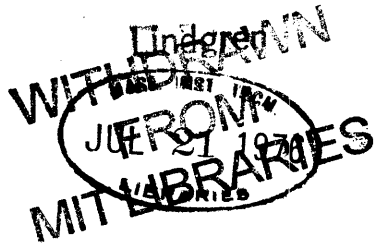MICROTECHNIQUES IN Pb-U DATING

OF MOROCCAN ZIRCONS

by

Marylee Witner Hull

S.B., Massachusetts Institute of Technology

(1975)

SUBMITTED IN

PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF

TECHNOLOGY

May 1976

Signature of Author...

Department of Earth and Planetary Sciences

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Thesis Supervisor

Accepted by...

Chairman, Departmental Committee on Graduate Students

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Submitted to the Department of Earth and
Planetary Sciences on May 11,1976 in partial
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ABSTRACT

Lead-uranium dating was performed on sedimentary zircons from Triassic and

Paleozoic samples collected in the Moroccan Meseta. Three methods for the process

of dissolution and loading were used.

The standard bomb method, requiring the use of ion exchange columns yielded

two valid data points, which, when plotted on a Pb-U concordia diagram, show

an age of formation of approximately 1560 mya. Most of the samples

processed by the standard bomb method, however, were contaminated by the

ion exchange columns.

Minibombs were constructed which which could dissolve small amounts of

zircon and did not require the use of ion exchange columns. In the first

minibomb technique, small numbers of zircons were dissolved. The resulting

solution was diluted with 3.1N HCl and aliquoted into lead-spiked and lead-

unspiked portions. It was found that the dilution added too much contamination

for the small amount of zircon used.

In the second minibomb technique, a spiked sample and an unspiked sample, each containing one zircon, were dissolved in separate bombs, thus eliminating the need for dilution. Comparison of the lead ratios obtained by this method and those previously measured using the standard bomb procedure were similar. Therefore, the second minibomb technique may be useful.
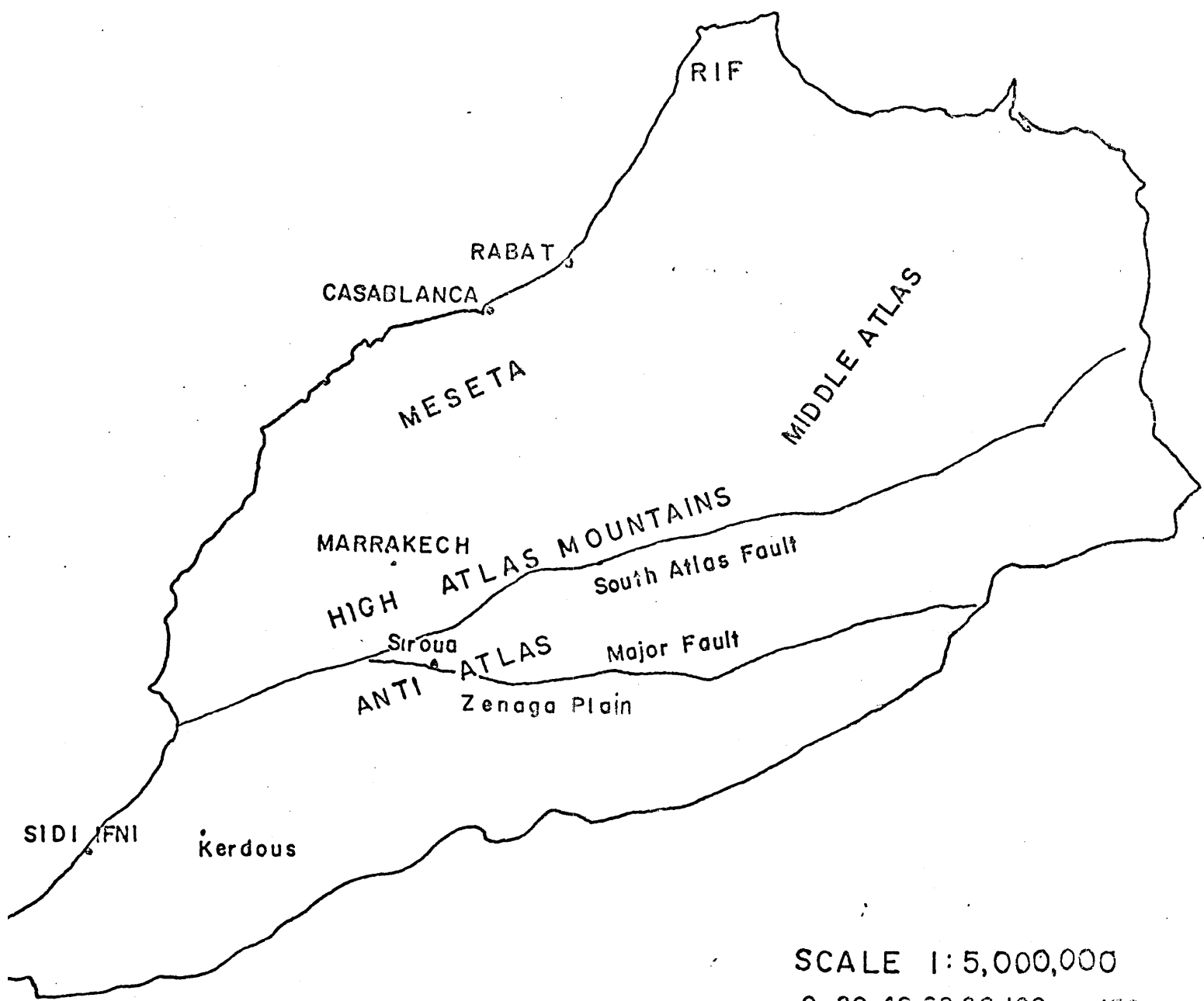
Thesis Supervisor: Patrick M. Hurley

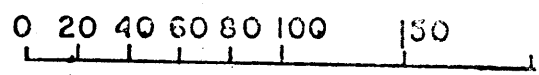Title: Professor of Geology and Geochemistry

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Figure 1. Map of Morocco. (Outline from The Times Atlas of the World, J. Bartholomew, ed., 1956, plate 88.

RIF

RABAT

CASABLANCA

MESETA

MIDDLE ATLAS

MARRAKECH

HIGH ATLAS MOUNTAINS

South Atlas Fault

Siroua ATLAS Major Fault

ANTI

Zenaga Plain

SIDI IFNI Kerdous

SCALE 1:5,000,000

0 20 40 60 80 100 150

I. Outline of the Geology of Morocco

Four separate regions in Morocco can be defined in terms of their different histories: the Anti Atlas, the Meseta, the Atlas Mountains, and the Rif. The Atlas Mountains provide the boundary between the Precambrian exposures of the Anti Atlas and the Paleozoic exposures of the Meseta. The Rif involves purely Tertiary activity.

