Staurolite Indicator of Regional Metamorphism

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Abstract

Different isotopic dating methods can be utilized to ascertain the geologic age of an area. Isotope geochronology continues to evolve with newer methods. Applying uranium and lead isotopic ratios gathered from the mineral staurolite, the relative age of when regional metamorphic thermal apex occurred of the southern Appalachian Mountains mainly Talladega Belt and the western Blue Ridge can be determined. The results will establish whether staurolite analyzes represent growth or cooling stages of metamorphism. These results once completed will provide additional isotopic evidence to support Rebekah Brosky's research. Experimental procedures involve rock crushing, handpicking, clean lab usage, ion exchange columns, and a thermal ionization mass spectrometer.

Introduction

This experiment is a continuation of Rebekah Brosky's master's thesis to gather more scientific data in evidence of Brosky's hypothesis that the mineral staurolite can determine whether or not regional metamorphism occurred in the southern Appalachian Mountains. After receiving her B.S. degree in biochemistry at Florida State University, Rebekah Brosky continued her chemistry route and focused in geochronology for her M.S. at Florida State University's geochemistry department. Her thesis was to ensure that staurolite analyses represent growth rather than cooling ages of metamorphism. Our purpose is to provide additional supporting isotopic evidence of her results.

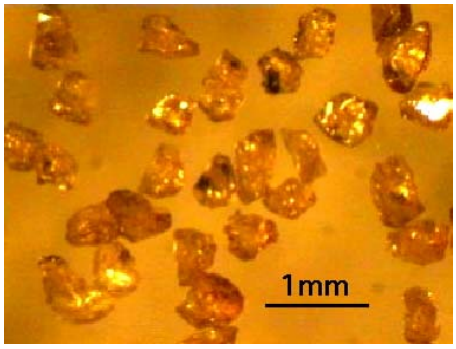
Regional metamorphism is the changing of rocks under high temperatures and pressures into new mineral and rocks. There are three types of rocks: igneous, sedimentary, and metamorphic. Igneous rock is formed from the cooling of hot magma and lava from volcanic activity. Sedimentary rock is formed from the deposits of sediments over a period of time. Metamorphic rock is the changing of an existing solid rock to another rock as the result of heat, pressure, and/or chemically active fluids. Sometimes multiple metamorphoses occur in a region.

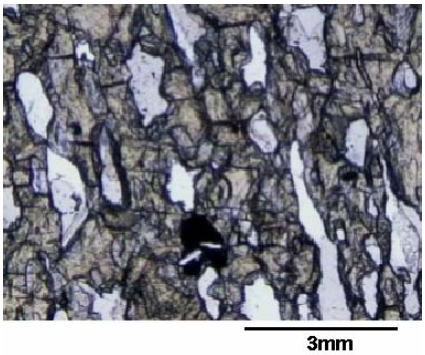
The time of metamorphism in an area can be determined through methods of dating rocks and minerals. The onset of regional metamorphism is not a brief event but can extend over millions of years, a long period for geologic time. As pre-existing rocks and sediments are buried during natural geologic processes, there is a gradual increase of temperature and pressure in the surrounding environment. Then, there is a quick and abrupt increase in temperature and pressure; this is the thermal apex, or thermal maximum. During this time, minerals melt and crystallize and undergo a variety of geochemical processes. The rocks and minerals gradually cool and erosion takes place causing uplift of those rocks that were buried and underwent metamorphism. Given the metamorphic cycle, isotopic dating is used only to *approximate* the time of the brief thermal apex. Geologically, the rocks quickly cool to the closure temperature of Pb-U diffusion in staurolite.

In order to determine when metamorphism occurred, the mineral staurolite is utilized because it is a "high-grade metamorphic mineral and has a high closure temperature to isotope diffusion" (Brosky 4). Meaning that when the parent atom uranium beta decays to the daughter atom lead, all radiogenic daughter atoms are still present in the mineral. It is a closed system therefore nothing is removed; no chemical movement occurs in or out of its chemical composition. The isotopic ratios are locked the moment the rocks reach the closure temperature of Pb-U diffusion.

