STUDY AND RESEARCH IN FIELD GEOCHEMISTRY
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Staurolite Indicates Regional Metamorphism

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ABSTRACT

Isotope geochronology has evolved with the correlation of the variation in the nature of lead isotopes and mineral ages. This science continues to evolve with the influence of newer and more advanced technological methods. Staurolite is studied by the independent method of mineral dating based on Uranium and Lead ratios. Experimental procedures include rock crushing processes, clean lab usage, and ion exchange columns. A thermal ionization mass spectrometer is used to measure concentration ratios of different isotopes. Analysis of the results will determine whether staurolite analyses represent growth or cooling stages of metamorphism. Ages of the sample will be established through Uranium-Lead isotope analyses.

INTRODUCTION

As proven in previous studies, the onset of regional metamorphism is not a brief event. It in fact progresses over millions of years. Metamorphism is the change of an existing solid rock to another rock as the result of heat, pressure, and/or chemically active fluids. A metamorphic cycle begins with a gradual build-up of extremely high temperatures and pressures, leading to a thermal apex. This thermal peak occurs quickly and ends abruptly. Gradual cooling and erosion then follow and end the cycle. Isotopic dating is used only to *approximate* the time of the brief thermal maximum. (Brosky, 18)

The time of metamorphism or even several metamorphisms in an area can be determined through methods of dating rocks and minerals. Knowing the dates or times of metamorphic cycles in an area of study is essential for scientists to perform other studies and make observations and predictions regarding geological changes or patterns in Earth. Though there have been many previous studies in determining metamorphic times, there still remains much doubt over the accuracy of the results. This controversy can be attributed to the different methods, materials, and techniques used in acquiring a date.

There are several considerations to make in order to precisely date metamorphic ages. All known isotopic dates, those from all minerals and whole-rocks within the area of study that have been dated by different isotopic methods, must be considered altogether to arrive at a common conclusion. All the data from these studies must be concordant, or else explainable. Also, geological relationships between and within the samples from an area must be examined. Logically, there must be geological evidence that confirms the

isotopic evidence in order to prove that a metamorphic event occurred at the approximated time.

The general area of interest in this study is the Southern Appalachian Mountains, particularly the Talladega belt and the basement of the western Blue Ridge. This basement was progressively metamorphosed from kyanite to silimanite, two different rock forms. It has been studied numerous times, always with the same, consistent, controversial results. For this experimental study, rock samples containing the mineral Staurolite were gathered from these mountain areas to use as study parameters for isotopic dating.

Staurolite is a silicate mineral containing iron and aluminum $(OH)_2Fe_2Al_9Si_4O_{22}$. (See Figure 1) It is Georgia's state mineral and abundantly found in the southern Appalachian Mountains. Staurolite is a high-grade metamorphic mineral that has a high closure temperature to isotope diffusion (over 500°C) as well as a high U-Pb ratio. Thus, it is considered one of the best single mineral chronometers to use in high-metamorphic grade terrain. Staurolite is a closed mineral system, meaning that no chemical movement occurs in or out of its chemical composition. The resistance to chemical weathering ensures its preservation as a mineral on sediments. Staurolite also preserves the majority of its radiogenic Pb isotopic composition. From these characteristics, it is probable that Staurolite will be a reliable indicator of metamorphism. (Deer, 151-160)

In the past, most geochronological dating done in the Southern Appalachians has been performed through isotopic analyses of K-Ar or ^{40}Ar-^{39}Ar mineral methods. However, these methods tend to produce poor limits of detection and allow for undesirable significant error in results. Researchers stipulated that in order to yield accurate geological dates with the K-Ar isotope system, radiogenic ^{40}Ar must be fully retained the instant the metamorphic event takes place. To complicate factors further, argon must not be incorporated into the structural phase, and the phase must have remained a closed system from the time of metamorphism to the time of analysis. Thus, K-Ar dates will always have uncertainty due to the introduction of argon in the method, and there is further uncertainty from the fact that most rocks do experience chemical movement in either the parent or daughter isotopes (their system does not remain closed). These uncertainty problems lead researchers and scientists to study other methods of dating with new technology and even different minerals.

