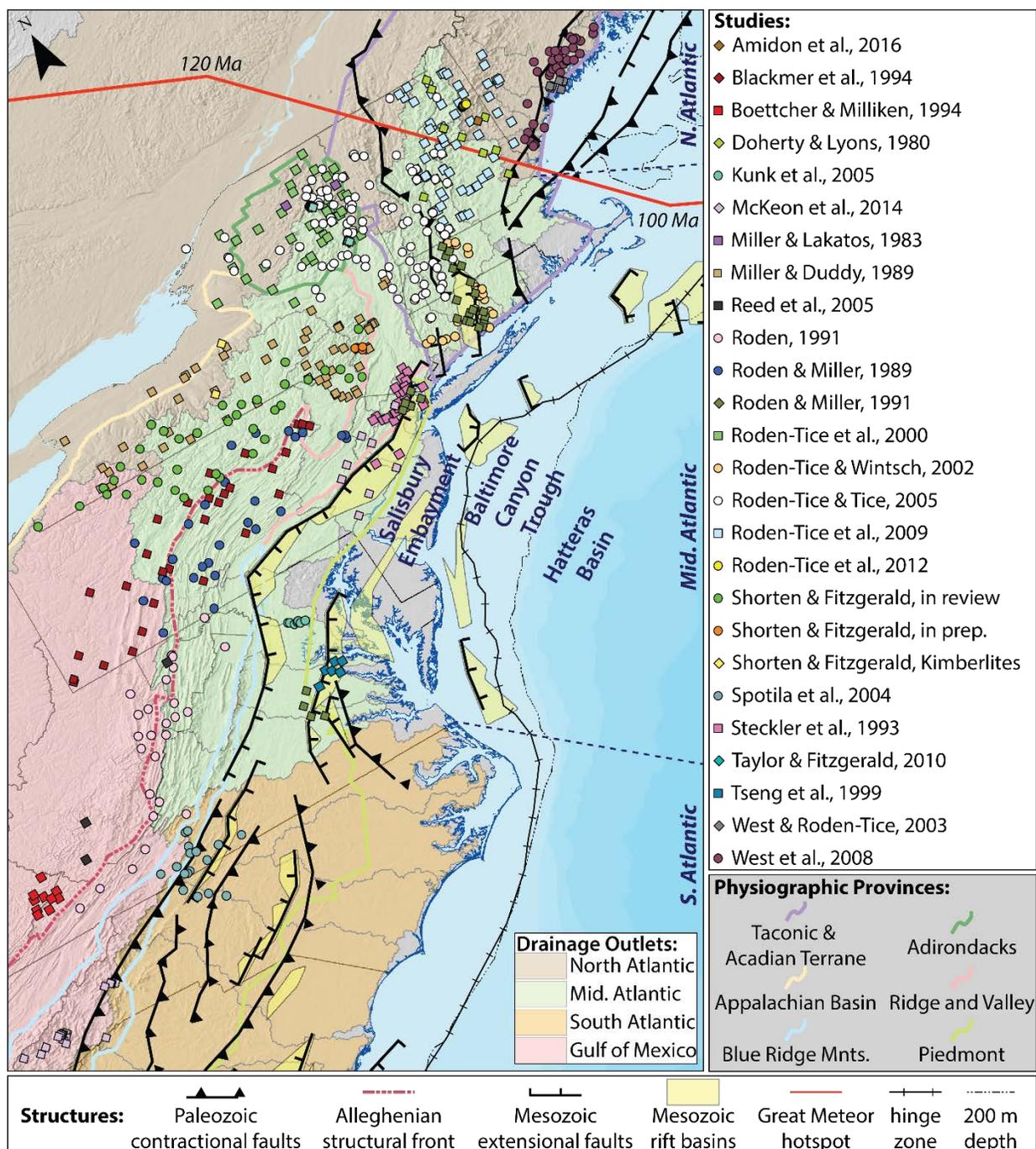


Figure 2. Map of eastern U.S. with sample locations from the 26 low-temperature thermochronology studies by color and symbol. Also included are the outline of the physiographic provinces (same colors as Figure 1), structural features and rift basins (Withjack et al., 2012), path of the Great Meteor Hotspot (Heaman and Kjarsgaard, 2000), continental hinge zone, bathymetry (200 m depth and 1000 m shading), and the Middle (Mid.) Atlantic offshore basins (i.e. Salisbury embayment, Baltimore Canyon trough, Hatteras basin; Pazzaglia and Brandon, 1996). Map rotated 30° counterclockwise.

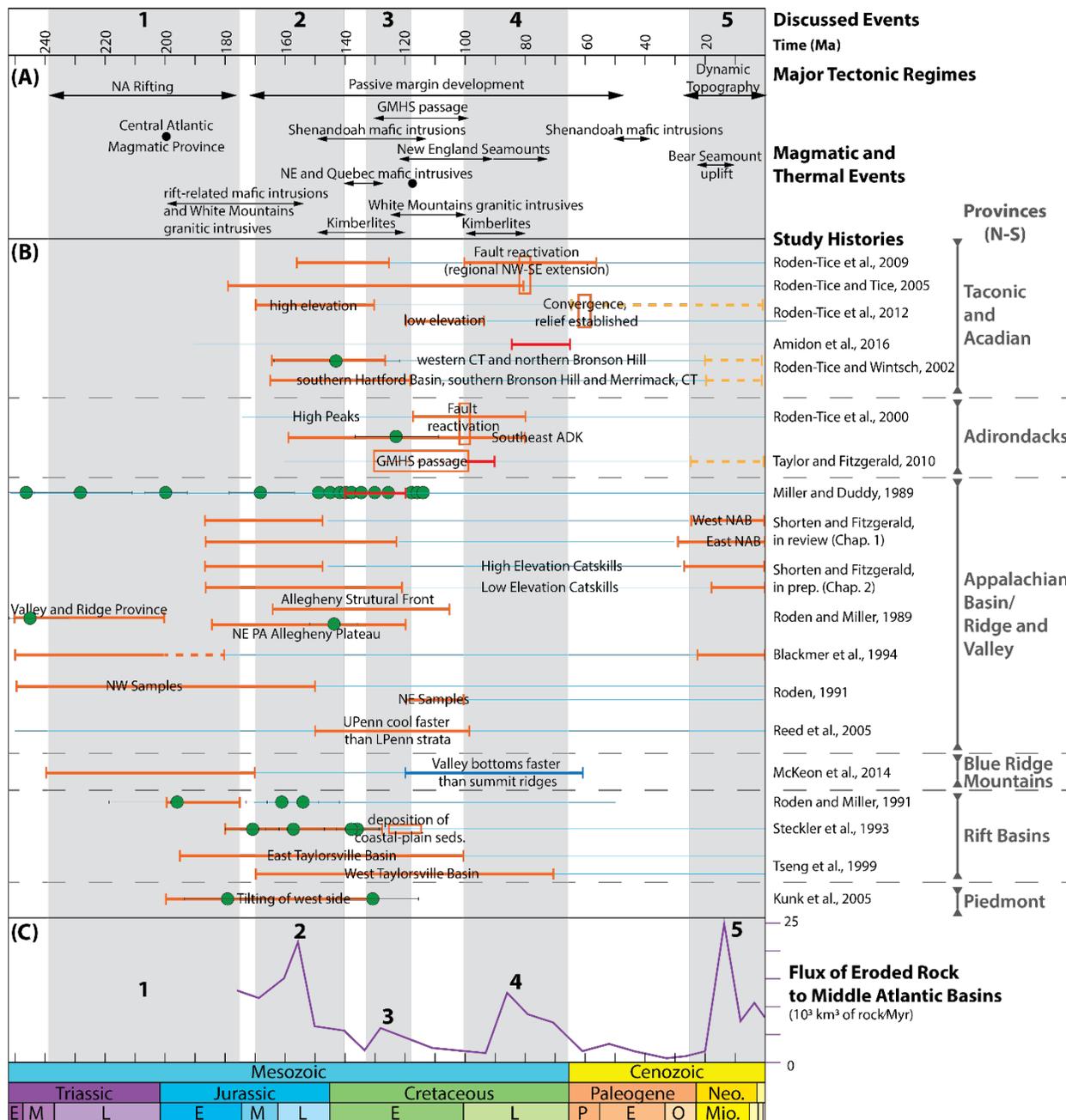


Figure 3. Comparison of modeled thermal histories (within catchments which drain into Mid. Atlantic) to geological events and offshore Mid. Atlantic sedimentation flux, highlighting the 5 periods of cooling discussed in text (grey shading). (A) Major tectonic regimes (Withjack et al., 1998; Moucha et al., 2008) and the syn- and post-rift magmatic intrusions of the eastern U.S. (de Boer et al., 1988; Pazzaglia and Brandon, 1996; Marzoli et al., 1999; Olsen et al., 2003). (B) Timing and duration of thermal events identified within low-temperature thermochronology studies which drain into the Mid. Atlantic, arranged from north to south and grouped by physiographic province. Colors and thickness differentiate periods and timing of very rapid cooling ($>5 \text{ }^\circ\text{C/Myr}$, red), rapid cooling ($\geq 1 \text{ }^\circ\text{C/Myr}$, orange), and slow cooling ($<1 \text{ }^\circ\text{C/Myr}$, blue). Green circles ($\pm 1\sigma$) are AFT ages with MTL $>14 \text{ }\mu\text{m}$ which indicate rapid cooling.

Figure 3. (continued) (C) Volume of solid-rock delivered into the Mid. Atlantic Basins (i.e. Salisbury Embayment, Baltimore Canyon Trough, and Hatteras Basin) per million years by mechanical erosion (i.e. sediment flux; Pazzaglia and Brandon, 1996).

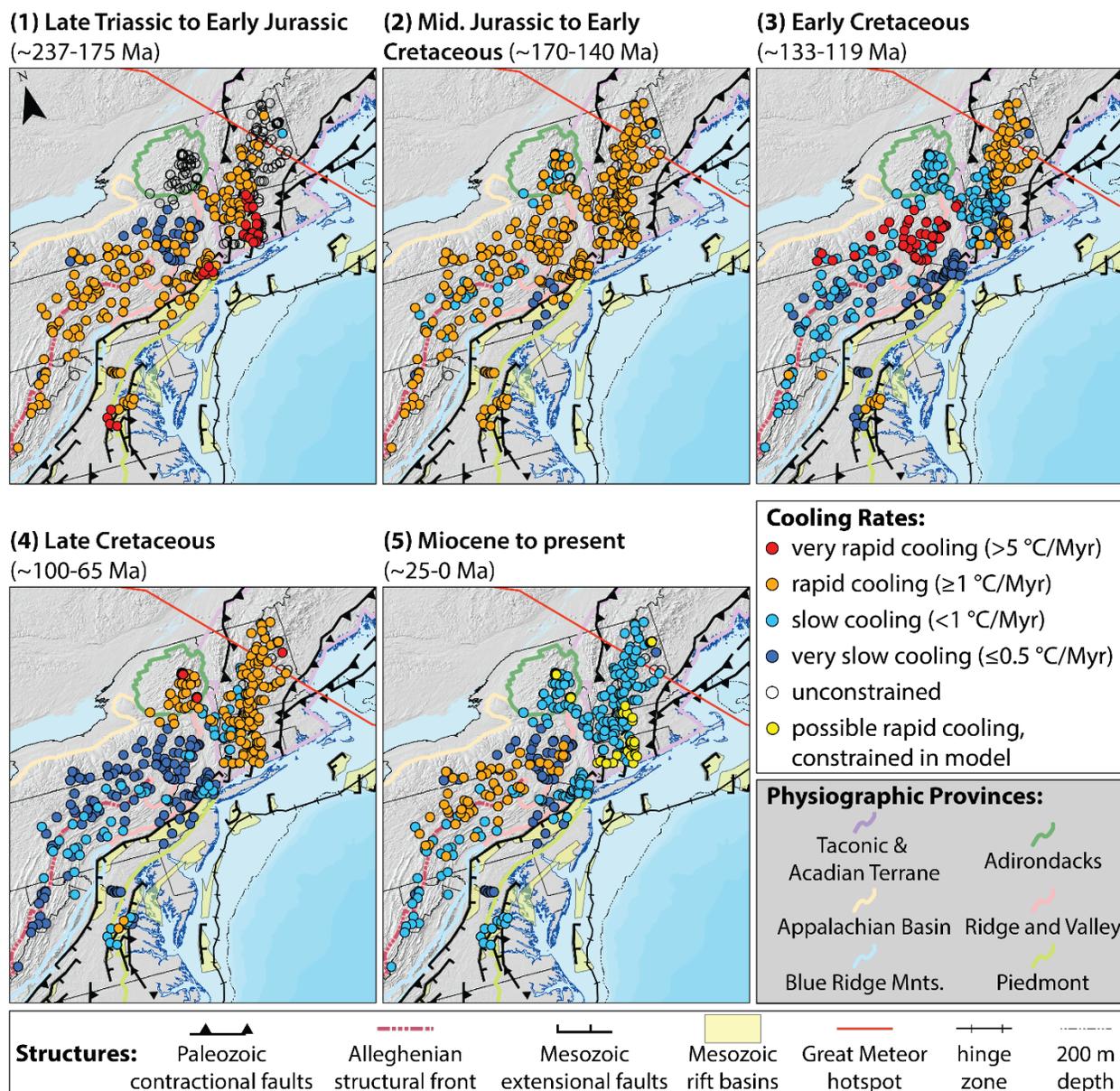


Figure 4. Maps of low-temperature thermochronology samples that lie within catchments which drain into Mid. Atlantic, colorized by rate of cooling during the 5 events discussed. Open circles indicate when a sample's thermal history does not include and/or constrain time-temperature paths within a time range. Yellow circles indicate model constrained Miocene cooling, which requires additional research to determine if it is real or which is an artifact of a first-generation annealing algorithm. Map rotated 15° counterclockwise.

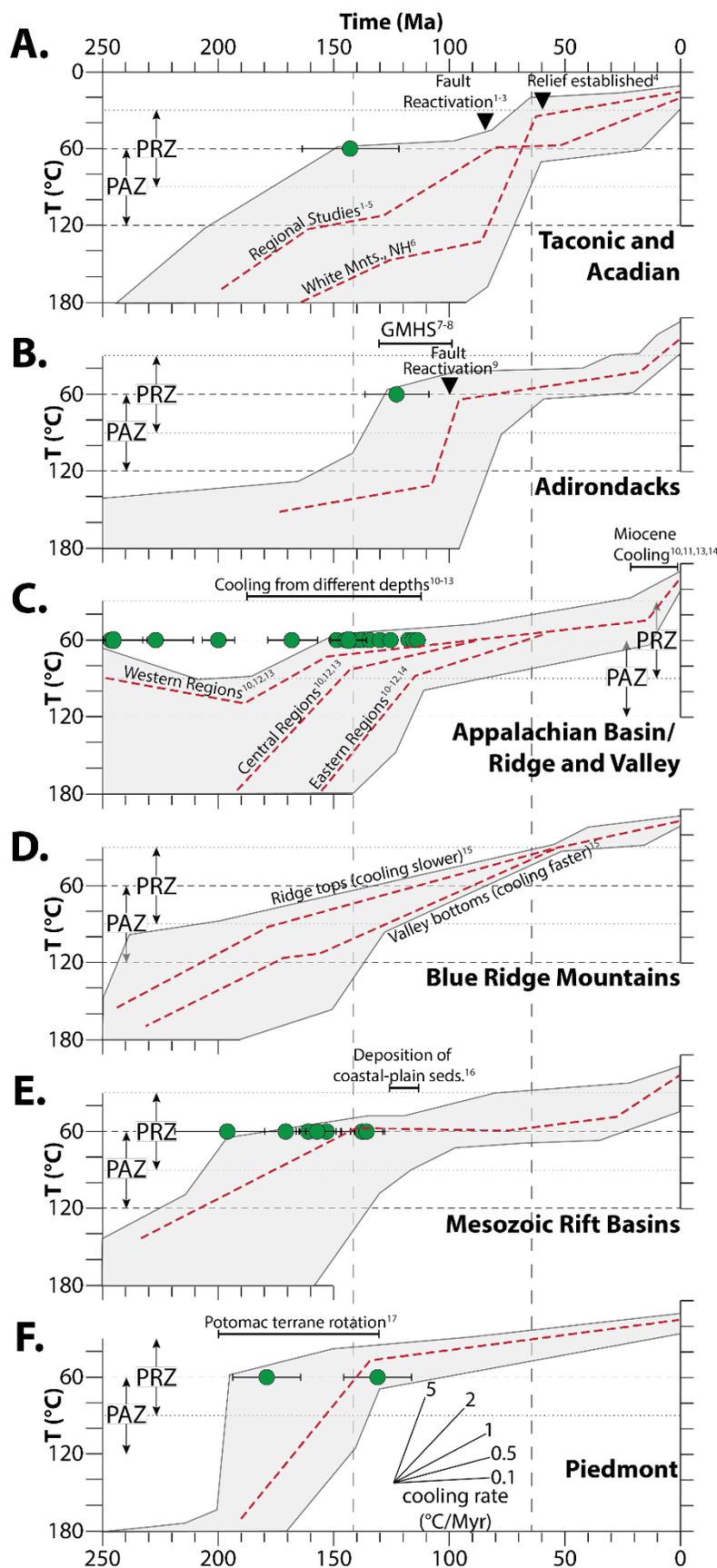


Figure 5. Schematic thermal history diagrams by province. Grey envelope represents the range of potential time-temperature (T-t) paths and the red dashed line is the best-fit thermal history constrained by published studies. AFT age of samples with mean track lengths $>14 \mu\text{m}$ indicate rapid cooling (green circles $\pm 1\sigma$). Timing and duration of relevant geologic events included. Dashed T-t paths illustrate differential cooling histories constrained within the province. Figure references: West and Roden-Tice, 2003¹; Roden-Tice and Tice, 2005²; Roden-Tice et al., 2009³; Roden-Tice et al., 2012⁴; West et al., 2008⁵; Amidon et al., 2016⁶; Heaman and Kjarsgaard, 2000⁷; Taylor and Fitzgerald, 2010⁸; Roden-Tice et al., 2000⁹; Shorten and Fitzgerald, in review¹⁰; Shorten and Fitzgerald, in prep.¹¹; Roden, 1991¹²; Blackmer et al., 1994¹³; Boettcher and Milliken, 1994¹⁴; McKeon et al., 2014¹⁵; Steckler et al., 1993¹⁶; Kunk et al., 2005¹⁷.

Table 1. Summary of information in Eastern North America Low-temperature Thermochronology Studies

| Study | Location (States) | Methods Measured | Where catchments drain to (% of Samples) | Provinces samples lie within (% of Samples) | Rock Type | Age-Elevation Profile | Low-T Therm. Modeling | Details |
|--|---------------------|---|---|--|------------------------------------|-----------------------|-----------------------|--|
| Amidon et al., 2017 | NH | AFT, AHe, Zr U-Pb, U/Th zonation profiles | 100% North Atlantic | 100% Taconic/Acadian Terrane | Igneous | AFT and AHe | Forward and Inverse | modeling of AFT and AHe age data; two forward models in HeFTy and inverse in QTQT |
| Blackmer et al., 1994 | PA | AFT and VR | 69% Mid. Atlantic, 31% Gulf of Mexico | 62% Appalachian Basin, 38% Valley and Ridge | Sedimentary | - | Forward | AFT annealing algorithm: Laslett et al., 1987; approach: Green et al., 1989 |
| Boettcher & Milliken, 1994 | KY & VA | AFT | 100% Gulf of Mexico | 100% Blue Ridge Mnts. | Sedimentary | - | Inverse | AFT annealing algorithm: Carlson, 1990; program: Corrigan, 1991 |
| Doherty & Lyons, 1980 | VT & NH | AFT and ZFT | 78% Mid. Atlantic, 22% North Atlantic | 100% Taconic/Acadian Terrane | Igneous | - | - | thermal conduction models, no AFT models |
| Kunk et al., 2005 | VA & MD | AFT and Ar-Ar | 100% Mid. Atlantic | 100% Piedmont | Metamorphic | - | - | Schematic thermal history diagrams and Ar-Ar spectra |
| Lakatos and Miller, 1983 | NY | AFT and ZFT | 100% Mid. Atlantic | 100% Appalachian Basin | Sedimentary | - | - | thermal trends based on AFT and ZFT ages and closure temperatures |
| McKeon et al., 2014 | NJ, PA, NC & SC | AHe and ZHe | 57% Gulf of Mexico, 27% Mid. Atlantic, 17% South Atlantic | 73% Blue Ridge Mnts., 17% Valley and Ridge, 10% Piedmont | Metamorphic | AHe | Inverse | HeFTy models of AHe data (RDAAM; Flowers et al., 2009). |
| Miller & Lakatos, 1983 | NY | AFT | 100% North Atlantic | 100% Adirondacks | Metamorphic | AFT | - | age-elevation profile used to estimate exhumation |
| Miller & Duddy, 1989 | NY | AFT | 74% Mid. Atlantic, 19% North Atlantic, 7% Gulf of Mexico | 86% Appalachian Basin, 14% Valley and Ridge | Sedimentary | - | - | Schematic thermal history diagrams based on AFT data |
| Reed et al., 2005 | WV | AHe, VR, fluid inclusion | 50% Gulf of Mexico, 50% Mid. Atlantic | 100% Appalachian Basin | Sedimentary | - | - | Schematic, exhumation rates calculated from T_{max} , AFT and AHe ages |
| Roden, 1991 | MD, VA & WV | AFT | 50% Gulf of Mexico, 46% Mid. Atlantic, 4% South Atlantic | 69% Valley and Ridge, 31% Appalachian Basin | Sedimentary | - | Inverse | AFT annealing algorithm: Laslett et al., 1987; approach: Green et al., 1989 |
| Roden & Miller, 1989 | PA | AFT | 96% Mid. Atlantic, 4% Gulf of Mexico | 70% Valley and Ridge, 30% Appalachian Basin | Sedimentary | - | - | thermal history based on AFT data (ages and CTLDs) and their closure temperatures |
| Roden & Miller, 1991 | MA, CT, NY, NJ & VA | AFT and ZFT | 100% Mid. Atlantic | 66% Taconic/Acadian Terrane, 31% Piedmont, 3% Valley and Ridge | Metamorphic & Sedimentary | - | Inverse | AFT annealing algorithm: Laslett et al., 1987 |
| Roden-Tice et al., 2000 | NY & VT | AFT and AHe | 65% North Atlantic, 35% Mid. Atlantic | 91% Adirondacks, 5% Appalachian Basin, 2% Taconic/Acadian Terrane, 2% Valley and Ridge | Metamorphic | - | Inverse | AFT annealing algorithm: Crowley et al., 1991; program: AFTINV (Issler, 1996) |
| Roden-Tice & Wintsch, 2002 | CT, MA & NH | AFT, AHe, ZFT | 100% Mid. Atlantic | 100% Taconic/Acadian Terrane | Metamorphic & Sedimentary | - | Inverse | AFT annealing algorithm: Crowley et al., 1991; program: AFTINV (Issler, 1996) |
| Roden-Tice & Tice, 2005 | NY, VT, NH, MA & CT | AFT and AHe | 57% Mid. Atlantic, 43% North Atlantic Adirondacks, 7% Valley and Ridge, 2% Appalachian Basin, 1% Canada | 46% Taconic/Acadian Terrane, 44% Adirondacks, 7% Valley and Ridge, 2% Appalachian Basin, 1% Canada | Metamorphic & Sedimentary | AFT | Inverse | AFT annealing algorithm: Crowley et al., 1991; program: AFTINV (Issler, 1996) |
| Roden-Tice et al., 2009 | NH, ME & VT | AFT | 70% Mid. Atlantic, 30% North Atlantic | 100% Taconic/Acadian Terrane | Igneous & Metamorphic | - | Inverse | AFT annealing algorithm: Crowley et al., 1991; program: AFTINV (Issler, 1996) |
| Roden-Tice et al., 2012 | NH | AFT | 100% North Atlantic | 100% Taconic/Acadian Terrane | Metamorphic | AFT | Inverse | AFT annealing algorithm: Ketchum et al., 2007; program: HeFTy v1.6.7 (Ketchum, 2005) |
| Shorten & Fitzgerald, in review | NY & PA | AFT, AHe, CAI | 71% Mid. Atlantic, 24% Gulf of Mexico, 5% North Atlantic | 100% Appalachian Basin | Sedimentary | - | Inverse | AFT annealing algorithm: Ketchum et al., 2007; program: HeFTy v1.9.1 (Ketchum, 2005) |
| Shorten & Fitzgerald, in press Chap. 2 | NY | AFT and AHe | 100% Mid. Atlantic | 100% Appalachian Basin | Sedimentary | AFT and AHe | Inverse | AFT annealing algorithm: Ketchum et al., 2007; program: HeFTy v1.9.1 (Ketchum, 2005) |
| Spotila et al., 2004 | VA & NC | AFT and AHe | 88% South Atlantic, 12% Gulf of Mexico | 65% Piedmont, 35% Blue Ridge Mnts. | Metamorphic | AFT and AHe | - | used age-elevation profiles but no thermal modeling |
| Steckler et al., 1993 | NY, PA & NJ | AFT and ZFT | 100% Mid. Atlantic | 62% Valley and Ridge, 38% Piedmont | Sedimentary, igneous & Metamorphic | - | - | thermal history based on AFT data (ages and CTLDs) and ZFT ages and their closure temperatures |
| Taylor & Fitzgerald, 2010 | NY | AFT and AHe | 100% North Atlantic | 100% Adirondacks | Metamorphic | AFT and AHe | Inverse | AFT annealing algorithm: Ketchum et al., 1999; program: HeFTy (Ketchum, 2005) |
| Tseng et al., 1999 | VA | AFT, Microthermometry, Gas Chromatography | 100% Mid. Atlantic | 100% Coastal Plain | Sedimentary | AFT depth profile | Inverse | AFT annealing algorithm: Laslett et al., 1987 |
| West & Roden-Tice, 2003 | ME | AFT | 100% North Atlantic | 100% Taconic/Acadian Terrane | Metamorphic & Sedimentary | - | Inverse | AFT annealing algorithm: Crowley et al., 1991; program: AFTINV (Issler, 1996) |
| West et al., 2008 | ME & NH | AFT and AHe | 97% North Atlantic, 3% Mid. Atlantic | 100% Taconic/Acadian Terrane | Sedimentary, igneous & Metamorphic | - | Inverse | AFT annealing algorithm: Crowley et al., 1991; program: AFTINV (Issler, 1996) |

Methods measured only includes the methods that were calculated/measured in the study (i.e. data integrated from previously published information not included in list). Percent of samples located within drainage outlets (where catchments drain to) and provinces were determined using ArcGIS and published figures (e.g. Poag, 1992; Pazzaglia and Brandon, 1996). Modern United States postal code abbreviations used for states. HeFTy (Ketchum, 2005), QTQT (Gallagher, 2012), and AFTINV (Issler, 1996) are thermochronometric and maximum paleotemperature modeling software packages. AFT - apatite fission track; AHe - apatite (U-Th)/He dating; Zr - zircon; VR - vitrinite reflectance; ZFT - zircon fission track; ZHe - zircon (U-Th)/He dating; CAI - concordant alteration index; Mid. - Middle; Mnts. - Mountains; RDAAM - radiation damage accumulation and annealing model.

Appendices

Appendix A: Supplementary material for Chapter One

Supplementary File A. AFT Sample Matrix

| Sample ID | State | Location | | Elev. (m) | Dep. Age | Depositional Group | Formation | Ref. Map |
|-----------------------|--------------|-----------------|--------------|------------------|-----------------|---------------------------------|--------------------|-----------------|
| | | Lat. | Long. | | | | | |
| Western Region | | | | | | | | |
| 36N | NY | 42.226 | -78.260 | 504 | LD | Conneaut | Cattaragus facies | 2,3 |
| 37N | NY | 42.100 | -78.443 | 455 | LD | Conneaut | Cattaragus facies | 2,3 |
| 38N | NY | 42.083 | -78.634 | 447 | LD | Conneaut | Chemug facies | 2,3 |
| 39P | PA | 41.971 | -78.630 | 403 | LD | Conneaut | Chadakoin | 4,5 |
| 40P | PA | 41.824 | -78.386 | 618 | LD | Catskill facies | Catskill | 1 |
| 42P | PA | 41.904 | -78.087 | 498 | LD | Conneaut | Chadakoin | 4,5 |
| 51N | NY | 42.073 | -79.745 | 443 | LD | Conewango | Oswayo and Venango | 2,3 |
| 53N | NY | 42.026 | -79.064 | 618 | LD | Conewango | Oswayo and Venango | 2,3 |
| Central Region | | | | | | | | |
| 3P | PA | 41.827 | -75.774 | 336 | LD | Catskill facies | Catskill | 1 |
| 4P | PA | 41.812 | -75.885 | 499 | LD | Catskill facies | Catskill | 1 |
| 5P | PA | 41.736 | -76.297 | 394 | ED | underlies Catskills (Canadaway) | Lockhaven | 1 |
| 7P | PA | 41.521 | -76.231 | 365 | LD | Catskill facies | Catskill | 1 |
| 8P | PA | 41.423 | -76.489 | 570 | EM | above Catskill | Burgoon Sandstone | 1 |
| 9P | PA | 41.363 | -77.082 | 233 | LD | Catskill facies | Catskill | 1 |
| 10P | PA | 41.441 | -77.101 | 384 | LD | Catskill facies | Catskill | 1 |
| 15N | NY | 42.068 | -75.572 | 464 | LD | West Falls | Upper Walton | 2,3 |
| 17N | NY | 42.075 | -76.042 | 328 | LD | West Falls | Upper Walton | 2,3 |
| 19N | NY | 42.126 | -76.270 | 233 | LD | West Falls | Upper Walton | 2,3 |
| 20N | NY | 42.033 | -76.412 | 304 | LD | West Falls | Upper Walton | 2,3 |
| 21N | NY | 42.014 | -76.566 | 396 | LD | West Falls | Gardeau | 2,3 |
| 22N | NY | 42.090 | -77.041 | 359 | LD | West Falls | Nunda | 2,3 |
| 24N | NY | 42.152 | -77.313 | 315 | LD | West Falls | Nunda | 2,3 |
| 28Pc | PA | 41.365 | -77.680 | ~ 1 km depth | ED | underlies Catskills (Canadaway) | Lockhaven | 1 |
| 34N | NY | 42.366 | -77.453 | 384 | LD | West Falls | Nunda | 2,3 |
| 35N | NY | 42.305 | -77.884 | 592 | LD | Canadaway | Machias | 2,3 |
| 43P | PA | 41.757 | -77.903 | 621 | LD | Catskill facies | Catskill | 1 |
| 55P | PA | 41.525 | -77.737 | 373 | LD | Catskill facies | Catskill | 1 |
| 56P | PA | 41.284 | -77.319 | 180 | LD | Catskill facies | Catskill | 1 |
| 57N | NY | 42.538 | -77.559 | 453 | LD | West Falls | Nunda | 2,3 |
| KS3 | NY | 42.259 | -76.518 | 337 | LD | West Falls | Upper Walton | 2,3 |
| Eastern Region | | | | | | | | |
| 45N | NY | 41.949 | -74.961 | 390 | LD | West Falls | Upper Walton | 2,3 |
| 48N | NY | 41.673 | -74.713 | 442 | LD | West Falls | Upper Walton | 2,3 |
| 49N | NY | 41.595 | -74.539 | 428 | MD | Hamilton | Moscow | 2,3 |
| 50N | NY | 41.957 | -75.239 | 341 | LD | West Falls | Upper Walton | 2,3 |
| G12 | NY | 42.342 | -75.406 | 339 | MD | Hamilton | Moscow | 2,3 |
| P12 | NY | 41.854 | -74.762 | 552 | LD | West Falls | Upper Walton | 2,3 |
| 15.2 | NY | 42.228 | -74.237 | 595 | MD | Hamilton | Moscow | 2,3 |

Samples listed numerically within regions.