Staurolite is a silicate mineral containing iron and aluminum $(OH)_2Fe_2Al_9Si_4O_{22}$. Georgia's state mineral is the focus mineral in this study and is abundantly found in the southern Appalachian Mountains. Having ideal characteristics for isotopic dating, staurolite is advantageous with a high closure temperature to isotope diffusion (over 500°C) as well as a high U-Pb ratio, being a closed mineral system, and also being resistant to chemical weathering ensures its preservation as a mineral on sediments. Depending on the angle observed staurolite has a golden-red-brown coloring. When looking for staurolite within rocks on location it is often found in conjunction with magnetite (black) and quartz (clear) and appears metallic dark-gray. See Figure 1 for examples.

Figure 1. Staurolite.





The mineral staurolite used in this experiment to determine the metamorphic age of the southern Appalachian Mountains. Larger rock samples were gathered by Rebekah in the basement of the western Blue Ridge mountains and the Talladega Belt of the southern Appalachians. Three samples were collected based on the size of the mineral inclusions. These samples were obtained from three locations: Cherokee Quarry near Tate, Georgia, River Rock Creek in Cherry Log, Georgia, and from Rebekah's Power and Forest field trip near Marble, North Carolina. Rock from the Cherry Log, Georgia site was the only sample used is this experiment for the additional evidence needed for Brosky's research.

The peak of regional metamorphism determined by Butler was around 470 million years ago, though the exact time of metamorphism in this area is very controversial as Rebekah goes into further detail. The western side of the southern Appalachians appears older than the eastern side; the ages tend to young toward the southeast. All samples should define a single isochron for the time of metamorphism. Isochron is from the Greek 'isos' meaning equal and 'chron' meaning time, so an isochron of the different samples should maintain an equal time period metamorphism occurred.

Geochronology is the estimation of time gone by using the radioactive properties of elements in minerals. Important measurement discoveries have been made in geochronology that have allowed this research to be possible. One is that mass spectrometry can provide accurate results in common lead contamination (See Table 9 in Brosky's appendix), the other, in isotopic ratios of $^{207}Pb/^{206}Pb$ abundance ratio and $^{238}U/^{235}U$ ratio. Other methods used to determine geochronology are Ar/Kr, Sr/Sr and Rb/Sr dating. Many of the geochronological dating done in the southern Appalachain Mountains by K-Ar or Ar-Ar mineral methods produce poor limits of detection for several reasons. Argon gas may diffuse out of the sample while still part of the environment. Argon is highly volatile and makes sample preparation, and thus data collection and ratio measurement, difficult.

The isotopes worked with in this research are those of lead and uranium. Four stable isotopes occur naturally for lead: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Three naturally occurring isotopes for Uranium exist: ^{234}U, ^{235}U, and ^{238}U. ^{235}U and ^{238}U decay independently with two very different decay rates. ^{235}U decays to ^{207}Pb and ^{238}U decays to ^{206}Pb. The high U-Pb ratios found in staurolite allow a sample to be used as a precise metamorphic chronometer, within ±10

million years. The primary focus of this study were isotope ratios $^{207}Pb/^{206}Pb$ and $^{238}U/^{235}U$. Isochrons of ^{238}U-^{206}Pb tend to be the most reliable in lead-uranium geochronology, especially for low U-Pb minerals.

The theory behind isotopic dating is that "the activity of a radioactive isotope decreases with time, but is still proportional to the number of parent atoms remaining at any time" (Brosky 4).

Equation 1: $N = N_o e^{-\lambda t}$

Equation 1 indicates the number of radioactive parent atoms (N) that remain at any time, t, of an original number of parent atoms (N_o) at t = 0.

Equation 2: $D = D_o + N(e^{-\lambda t} - 1)$

Equation 2 is normally used to determine age by geochronology. But this equation can only be applied if four conditions are met. (1) The ratio of radiogenic daughter to parent atoms remaining only changes from radioactive decay. The mineral must be a closed system. (2) The original amount of daughter atoms before radioactive decay must exist and be real, this can be determined from an isochron plot. (3) The decay constant (λ) for the parent atom must be known. (4) The respective daughter and parent atoms present after radioactive decay (at present time) must be evaluated and measured accurately. Before a time period can be considered an 'age,' there must also be supporting geological evidence. (Brosky 4-6). The parent atoms (radioactive) in this study are $^{238}U/^{235}U$ and the daughter atoms (radiogenic) are ^{206}Pb and ^{207}Pb, respectively. The focus ratios can be substituted into equation 2 creating equation 3 and equation 4.