Two newly measured ratios that are giving way to a new independent method of dating minerals that contain Uranium are $^{207}Pb/^{206}Pb$ and $^{238}U/^{235}U$. This is caused by the decay of ^{235}U to ^{207}Pb and also the decay of ^{238}U to ^{206}Pb. They both decay independently and with two completely different decay rates. Uranium has three naturally occurring isotopes: ^{234}U, ^{235}U, and ^{238}U, and lead has four that occur naturally: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. ^{235}U and ^{238}U are radioactive, while ^{206}Pb and ^{207}Pb are radiogenic and stable. (Brosky, 3) A relatively high U-Pb ratio allows a sample to be used as a precise metamorphic chronometer. A great benefit of U-Pb dating methods over the K-Ar techniques is that within reasonable amount, radiogenic inclusions do not significantly affect the accuracy of an age.

The newly introduced U-Pb method can illustrate its effectiveness through staurolite. Since this mineral portrays many optimal qualities of a good chronometer, accurate results are expected through experimental and isotopic analysis. In a previous study and also the first part of this one, staurolite ages were both concordant. "Nonetheless, a bit more evidence is necessary to ensure that staurolite analyses represent growth rather than cooling ages" (Brosky, 38).

METHODS AND MATERIALS

CRUSHING

Samples of the mineral were separated from the whole rock using a rock crusher (this had previously been done for us). The pieces of crushed rock were then reduced to a fine grain size with a mortar and pestle, and sieved, while collecting samples between 74μm and 105μm. We found that larger grains contained excess black and white inclusions, which we believe to be magnetite and quartz, though this has not been tested for certain. Even the grains $74\mu m \leq x \leq 105\mu m$ contained some inclusions, so running each sample through a Franz Isodynamic Magnetic Separator helped to eliminate extraneous magnetic particles. We experimented with different front and side tilt angles as well as the amperage to find optimal utilization of the machine. After this stage of separation, the "clean" minerals, those without inclusions, had to be hand picked under a binocular microscope. This was a very tedious and time-consuming process that lasted about four continuous days for each 20mg sample. Different methods for picking these particles were tested. I found that they were easier to separate in a drop of water on a microscope slide. A piece of thin wire was used to push aside the dirty particles, while the pure ones were left in the water droplet.

Approximately 20mg of pure particles from each sample were collected into separate 10ml Pyrex beakers. These mineral samples were cleaned to remove any surface impurities acquired from handling. The cleaning procedure had to be performed carefully to avoid losing any of the samples. Cleaning procedure: fill the beaker halfway with 2% HNO_3, and place in an ultrasonic bath for 20 minutes. Then remove the acid from the beakers using clean 200μl pipette tips. Be sure not to touch the sample, and use a different pipette tip for each sample. Fill each beaker halfway with quartz-distilled (QD) water and remove the liquid just as before. Do this a total of 3 times to completely dilute the acid. Rinse with distilled acetone to absorb excess water from the sample. Pipette out most of it, leaving only enough to cover the sample. Then cover beakers in foil, and place in an oven (not a hot plate) at 100°C just long enough to evaporate the last bit of moisture. Let the beakers cool to room temperature and weigh them to figure the new mass, since some may have been lost while cleaning.

IN THE CLEAN LAB

Now working in a clean lab, we transferred the samples into clean 15ml Teflon containers with screw-on lids. Placing samples that "attached" to the Pyrex beakers in a sonicator for a few minutes loosened the particles.

SPIKING THE SAMPLES

*Note on the addition of ^{205}Pb and ^{235}Pb spikes:

Technically, lead does not need to be spiked, but it is a precise method that is fairly simple to perform, experimentally. The main purpose for spiking the samples is to determine the ^{206}Pb and ^{238}U concentrations in the samples, as well as their ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb isotopic compositions. Since the $^{206}Pb/^{238}U$ ratio is what is needed, a known amount of ^{205}Pb spike is added to the samples in order to later measure the $^{205}Pb/^{206}Pb$ ratio. The Lead spike was prepared from ^{205}Pb obtained from the University of Toronto. It is essentially 100% pure. The $^{238}U/^{235}U$ ratio for our Uranium spike is 0.00175, approximately 99% pure. It is an enriched Uranium that was originally prepared at the Oak Ridge National Laboratory. The concentration of ^{235}U in a sample equals the concentration of ^{235}U in the spike times the amount of spike added to the sample.