Lat.: Latitude; Long.: Longitude; Elev.: Elevation; Dep. Age: Depositional age; Ref. Maps: Reference maps
 EM: Early Mississippian (359-345 Ma); LD: Late Devonian (383-359 Ma); MD: Middle Devonian (393-383 Ma); ED: Early Devonian (419-393 Ma)

See next page for reference (ref.) maps.

Supplementary File A. AFT Sample Matrix**Reference (Ref.) Maps:**

- 1 Garrity, C.P., and Soller, D.R., 2009, Database of the Geologic Map of North America; adapted from the map by J.C. Reed, Jr. and others (2005): U.S. Geological Survey Data Series 424
- 2 NYS Museum, NYS Geological Survey, NYS Museum Technology Center, 1999, 1:250,000 Bedrock geology of NYS, data is distributed in ARC/INFO or EXPORT format (with ".e00" extension) in 5 separate files based on printed map sheets, <http://www.nysm.nysed.gov/gis.html>.
- 3 D. W. Fisher; Y. W. Isachsen, L. V. Rickard, 1970, Geologic Map of New York State, consisting of 5 sheets: Niagara, Finger Lakes, Hudson-Mohawk, Adirondack, and Lower Hudson, New York State Museum and Science Service, Map and Chart Series No. 15, scale 1:250000.
- 4 Pennsylvania Bureau of Topographic and Geologic Survey, Department of Conservation and Natural Resources, 2001, Bedrock Geology of Pennsylvania, edition: 1.0, digital map. Retrieved from
- 5 Berg, T. M., Edmunds, W. E., Geyer, A. R., and others, compilers, 1980, Geologic map of Pennsylvania: Pennsylvania Geological Survey, 4th ser., Map 1, 2nd ed., 3 sheets, scale 1:250,000.

Supplementary File B. Inverse Thermal Models

In this supplementary file, the development of post-depositional constraints and inverse thermal models which did not work are discussed. Then, the models for all 38 of the samples are presented. All samples were modeled using inverse thermal modeling in HeFTy (Ketcham, 2005) and in this supplementary file the following information is presented for each sample: the time-temperature history path envelopes (good paths in purple and acceptable paths in green), the best-fit (black path) and weighted mean path (thick blue path), and the constraint boxes which includes stratigraphic age and paleo-temperature (olive box; Woodrow et al., 1973); AFT track length distribution, calculated track length distribution based on best-fit path; model goodness-of-fit (GOF) statistics and the age of the oldest fission track that has not been completely annealed (“Old”; Ketcham, 2005); AHe diffusion profile and GOF statistics when present; and vitrinite reflectance (%R_o) output, which includes modeled and measured values (“>” sign means the %R_o calculation does not include a depositional event).

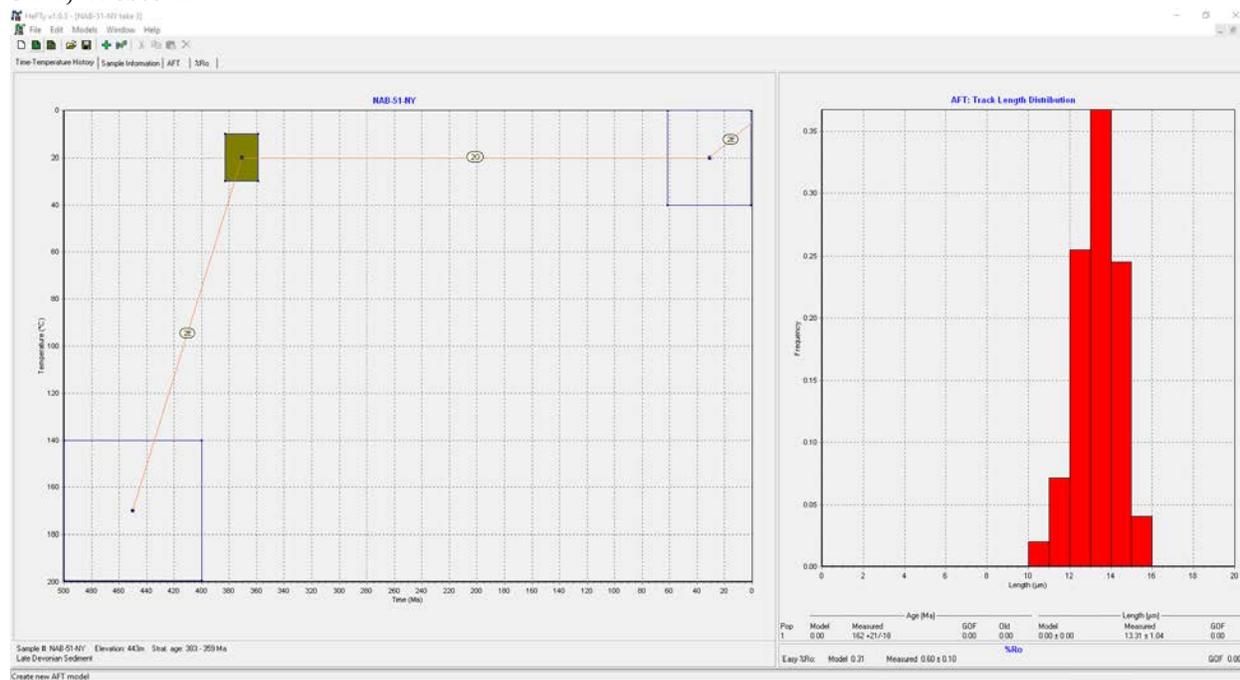
B1. Development of post-depositional constraints used in inverse thermal modeling

Several iterations of models were run to determine the most likely thermal histories. First, only the provenance (Acadian/Taconic sources; Ver Straeten, 2009), stratigraphic/depositional age (Table 1) and paleo-temperature (25 ± 10 °C; Woodrow et al., 1973), and present-day conditions (5 ± 5 °C; Hijmans et al., 2005) were used to constrain inverse thermal models (Attempt 1). However, using only these constraints produced no good or acceptable paths. The addition of a large post-depositional constraint box, ranging from ca. 360-0 Ma and ~0-190 °C, allowed the models to explore the T-t space and begin to constrain T-t paths (Attempt 2). Another constraint box was then added to resolve the Cenozoic thermal history (60-0 Ma), but the box was left wide (0-100 °C) so as not to force paths to resolve a rapid cooling event

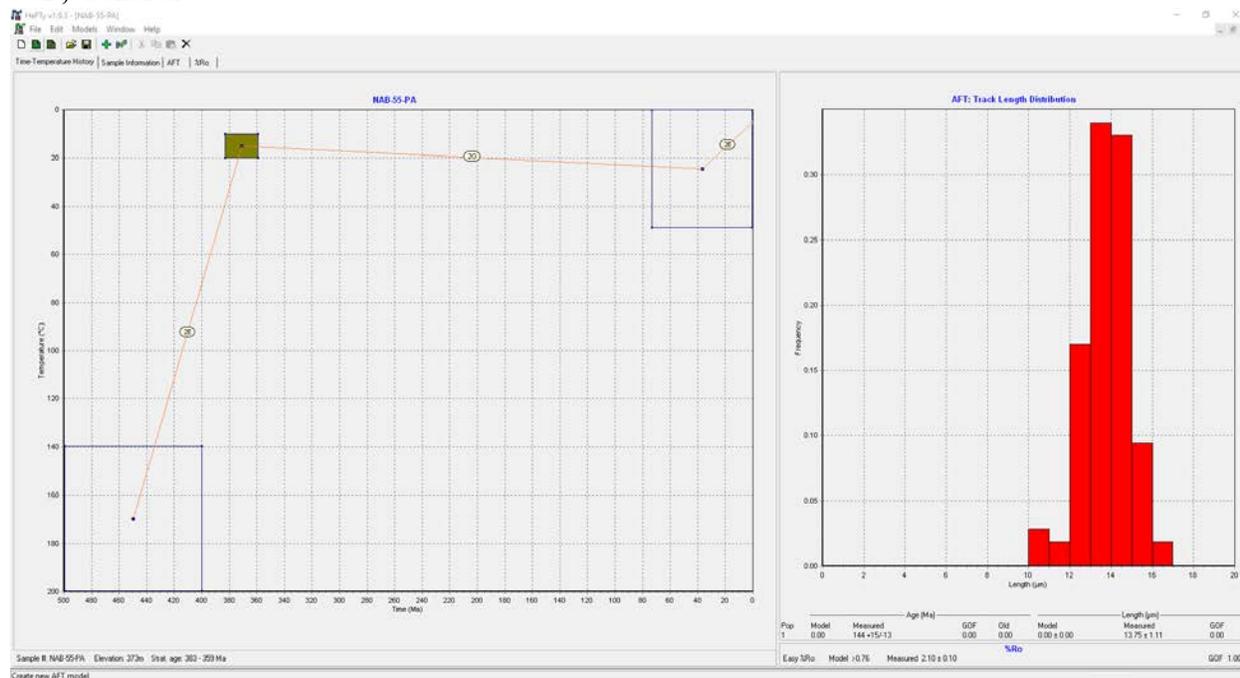
(Attempt 3). Finally, based on the thermal history trends constrained by the broad constraint boxes (attempts 1-3) and the geologic events affecting the eastern North America, the constraint boxes were further divided to better resolve the post-depositional thermal history (Attempt 4). Constraint boxes are not tightly constrained by temperature but are divided into the following time ranges: (1) ca. 360-200 Ma (deposition and rifting of eastern North America); (2) ca. 200-60 Ma (post-rift passive margin development); (3) ca. 60-0 Ma (Cenozoic history and development of dynamic topography). Note that with every attempt and addition of relevant constraint boxes the goodness-of-fit statistics for the best-fit T-t path increased.

Attempt 1. Provenance, stratigraphic and present-day condition constraints only. For all models 10,000 paths were tried, with no constrained good or acceptable paths.

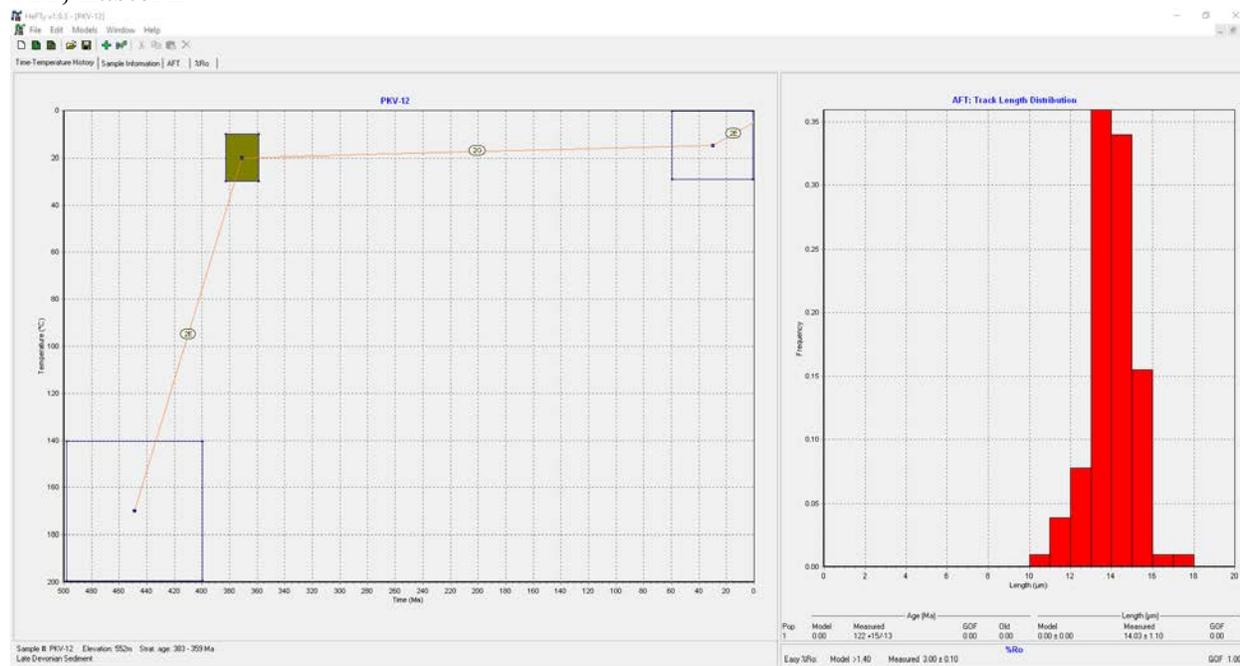
51N, Western



55P, Central

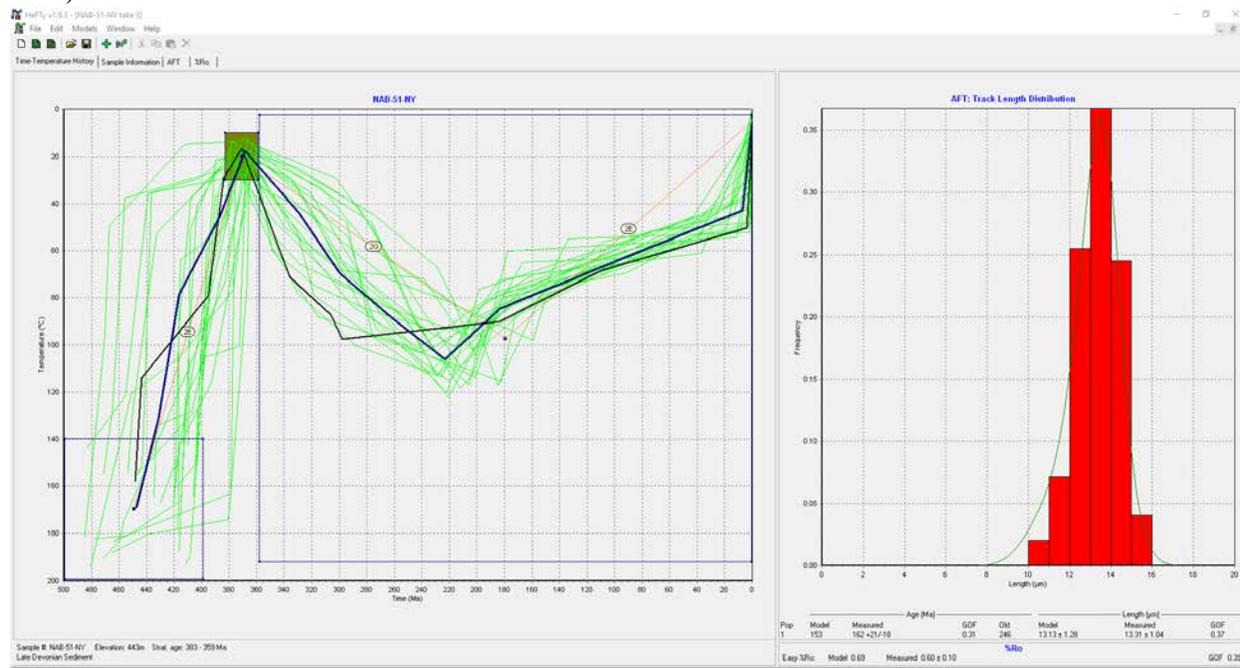


P12, Eastern

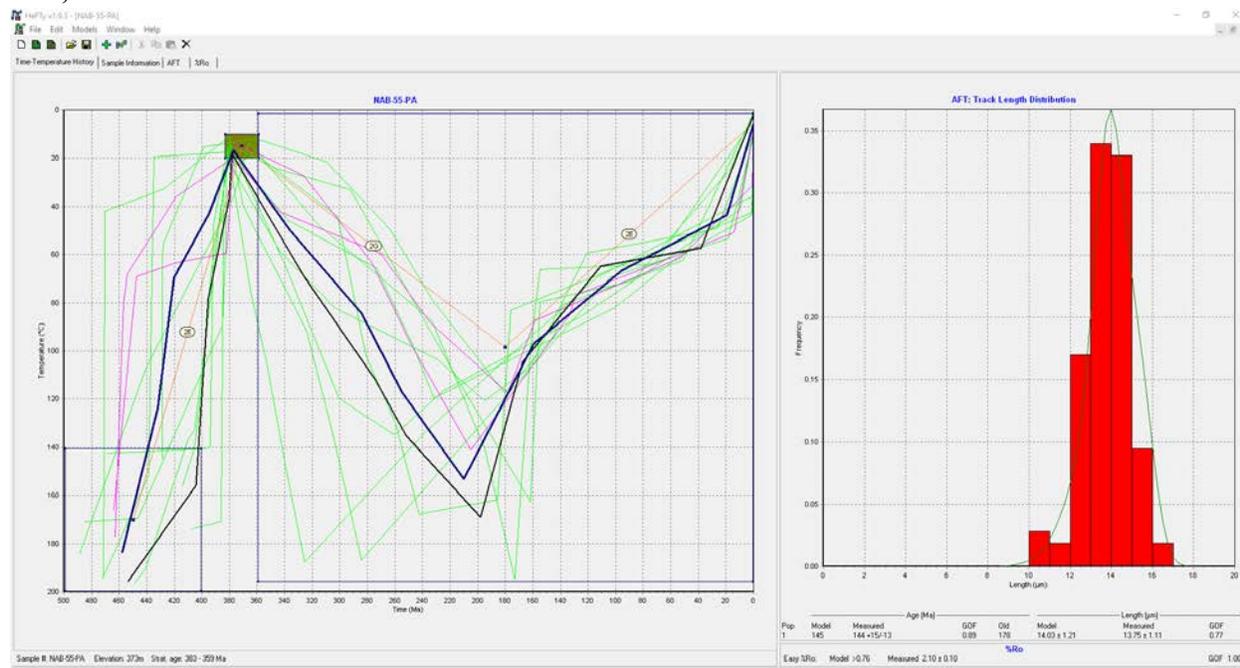


Attempt 2. Provenance, stratigraphic and large constraint box post-deposition. For all models 10,000 paths were tried with various resolution of thermal histories.

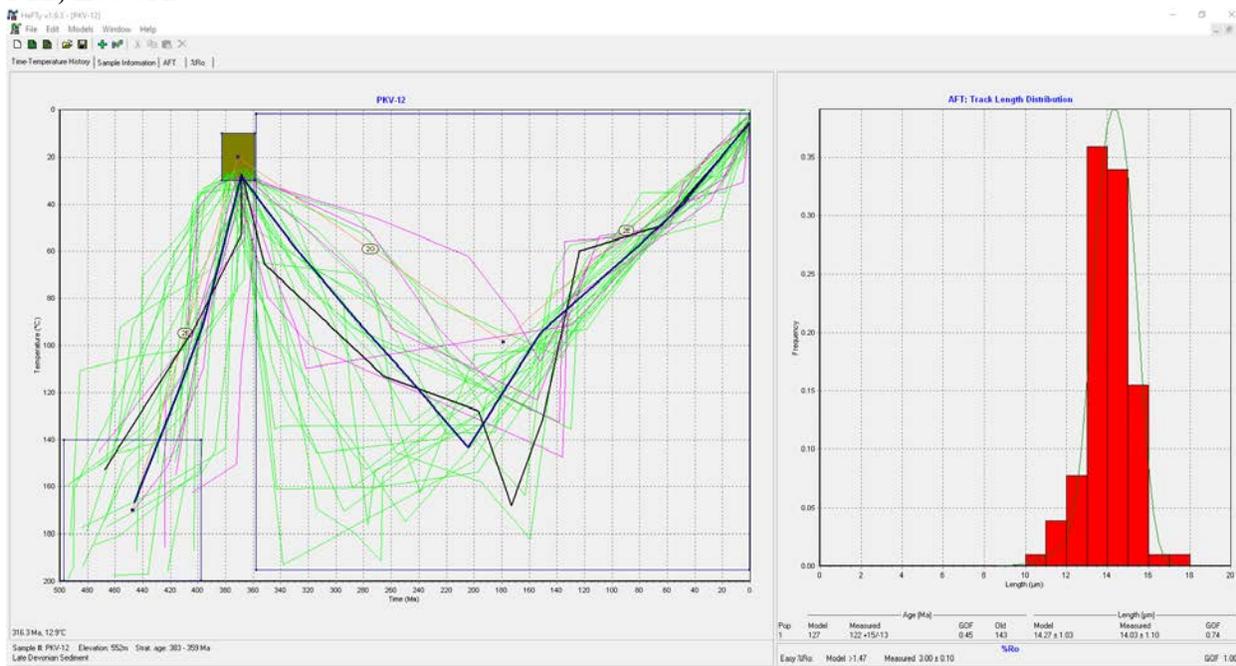
51N, Western



55P, Central

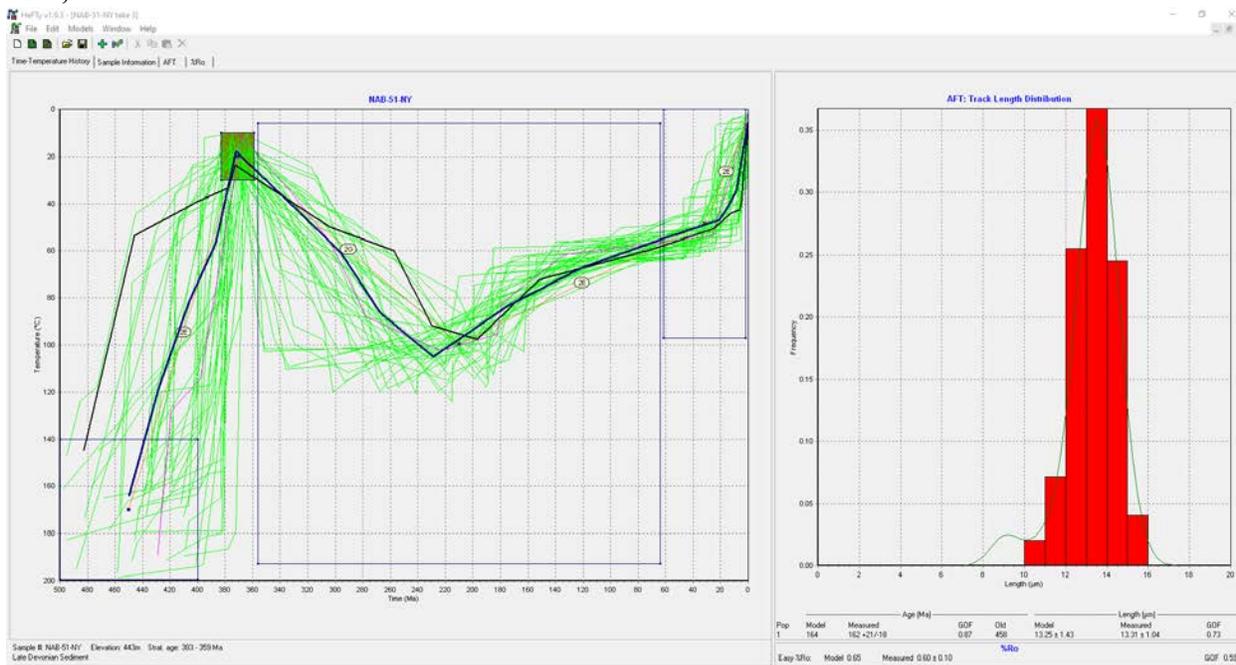


P12, Eastern

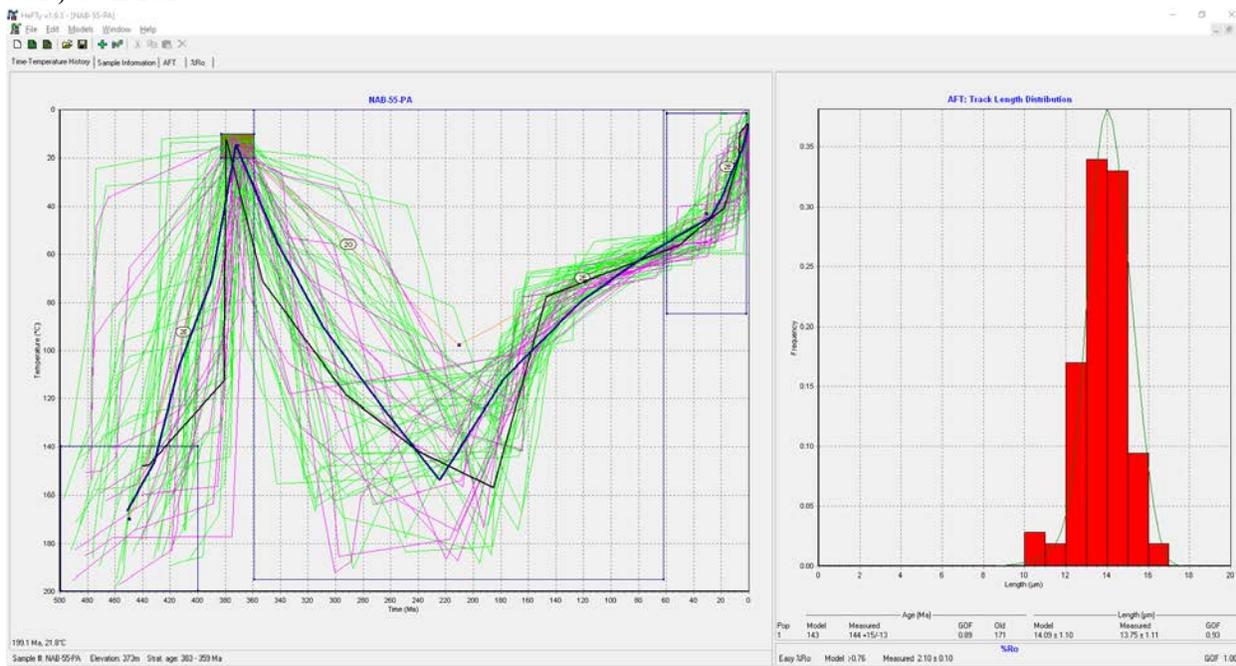


Attempt 3. Provenance, stratigraphic and two post-deposition constraint boxes with one focused on the Cenozoic thermal history. For all models 10,000 paths were tried.

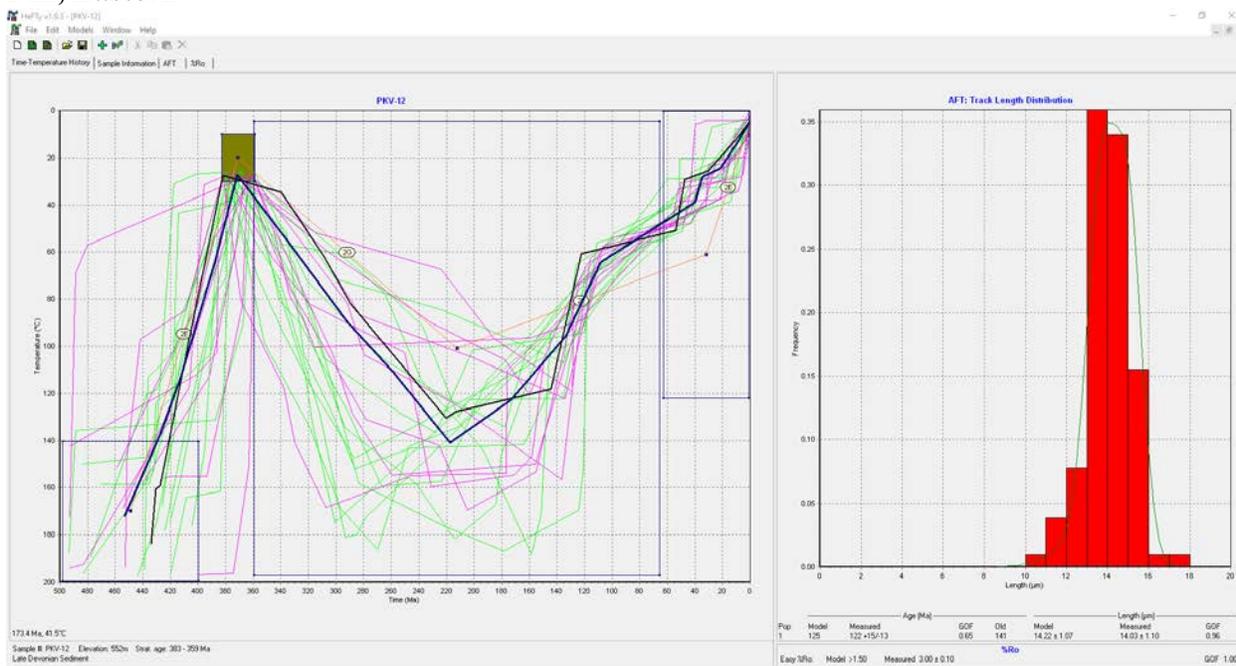
51N, Western



55P, Central



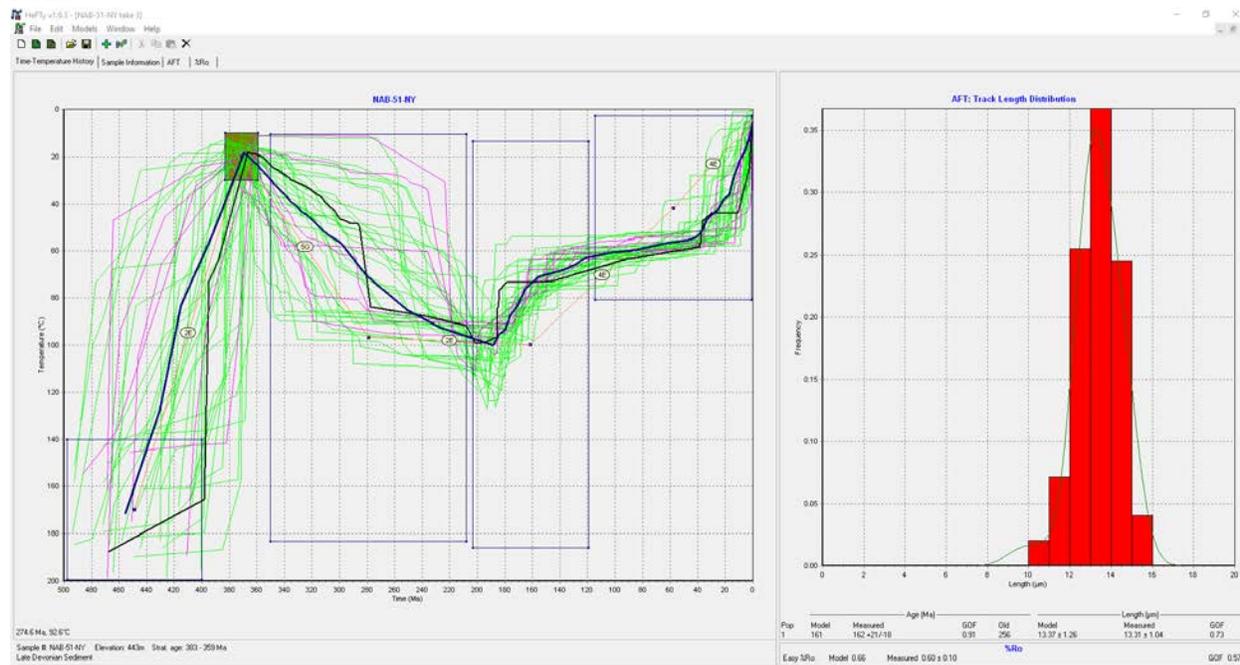
P12, Eastern



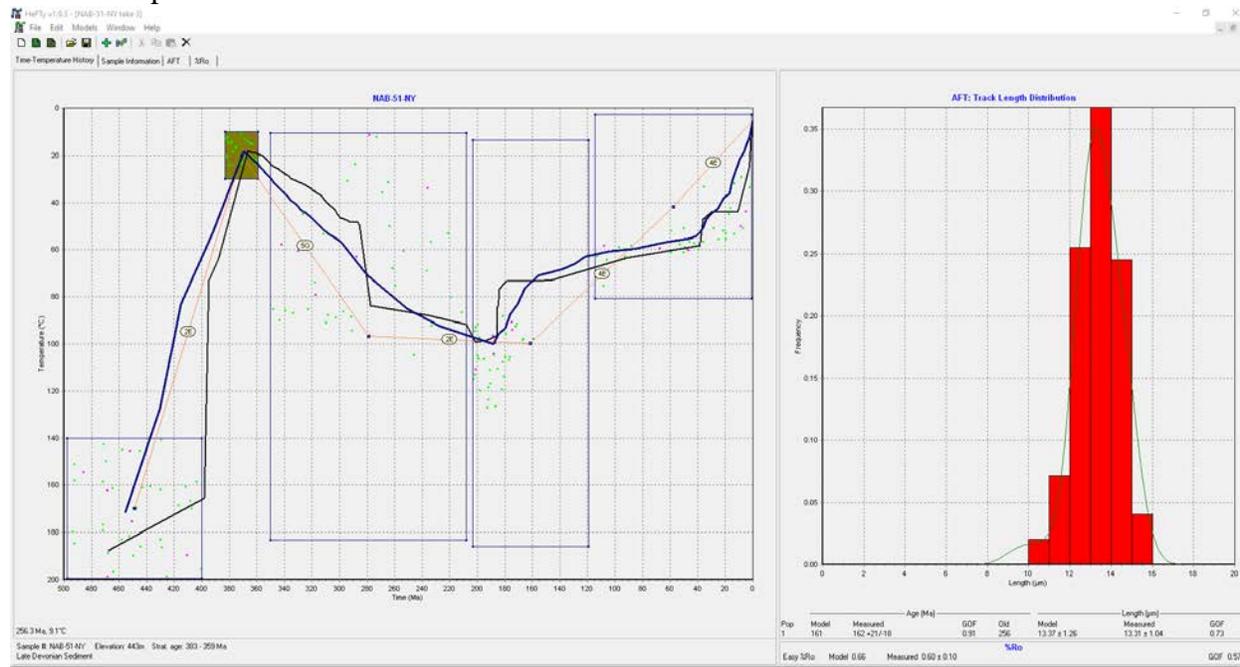
Attempt 4. Provenance, stratigraphic and three post-deposition constraint boxes. Both time-temperature paths and constraint points are shown. Points may represent local temperature minimums or maximums and can be useful in examining times/temperatures of peak heating and onset of changes in cooling rate constrained by inverse thermal models (Ketcham, 2005).