The Atlas Mountains did not begin to form until the middle of the Jurassic, at which time, there was only a modest amount of uplift. The sharp terrain of overturned anticlines and flysch did not begin to take shape until early Cretaceous time. This activity continued through the Oligocene and Miocene when compressive forces folded the sediments and then overturned the folds.

As a barrier between the Meseta and the Anti Atlas, the Atlas Mountains have really been effective only since the Cretaceous. The height of these mountains has made them the source for the younger sediments in the Meseta and those in the low areas of the Anti Atlas from Cretaceous or Tertiary times through the present. Thus, the effect of the Atlas Mountains on the adjacent Meseta has lasted only since the start of the Teriary.

As the samples used in this study represent Paleozoic and Triassic sedimentary rocks from the Meseta, it is important to reconstruct the history of Morocco prior to the Jurassic period. The Anti Atlas block is an Eburnian(1800 my) igneous-metamorphic terrain, probably abutting the Reguibat massif of northwest Africa until late in the Precambrian when a Pan-African event pulled it apart from the West African craton. This event has been dated at between 650 my and 570 my. The Pan-African orogeny involved massive rhyolitic and andesitic volcanism and granitic plutonism

along the edge of the Anti Atlas. The effect of this event was to reset the ages in much of the bounding region.

The Meseta, now separated from the Anti Atlas by the Atlas Mountains, is a very different landform. Mainly serving as a basin to receive sediments from whatever sources existed on the continent, it has been measured to be 5 km. deep. This depthe was measured from the earliest known Paleozoic sediments.[1] Geologists have had difficulty tracing the strata produced in the Meseta because of the persistent faulting that has taken place throughout its history.

Outcrops of Paleozoic granites are evident throughout the Meseta. One such outcrop, the Tichka Massif, gives evidence of three separate igneous rocks emplaced at about the same time.[2] The granite is surrounded by quartz diorite and mafic diorite. Because of the pod-like shape of these outcrops, they are thought to be diapirs or large plutons. Indeed, gravity surveys have shown that the material extends underground far from the outcrops and is fairly shallow.[3] Near the Atlantic coastline, the Paleozoic beds exhibit tight southeast-dipping fods.

It is believed by some investigators[4] that, during the early Paleozoic, the small Proto Atlantic Ocean began to close causing underthrusting of the Meseta. It was closed by mid to late Paleozoic time, but marine sedimentary rocks show that it was open again later in the Paleozoic[5] at least on a small scale along parts of the African coast.

The subduction of the Atlantic lithospheric plate underthrusting the Meseta may have caused many of the structural features visible today. The tight

1. P.M. Hurley, et al., "A Plate Tectonics Origin for Late Precambrian-Paleozoic Belt in Morocco," Geology(July 1974), 343.
2. T.A. Vogel and B.M. Walker, "The Tichka Massif, Morocco..," Lithos, 8 (1975), 31.
3. W.H. Kanes, et al., "Moroccan Crustal Response to Continental Drift," Science, 180(1973), 951.
4. P.E. Schenk, "Southeastern Canada, Northeastern Africa, and Continental Drift," Can. Journal of Earth Science(1971).
5. L. de Loczy, "Synchronous Diastrophic Events...," in Amer. Assoc. of Petroleum Geol. Memoir 23, C.F. Kahle, ed.,253.

folds near the coast are thought to be a drag response to the subduction.
Granite plutons of Paleozoic age dotting the Meseta are comparable to those
in other subduction zones. Final collision probably occurred in the Hercynian.

Toward the end of the Triassic, the current Atlantic Ocean began to open
as North America and Africa pulled apart. The tension in the Moroccan crust
is evidenced by the large horsts and grabens formed in the late Triassic
and early Jurassic terrain. During the Jurassic, this faulting ceased as
new crust was being added between the shores of North America and Morocco.[6]
The horsts and grabens formed are parallel to the Atlantic coast of Morocco
indicating the basic direction in which the spreading took place. The
spreading direction is approximately parallel to the direction of under-
thrusting during the Paleozoic. However, it is not certain that the location
of the separation line between North America and Morocco corresponds with the
suture that resulted from the closing of the Proto Atlantic.

Subsequent uplift of these filled Jurassic basins occurred in Alpine
times so that they now constitute part of the structure and stratigraphy
of the High Atlas Mountains.

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6. W.H. Kanes, et al., op. cit., p. 952.

II. Experimental Objectives

Six sand and sandstone samples collected from the Meseta were processed in order to provide geologically interesting material for the microchemical techniques to be examined in this thesis. The objective was to carry out lead-uranium dating on the zircons they contained. These samples came from late Paleozoic and early Triassic formations.

Firstly, it was important to determine the source of the sediments filling the Meseta basin. Several possible sources of zircons exist within the boundaries of Morocco. One likely candidate is the Pan-African volcanic material separateing the Anti Atlas stable block from the Meseta. Another source might be the paleozoic plutonic exposures widely visible on the Meseta. Lastlyin Morocco are the Anti Atlas chains. The Atlas Mountains and the orogeny associated with the Rif came later and would not have influenced these sediments.

One theory, though, is that the Meseta was not originally part of Morocco. As the nature of the South Atlas Fault is in Question, it has been suggested that the Meseta was transported along this strike-slip fault to its present location. There exists the possibility, then, that many of the Paleozoic sediments of the Meseta have their source on the other side of the Atlantic.

Dating the Moroccan zircons can give two important pieces of information. Of basic importance is the question of the historical position of the Meseta. The ages of the zircons will show whether their sources can be explained to be in Morocco or whether they must be somewhere else. If the age of the sedimentary zircons does does correspond with that of one of the igneous formations or if it falls somewhere in between the ages of the igneous formations of Morocco, we can deduce which landforms had positive expression through the early Triassic.

Another purpose of this work is to initiate a series of experiments to determine the boundaries of the various tectonic activities that have affected Morocco. The Proto Atlantic closed forming a suture line at the edge of the Meseta. In the Mesozoic, The Atlantic opened along a line somewhat parallel to the suture but possibly not exactly the same line. The possibility exists that either part of the North American continent is now attached to Morocco or that part of Morocco is attached to North America. There is very little evidence of a suture in the present-day Meseta. It is therefore possible that the suture exists somewhere on the North American continent. Collecting samples from the Paleozoic formations along the east coast of North America would allow a study of the zircons found in them. A zircon age similar to that of the Meseta zircon age would be convincing evidence that part of the Pre-Atlantic Meseta is now part of North America. Rubidium-strontium age studies of the igneous rocks of the eastern United States seaboard yield ages of 600 my to 250 my.[7] The only areas in North America which have ages comparable to that of the Eburnian orogeny as in the Anti Atlas are found along the Grenville front and in the Churchill province of Canada. Thus, if the Meseta zircons are derived from the typical West African craton, they should be very distinctive in North America.