The amount of spike added to the samples must be accurate up to as many decimals places as possible, so we calibrated the pipettes that would be used with the assumption that 1g=1ml (H_2O). We obtained a ^{205}Pb and a ^{235}U spike from Dr. Odom. He gave us 1.5699g (≈1.5699ml) and diluted it with approximately 4.4301ml QD H_2O. This ^{205}Pb spike concentration had to be calibrated, so 500μl was put into each of three Teflon containers, closed tightly, to be used in the last stage of the clean lab processes. An equal, calculated amount of ^{205}Pb spike was added to each sample as well as two blank samples. We diluted the portion of ^{235}U spike that Dr. Odom gave us ten times with the QD water. This did not have to be calibrated, since we used exact amounts from our calibrated pipettes. Unlike the lead spike, different, calculated amounts of the ^{235}U spike were added to each sample and the blanks. (Refer to Table 1)

***SAMPLE DISSOLUTION**:*

A standard mixture of acids was made in order to dissolve the solid particles into a liquid form. This mixture is a 4:3:2:1 ratio of 6N HCl, HNO_3, $HclO_4$, and HF, respectively. We made this mixture in a Teflon bottle with the following amounts of each acid: 24ml:18ml:12ml:6ml. Three milliliters of this dissolution mix were added to each of our samples along with the proper spike amounts. The Teflon containers were tightly sealed and placed on a hotplate at temperature setting 150 (this hot plate has not been calibrated, thus its accurate temperature is unknown). The average time elapse for the minerals to dissolve in the dissolution mix is 2-3 weeks at this setting.

*At present, the samples are almost completely dissolved, so the following procedures are the guidelines for what will be performed. Note that there is the possibility of slightly altering steps of experimental procedures as a result of uniqueness within individual samples.

PREPARATION FOR COLUMNS

After the minerals are completely in liquid form, they must be evaporated to dryness. This is done in a hotbox with the covers removed from the containers. The temperature setting is raised to 250 for 1-2 hours. Once all liquid is completely evaporated, *add 3ml 6N HCl to each sample and each blank, washing down the inside walls of the Teflon

beakers. Evaporate this to dryness between temperature setting150-175. Then the temperature must be raised to about 250 again 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 (including the blank samples), cover, and let sit for 30-60 minutes so that the entire sample dissolves completely. Pour or pipette solution in separate, clean centrifuge tubes, rinsing the remainder from the beakers with a few drops of the 7N HNO_3 into the tubes. Centrifuge them for 1-2 minutes, until the solution is clear and any remaining solid is collected at the bottom of the tube. Record the total volume of liquid solution using pipette measuring.

URANIUM COLUMNS

Following the procedures for 400 Microliter Anion Columns, (Refer to Table 2) Uranium will be extracted and collected from the three samples and the two blanks. After the columns are made, cleaned, and conditioned, a fraction of the sample will be collected and saved for Lead collection. Collect this part in clean Teflon containers during the sample processing section of the table from "load sample 0.5ml 7N HNO_3" to "wash 2ml 6N HCl." These samples can be set aside until Lead collection begins. Continue with Uranium collection by following the remaining procedures of the table. Collect this fraction in separate Teflon containers. Add 1 drop 0.025N H_3PO_4 and dry on the hotplate at a temperature setting between 150 and 175, as stated on last step of the table. To clean the Uranium fraction, add 3 drops 7N HNO_3 and dry, just as before. Repeat the 3 drops two more times. Sample will end in dryness state. Set aside to use during loading.

LEAD COLUMNS

Evaporate the lead fraction of the samples and the blanks to dryness. Rinse them with 0.5N HBr and dry them, repeating this two more times. Then follow the procedures of Pb Columns: 40 Microliter Anion Columns (Refer to Table 3). Once the columns are made, cleaned, and conditioned, perform the first stage sample processing, collection the lead and drying it again. Lead collection must be done twice to ensure purity of the sample collected, so re-make the columns with new resin, clean, and condition them as before, and proceed to the second stage processing of the table, this time loading the part of the sample that has already gone through the columns once (it is in dryness state, and will be loaded with the first step of sample processing). 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 Pb standard to each of the three containers with 500μl of the spike. These calibration samples must be evaporated to dryness as well.