51N, Western

Paths

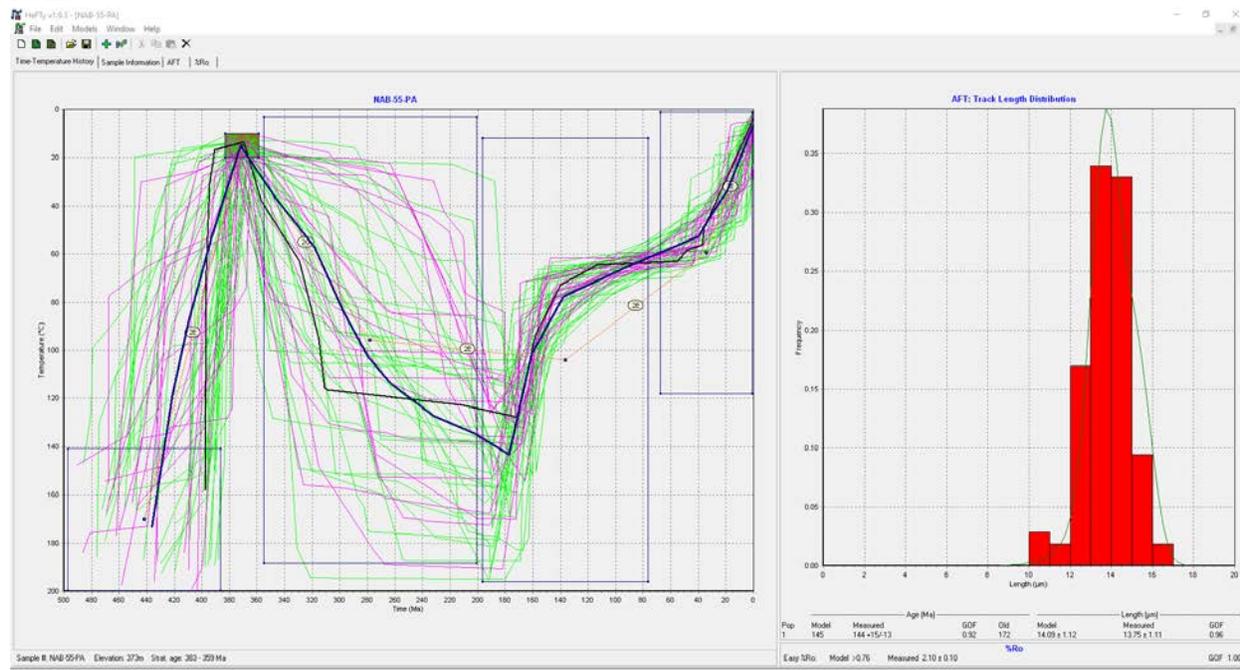


Constraint points

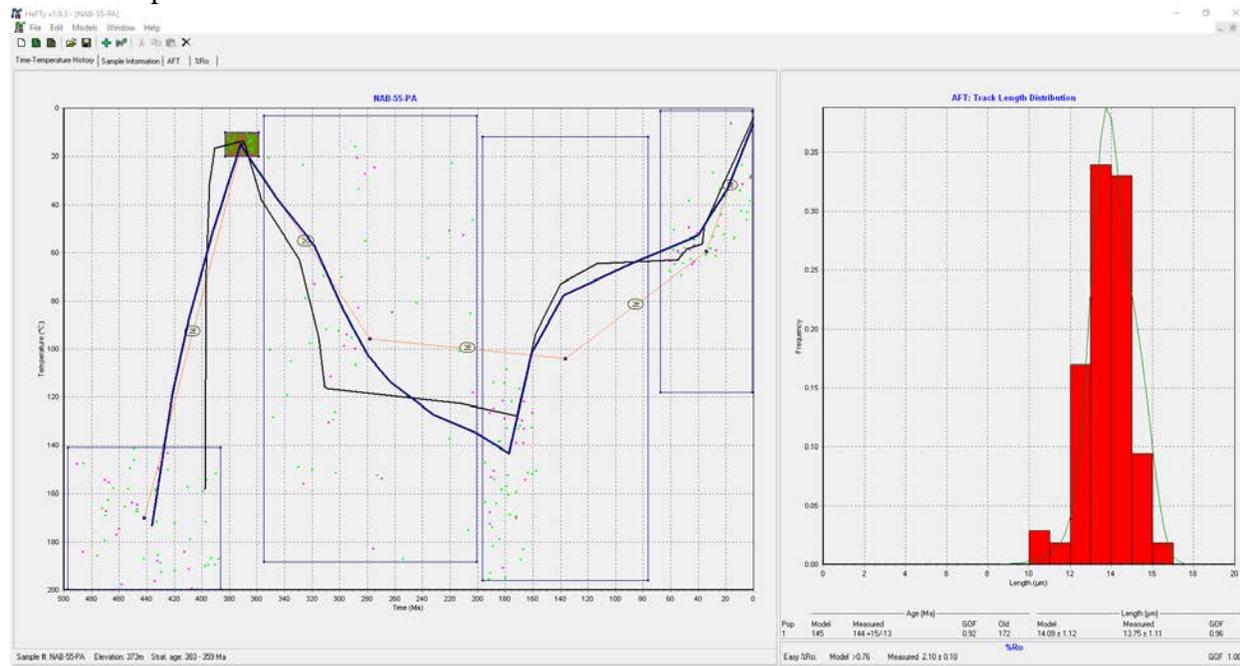


55P, Central

Paths

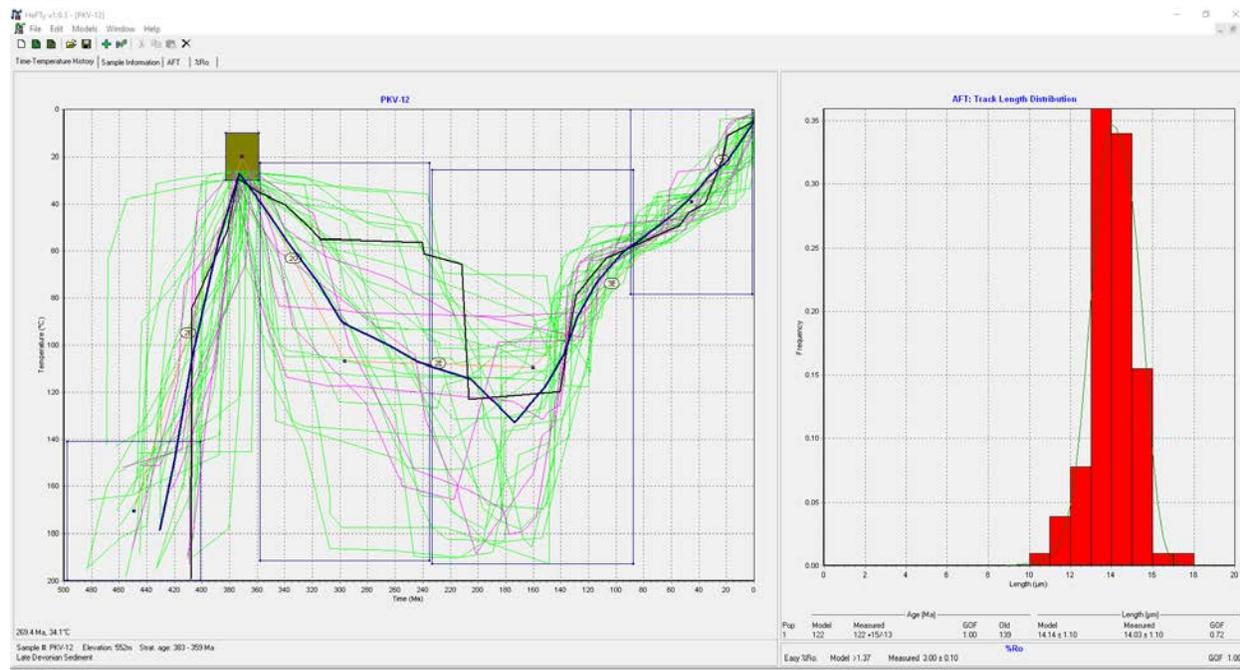


Constraint points

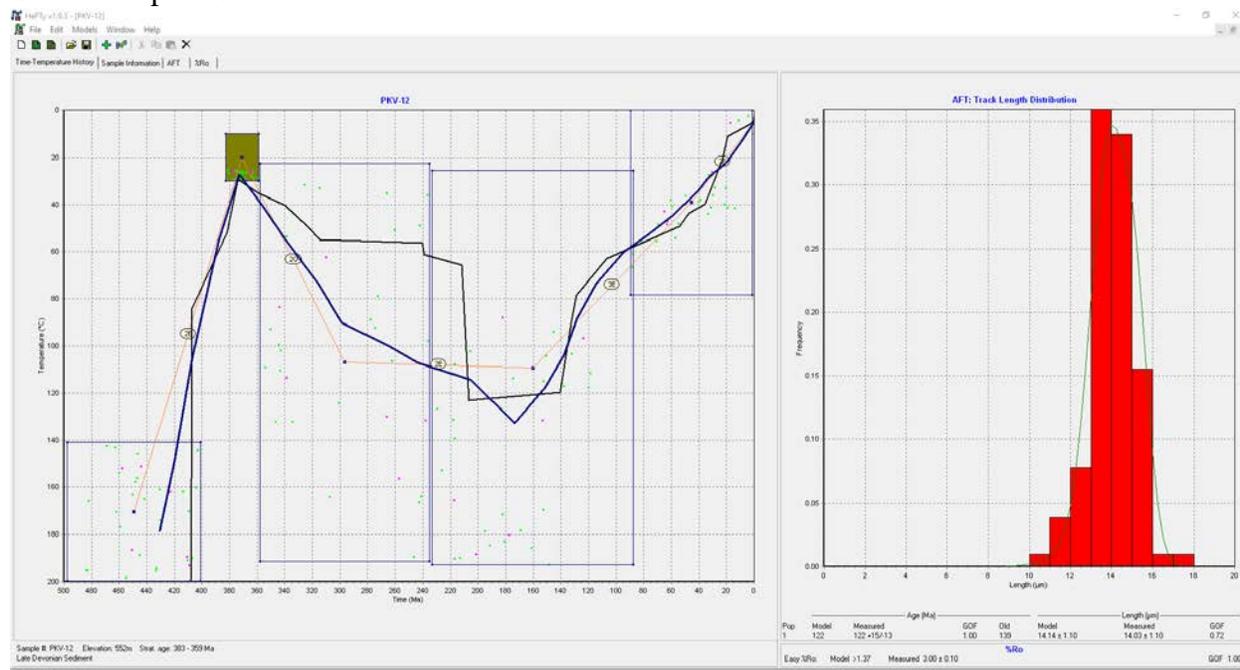


P12, Eastern

Paths



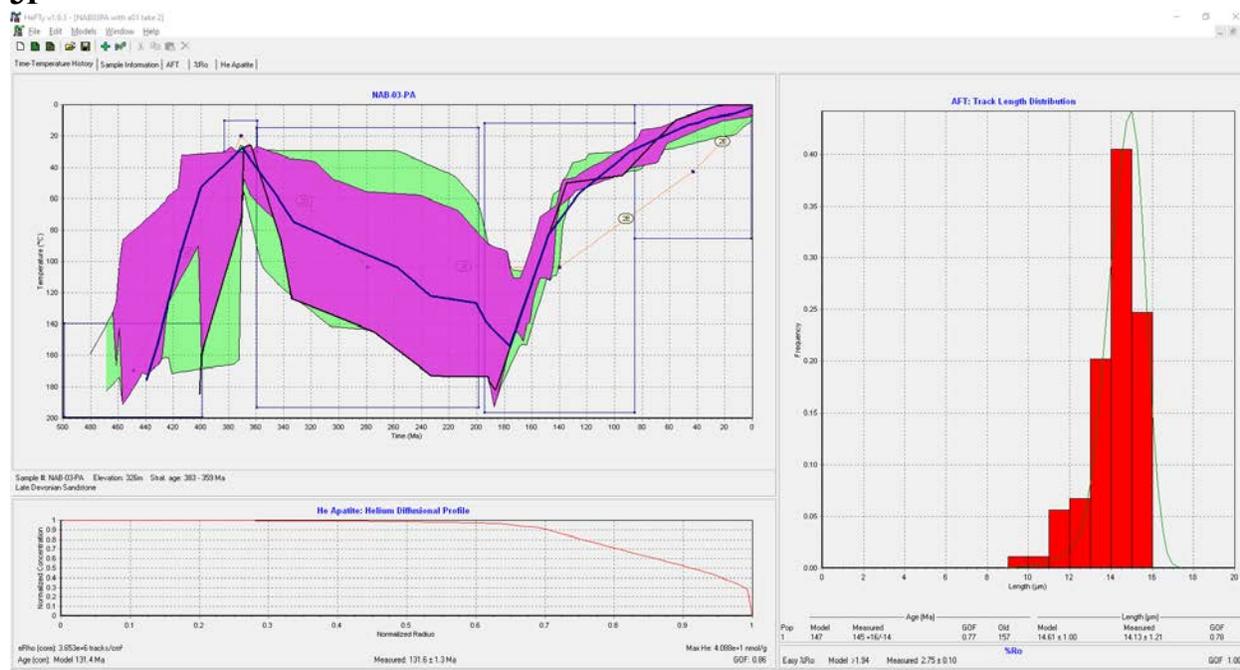
Constraint points



B2. Inverse Thermal Models

As stated in the thermal history interpretation discussion within Chapter 1, six representative inverse thermal models were used to demonstrate the time-temperature history trends. However, the trends were based on the thermal trends revealed in models from all 38 of the samples. Inverse thermal models are presented in numerical sample order.

