

**DATING THE THERMAL MAXIMUM OF THE
BEEKMANTOWN GROUP USING FISSION TRACKS IN
RADIATION-DAMAGED DETRITAL ZIRCON**

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ABSTRACT

Zircon from Cambrian and Precambrian rocks in and around the Adirondacks were used to develop a methodology for High-Density Fission-Track (HDFT) dating, and this dating technique to understanding the thermal evolution of the Beekmantown Group in New York State. This new dating technique allowed dating of the thermal history of grains that are older (>300 Ma) and have higher tracks densities than those analyzed using traditional optical microscopes. Annealing experiments were conducted on zircons from the Willsboro-Lewis pegmatite to understand thermal annealing in conditions similar to those experienced by strata that blanket the Grenville Basement of NY State. The annealing experiments show that fission tracks are annealed well below the temperature required to remove internal radiation damage as measured by Raman spectroscopy (i.e. crystal disorder). This finding indicates that after heating, a zircon grain retains radiation damage, which then affects the systematics of track retention and annealing.

Dating of samples around the Adirondacks and in the Taconic Range shows a clear pattern of thermal resetting that is pronounced, but not dramatic, in the east. For samples to the west, component populations are older than the age of deposition, and therefore the populations reflect cooling ages of the Grenville source rock that has its own distinct thermal history (Montario and Garver, 2009). Most samples in the Mohawk corridor are not reset, and thus did not get to temperatures in excess of c. 200°C. Those that are partly reset show that heating was not widespread and that the thermal pattern suggested by the CAI and fluid inclusion data likely represents two different post-depositional events. For the north-south transect including the eastern Adirondacks, the Taconics, rocks in the mid-Hudson, and south to SE Pennsylvania, samples have a clear southward-increasing thermal signal from the Alleghanian (c. 264-270 Ma), and they have been locally been reset by a thermal event associated with Atlantic rifting (c. 188-190 Ma).

Zircon from several samples of the Cambrian Potsdam and the Galway formations were dated by both HDFT dating and U/Pb dating. Approximately 90% of the U-Pb ages from detrital zircon fall between 950-1200 Ma, which indicates they are derived almost entirely from Grenville age rock. Zircon FT (ZFT) ages from the same samples have component populations of cooling ages at ~540 Ma, ~780 Ma, ~1200 Ma. The HDFT data indicate that strata on both sides of the Adirondacks have not seen widespread post-depositional resetting (i.e. all strata have remained below temperatures of c. 200-250°C) and strata on the west side had peak temperatures that were lower than strata on the east side. This finding indicates that heating was local and not widespread. A key sample in the eastern Adirondacks (Whitehall), yields two component populations at 270 Ma (-30.6/+34.4) and 460 Ma (-22.0/+23.1), which suggests that this part of the Adirondacks experienced heating associated the Alleghanian and Taconian orogenic events, and this heating was only to the lower range of zircon annealing (i.e. 200-250°C). Overall these findings suggest that there was an overall increase in thermal maturity of cover strata eastward to the Taconic front supporting models that invoke a regional east-to-west flow of fluids and gas.

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TABLE OF CONTENTS

Abstract.....	iii
Acknowledgements	iv
Summary	S-1
Introduction	1
Geologic Background	3
Technique Development and Experiments	5
Development of HDFT dating	6
Sample preparation and analysis	6
Application of HDFT dating	8
Annealing experiments.....	8
Raman Spectroscopy	12
Application of HDFT dating too Cambrian strata of NY State	15
Provenance of Cambrian Strata	15
Thermal events – differentially annealed grains.....	18
Basal unconformity – Potsdam Formation near Whitehall.....	19
Alpha dose screening.....	19
Samples from the Taconic Allochthon.....	21
Mohawk Corridor Samples.....	22
Conclusions on the thermal evolution of central and eastern NY State.....	24
Unannealed samples.....	24
Annealed or partly annealed samples.....	25
Papers and abstracts supported by this NYSERDA grant	25
References Cited in this report	26

Figures and tables

Figure 1: Map showing Precambrian terranes in the Appalachians	2
Figure 2: Plot of spontaneous track density vs. detrital grain ages	8
Figure 3: Distribution of pit width measurements from annealing experiments	11
Figure 4: Raman scattering in annealed samples from the Willsboro-Lewis pegmatite.....	13
Figure 5: Image of etch pits from annealed grains with induced tracks	14
Figure 6: SEM images of a zircon with very high track density from the Cambrian Potsdam Formation	14
Figure 7: U/Pb ages of detrital zircon from three Cambrian samples.....	17
Figure 8: Estimated alpha dose in grains from a sample of the Potsdam Fm	20
Figure 9: Statistical analysis of samples from the Taconic Allochthon	22
Figure 10: Simplified map of samples and results from the Mohawk corridor.....	23
Table 1: Summary of pit width measurements from the Willsboro-Lewis Pegmatite zircons	12
Table 2: Summary of unreset ZFT ages from Potsdam and Galway formations	15
Table 3: Summary of reset ZFT ages from the Potsdam and Galway formations.....	19
Table 4: Summary of partly reset ZFT ages in north to south transect.....	21

Dating the thermal maximum of the Beekmantown Group using fission tracks in radiation-damaged detrital zircon

SUMMARY

Paleozoic strata in central and eastern New York State have abundant resources of natural gas that is poorly understood in terms of the timing of maturation and migration. Clastic strata at the base of the stratigraphic section that sits above the Precambrian basement rocks, which are well exposed in the Adirondacks, provide important clues as to the timing of heating because they contain minerals (notably zircon – $ZrSiO_4$) that are well suited for dating low-temperature thermal events. To use zircon to date low-temperature thermal events in NY State, the systematics of how fission tracks anneal were investigated in very old, highly damaged grains, which are typical in this setting.

High-Density Fission-track (HDFT) dating reveals that: 1) most of the strata that sit above the Adirondack basement massif were not heated to temperatures above c. 200-250°C; 2) rocks on the east side of the Adirondacks (near the Taconic front) were hotter than rocks on the west side by about 50-100°C (near the Tug Hill Plateau); 3) unreset fission track ages from Cambrian strata on the western part of the Adirondacks indicate that the Grenville basement massif experienced two primary cooling episodes at c. 540 and 780 Ma; 4) partly reset fission track ages from the eastern part of the Adirondacks indicate that cover strata experienced a significant thermal event at 270 Ma (-30.6/+34.4) and 460 Ma (-22.0/+23.1).

These findings also suggest that the low-temperature thermal history of these rocks was complicated because the rocks appear to have been heated to c. 200°C more than once: data from this project suggest that heating occurred in the Taconic and Alleghanian orogenies, although Acadian heating cannot be ruled out. Overall, these findings suggest that there is an overall increase in thermal maturity of cover strata eastward to the Taconic front, which supports models that invoke a regional east to west flow of fluids and gas. In addition, the thermochronological data supports those models of gas generation and migration that invoke multiple periods of heating as opposed to a single defining thermal event.

INTRODUCTION

This research was focused on determining the timing of heating events that have affected Cambrian rocks in New York State to gain a better understanding of the timing of thermal maturity of oil- and gas-prone strata. The thermochronological history (temperature-time history) of New York is poorly constrained, but several paleothermometry (temperature only) techniques have been applied to provide a partial picture of this thermal history (Bradley and Kidd 1991; Sarwar and Friedman 1995; Weary et al., 2001; Smith et al. 2003; Smith 2006; Lim et al. 2005 Collins-Waite 1991; Selleck 2008). These approaches include conodont alteration, fluid inclusion analysis, fission-track dating (mainly apatite), vitrinite reflectance, clay diagenesis, and monazite growth. However, these techniques do not converge on the timing of the thermal maximum in New York, but instead they result in puzzling data set that provides a fragmentary view of the spatial and temporal history of heating. Together the data would seem to indicate that the rocks experienced more than one period of heating, thus complicating the picture. This thermal evolution is extremely important for understanding oil and gas generation and migration because the temporal framework provides key information that drives exploration models. A possible reason for this ambiguous result is that strata in New York have been affected by several low-temperature thermal events (mostly low, below 200°C) and the multiplicity of events have affected the systematics of these thermal indicators.

There is a relatively well known framework as to when rocks have been significantly heated in eastern NY State, so one way to approach this problem is to evaluate which of these events played the most significant roll in heating the Paleozoic section. Based on well-established geological evidence, there are several likely times when thermal events occurred: 1) during the Taconic orogeny, by way of fluids migrating in advance of thrust sheets (~450 Ma) (i.e. Whitney and Davin, 1987; Smith, 2006); 2) during the Acadian orogeny, through burial and basement-derived fluids (~370 Ma); 3) during or following the Alleghanian, through burial (~270-290 Ma) (i.e. Friedman and Sanders, 1982); and 4) during Mesozoic heating and high heat flow associated with rifting of the Atlantic or the Palisades orogeny (180-190 Ma) (i.e. Steckler and others, 1993; see Montario and Garver, 2009 for summary and discussion). It is important to understand how these events affected strata in New York State because they are vital to oil and gas maturation and migration that was accompanied by significant fluid flow.

This research involved developing a new dating technique that holds promise for being able to date multiple low-temperature thermal events (Garver et al., 2005). The general technique employs fission track dating in zircon ($ZrSiO_4$), which is a common accessory silicate mineral with trace amounts of uranium, which decays though time by spontaneous fission and alpha decay (see Garver, 2008). Alpha decay (driven by the decay of uranium to lead) causes a crystal to accumulate radiation damage through time, and this disintegration process acts to change the crystal properties over time. Fission decay is different, and much less common (Garver, 2008). The daughter product of fission decay is a single fission track, which

represents the damage in the crystal from two sub-equal fission fragments recoiling from on another after the fission event: these tracks are relatively large and can be viewed optically with a microscope (Wagner and van den Haute, 1992; Garver, 2008). Annealing or healing of fission tracks generally occurs when the crystal is brought to temperatures of 200-300°C, but the temperature of annealing varies with radiation damage, an essential crystallographic property of a zircon. This annealing is important because it essentially resets the radiometric clock of this particular system. This project was aimed at exploiting this difference by dating detrital zircon from Cambrian strata that have been heated. To do this, it was first necessary develop a method of counting tracks in very old, track-rich grains, which is nearly impossible using traditional techniques (see Bernet and Garver, 2005). Counting tracks in this old zircon grains with high track densities was accomplished using a Scanning Electron Microscope (SEM) to count track densities, and this new technique allows dating old damage zircon crystals that were previously impossible to date. This development means that this technique can be used to evaluate the Paleozoic thermal history of NY State for the first time. It was also necessary to better understand the annealing characteristics of zircon, so annealing experiments were conducted in the laboratory.

