JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 107, NO. B11, 2296, doi:10.1029/2001JB001094, 2002

The ^{40}Ar-^{39}Ar laser analysis of K-feldspar: Constraints on the uplift history of the Grenville Province in Ontario and New York

Margaret M. Streepey,[1] Chris M. Hall, and Ben A. van der Pluijm
Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, USA

Received 27 August 2001; revised 5 April 2002; accepted 10 April 2002; published 15 November 2002.

[1] A comprehensive geochronologic database describes a period of late extension across the Metasedimentary Belt (MB) of the Grenville Province in northeastern North America. Because extension continued through much of the young unroofing history of the region, these data do not bracket the timing of final extension across all shear zones and do not constrain the timing of final juxtaposition of terranes. Analysis of K-feldspar in the MB by the ^{40}Ar-^{39}Ar method can give information on the very latest perturbations in the area since K-feldspars have multiple, low closure temperatures, ranging from about 150° to 300°C. These multiple diffusion domains require temperature-time modeling to fully interpret argon release spectra. This modeling requires precise knowledge of the temperature of degassing of each step, which usually requires the use of a resistance furnace for sample analysis. We establish a first-order relationship between laser power and temperature, which can be used for multidiffusion domain modeling of K-feldspars. Comparison of samples analyzed by both methods reveals virtually no difference between the systems, supporting the validity of K-feldspar analyses by laser step heating. Our data suggest that using the laser for K-feldspars can give results that are geologically reasonable, precise, and easier to collect. In this case, these data are then applied to the cooling history of the North American Grenville Province. Our K-feldspar analyses show that the latest extensional motion along shear zones in the MB is after 900 Ma, and the region is uplifting as a uniform block by 780 Ma. *INDEX TERMS:* 8109 Tectonophysics: Continental tectonics—extensional (0905); 1035 Geochemistry: Geochronology; 9619 Information Related to Geologic Time: Precambrian; 1094 Geochemistry: Instruments and techniques; 8102 Tectonophysics: Continental contractional orogenic belts; *KEYWORDS:* Grenville, Ar-Ar, K-feldspar, geochronology, extension, North America

Citation: Streepey, M. M., C. M. Hall, and B. A. van der Pluijm, The ^{40}Ar-^{39}Ar laser analysis of K-feldspar: Constraints on the uplift history of the Grenville Province in Ontario and New York, *J. Geophys. Res.*, *107*(B11), 2296, doi:10.1029/2001JB001094, 2002.

1. Introduction

[2] The southeastern portion of the Grenville Province of northeastern North America is a very well studied section of a Precambrian orogenic belt, with evidence that the latest episodes of contractional deformation in the study area are at circa 1040 Ma [*McLelland et al.*, 2001; *Davidson*, 1998; *Rivers*, 1997; *McEachern and van Breemen*, 1993]. There is an abundant database of geochronologic information in the region, yielding a detailed temperature-time history from this latest episode of contraction to its late extensional history. Because the metamorphic and cooling histories are so well constrained, it is an ideal area for tests of new approaches to thermochronometry which can address the exhumation history of the area.

[3] The laterally continuous Grenville Province in North America ranges from Labrador, Canada, down through southern Ontario and New York State, with outliers of Grenville-aged rocks occurring down the eastern coast of North America and in Texas. To the west, the Grenville Front Tectonic Zone juxtaposes the Grenville belt with Archean subprovinces (Figure 1). In southern Ontario and New York, the Grenville Province is divided into three lithotectonic belts, the Gneiss Belt, the Metasedimentary Belt, and the Granulite Terrane, defined by distinct geological and geophysical differences [*Wynne-Edwards*, 1972]. These crustal slices are separated by ductile shear zones, with the Metasedimentary Belt boundary zone separating the Gneiss and Metasedimentary Belts, and the Carthage-Colton shear zone separating the Metasedimentary Belt and the Granulite Terrane.

[4] The Metasedimentary Belt (MB) of the Grenville Province in Ontario and New York is composed primarily of greenschist to granulite facies metasediments, with major ductile shear zones separating terranes with distinct metamorphic and cooling histories (Figure 1). A combination of structural/kinematic studies, petrologic analysis, and geo-

---

[1] Now at Department of Geological Sciences, Florida State University, Tallahassee, Florida, USA.

0148-0227/02/2001JB001094$09.00

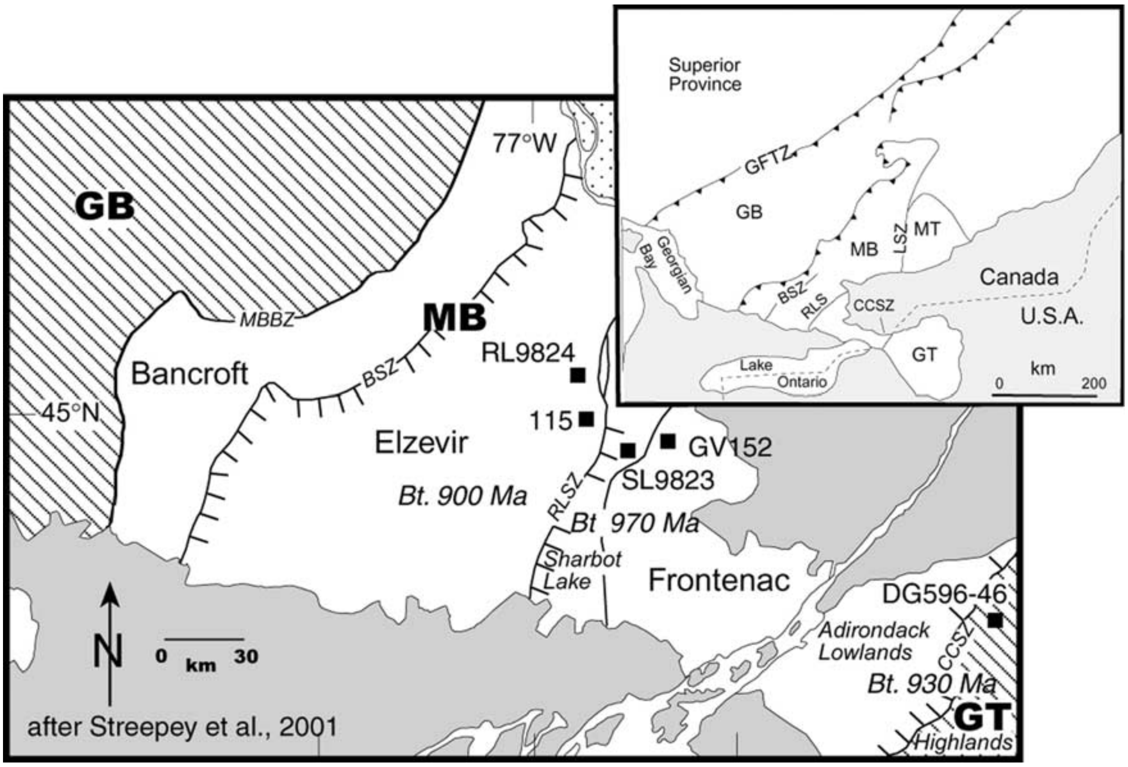

Figure 1. Generalized map of the Metasedimentary Belt in the Grenville Province (inset map shows the North American Grenville Province). The positions of the late extensional shear zones are shown with tick marks indicating the latest sense of motion (BSZ, Bancroft Shear Zone; RLSZ, Robertson Lake Shear Zone; CCSZ, Carthage Colton Shear Zone). MBBZ, Metasedimentary Belt Boundary Zone; GB, Gneiss Belt; GT, Granulite Terrane; MT, Morin Terrane; LSZ, Labelle Shear Zone; GFTZ, Grenville Front Tectonic Zone. Locations of K-feldspar samples in this study are shown, and biotite ^{40}Ar-^{39}Ar ages for each domain are indicated for reference (ages from *Busch and van der Pluijm* [1996] and *Streepey et al.* [2000]). Paleozoic cover indicated in gray.

chronologic investigations have given detailed temperature-time paths over most of the area [*Cosca et al.*, 1991, 1992; *Mezger et al.*, 1991, 1993; *van der Pluijm et al.*, 1994], which outline a tectonic history that spans over 200 Myr.