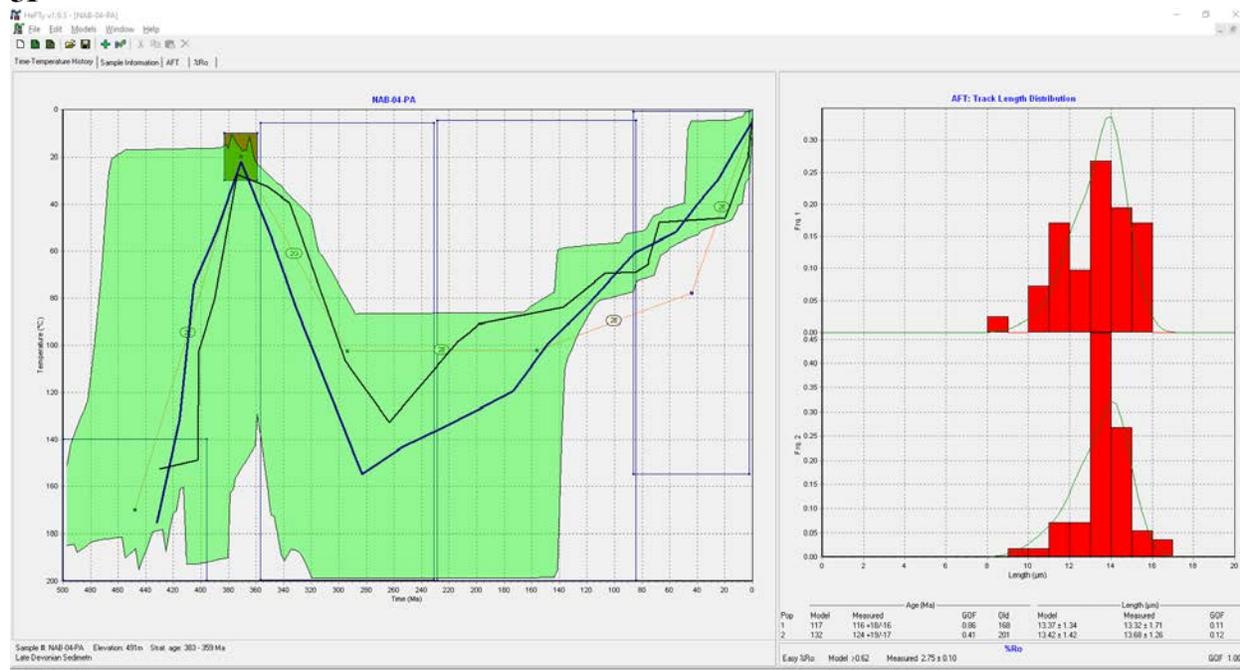
3P



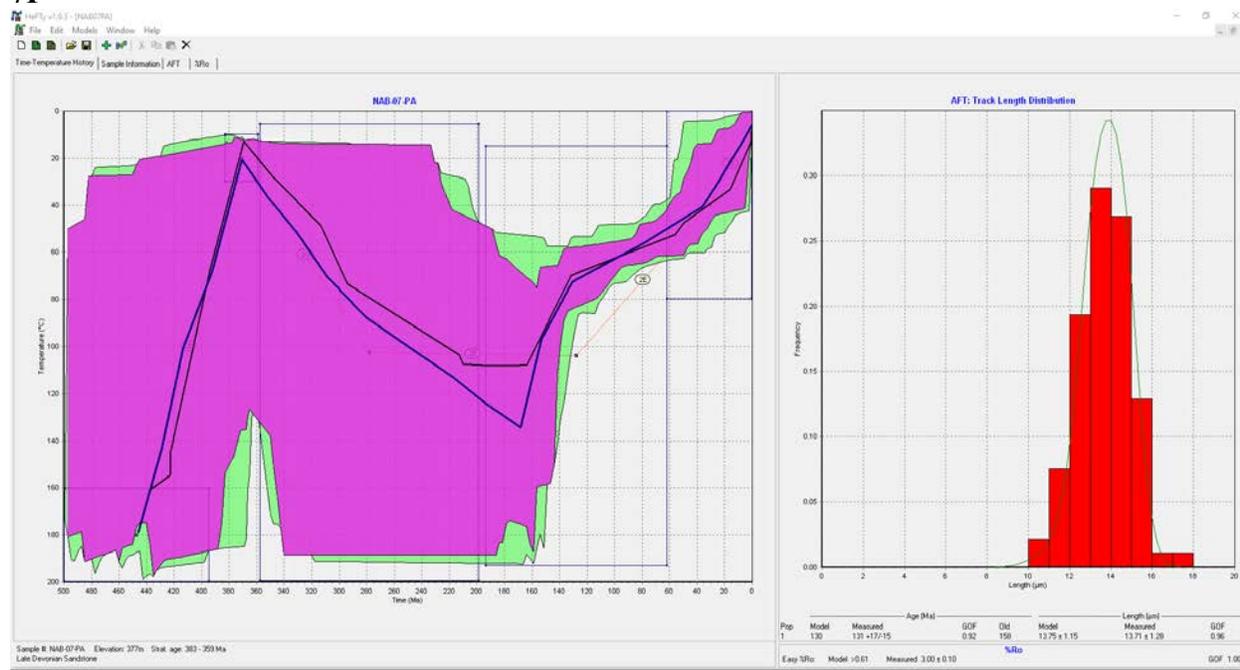
4P



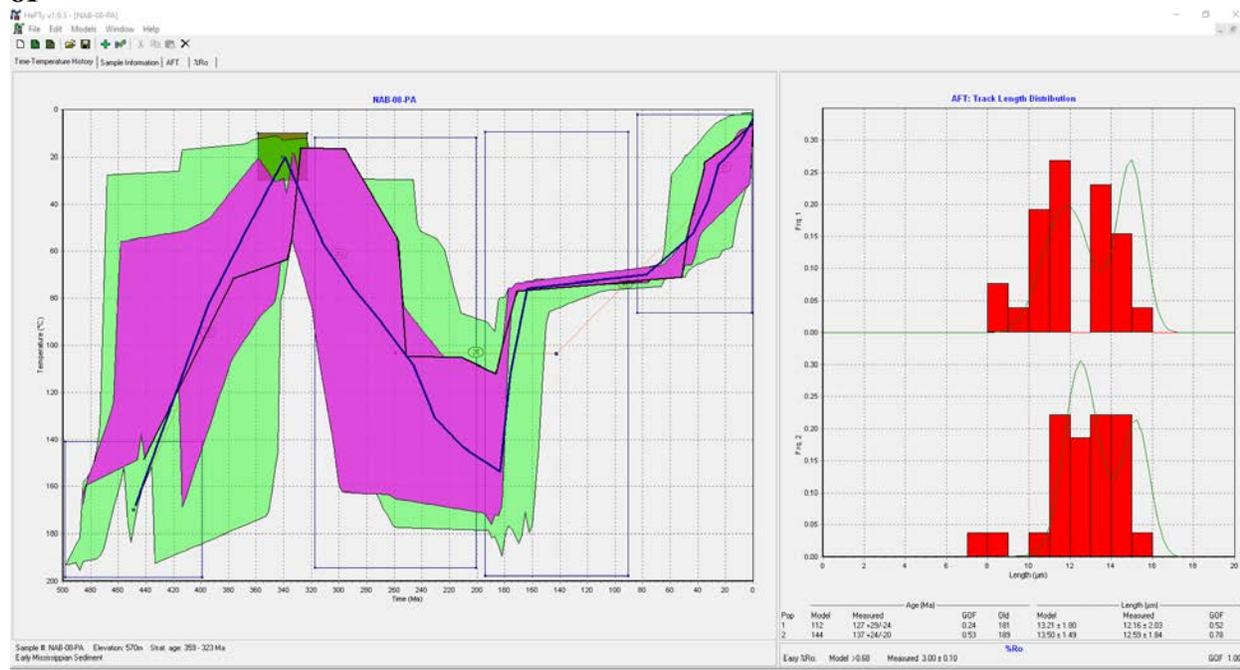
5P



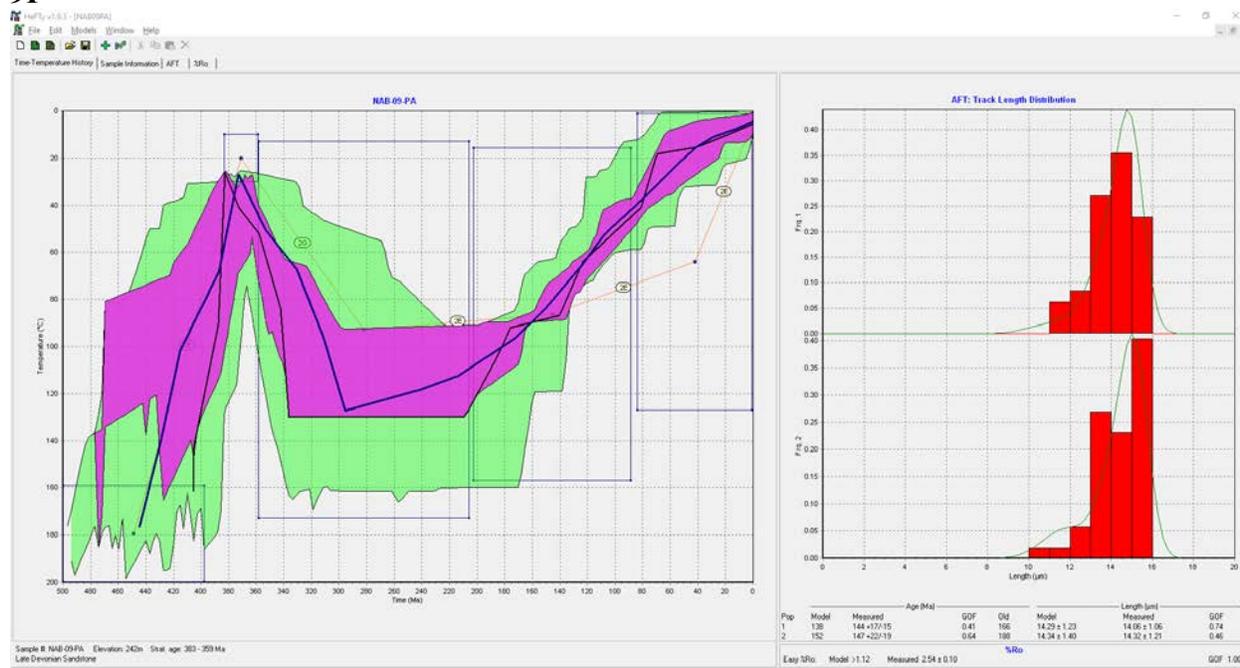
7P



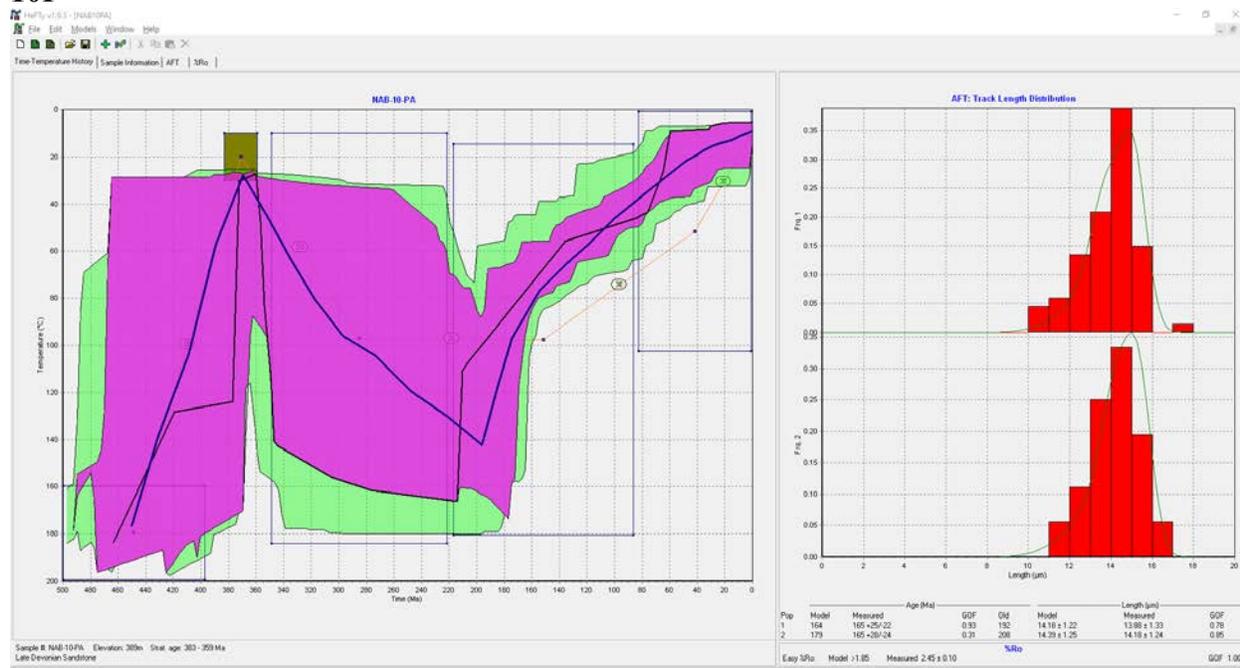
8P



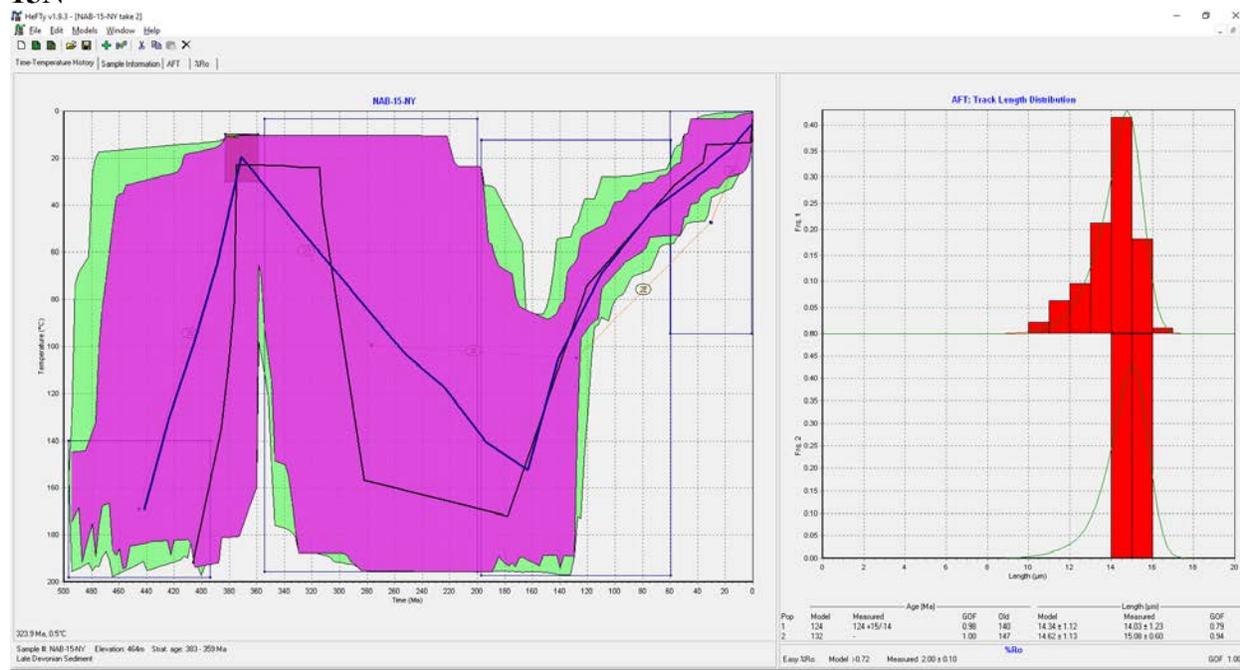
9P



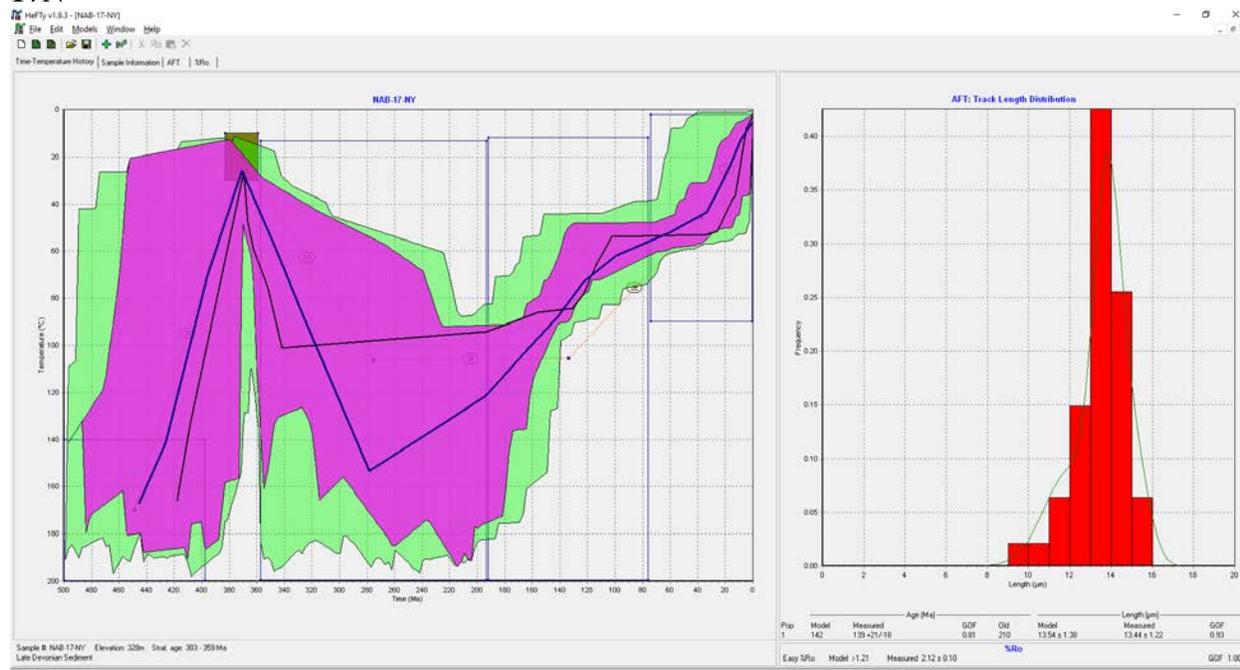
10P



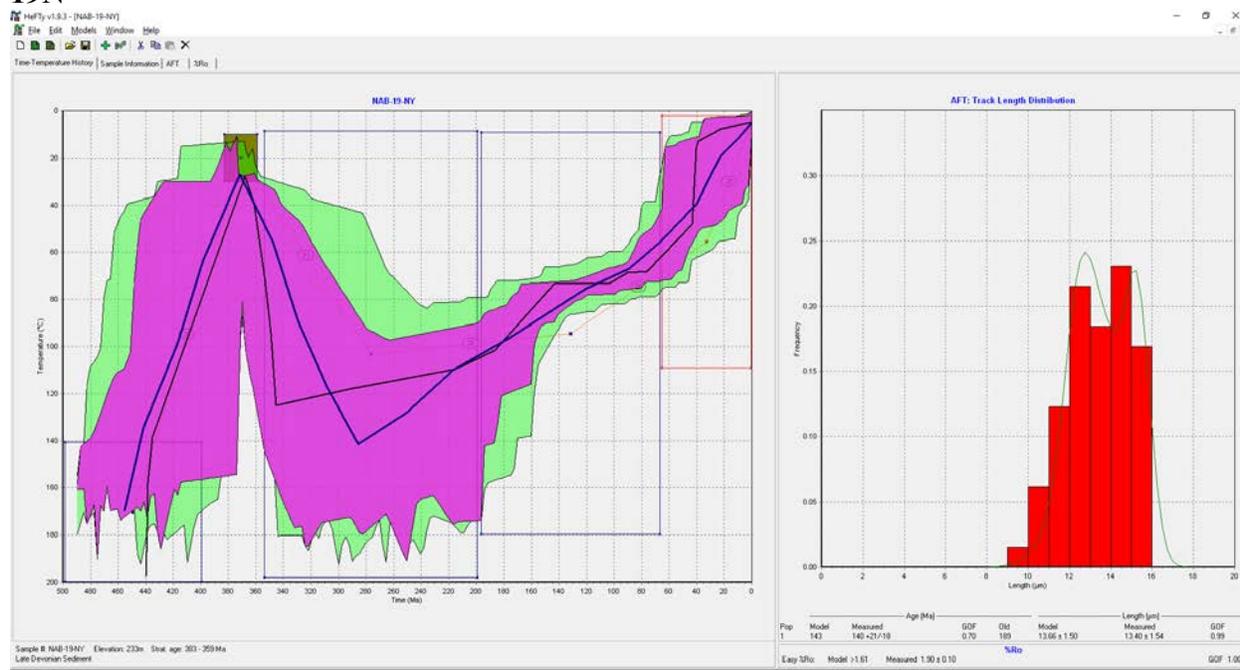
15N



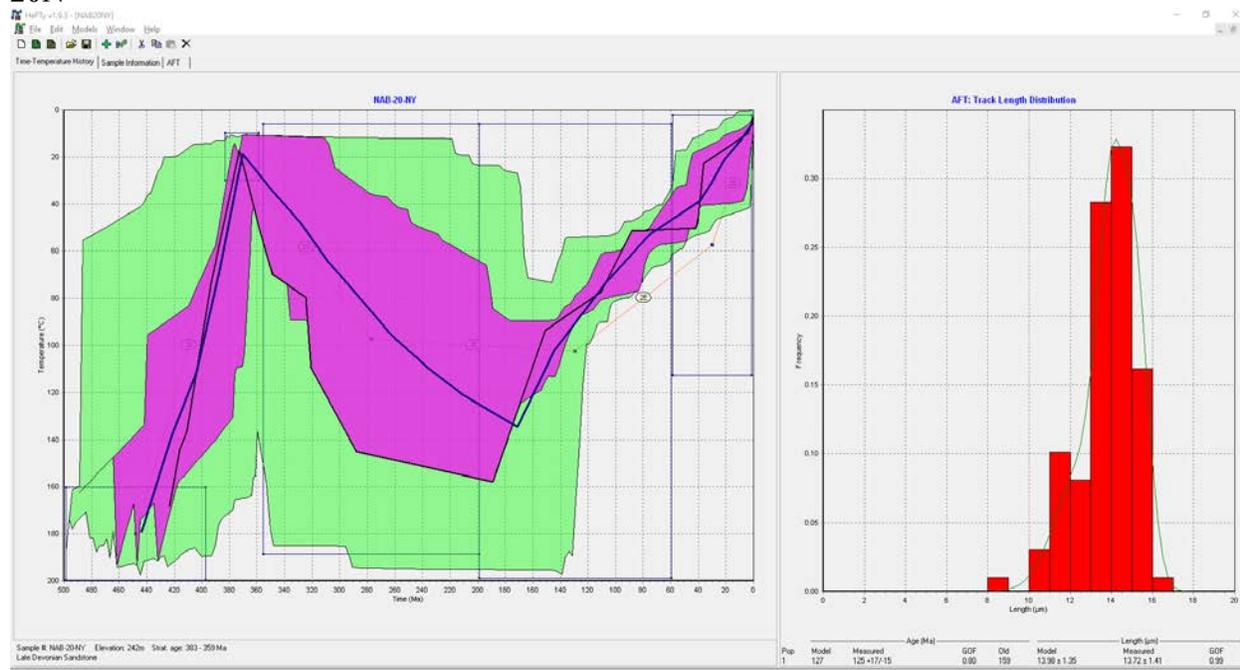
17N



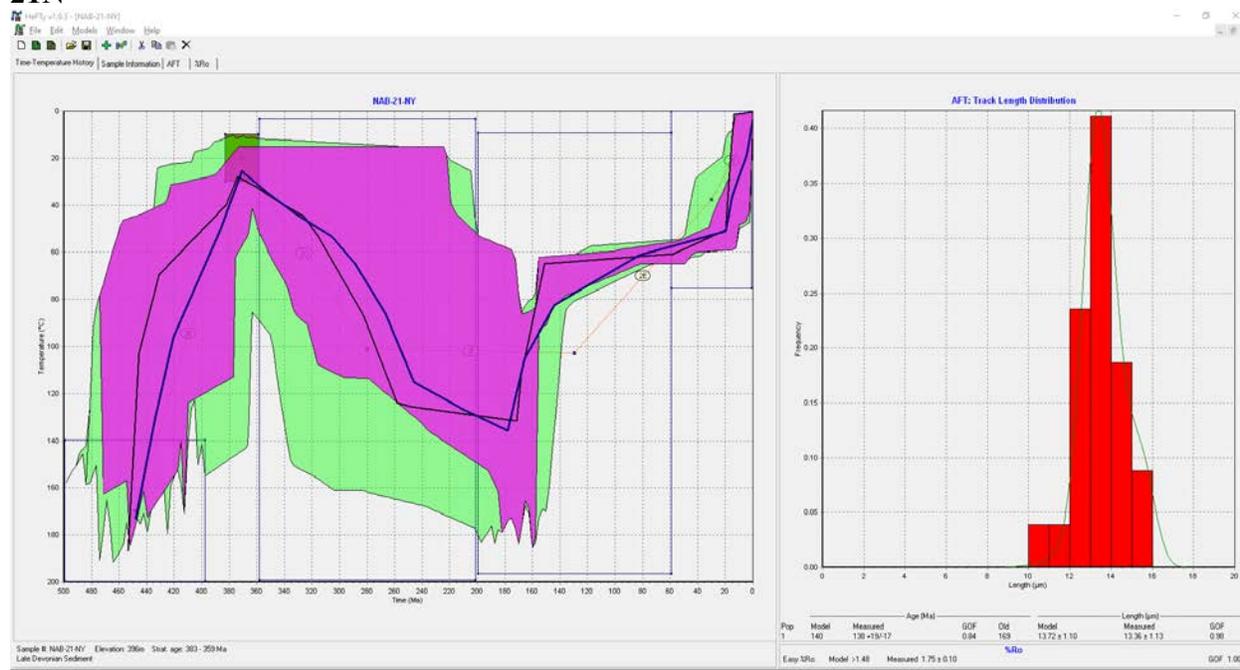
19N



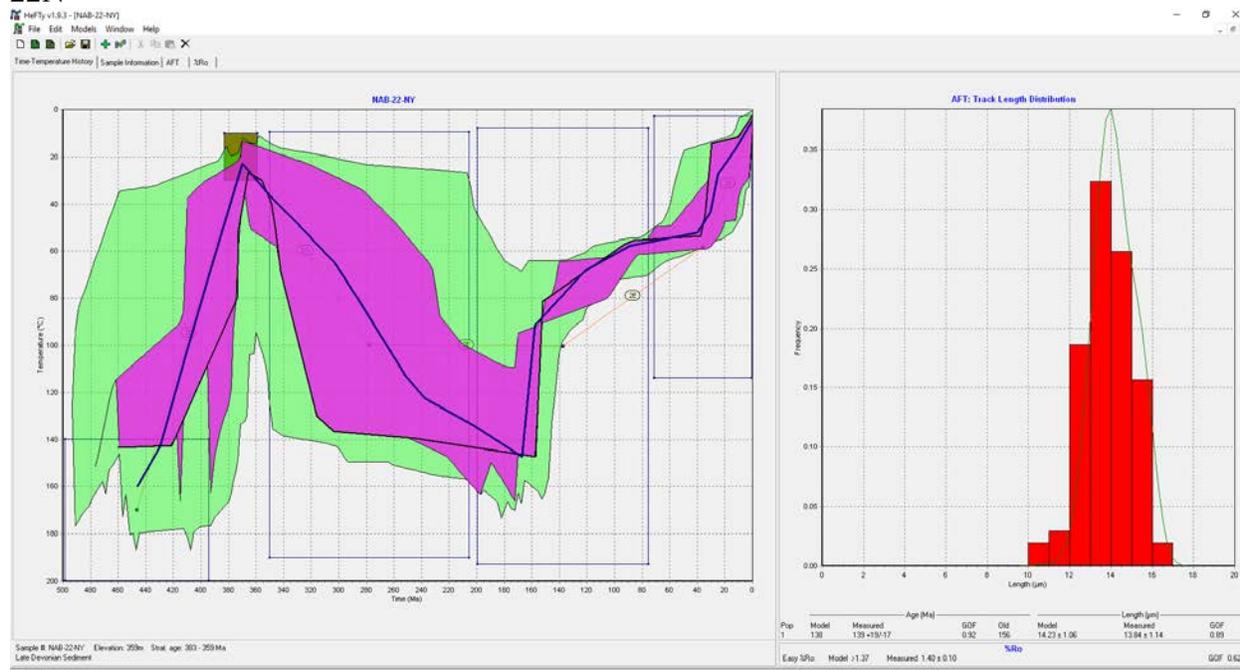
20N



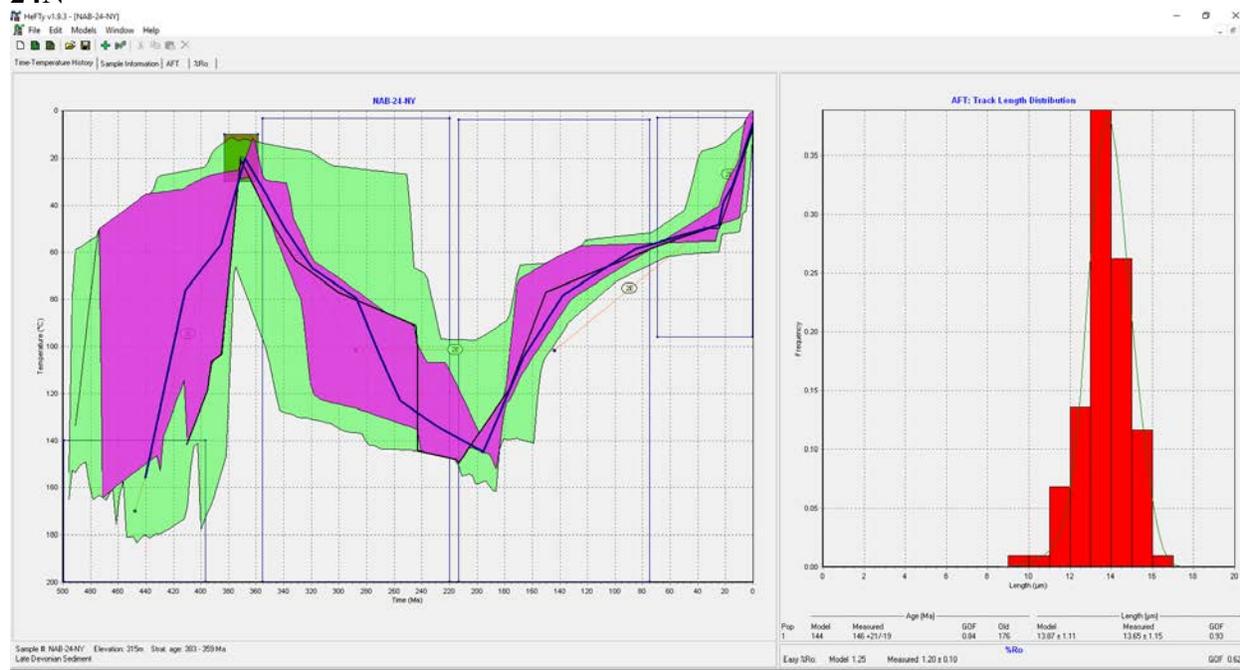
21N



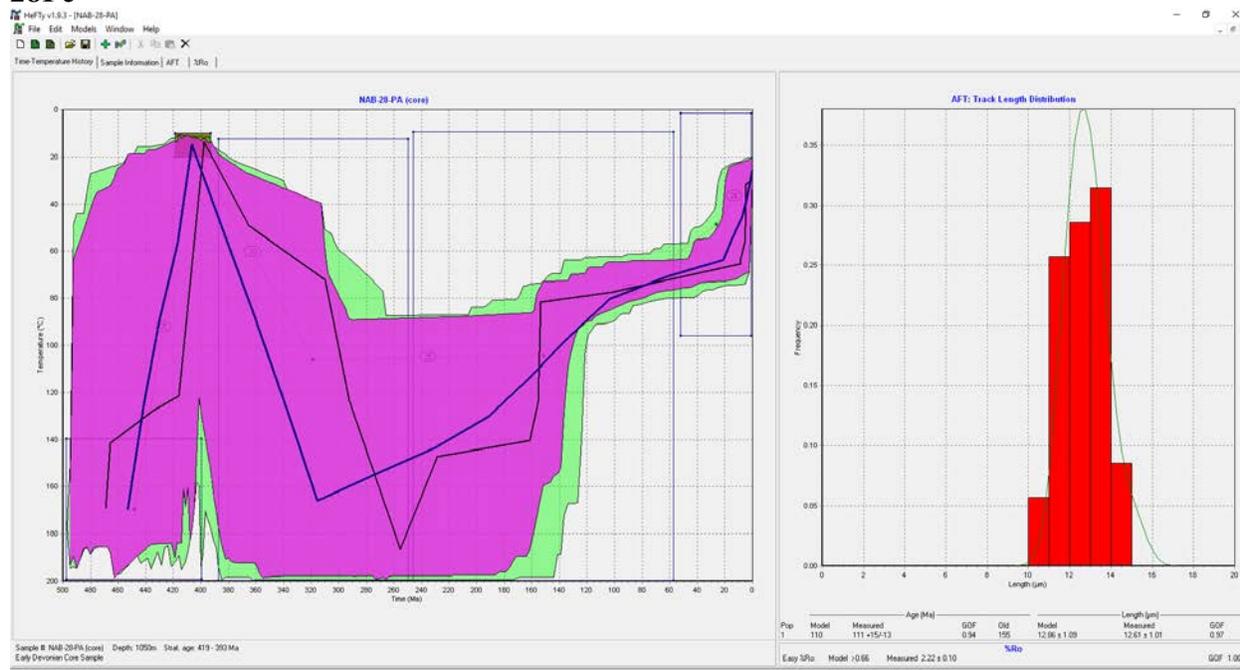
22N



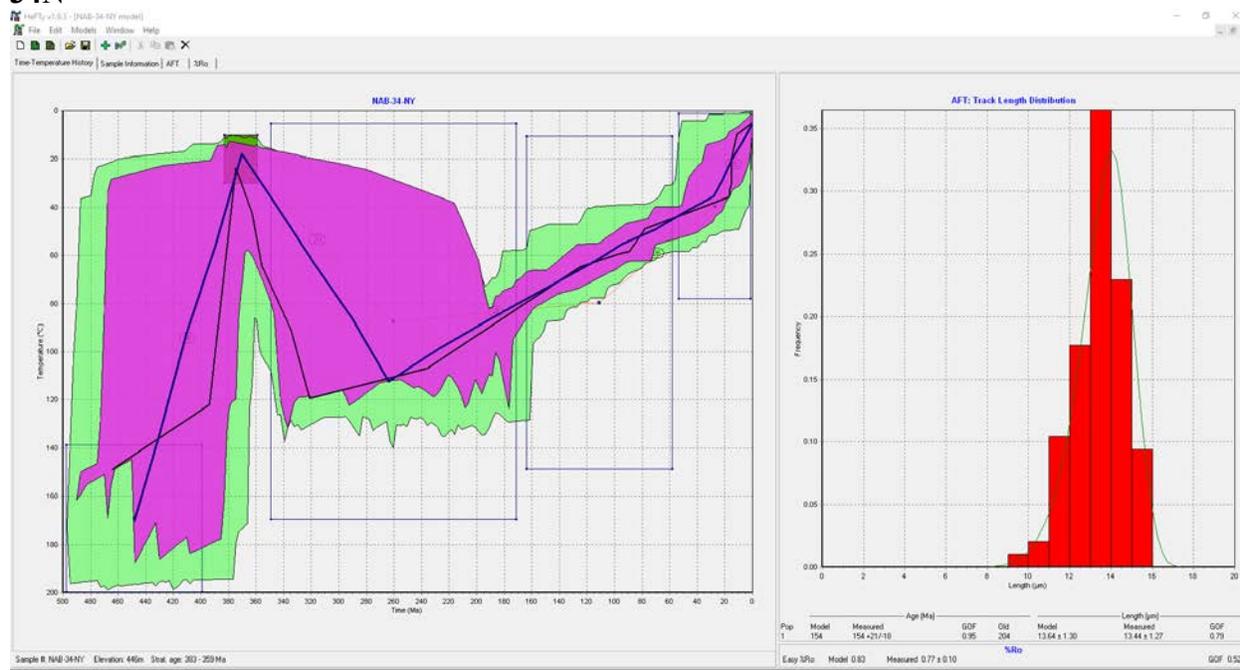
24N



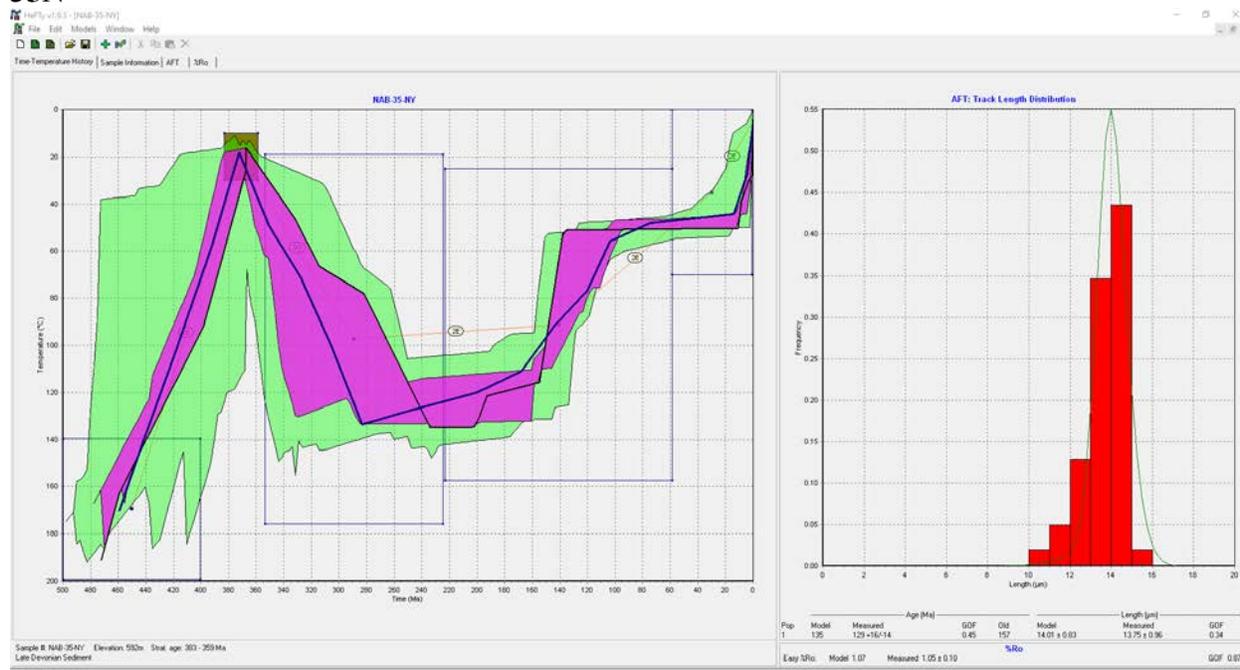
28Pc



34N



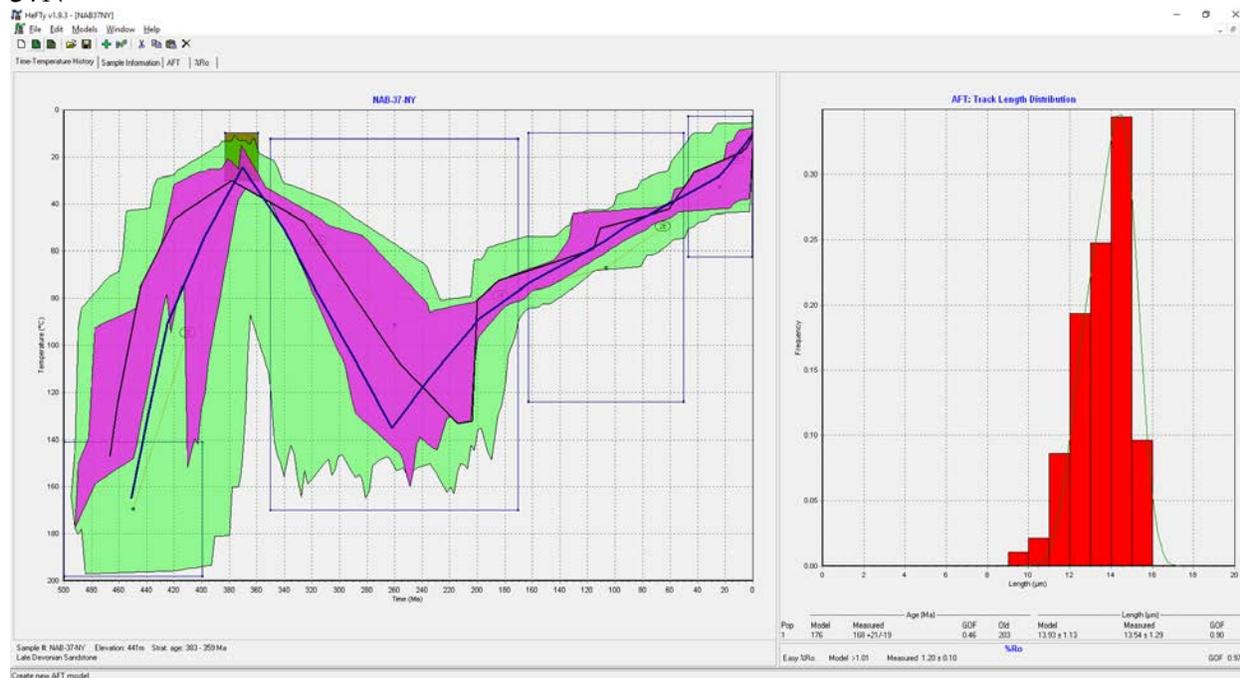
35N



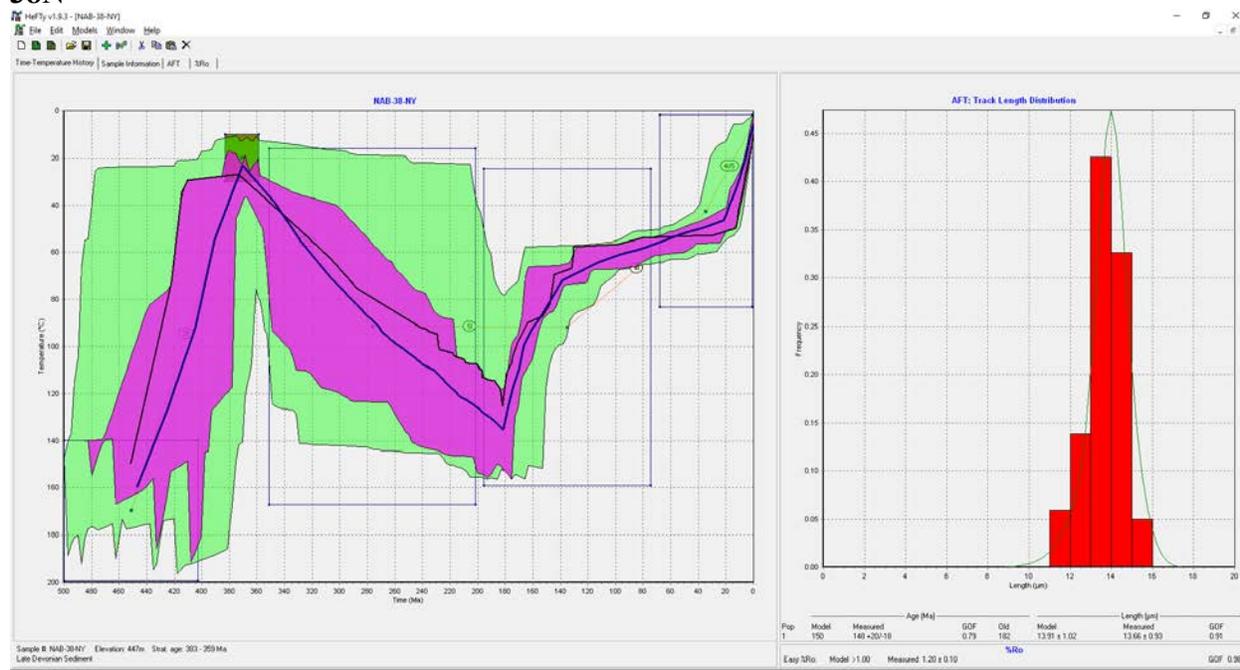
36N



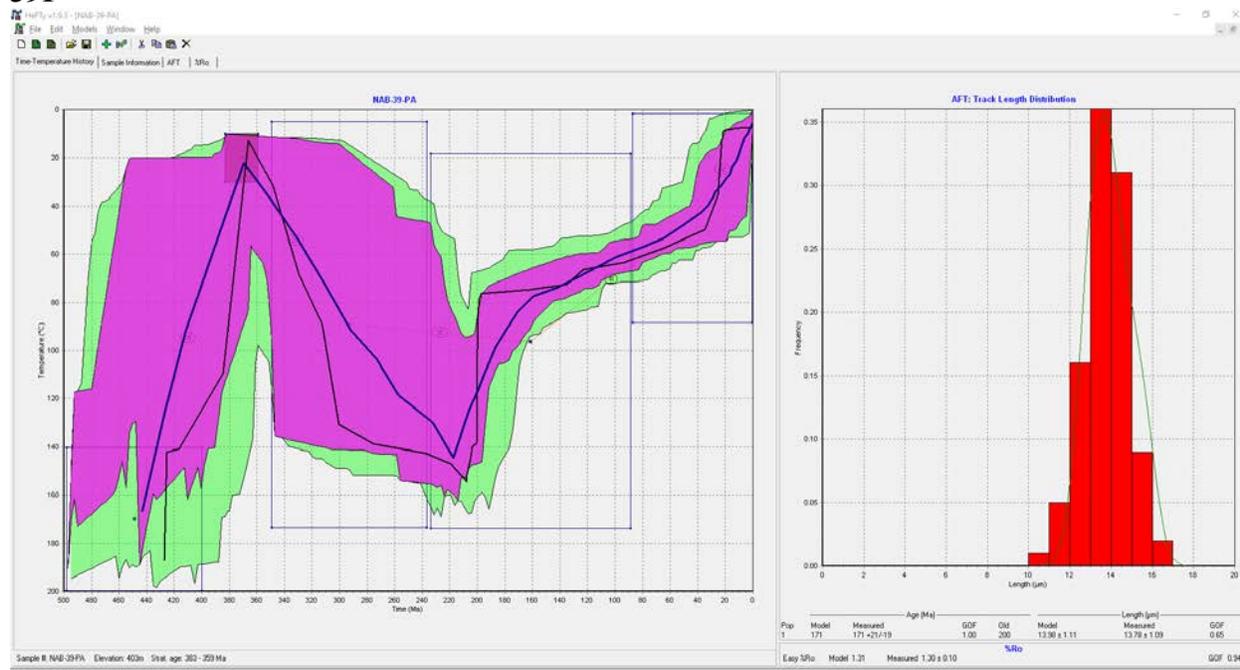
37N



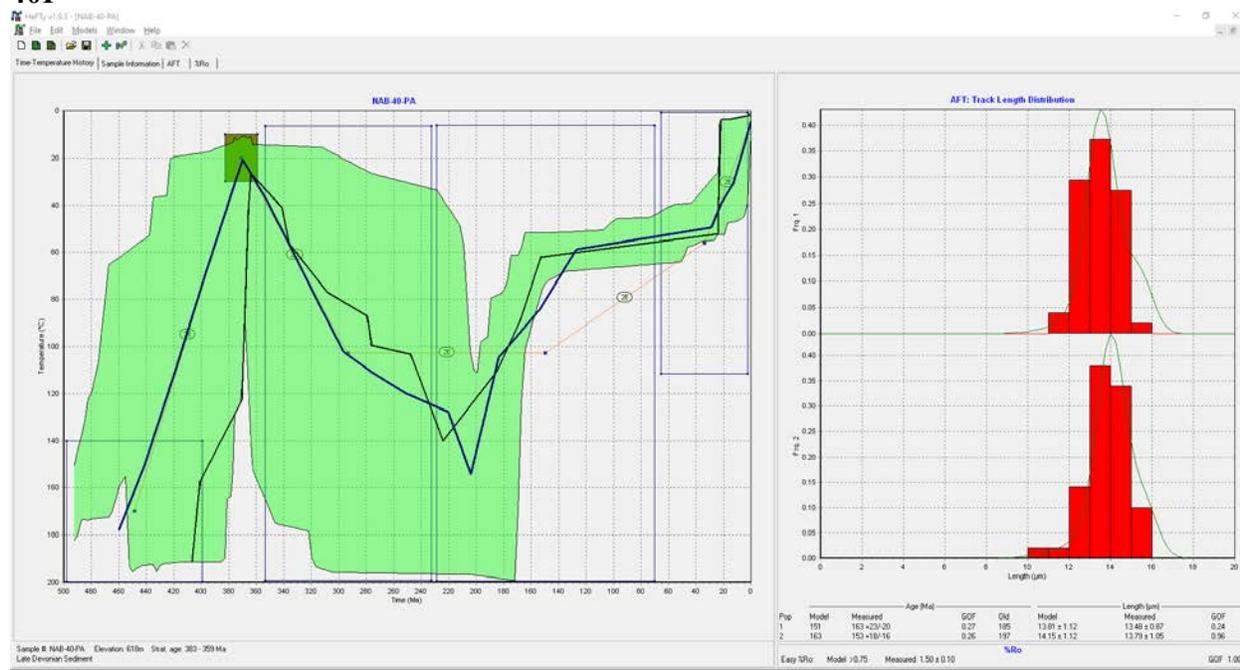
38N



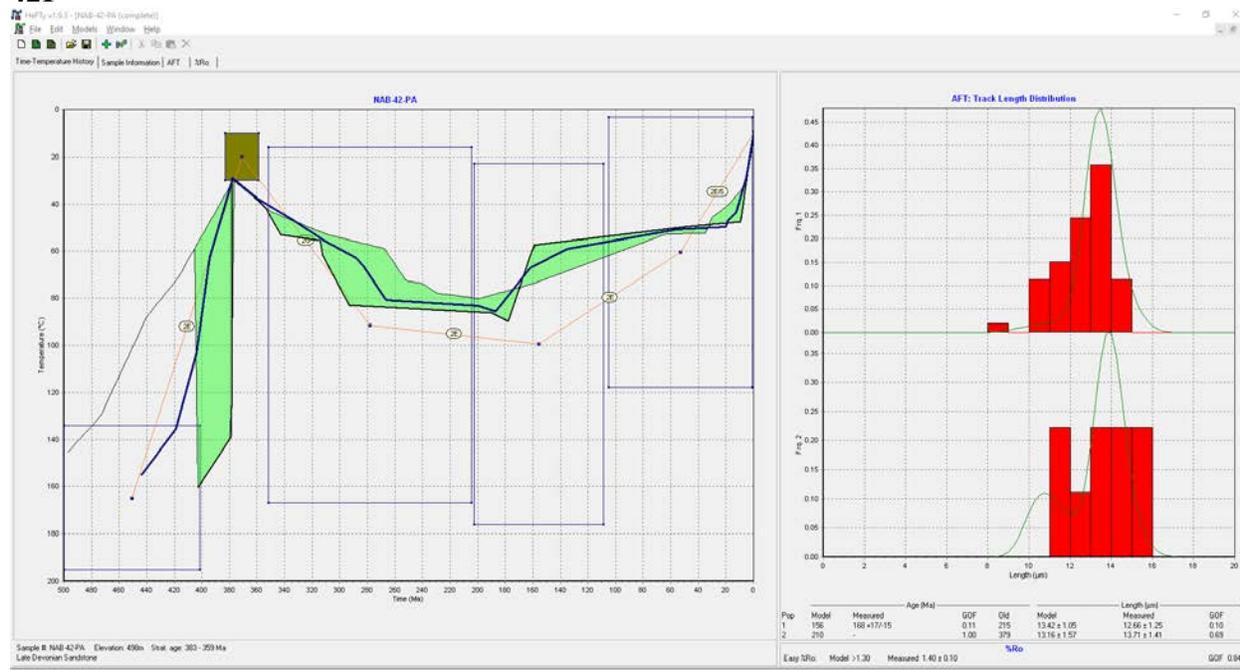
39P



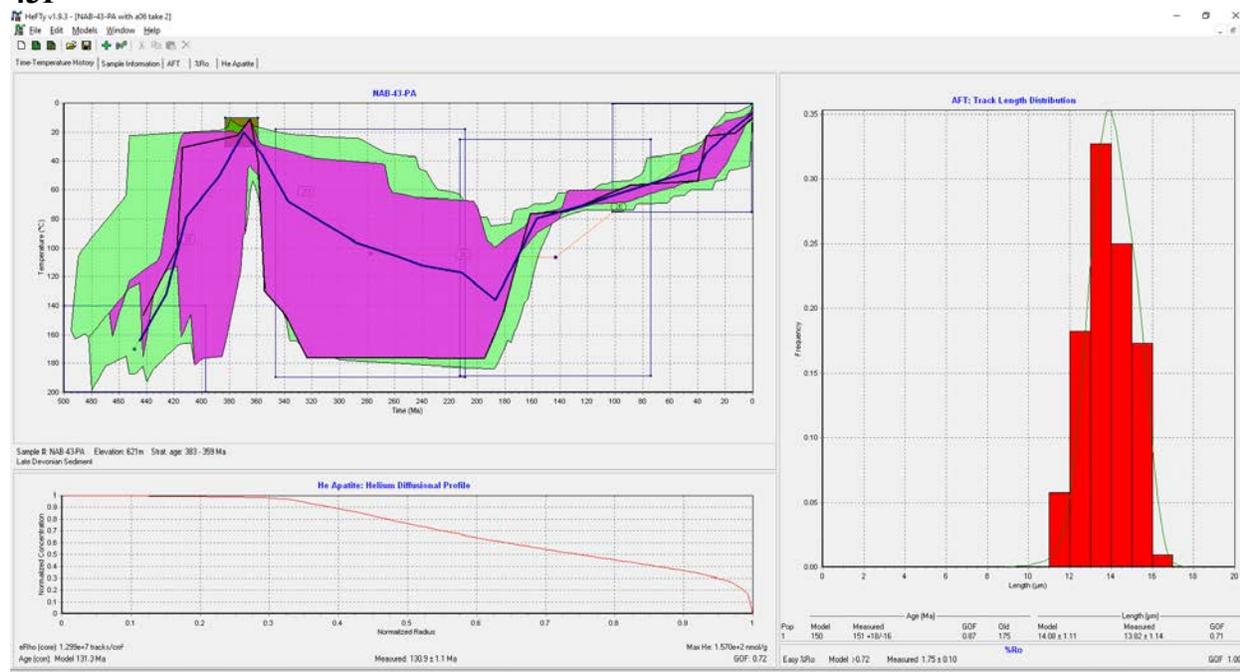
40P



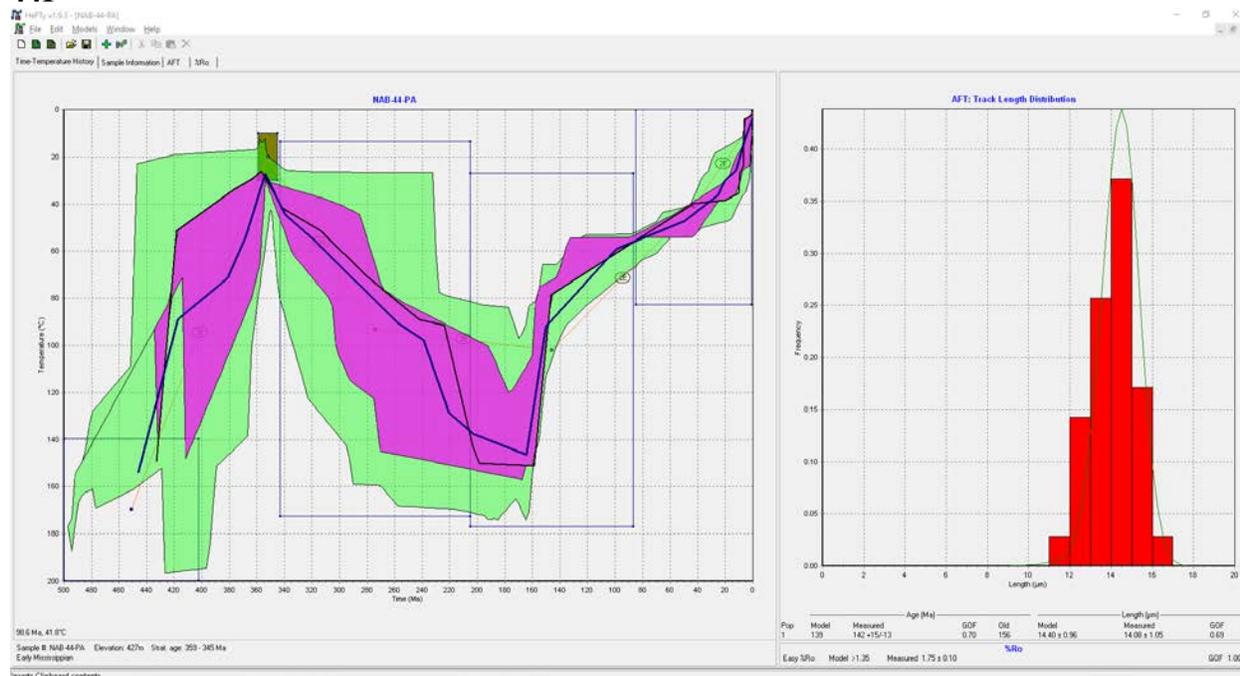
42P



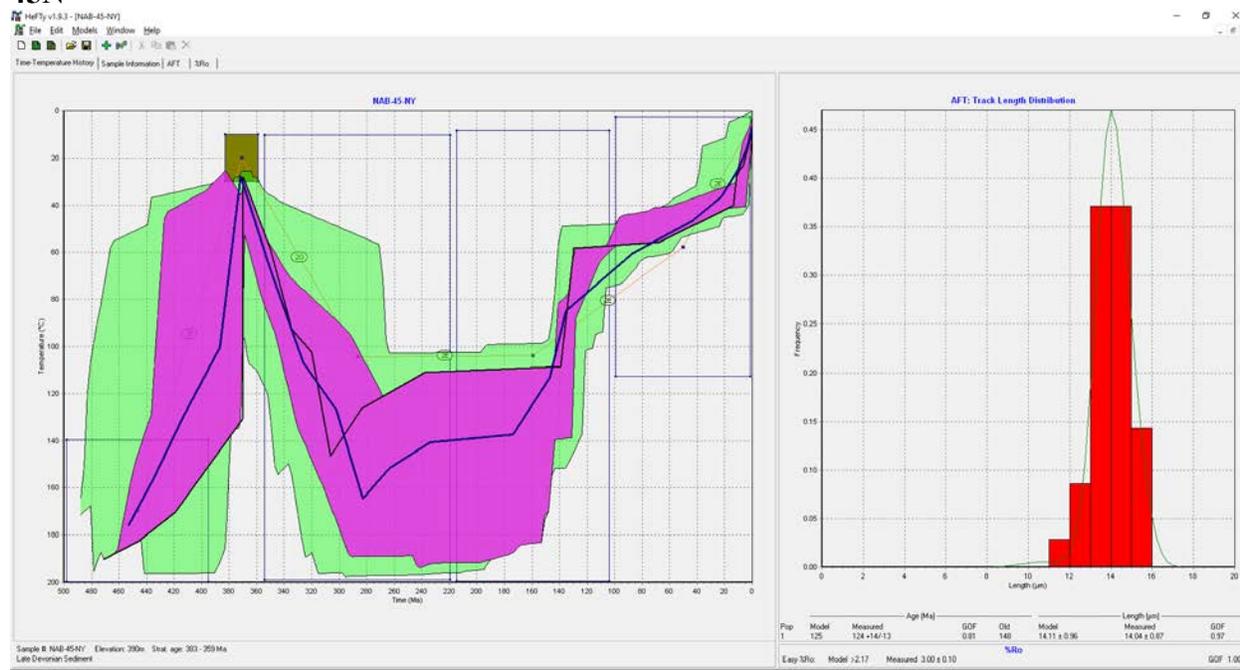
43P