Equation 3: $^{206}Pb/^{204}Pb = {}^{206}Pb_o/^{204}Pb + {}^{238}U/^{204}Pb\ (e^{-\lambda t} - 1)$

Equation 4: $^{207}Pb/^{204}Pb = {}^{207}Pb_o/^{204}Pb + {}^{235}U/^{204}Pb\ (e^{-\lambda t} - 1)$

Any ^{204}Pb observed during the isotopic analyses, in excess of laboratory blank, is considered common lead and is evidence that the mineral did initially contain lead at the time the sample staurolite crystallized.

Methods and Materials

With the samplings gathered from the Cherry Log, Georgia, location (ChLS label), the larger rock samples were cut into manageable pieces with the rock crusher located on Florida State University's campus. Using a rock slicer, the smaller rocks were segmented into three samples: ChLS 2, ChLS 3, and dChLS 2. Afterwards usage of a hammer crushed the samples and then using the mortar and pestle grinded. To guarantee purity of the sample and a consistent size, the crushed grains went through sifters throughout the grinding process. The sieve sizes applied to ensure the least amount of inclusions on the samples were 74-105µm.

After the sieving of the grains, a Franz Isodynamic Magnetic Separator was utilized to separate the more magnetic grains from those of less magnetism. A high tilt was used on the magnetic separator, because staurolite is of the middle ground: not too magnetic but not completely non-magnetic, which is difficult to separate. There was a definite difference between the grain colorization once separated. The sample containing the most staurolite was more a brighter red color than the other less magnetic which was dark gray colorization. Staurolite is often found with magnetite and quartz, which can explain the differences in colorization. Magnetite is a black mineral and quartz is clear. After going through the magnetic separator a couple of times a sample containing a lot of staurolite was achieved which was a red-brown coloration.

Once the particles were differentiated based on magnetism, the difficult task of separation by hand began. Using a binocular microscope, the samples were hand picked keeping the sample grains that had the least amount of inclusions (black specs of magnetite or large amounts of quartz). These samples without inclusions were considered 'clean.' Collecting 'clean' samples took three days for three people to gather three samples worth of a target sample size of 20mg. The 'clean' sample sizes collected were 22mg ChLS2, 17mg ChLS3, and 25mg ChLS 2. Under the binocular microscope, petri dishes and microscope slides were used to contain the staurolite grains. Tiny wires not much thicker than a strand of hair were used as tools. The samples were collected in clean 10ml Pyrex beakers.

Before continuing with the samples, Teflon contains and bottles, centrifuge tubes, and pipette tips that were to be used in holding, moving, and storage of the samples had to be cleaned. 200μL pipette tips were calibrated to ensure their accuracy. To avoid contamination clean lab procedures were employed with the equipment used with the samples. Working with such microscopic sample sizes, even dust particles and other tiny impurities can alter results. The clean lab in the isotopic geochemistry department at NHMFL Tallahassee was utilized. Please refer to the Appendix Experimental Procedures on procedures followed in the clean lab.

Once enough grains of staurolite were collected, they were first soaked in a 2% nitric solution in an ultrasonic bath for 15-20 minutes in Pyrex beakers. The samples were transferred into clean 15ml Teflon containers with screw-on lids. Placing samples that "attached" to the Pyrex beakers in a sonicator for a few more minutes loosened the particles. Afterwards, a small pipette was used to extract the HNO_3 without taking any of the grains of staurolite. Then the samples were rinsed with quartz-distilled (QD) which was extracted with the pipette using different tips each time, repeated two more times. Acetone was put in the samples to dry out the DI and extracted as much acetone with taking any of the particles. The remaining acetone was evaporated by putting the samples in the oven around 10˚C, and checked often. Be careful evaporating the acetone, if left too long in the oven the particles will start to pop out of the Teflon beakers. After evaporation of the liquids, let the beakers cool, then weigh, because some sample might have been lost during cleaning.