[5] Initial metamorphism of the region, during the first cycle of Grenville orogenesis, is documented by U/Pb analyses of sphene and zircons at circa 1150 Ma [e.g., *Rivers*, 1997, and references therein]. This age of metamorphism is seen in most of the MB and is followed by a second period of metamorphism and deformation at circa 1050 Ma [*Mezger et al.*, 1993; *Busch et al.*, 1997; *Streepey et al.*, 2001]. This later period of activity is not recorded in several terranes of the MB, leading to hypotheses that these terranes were both laterally (along strike) and vertically separated during this period. Later, postorogenic, extension is documented along the Robertson Lake Shear zone (RLSZ) (separating the Elzevir and Sharbot Lake/Frontenac domains) and the Carthage-Colton shear zone (CCSZ) at the eastern edge of the MB (separating the Adirondack Lowlands of the Frontenac from the Adirondack Highlands of the Granulite Terrane) [*Busch et al.*, 1996; *Streepey et al.*, 2000]. This motion is primarily constrained by ^{40}Ar-^{39}Ar analyses of hornblende and biotite in the regions adjacent to the shear zones. Hornblende ages on the hanging wall side of the RLSZ are ~100 Myr older than those in the footwall. The same displacement is seen across the CCSZ.

[6] The closure temperature of hornblende to the argon system is ~500°C [*McDougall and Harrison*, 1999], which is close to the peak temperatures recorded during the amphibolite facies conditions of metamorphism in most of these areas. Therefore hornblende analyses give information on the early, postmetamorphic portion of the cooling history and show that, during this early portion of cooling, the terranes comprising the MB were at different crustal levels. The closure temperature of biotite to the argon system is ~300°C, which yields information on the later, extensional portion of the MB's cooling history. Across the RLSZ, biotite ages vary by almost 100 Myr [*Busch and van der Pluijm*, 1996]. However, biotite ages are the same across the CCSZ, which brackets the time of final extension across this shear zone (after the timing of closure to the hornblende system and before the timing of closure to the biotite system [*Streepey et al.*, 2000]). Therefore argon analyses of biotite constrain the timing of final motion across the CCSZ but do not constrain the latest history of the RLSZ (Figure 2).

[7] Obtaining accurate information on the low-temperature portion of the cooling histories of ancient metamorphic terranes is, at best, difficult. Fission track work on apatites in this region, with a closure temperature of ~125°C, generally gives ages that are Mesozoic [*Roden-Tice et al.*, 2000]. An approach that bridges the temperature

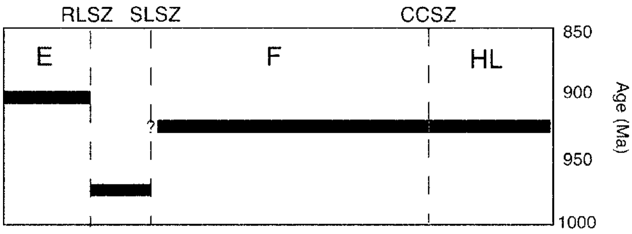

Figure 2. Profile across the Metasedimentary Belt with average biotite ages for each domain shown. Offsets in biotite ages occur across shear zone boundaries. In the Elzevir (E) domain, biotite ages are 900 Ma. Over the Robertson Lake Shear Zone (RLSZ) they increase to 970 Ma. Across the Sharbot Lake Shear Zone (SLSZ), biotite ages appear to decrease to circa 930 Ma in the Frontenac (F) domain. There is no offset in biotite ages across the Carthage Colton Shear Zone (CCSZ), indicating that the final episode of extension motion occurred along this zone before 930 Ma.

gap is the ^{40}Ar-^{39}Ar analysis of K-feldspar. The closure temperature of K-feldspar to the argon system, although debated, is known to be less than 300°C [*McDougall and Harrison*, 1999]. Potassium feldspars are ubiquitous in the MB, and, therefore, an excellent choice for a regional comparison of late cooling histories. The addition of K-feldspar analyses to our current database of geochronologic data provides over 300 million years of temperature time information and geochronologically constrains this area, from its early stages of contractional activity through the transition to extension, to a time during which the entire area was unroofing as a coherent block.

[8] There is considerable debate over the method of interpretation of argon analyses from slowly cooled K-feldspars [e.g., *Harrison*, 1990; *McDougall and Harrison*, 1999; *Parsons et al.*, 1999]. At the center of the discussion lies the hypothesis that feldspars have multiple, discrete diffusion domains, different from amphibole or phyllosilicate in which a single diffusion length-scale is used to describe volume diffusion in the grain. In feldspar, diffusion domains vary in size and their associated closure temperatures range from about 150 to 300°C. The multiple diffusion domain (MDD) hypothesis, proposed by *Lovera et al.* [1989] states in general terms that each of these domains retains argon at different closure temperatures, so that a single grain preserves a cooling history, rather than a single cooling age. The ^{39}Ar release data are combined with the apparent age and the temperature of degassing to model the temperature-time history of a single grain. The key underlying assumption in MDD theory is that degassing behavior in the laboratory matches degassing behavior in nature, so that multiple diffusion domains are not the product of structural breakdown of the feldspar at high temperatures. It has been shown that age spectra from slowly cooled K-feldspars differ from those predicted by single-diffusion domain theory as proposed by *Dodson* [1973]. *Lovera et al.* [1989, 1991, 1993] calculated the difference between the actual ^{39}Ar release and the predicted spectra to find the number of domains and their closure temperatures that best fit the actual spectra.

[9] When analyzing potassium feldspars, it is important to have precise temperature control during degassing of samples. Most feldspar analyses are performed in a resistance furnace, where thermocouples directly measure the temperature inside the crucible. However, furnace methods of analysis are cumbersome, requiring prolonged periods of temperature cycling and dwelling at a specific temperature for a certain length of time to thoroughly degas the sample. One of the greatest strengths of a laser step-heating method, as opposed to the resistance furnace method, is the speed and precision of analysis. However, there is no direct temperature information for the laser method, which is required for temperature-dependent modeling. In this paper, a new method is introduced for equating laser power with temperature of degassing. When matching the laser results with results from the standard resistance furnace method, the laser step-heating method is shown to be a quick and reliable alternative to resistance furnace analysis. These results in the Grenville Province constrain the latest uplift history in the MB and give information on the evolution of orogenic belts, most importantly, how long it takes for the crust to begin to stabilize after orogenesis.

2. Methods

[10] Samples were collected across the RLSZ, in the Elzevir and Frontenac domains and across the CCSZ into the Adirondack Highlands (Figure 1). Hand samples were crushed, cleaned, and sieved. K-feldspar grains were separated using standard separation techniques followed by handpicking under a binocular microscope to ensure that the resulting sample was pure feldspar. For both resistance furnace and laser analyses, three to five grains were loaded into Al foil packets and irradiated at the University of Michigan Ford Phoenix reactor at position L67 for 120 mWh. The standard MMhb-1 (age 520.4 Ma [*Samson and Alexander*, 1987]) was also irradiated and measured to calculate neutron flux in the reactor. Samples analyzed by the resistance furnace method were loaded into a high-vacuum sample chamber above the furnace. Single grains were loaded into individual wells on Cu trays for argon analysis using the laser system.