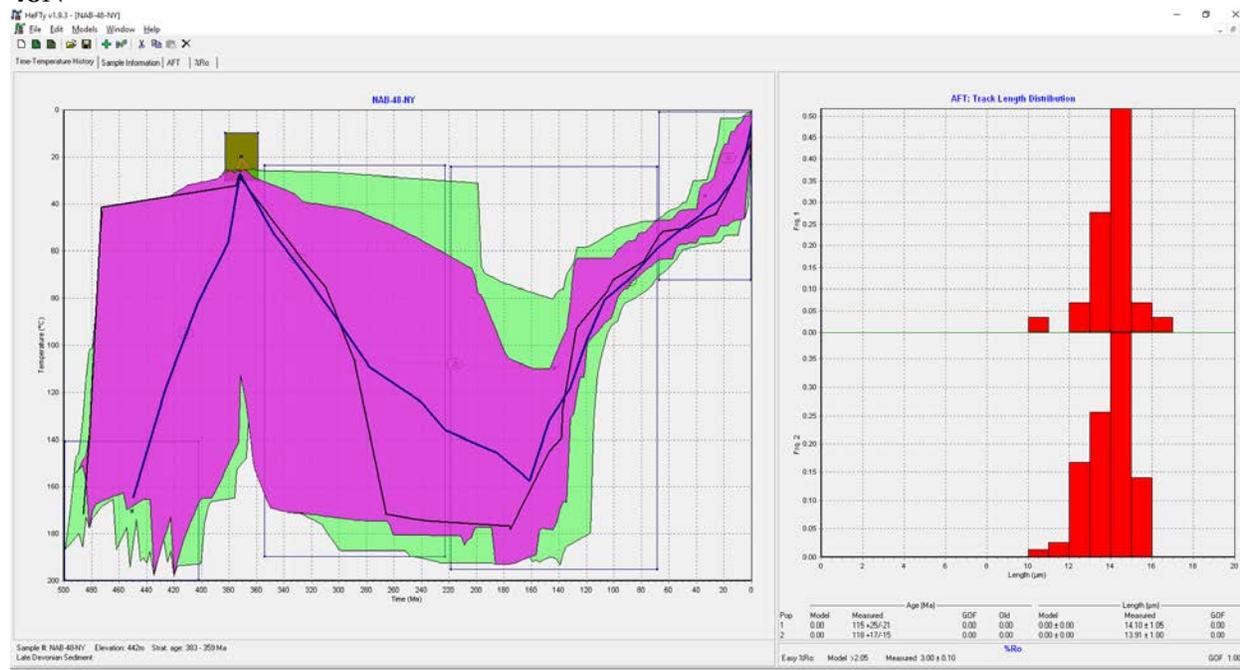
44P



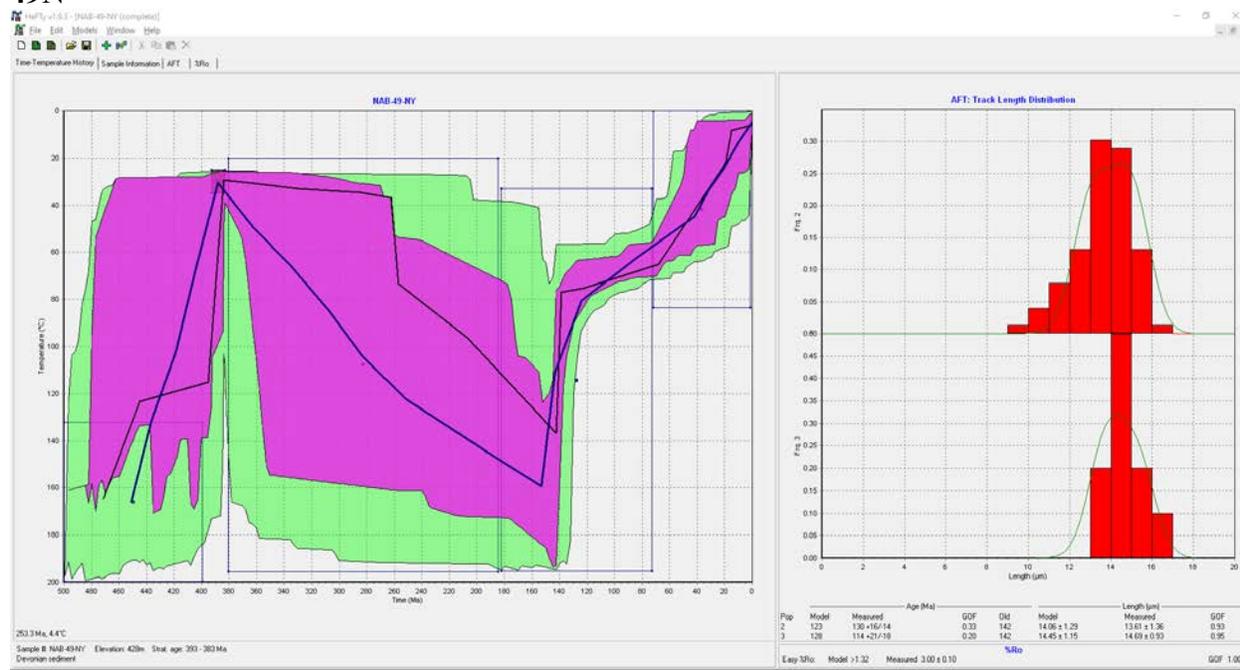
45N



48N



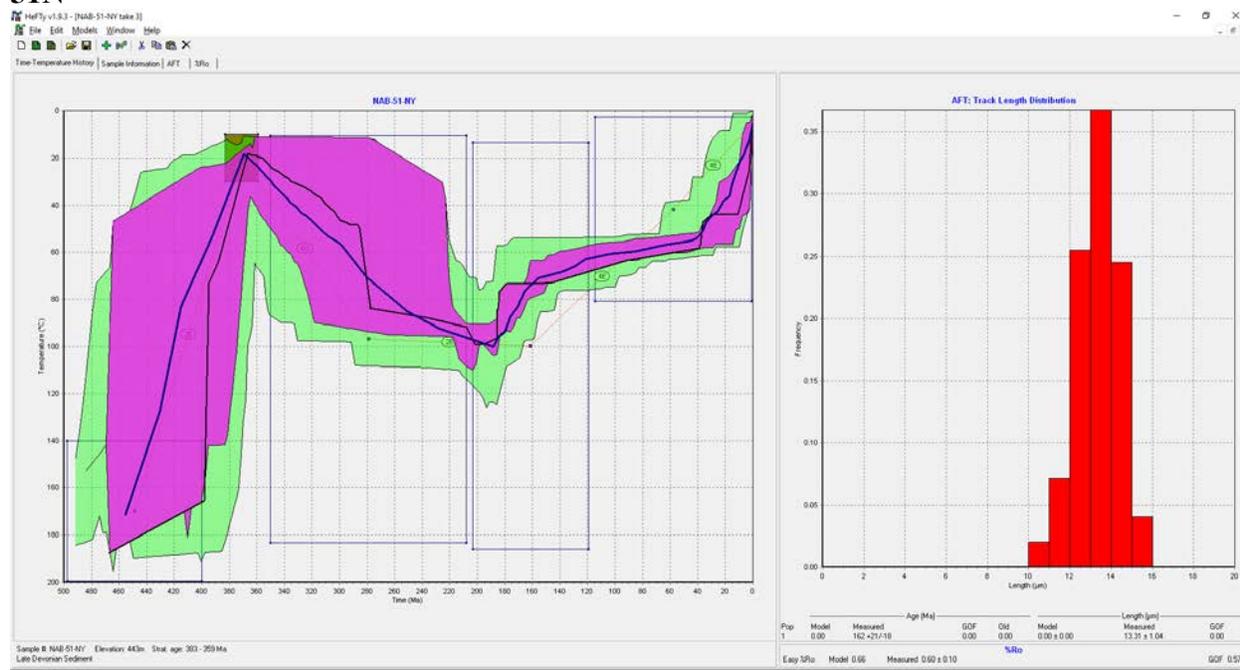
49N



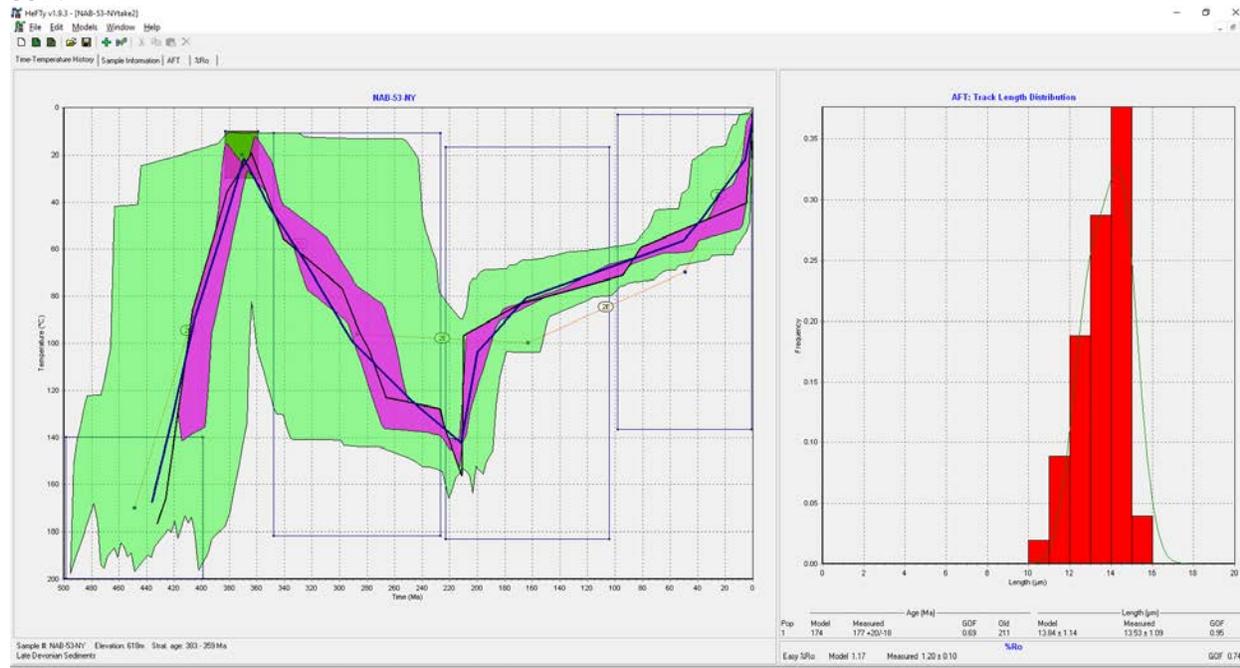
50N



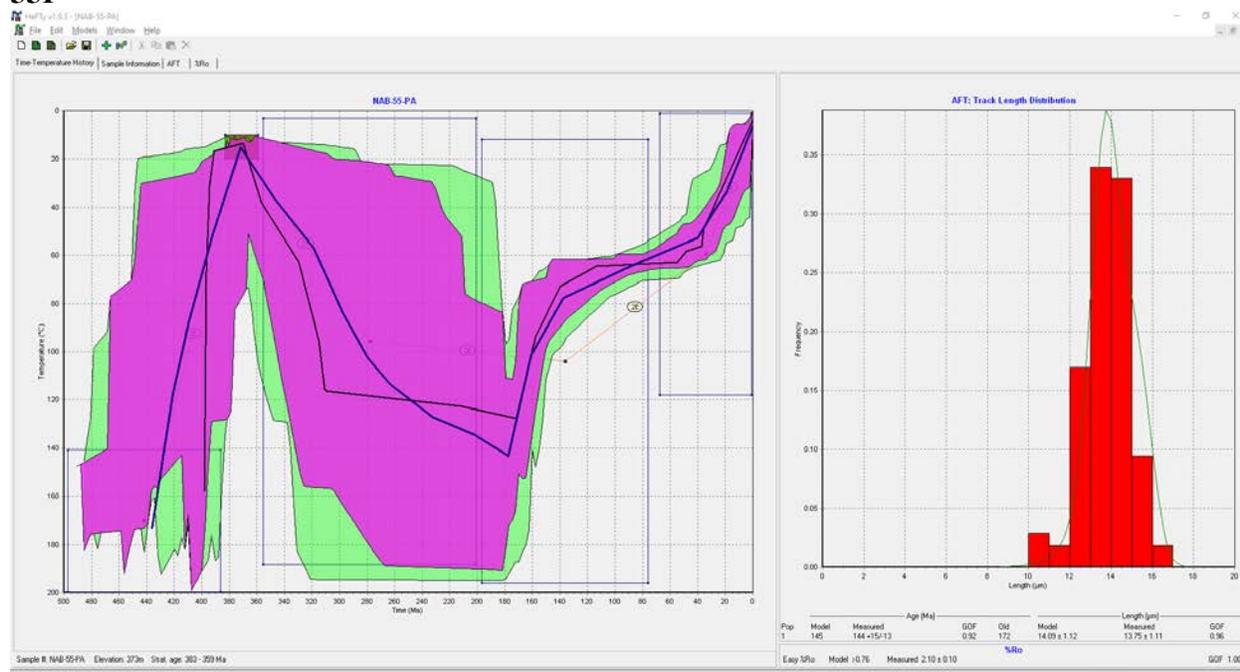
51N



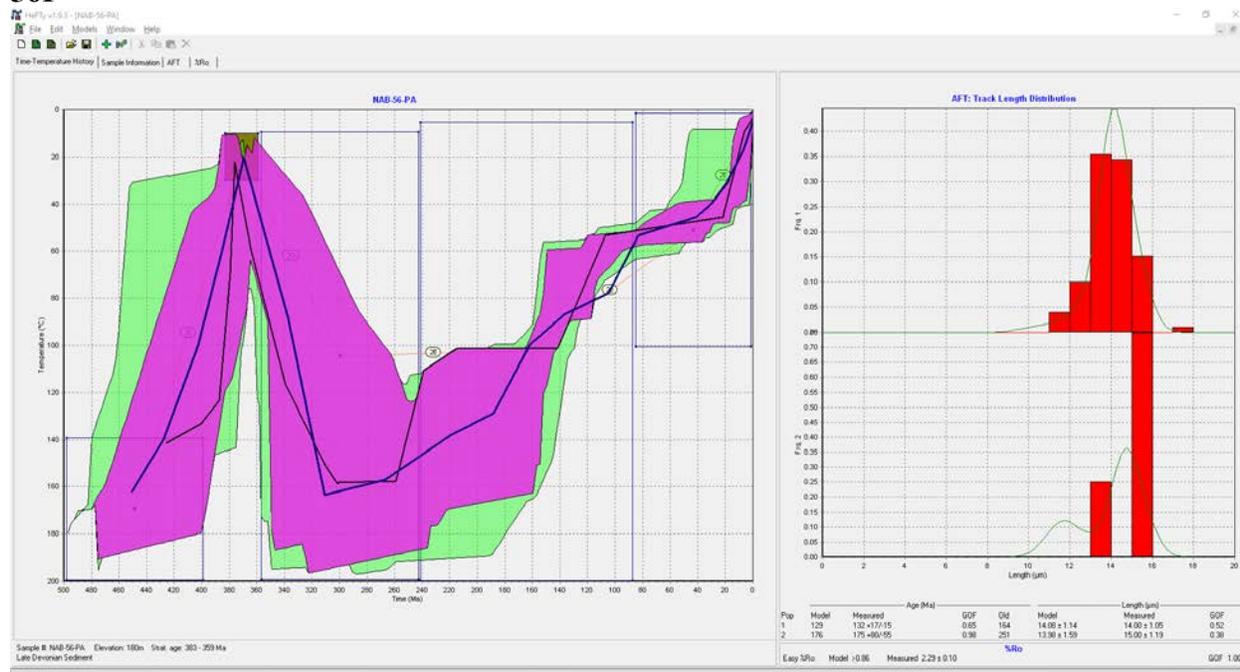
53N



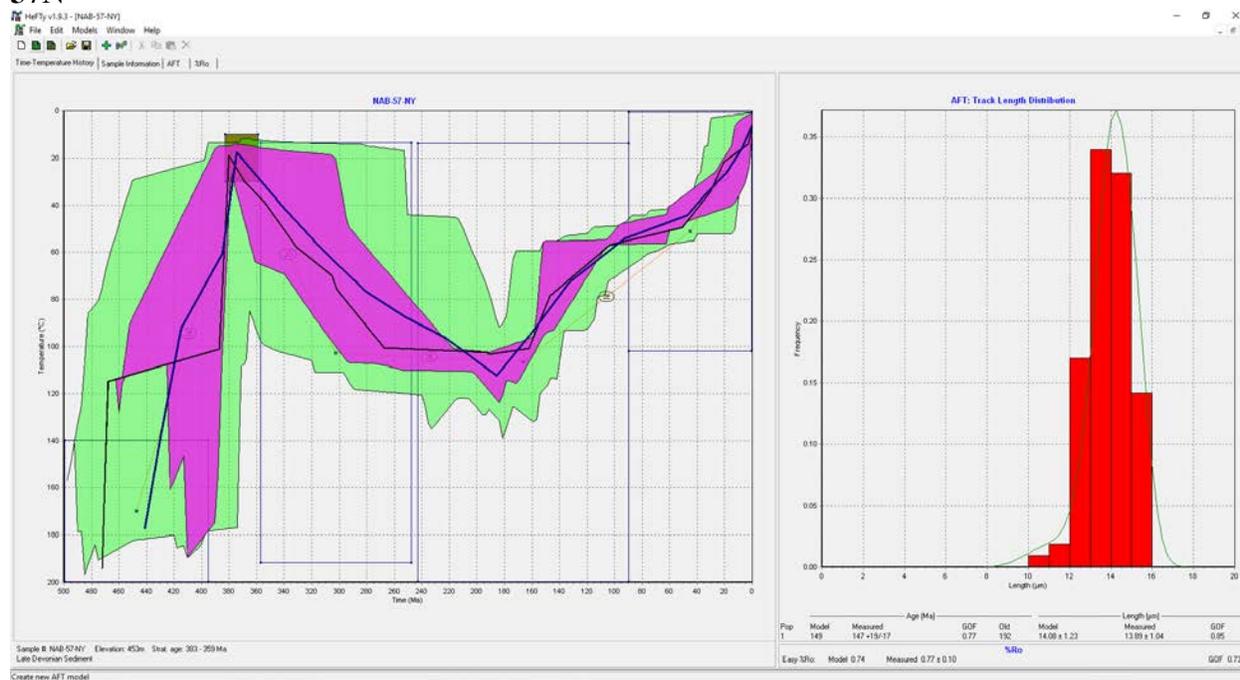
55P



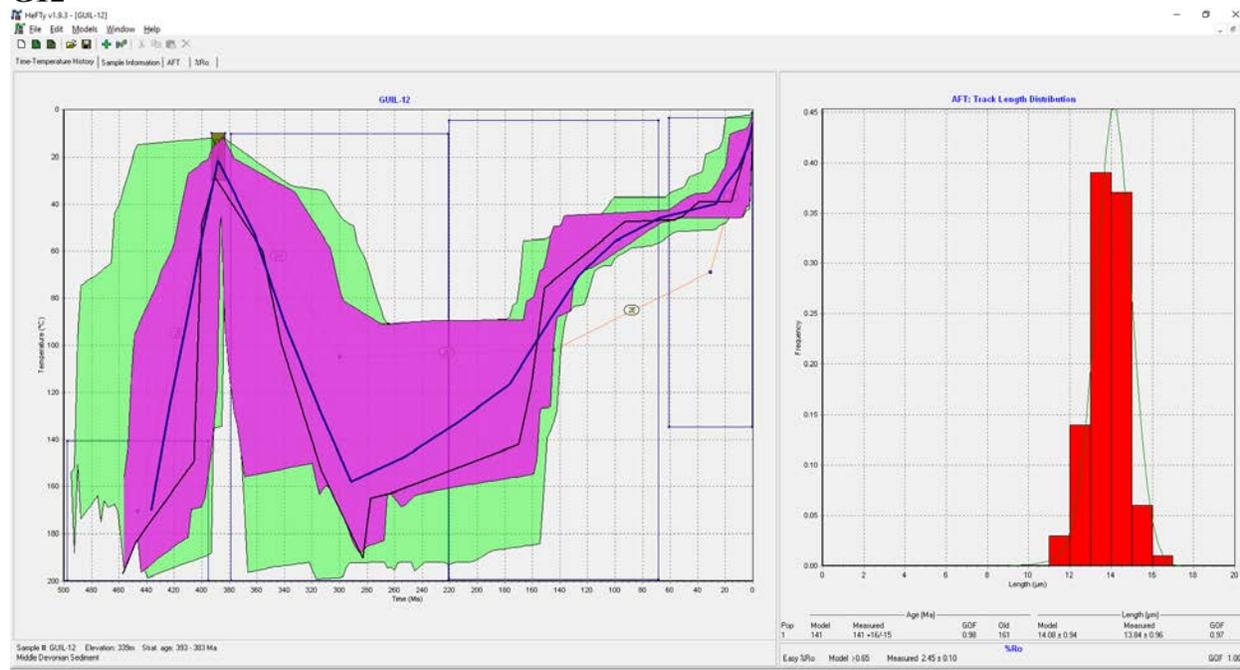
56P



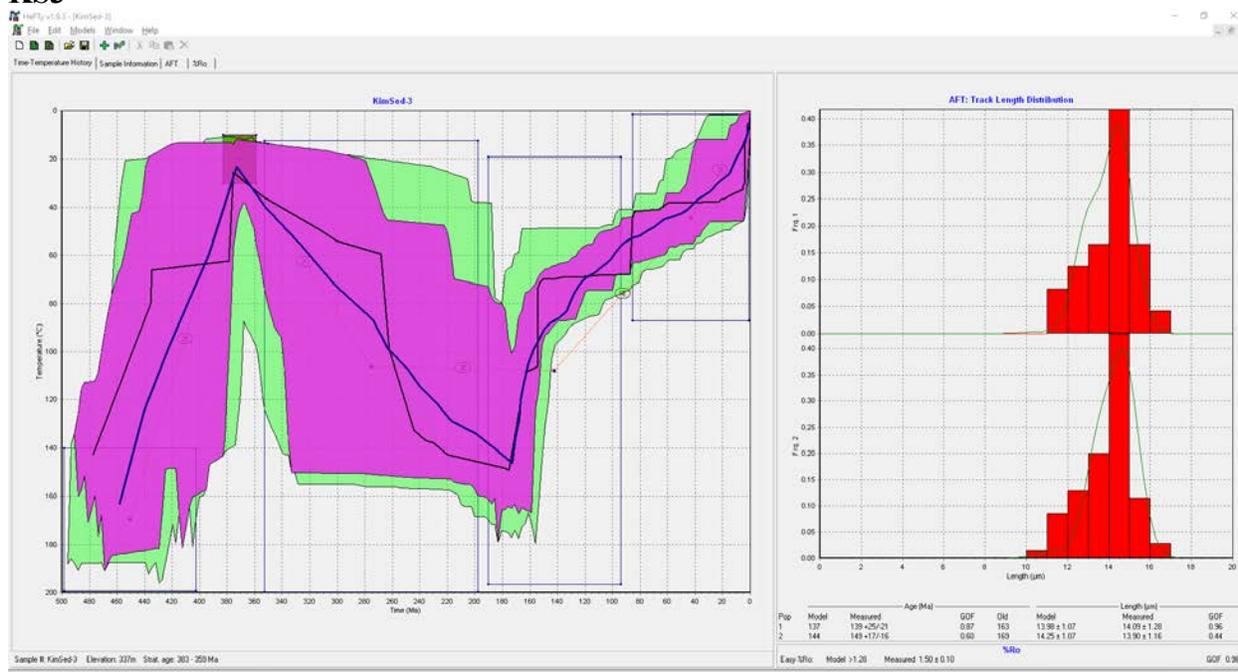
57N



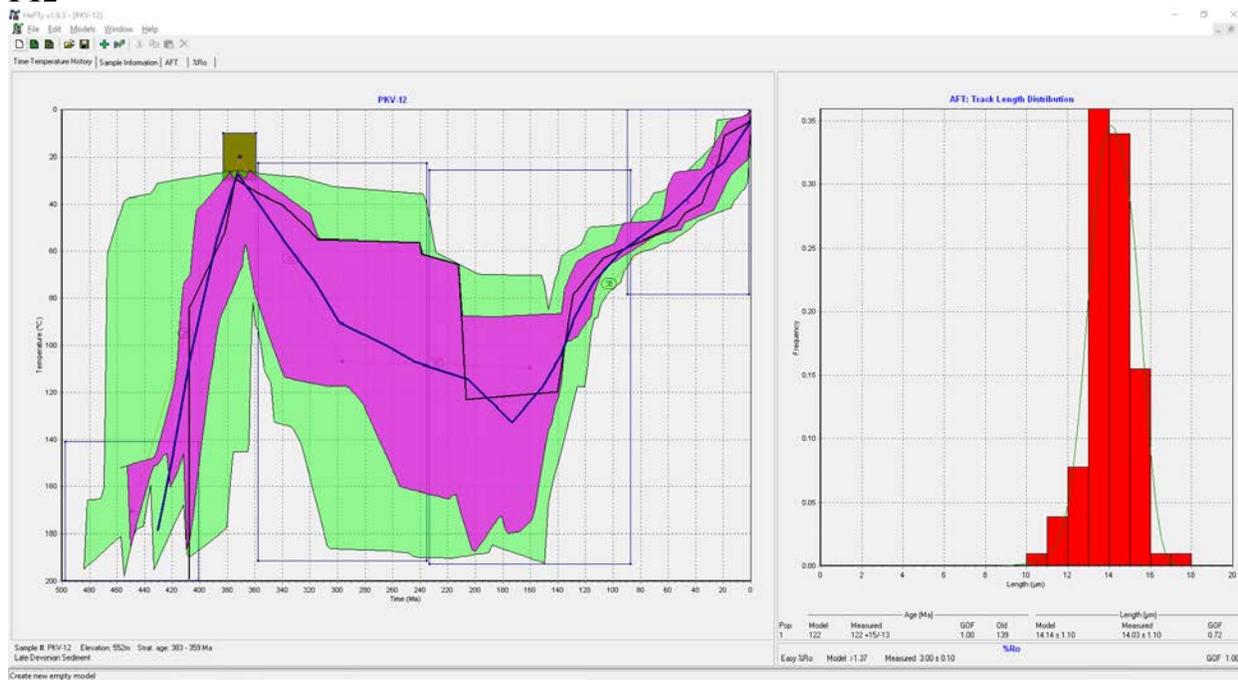
G12



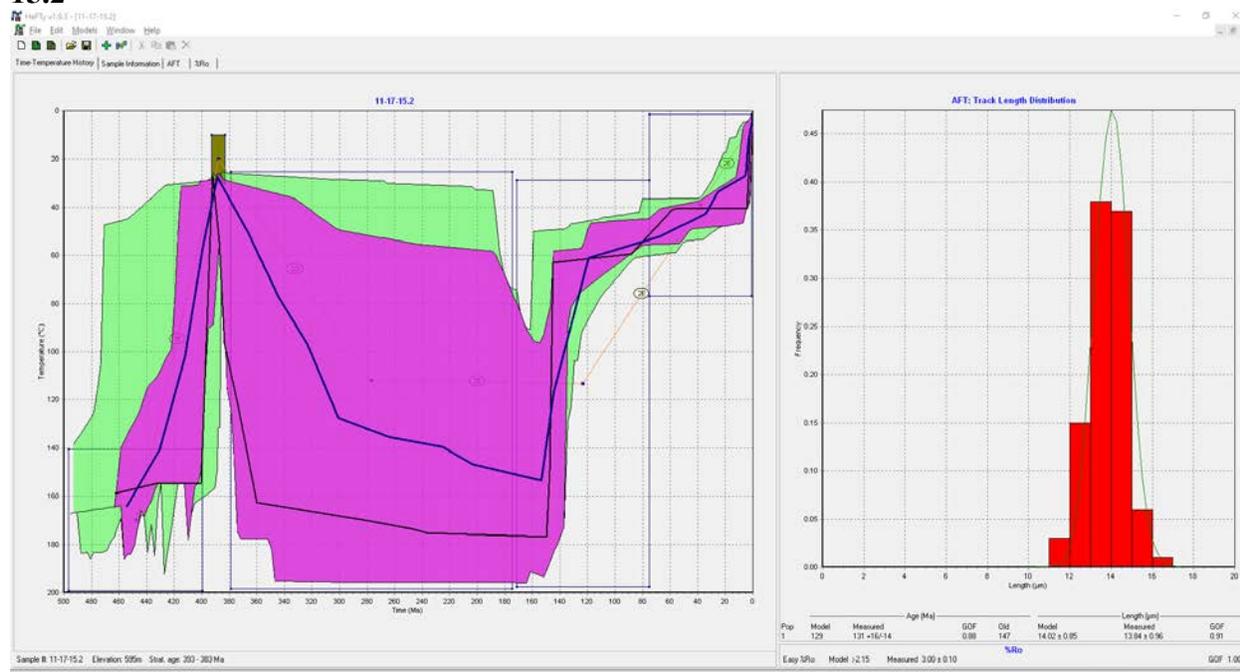
KS3



P12

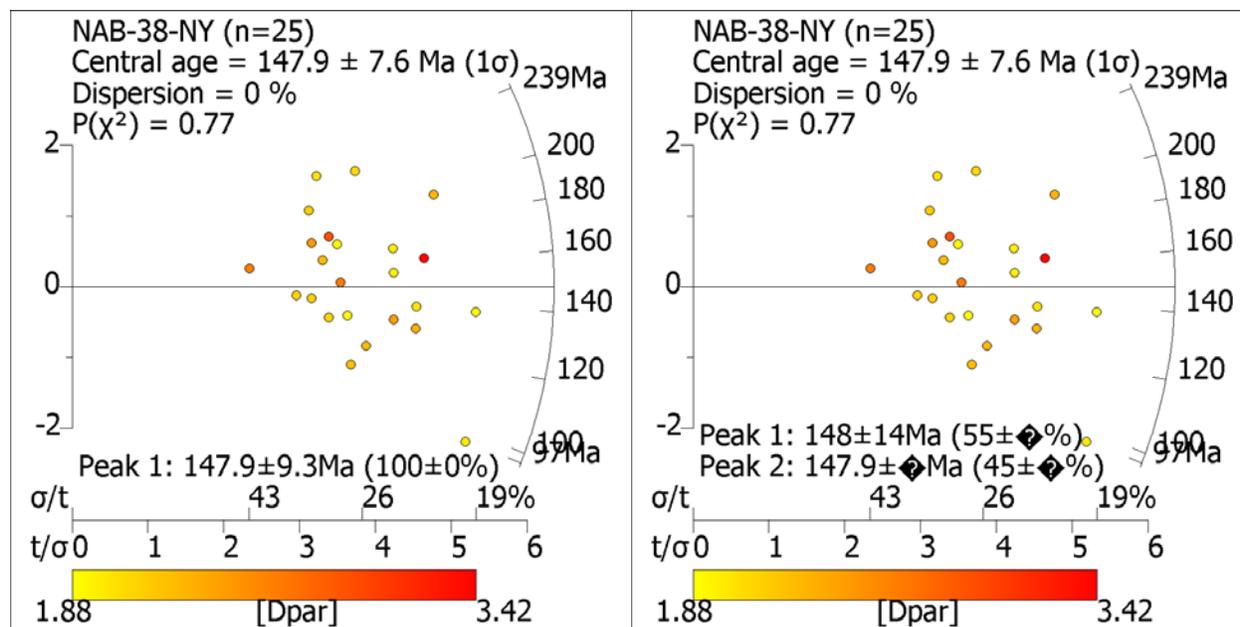


15.2



Supplementary File C. Radial Plots

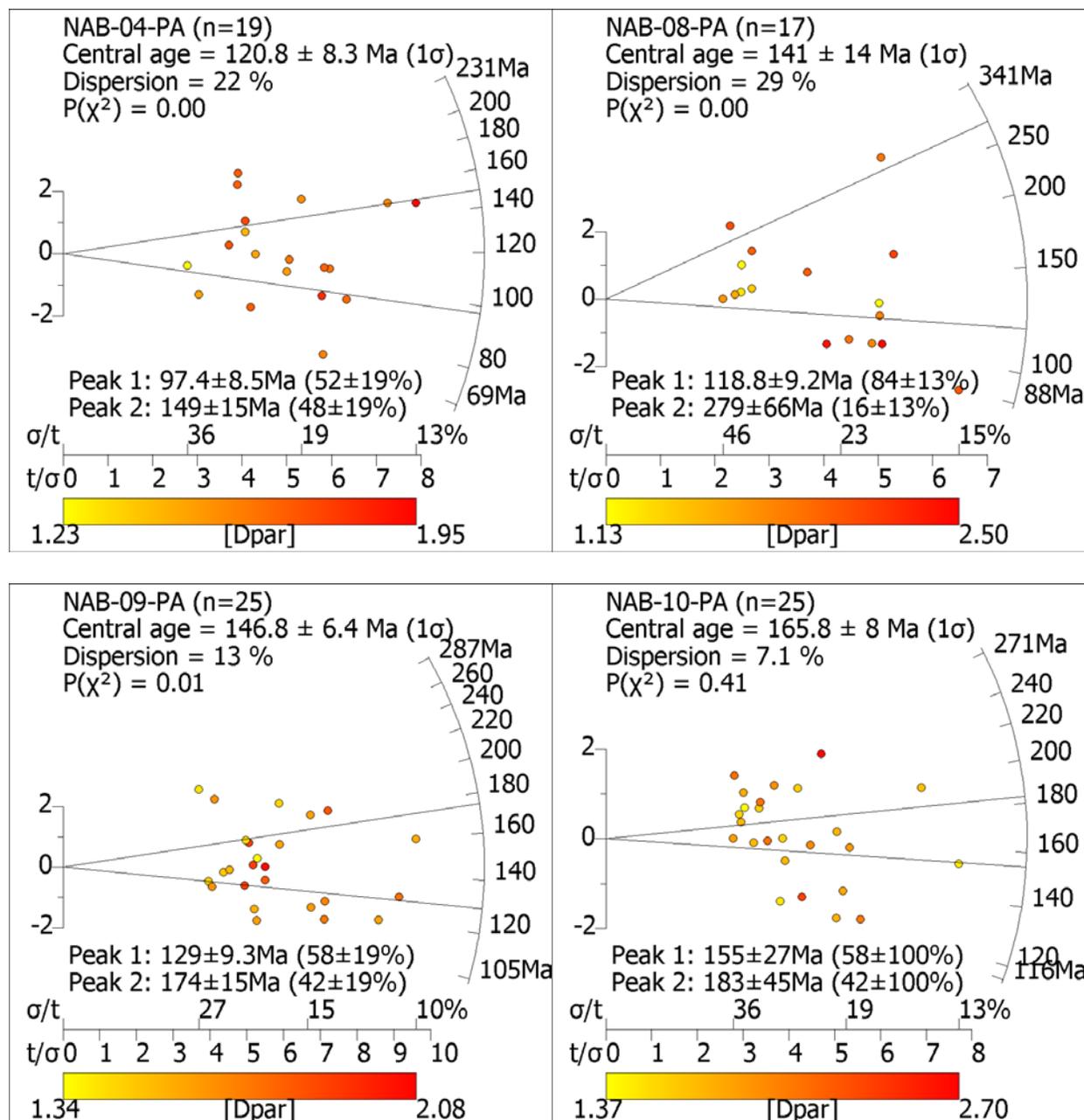
It is common for detrital samples, such as this study's Devonian sandstone samples, to exhibit single-grain AFT age dispersion and contain multiple kinetic populations. Radial plots are a useful tool for displaying single-grain ages, analytical uncertainties and measurement precision (i.e. standard error; Galbraith, 1990). As stated in chapter 1, RadialPlotter (Vermeesch, 2008) was used to visualize the age spread and determine