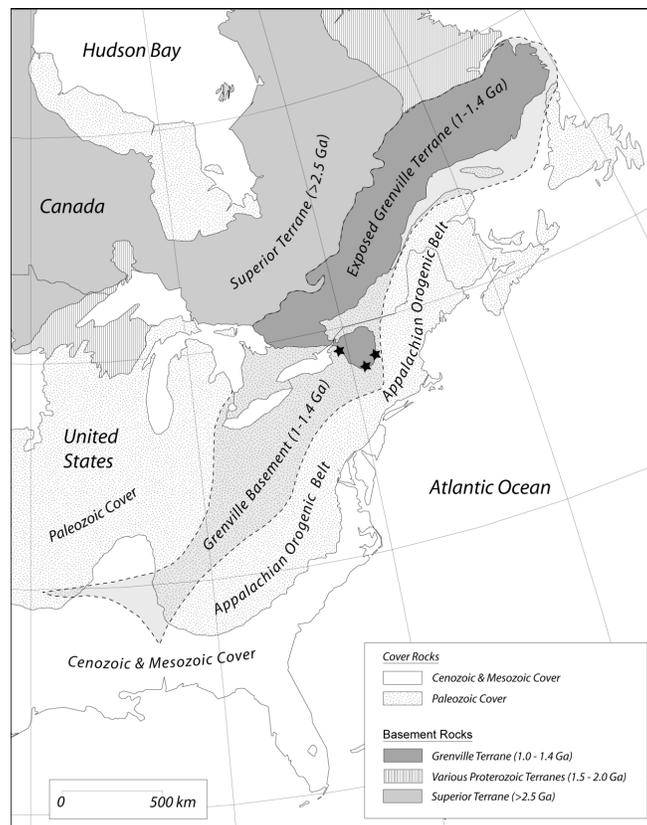


Figure 1: Distribution of Precambrian terranes and Paleozoic and Mesozoic cover strata of eastern North America. This study focuses on an exposure of Grenville-age basement rocks in the Adirondacks and cover strata in New York State. Stars indicate sample locations that are highlighted in this final report and they essentially represent the location of the western Adirondacks, the Mohawk Valley, and the eastern Adirondacks. Modified from the USGS North America Tapestry of Time and Terrain map (Barton et al., 2003).

This report presents this new dating technique, explains the annealing experiments, and then presents the cooling ages determined for the Cambrian cover strata in NY State. This latter data set on the timing of thermal events is relevant to models aimed at explaining the maturation and migration of natural gas in New York State.

GEOLOGIC BACKGROUND

Lower Paleozoic rocks in the northern Appalachians (New York State) rest unconformably on Precambrian basement terranes, which are well exposed in the Adirondacks. The units of interest are the Cambro-Ordovician Beekmantown Group (including the basal Potsdam Sandstone), and the overlying Trenton-Black River groups. This relatively thin succession (c. 150-200 m) rests unconformably on Grenville basement (Fisher, 1977). The E-W-trending Mohawk Valley provides an excellent transect perpendicular to the orogenic belt. The rocks are relatively well studied in terms of Conodont alteration (or CAI) (Harris et al., 1978; 1979) and fluid inclusion studies (see Weary et al. 2001, Lim et al., 2005, and Repetski et al., 2006, for summaries).

It is not known when the thermal maximum occurred in the Lower Paleozoic of eastern New York, and it is likely that these rocks saw more than one period of heating. A brief overview of the stratigraphic evolution is helpful here to place different heating hypotheses into context, and then four competing hypotheses are reviewed.

Strata of the Beekmantown Group represent a Cambro-Ordovician passive margin following the breakup of Rodinia (Heitzler and Harrison, 1998). One of the most important units for our analysis is the Cambrian Potsdam Formation because these clastic rocks are rich in detrital zircon. In New York State, the Potsdam Formation is the basal unit of the Paleozoic cover strata that sit unconformably above the Grenville basement, and this contact is well exposed around the Adirondack Mountains. The depositional age of the Potsdam Formation varies from upper middle Cambrian to lower upper Cambrian in New York State (Fisher 1977; Selleck 1997; Landing 2007). The depositional environments for the Potsdam Formation vary around the marine-nonmarine interface (Otvos 1965; Selleck 1997). The overlying Galway Formation consists of interbedded carbonate and quartz clastic sandstones that overlie the Potsdam Formation, and is equivalent to the Theresa Formation of southwestern New York and the Rose Run Formation of Ohio (Janssens 1973; Fisher 1977). These units, which grade upward into carbonates of the Beekmantown Group, represent a widespread transgressive sequence from the Late Cambrian to the Early Ordovician. Sandstones of the Galway Formation have been the focus of oil and gas exploration in New York over the

past few years because of the large plays discovered in the Theresa Formation of Ohio (Harris et al., 1978; Hart et al. 1996).

The Potsdam and Beekmantown Group rocks were buried by an east-thickening clastic wedge from the Taconic orogeny (c. 450 Ma), and then a similar east-thickening clastic wedge of the Middle to Upper Devonian Catskill delta (c. 370 Ma) (Fisher 1977; Rickard, 1975). What is not known is the extent of burial during the Alleghanian orogeny because there is currently no trace of rocks of this age in this part of the orogenic belt - farther to the south in Pennsylvania there are 2-6.4 km of these strata (Friedman and Sanders, 1982): a big question is how thick was the stratigraphic section in NY. The Palisades orogeny is marked by crustal extension and high heat flow in the early Mesozoic (c. 180 Ma): the major features are the Newark, Hartford, and Deerfield basins in NJ, NY, CT, and MA (i.e. Steckler and others, 1993). Finally, PA, NY and New England were affected by an interesting short-lived kimberlitic intrusive event (see Weary et al., 2001; Repetski et al., 2002). While the volume of kimberlitic material is minuscule, the dikes are regionally widespread and therefore might signal a time of an elevated geotherm. Four hypotheses for the timing of heating, which are not mutually exclusive, stand out and need to be evaluated.

A) Taconic fluids migrating in advance of thrust sheets (~450 Ma). This hypothesis is supported by evidence of hydrothermal fluids along high-angle basement cutting faults that appear to cut Ordovician and older rocks. The fluid flow has a general spatial congruence with isotherms and the orogenic front (Whitney and Davin, 1987; Smith and Nyahay, 2004; Smith, 2006). In terms of hydrocarbons, this hypothesis implies that the Cambro-Ordovician rocks are over-mature with respect to the overlying strata. It also implies that the primary model for exploration should be focused on narrow negative flower structures with saddle dolomite in the Black River Group, and that there are many occurrences of these gas-rich deposits hidden below the Devonian in the southern half of the state (Smith 2006).

B) Acadian burial and basement-derived fluids (~370 Ma). This hypothesis calls on burial by both Taconian and Acadian clastic wedges, and then fluids driven by orogenic contraction that involved basement rocks. These fluids include Mississippi Valley Type (MVT) lead-zinc-bearing fluids, which are reasonably well dated elsewhere in the orogenic belt between 375 and 360 Ma (see summaries in Kesler and van der Pluijm, 1990; Leach et al., 2001; and Rasmussen et al., 2003). An important implication of this hypothesis is that it opens the Devonian for exploration and that structures in the Devonian are reliable exploration tools. For example, reservoirs in the Steuben Field in south central NY occur below synclinal sags in the Devonian strata, and this structural occurrence is consistent with gas accumulation in regions of Riedel-tensile, low-pressure environments along NW-striking strike-slip faults (Rasmussen et al., 2003, p. 4.11). The implication here, compared to the Taconian hypothesis is that the Devonian strata and structures in those strata are useful for exploration and they do not obscure it.

C) Alleghanian burial (~270-320 Ma). This hypothesis is supported by observations of maturation of Devonian strata in the Catskills, zircon FT ages (c. 320) (Laktos and Miller, 1983; see also Johnsson, 1986), and multi-diffusion domain (MDD) models of K-feldspar in basement rocks (Heitzler and Harrison, 1998). It is also supported by a number of K/Ar ages of MVT deposits regionally (278-322 Ma) (Hearn et al., 1987; Leach et al., 2001). It has been proposed that strata from the Alleghanian basin covered all of New York State (c. 4-6 km - Sarwar and Friedman, 1995) and then subsequently completely removed by the Jura-Cretaceous (i.e. Laktos and Miller, 1983 and Roden-Tice et al., 2000; Roden-Tice and Tice, 2005). There are several implications for this timing, but a key element is whether this event is an overprint or a main driving event for fluids and/or regional heating. If it is an overprint, the regional extent of burial and the thickness across the state become key aspects of the problem.

D) Mesozoic heating and high heat flow (at ~145 Ma and/or 180 Ma). This hypothesis requires that maximum paleo-temperatures are in large part related to high heat flow associated with Triassic rifting well north of the Newark basin (i.e. Hudson and Taconics as proposed by Garver and Bartholomew, 2001) and also east in the Rome trough (Repetski et al., 2006). High heat flow with associated kimberlitic intrusions could have also affected maximum paleo-temperatures regionally (see Roden-Tice et al., 2000; Weary et al. 2001, and Roden-Tice and Tice, 2005). These cases require a period of exceptionally high geothermal gradient that has a distinct spatial distribution. A crucial implication of this hypothesis is that there are local areas or structures with a strong thermal overprint that likely affected the occurrences of natural gas.