[11] The tantalum resistance furnace was initially conditioned through a series of high-temperature cyclings and dwellings at selected temperatures, from 400°C to 1750°C. Temperature in the furnace was monitored through the use of a thermocouple inserted into the base of the Ta crucible. This thermocouple measures temperatures in the external portion of the furnace; temperatures within the crucible were then determined indirectly. In our experience with the Ta furnace at the University of Michigan, temperature differences of several hundred degrees Celsius are possible between the external thermocouple and the location of the sample package. In order to estimate the actual sample temperature, a thermal model incorporating heat capacity, radiative heating, radiative cooling, and conductive heat losses was fit to measured internal temperatures measured before samples were loaded. Temperatures estimated by this model, which uses the measured external temperature as an input parameter, mimic the known time and temperature lag of the samples within the Ta furnace, which was determined directly in a separate experiment. The results of this thermal

model were automatically logged every 5 s. The resulting time-temperature history of the sample during was then used to model the sample's diffusion parameters. This complex thermal trajectory information is incompatible with the standard data reduction methods of *Lovera et al.* [1989, 1991]. Instead, a variant of the method briefly described by *Hall* [1990] and *Meert et al.* [2001], and described below, was adapted to analyze the data. To test this technique against the Lovera method, published data from *Heizler and Harrison* [1998] were reanalyzed using the reduction method by *Hall* [1990]. The two procedures were found to be compatible.

[12] For analysis, irradiated foil packets containing three to five grains of feldspar were dropped from the sample chamber into the molybdenum-lined crucible with the use of a magnet. Foil on the sample packets burned off at very low temperatures and did not affect our results. The individual heating schedules for samples varied, depending on the size of the sample and its gas release. In the very early portion of the release (before obtaining a significant signal of ^{39}Ar), steps were 50°C to 100°C. At the earliest appreciable signals of ^{39}Ar, the step size was decreased to 10°C increments until melting of the sample. In many instances, it was necessary to run multiple steps at one temperature to fully degas the sample. As samples required more than one day of analysis, the system was cooled at the end of each working day, and any remaining gas in the system during cooling was collected and included in analysis. Using an automated system, a specified temperature was obtained through computer control. The sample was allowed to dwell at a temperature for thirty minutes before inletting gas into the mass spectrometer. The resistance furnace and laser samples were run on the same VG1200 mass spectrometer. Sample signals for feldspars were large enough to require analyses using the Faraday collector almost exclusively. In general, a single feldspar packet required a minimum of approximately 80 to 100 steps to fully degas.

[13] For laser analysis, single, irradiated grains were loaded into individual wells in a Cu tray. K-feldspars were step heated until fusion using an argon-ion laser and analyzed on the VG1200 mass spectrometer also used to analyze resistance furnace samples. Individual steps comprised heating for sixty seconds with a defocused beam followed by two minutes of gas purification using two 10 l/s SAES getters (ST101 alloy) and a liquid N_2 cold finger. Laser line blanks were generally run after every six steps. As with the resistance furnace, individual heating schedules varied as a function of the gas release of the sample. However, sample step sizes were between 10 and 20 mW during the major release of ^{39}Ar. In general, it required between 80 and 100 steps to thoroughly degas a single feldspar grain with the laser. However, the speed of laser analysis cut the laboratory time needed to fully degas a sample nearly in half compared to that required for furnace analysis.

3. Results

[14] K-feldspars analyzed by the resistance furnace did not generally yield smooth release patterns. Spectra and argon data tables are included in a data repository[1]. Anomalous K/Cl ratios in initial steps probably indicate the presence of fluid inclusions, which do not affect the release spectra at higher temperatures. There is evidence for widespread, postgranulite facies, chlorine-rich fluid infiltration in this part of the Adirondacks [*Morrison and Valley*, 1988], and fluid inclusions are probably related to this event in New York. It is likely that significant amounts of fluid were present in similar rocks in Ontario and may also explain the anomalous K/Cl ratios found in the early release of those K-feldspars as well. Some disturbance of resulting spectra may also be due to the analysis of multiple grains at once, rather than degassing individual grains. Spectra produced by laser-line analysis were generally much cleaner than furnace analyses and therefore easier to interpret. K/Cl and K/Ca ratios in initial steps indicate that fluid inclusions may affect the apparent ages in the first few steps; however, their contribution does not appear to last past those few steps.

4. Modeling

[15] The MDD model was developed in the late 1980s, when it was first hypothesized that the wide range of apparent argon ages seen within single K-feldspar samples might be due to a distribution of diffusion domain sizes within the mineral. To test and apply this idea, an analytical technique that combines laboratory degassing experiments with numerical inversion procedures has been developed to extract cooling history information from feldspars [e.g., *Lovera et al.*, 1989, 1991]. A key part of the method involves careful control of temperature in the laboratory to constrain the diffusion parameters of the feldspar samples.

[16] As was previously noted, it proved to be difficult to adapt the Ta furnace data to the data reduction techniques of *Lovera et al.* [1989, 1991]. Instead a modification using the method of *Hall* [1990] and *Meert et al.* [2001] was used, which was tested for compatibility by analyzing published results using both methods. An advantage of this technique is that it does not require a subjective assignment of the number of discrete domain sizes, and it is computationally extremely efficient, generating a complete fit of the measured argon release pattern and age spectrum within a few seconds on a personal computer.

[17] The first step to fitting a set of domains to the observed ^{39}Ar release pattern is to discretize the range of possible domain sizes. This is a common first step in many methods of geophysical inverse theory [e.g. *Menke*, 1984]. Several discretization schemes are possible, such as choosing a pre-exponential factor D_0 and then allowing for a discrete set of evenly spaced values for the size parameter a, thereby yielding a set of frequency factor values D_o/a^2. This is conceptually similar to the scheme of *Lovera et al.* [1989, 1991], who, although allowing for a continuum of domain sizes, base the fit on a set of values for r/r_o, where r_o is the size of the smallest domains. Instead, we have chosen to consider an evenly spaced set of closure temperatures (T_c) that can be converted back into domain sizes using a rearranged version of the closure temperature equation of *Dodson* [1973]:

$$\ln\left(\frac{Do}{a^2}\right) = \frac{E}{RT_c} + \ln\left(\frac{E}{R}\right) - 2\ln(T_c) + \ln\left(-\frac{dT_c}{dt}\right) - \ln(A). \quad (1)$$

Here A is a parameter which depends upon the geometry of the problem and takes on the values 55, 27, or 8.7 for the sphere, cylinder, or infinite slab, respectively. This system has the advantage that the T_c parameter, which is the most important factor for tectonic interpretation, is guaranteed to be uniformly represented in the discretization over the expected range of blocking temperatures.