The Moroccan Meseta is quite small relative to North America, however. It is important to know where to look for Moroccan zircons. It has been proposed that the South Atlas Fault system is the eastern end of a transform fault that cuts across the Mid-Atlantic Ridge.[8] Below the latitude of the South Atlas Fault, the ridge is shifted slightly to the east. It has been noted that the Canary Islands, just off the coast of Morocco, may have some material on the easternmost island which resembles Moroccan Jurassic

7. P.M. Hurley, personal communication.
8. W.C. Pitman and M. Talwani, "Sea-Floor Spreading in the North Atlantic" Geol. Soc. America Bull., 83(1972), 635.

sediment.[9] There is also evidence of folding and volcanism on the Canaries that resemble the Miocene activity of the South Atlas Fault. Therefore, it seems likely that the Canary Islands fall along the South Atlas Fault line and are part of the Moroccan Meseta. The line that connects the South Atlas Fault with the Canary Islands and the offset in the Mid-Atlantic Ridge should intersect the North American continent in an area most likely to have Moroccan sediments. There is some question as to where the intersection is. Some have proposed that the New England seamounts are the westernmost expression of of this fault.[10] It is possible, though, that the fault extends farther south. In either case, it would be most likely to find Moroccan sedimentary rocks in the New England area.

Therefore, the two geologic purposes of this work are to find the source of the Meseta sediments and to lay the groundwork for further tectonic reconstruction through the age-dating of detrital zircons.

In dating the Moroccan zircons, several techniques were used. The experimental objective of this work was to develop the microtechnique of age-dating after first using the standard procedure and equipment. Development of the micro-technique first involved reproducing data already obtained using the standard method. After the initial testing of the microtechnique using minibombs constructed by the MIT geology machine shop, the plan was to use these minibombs to find the ages of single zircon grains found in the larger mixed suites. In this way, it would be possible to more accurately determine the sources which contributed to the Paleozoic and Triassic zircons.

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9. _Ibid._, p. 634.
10. _Ibid._, p. 634.

Sample Descriptions

The samples used in this study were collected in the northern part of the Moroccan Meseta and in the Casablanca area by John Lorenz and Guy Padgett of the University of South Carolina. The sample descriptions are as follows:

8530- Lower Carboniferous graded fluxoturbidite
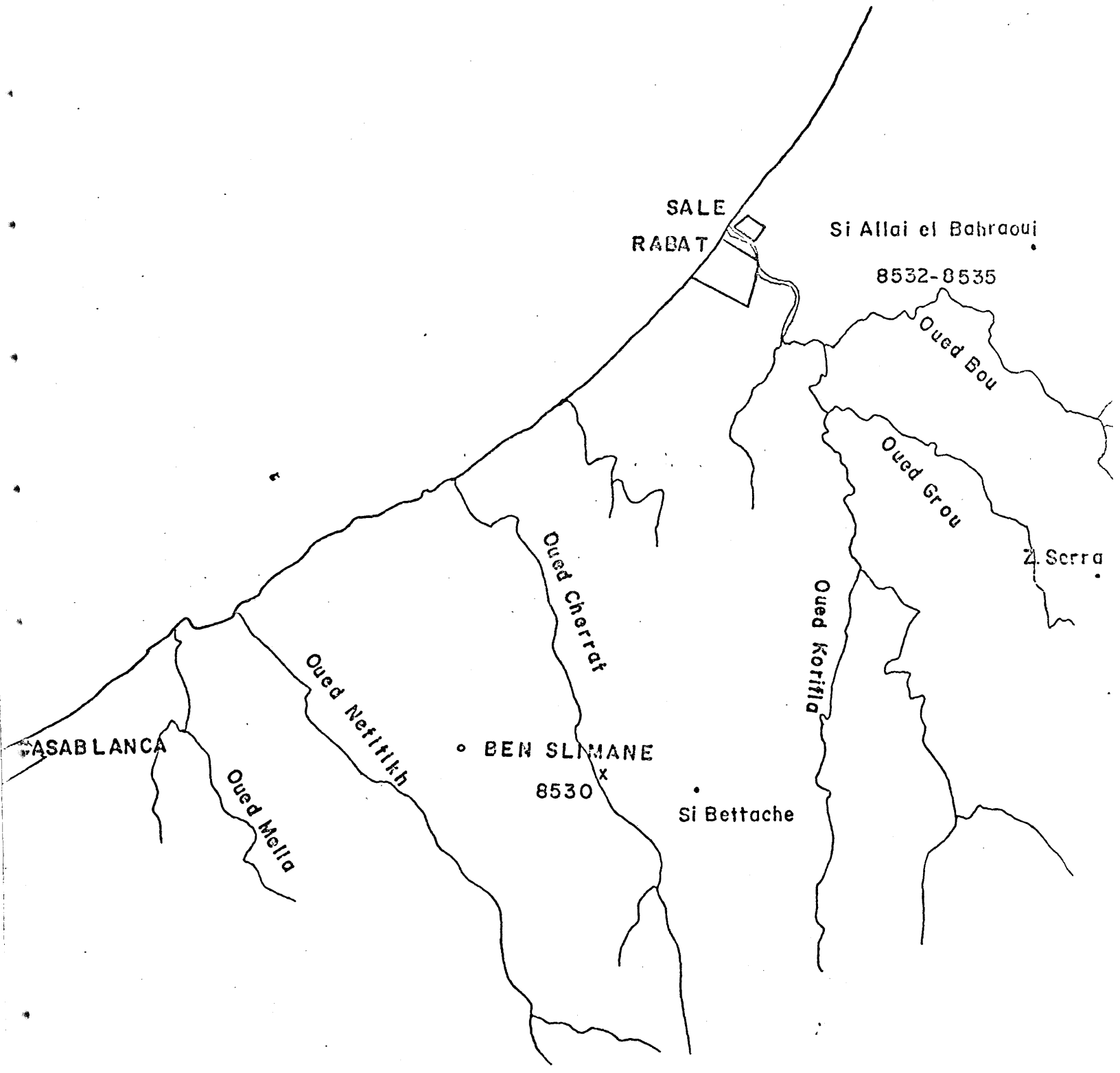
8532- Basal Triassic red sandstone

8533- Triassic red sandstone

8534- Basal Triassic red sandstone and shale

8535- Triassic red sandstone and shale

8536- Dark heavy beach sand from Omor Rbia, 60 km. south of Casablanca

Figure 2. Map of the northwestern Meseta including the sample locations of numbers 8530, 8532, 8533, 8534, and 8535.

SALE
RABAT

Si Allai el Bahraoui

8532-8535

Oued Bou

Oued Grou

Z. Serra

Oued Chorrat

Oued Korifla

Oued Nefifikh

CASABLANCA

Oued Mella

BEN SLIMANE

8530

Si Bettache

III. Standard Bomb Procedure

Preparation of the samples for mass spectrometry involved two processes: the physical separation and cleaning of the zircons and the chemical separation of the various components of the zircons. For the first process, no concern was taken for the introduction of chemical impurities from the air or the equipment used. It was assumed that the later cleaning would remove any recently added lead or uranium. In the second process, however, great care was taken to avoid lead contamination.