Note that these specific hypotheses are not mutually exclusive, but some temporal control on the timing will clearly constrain models for basin evolution and hydrocarbon maturation and migration. As we show in the next section, radiation-damaged zircons can retain a memory of more than one thermal event. In the next section we provide the background and the experimental details of how we use fission tracks in radiation damaged detrital zircon to evaluate the timing of heating.

TECHNIQUE DEVELOPMENT AND EXPERIMENTS

One of the most pressing issues with respect to dating the thermal maximum in New York State is that much (or most) of this heating has apparently occurred in a temperature window between c. 150-300°C, which is a difficult temperature range to date because these low-grade metamorphic conditions do not produce primary datable minerals. This observation means that traditional dating techniques have largely failed to result in a clear understanding of the timing of heating. To address this issue one needs to rely on minerals that are reset in this thermal window, and fission track dating is well suited to this task (Garver, 2008). However, in very old rocks fission track dating is difficult because track densities are extremely high, and this hampers our ability to quantify the daughter in this radiometric dating technique.

DEVELOPMENT OF HDFT DATING

Fission-track dating relies on the determination of the track density left by the spontaneous fission of ^{238}U in a crystal (Garver, 2008). In relatively old rocks, like the lower Paleozoic strata in New York State, the density of fission tracks in zircon is extremely high because so much time has elapsed since the rocks have cooled to near ambient temperatures. Thus because the track density is so high, traditional FT dating cannot be applied because optical identification of individual fission tracks cannot distinguish individual etched tracks because overlap is so common (etched fission tracks are about $1\ \mu\text{m}$ wide and about $10\ \mu\text{m}$ long in zircon). These limitations stem from the fact that optical microscopes have maximum magnification of $\sim 1250\text{-}1500\times$ and have difficulty resolving objects that approach the nanometer scale. Latent fission tracks in zircon (i.e. those in their natural state) are typically $8\text{-}10\ \mu\text{m}$ long (8000 to $10,000$ nm) but only $2\text{-}5$ nm wide. In all approaches to FT dating, chemical etching is used to enlarge track width so that they can be evaluated and counted using a microscope (Fleischer et al 1975; Wagner & van den Haute, 1992; Tagami & O'Sullivan, 2005; Garver 2008). High-density fission-track (HDFT dating) involves etching fission-tracks so that the width is narrower, and as a result there is less overlap of individual tracks and this allows us to count grains with much higher track densities (see Montario and Garver, 2008). However, because the tracks are narrower, they tend to be below the limit of identification using an optical microscope, so the solution is to use a higher resolution imaging system. The principal approach is to etch the tracks for a shorter time so their enlarged width is closer to their latent state, and then use a high-resolution Scanning Electron Microscope (SEM) to count grains with a High-Density (HD) of fission tracks (FT). In effect, the only real difference is that in this new technique, a SEM replaces a traditional optical microscope. Much of our early effort in this project was to develop the procedures of this new approach. To count fission tract densities using an SEM, a routine was developed that is relatively practical and can be applied to a wide range of grain ages (first published in Montario and Garver, 2008).

Sample preparation and analysis

Samples of polished and etched zircon grains are coated using a vacuum sputter coater with a gold-palladium target at ~ 50 mTorr using argon gas and a vacuum pump to produce a coating estimated to be $\sim 80\text{-}100\ \text{\AA}$ ($8\text{-}10$ nm) thick. The FT mount was then attached to a standard flat top SEM sample holder, and copper tape was used to hold the mount in place, and conductive silver (Ag) paint was then applied to both the edge of the Teflon[®] and mica extending to the copper tape to complete a path to the grounded SEM stage.

All imaging for this study was done on a Zeiss EVO 50 scanning electron microscope. An Everhart-Thornley detector was used for the collection of SE images and a QBSD was used for collection of backscattered electron (BSE) images. All images were taken with under high vacuum, at least 10^{-5} Torr, with an accelerating voltage (EHT) of $17\ \text{keV}$, a working distance of ~ 10 mm, and a beam current of 100

μA . Due to the differences in SEM software, noise reduction is handled differently between brands. We used a scan resolution of 1024x768 and a scan time of 2.7 minutes for each image. Higher resolutions are possible but require significantly more time for data collection and we found that this didn't significantly increase image usefulness. Through experimentation, it was determined that the smaller resolution images and 2.7 minute scan time were more than sufficient for track identification. The Zeiss EVO 50 series also allows the user to collect SE and BSE images simultaneously, which speeds up the spontaneous track imaging process.

In developing HDFT dating, it was determined that four images are needed to evaluate and count each dated grain. The first image is of the etched zone on the zircon grain to be counted; this includes a SE and a BSE image. Although the BSE image is used for direct track analysis, the two images compliment each other when counting tracks (and both are sometimes required to aid in track identification). The second image taken is of the entire grain and surrounding area, this is taken to ensure the grain can be located again. This image is also used to make sure the mica print and grain have the correct orientation. To align the grain image with the mirror image on the mica, the entire image of the mica is rotated on the SEM by changing the scan direction of the electron beam. This allows the user to rotate the mica image to the correct orientation in the same way an eyepiece grid can be rotated to correct for mounting irregularities. The fourth and final image is a uranium map created by irradiating the zircons with thermal neutrons. The induced tracks are registered in mica so they have a slightly different look than those tracks formed in zircon when imaged on the SEM. The lighter areas and glowing tracks in all the images are caused by the electron beam charging certain locations on the sample.

During the imaging process, magnifications used were between 3000x and 6500x in even and round increments. On SEM images that were counted for this study, image sizes range from ~ 217 to $1012 \mu\text{m}^2$ at (at 3000x and 6500x respectively). Note that with typical settings on an optical microscope, the counting area ranges from about $\sim 65 \mu\text{m}^2$ to $\sim 6500 \mu\text{m}^2$. Thus we count a smaller area using the SEM (as compared to an optical microscope), which makes sense given the fact we are counting at higher magnification.

For track density analysis, the entire image area is counted and the size of the counted area is determined. The track pits are counted using ImageJ software, which is available from the National Institute of Health. The software allows the pits to be marked and then the program counts the number of marks placed on the image. The program cannot automatically count track pits without marking them first. ZFT ages were calculated using the Zeta method (Hurford, 1996) and peak fitting of calculated ages was done using Binomfit (Brandon, 1996; Bernet and Garver, 2005). We reported the first HDFT ages, from this study, in 2008 and 2009 (Garver and Montario, 2008; Montario and Garver, 2008; Montario et al., 2008; and Montario and Garver, 2009).

APPLICATION OF HDFT DATING

HDFT dating using SEM allows dating of Precambrian and Paleozoic low-temperature cooling events, which has not been previously possible using fission track dating of zircon (see Bernet and Garver, 2005). The technique has focused attention on the low-temperature thermal evolution of the Grenville basement and Cambro-Ordovician cover rock in New York State. This technique was used for the first time on detrital zircon from lower Paleozoic strata (mainly Cambrian and Ordovician clastics) around the Adirondacks, the Mohawk Corridor and in the Taconics.

The specific grain-to-grain age variation provide important clues as to the thermal evolution of these different areas. Using this new technique, a total of 1304 zircon grains were dated from 29 samples across New York State, mainly from Cambrian cover strata (Potsdam and Galway formations) that rests above the Precambrian basement rock. Because this technique was developed specifically to attack this geologic problem, this data are first of a kind and no comparable studies have been done elsewhere in the world. The results show that dated grains can have with track densities as high as 3×10^8 tk/cm², which is about an order of magnitude higher than the highest densities counted optically (Fig. 1). This technique has allowed dating of grains at the extreme end of the current old boundary between 500 to 900 Myr (i.e. Montario and Garver, 2009). Because this technique has never been applied before, it is technically now possible to date very old low-temperature thermal events, which has been first used on rocks in NY State.

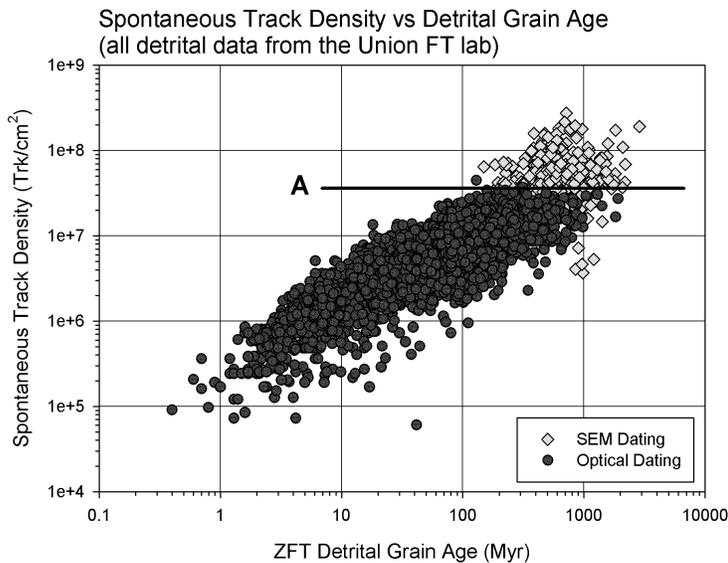


Figure 2: Plot of spontaneous track density vs. detrital grain age for over 5000 zircon grains (from various studies in the Union College FT lab). Dark points are grains dated using traditional identification of tracks with a light microscope at 1250x; Light diamonds are track densities determined using the SEM-HD-FT dating technique. The upper limit of track densities that can be determined by traditional ZFT dating is about 2×10^7 tr/cm². Much older grains, with track densities $>2 \times 10^7$ tr/cm² (shown by line A) can be routinely dated with this new technique.

ANNEALING EXPERIMENTS

Part of this work was focused on understanding how elevated temperatures cause annealing of fission tracks in nature. As such, it is important to determine how tracks shorten in zircon, and how internal

radiation damage in the zircon affects the annealing process. For this part of the study, natural zircon (ZrSiO_4) from the Adirondacks was studied in the laboratory. Essentially, these zircon crystals were heated to see the process of annealing and internal repair that occurs at elevated temperatures (Marsellos et al., 2008; Montario et al., 2008).