multiple kinetic populations on samples which failed the χ^2 test. Samples which passed the χ^2 test were not input into RadialPlotter as their radial plots would only constrain a single population or, if forced to constrain multiple populations, would result in populations of similar age (example below).

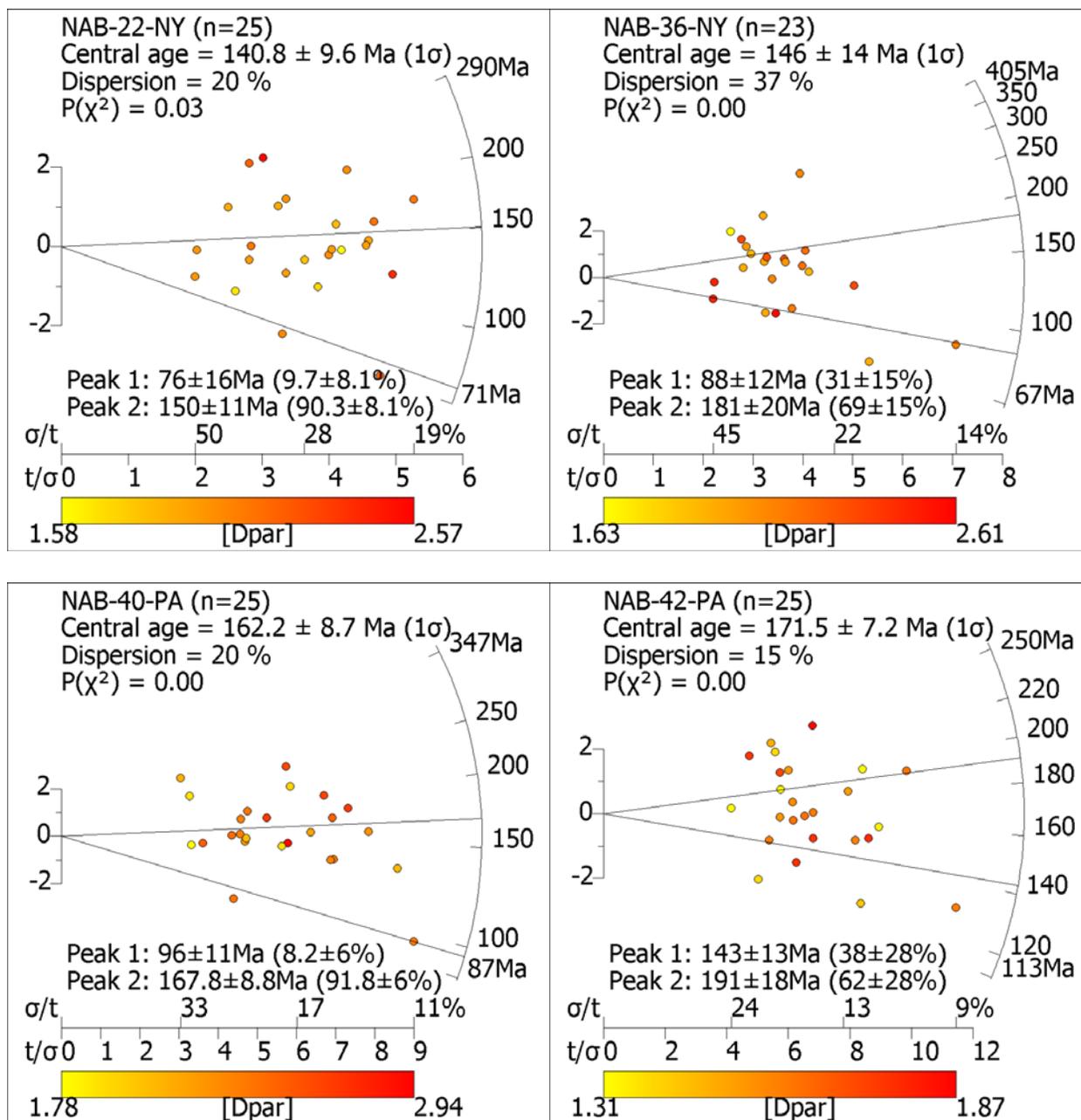


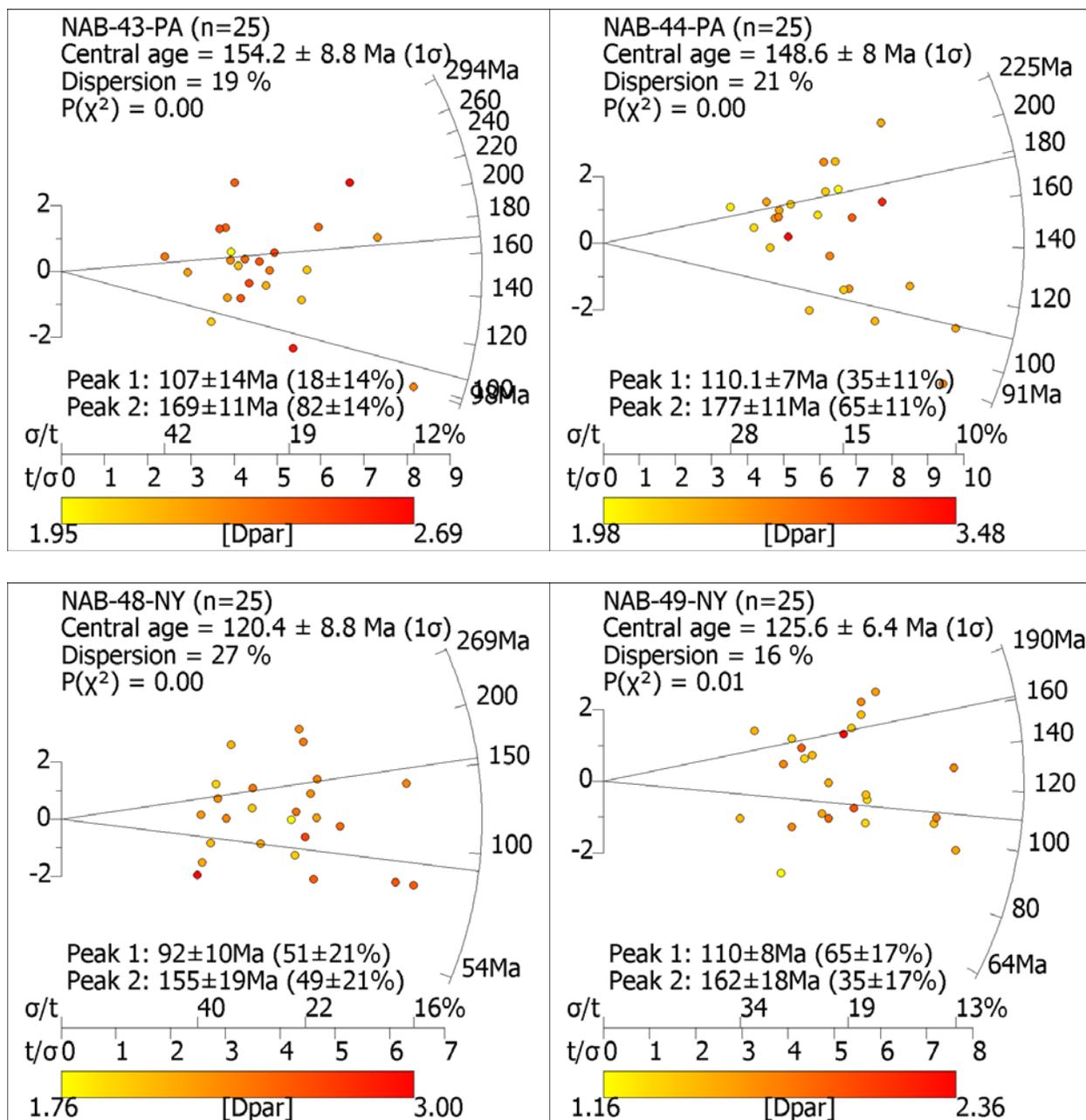
Example of radial plotting a sample (38N) which passed the χ^2 test (76.7 %). The plot on the right was allowed to automatically generate populations while the plot on the left was forced to produce two populations.

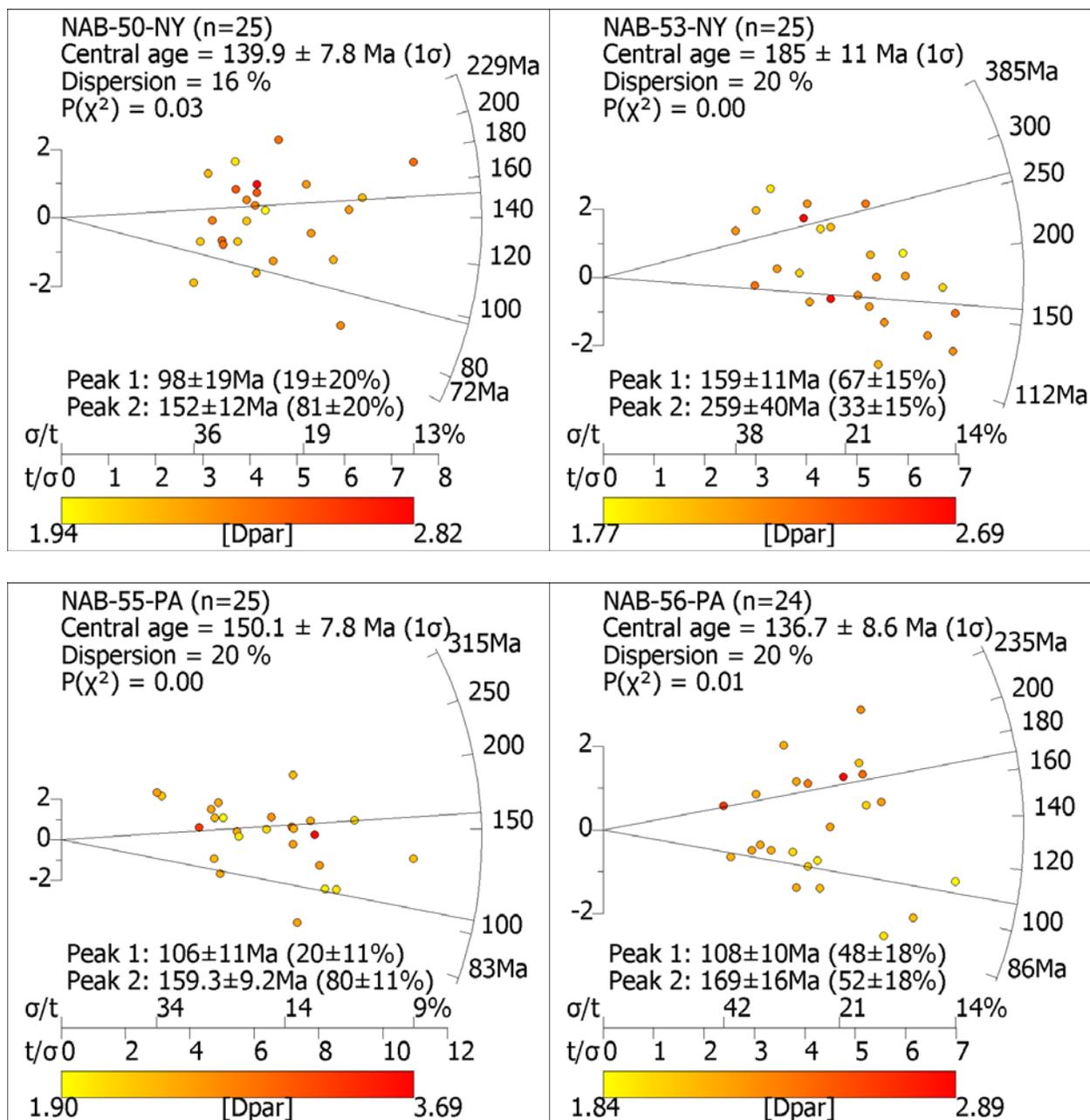
RadialPlotter automatically determined mixture models and generally produced two kinetic populations in samples which did not pass the χ^2 test (see Table 1 for χ^2 percentages). This information was utilized in inverse thermal modeling program HeFTy (Ketcham, 2005) to

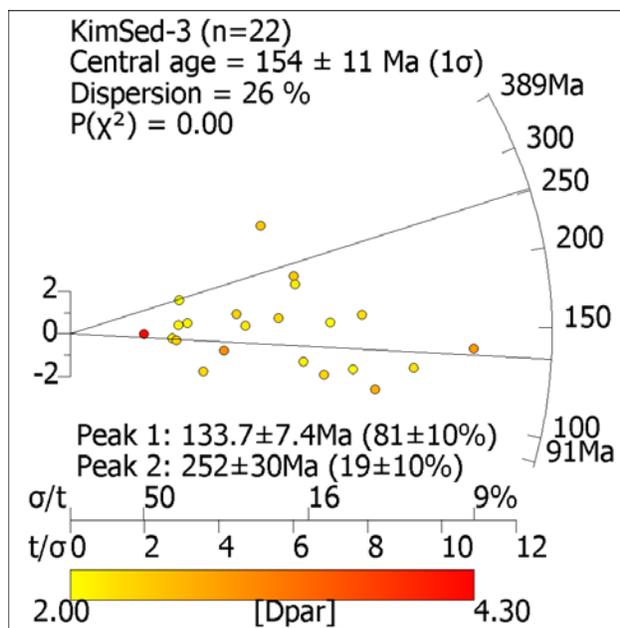
define kinetic populations. Below are the radial plots of the 17 samples which did not pass the χ^2 test, displayed in numerical order.