As five of the six samples used were sandstones, they had to be disaggregated first. The other sample was a beach sand and could be used in original form. The disaggregated material was then put through a stack of sieves of the following mesh sizes: 50, 270, and 325. The material larger than 50 mesh was set aside to be reground if needed. All of the zircons found have been much smaller than this material. The powder less than 325 mesh was also set aside. Although this material was often found to contain a high proportion of zircons, it was difficult to work with and was used only as a last resort. The grains between 50 and 325 mesh continued through the process.

In order to separate the zircons of specific gravity 4.68 from the other minerals of specific gravity 2 to 3 in the sample, a heavy liquid separation using acetylene tetrabromide of specific gravity 2.955 was performed. The light fraction, mostly quartz and feldspar, was discarded, and the heavy fraction cleaned several times in acetone.

Those samples which had come from sandstones were heavily coated with oxidized iron. They were cleaned by being heated in 6N HCl under a heat lamp until all the iron was dissloved. Water and acetone were used to clean out the HCl.

At this point, the remaining grains were put through a second heavy liquid

separation of methylene iodide, whose specific gravity is 3.3. This liquid

floated some of the minerals that remained from the previous separation

but sank the zircons and a few other minerals. One of the minerals that

sank along with the zircons was magnetite. After the heavy separate was

removed and cleaned with acetone, the magnetite was removed with a hand

magnet.

The next separation was performed with a Franz magnetic separater. Zircon

is one of the least magnetic minerals in the sample. Magnetic separations

were made with the magnet current set at 1.5Amps, the pitch at 10°, and

the yaw set at 15°, 10°, 5°, 2°, and finally at 1°. Of the grains that

were nonmagnetic at the 2° setting, usually at least 30% were zircons and

often as many as 90% were. The further division at a 1° setting was made

to obtain two usable fractions of zircons.

These two fractions were then washed in warm, high-purity 7N HNO_3 for

two 15-minute periods. They were then washed in 4* water for two more

15-minute periods. This cleaning was supposed to remove any lead or uranium

that had become attached to the surfaces of the grains through exposure to

impure air or metal.

Immediately after cleaning, the grains were dried under a heat lamp and

put through another stack of very clean sieves. The mesh sizes used were

150, 250, and 325. This way, both the magnetic fraction and the nonmagnetic

fractions could be further subdivided into three size fractions apiece.

It was hoped that the results of several size fractions could be plotted

on a lead-uranium concordia graph to form a well-substantiated line.

The chemical process of dissolution followed. The procedures used were

basically those of Krogh.[11] A small amount of pure zircon, usually weighing

11. T.E. Krogh, "A Low-contamination Method for Hydrothermal Decomposition of Zircon and Extraction of U and Pb for Isotopic Age Determination," Geochimica et Cosmochimica Acta, 37(1973).

between 1 and 10 mg., was selected by hand picking with a paintbrush and discarding the nonzircon grains from the sample. The zircons were placed in the teflon capsule of the bomb used. Approximately 2 ml. of concentrated ultrapure HF and a few drops of HNO_3 were added to the zircons. The assembled bomb was heated in a 205°C oven for a week.

After the bomb had cooled, the liquid in the capsule was evaporated, and a large drop of U^{235} spike was placed in the capsule and weighed. Approximately 2 ml. of 3.1N HCl were added to the capsule, and the bomb was placed in the oven overnight.

When the bomb had cooled again, the liquid was aliquoted into two small beakers, and a weight of Pb^{208} spike was added to one aliquot. The two portions were then put through ion exchange columns whose purpose was to separate the lead and uranium ions from each other and from all the other ions present. Pure samples of lead and uranium were obtained, and the recovery rate for these two elements was estimated to be 98%.

Column Procedure

The column apparatus was partially enclosed by plastic shields, and a steady flow of filtered air was pumped into the enclosure and allowed to escape through an opening in the front. This process created a clean, dust-free environment for the columns.

In the use of the ion exchange columns, it was first necessary to remove any used resin from the columns. Approximately one column length of 6.2N HCl was poured into the empty column and allowed to drip through the frit in order to remove any lead that remained in the column. When that had dripped through into the plastic container beneath, a column length of 4* water was was poured in and allowed to drip through to remove the uranium.

Next, the resin, Dowex 1x8 200-400 mesh, was added. The resin was kept in a slurry in 4* water, and enough of this slurry was added to provide a 3/4" column of resin when the excess water had dripped out. In order to clean the resin, one column length of 6.2N HCl was added and allowed to drip through. An equal amount of 4* water was then added. A conditioning step was performed at this point. One column length of 3.1N HCl was added. The columns were then ready for the sample.

The spiked and unspiked aliquots were added to separate columns. After the acid had dripped through, the zirconium was eluted with one column length of 3.1N HCl. All the liquid that had been collected from the columns up to that point was discarded, and the teflon beakers used in the aliquoting process were placed under the columns in order to collect the lead fractions.

The lead was eluted with a column length of 6.2N HCl. It was then allowed to evaporate under a heat lamp in a laminar flow of air. During the evaporation, the beakers were placed on a sloping surface with their spout sides

low. This way, the final deposit of lead can be located.

As the uranium spike had been added before the aliquots were made, the uranium solution was eluted from both the lead spiked and the lead unspiked columns. This was accomplished by pouring a column lengthof 4* water through each column. The uranium was collected in a small teflon beaker and evaporated in the manner described above.

Sample Loading

To prepare the sample for mass spectrometry, two or three drops of 0.75N H_3PO_4 were pipetted into the beakers of the evaporated lead and uranium. The beakers were heated under a heat lamp to equilibrate the solution. The spiked and unspiked portions of lead were loaded onto separate Re filaments which had previously been cleaned by being heated with an electric current of 4Amps in a vacuum chamber. This process of heating was a precautionary measure to prevent material of any sort that might stick to the filament from contaminating the load.

A large drop of silica gel solution was pipetted onto the filament and allowed to dry under the heat lamp. Generally, a second drop was then pipetted onto the filament and allowed to dry. In a similar manner, two or three drops of the lead-H_3PO_4 solution were pipetted onto the silica gel and allowed to dry. The final product looked like a lumpy, transparent glass. The filament was then subjected to a slowly increasing current of between 0 and 2.5 Amps. The lead oxidized, and the excess H_3PO_4 was driven off as a gas. When the flow of gas diminished, the filament was ready to be loaded into the mass spectrometer. The appearance of the load was usually ashy black.

The uranium loading process was slightly different. The filament used did not need to go through the process of heating and evacuation because there was virtually no uranium contamination in the air. One drop of Ta_2O_5 solution was pipetted onto the filament and allowed to dry under the heat lamp. Then, two drops of the uranium-H_3PO_4 solution were pipetted onto the filament and allowed to dry. The filament was then subjected to a 2.5 Amp current, and the substance on the filament turned from a thin, beige coating to a shiny black one.