In these experiments, natural fission tracks were annealed (removed), and then new tracks were induced using neutron irradiation. These with so that we could ensure that our empirical observations were based on grains with an exactly similar number of fission tracks that formed under the same conditions. It has been known for some time that alpha-radiation damage affects closure temperatures, annealing characteristics, and etching characteristics of zircon (Brandon et al., 1998; Rahn et al., 2004; Garver et al., 2005; Bernet, 2009). This part of the study was conducted to understand the effects long-term (>100 Myr) alpha-radiation damage has on the stability of fission tracks.

Large pegmatitic zircons (mm in size) were obtained from the Willsboro-Lewis Pegmatite where are part of the Grenville basement rocks in the eastern Adirondacks (courtesy of M. Lupulescu, NY State Museum – summarized in Montario et al., 2008). Our analysis indicates that these zircons have a fission track age of 513 ± 30 Ma with typical uranium concentrations of c. 150-350 ppm. The newly determined fission track age indicates that these rocks where heated enough to reset the fission track system in the Paleozoic, but not necessarily at ~ 513 Ma (see Montario, 2010). These zircons were used to understand their crystal-specific properties.

For annealing and Raman studies, the zircons were first heat treated to determine the temperature of fission track annealing, which was achieved by holding the zircons at 750°C for 1 hr. The principal hypothesis considered here is that internal radiation damage remains in the zircon well after fission tracks are annealed and we want to determine how much remains after different annealing increments. The reason this is important is that grains with radiation damage have a lower retention for fission tracks, and therefore they can get reset (or annealed) easily. As such, the relationship between annealing of fission tracks and the amount of radiation damage in a particular grain needs to be determined. The objective is ultimately to understand why some of the dated grains in the study are reset (young) and why some are not: this allows an understanding of the significance of this new dating technique.

In this experiment, different aliquots of the Willsboro-Lewis Pegmatite zircon were progressively annealed to temperatures of 750° , 850° , 950° and 1050°C for 20 hr. After this first annealing, grains were sent to the Oregon State University nuclear reactor and fission tracks were induced by neutron irradiation of ^{235}U (the ratio of ^{235}U to ^{238}U is constant in nature, so this technique allows determination of total uranium concentration). After irradiation, the samples were then polished and etched (using the same etchant and etching time for all samples).

The SEM images are used to measure the pit size (Fig. 2) because of the limits on optical microscope magnification and quality. The etchability (or chemical reactivity) of the track pits is used as a proxy for radiation damage in this situation. This inference is based on the fact that at this point we have controlled all other variables, so if a track in one grain widens further in a given time at a given temperature, then the variation must be due to inherent radiation damage. The way this variation is quantified is to measure the size of the fission track that intersects the grain surface, which is referred to as the etch pit.

Approximately 500-700 pit measurements were collected from each annealed aliquot. The aliquots heated to higher temperatures have smaller pits after the same etch time, indicating they are less susceptible to etching, and therefore have less radiation damage. These data suggest that radiation damage is more robust than fission damage and that radiation damage affects the systematics of this dating technique. This matters in the understanding of the thermal history of New York State because these data confirm a long-held belief that radiation damage affects the cooling age distribution that we get using the HDFT technique. Previously, this inference was untested, and these results verify the suspicion that the young reset FT grain ages largely reflects annealed grains that have low track retention. In other words, these data provide confidence that the young FT ages reflect thermal resetting in a particular type of zircon: one that has high damage and is mineralogically distinct from other grains.

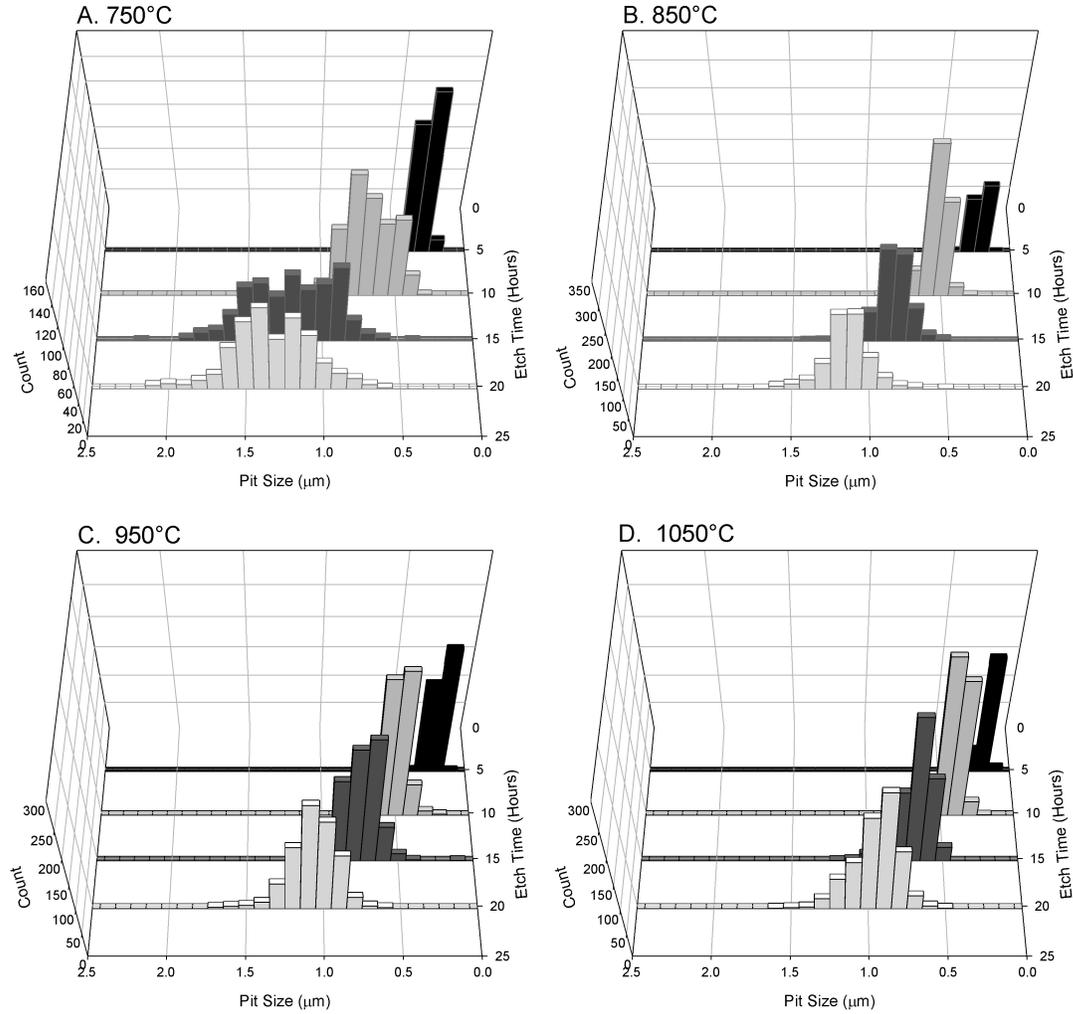


Figure 3: This plot shows pit size measurements of induced tracks compared to etch time in zircon from the Willsboro-Lewis pegmatite. Each aliquot of zircon was initially annealed at progressively higher temperatures (750°, 850°, 950°, and 1050°C) to eliminate spontaneous tracks. The aliquot pre-annealed at 750°C has much larger pit sizes after the same etch time. Because the fission tracks have been induced by neutron irradiation, the difference in etch pit size must be a function of grain etchability (susceptibility to chemical attack). Assuming the only unconstrained variable in this experiment is variation in internal damage, the pit size is a proxy for remnant radiation damage (Holland and Gottfried, 1955, Woodhead et al., 1991; Weber et al., 1994, Riley and Garver, 2004). The grains annealed at only 750° C (far plot), have larger etch pits because they retain the most internal radiation damage, which facilitates etching and track enlargement (Brandon et al. 1998; Tagami and O’Sullivan, 2005; Garver et al., 2005). Grains annealed at higher temperatures are more crystalline because more radiation damage has been annealed and therefore track revelation is slower. Note that etching was done after irradiation, in a controlled laboratory oven for all samples at exactly the same time.

Table 1: Summary of pit width measurements from the Willsboro-Lewis Pegmatite zircons

Pre-Annealing Temperature (Celsius)	Average Pit Width After:			
	5 Hour Etch (μm)	10 Hour Etch (μm)	15 Hour Etch (μm)	20 Hour Etch (μm)
<i>750°C</i>	0.30	0.66	1.17	1.29
<i>850°C</i>	0.21	0.53	0.80	1.10
<i>950°C</i>	0.19	0.50	0.73	1.03
<i>1050°C</i>	0.17	0.42	0.66	0.92

Note: Average track pit size for each etching interval. Each of these aliquots were pre-annealed for 30 hr at the temperature listed, tracks were then induced in the zircon by neutron irradiation. After mounting and polishing, pit width was measured at 5 hr etch increments (5, 10, 15 and 20 hr). All mounts were etched at the same time in the same etchant. Pits widths are in micrometers, and reproducibility on the pit size measurements was ~ 0.03 micrometers.

RAMAN SPECTROSCOPY

Raman Spectroscopy is an analytical technique that allows measurement of the crystalline structure of a zircon. This measurement is important because the long-term accumulation of radiation damage causes the crystalline structure to degrade, or the crystal becomes less crystalline and more amorphous. This process of radiation-driven damage is commonly referred to as “amorphousization” and it represents an important change that a zircon crystal goes through over millions or billions of years that results in a loss of crystallinity (Ewing, 1994). These experiments are designed to understand what happens to zircon crystals over time. Raman spectroscopic analysis was performed on each of eight pre-annealed aliquots, four of which were irradiated as discussed above. A total of forty Raman measurements were completed for this part of the experiment. The Raman data from the step heating experiment clearly show that some amount of alpha-radiation damage is annealed out at each temperature interval, and this was quantified by measurements of the FWHM of the ν_3 wavelength (Fig. 3). In the pit-width experiment, fission tracks were fully annealed in these Willsboro-Lewis Pegmatite zircon after one hour at 750°C. This result indicates that there is still a significant change in the crystal order, at higher annealing temperatures, well above the temperature required to anneal fission-tracks (at 750°C). The key finding here is that fission tracks are annealed well below the temperature required to remove what is assumed to be a significant portion of the internal radiation damage (here crystal disorder). Thus, if fission tracks are annealed in a natural sample, it can be concluded that a significant fraction of the radiation is not annealed. Full recovery of crystalline order over very short timescales probably occurs at temperatures above 1300°C (Zhang et al., 2000; Nasdala et al., 2002).