In the clean lab, the granular staurolite samples need to be dissolved into liquid. Dissolution mixture of a 4:3:2:1 ratio of 6N HCl, HNO_3, $HClO_4$, and HF, respectively, was blended in a Teflon bottle. Three milliliters were added to each of the samples and two blanks with the proper spike amounts. A known amount of ^{205}Pb spike was added to measure the $^{205}Pb/^{206}Pb$ isotopic ratio. ^{205}Pb is artificially produced and does not occur naturally. Essentially 100%

pure, ^{205}Pb was synthetically produced and obtained from the University of Toronto. The $^{238}U/^{235}U$ ratio for our Uranium spike is 0.00175, also added to the three samples and the two blanks. The ^{235}U is enriched uranium approximately 99% pure prepared and obtained from the Oak Ridge National Laboratory in Tennessee. The portion of ^{235}U spike was diluted ten times with quartz-deionized water (QD). The amounts of spike added to each sample is summarized in Figure 2.

Figure 2. Amounts of ^{235}U spike and ^{205}Pb spike added to each sample.

Sample	**^{205}Pb (g)**	**(μL)**	**Actual**	**^{235}U (g)**	**(μL)**	**Actual**
$ChLS_2$	**0.500**	**499**	**500**	**0.278**	**278**	**280**
$ChLS_3$	**0.500**	**499**	**500**	**0.215**	**215**	**215**
$dChLS_2$	**0.500**	**499**	**500**	**0.316**	**316**	**315**
Blank 1	**0.500**	**499**	**500**	**0.266**	**266**	**265**
Blank 2	**0.750**	**749**	**750**	**0.500**	**499**	**500**

The five Teflon containers were tightly sealed and placed on a hotplate at approximately 150° (the accurate temperature is unknown just markings on the instrument). The containers remained in the dissolution mix until all the grains were dissolved. This took approximately 3 weeks at this setting.

This is the point reached at the end of the time period of the internship. Explanations of the remaining procedures still to be executed follow.

After the particles are fully dissolved, they undergo evaporation to dryness and rinsing series to further clean the samples. The first evaporation is in the hotbox with the temperature at 250° for 1-2 hours. Once solution is evaporated, add 3mL 6N HCl to each sample and each blank, make sure to wash down the inside walls of the Teflon beakers. Evaporate this to dryness between temperatures 150-175. Then raise the temperature to about 250° for 1-2 hours to dry off any remaining $HClO_4$. Repeat with the 3mL 6N HCl two more times, then remove the beakers from the hotplate to cool. At room temperature, add 1mL 7N HNO_3 to each beaker of dried sample and dried blanks. Recover containers and leave alone for 30-60 minutes, until entire sample has completely dissolved again. In separate, clean centrifuge tubes pipette solutions and rinse the remainder from the beakers with a few drops of the 7N HNO_3 into the tubes. Centrifuge for 1-2 minutes, until the solution is clear and any remaining solid is collected at the bottom of the tube. Using pipettes, measure and document the total volume of liquid solution.

The samples must then go through ion exchange columns that separate lead and uranium from the rest of the sample. Ion exchange separation works by exchanging similar ions. An ion attached to a resin is exchanged for one in solution of the same charge, hence the name ion, a charged particle. There are two types of ion exchange: anion exchange, which involves the exchange of negative ions, and cation exchange, which exchanges positive ions. Uranium and

lead are extracted from the samples through separate anion exchange columns with an anion resin and several acid solutions.

The extraction processes for both elements are similar though different acids and resins are employed. The columns, Pb column: 40 Microliter Anion Columns and U column: 400 Microliter Anion Column, are loaded with the proper resins, and then prepared involving cleaning and conditioning the columns before sample is added. Uranium is collected once after loading and washing the sample; whereas, lead is collected twice. Between each collection of lead, remaking the resin column, cleaning and conditioning is necessary. When all uranium and lead are extracted and collected, samples are evaporated to dryness. This entire extraction procedure takes a long time since every last drop of sample must go through the column between each acid added. Refer to Appendix for outlined lead and uranium procedures in worksheets on this process.