The pipettes used during this procedure were glass. One pipette was designated for each separate process, and the pipettes were rinsed thoroughly with 4* water before and after each use. When not in use, the pipettes were kept well wrapped in plastic. The beakers used to collect the samples had been rinsed in 1:1 HCl and water, soaked in a detergent bath for several days, rinsed in 2* water, and then soaked in hot 1:1 HNO_3 for 30 minutes. After being rinsed in 1* water, they were left to drip dry between two layers of tissue. Clean beakers were kept in a sealed plastic box.

Equipment Needed for Column Procedure and Loading

5" long sections of Teflon FEP tubing with the lower $1\frac{1}{2}$" shrunk to hold a porous polyethylene disc

Dowex 1x8 200-400 mesh, chloride form in slurry with 4* water

Ultrapure 6.2N HCl

Ultrapure 3.1N HCl

5 ml. teflon beakers(for uranium)

3 ml. teflon beakers(for lead)

30 ml. plastic beakers(waste liquid from columns)

Ultrapure 0.75N H_3PO_4

Ultrapure silica gel

3 glass pipettes

Syringe

Heat lamp in laminar flow of air

Contamination

It was found from mass spectrometry that a large amount of lead contamination had entered most of the samples. The contamination level varied from sample to sample to sample and sometimes between the two aliquots of the same sample. This variation in contamination eliminated the possibility that the problem was in the laboratory air, incomplete cleaning of the bombs, or bad loading procedure.

The most likely source of the contamination was in the ion exchange columns. Although the prescribed cleaning procedures were used, the columns dripped more and more slowly with time, indicating that the frit was being gradually clogged. The columns were being used by several people and were used for separating lead and uranium from whole rock samples as well as zircon samples. It was likely that the lead contamination was caused by whole rock compounds that did not respond to the cleaning procedure.

In the future, separate sets of columns should be used for whole rock lead work and zircon work. Also, the columns should be cleaned regularly with HF to insure that all the lead is cleaned out and one set of results does not perpetuate itself with each use of the columns. The HF cleaning, while a strong measure, should be carried out after four or five uses of the columns.

$$\frac{(Pb^{207})_{AC}}{mole} = \frac{(7/6)_{AC}}{(8/6)_{AC}+(7/6)_{AC}+(6/6)_{AC}+(4/6)_{AC}}$$

$$\frac{(Pb^{206})_{AC}}{mole} = \frac{(6/6)_{AC}}{(8/6)_{AC}+(7/6)_{AC}+(6/6)_{AC}+(4/6)_{AC}}$$

$$\frac{(Pb^{204})_{AC}}{mole} = \frac{(4/6)_{AC}}{(8/6)_{AC}+(7/6)_{AC}+(6/6)_{AC}+(4/6)_{AC}}$$

2. Find the amount of each isotope of contaminant lead, Pb_x, present in one mole of total contaminant lead by the same process as in 1. Using North Atlantic common lead, the ratios are:

$$(8/6)_x = 2.67$$
$$(7/6)_x = .828$$
$$(6/6)_x = 1$$
$$(4/6)_x = .0523$$

3. Solve for the number of moles, N, of contaminant subtracted from one mole of aliquot A's lead in order to change the A ratios to the uncontaminated B ratios. Using the 7/6 ratios:

$$\frac{(Pb^{207})_{AC} - N(Pb^{207})_x}{(Pb^{206})_{AC} - N(Pb^{206})_x} = (7/6)_{BL}$$

The value obtained for N may be checked by following the same procedure with the 6/4 ratios.

4. Using the known value for N, solve for $(8/6)_{AL}$.

$$\frac{(Pb^{208})_{AC} - N(Pb^{208})_x}{(Pb^{206})_{AC} - N(Pb^{206})_x} = (8/6)_{AL}$$

Results

_ Two valid data points were obtained from the procedure described above. The numerical values given by the two samples are summarized in the following table.

| Sample	Pb^{208}/gm	Pb^{207}/gm	Pb^{206}/gm	$\dfrac{Pb^{206}}{U^{238}}$	$\dfrac{Pb^{207}}{U^{235}}$	$\dfrac{Pb^{207}}{Pb^{206}}$ a
8534NM	17.35	11.99	128.18	.1586	2.0461	1490my
8536M -250	16.00	13.27	148.64	.12550	1.5443	1410my

The plot of these points on the lead-uranium concordia diagram allows a cord to be drawn. This cord intersects the curve at an age of 1560 my.

This intercept age an d the Pb^{207}/Pb^{206} ages for the two samples are all younger than the corresponding ages obtained from beach sands in the North African countries east of Morocco. The Pb^{207}/Pb^{206} ages of these sands fall between 1635 my and 1967 my, and their upper intercept is at 1735 my.[12]

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12. H. Gaudette, personal communication.

Figure 3. Uranium-lead concordia diagram showing the positions of the Pb^{206}/U^{238}-Pb^{207}/U^{235} values for samples 8534 and 8536. The cord intersects the curve at approximately 1560 my. It is, therefore, assumed that this is the age of formation of the zircons.
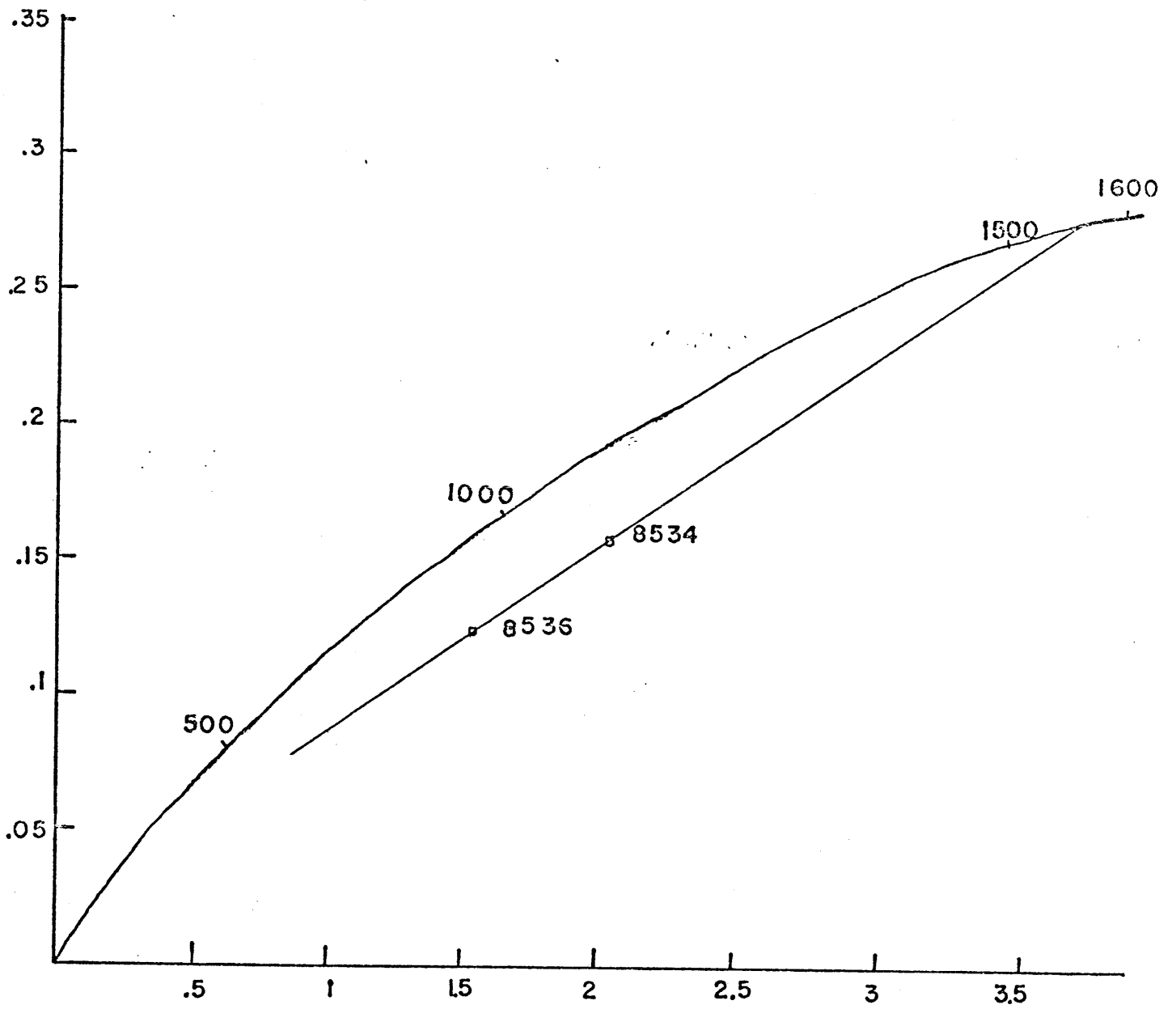
IV. The Minibomb