The implications from the Raman data are consistent with the pit size measurements because they indicate that at that higher temperatures anneal more radiation damage. This finding is not a surprise, but the fact that the radiation damage appears to be progressively removed over such a wide temperature range is a new

and distinctive finding. A key implication of these data is that even after heating, zircon grains likely inherit radiation damage between geologic events, and these experiments show this conclusively for the first time. Because the amount of radiation damage varies with time and uranium concentration (Marsellos and Garver, 2010), the inherited damage will be different for each grain, resulting in some grains that are more susceptible to annealing. This inherited damage likely affects the systematics of this geochronologic system.

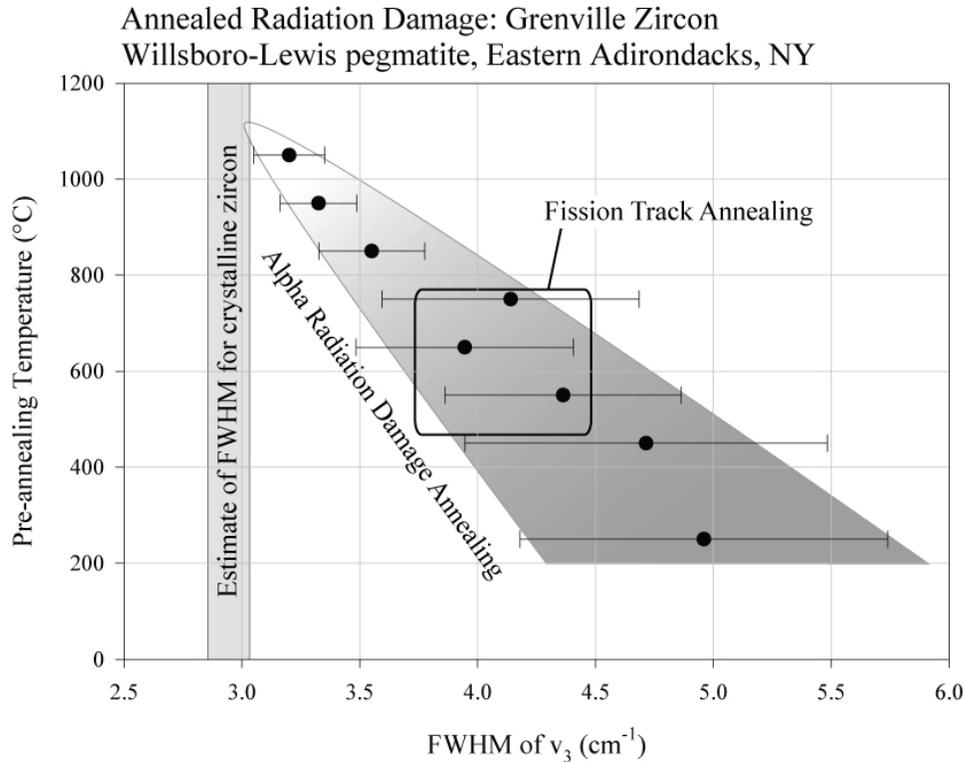


Figure 4: Plot showing Raman scattering full width half maximum (FWHM), which is used as a proxy for radiation damage in the crystal structure of zircon. The FWHM value is a measure of the ν_3 [SiO₄] wavenumber and a shift to smaller FWHM values reflects greater crystallinity and less internal disorder in the zircon (Nasdala et al., 2004). Each data point represents the average of five individual grains and error bars represent the standard deviation of those measurements. The grey bar represents what is thought to be the FWHM value of undamaged crystalline zircon. 99% of the fission tracks were annealed in this sample after a one hour heating at 750°C. All zircon were heated for 30 hours before Raman analysis were conducted.

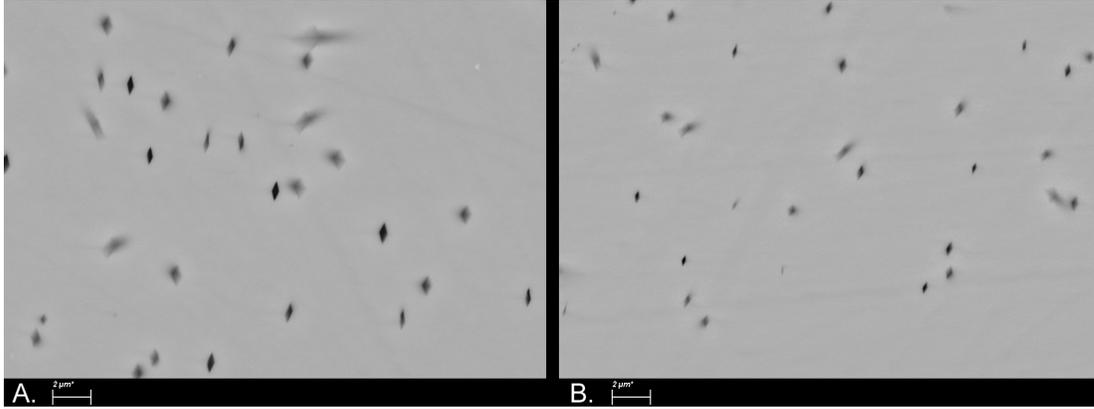


Figure 5: Image of etch pits of induced fission tracks in annealed zircon from the Grenville Willsboro-Lewis pegmatite, eastern Adirondacks, New York. (a) SEM image of etch pits of induced tracks in grain that had been previously annealed at 750°C for 30 hours and (b) zircon previously annealed at 1050°C for 30 hours. These grains were etched under identical conditions. The induced track density is about the same in each case ($\sim 5 \times 10^6$ tracks/cm²), but the size of track pit is considerably smaller in those annealed at higher temperatures.

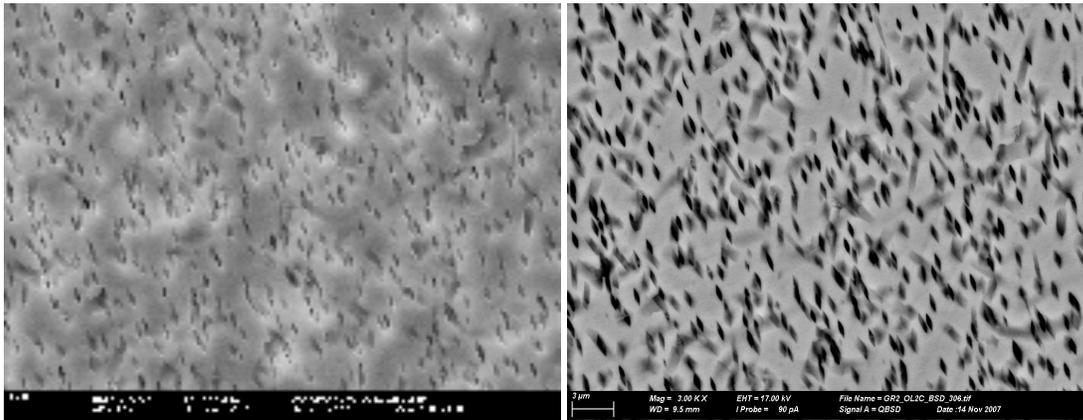


Figure 6. SEM images of a zircon with very high track density from the Cambrian Potsdam Formation. [a] secondary electron (SE) image is of a high track density grain that has been chemically etched and imaged on the SEM. Track pits here are typically ~ 500 to 1000 nanometers (0.5 to $1 \mu\text{m}$) (scale bar present in bottom left corner of image). These pits would be far too small to count on an optical scope and would make this sample undatable. There are ~ 600 track pits on this image, a track density of 5.90×10^7 tracks/cm². [b] backscatter electron image of the same grain.

APPLICATION OF HDFT DATING TO CAMBRIAN STRATA OF NY STATE

This section presents results from HDFT dating on Cambrian strata that are mainly from the lower Beekmantown Group in New York State. This section first presents those samples that show no evidence of thermal resetting (mainly to the west), and the next section reviews those samples that show evidence of annealing and resetting of fission track grain ages.

PROVENANCE OF CAMBRIAN STRATA

One important finding from this work is the determination of cooling ages on detrital zircon from Cambrian strata that directly relate to the early evolution of rocks now exposed in the Adirondacks (published now in Montario and Garver, 2009). This work allows a better understanding of the evolution of the Adirondacks and how the old Precambrian rock was uplifted and exhumed to the surface following the Grenville orogeny (~1.1 Ga). This finding is important because erosion of the early Adirondack basement rocks provided a large quantity of sediment to adjacent basins, and these are one group of strata that are gas prone in New York State (and adjacent states and provinces). Data related to when and how these strata were deposited is important to developing a sedimentological framework for strata, facies, and basin deposits. These data also provide us with key insight on the “starting point” for radiation damage in zircon grains that then later were heated (discussed below).