[18] It is possible to set the number of allowed values of T_c to be so high that the discretization interval is fine enough to closely approximate a continuum. The suite of possible domains is a uniformly distributed set of 251 discrete domains having closure temperatures [*Dodson*, 1973] ranging from 50°C to 300°C, using infinite slab geometry and assuming a cooling rate at closure of 0.5°C/Myr. Therefore the allowed domain set has a temperature resolution of 1°C, which should be adequate for describing any reasonable set of actual domains. Having constructed a set of allowed domain closure temperatures, it is necessary to perform the forward modeling calculation for the expected gas release of each potential domain for the experimental conditions experienced by the K-feldspar sample. That is, for a given set of experimental times and temperatures, it is necessary to calculate the fraction of ^{39}Ar expected to be released by each domain. This can be accomplished using the well known diffusion equation solutions of *Carslaw and Jaeger* [1990] for each domain. For example, for spherical geometry, the fraction of gas released $f[x]$ is given by

$$f(x) = 1 - \frac{6}{\pi^2} \sum\nolimits_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 x\right), \tag{2}$$

where x is defined as

$$x = \int_0^t \frac{D}{a^2}(\tau) d\tau. \tag{3}$$

An Arrhenius relationship is assumed for the diffusion parameters of each domain, such that

$$D = D_0 \exp\left(-\frac{E}{RT}\right). \tag{4}$$

The inverse problem of fitting a set of domains to the experimentally measured ^{39}Ar release pattern can now be stated as follows: let the number of allowed domains be n, the number of step-heating fractions be m, and the ith fraction of ^{39}Ar released by the jth domain be denoted as p_{ij}. A matrix $\mathbf{P}$ can be defined as

$$\mathbf{P} = \left[p_{ij}\right]. \tag{5}$$

Let ϕ_i be the fraction of the mineral represented by the ith domain and ϕ is the vector consisting of all the ϕ_i. The problem of fitting the domain distribution to the measured volume release $\mathbf{d}$ can be stated as solving, in the least squares sense,

$$D = P\phi. \tag{6}$$

This is a highly underdetermined problem as m is typically $\ll n$. However there are two constraints that greatly restrict the allowed solution space. First, the sum of the domain fractions must equal one, and, secondly, there can be no negative contributions. Therefore, in addition to equation (6), it is necessary to satisfy

$$\sum_{i=1}^{n} \phi_i = 1 \tag{7}$$

$$\phi_i \geq 0. \tag{8}$$

The combination of equation (6) with constraints (7) and (8) constitutes a standard problem in quadratic programming, and we used the algorithm outlined by *Mifflin* [1978].

[19] As written, equation (6) produces an unrealistic model, as it yields a solution that minimizes the absolute misfit of gas volume release. This heavily weights large fractions and tends to ignore small, low temperature fractions, which hold most of the information regarding the smallest domains. Equation (6) can be modified to weight the equations to give a solution with nearly constant relative error. If an expected relative error of 1% is assumed, subject to a minimum absolute fraction error of 1×10^{-5}, then the ith fraction would be expected to have an error σ_i of

$$\sigma_i = 0.01 d_i \quad d_i \geq 0.001 \text{ or } 1 \times 10^{-5}, \tag{9}$$

otherwise a weighting matrix $\mathbf{W}$ can be defined as

$$\mathbf{W} = \mathrm{diag}[1/\sigma_1] \tag{10}$$

And equation (6) can be modified to yield a best fit with nearly constant relative error using

$$\mathbf{Wd} = \mathbf{WP\Phi}. \tag{11}$$

In the above scheme, the discretization process produces a set of T_c and therefore an equivalent set of $\ln[D_o/a]$ values. However, the activation energy E has not been determined. *Lovera et al.* [1989, 1991] showed that if for the earliest gas fractions, all domains are experiencing just the beginning stages of gas loss, an Arrhenius plot will yield a linear array parallel to the true activation energy. Unfortunately, if some domains become highly depleted during the earliest fractions, the activation energy determined by this procedure can be biased, possibly to erroneously low values. Since the quadratic programming solution method is computationally efficient, it is possible to test the behavior of the solution for a wide range of activation energies. There seems to be very little difference in the goodness of fit over the rather broad range from 45 to beyond 60 kcal/mol. This means that the volume release pattern alone, or for that matter the Arrhenius plot, does not constrain the value of the activation energy. As pointed out by *Hall* [1990] and *York and Hall* [1990] this holds true for other published studies of K-feldspar, including ones with heating schedules that include temperature cycling. Using this method with resistance furnace data, it can be shown that a broad range of diffusion activation energies can be made to fit laboratory data [*York and Hall*, 1990]. Given that plus the lack of direct laboratory temperature estimates, it is not possible to accurately estimate this parameter from the data, and instead, a typical value for K-feldspar of 50 kcal/mol was assumed.

[20] The age spectra can either be fit visually or the same quadratic programming algorithm can be used to fit the volume release pattern to create a monotonically cooling thermal history that fits the volume release and the measured age spectrum. Instead of fitting temperature to time, one fits time, or more precisely $\delta[e^{\lambda t}\text{-}1]$, as a function of temperature. Requiring that these values are nonnegative assures monotonic cooling.

[21] In this study, argon isotopes from single crystals of K-feldspar that were analyzed using a laser mimic the types of data seen in standard resistance heater experiments. Using a single added free parameter in the model, it may be possible to analyze these data in the multidomain style. For this conversion it is necessary to convert laser power to temperature, as temperature cannot be measured directly during laser analyses as is done with samples analyzed using the resistance furnace. The basic assumption to convert laser power into a proxy for temperature involves the mechanism for heat loss for a sample that is laser step heated. *Hall et al.* [1988] demonstrated, using data from an infrared pyrometer, that to a very good approximation, cooling of a heated mineral grain in a UHV vacuum system could be accounted for via blackbody radiation and that thermal losses from conduction were negligible. Given this assumption, sample temperature at steady state will be determined by a balance of laser power absorption and blackbody radiation. Therefore, using the Stefan-Boltzmann law, the relationship between laser power and temperature can be written as

$$\alpha P = T^4 - T_0^4,$$

where P is laser power, T is absolute temperature, and T_0 is ambient temperature. The parameter α is a proportionality constant that will depend on the sample's reflectivity, emissivity, grain size, opacity, the laser beam size and other details of the system's optics. It is not possible to assign α accurately from first principles but, given both the expected degassing temperatures for K-feldspars [400°–1100°C] and the actual laser powers used, we can roughly estimate that for our experiments α should have values of about $2–3 \times 10^9$ with P measured in mW and T measured in K.

[22] Both the furnace and laser models require an input parameter constraining the maximum age of the samples. The closure temperature of K-feldspar is generally taken to be lower than the closure temperature of biotite, which is estimated at 300°C [*McDougall and Harrison*, 1999]. Since biotite ages are well known in this part of the Grenville, we have assigned maximum ages of the K-feldspar based on ^{40}Ar-^{39}Ar of biotites taken from rocks adjacent to the samples analyzed in this study (Figure 1). Because biotite ages are different in the MB, different maximum ages were used in models depending on sample location.

[23] Once the argon release pattern has been fit, the resulting set of domains with nonzero volume contributions is assigned argon closure ages in order to fit the measured apparent age spectra. This was done assuming monotonic cooling from temperatures above the maximum allowed closure temperature, and allowance was made for possible disturbances of the spectrum of each domain because of slow cooling through the closure temperature. This correction used a method similar to that outlined by *Onstott et al.* [1989] and *York* [1984]. The resulting age-temperature pairs can then be used as the basis for constructing a possible cooling history for the sample. Of course, the derived cooling trajectory is not the only possible cooling history that can fit the data; multiple episodes of reheating and argon loss are also possible. However, the fitted cooling trajectory will be close to the lowest possible cooling rates that can fit the data. This model is nonunique and it is not required by the data. It is, however, perfectly compatible with them.

[24] The K-feldspar data and the model fit to the age spectra for samples analyzed using the resistance furnace (both ages and ^{39}Ar release) are shown in Figure 3, and those analyzed using the laser are shown in Figure 4. For all laser analyses, a range of models with a variety of α values is shown. The temperature-time paths that result from the multidiffusion domain analysis are also shown. Although these models yield information about the late, low-temperature portion of the thermal history of a sample, this part of the model represents a small amount of the total ^{39}Ar released by the sample. Therefore the very young portions of the temperature-time paths of these samples can be highly variable but do not necessarily represent a significant event. This may instead be an artifact of the model trying to fit data that are not robust and do not represent a significant amount of the gas release of the sample. Therefore, in the tectonic interpretations, it is important to focus on the portion of the cooling history that occurs immediately after the closure of biotite.