LOADING SAMPLES ONTO FILAMENTS

Making and loading the filaments takes place under the loading hood (out of the clean lab). In advance, make and degas several filaments.

FOR URANIUM

Use single Re (Rhenium) 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 our 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 Re filaments. Dissolve each dry sample in 0.25N HNO_3. Then, mix silica gel (ultrasonic it for 20 minutes before using), H_3PO_4, HNO_3/sample in a micro-pipette. 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.

THEFINNIGEN/MAT 262 MASS SPECTROMETER

*Note on the mechanics of the mass spectrometer (See Figure 2):

The FINNIGEN/MAT 262 is a Thermal Ionization Mass Spectrometer that used heat to measure concentrations of isotopes of an element based on their masses. This machine consists of a variety of components: an ion source, an analyzer, a detector, a vacuum system, electronic power & current supply, and computer software. The source generates the ions as an electric current is passed through a filament that is increased to reach high temperatures up to 1300°C. The maximum temperature that it reaches varies from different elements. At this max temperature, the element on the filament is evaporated into positive ions. The positive ions are accelerated through narrow slits in 5 parallel disks 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, consisting of a curved flight tube and an electric magnet. As ions enter the magnetic field, they are deflected according to their mass. The lighter ions are deflected more than the heavier ones. These deflections create ion beams, each representing different isotopes of the element, heading toward the detector. The detector is composed of 6 moveable faraday cups that are statistically pre-positioned to catch the ions by their mass. The cups are connected to a ground wire that creates a small electrical current after the charge of the wire passes through a resistor. The current at each cup is proportional to the number of ions that hit that cup. These currents are read by an electrometer. The data is sent to a computer where the ratio of ion currents can be determined.

Once the samples are loaded onto filaments, they are attached to a magazine wheel and covered with plates. Since a magazine only holds 15 samples at a time, do two runs- one for the Uranium samples, and one for the Lead samples. Put the magazine into the mass spec and begin pressuring it down. Follow operating procedures found in the user's manual of the spectrometer. Notes for previous staurolite samples are found in the MAT 262 mass spec notebook, 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

^{235}U and ^{238}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 measures. 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.

ANALYZING THE DATA

Data is collected from the computer of the mass spectrometer in blocks of 5-10 runs. This data is then documented into spreadsheets that layout all the information needed for the calculations and graphs. Since nearly identical work has previously been performed in our lab on Uranium and Lead studies of staurolite, we will use the same spreadsheets and formulas to plot and graph our data. We will also the same equations to calculate a date of the age of our rock samples. Plots will include isochrons of the beta decay of ^{238}U to ^{206}Pb as well as ^{235}U to ^{207}Pb, by plotting different lead and uranium concentration ratios (See Figure 3). A best-fit line is set through the data, with a slope that corresponds to an age and an uncertainty level. This established date is then compared to dates of differently measured isochrons in order to find a certainty level of concordance.

EXPECTED 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. Concordance of these isotopes should be achieved and correlate to that of Rebekah's previous results of the same samples. 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 it indistinguishable from that of the isochrons.

DISCUSSION AND CONCLUSION

In conclusion, the present study and experimentation on staurolite samples will be continued after this documentation. The results that are achieved will be compared to Rebekah's results. Then, a conclusion can be made and discussed further.

FIGURES AND TABLES

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

Table 1: Amounts of ^{235}U spike and ^{205}Pb spike added to each sample

Date:		
Analyst:		
Column No.		
Sample No.		
Cleaning		
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		

Table 2: Worksheet for Lead, 40 Microliter Anion Columns

Column no.		1	2	3	4
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 dps 7N HNO3 2x					