Table 2: Summary of unreset ZFT ages from the Potsdam Formation & Galway Formation

Sample	Peak	Population (%)	Age (Ma)	Error -1 σ	Error +1 σ	n
<i>Potsdam Formation – Lake George, NY</i>						
M-07	P ₁	63%	540	42	46	50
	P ₂	37%	720	76	74	
<i>Galway Sandstone – Mosherville</i>						
M-09	P ₁	29%	580	67	75	49
	P ₂	61%	860	98	110	
	P ₃	10%	1400	360	470	
<i>Potsdam Formation – Fisher’s Landing, NY</i>						
M-19	P ₁	14%	550	90	110	48
	P ₂	86%	800	47	49	
<i>All Samples Combined</i>						
	P ₁	34%	540	33	35	147
	P ₂	59%	780	63	69	
	P ₃	5%	1200	330	450	

Note: Fission track ages ($\pm 1\sigma$) were determined using the Zeta method, and ages were calculated using Binomfit (Brandon). A Zeta factor for zircon of 337.6 ± 9.2 ($\pm 1\sigma$) is based on nine determinations from the Fish Canyon Tuff, Buluk tuff, and Peach Springs Tuff. Glass monitors (CN5 for zircon), placed at the top and bottom of the irradiation package were used to determine the fluence gradient. All samples were counted using the methods described in Montario & Garver (2008).

Some background is required here to frame why this sort of information is important. Studies of Precambrian terranes (like the Grenville rocks of the Adirondacks) using detrital zircon have been the domain of U-Pb dating techniques which now are fast and precise (Gehrels et al., 2008). U-Pb dating of single zircon grain provides the crystallization age of that zircon, which can be derived from different source rocks and then deposited in nearby basins. However, it is clear that the uplift and exhumation of source rock is intimately linked to basin sedimentation, and therefore when studying basins and the source of clastic detritus, we are commonly concerned with cooling ages (FT) as opposed to crystallization ages (U-Pb). While this difference may seem subtle, it is not. One technique dates the time a rock forms (U-Pb), while the other dates the time rock is brought to the surface by mountain building processes (FT) and this latter age is what matters when sedimentation is linked with source rock evolution (Bernet and Garver, 2005).

With HDFT dating it is now possible to study the low-temperature evolution of these terranes using the fission-track (FT) dating method, and combining these two techniques provides a unique look at the thermal evolution of Precambrian terranes. Part of this work focused on detrital zircon from the upper Middle Cambrian to lower Middle Cambrian Potsdam and Galway Formations in New York. These strata unconformably overlie the Precambrian Grenville basement terrane and for some samples we analyzed zircon by both dating techniques (i.e. grains were analyzed by both U-Pb and FT dating).

Results show that approximately 90% of the U-Pb ages from detrital zircon fall between 950-1200 Ma, which is consistent with previously published idea that they are derived almost entirely from underlying Grenville age rock (i.e. Gaudette et al., 1981). Zircon FT (ZFT) ages from the same suite of sample have component populations of cooling ages at ~540 Ma, ~780 Ma, ~1200 Ma and single grain ages as old as 2.1 Ga. If we put these two data sets together, we can estimate the total maximum amount of radiation damage that typical grains could have, and this is important in understanding annealing in later heating events (discussed below).

An important observation from the FT cooling ages from these Cambrian strata is that it is now known that there has not been widespread resetting on either side of the Adirondacks. This is known this because component populations of cooling ages are older than the age of deposition, and therefore the principle population likely reflects the cooling ages of what was almost exclusively Grenville source rock. The ZFT component populations older than Grenville tectonic events (fission track age >1.6 Ga) suggest that these old grains, and the zircon with old U-Pb ages, were transported from other nearby Precambrian terranes, such as the Superior or Yavapai-Mazatzal terranes (i.e. Dickinson and Gehrels 2008). These FT data show that the Potsdam and Galway Formations have not seen heating significant enough to reset fission tracks in zircon since deposition and the heating in the source rocks at 540 Ma corresponds to the breakup of

Rodinia and the rifting of the Iapetus Ocean (see Kumarapeli et al. 1990; Coish and Sinton 1991; Aleinikoff et al. 1995; Cawood et al. 2001).

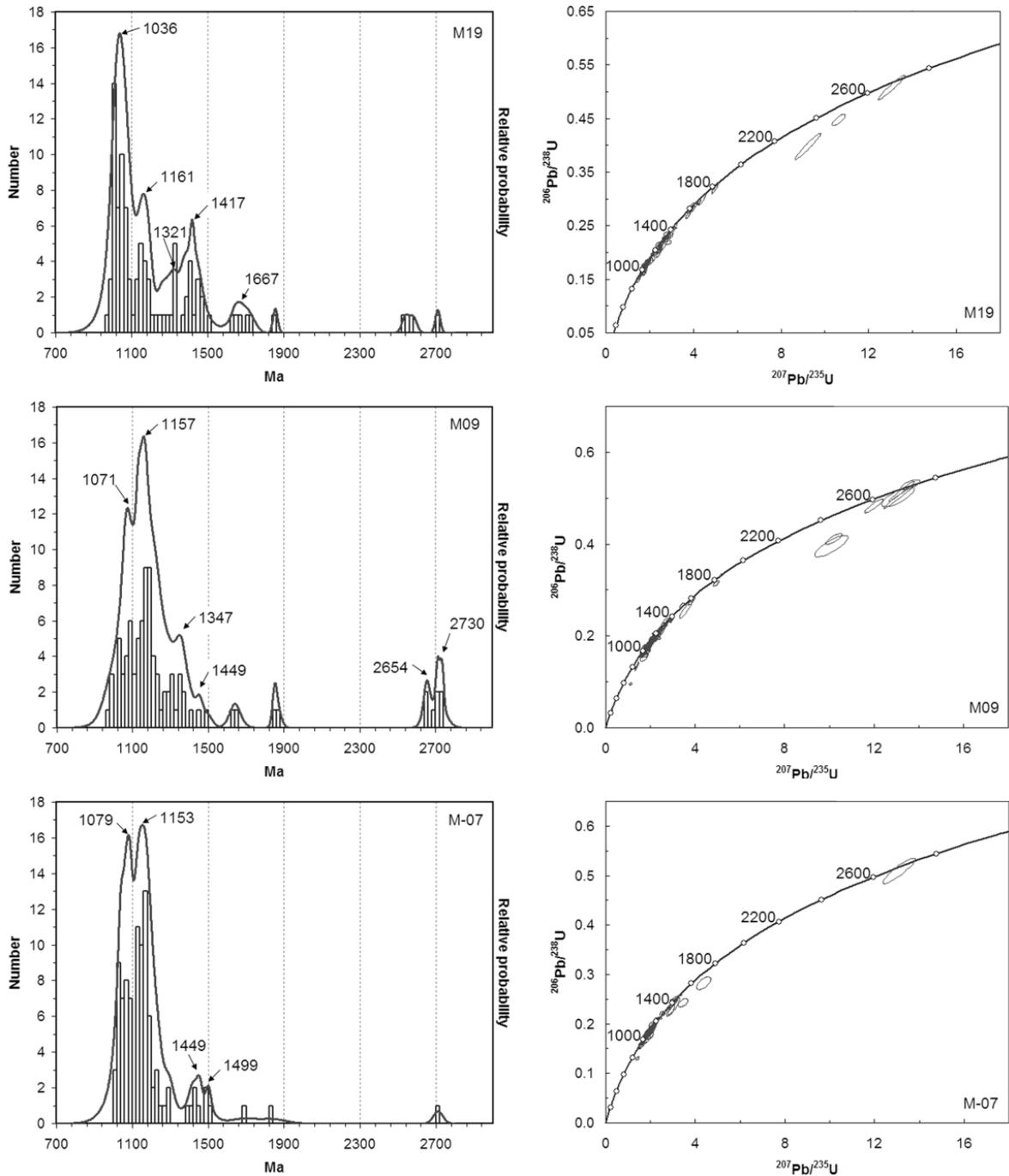


Figure 7. Detrital zircons have crystallization ages that indicate the source of the Cambrian clastic strata was dominated by rocks formed in the Grenville. Probability density and concordia plots for U-Pb analysis for samples M-19, M-09, and M-07. Peak ages are labeled in the probability density plot. Data point error ellipses for the concordia plots are 68% confidence intervals (from Montarico and Garver, 2009).

THERMAL EVENTS - DIFFERENTIALLY ANNEALED GRAINS

Most of the samples from the eastern Adirondacks, and the Taconics have a large fraction of reset zircons (annealed since deposition) and many grain ages are younger than depositional age. Thus these rocks have evidence of being heated after deposition in the range of 200° C or higher. This pattern of partial or incomplete resetting indicates that these samples were brought to elevated temperatures sufficient to anneal tracks in grains with high radiation damage, but not in zircon grains with low damage. Samples in this group therefore have grains that have been annealed, grains that have been partially annealed, and potentially grains that have not been annealed at all and therefore have their original fission-track distribution. Therefore we refer to such samples as having been *differentially annealed*, which means that to extract the valuable information from them in terms of when they were heated, we need to isolate the young grain ages that represent the latest heating episode.

In general, it was discovered that the rocks have been hottest (c. 200°C or greater) in the eastern edge of the State, including the eastern Adirondacks, the eastern Mohawk, and the Taconics: all rocks to the west experienced peak temperatures that were lower ($\leq 200^{\circ}\text{C}$). These data support models that infer large-scale east to west regional fluid flow. We break these findings down by sector: 1) On the west side of the Adirondacks, detrital zircon from the Cambrian Potsdam Formation are completely unreset and reveal detailed information about the underlying Grenville terrane. This result is consistent with paleothermometry that demonstrate that cover strata on western side of the Adirondacks have not been heated significantly (Conodont Alteration Index – CAI – of 2). The detrital zircons have U/Pb ages that are almost exclusively Grenville (c. 1000-1100 Ma), but ZFT cooling ages that reflect post-Grenville exhumation (780 Ma) and a subsequent widespread thermal event likely associated with rifting of the Iapetus ocean (~540 Ma). 2) On the east side of the Adirondacks, a number of paleothermometers indicate that the lower Paleozoic strata were subjected to the some of the highest post-depositional temperatures in the region. Our ZFT grain ages from the eastern Adirondacks are largely unreset, and therefore maximum temperatures did not greatly exceed 200-250°C. A small fraction of reset radiation-damaged zircon grains provides information about post-depositional thermal events. Virtually all the reset grains yield Taconic cooling ages. However, a small fraction of the reset grains (15%) indicate that these rocks experienced heating related to the Alleghenian orogeny. 3) The effects of the Alleghenian thermal anomaly are better developed to south in the Taconic allochthon. Our ZFT grain ages from five samples within the center part of the allochthon show resetting at c. 264 Ma. Farther to the south, in Pennsylvania, all detrital zircon from the Cambrian Chickies Formation have ZFT grain ages that are fully reset to c. 270 Ma. These ZFT data provide a more detailed understanding of the temporal and spatial effects of the thermal veil related to Alleghenian orogenesis that undoubtedly affected migration and maturation of hydrocarbons in Paleozoic strata. Some specific areas of interest are discussed below.