Because of the contamination problem encountered using the standard bomb procedure, a new method was needed in which the ion exchange columns were not used. As success had been achieved at the Institut du Physique du Globe[13] using minibombs for the dissolution of single zircons without using any column work, we decided to try this method in the dating of the Moroccan zircons.

The minibomb is made up of several parts. A teflon capsule held by a thin teflon sleeve holds the zircon grain and dissolving acid. Lateral pressure on the capsule is exerted by a monel cylinder slightly taller than the capsule. Pressure is exerted on the top of the capsule by a monel disc which has the same diameter as the capsule and fits inside the cylinder on top of the capsule. The top of the disc is raised above the top of the cylinder. On top of this disc is placed a larger disc with a spring on it. This larger disc exerts pressure directly on the smaller disc in order to keep the capsule shut. The whole assemblage is enclosed in a monel casing with a screw-on lid. This lid must be screwed very tightly to put pressure on the spring, which in turn puts pressure on the larger disc.

13. J. Lancelot, A. Vitrac, and C.J. Allegre, "Uranium and Lead Isotopic Dating with Grain by Grain Analysis: A Study of Complex Geological History with a Single Rock," Earth and Planetary Science Letters, 29(1975),

Figure 4. The top(above) and bottom(below) of the outer casing of the
minibomb. The drawings are in cross-section, and the thread
pattern is printed on the bottom piece. All dimensions are
in inches.

1.96

.89

1.01

1.688

.26

1.8

1.926

1.015

1.168

1.688
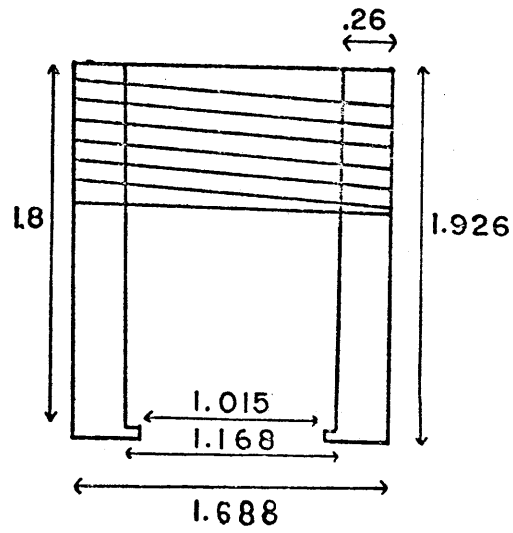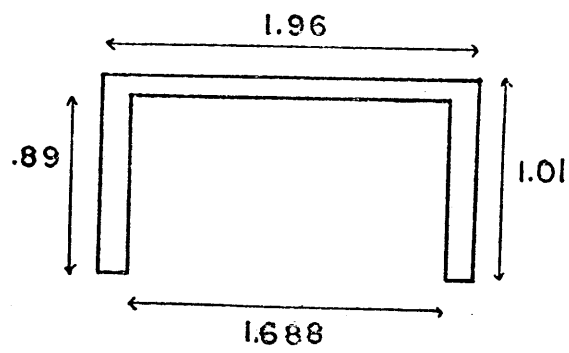
Figure 5. Cross-sections of minibomb parts, from upper to lower: 1. The large

pressure disc containing the well which houses the spring.

2. The small pressure disc, which fits inside the inner cylinder.

3. The inner cylinder.

4. The bottom piece made of two concentric discs. This piece

fits into the bottom of the outer casing and supports the inner

cylinder and the capsule.

Dimensions in inches.

.715

.312

.472

1.168

.840

.156

1.168

1.535

.85

1.168

.118

.117

.235

1.105
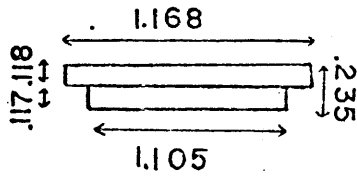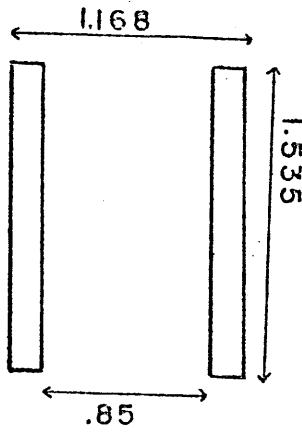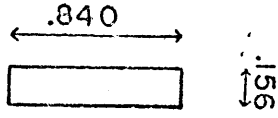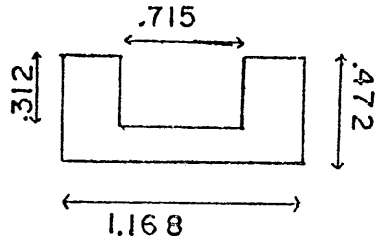
Figure 6. Cross-sections of the parts of the teflon capsule, from upper

to lower: 1. Lid of the capsule.