[25] To check the validity of the laser models, it is critical to compare a single sample analyzed by both the laser and furnace methods. Figure 5 shows the combined temperature-time paths for sample 115, from the Elzevir domain (see Figure 1), analyzed by both the laser and resistance furnace methods. ^{40}Ar-^{39}Ar ages of biotites in this region are ~900 Ma, which gives us a good estimate of the maximum age to use for feldspar models. Model spectra fit the data well in each case. Temperature-time data are plotted for multiple values of α for sample 115 and compared to temperature-time data from the furnace sample at an activation energy of 50 kcal/mol. Although changing the α parameter shifts the temperature-time curve, the shape of the curve and the absolute temperature-time history of the sample are in good agreement for both our laser and furnace analyses. Therefore K-feldspar data obtained through laser step-heating analysis can be modeled using the multidiffusion domain theory and compared with K-feldspar samples analyzed by the more traditional resistance furnace method.

5. Discussion

[26] Sample locations are plotted in Figure 1, along with associated ^{40}Ar-^{39}Ar biotite ages that are used for reference. Samples 115, GV152, and DG596-46 were all analyzed using the resistance furnace, whereas 115, RL9824, and SL9823 were analyzed using the laser. Collectively, these samples span the eastern Metasedimentary Belt of the

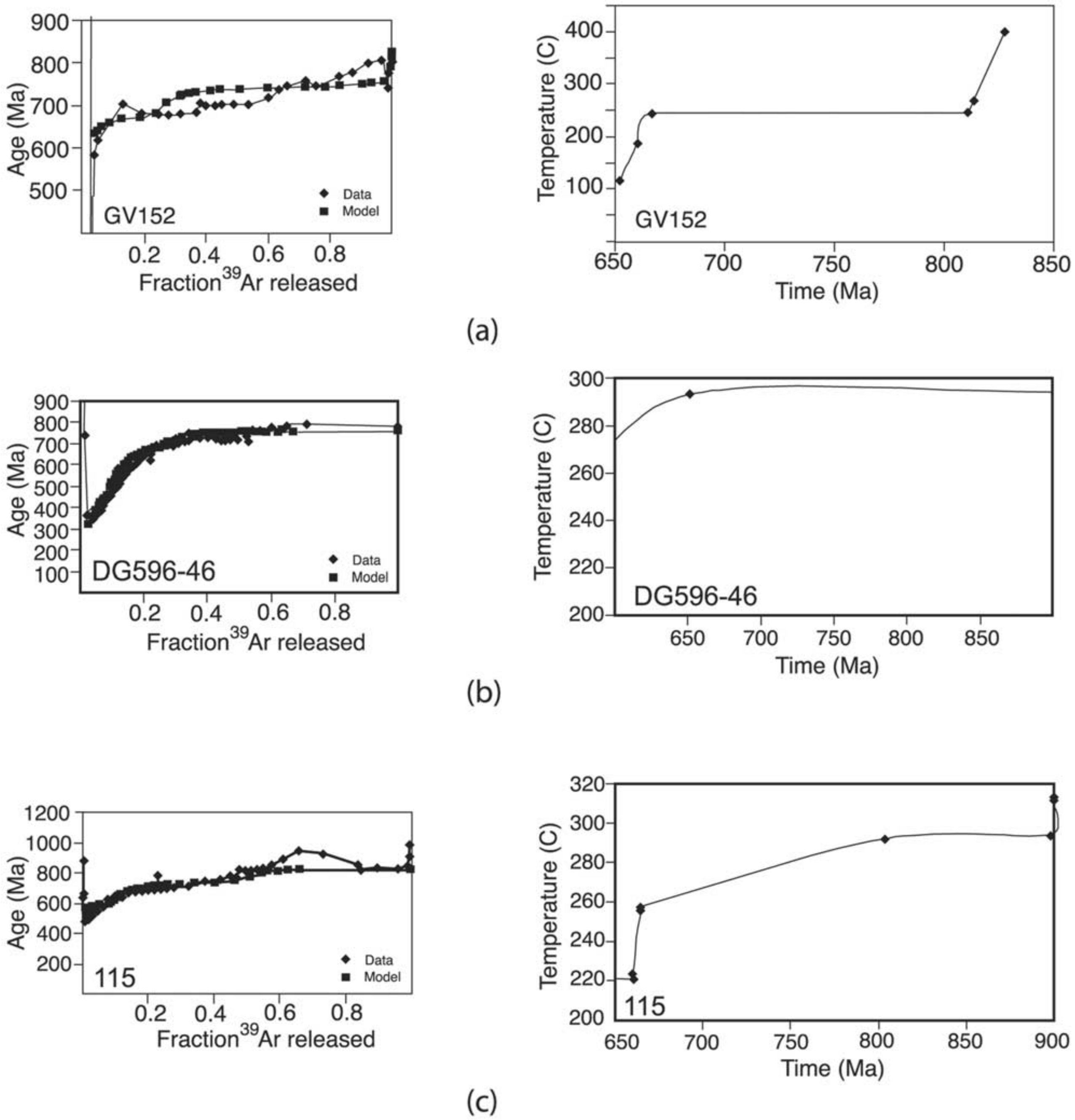

Figure 3. Model age spectra plotted with actual age spectra for samples analyzed in the Ta furnace. Model temperature-time curves for each sample are also shown. Activation energies for models were uniformly 50 kcal/mol. Maximum model ages for the K-feldspar were constrained using biotite ^{40}Ar-^{39}Ar ages (see Figures 1 and 2) for (a) sample GV152, (b) sample DG596-46, and (c) sample 115.

Grenville Province in Ontario and New York. This region includes at least two fundamental tectonic boundaries, the Robertson Lake shear zone (RLSZ) and the Carthage-Colton shear zone (CCSZ). As discussed (see above) previous hornblende and biotite ^{40}Ar-^{39}Ar ages constrain the timing of latest extension across the CCSZ at 945 Ma [*Streepey et al.*, 2001] but do not provide such a constraint across the RLSZ, where there is still offset across the boundary at circa 900 Ma. Analysis of the temperature-time paths for these K-feldspar samples show that, even though there are offsets among our samples at circa 900 Ma, cooling histories over the eastern portion of the MB are the same within ~30 Myr starting at 800–780 Ma (Figure 6).