Table 3: Summary of reset ZFT ages from the Potsdam Formation & Galway Formation

Sample	Peak	Population (%)	Age (Ma)	Error -1 σ	Error +1 σ
<i>Willsboro-Lewis Pegmatite – Eastern Adirondacks</i>					
LC-1 (12 grains)	P ₁	100%	513	29	31
<i>Potsdam Formation – Whitehall, NY</i>					
M-06 (57 grains)	P ₁	11%	290	29	33
	P ₂	44%	480	70	81
	P ₃	45%	680	75	83

Note: Fission track ages ($\pm 1\sigma$) were determined using the Zeta method, and ages were calculated using the computer program Binomfit (Brandon). ζ_{CN5} of 337.6 ± 9.2 ($\pm 1\sigma$) is used in age determination and is based on nine determinations of the Fish Canyon Tuff, Buluk Tuff, and Peach Springs Tuff. Glass monitors (CN5 for zircon), placed at the top and bottom of the irradiation package were used to determine the fluence gradient. All samples were counted using the methods described in Montario & Garver (2008).

Basal Unconformity – Potsdam Formation near Whitehall

The grain ages obtained from the Potsdam Formation, near Whitehall, NY, are partly reset and very instructive because they have been studied in detail. The grain-age distribution is over-dispersed (wider range of ZFT ages than expected from a single-source sample) but there are young grain ages not seen in the Potsdam Formation elsewhere (Montario and Garver, 2009). The location of this sample has also seen post-depositional hydrothermal alteration by fluids with temperatures in excess of 200°C (Selleck, 1997; 2008). Studies of monazite and xenotime from this same unit (same outcrop) show mineral growth at c. 450 Ma (see Selleck, 2008). Our data are compatible with this finding, but it would appear that radiation-damaged zircon also record a younger thermal event as well. Assignment of these young, reset ages from the ZFT ages is not simple because single grain ages have relatively low precision. The following section will review possible methods that our group has used to extract young reset component ages in the Potsdam Formation from Whitehall NY.

Alpha Dose Screening

This proposed screening method involves estimating the alpha dose that the zircon grain would have received by the time it was heated. This process involves double dating the zircon using U-Pb and fission-track dating (thus it is time intensive and expensive). The reason being is that for any given grain, the uranium and thorium concentrations are needed to calculate a reasonable alpha dose estimate. The alpha dose estimate is calculated using the formula $D_{\alpha} = 8^{238}\text{U}(e^{a_{1t}} - 1) + 7^{235}\text{U}(e^{a_{2t}} - 1) + 6^{232}\text{Th}(e^{a_{3t}} - 1)$, which approximates the number of alpha decay events with time (see details in Ewing, 1994). Thorium concentrations are not calculated during the FT dating process; therefore we must analyze the grains by U-Pb LA-MC-ICPMS, which provides a U/Th ratio that can be used for precise alpha dose calculations. The

time factor needed for the estimate of alpha dose is calculated by subtracting the ZFT cooling age of each grain from the ZFT cooling age of Grenville source rock, this is ~780 Ma (Montario and Garver, 2009). The difference between these two numbers represents the time that grain had to accrue alpha damage between Grenville cooling and the next heating event to anneal fission tracks in that grain. Any grains from the Grenville Province would have been reheated and reset during Ottawan orogenesis and would not be older than ~780 Ma.

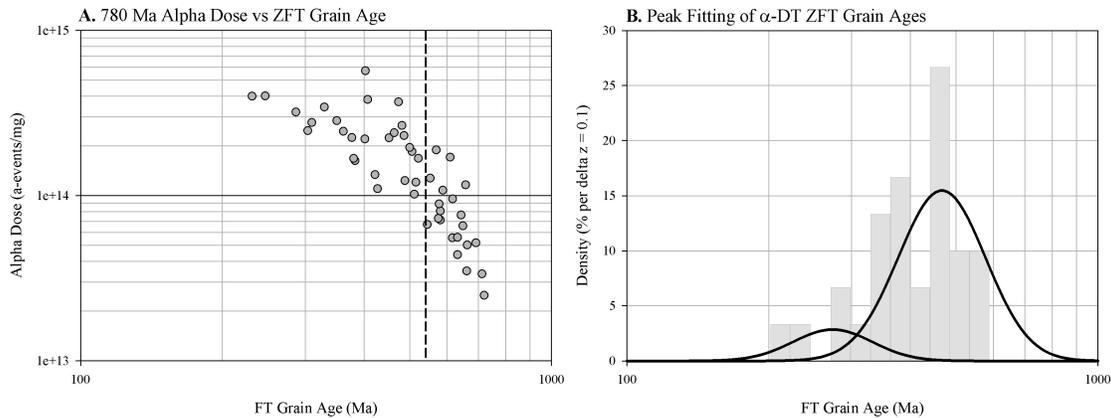


Figure 8. (a) Plot of estimated alpha dose accrued by each grain after Grenville cooling at 780 Ma. The dashed black line represents the approximate time of deposition of the Cambrian Potsdam Formation. Grains with an estimated alpha dose of higher than 1×10^{14} α -events/mg extracted for statistical analysis. (b) Statistical analysis of the grains with an alpha dose above 1×10^{14} α -events/mg yielded two component populations at 460 Ma and 270 Ma.

There are several important aspects of this alpha dose calculation plot (Fig. 4a) that need to be considered. First, there is an increase in the scattering of the data after a dose of 1×10^{14} α -events/mg. Second, all of the grains with reset ZFT ages fall above this same calculated alpha dose. It is interesting to note that the point at which the scatter in the data increases corresponds to the time of deposition of the Potsdam Formation, Upper Middle Cambrian to Lower Upper Cambrian in New York State (Fisher, 1977; Selleck, 1997; Landing, 2007). With this in mind, the selection of a threshold value of 1×10^{14} α -events/mg was used as a cut off values for extracting grains for analysis. This is not to suggest that this number will work for all detrital ZFT suites, but for this particular data set it appears to be the α -dose threshold for resetting.

Table 4: Summary of partly reset ZFT ages from the Chickies Formation, Potsdam Formation and Austin Glen Member

Sample	Peak	Population (%)	Age (Ma)	Error -1 σ	Error +1 σ	n
<i>Chickies Formation – Chickies Rock, PA</i>						
M-20	P ₁	100%	270	13	14	25
<i>Austin Glen Member – Catskill, NY</i>						
M-26	P ₁	9%	185	12	13	105
	P ₂	85%	260	9	9	
	P ₃	6%	500	50	56	
<i>Potsdam Formation – Whitehall, NY</i>						
M-06	P ₁	7%	290	28	31	93
	P ₂	35%	490	69	80	
	P ₃	54%	620	47	51	
	P ₄	4%	1860	250	282	

Note: Fission track ages ($\pm 1\sigma$) were determined using the Zeta method, and ages were calculated using the computer program Binomfit (Brandon). A Zeta factor for zircon of 337.6 ± 9.2 ($\pm 1\sigma$) is based on 9 determinations from the Fish Canyon Tuff, Buluk tuff, and Peach Springs Tuff. Glass monitors (CN5 for zircon), placed at the top and bottom of the irradiation package were used to determine the fluence gradient. All samples were counted using the methods described in Montario & Garver (2008).

This α -dose threshold (α -DT) allows extraction of young reset grains without arbitrarily (or statistically) picking one grain over another, which is especially important when populations of grain ages overlap (see Bernet and Garver, 2005). Applied to the Potsdam Formation sample from Whitehall, a clear picture of the more recent thermal events is revealed. Peak-fitting analysis of the α -DT grains yields two component populations at 270 Ma (-30.6/+34.4) and 460 Ma (-22.0/+23.1) (Fig. 4b), which are likely the primary ages of thermal events that affected this area of New York State. The 460 Ma component population, 86% of the total grain population, corresponds well to the Taconic Orogeny, while the 270 Ma component, 14% of the total grain population, corresponds to the Alleghenian Orogeny. The 460 Ma population also agrees with results of microprobe dating of monazite and xenotime from the Potsdam Formation of the eastern Adirondacks (Selleck et al., 2008). In Pennsylvania, in the anthracite belt, the Chickies Formation (Potsdam equivalent) is totally reset and yields a single grain-age population of 270.4 ± 13 Ma, which is similar to the young population from the Potsdam Formation in the eastern Adirondacks. This result suggests that Alleghenian heating to the south was more intense, resetting the entire grain population.

Samples from the Taconic Allochthon

A total of 237 grains from five samples from rocks of the Taconic allochthon were dated. These samples are not fully reset, but they do have a significant fraction of grains younger than depositional age, and therefore a good memory of low-temperature resetting. Statistical analysis of these samples yields four component populations at 188, 264, 480 and 700 Ma (Fig. 5). Compared to samples in the Mohawk and

the Adirondacks, samples from the Taconic Allochthon appear to have been affected most strongly by later thermal events. The 264 Ma component age is comprised of the largest percentage (~36%) of the total population of reset grains and is likely associated with Alleghenian heating. The youngest peak is relatively minor (5%) and is almost certainly associated with Mesozoic heating due to rifting. The two other component ages (59%) are more difficult to interpret with confidence because of the large fraction of young reset grains, but they may be associated with Taconic heating (480 Ma) and then a number are unreset grains from the original Grenville source rock (700 Ma).