2. Base of the capsule.

3. Sleeve which fits over the assembled capsule.

.795

.984

.4

.669

.198

.410

.723

1.145

.826

15°

.196

.787

1.4

.0196
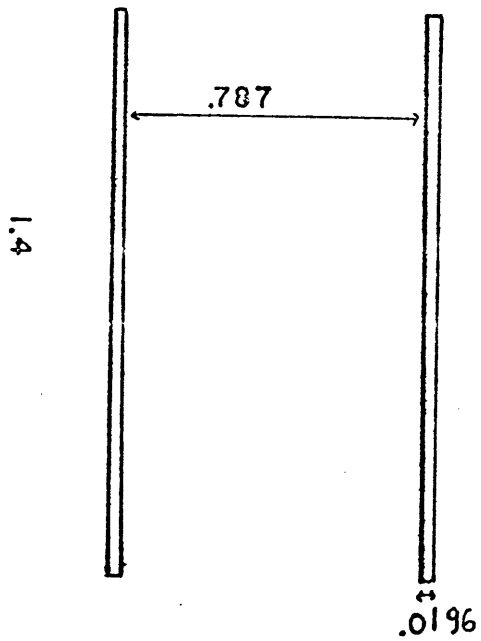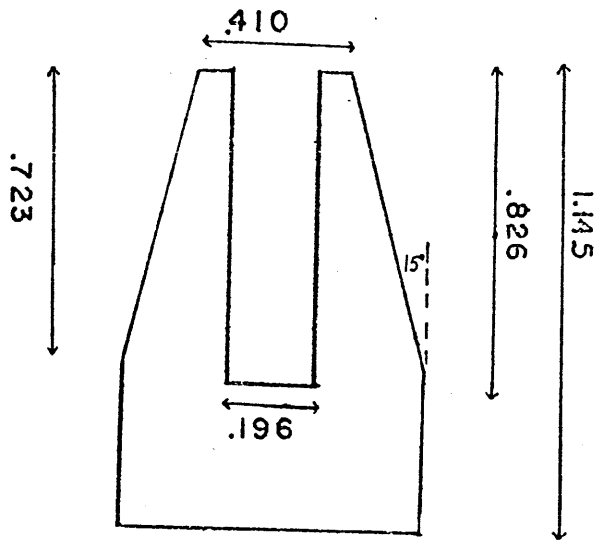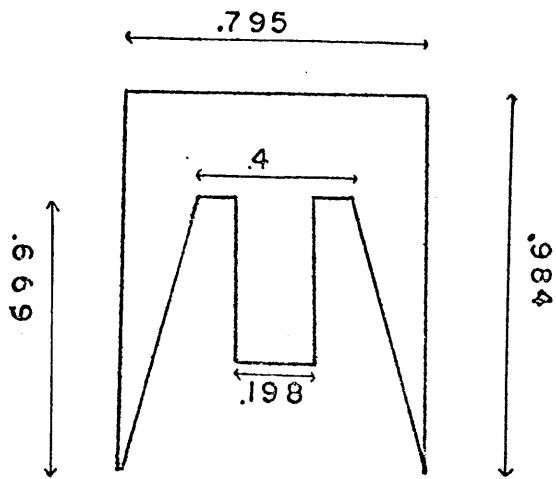
First Minibomb Technique

The new teflon capsules and sleeves were cleaned in the same way that all the other teflon and glassware were. They were rinsed in a 1:1 mixture of reagent grade HCl and tap water. Next, they were soaked in a detergent solution for 3 days. After being rinsed with 2* water, they were soaked in a near boiling 1:1 solution of reagent grade HNO_3 and tap water. The Pieces were left to dry between 2 layers of tissue. The bombs were then cleaned by loading the capsule with 2 drops of ultrapure HF and leaving the assembled bombs in a $205^{0}C$ oven overnight. The procedure was repeated with fresh acid for a second night.

Between uses, the bombs were cleaned by soaking all the parts except for the spring in a weak solution of HNO_3 and tap water for 2 hours. They were then rinsed and left to dry in the open air. The spring was quickly corroded if put in the acid solution, so it was cleaned by rinsing with tap water. The bomb was then assembled and given the same double overnight cleaning described above.

In loading the bomb, a plasticpipette was used for the HF. Every pipette was used only once and then discarded. Two drops of HF were added to the 2 or 3 zircons in the capsule, and the bomb was placed in the oven for a period of between 16 and 24 hours. A teflon beaker was labeled and weighed, and the contents of the capsule were placed in the beaker. After covering the beaker and placing it in a well-wrapped box, we put 2 drops of ultrapure 11.2N HCl into the capsule and put the bomb back in the oven for a period of from 8 to 16 hours. In this way, most of the lead from the zircons could be extracted from the dissolution capsule. The HCl was deposited in the same beaker, after the bomb had cooled. The contents of the beaker were evaporated to dryness during the first trials according to the procedure

of Lancelot et al.[14]

For the purpose of spiking such small amounts of solution, both the lead and uranium spikes were diluted in 3.1N HCl. Good values for the U^{238}/U^{235} ratio were obtained using a U^{235} spike concentration of 7×10^{-10} moles U^{235}/ml. The concentration of the Pb^{208} spike used was 1.6×10^{-9} moles Pb^{208}/ml.

After the sample had evaporated, one drop of the dilute U^{235} spike was weighed into the beaker. At this point, more 3.1N HCl was added to increase the volume of liquid in the beaker to approximately 1 ml. After being allowed to equilibrate for a few minutes, the loution was aliquoted, and one drop of the dilute Pb^{208} spike was weighed into the beaker.

The two aliquots were then evaporated to dryness and loaded onto filaments for mass spectrometry. The loading procedure used was the same as that used for loading the lead solutions onto filaments in the standard bomb procedure. The following table of results shows that there was a large amount of contamination introduced during this procedure. For comparison, I have placed one of the successful results from the standard bomb method at the top.

Sample	weight of zircon (grams)	weight of acid added (grams)	$\dfrac{Pb^{208}}{Pb^{206}}$	$\dfrac{Pb^{207}}{Pb^{206}}$	$\dfrac{Pb^{206}}{Pb^{204}}$
8536N	.0071	4.1203	.408	.2022	124.97
8532	.0004	.2622	1.4716	.5882	33.032
8532	.0007	1.4733	1.7425	.7907	
8534	.00015	.4311		.7673	
8536	.0002	.5963		.6708	26.315

It is evident that the ratio of 3.1N HCl added and the weight of the zircons used is somewhat proportional to the quality of the results. Using such small amounts of zircon made the lead content of the reagent critical, and our HCl was not pure enough to be used in such large quantities.

14. Ibid.

Second Minibomb Technique

A second technique was used to reduce the need for reagents and to intensify the efforts to keep the sample clean. For this method only one zircon was dissolved in each bomb to reduce the error of selecting grains. A zircon was picked with a paintbrush and deposited in the teflon capsule. A second zircon of similar size and shape was placed in another capsule. Two drops of HF were pipetted into each capsule using the plastic disposable pipettes. Into one of the capsules were weighed one pipette drop each of the dilute U^{235} spike and the dilute Pb^{208} spike. Both capsules were placed inside their metal casings and left in the oven overnight.