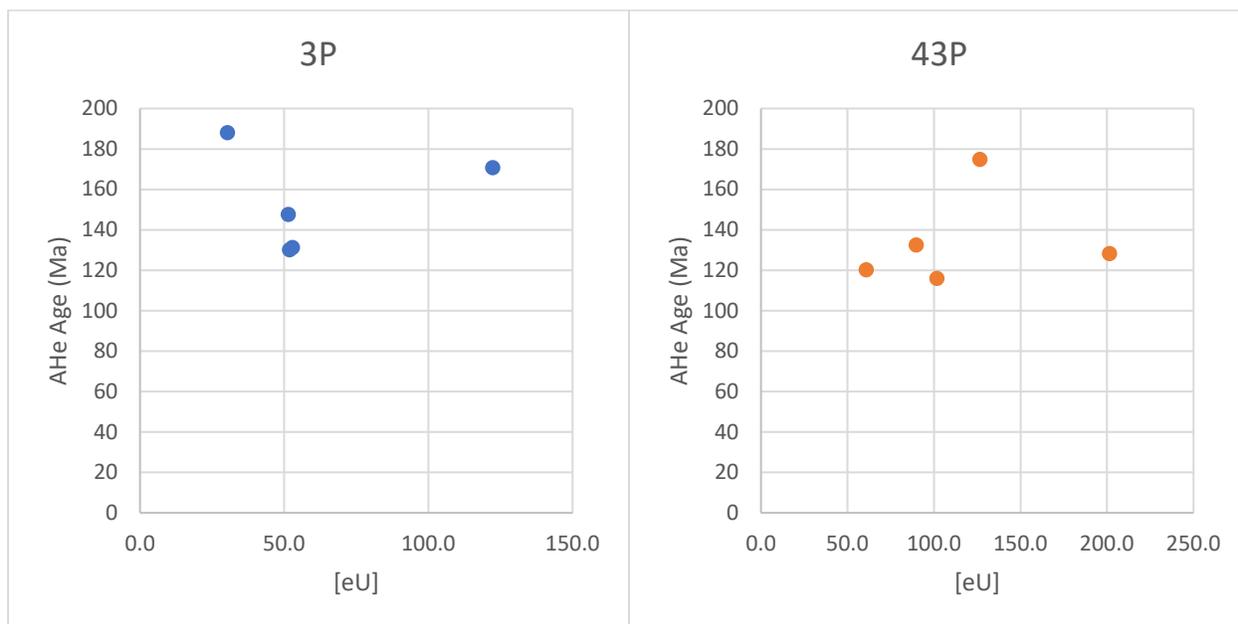




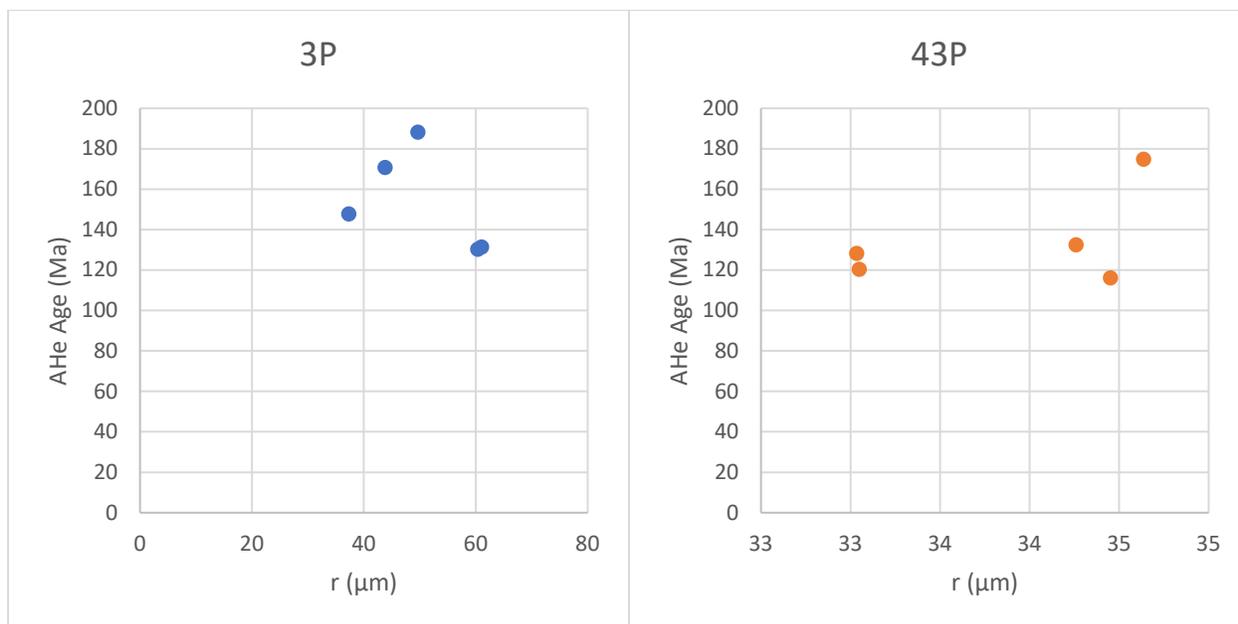


Supplementary File D. Apatite (U-Th)/He Dating

As discussed in AHe Data section of Chapter 1, AHe single-grain ages vs. [eU] display weakly negative to no trend.



AHe single-grain ages vs. grain size (approximated by “r”: radius of a sphere with an equivalent surface area to volume ratio as the apatite grain) display a weakly positive trend.



Supplementary File E. Shorten's Zeta Calibration

Apatite age standards (Fish Canyon Tuff, Durango, and Mt. Dromedary apatite) were counted to determine a personal zeta age calibration factor for fission-track dating (e.g. Hurford and Green, 1983). Before counting fission-tracks in apatite to familiarize Shorten with fission-track recognition and counting techniques, track densities in 6 external mica detectors of standard glasses (CN1, CN2 and CN5) were counted. Track densities counted from standard glasses were compared to those obtained by experienced fission-track workers at Syracuse University (e.g. Paul Fitzgerald and Paul O'Sullivan).

The zeta calibration results are listed in Table E1 and graphed in Fig. E2. A sample weighed mean zeta (the weighted mean of all determinations for each age standard) of 366 ± 35 was determined for the Fish Canyon Tuff apatite, 356 ± 10 for Durango apatite and 345 ± 26 for the Mt. Dromedary apatite. An overall weighted mean zeta of 356 ± 13 ($\pm 1\sigma$) was used when determining unknown apatite ages.

Table E1. Individual zeta determinations and SWMZ values for age standard apatites

| Age standard (Age $\pm 2\sigma$) and apatite mount ID | No. of Grains | Standard Track Density ($\times 10^6\text{cm}^{-2}$) | Spontaneous Track Density ($\times 10^6\text{cm}^{-2}$) | Induced Track Density ($\times 10^6\text{cm}^{-2}$) | χ^2 prob. (%) | Var. (%) | Zeta ($\pm 1\sigma$) |
|---|------------------|---|--|--|--------------------------|-------------|------------------------|
| Fish Canyon Tuff (27.8 ± 0.5 Ma) | | | | | | | |
| UA009-02 (FCT-11) | 25 | 1.702 (5675) | 0.1805 (256) | 2.034 (2885) | 99.7 | 0 | 369 ± 25 |
| UA011-01 (FCT-14) | 25 | 1.72 (5554) | 0.1958 (276) | 2.317 (3267) | 93.6 | 0 | 383 ± 25 |
| UA013-01 (FCT-3a) | 25 | 1.967 (6475) | 0.2132 (306) | 2.537 (3640) | 75.6 | 0 | 337 ± 21 |
| SWMZ = 366 ± 35 | | | | | | | |
| Durango (31.4 ± 0.5 Ma) | | | | | | | |
| UA009-01 (DUR-4) | 29 | 1.69 (5675) | 0.2205 (297) | 2.21 (2976) | 22.1 | 1 | 373 ± 24 |
| UA009-11 (DUR-6a) | 28 | 1.805 (5675) | 0.2053 (362) | 2.08 (3669) | 80.8 | 0 | 353 ± 21 |
| UA009-12 (DUR-6b) | 25 | 1.816 (5675) | 0.2386 (378) | 2.369 (3753) | 66.4 | 0 | 344 ± 20 |
| UA009-13 (DUR-7b) | 25 | 1.827 (5675) | 0.2319 (361) | 2.407 (3746) | 65.9 | 0 | 358 ± 21 |
| SWMZ = 356 ± 10 | | | | | | | |
| Mt Dromedary (98.7 ± 0.5 Ma) | | | | | | | |
| UA009-03 (DROM-2b) | 25 | 1.713 (5675) | 0.9046 (576) | 2.959 (1884) | 6.9 | 15 | 380 ± 19 |
| UA009-04 (DROM-2c) | 25 | 1.725 (5675) | 1.1154 (518) | 3.583 (1664) | 27.6 | 14 | 370 ± 19 |
| UA011-04 (DROM-13a) | 25 | 1.723 (5554) | 1.1413 (577) | 3.248 (1642) | 60.2 | 0 | 329 ± 17 |
| UA011-05 (DROM-13b) | 25 | 1.725 (5554) | 0.917 (499) | 2.758 (1501) | 8.1 | 14 | 347 ± 19 |
| SWMZ = 346 ± 26 | | | | | | | |
| OWMZ = 356 ± 13 | | | | | | | |

Brackets show number (no.) of tracks counted. Standard and induced track densities measured on mica external detectors ($g=0.5$) and spontaneous tracks densities on internal mineral surfaces ($g=1$). All samples pass the chi-squared test, with probabilities $>5\%$ (χ^2 prob.) and low single-grain age variation (Var.) indicating a single age population. SWMZ = sample weighted mean zeta ($\pm 1\sigma$); OWMZ = overall weighted mean zeta ($\pm 1\sigma$).

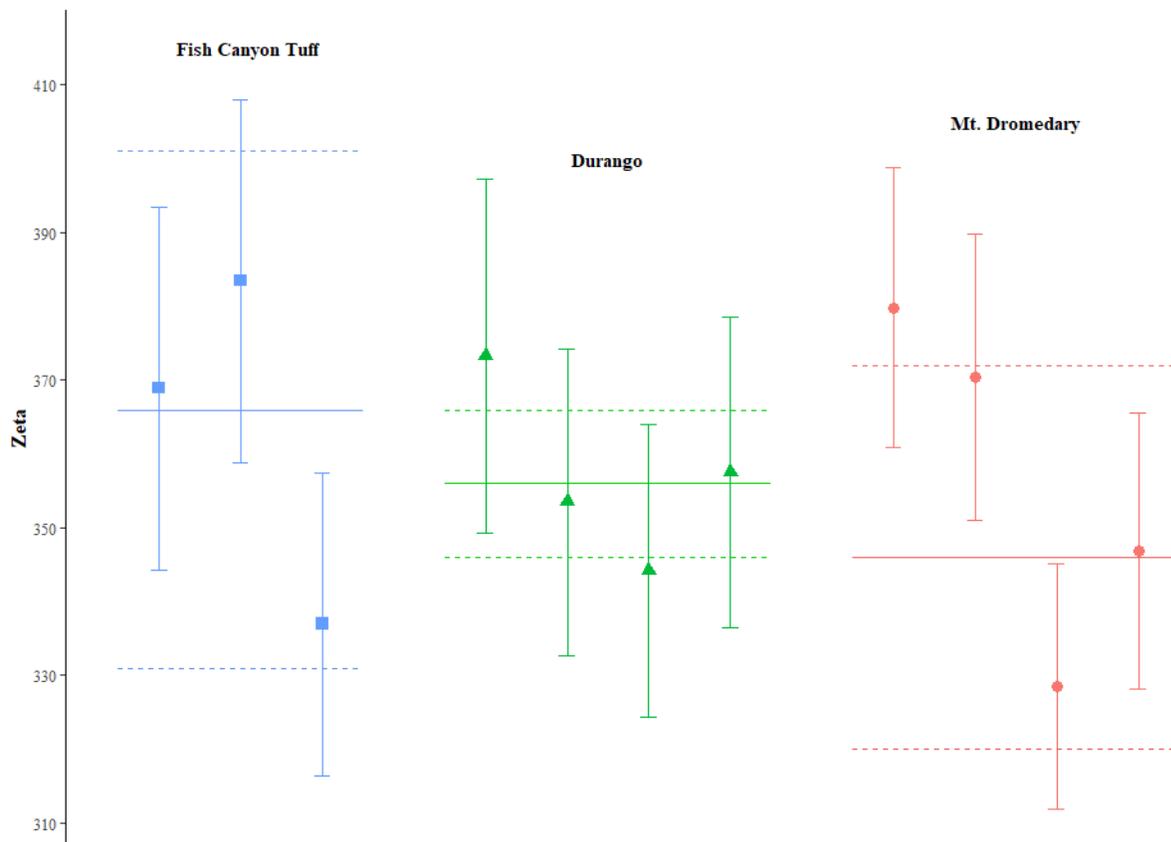


Figure E2. Repeated determinations of zeta for the apatite age standards Fish Canyon Tuff, Durango and Mt. Dromedary. Error bars are 1σ . The sample weighted mean zeta for each age standard is shown as a horizontal line $\pm 1\sigma$ (dashed lines).

Appendix B: Supplementary material for Chapter Two

Supplementary Table 1. Summary of apatite fission-track thermochronology results.

| Sample (Strat. Age) | Lat. (°N), Elev. (m) | Long. (°W) | No. of Grains | Standard Track Density ($\times 10^6 \text{ cm}^{-2}$) | Spontaneous Track Density ($\times 10^6 \text{ cm}^{-2}$) | Induced Track Density ($\times 10^6 \text{ cm}^{-2}$) | χ^2 prob. (%) | Var. (%) | Age (Ma) ($\pm 1\sigma$) | Mean Track Length (μm) | Std. Dev. (μm) | D_{par} (μm) |
|------------------------|-------------------------|------------|------------------|--|---|---|--------------------------|-------------|-------------------------------|---|-----------------------------------|--------------------------------|
| CAT-1 (LD) | 41.9989, 1272 | -74.3852 | 18 | 1.05 (6671) | 1.3152 (862) | 1.831 (1200) | 20.1 | 12 | 133 \pm 7 | 12.5 \pm 0.2 (34) | 1.4 | 2.34 (0.3) |
| CAT-2 (LD) | 42.0023, 1112 | -74.4022 | 14 | 1.06 (6671) | 0.8939 (399) | 1.304 (582) | 71.0 | 0 | 128 \pm 9 | 12.9 \pm 0.3 (22) | 1.6 | 2.15 (0.3) |
| CAT-3 (LD) | 42.0074, 871 | -74.4204 | 25 | 1.071 (6671) | 1.556 (1705) | 2.224 (2437) | 66.1 | 0 | 132 \pm 5 | 12.9 \pm 0.2 (100) | 1.6 | 2.22 (0.3) |
| CAT-5 (MD) | 41.9318, 441 | -74.3359 | 21 | 1.081 (6671) | 1.0485 (698) | 1.648 (1097) | 16.0 | 11 | 122 \pm 7 | 12.8 \pm 0.2 (40) | 1.2 | 2.39 (0.4) |
| CAT-6 (MD) | 41.9731, 281 | -74.3128 | 20 | 1.091 (6671) | 1.0609 (449) | 1.843 (780) | 17.6 | 16 | 114 \pm 8 | 13.1 \pm 0.2 (32) | 1.1 | 2.38 (0.4) |

Samples listed numerically from highest to lowest elevation, with stratigraphic age: LD – Late Devonian (383-359 Ma); MD – Middle Devonian (393-383 Ma). Location, elevation, and number of grains counted for AFT age included. Standard and induced track densities were counted on mica external detectors and spontaneous track densities were counted on internal apatite mineral surfaces, with the track count in parentheses. All samples were crushed and apatites were separated using conventional heavy liquid and magnetic separation techniques. Apatites were mounted and prepared for AFT thermochronology using standard methods (e.g. Kohn et al., 2018). Chi-square probability (χ^2 prob.) determines if grains are from a single age population; if the χ^2 value is $>5\%$, it is likely that there is a single age population. Age variation (Var.) is the relative standard deviation of the central age and when variation is low ($<15\%$) the data are consistent with a single population. The external detector method (e.g. Gleadow, 1981) and zeta calibration approach (Hurford and Green, 1983) was used with a zeta of 353 ± 13 ($\pm 1\sigma$) for Shorten. Central ages are reported (Galbraith and Laslett, 1993). When possible, 100 horizontal confined fission-track lengths per sample were measured using a projection tube and a digitizing tablet (number of tracks measured in parentheses) and standard deviation of fission-track lengths (Std. Dev.) is reported. Mean D_{par} calculated from D_{par} measurements on grains used for AFT age, with std. dev. in parentheses.

Supplementary Table 2. Summary of (U-Th)/He results.

| Grain # | Dim. Mass (mg) | r (μm) | length (μm) | U (ppm) | Th (ppm) | Sm (ppm) | eU | ^4He (nmol/g) | F_T | Raw Age (Ma) | Corr. Age (Ma) | Full Unc. (Ma) | Analytic Unc. (Ma) |
|---|----------------|---------------------|--------------------------|---------|----------|----------|------|------------------------|-------|--------------|----------------|----------------|--------------------|
| CAT1, Honesdale Formation of the West Falls Group (Late Devonian), 41.9989 °N, -74.3852 °W, 1272 m elevation | | | | | | | | | | | | | |
| a1 | 2.9 | 50.27 | 124.80 | 6.78 | 23.57 | 17.68 | 12.3 | 6.025 | 0.711 | 89 | 124 | | 5.9 |
| a2 | 2.8 | 48.97 | 133.04 | 10.82 | 23.91 | 21.07 | 16.4 | 18.757 | 0.708 | 206 | 288 | | 9.8 |
| a4 | 5.4 | 63.79 | 186.75 | 0.18 | 2.25 | 1.36 | 0.7 | 1.281 | 0.758 | 323.66 | 424 | | 30.3 |
| a5 | 7.5 | 69.15 | 243.03 | 23.42 | 44.63 | 33.82 | 33.9 | 28.603 | 0.789 | 153 | 193 | | 5.7 |
| a6 | 8.7 | 75.88 | 194.29 | 0.11 | 3.05 | 32.58 | 0.8 | 9.593 | 0.792 | 1545.24 | 1850 | | 69.2 |
| <i>Mean age $\pm 1\sigma$ (% std. dev.) of all: 576 \pm 721 (125%)</i> | | | | | | | | | | | | | |
| <i>Mean age $\pm 1\sigma$ (% std. dev.) of grain 1 & 5: 159 \pm 49 (31%)</i> | | | | | | | | | | | | | |
| CAT3, Upper Walton Formation of the West Falls Group (Late Devonian), 42.0074 °N, -74.4204 °W, 871 m elevation | | | | | | | | | | | | | |
| a1 | 6.0 | 64.34 | 133.12 | 14.30 | 74.99 | 31.06 | 31.9 | 14.933 | 0.769 | 85 | 111 | | 3.5 |
| <i>Mean age $\pm 1\sigma$ (% std. dev.): 111 \pm 3 (0%)</i> | | | | | | | | | | | | | |
| CAT5, Moscow Formation of the Hamilton Group (Middle Devonian), 41.9318 °N, -74.3359 °W, 441 m elevation | | | | | | | | | | | | | |
| a1 | 1.3 | 39.02 | 168.79 | 26.92 | 25.60 | 75.61 | 32.9 | 14.750 | 0.637 | 81 | 126 | 20.39 | 1.1 |
| a2 | 1.4 | 40.16 | 141.41 | 14.47 | 0.00 | 21.92 | 14.5 | 8.720 | 0.652 | 109 | 164 | 22.23 | 2.8 |
| a3 | 9.2 | 81.00 | 273.30 | 1.54 | 12.39 | 12.86 | 4.5 | 6.271 | 0.806 | 251 | 309 | 22.61 | 3.4 |
| a4 | 6.0 | 75.59 | 137.58 | 5.43 | 108.06 | 21.46 | 30.8 | 10.986 | 0.786 | 65 | 83 | 5.99 | 0.6 |
| a5 | 2.5 | 53.56 | 169.22 | 22.55 | 107.94 | 22.66 | 47.9 | 26.276 | 0.714 | 100 | 140 | 10.23 | 1.2 |
| <i>Mean age $\pm 1\sigma$ (% std. dev.) of all: 164 \pm 86 (52%)</i> | | | | | | | | | | | | | |
| <i>Mean age $\pm 1\sigma$ (% std. dev.) of grain 1, 2, 4 & 5: 128 \pm 34 (27%)</i> | | | | | | | | | | | | | |

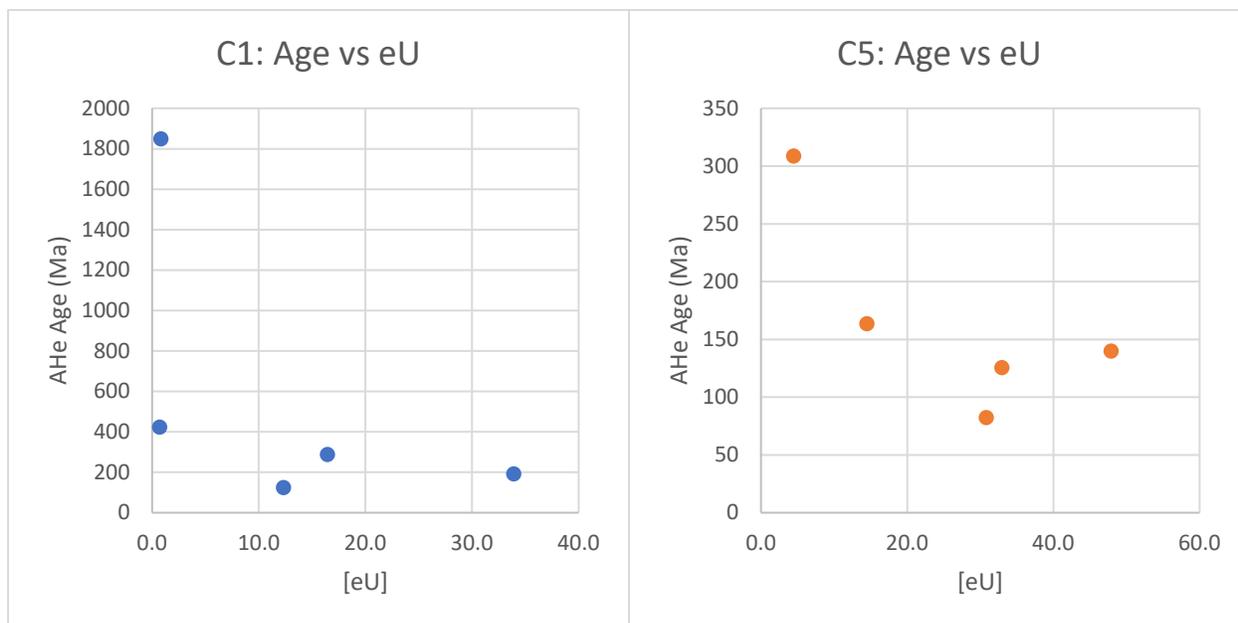
Analyses were completed by CU TRaLL. Dim. Mass = dimensional mass of grain calculated from crystal volume and average apatite density; r = radius of a sphere with equivalent surface area to volume ratio as the grain; l = longest dimension of the grain. Concentrations of U, Th and Sm measured via isotope dilution on an ICP-MS. eU is the effective Uranium, calculated as $[U] + 0.235[\text{Th}]$ (e.g. Flowers et al., 2009). Grains were degassed by heating with a laser to determine the amount of ^4He (nmol/g) in the grain. Alpha ejection correction (F_T) is a measure of the amount of He ejected from the crystal, values <0.65 (grey) indicate that a significant amount of He was ejected (Farley et al., 1996; Farley, 2002). Each grain degassed was followed by a re-extract to ensure there was no ^4He gas remaining in the crystal. If residual ^4He was measured the sample was rejected, as this typically indicates the presence of [U]-rich inclusions. Ages and F_T were calculated using methods described in Ketchum et al. (2011). Raw Age = age calculated from isotope concentrations, without F_T correction; Corr. Age = age calculated from isotope concentrations, with F_T correction (outliers in red, italics); Error = 2σ analytical uncertainty (not incorporating F_T uncertainty). Summarized in italics is the mean age of the single-grain corr. ages with 1σ error on the ages and in bold italics the mean age and 1σ error without outliers, with coefficient of variation (% std. dev.) in parenthesis. Exclusion of outliers is discussed in text. Averaging grain ages and determining variation of single-grain ages is after Ault et al. (2013). Coefficient of variation (% std. dev.) is calculated from the ratio of the standard deviation to the mean and indicates the variation of single-grain ages from the mean age.

Supplementary Table 3. CU TRaIL notes on apatite grains used for AHe analyses.

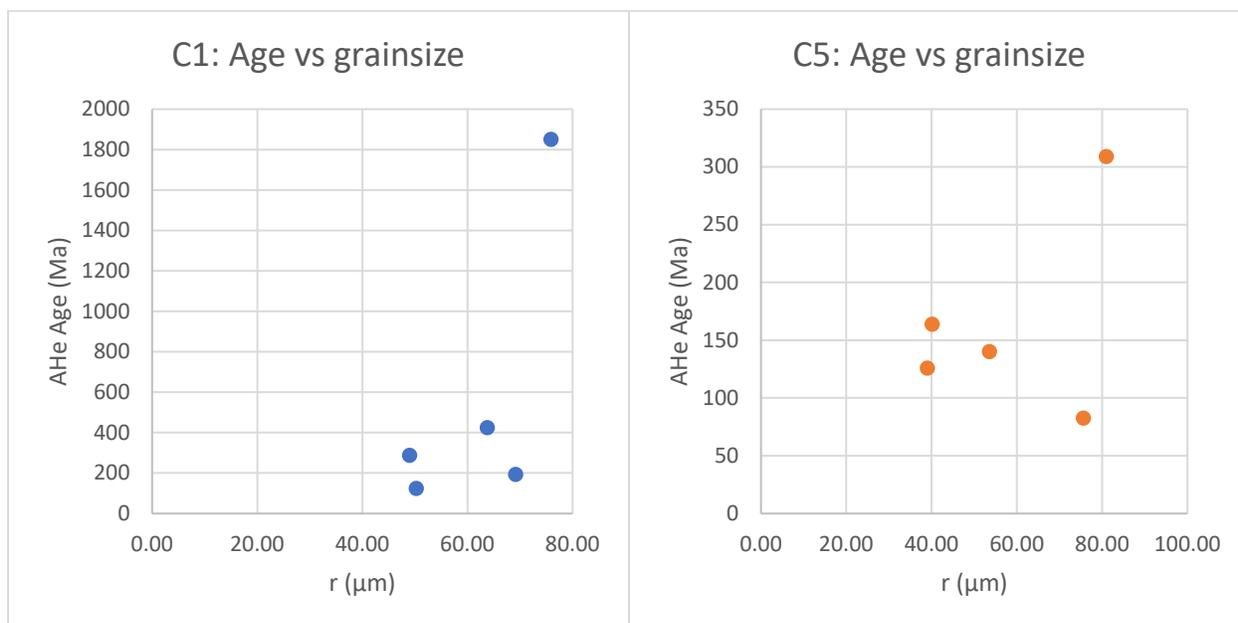
| Grain # | Corr. Age (Ma) | Analytic Unc. (Ma) | Notes |
|---|----------------|--------------------|--|
| CAT1, Honesdale Formation of the West Falls Group (Late Devonian), 41.9989 °N, -74.3852 °W, 1272 m elevation | | | |
| a1 | 124 | 5.9 | broken segment, surface heavily pitted, tough to see inclusions, goes completely dark in XPL, fractures and brownish coloration |
| a2 | 288 | 9.8 | broken segment, surface heavily pitted, tough to see inclusions, goes completely dark in XPL, fractures and brownish coloration |
| a4 | 424 | 30.3 | broken end, many surface pits though interior appears clear. Crack visible inside. Goes completely dark in xpl, but may have small inclusions |
| a5 | 193 | 5.7 | many surface pits, but interior appears clear. Fracture shines in XPL. Broken segment. May have inclusions |
| a6 | 1850 | 69.2 | many surface pits, but interior appears clear. dark in XPL. Broken segment. Brownish coloration in the interior. May have small inclusions |
| <p><i>Mean age ± 1σ (% std. dev.) of all: 576 ± 721 (125%)</i> <i>Mean age ± 1σ (% std. dev.) of grain 1, 2 & 5: 202 ± 82 (41%)</i> <i>Mean age ± 1σ (% std. dev.) of grain 1 & 5: 159 ± 49 (31%)</i></p> | | | |
| CAT3, Upper Walton Formation of the West Falls Group (Late Devonian), 42.0074 °N, -74.4204 °W, 871 m elevation | | | |
| a1 | 111 | 3.5 | large, 2 fractured ends, no visible inclusions, surface a bit marked but most is clear enough to see through |
| <p><i>Mean age ± 1σ (% std. dev.): 111 ± 3 (0%)</i></p> | | | |
| CAT5, Moscow Formation of the Hamilton Group (Middle Devonian), 41.9318 °N, -74.3359 °W, 441 m elevation | | | |
| a1 | 126 | 1.1 | clear, no inclusions, looks like 2 pyr |
| a2 | 164 | 2.8 | clear, no inclusions, looks like 1 pyr |
| a3 | 309 | 3.4 | very rounded, heavily pitted, no obvious inclusions, some marks and fractures could obscure small incl., blue and reddish brown intf colors, seems to be apatite (lower relief than zircons in same sample) |
| a4 | 83 | 0.6 | very rounded, heavily pitted, could be broken tip, no obvious inclusions, some marks and fractures could obscure small incl., blue and reddish brown intf colors, seems to be apatite (lower relief than zircons in same sample) |
| a5 | 140 | 1.2 | very rounded, heavily pitted, no obvious inclusions, some marks and fractures could obscure small incl., blue and reddish brown intf colors, seems to be apatite (lower relief than zircons in same sample) |
| <p><i>Mean age ± 1σ (% std. dev.) of all: 164 ± 86 (52%)</i> <i>Mean age ± 1σ (% std. dev.) of grain 1, 2, 4 & 5: 128 ± 34 (27%)</i></p> | | | |

Supplementary File A. Apatite (U-Th)/He Dating

AHe single-grain ages vs. effective uranium [eU] display a weakly negative to no trend.



AHe single-grain ages vs. grain size (approximated by “r”: radius of a sphere with an equivalent surface area to volume ratio as the apatite grain) also display no trend.