[27] Figure 7 is a schematic diagram showing the tectonic evolution of the eastern MB, as constrained by previous geochronologic and structural work in the RLSZ, CCSZ, and their bounding domains and the new feldspar data reported here. At circa 1050 Ma, the entire region was affected by transpressional deformation, juxtaposing ter-

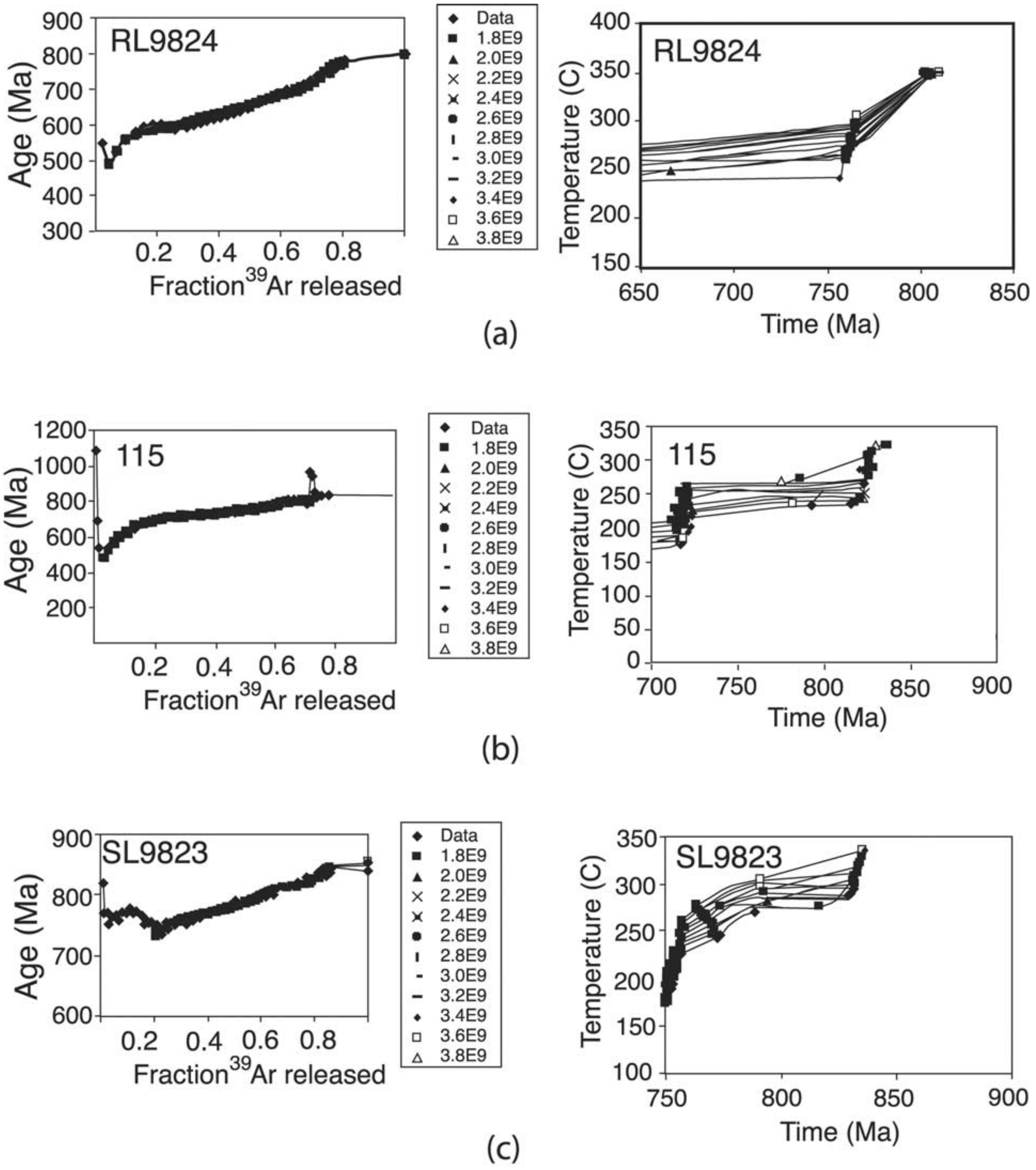

Figure 4. Model age spectra plotted with actual age spectra for samples analyzed using the laser. Models were calculated for a range of α values (see text for definition). Resulting temperature-time curves for each model are also shown. Biotite ^{40}Ar-^{39}Ar ages constrain the maximum K-feldspar model ages for (a) sample RL9824, (b) sample 115, and (c) sample SL9823.

ranes that had been laterally separated. One hundred million years later, at circa 945 Ma, the eastern MB was undergoing extension, reactivating both the RLSZ and the CCSZ. After 900 Ma, a final episode of extension occurred along the RLSZ, adjusting the Elzevir, Frontenac (and Adirondack Lowlands), and Adirondack Highlands to their current positions relative to one another. By approximately 780 Ma, the region was cooling as a coherent block, signaling the end of regional tectonic activity. Later perturbations associated with the opening of Iapetus at circa 650 Ma appear to be recorded in some of our K-feldspar samples, which are in agreement with pulses of activity recorded in K-feldspar in the eastern Adirondacks [*Heizler and Harrison*, 1998]. However, the event does not cause widespread resetting of K-feldspars in the western portions of the Metasedimentary Belt. This Appalachian rift-drift event

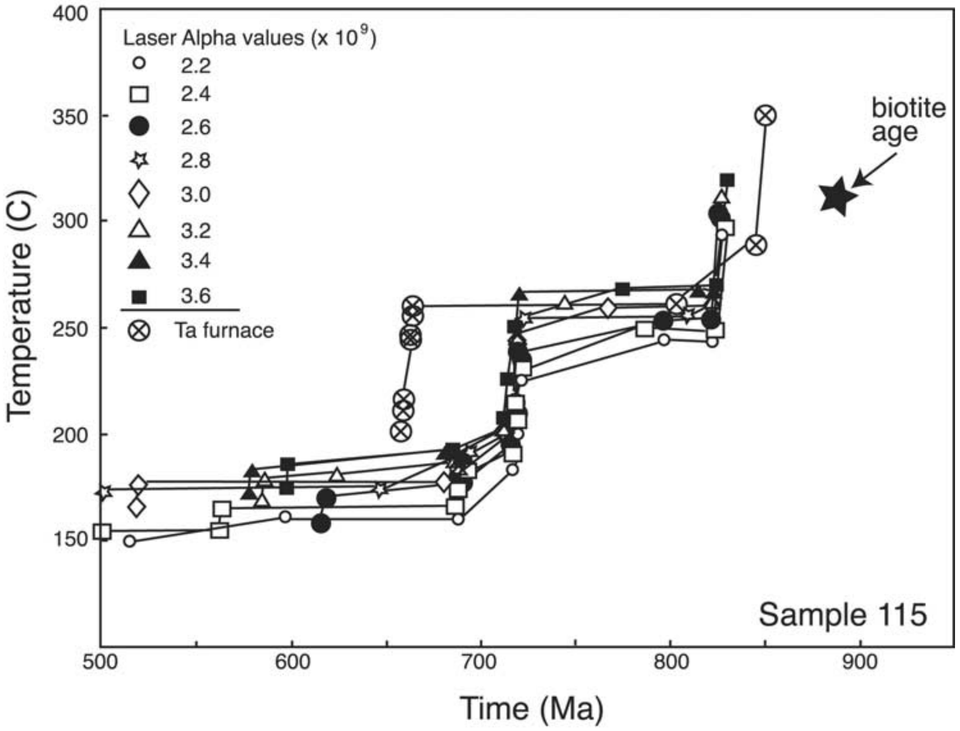

Figure 5. Plot of model cooling histories for sample 115 obtained by both the Ta furnace and the laser line. Cooling curves are in good agreement until circa 750 Ma, when the small volume of gas release makes the model fit difficult.

was apparently not significant in the area and did not reactivate the CCSZ or RLSZ.

6. Conclusions

[28] In this study, a new approach to K-feldspar thermochronology is presented. The modeling work shows that laser step-heating is a powerful method to analyze slowly cooled K-feldspars in ancient terranes that provides a viable alternative to the time intensive, and more cumbersome, resistance furnace method of analysis. In addition, new data provide information on the previously unconstrained, latest history of the Grenville Province of Ontario and western New York.