After the bombs had cooled, the capsules were removed and the contents evaporated by placing the contents in separate covered teflon vessels under a heat lamp. Two drops of 0.75N H_3PO_4 were pipetted into each capsule. The capsules were then placed in their respective teflon evaprating vessels and allowed to heat for a few minutes to equilibrate the acid and powdered zircon.

The pipette used to take up this solution and load it onto the filament was washed in 6.2N HCl and 4* water before and after loading. As much of the sample as possible was loaded onto the filament as the original sample had been so small. Otherwise, the loading procedure was the same as the lead loading procedure discussed before.

The cleaning procedure between uses of the bomb was changed. Each time the bomb was used, the capsule and the sleeve took on a residue from the metal parts of the bomb.. This residue did not come off during the normal cleaning procedure. Therefore, the teflon pieces were washed well in 1:1 reagent grade HCl and water. After being rinsed in 2* water, they soaked in a near boiling solution of 1:1 reagent grade HNO_3 and water for 30 minutes to an hour. This process was very effective in removing the residue and was used after each

use of the bomb. The metal parts of the bomb except for the spring were soaked

in a dilute solution of HNO_3 for two hours, rinsed, then allowed to dry.

The bomb was then loaded with two drops of HF and left in the oven overnight.

This procedure was repeated a second night.

To test these new cleaning and loading procedures, several measurements of

lead isotope ratios were made on a zircon sample from Tunisia. The ratios

from this sample had previously been measured by Professor Henri Gaudette of

the University of New Hampshire. The following table shows the comparison

of his results using the standard bombs under ideal conditions and my results

using the small bombs.

Sample 8180	$\dfrac{Pb^{208}}{Pb^{206}}$	$\dfrac{Pb^{207}}{Pb^{206}}$	$\dfrac{Pb^{206}}{Pb^{204}}$
Standard bomb	.15347	.10055	1050
Minibomb	.46157	.20332	146.006
	.31483	.16490	180.101

It is apparent that the standard bomb contamination level was lower than

the minibomb level. The amount of contaminant lead in each minibomb load

was calculated to be 1.3 ng. However, these measurements show a great improve-

ment over the measurements made with the first minibomb technique. It is

possible to correct for the lead contamination in these measurements with a

fair degree of confidence. The ratio of the contaminating lead in this

technique was calculated to be approximately 1:36:17:41 for $Pb^{204}:Pb^{206}:Pb^{207}:Pb^{208}$.

The weight of the zircon grain used had to be estimated. The error in such

an estimation does not affect the corrected values of the lead isotope ratios

much. It does cast doubt, however, on the value of the uranium-lead ratios

obtained by this method. More precise measurement of single grain weights is

needed before these values can be used on a uranium-lead concordia plot.

Assets and Problems of the Minibomb

Usage of two minibombs, one containing a spiked sample and the other, an unspiked sample, simulates the situation in which one larger sample is split into smaller aliquots. The ratios of Pb^{208}/Pb^{206}, Pb^{207}/Pb^{206}, and Pb^{206}/Pb^{204} were measured on the unspiked sample. The ratios Pb^{208}/Pb^{206} and U^{238}/U^{235} were measured on the spiked sample. Whereas, in the standard bomb procedure, three filaments had to be loaded to make all the necessary measurements, this method requires only two filaments. This amounts to a saving in filaments and in loading time.

It was found that a single zircon grain larger than 150 mesh created a strong enough signal on the mass spectrometer to measure even the very high ratios of Pb^{206}/Pb^{204}. Two difficulties were encountered, though. First, the signal is slightly less stable using the minibomb technique. This problem is at least partly caused by the presence of many other elements like zirconium, which are removed by the resin in the ion exchange columns. These elements cause the load to be less well-ordered and, therefore, less stable.

The second problem is the large number of peaks indicating the various elements present. The uranium peaks, though strong enough to be measured, are often hard to distinguish from the surrounding peaks.

Aside from the results obtained using the minibombs, their design has important effects on the ease with which they can be used. The design is especially good for removing the teflon capsule after the assemblage has been in the oven. It is easy to get the inner monel cylinder out of the outer casing and force the teflon capsule out. This is important because the teflon capsule and sleeve flow during their time in the oven and can stick to the sides of the cylinder. Their small size would make them difficult to remove if both ends of the inner cylinder were not open.

Evaporation of the liquid from the capsule is one of the hazards of the minibomb because there is so little acid placed in the capsule to begin with. Any loss of acid and dissolved zircon would lessen the possibility of getting strong enough signals during the mass specrtoscopy. Again, the design provides a solution to this problem. The small pressure disc that fits on top of the capsule is in contact with the larger pressure disc that fits inside the top of the caseing. Thus there is direct pressure on the capsule to keep it tightly sealed. The spring seated in the upper pressure disc moderates the pressure created by screwing the top on. However, it also provides a continuous force on the small pressure disc while the capsule is undergoing flowage during heating. A slight shortening of the capsule does not drastically reduce the pressure on it. The top must, therefore, be screwed on tightly.

Several of the capsules used experienced shortening during the course of several uses. The teflon capsule and sleeve flared out at the bottom of the capsule. As there was no direct pressure on the inner cylinder, it was not prevented from moving slightly and allowing the teflon to flow under it.

The shortening of the capsules caused the small pressure disc to seat lower in the inner cylinder. At the point at which the pressure disc's top was nearly leve with the top of the inner cylinder, a steady state was reached. The capsule remained the same length and did not expand at the bottom any more. This result suggests that, in the future, the design of these minibombs should be modified to allow for a shorter capsule and a small pressure disc more nearly level with the inner cylinder.

One other problem experienced with the bombs was that the heavy tightening needed to create sufficient pressure tended to chip and deform the threads on the outer casing. It was apparent that the extreme tightening might shorten the life of the bomb.

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Appendix

Rubidium-strontium dating has been performed on many of the exposures of
Precambrian and Paleozoic plutonic and volcanic material in Morocco. As these
are the possible sources of Mesozoic zircons, their ages are important for com-
parison with the ages determined for the Meseta zircons.

Area	Exposure	Ages in millions of years				
		15	16	17	18	19
Bas Dra	Ain Tamousift granite	1895±20	1900			
	Aounet n'Ait Oussa "	1890±90				
	Oued Chaiba granite	1640±32				—
Kerdous	Jbel Ouiharem gneiss	1700				
	Tazeroualt granite	1905±25	1900	1700		
	Oued Amarheus "	1900		1900		
	Tasserhirt granite	1900	1600±30	1800		
	Tahala granite	1920±40	1900		1920	
	Kerdous rhyolites	580-380				
	Tafraoute granite		530	500±27	530	
Zenaga	Azguemerzi granite	1865±25	1850±30	1850±50		
	Tazenakht granite	1735±15	1740±30	1744±32		
	Timcharhine pegmatite	1800				
Siroua	Askaoun granite	690	690			
Ouarzazate	Ouarzazate volcanics	550-380		410±26		
Ifni	Alouzad granite	2217±44				
	Ifni rhyolites	631-603				
Meseta	Tichka massif					313-30

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