First, uranium is collected in separate clean Teflon containers from the 400 Microliter Anion Columns once made, cleaned and conditioned. A portion of each sample needs to be set aside until lead collection begins during the sample processing section from "load sample 0.5ml 7N HNO_3" to "wash 2ml 6N HCl." Continue with uranium collection by following the remaining procedures of the worksheet. Collect this fraction in separate Teflon containers. Add 1 drop 0.025N H_3PO_4 and dry on the hotplate between 150 and 175°. To clean the uranium fraction, add 3 drops 7N HNO_3 and dry same as above, repeat the 3 drops two more times. Sample will end in dryness state. Set aside for use in loading.

Next is lead separation from the samples. Evaporate the lead fraction of the samples and the blanks to dryness. Rinse them with 0.5N HBr and dry, repeat two more times. Continue to follow the worksheet procedures. Once the 40 Microliter Anion Columns are made, cleaned, and conditioned, execute the first run of the sample, collect the lead and dry. Reconstruct the columns with new resin, then clean and condition, as previously. To ensure purity of lead collected, separation must be done twice. Unlike uranium at 400µL, lead columns are even smaller at 40µL. Proceed to the second run of lead separation. Loading the portion of sample that has already been lead separated once and has been dried. Follow the first step of process again and continue. After adding one drop of H_3PO_4 to each collected fraction, evaporate to dryness on hotplate at temperature setting 150-175°. At this time, recall the ^{205}Pb spike samples that were set aside to be calibrated. Add 500µL of lead standard to each of the three containers with 500µL of the spike. These calibration samples must be evaporated to dryness as well.

Before being able to test the isotopic ratios, the uranium and lead need to be loaded on filaments. Making and loading the filaments takes place under the loading hood, not in the clean lab. Making and degassing several filaments can be done while waiting for samples to dissolve. See Figure 3a for an example of a single Re filament.

For uranium, use single Rhenium (Re) filaments. Load colloidal graphite onto degassed, clean filament, and heat gently (0.1A at a time) to evaporate the water. This gives a uniform graphite layer to load the sample onto. Add enough 0.1N HNO_3 to dissolve each uranium fraction sample. Once dissolved, load each sample onto separate filaments with the graphite coating. Gently heat the sample until it is dry. Then add another coat of colloidal graphite on top of the

sample and heat, making a "graphite sandwich." In this experiment, a total of three samples, two blanks, and three standards will be loaded onto filaments. Record the total volume (μl) that is loaded onto each filament (measuring with pipette that is used to load). Load 3 different amounts of the standards: 0.50μL, 1.00μL, and 2.00μL. The standard that is used is the 1000ppm ICPMS Uranium standard. Dilute 2μL of this standard with 8μL QD water.

For lead, use zone-refined single Rhenium filaments. Dissolve each dry sample in 0.25N HNO_3. Then, mix silica gel (Refer to notes on silica gel for Pb in Appendix), H_3PO_4, HNO_3/sample in a micropipette. Then load the entire mixture onto a degassed filament, one drop at a time, gently drying between drops. Here, three samples, two blanks, three standards, and three ^{205}Pb spike calibrations will be loaded. Again, record the actual volume that is loaded onto each filament. The amounts of the standards are as follows: 0.50μL, 1.50μL, and 2.50μL. The standard that is used is the NBS 981 standard.

Figure 3. a)Single Re Filament b)Magazine c)Magazine in TIMS Chamber

The FINNIGEN/MAT 262 Thermal Ionization Mass Spectrometer (TIMS) is located in the Geochemistry department at the National High Magnetic Field Laboratory in Tallahassee, Florida. This instrument uses heat to determine the concentrations of isotopes of an element based on their masses and consists of a variety of components: an ion source, an analyzer, a detector, a vacuum system, electronic power & current supply, and computer software. Please refer to an example in the Appendix.