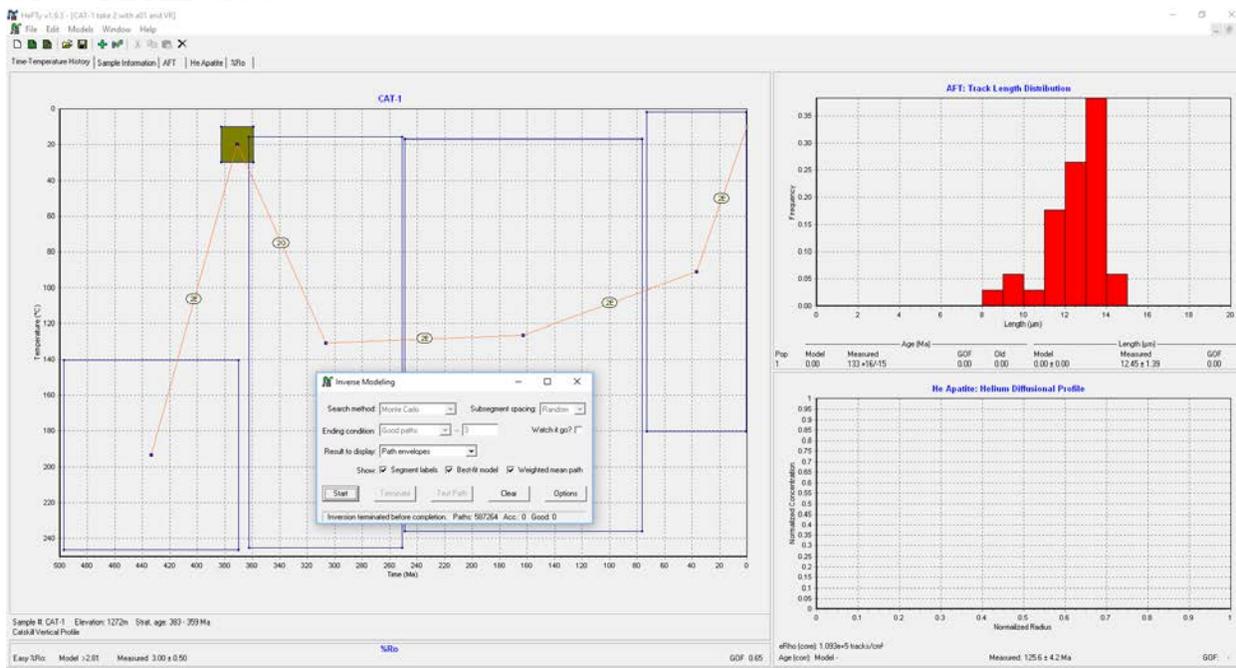


Supplementary File B. Inverse Thermal Models

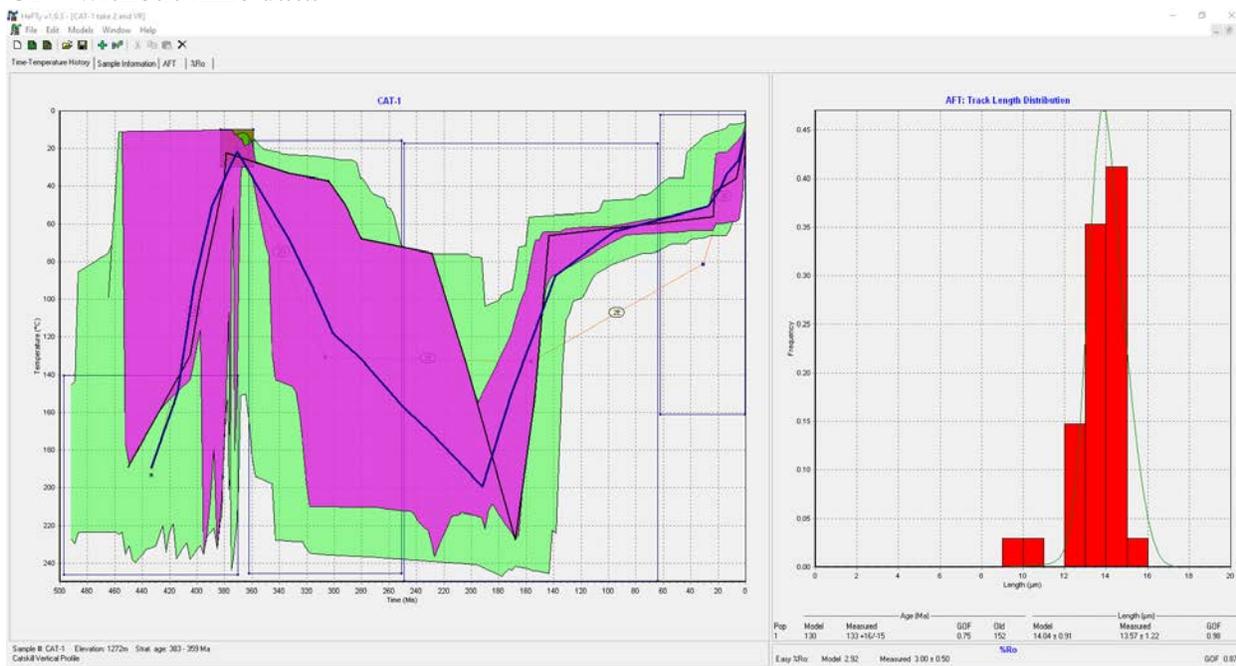
In this supplementary file, the screenshots of HeFTy (Ketcham, 2005) inverse thermal models are included. The following information is presented for each sample: the time-temperature history path envelopes (good paths in purple and acceptable paths in green), the best-fit (black path) and weighted mean path (thick blue path), and the constraint boxes which includes stratigraphic age and paleo-temperature (olive box; Woodrow et al., 1973); AFT track length distribution, calculated track length distribution based on best-fit path; model goodness-of-fit (GOF) statistics and the age of the oldest fission track that has not been completely annealed (“Old”; Ketcham, 2005); AHe diffusion profile and GOF statistics when present; and vitrinite reflectance (%R_o) output, which includes modeled and measured values (“>” sign means the %R_o calculation does not include a depositional event). See Chapter 1 supplementary information for further discussion on development of inverse thermal models and constraints.

In this file, thermal models constrained with and without additional apatite (U-Th)/He (AHe) dates are included. AHe data contained single-grain age variation with outliers significantly older than AFT ages (Table 2). The addition of AHe data in inverse thermal modeling generally yielded more tightly constrained time-temperature path envelopes through the PRZ (~30-90 °C) but sample C1 was unable to model any good or acceptable paths using both AHe and AFT data. Given that AHe single-grain ages contained significant variation and AFT data contains the kinetic parameter (i.e. fission track length), as discussed in the paper, when the model was unable to produce paths with AHe and AFT data, AFT data was used exclusively.

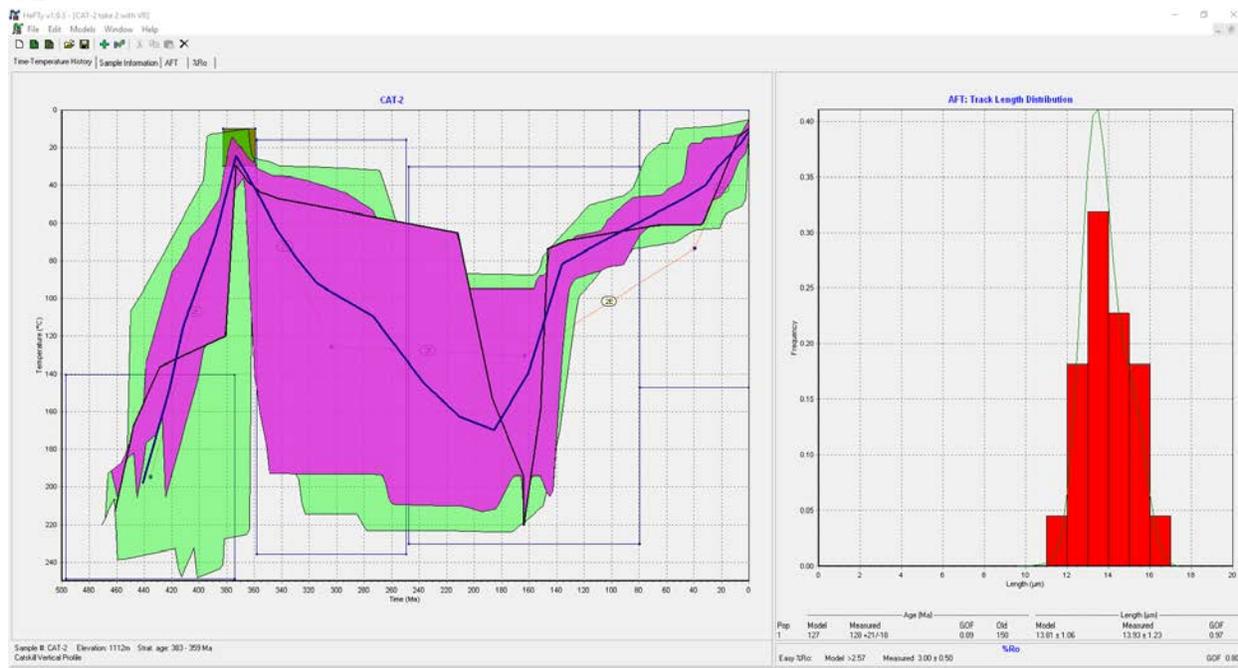
C1 – with AHe data



C1 – without AHe data



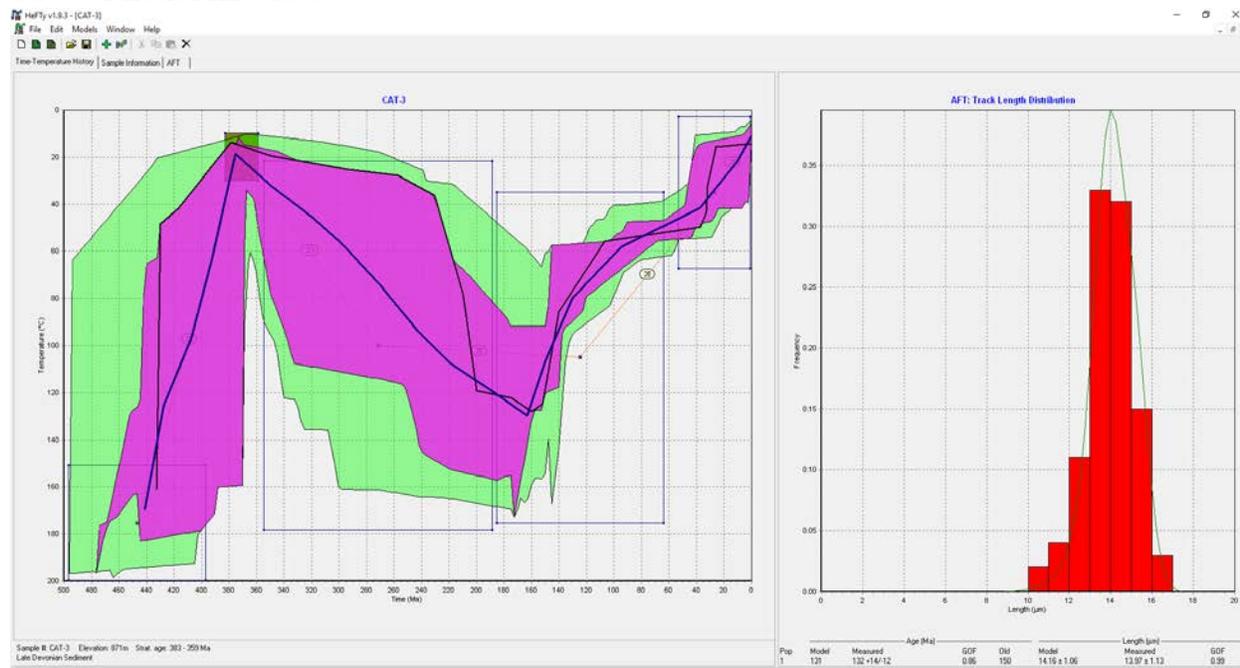
C2



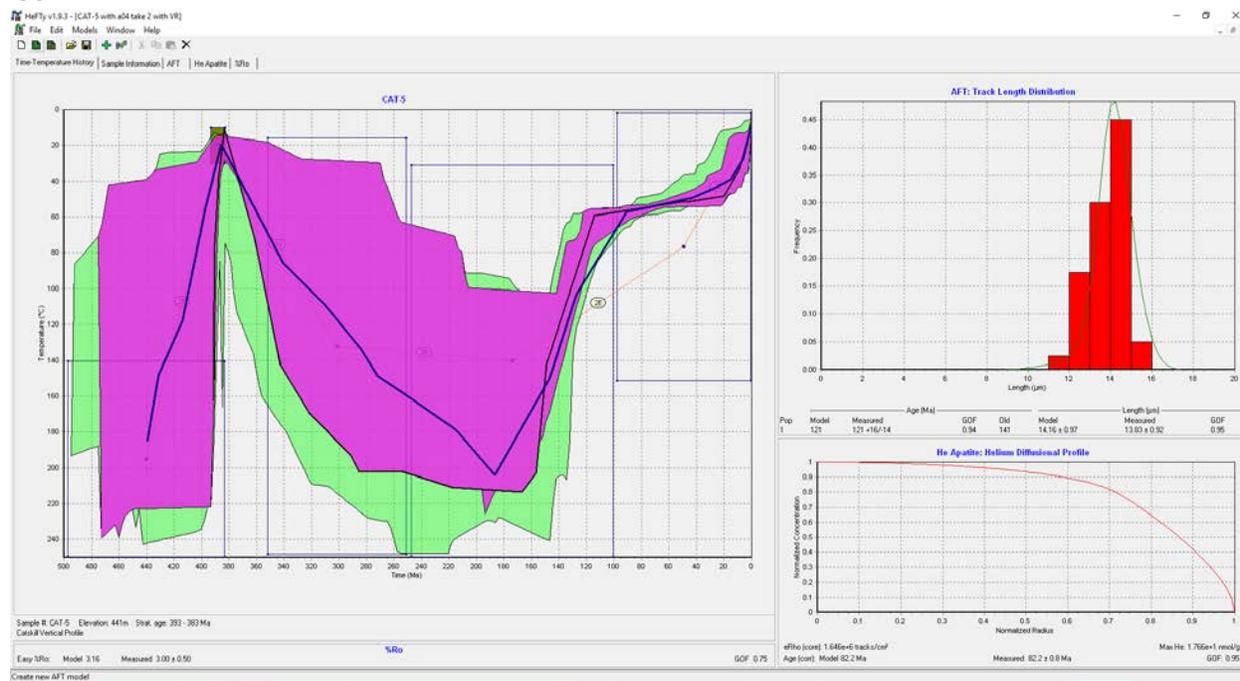
C3 – with AHe data



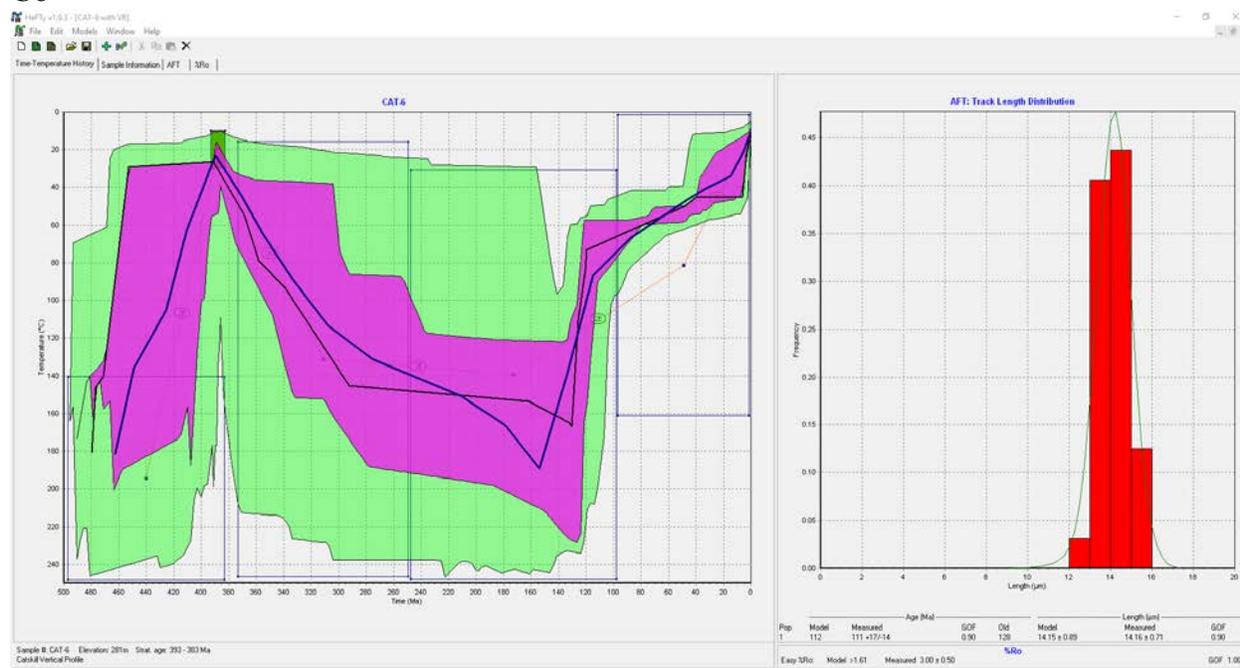
C3 – without AHe data



C5



C6



Appendix C: Supplementary material for Chapter Three

Appalachian Low-Temperature Thermochronology Database (AppLTDB) Information Guide:

| |
|---|
| Database was created without spaces to allow for seamless loading into ArcGIS. |
| Can be ordered in alphabetical order (row # and Ref_Order) or from north to south (N-S_Order), which was determined by arranging studies by latitude. |
| Location Data: |
| Sample ID and location data (latitude/longitude in decimal degrees) is from published tables (Table), GPS measured values (Measured), manually georeferenced pdfs in ArcGIS (Manual_Georef) or published georeferenced figures (GeoTiff). |
| Elevation (meters) is from published tables (Table), text of the paper (Text), GPS measured values (Measured) or estimated on Google Earth Pro (GoogleEarthPro). Negative values indicate depth of sample below surface. |
| AFT Age Data: |
| Apatite fission-track ages (AFT_age; Ma), 1-sigma error (AFT_1sig), chi-squared % values (chi2; when reported), mean track length (MTL; μm), and standard deviation (Std_Dev; μm) |
| AHe Age Data: |
| Apatite (U-Th)/He ages (AHe_age; Ma), 2-sigma analytical error (AHe_2sig) and single-grain age variation (Var; when reported) |
| Physiographic Provinces: |
| Physiographic province (Province) polygons were determined and drawn into ArcGIS from Soeder et al. (2014). Polygon layer was joined with sample point data to determine province of each sample location. |
| Rift Basins (Rift_Basins) polygons were drawn into ArcGIS from Withjack et al. (2012). Polygon layer was joined with sample point data to determine if sample lay within a rift basin. Output dash if not within rift basin. |
| Lithology |
| United State lithologic maps from the USGS The State Geologic Map Compilation (SGMC) Geodatabase of the Conterminous United States (Horton, 2017). Polygon layer was joined with sample point data to determine lithology of each sample location. |
| Information includes: original map unit label from state geologic maps (ORIG_LABEL); SGMC map unit label (SGMC_LABEL); unique value for every unite in the SGMC (UNIT_LINK), also the easiest way to look up details on the USGS Mineral Resources Online Spatial Database; USGS state agency code (SOURCE); unit formational/depositional age (UNIT_AGE); lithology ranked by the SGMC compiler as a major component of the geologic unit (ROCKTYPE1); lithology ranked by the SGMC compiler as the second major component of the geologic unit (ROCKTYPE2). |
| HydroSHEDS Database |
| USGS database of geo-references catchment boundaries (Lehner et al., 2008). Database name is an abbreviation of: H ydrological data and maps based on S Huttle E levation D erivatives at m ultiple S cales (http://www.hydrosheds.org). |
| Drainage polygon layer was joined with sample point data to determine which catchment each sample location was within. |
| Which part of the Atlantic (i.e. North, Middle, or South) or Gulf of Mexico catchments drain to (Drain_To) was determined using Pazzaglia and Brandon (1996). |

Appalachian Low-Temperature Database (April 2018)

Table with columns: Row No, Well Code, Well Name, State, County, Township, Range, Section, Easting, Northing, Elevation, Log Data, Core Data, Lithology, Rock Type, Rock Type 2, Rock Type 3, Lithology 2, Lithology 3, Lithology 4, Lithology 5, Lithology 6, Lithology 7, Lithology 8, Lithology 9, Lithology 10, Lithology 11, Lithology 12, Lithology 13, Lithology 14, Lithology 15, Lithology 16, Lithology 17, Lithology 18, Lithology 19, Lithology 20, Lithology 21, Lithology 22, Lithology 23, Lithology 24, Lithology 25, Lithology 26, Lithology 27, Lithology 28, Lithology 29, Lithology 30, Lithology 31, Lithology 32, Lithology 33, Lithology 34, Lithology 35, Lithology 36, Lithology 37, Lithology 38, Lithology 39, Lithology 40, Lithology 41, Lithology 42, Lithology 43, Lithology 44, Lithology 45, Lithology 46, Lithology 47, Lithology 48, Lithology 49, Lithology 50, Lithology 51, Lithology 52, Lithology 53, Lithology 54, Lithology 55, Lithology 56, Lithology 57, Lithology 58, Lithology 59, Lithology 60, Lithology 61, Lithology 62, Lithology 63, Lithology 64, Lithology 65, Lithology 66, Lithology 67, Lithology 68, Lithology 69, Lithology 70, Lithology 71, Lithology 72, Lithology 73, Lithology 74, Lithology 75, Lithology 76, Lithology 77, Lithology 78, Lithology 79, Lithology 80, Lithology 81, Lithology 82, Lithology 83, Lithology 84, Lithology 85, Lithology 86, Lithology 87, Lithology 88, Lithology 89, Lithology 90, Lithology 91, Lithology 92, Lithology 93, Lithology 94, Lithology 95, Lithology 96, Lithology 97, Lithology 98, Lithology 99, Lithology 100, Lithology 101, Lithology 102, Lithology 103, Lithology 104, Lithology 105, Lithology 106, Lithology 107, Lithology 108, Lithology 109, Lithology 110, Lithology 111, Lithology 112, Lithology 113, Lithology 114, Lithology 115, Lithology 116, Lithology 117, Lithology 118, Lithology 119, Lithology 120, Lithology 121, Lithology 122.

Appalachian Low-Temperature Database (April 1988)

Table with columns: Row No., Well No., Sample ID, Longitude, Latitude, Elevation, etc. The table contains detailed geological data for various wells in the Appalachian region, including sample numbers, coordinates, elevations, and lithological descriptions.

Supplementary Table 2. Summary of information on samples with mean apatite fission-track lengths $>14 \mu\text{m}$

| Study | Lat., Long. (°) Elev. (m) | AFT Age (Ma) ($\pm 1\sigma$) | χ^2 prob. (%) | Mean Track Length (μm) | Std. Dev. (μm) | Physiographic Province | Catchment Drainage Outlet |
|----------------------|------------------------------|---|--------------------------|--|-----------------------------------|---------------------------|---------------------------------|
| Kunk et al., 2005 | 39.028, -77.279 72 | 131 \pm 16 | 1 | 14.0 | 1.2 | Piedmont | Mid. Atlantic |
| Kunk et al., 2005 | 38.972, -77.138 80 | 179 \pm 15 | 43 | 14.3 | 1.4 | Piedmont | Mid. Atlantic |
| Miller & Duddy, 1989 | 42.421, -74.465 352 | 145 \pm 14 | 75 | 14.1 | 1.1 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 42.931, -76.589 191 | 142 \pm 20 | 2 | 14.6 | 1.2 | Appalachian Basin | North Atlantic |
| Miller & Duddy, 1989 | 42.812, -74.699 446 | 246 \pm 17 | 61 | 14.2 | 1.2 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 42.972, -76.048 306 | 228 \pm 17 | 65 | 14.8 | 1.1 | Appalachian Basin | North Atlantic |
| Miller & Duddy, 1989 | 42.916, -76.764 135 | 149 \pm 9 | 24 | 14.4 | 1.5 | Appalachian Basin | North Atlantic |
| Miller & Duddy, 1989 | 42.948, -77.316 209 | 200 \pm 7 | 85 | 14.1 | 1.4 | Appalachian Basin | North Atlantic |
| Miller & Duddy, 1989 | 42.183, -74.094 804 | 126 \pm 10 | 10 | 14.5 | 1.0 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 41.48, -74.725 388 | 159 \pm 19 | 3 | 14.0 | 1.2 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 41.454, -74.874 275 | 135 \pm 17 | 1 | 14.1 | 1.1 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 41.57, -75.01 237 | 130 \pm 8 | 84 | 14.1 | 1.1 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 41.867, -74.999 558 | 168 \pm 11 | 39 | 14.4 | 1.0 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 41.98, -75.225 406 | 140 \pm 11 | 18 | 14.4 | 1.2 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 42.32, -77.401 410 | 142 \pm 12 | 91 | 14.0 | 1.3 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 41.749, -74.507 339 | 114 \pm 9 | 17 | 14.1 | 1.0 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 42.099, -74.567 612 | 118 \pm 9 | 16 | 14.1 | 1.3 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 41.998, -74.406 1105 | 116 \pm 23 | 81 | 14.6 | 1.3 | Appalachian Basin | Mid. Atlantic |
| Miller & Duddy, 1989 | 41.915, -74.275 486 | 138 \pm 14 | - | 14.5 | 0.7 | Ridge and Valley | Mid. Atlantic |

| Study | Lat., Long. (°) Elev. (m) | AFT Age (Ma) ($\pm 1\sigma$) | χ^2 prob. (%) | Mean Track Length (μm) | Std. Dev. (μm) | Physiographic Province | Catchment Drainage Outlet |
|-------------------------------|------------------------------|---|--------------------------|--|-----------------------------------|-----------------------------------|---------------------------------|
| Roden & Miller, 1989 | 40.932, -75.186 404 | 144 \pm 8 | 5 | 14.0 | 1.2 | Ridge and Valley | Mid. Atlantic |
| Roden & Miller, 1989 | 40.511, -77.581 135 | 245 \pm 13 | 5 | 14.1 | 1.7 | Ridge and Valley | Mid. Atlantic |
| Roden & Miller, 1991 | 41.066, -74.027 72 | 161 \pm 12 | 85 | 14.1 | 1.6 | Hartford Rift Basin | Mid. Atlantic |
| Roden & Miller, 1991 | 40.959, -74.185 76 | 196 \pm 23 | 98 | 14.8 | 1.0 | Hartford Rift Basin | Mid. Atlantic |
| Roden & Miller, 1991 | 41.389, -72.613 102 | 154 \pm 11 | 58 | 14.0 | 1.4 | Hartford Rift Basin | Mid. Atlantic |
| Roden-Tice & Wintsch, 2002 | 42.46, -72.26 159 | 143 \pm 21 | - | 14.1 | 1.2 | Taconic and Acadian Terrane | Mid. Atlantic |
| Roden-Tice et al., 2000 | 44.05, -73.46 83 | 123 \pm 14 | - | 14.0 | 1.4 | Adirondacks | North Atlantic |
| Steckler et al., 1993 | 40.888, -74.167 51 | 136 \pm 7 | 27 | 14.3 | 1.0 | Newark Rift Basin | Mid. Atlantic |
| Steckler et al., 1993 | 41.111, -74.063 157 | 157 \pm 10 | 1 | 14.2 | 1.1 | Newark Rift Basin | Mid. Atlantic |
| Steckler et al., 1993 | 41.016, -74.272 93 | 138 \pm 9 | 35 | 14.1 | 1.1 | Newark Rift Basin | Mid. Atlantic |
| Steckler et al., 1993 | 41.238, -74.005 53 | 171 \pm 9 | 36 | 14.1 | 1.1 | Newark Rift Basin | Mid. Atlantic |

This table summarizes the pertinent information from the AppLTDB (Supplementary material) collected on samples with mean apatite fission-track lengths $>14 \mu\text{m}$. AFT age likely represents the timing of rapid cooling for that sample (i.e. Gleadow et al., 1986; Green et al., 1989). Physiographic province and catchment drainage outlet are included for reference with figure 5 and the discussion. Lat. = latitude; Long. = longitude; Elev. = elevation; AFT = apatite fission-track; Std. Dev. = standard deviation.

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Vita

Chilisa M. Shorten

cmshorte@syr.edu

Department of Earth Sciences
Syracuse University

EDUCATION

Ph.D. in Earth Sciences 2013 – 2018
Department of Earth Sciences, Syracuse University

B.S. Cum Laude in Geology 2007 – 2010
Department of Geology and Environmental Science, University of Pittsburgh

PROFESSIONAL AND TEACHING EXPERIENCE

Syracuse University Department of Earth Sciences, **Teaching Assistant** 2013 – 2018

Chevron Energy Technology Company, **Earth Science Internship** Summer 2017

Syracuse University Department of Earth Sciences, **Teaching Instructor** Summer 2016

Environmental Resources Management, **Associate Geologist** 2011 – 2013

Groundwater and Environmental Services, **Staff Geologist** 2010 – 2011

PUBLICATIONS

Shorten, C.S. & Fitzgerald, P.G. (in review). Post-orogenic thermal history and exhumation of the Northern Appalachian Basin: Low-temperature thermochronologic constraints. *Basin Research*.

PRESENTATIONS

Shorten, C.S. & Fitzgerald, P.G. (2018). Post-Orogenic Exhumation of the Northern Appalachian Basin and the Timing of Hydrocarbon Generation: Low-Temperature Thermochronological Constraints from New York and Pennsylvania. *AAPG Annual Convention and Exhibition*, abstract no.2832784. Poster, AAPG ACE, Salt Lake City, UT.

Shorten, C.S. & Fitzgerald, P.G. (2018). Post-Orogenic Exhumation of the Northern Appalachian Basin and the Timing of Hydrocarbon Generation: Low-Temperature Thermochronological Constraints from the Northern Appalachian Basin and the Catskills. *GSA Abstracts with Programs*, v.50, no.2, paper no.14-3. Oral Presentation, NE GSA Meeting, Burlington, VT.

Shorten, C.S. & Fitzgerald, P.G. (2017). Post-orogenic thermal history and exhumation of the Northern Appalachian Basin constrained through low-temperature thermochronology. *GSA Abstracts with Programs*, v.49, no.2, paper no.14-11. Poster, NE/NC GSA Meeting, Pittsburgh, PA.

Shorten, C.S. & Fitzgerald, P.G. (2015). Post-orogenic thermal history and exhumation of the Northern Appalachian Basin constrained through low-temperature thermochronology. *GSA Abstracts with Programs*, v.47, no.7, p.799, paper no.316-7. Poster, GSA Annual Meeting, Baltimore, MD.

ACADEMIC AWARDS AND CERTIFICATIONS

SU Outstanding Teaching Assistant Award 2017

Certificate in University Teaching, SU Graduate School and Dept. of Earth Science 2017

Certificate of Professional Development, SU Women in Science and Engineering 2016

K. Douglas Nelson Award for graduate research in geophysics and tectonics 2015

PROFESSIONAL MEMBERSHIPS

AAPG (since 2013); **AAPG Division of Professional Affairs** (provisional member, since 2018);
GSA (since 2013); **GSA Structure and Tectonics Division** (since 2014); **AGU** (since 2013)