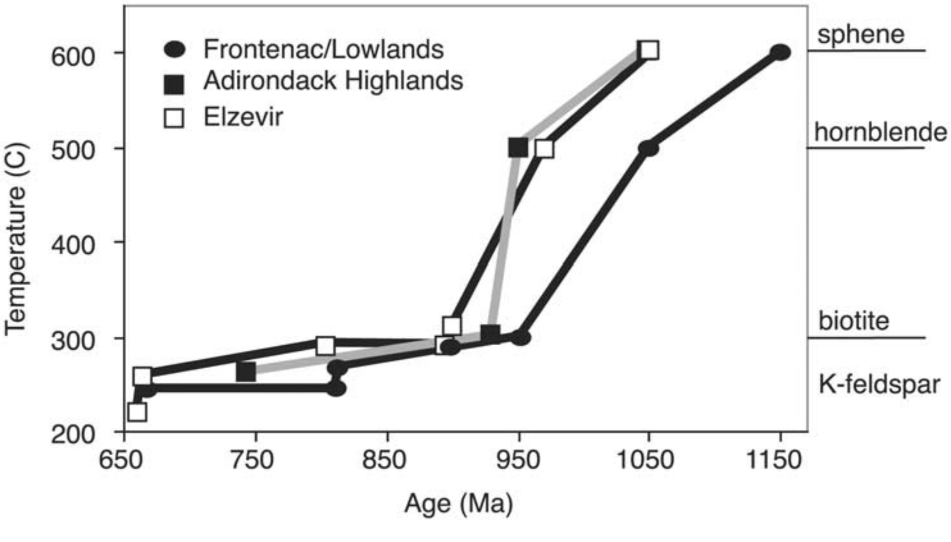

Figure 6. Composite temperature-time paths for Frontenac domain, Elzevir domain, and Adirondack Highlands. Sphene ages from *Mezger et al.* [1991, 1993]; hornblende and biotite ages from *Cosca et al.* [1991], *Busch et al.* [1996], and *Streepey et al.* [2000]. Domains have distinct metamorphic histories. Plot clearly shows that all domains are at the same temperatures (and therefore depths) by circa 780 Ma.

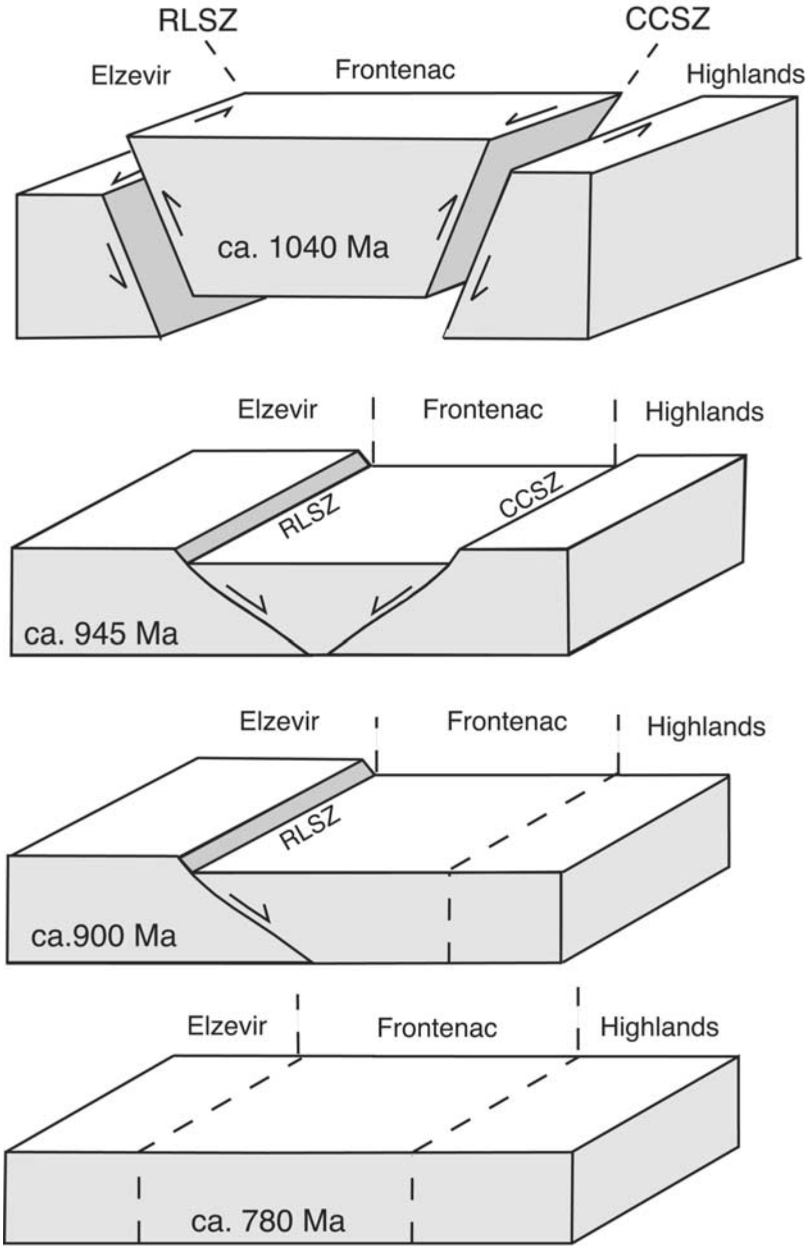

Figure 7. Schematic tectonic scenario for eastern Metasedimentary Belt. At circa 1040 Ma, entire area undergoes transpression. Approximately100 Myr later, there is a transition to extension. By circa 930 Ma, extension has ceased along the CCSZ. By 780 Ma, extension has ceased along the RLSZ, and entire block is unroofing as one coherent unit.

[29] It is essential to constrain the timing of deformation in order to understand the process of orogenic evolution, particularly the mechanisms that modify mountain belts after their last episodes of contraction. K-feldspar analyses show the latest episodes of deformation at circa 780–800 Ma in the eastern MB, and thus limit the amount of time needed (at least in the Grenville Province) for the crust to stabilize and uplift as a uniform block after a protracted history of contraction. It is known that postorogenic extension is a common feature in mountain belts, and that the physics controlling uplift and extension of mountain belts changes little even if the kinematics of plate motion that drive orogenesis are unique for individual mountain belts. Therefore this temporal information can be used as the framework for modeling the factors that control modification of the crust (for example, gravitational collapse and mantle delamination) after orogenesis.

[30] **Acknowledgments.** This work was funded by National Science Foundation (NSF) grant EAR-9627911 (to B.v.d.P.), the University of Michigan F. Scott Turner fund (to M.M.S.). Neutron irradiations were provided by the Phoenix-Ford Reactor at the University of Michigan. We would like to thank Oscar Lovera for assistance with argon data reduction software and Marcus Johnson for technical assistance in the Radiogenic Isotope Geology Laboratory at the University of Michigan. Thanks to Matt Heizler and Andrew Hynes for reviews that improved the manuscript. Eric

Essene is thanked for insightful comments on a review of an earlier version of the manuscript.

References

Busch, J. P., and B. A. van der Pluijm, Late orogenic, plastic to brittle extension along the Robertson Lake shear zone: Implications for the style of deep-crustal extension in the Grenville orogen, Canada, *Precambrian Res.*, *77*, 41–57, 1996.

Busch, J. P., B. A. van der Pluijm, C. M. Hall, and E. J. Essene, Listric normal faulting during postorogenic extension revealed by ^{40}Ar/^{39}Ar thermochronology near the Robertson Lake shear zone, Grenville Orogen, Canada, *Tectonics*, *15*, 387–402, 1996.

Busch, J. P., K. Mezger, and B. A. van der Pluijm, Suturing and extensional reactivation in the Grenville Orogen, Canada, *Geology*, *25*, 507–510, 1997.