The TIMS works by having an electric current pass through and heat the filaments until the temperature reaches approximately 1300°C. The maximum temperature reached varies between elements. At this maximum temperature, the sample evaporates from the filaments in the form of positive ions. These ions accelerate through slits in 5 round metallic parallel plates that increase negatively in voltage up to energies of 10,000 volts. The slits focus the ions into a narrow ion-beam toward the analyzer. The analyzer consists of a curved light tube and electric magnet. As ions enter the magnetic field they are deflected. The lighter ions are deflected more than the heavier ions. Ion beams, each beam a different isotope of the element, are left in the magnetic field and lead toward the detector. The detector contains six movable Faraday cups that are pre-positioned to catch the ions. The cups are connected to grounded wires where a charge passes through a resistor and sets a small current. The current at each cup is proportional

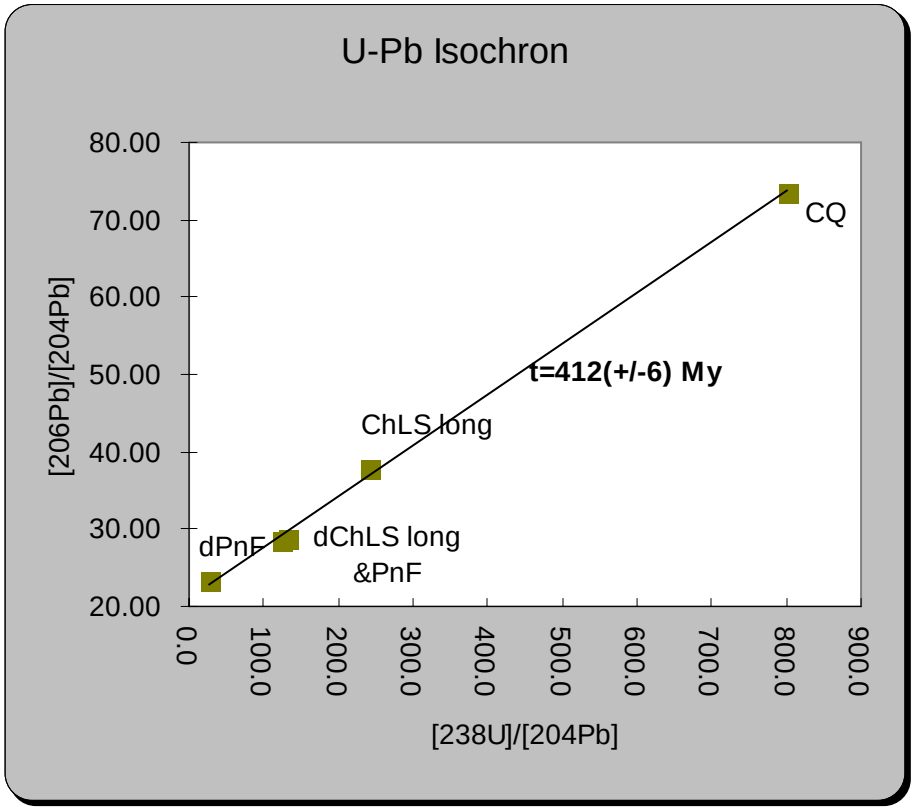
to the number of ions hitting that cup. The currents are read by an electrometer and data is sent to a computer, where the ratio of ion currents can be determined.

Once filaments are loaded with samples, they are then attached and covered to a magazine wheel. Please see Figure 3b. The magazine is placed inside the chamber of the mass spectrometer. Please see Figure 3c. The magazine can hold 15 samples at a time. Two runs are needed, because can only run either lead or uranium, cannot run both at the same time. Once the magazine is in the mass spectrometer, depressurizing begins. Follow operating procedures found in the user's manual of the spectrometer. Also look for previous staurolite samples run on the MAT 262 in the mass spec lab book, and should be followed for consistency and accuracy. Use the static U program, taking 2-5 blocks of 5-10 runs for each uranium sample, measuring ^{238}U and ^{235}U at 1700°C-1800°C. For Lead samples, different methods are used for each different ratio measurement. Here, different Pb isotopes for samples versus blanks versus spike calibrations versus standards will be measured. Spike calibration: $^{204}Pb/^{205}Pb$, blanks: $^{208}Pb/^{205}Pb$, samples and standards: $^{208}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$, $^{208}Pb/^{207}Pb$, and $^{204}Pb/^{205}Pb$. Lead data will be collected in 5 blocks of 5-10 runs each, at an average temperature between 1200°C-1350°C.