Table 3: Worksheet for Uranium, 400 Microliter Anion Columns

Figure 1: Staurolite, Quartz, and Magnetite inclusions in rock sample

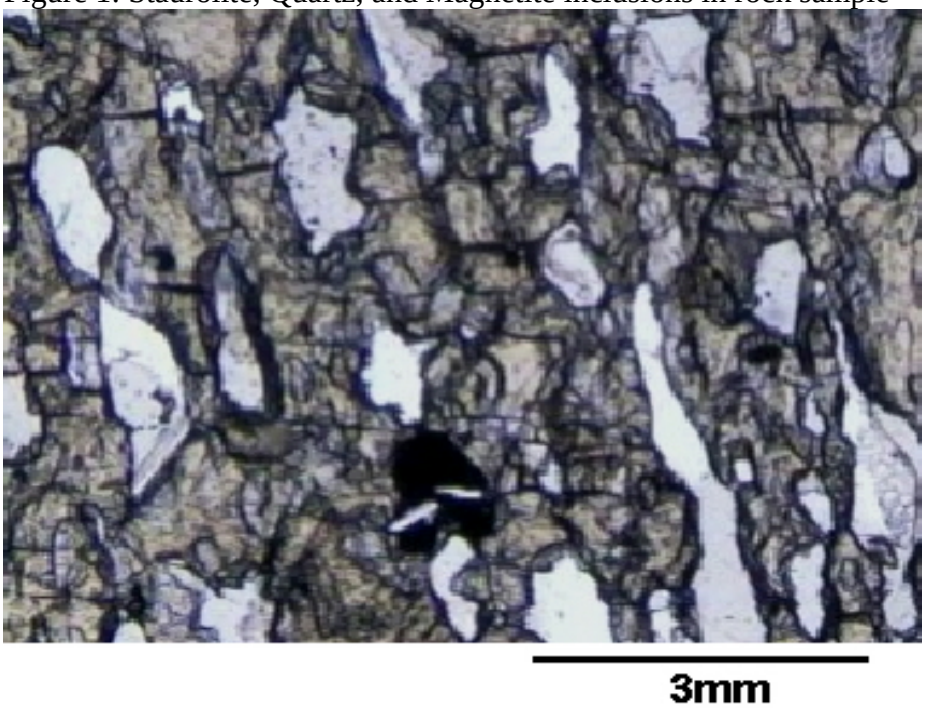
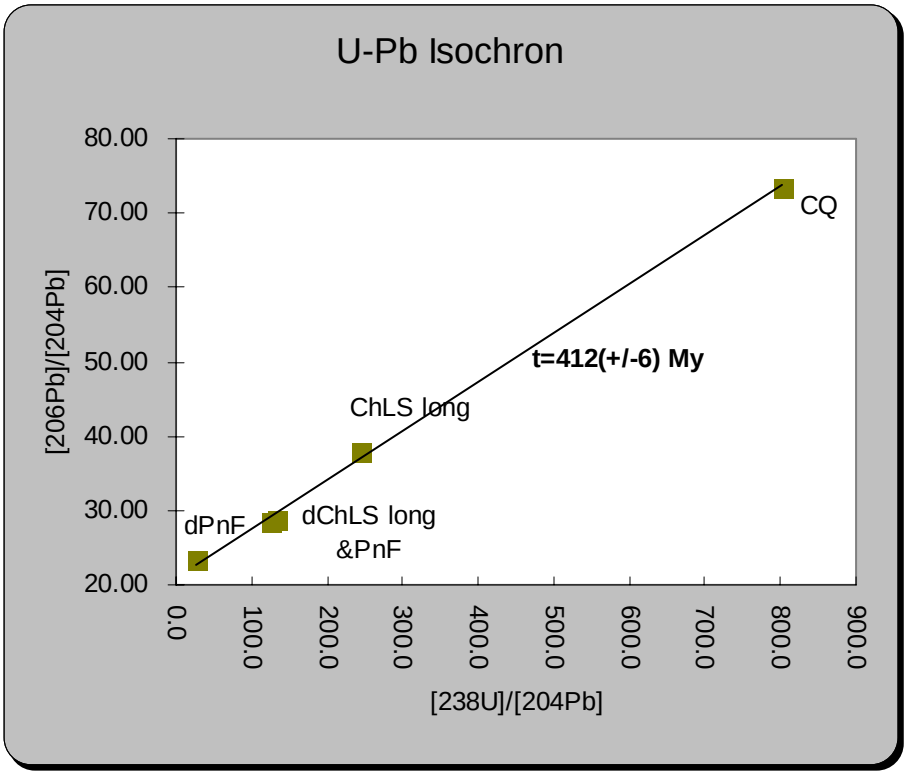


Figure 2: Thermal Ionization Mass Spectrometer

Figure 3: Uranium-Lead isochron showing decay of ^{238}U to ^{206}Pb



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