Carslaw, H. S., and J. C. Jaeger, *Conduction of Heat in Solids*, 510 pp., Clarendon, Oxford, England, 1990.

Cosca, M. A., J. F. Sutter, and E. J. Essene, Cooling and inferred uplift/erosion history of the Grenville orogen Ontario: Constraints from ^{40}Ar-^{39}Ar thermochronology, *Tectonics*, *10*, 959–977, 1991.

Cosca, M. A., E. J. Essene, M. J. Kunk, and J. F. Sutter, Differential unroofing within the Central Metasedimentary Belt of the Grenville orogen: Constraints from ^{40}Ar-^{39}Ar thermochronology, *Contrib. Mineral. Petrol.*, *110*, 211–225, 1992.

Davidson, A., An overview of Grenville Province geology, Canadian Shield, in *Geology of the Precambrian Superior Province and Precambrian Fossils in North America*, edited by S. B. Lucas and M. R. St-Onge, *Pap. Geo. Surv. Can.*, *7*, 205–270, 1998.

Dodson, M. H., Closure temperature in cooling geochronological and petrological systems, *Contrib. Mineral. Petrol.*, *40*, 259–274, 1973.

Hall, C. M., A method for estimating diffusion parameters and thermal histories from K-spar ^{40}Ar/^{39}Ar data, *Eos Trans. AGU*, *71*, 1297, 1990.

Hall, C. M., J. D. Redman, P. W. Layer, and D. York, ^{40}Ar/^{39}Ar Ages from a fully automated laser microprobe, *Eos Trans. AGU*, *69*, 520, 1988.

Harrison, T. M., Some observations on the interpretation of feldspar ^{40}Ar/^{39}Ar results, *Chem. Geol.*, *80*, 219–229, 1990.

Heizler, M. T., and T. M. Harrison, The thermal history of New York basement determined from ^{40}Ar/^{39}Ar K-feldspar studies, *J. Geophys. Res.*, *103*, 29,795–29,814, 1998.

Lovera, O. M., F. M. Richter, and T. M. Harrison, The ^{40}Ar/^{39}Ar thermochronometry for slowly cooled samples having a distribution of diffusion domain sizes, *J. Geophys. Res.*, *94*, 17,917–17,935, 1989.

Lovera, O. M., F. M. Richter, and T. M. Harrison, Diffusion domains determined by ^{39}Ar released during step heating, *J. Geophys. Res.*, *96*, 2057–2069, 1991.

Lovera, O. M., M. Heizler, and T. M. Harrison, Argon diffusion domains in K-feldspar, II, Kinetic properties of MH-10, *Contrib. Mineral. Petrol.*, *113*, 381–393, 1993.

McDougall, I., and T. M. Harrison, *Geochronology and Thermochronology by the ^{40}Ar/^{39}Ar Method*, 2nd ed., 212 pp., Oxford Univ. Press, New York, 1999.

McEachern, S. J., and O. van Breemen, Age of deformation within the Central Metasedimentary Belt Boundary Thrust Zone, southwest Grenville orogen—Constraints on the collision of the mid-Proterozoic Elzevir terrane, *Can. J. Earth Sci.*, *30*, 1155–1165, 1993.

McLelland, J., M. Hamilton, B. Selleck, J. McLelland, D. Walker, and S. Orrell, Zircon U-Pb geochronology of the Ottawan Orogeny, Adirondack Highlands, New York: Regional and tectonic implications, *Precambrian Res.*, *109*, 39–72, 2001.

Meert, J. G., C. Hall, A. Nedelec, and M. O. M. Razanatseheno, Cooling of a late-syn orogenic pluton: Evidence from laser K-feldspar modelling of the Carion granite, Madagascar, *Gondwana Res.*, *4*, 541–550, 2001.

Menke, W., *Geophysical Data Analysis: Discrete Inverse Theory*, Academic, San Diego, Calif., 1984.

Mezger, K., C. M. Rawnsley, S. R. Bohlen, and G. N. Hanson, U-Pb garnet, sphene, monazite, and rutile ages: Implications for the duration of high-grade metamorphism and cooling histories, Adirondack Mts., New York, *J. Geol.*, *99*, 415–428, 1991.

Mezger, K., E. J. Essene, B. A. van der Pluijm, and A. N. Halliday, U-Pb geochronology of the Grenville orogeny of Ontario and New York: Constraints on ancient crustal tectonics, *Contrib. Mineral. Petrol.*, *114*, 13–26, 1993.

Mifflin, R., A feasible descent algorithm for linearly constrained least squares problems, in *Nonsmooth Optimization: Proceedings of a IIASA Workshop March 28–April 8 1977*, edited by C. Lemarechal and R. Mifflin, pp. 103–130, Pergamon, New York, 1978.

Morrison, J., and J. W. Valley, Post-granulite facies fluid infiltration in the Adirondack Mountains, *Geology*, *16*, 513–516, 1988.

Onstott, T. C., C. M. Hall, and D. York, ^{40}Ar/^{39}Ar thermochronometry of the Imataca complex, Venezuela, *Precambrian Res.*, *42*, 255–291, 1989.

Parsons, I., W. L. Brown, and J. V. Smith, ^{49}Ar/^{39}Ar thermochronology using alkali feldspars; real thermal history or mathematical mirage of microtextures?, *Contrib. Mineral. Petrol.*, *136*, 219–229, 1999.

Rivers, T., Lithotectonic elements of the Grenville Province: Review and tectonic implications, *Precambrian Res.*, *86*, 117–154, 1997.

Roden-Tice, M. K., S. J. Tice, and I. S. Schofield, Evidence for differential unroofing in the Adirondack Mountains, New York State, determined by apatite fission-track thermochronology, *J. Geol.*, *108*, 155–169, 2000.

Samson, S. D., and E. C. Alexander, Calibration of the interlaboratory ^{40}Ar-^{39}Ar dating standard, Mmhb-1, *Chem. Geol.*, *66*, 27–34, 1987.

Streepey, M. M., B. A. van der Pluijm, E. J. Essene, C. M. Hall, and J. F. Magloughlin, Late Proterozoic (circa 930 Ma) extension in eastern Laurentia, *Geol. Soc. Am. Bull.*, *112*, 1522–1530, 2000.

Streepey, M. M., E. L. Johnson, K. Mezger, and B. A. van der Pluijm, Early history of the Carthage-Colton Shear Zone, Grenville Province, northwest Adirondacks, New York (U.S.A), *J. Geol.*, *109*, 479–492, 2001.

van der Pluijm, B. A., K. Mezger, M. A. Cosca, and E. J. Essene, Determining the significance of high-grade shear zones by using temperature-time paths, with examples from the Grenville orogen, *Geology*, *22*, 743–746, 1994.

Wynne-Edwards, H. R., The Grenville Province, in Variations in tectonic styles in Canada, edited by R. A. Price and R. J. W. Douglas, *Spec. Pap. Geol. Assoc. Can.*, *11*, 263–334, 1972.

York, D., Cooling histories from ^{40}Ar/^{39}Ar Age spectra: Implications for Precambrian plate tectonics, *Annu. Rev. Earth Planet. Sci.*, *12*, 384–409, 1984.

York, D., and C. M. Hall, Sensitivity of ^{40}Ar/^{39}Ar derived thermal histories to diffusion parameter estimates, *Eos Trans. AGU*, *71*, 1297, 1990.

C. M. Hall and B. A. van der Pluijm, Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1063, USA. (cmhall@umich.edu; vdpluijm@umich.edu)

M. M. Streepey, Department of Geological Sciences, Florida State University, Tallahassee, FL 32306, USA. (streepey@quartz.gly.fsu.edu)