Anticipated Results

Data collected from the TIMS will be plugged into spreadsheets already created by Brosky. The results expected should correlate with Brosky's research results. Isochrons of ^{238}U-^{206}Pb tend to be the most reliable in lead-uranium geochronology, especially for low U-Pb minerals. The age of this isochron should be indistinguishable from the isochron obtained from ^{235}U-^{207}Pb. Refer to Figure 4. Concordance will be evaluated of these isotopes and should be achieved and correlate to that of Rebekah's previous results of the same samples. Causes of discordia are (1) episodic lead loss, (2) continuous diffusion of lead from mineral crystals, (3) chemical weathering. Rebekah's results of the U-Pb dating of staurolite indicate that the thermal peak of metamorphism in the studied part of the western Blue Ridge took place between 406 & 418 million years ago. This date is defined by her isochrons, and is significant because this time period has never before been so narrowly defined for the southern Appalachians. Rebekah's conclusions are based upon good analytical agreement with the data. There is a U-Pb isochron and a Pb-Pb isochron plot with low standard error as well as a Concordia plot with an age that is indistinguishable from that of the isochrons.

Figure 4.



Discussion

During the fall semester 2002, progress on this project and experiment regarding staurolite will be continued. Then, the results obtained can finally be compared to Rebekah Brosky's and a definite conclusion will be made.

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Appendix

Clean Lab

Teflon Beakers

- Wipe with acetone and methanol to remove any labels, finger grease and surface debris
- Rinse with DI H2O
- Soak in 3:1 ratio of HCl/Nitric Acid (Aqua Regia) for at least 24 hours
- Rinse with DI H2O, 3 times
- Soak in 1:1 Nitric Acid for at least 48 hours, can remain here for a long time if you don't need them right away
- Rinse with DI H2O, 3 times
- Fill up halfway with reagent HF and close cover tightly, leave at 100˚C for at least four hours. Let cool off and pour the HF out.
- Rinse with DI H2O, 5 times
- Rinse with QD H20, 3 times
- Leave the beakers on a hot plate at a low T ~ 50˚C to dry out
- Put covers on the beakers and close them tightly; store them in a clean ziplock bag

Centrifuge and Pipette tips

- Rinse with DI H2O
- Soak in 1:1 Nitric Acid and QD for approximately four hours on hot plate
- Make sure nitric bath is not too hot and plastic is not exposed to nitric for more than 8-10 hours, the nitric will eat them up
- Rinse with DI H2O 3 times
- Rinse with QD H2O 3 times
- Close the centrifuge tubes and wrap them in saran wrap
- Place the pipette tips in the clean pipette tip box

Cleaning the samples

- 2% HNO3 in ultrasonic bath (sonicator) for 15-20 minutes
- Use small pipette to extract the HNO3 without taking any of the sample
- Rinse with DI
- Extract the DI
- Rinse with DI
- Extract the DI
- Put in acetone to dry out the DI
- Extract as much acetone you can with taking any of the sample
- Evaporate the remaining acetone by putting the samples in the oven around 10˚C

Sample Dissolution for Pb chemistry

- Weigh sample into a clean beaker
- Add about 5-7 mL of HF : HBr (7:3) dissolution mix. Good practice to add this slowly, making sure any powder clinging to the sides of the beakers gets washed down completely.
- Close the cover tightly, leave the beakers overnight on the hot plate at ~125degrees
- Next day, remove the caps, evaporate to dryness.
- Add 0.5 mL 0.5N HBr, washing down beaker sides.
- Evaporate to dryness
- Repeat 0.5N HBr step 2 more times.
- Remove the beakers from the hotplate to cool off.
- Add 0.5 mL 0.5N HBr to the beakers, let them sit for about 30-60 minutes to assure the dissolution of all the sample.
- Pour the solution into clean centrifuge tubes, rinse the remainder from beakers with small amount of 0.5N HBr into the tubes.
- Centrifuge them for 1-2 min. until the solution is clear.
- Load the samples onto clean and conditioned 40 uL Anion columns [(AG1-X8), 100-200 mesh] following the guidelines on Pb worksheet.