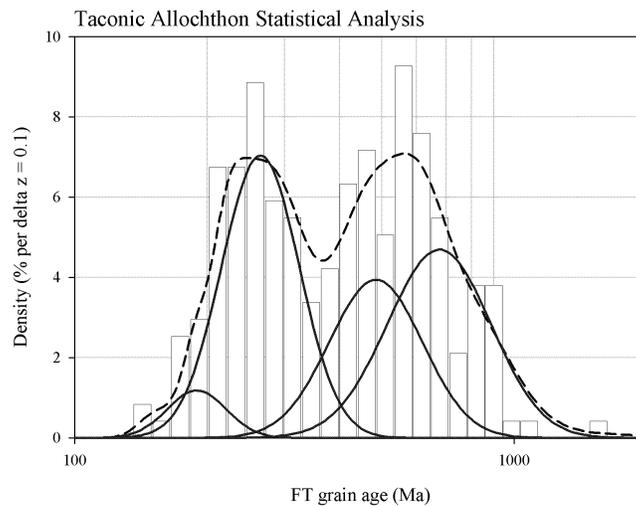


Figure 9. Statistical analysis of grain ages from samples within the Taconic Allochthon. Solid black lines are component populations at 188, 264, 480 and 700 Ma. The ZFT data shows that there is a clear signal from Alleghenian heating within the Taconic Allochthon.

Mohawk Corridor Samples

The original focus of the HDFT dating technique was to date the timing of thermal events associated with the formation of gas deposits in New York State. For this project the main sampling target was well-exposed zircon-bearing quartz sandstones of the Beekmantown Group and sandstones of the Taconic flysch in the Mohawk corridor. Conodont alteration index (CAI) values and fluid inclusion homogenization temperature data from strata in the Mohawk Corridor show a clear increase in temperatures from west to east, perpendicular to the Taconic orogenic front and its extension to the south (Fig. 6) (Harris et al., 1978, 1979; Repetski et al., 2002, 2005, 2006).

The results of peak fitting of the over-dispersed, single-grain fission-track ages for samples from the Mohawk Corridor show that almost all samples are unreset, which is surprising given the indicated paleotemperatures implied by CAI and fluid inclusion data. Of all the samples in this transect, only two have a significant number of grain ages younger than deposition and combined give an young age of 342 Ma, but this is defined by are only 3 grains, so that number has low precision. Samples with reset grains

include: M-18 (RCG Core #75NY-21) yielded three component populations at 375 Ma and 595 Ma and 861 Ma, based on 38 grains. M-16 (Yatesville) yielded four component populations at 340 Ma, 520 Ma, 680 Ma and 1100 Ma based on 106 grains.] All other samples are unreset, and therefore it is clear that this part of the NY stratigraphic section has not been heated appreciably (c. 200-250° C). Sample of unreset rocks include: M-17 (Palatine Bridge) yielded one population at 785 Ma based on 22 grains. M-15 (Kecks Corners) yielded two component populations at 674 Ma and 964 Ma based on 47 grains. M-14 (RCG Core #75NY-13) yielded two component populations at 672 Ma and 1376 Ma based on 43 grains. M-12 (Edinburg) yielded two component populations at 618 Ma and 905 Ma based on 50 grains. M-11 (Hoffmans) yielded two component populations at 502 Ma and 845 Ma based on 45 grains. M-10 (Bunns Corners) yielded two component populations at 587 Ma and 945 Ma based on 45 grains. M-8 (Corinth) yielded two component populations at 534 Ma and 704 Ma based on 35 grains. M-4 (RCG Core #75NY-1) yielded two component populations at 525 Ma and 682 Ma based on 49 grains.

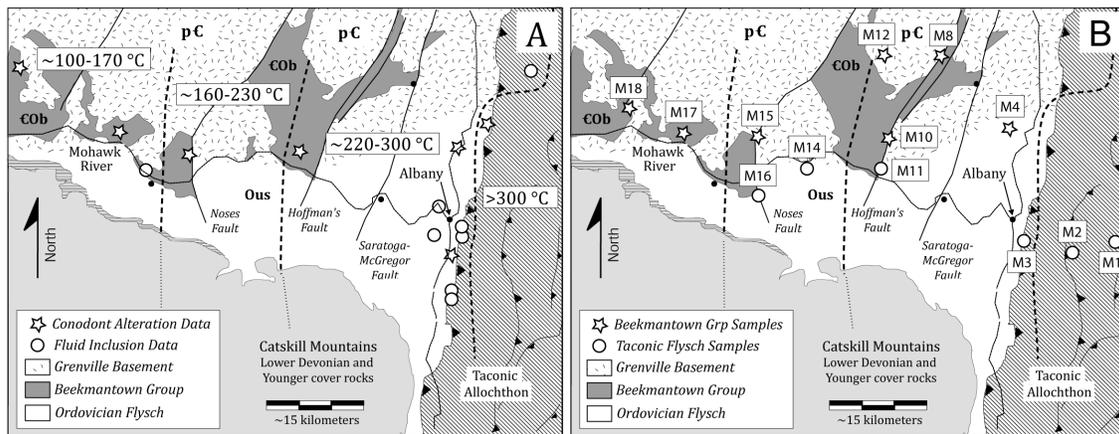


Figure 10. [a] Simplified geologic map of the Mohawk Corridor in eastern New York State. These rocks and others to the west are well-studied for paleothermometry. It is clear that there is a profound increase in maximum temperatures up to and in the Taconic thrust belt. Temperature ranges labeled on this map are based on CAI data from Harris et al. (1978 and 1979) and Repetski et al. (2002), as well as fluid inclusion data from Lim et al. (2005) and Sarwar and Friedman (1995). b: Sample Locations from the Mohawk Corridor transect.

The results from the samples in the Mohawk Corridor do not correspond to the heating pattern suggested by the CAI and fluid inclusion data. It is interesting to note that the samples that show any resetting are located on what would be the cool end of the Mohawk Corridor where CAI and fluid inclusion data indicated low peak temperatures.

Samples were also collected from the only known core of deep strata in the southwestern section of the state. The Olin well, from Steuben County New York, has 6" core from the base of the Beekmantown Group, including the Galway and Potsdam Formations. The Olin well has a maximum depth of 4,114 meters (13,496 ft) and provided an opportunity to study samples that occur well away from the early

Paleozoic orogenic front. The results suggest that these strata have not seen significant post depositional heating since deposition in the Cambrian.

Grain ages from the Potsdam Formation at the base Olin Well show that very little heating took place at the base of the Olin Well (i.e. at the base of strata in central NY State). Statistical analysis of the grain ages from the samples with reset grain ages from the Olin well yield component populations at 510 Ma and 730 Ma and a single grain that is younger than deposition but the error is too large to include in this analysis. A sample from the Galway Fm (Theresa Fm.) from slightly higher in the well, have component populations at 610 Ma and 800 Ma.

CONCLUSIONS ON THE THERMAL EVOLUTION OF CENTRAL AND EASTERN NEW YORK STATE

UNANNEALED SAMPLES

1. U-Pb ages from detrital zircon of the Potsdam and Galway Formations indicate derivation of these units almost entirely from the Precambrian Grenville terrane. Pre-Grenville ZFT cooling ages suggest that a small fraction (~10%) of the zircons with older U-Pb ages may have been derived from nearby Superior and Yavapai-Mazatzal terranes. The other possibility for these pre-Grenville ZFT ages is that these zircon grains are derived from metasedimentary rocks, such as the Irving Pond Quartzite, within the Grenville terrane. This second possibility is less likely as ZFT ages from the Grenville terrane would have all been fully reset during Ottawan Orogenesis.

2. ZFT ages of detrital zircon from the Potsdam and Galway Formations record the cooling history of the Grenville terrane following peak metamorphism at c. 1.0-1.1 Ga. The two ZFT cooling ages may correspond to post-orogenic exhumation (c. 780 Ma) and rifting related to the opening of the Iapetus Ocean and break up of Rodinia (c. 540 Ma). The small percentage (~5%) of older ZFT cooling ages (>1.0 Ga) probably represents grains derived from the Superior or Yavapai-Mazatzal terranes to the west of NY State.

3. The ZFT ages presented here suggest that significant post-Devonian deposition and burial over the Adirondacks did not occur. The old ZFT ages (i.e. not reset) are not consistent with widespread heating to temperatures >190°C due to 8-10 km of burial as suggested by other workers (Johnsson, 1986; Sarwar and Friedman, 1995). In fact these ZFT data refute any ideas that require significant post Devonian burial of the Grenville basement in this area. The ZFT ages from these Adirondack samples also do not support the idea of widespread Taconic heating, however, Taconic heating events could have been the result of localized fluids. Additional samples from the Adirondack region could provide more insight. It is possible that these heating events were not long enough or hot enough to affect the annealing kinetics of fission tracks in zircon.

ANNEALED OR PARTLY ANNEALED SAMPLES

1. These thermochronological data suggest that the well known CAI isotherm maps for NY State (Weary et al., 2001) reflect a combination of several heating events, especially for those areas with CAI values >4 in the central and eastern part of the State. Heating related to Mesozoic rifting, Alleghenian burial, and Taconic fluids appear to be likely candidates for the variable but high CAI values in the eastern part of the state. While the wide swath of CAI 4 values covering the middle and southern section of the state could be a result of cooling after the Acadian orogeny.

2. The alpha dose screening method developed as part of this study allows extraction of meaningful component grain populations from over-dispersed grain-age data. While it is desirable to have thorium concentration data for complete alpha dose estimates, it is probably not necessary. Because Thorium accounts for roughly 5-10% of the total alpha does, it is probably acceptable to use the eU parameter, 1.5:1 (U:Th), for calculating alphas dose estimates.

3. ZFT ages show Alleghenian heating has affected a majority of the reset zircon grains in the Taconic Allochthon. The percentage of grains reset to Alleghenian ages increases from north to south along the allochthon and farther to the south in to Pennsylvania, suggesting heating was more intense to the south.

4. A small population of grain ages from samples in Hudson Valley apparently were heated in the Mesozoic and this heating is likely related to rifting and intrusives (see Hudson valley example in Garver et al., 2005).

PAPERS AND ABSTRACTS SUPPORTED BY THIS NYSERDA GRANT

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