U Column Procedure Worksheet

(U only) 400 Microliter Anion Columns (U only)

(AG1-X8, 200-400 mesh)

Date: Analyst:

Column no.		1	2	3	4	5	6	7	8	9	10	11	12
Sample no.													
Cleaning	**Time**												
3ml 7N HN03													
3ml 7N HN03													
2ml H2O													
3ml 6N HCl													
3ml 6N HCl													
2ml H2O													
Conditioning													
1ml 7N HNO3 (32 dr)													
1ml 7N HNO3 (32 dr)													
Sample Processing													
Load sample 0.5ml 7N HNO3 (16 dr)													
Wash 0.5ml 7N HNO3 (16 dr)(~~beaker rinse~~)													
Wash 0.625ml 7N HNO3 (20 dr)													
(Load plus 7N HNO3 wash totals ~1.6ml, or ~4 column volumes.)													
(Save HNO3 washes on all critical samples until U is run; it does contain more U.)													
Wash 2ml 6N HCl (64 dr)													
Collect U 0.6ml 1N HBr (20 dr)													
Collect U 0.6ml 1N HBr (20 dr)													
Add 1 drop 0.025N H3PO4 and dry													

Add to dry U 3 drs 7N HNO3 3x'

Pb Column Procedure Worksheet

Pb Columns

	(Pb only) 40 Microliter Anion Columns (Pb only)												
Date:	(AG1-X8), 100-200 mesh)												
Analyst:													
Column No.		1	2	3	4	5	6	7	8	9	10	11	12
Sample No.													
Cleaning	**Time**												
1ml 0.25N HNO3													
0.5ml 0.25N HNO3													
0.5ml 0.25N HNO3													
0.5ml 6N HCl													
Conditioning													
0.2ml 0.5N HBr													
0.2ml 0.5N HBr													
0.2ml 0.5N HBr													
1st satge Sample Processing													
Load sample 0.5ml 0.5N HBr													
Wash 0.5ml 0.5N HBr													
Wash 0.2ml 2N HCl													
Collect Pb 0.7ml 6N HCl													
Add 2 drops 0.025N H3PO4													
to the beaker, dry													
Add 0.5ml 0.5N HBr, dry, repeat 2 X's													
Cleaning & Conditioning													
the same as above													
2nd stage Sample Processing													
Load sample 0.5ml 0.5N HBr													
Wash 0.5ml 0.5N HBr													
Wash 0.2ml 2N HCl													
Collect Pb 1.5ml 0.4N HCl													
Add 1 drop 0.025N H3PO4													
to the beaker, dry													

Note on Silica Gel for Pb:

- Before using it, mix it with the mixer in the clean lab for a few minutes next to the sonic bath, then ultrasonic it for about 10-15 min and mix again. This improves the quality of the silica gel a lot!
- Before loading samples check quality of the silica gel by loading it on a filament. Silica gel should be a nice powdery white bed on the filament without any cracks and should stick firmly to the filament if mixed with H_3PO_4.

Filament Loading Procedure for Pb

- Use single commercial Re filaments.
- Melt 2 strips of parafilm on filament at ~ 1 Amp.
- Take 1.5 – 2 uL of the concentrated silica gel and about 1 uL of 0.25M H_3PO_4.
- Pick up a suitable amount of sample in 0.25N HNO_3. Give samples some time to dissolve in the beaker, before picking it up.
- Mix sample, silica gel, and H_3PO_4 on an extra parafilm and load it in tiny drops on the filament and let dry at ~1 Amp.
- Increase current in 0.1 Amp steps (each step 10 sec) to ~1.8 Amp. Wait until all the H_3PO_4 has evaporated (white smoke) and flash very briefly at dull red ~ 2.0-2.2 Amp
- After that silica gel should be a nice powdery white bed on filament.

The Mass Spectrometer