PBDAT for MS-DOS

A COMPUTER PROGRAM FOR IBM-PC COMPATIBLES FOR PROCESSING RAW Pb-U-Th ISOTOPE DATA

Version 1.00a

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UNITED STATES GEOLOGICAL SURVEY

OPEN-FILE REPORT 88-542

Rev. September 21, 1988

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INTRODUCTION

PBDAT for MS-DOS takes raw Pb-U-Th isotope data (either typed in from the keyboard or from LOTUS 1-2-3 or other ASCII files), including all relevant data from the chemistry laboratory, and calculates elemental and isotopic concentrations, isotope ratios, apparent ages, uncertainties and error-correlations in these values using the algorithms developed in Ludwig (1980). The resulting data (figure 1) is corrected for instrumental mass-fractionation, laboratory blanks, and the initial Pb of radiogenic samples[1]. Data defining the particular spikes and blanks of a particular laboratory are entered by each user, and stored as user-specific data files on the same disk or directory as **PBDAT** itself. Because of this feature, several different laboratories can use the same program without program modification.

Raw data that has been stored as an ASCII file can be converted as a batch (either in whole or in part) to a reduced-data file which is compatible with the **ISOPLOT for MS-DOS** plotting program (Ludwig, in press). **PBDAT for MS-DOS** (or **PBDAT** for short) can accept data from laboratories using a variety of spikes, including ^{208}Pb, ^{206}Pb, ^{205}Pb, ^{235}U, ^{233}U-^{236}U, and ^{230}Th. These spikes can be delivered either to a liquid aliquot or to the total sample, for any combination of Pb and U/Th. Keyboard data-input is managed by a friendly and error-resistant **FORM** screen which makes extensive use of **HELP** screens and error-trapping.

PBDAT for MS-DOS, a compiled program written in QUICK BASIC 4.0, is a complete implementation of the earlier **PBDAT200** program[2] (Ludwig, 1985b). If you would like a copy of the current version of this program, please write to me directly and enclose a disk formatted on your computer. You may also request the source-code, provided as an ASCII file on another similarly-formatted disk. The code is lengthy, however, and QUICK BASIC 4 may look unfamiliar to users of other dialects of BASIC.

The decay constants used by **PBDAT** are those recommended by the I.U.G.S. Subcommission on Geochronology (Steiger and Jäger, 1977): .155125 x 10^{-9} /yr for ^{238}U, .98485 x 10^{-9} /yr for ^{235}U, .049475 x 10^{-9} /yr for ^{232}Th, and present-day $^{238}U/^{235}U$ = 137.88.

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[1]But not for uncertainties in the decay constants of U and Th, nor the uncertainty in the $^{238}U/^{235}U$ ratio of terrestrial uranium. The decay constants and U-isotope ratio used by **PBDAT** are those recommended in Steiger and Jäger (1977).

[2]Written in HP BASIC for Hewlett-Packard Series 200/300 computers.

HARDWARE REQUIRED

PBDAT for MS-DOS requires an IBM-PC compatible computer[1] with at least 256 kbytes of memory, running under DOS 2.0 or later. The program assumes that the printer is connected to the parallel port (LPT1) of the computer. Use of data files as input (instead of typed-in values) requires a program that can create ASCII text files (preferably a spreadsheet-type program such as LOTUS 1-2-3).

GETTING STARTED

You'll need DOS present either in one of the disk drives (if you're using a two-floppy system) or accessible from the hard disk via the PATH statement in your AUTOEXEC.BAT file. For a hard disk system, copy the **PBDAT** disk onto a subdirectory; for a two-floppy system, put the **PBDAT** disk in the other drive. Change the default drive and path to be that of **PBDAT**, so that the HELP files will be accessible. For example, if **PBDAT** were on the disk in drive **A:** under subdirectory **\PROGS\PB**, you would type **A: {ENTER}**, then **CHDIR \PROGS\PB**). Type **PBDAT {ENTER}** to start the program. After a few seconds, the screen will display:

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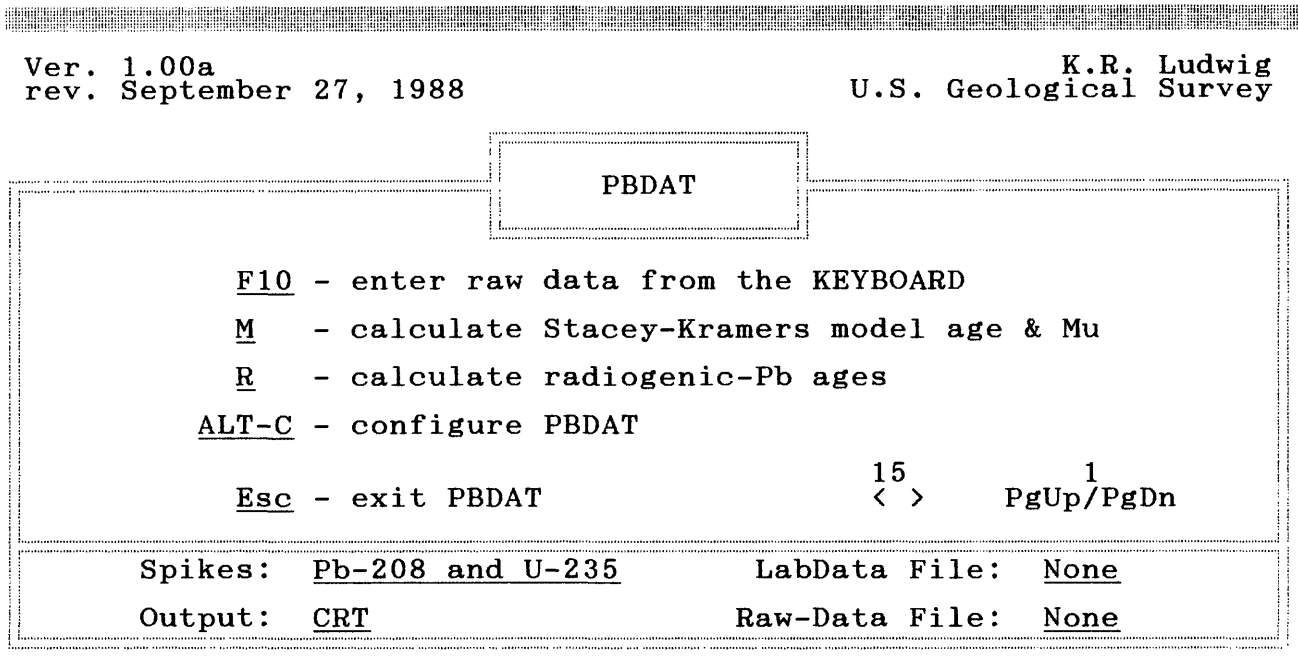
[1] You can use a Texas Instruments (TI) computer running under Romberg & Romberg's EMULATE program, but only if you invoke **PBDAT** by typing **PBDAT TI** instead of just **PBDAT**.



F1 HELP	F2 DOS	F3 Pb208 SPIKE	F4 U235 SPIKE	F5 LABDATA
F6 DATAFILE	F7 USE PRINTER	F8 Pb205 SPIKE	F9 233/236 SPK	F10 KEYBOARD

I'll refer to the above display as the Top-Level Screen. Use the function keys to specify which spikes you're using and where to direct your output. In PBDAT, the F1 key is always defined as a HELP key that will show you detailed information about the uses of the function keys or how to fill out a data form. I suggest that you make extensive use of the HELP screens the first few times you use PBDAT.

When you first run PBDAT, you'll need to configure the way the program operates by pressing ALT-C (configure PBDAT). The PBDAT configuration form will look like this:

PBDAT CONFIGURATION

```
Screen: Monochrome (M) or Color (C) ... M
        #lines in output (25 or 43) ... 25

  Reduced-data format for Pb ratios ... 1
       206/204-207/204-208/204  (1)
       204/206-207/206-208/206  (2)

Reduced-data format for radiogenic-Pb ... 1
         207Pb/235U-206Pb/238U  (1)
         238U/206Pb-207Pb/206Pb  (2)

 Default disk\path for  LabData files ... C:\PBDAT
 Default disk\path for Raw-Data files ... C:\LOTUS
```

ENTER - Enter One CTRL-ENTER - Enter All
F1 - Help F9 - Recall one F10 - Recall All

Enter the type of monitor you're using and, if you have an EGA or VGA screen, the number of lines in your output screens (25 is normal, 43 will show you more per screen, but at the cost of some legibility and clutter).

You can select how you want your reduced-data calculated for both the total-Pb ratios and the radiogenic-Pb ratios. Entering 1's for both will give you the "normal" formats, with 206/204-207/204 - 208/204 for total-Pb and the usual concordia-plot ratios of 206/238 - 207/235 for the radiogenic-isotope ratios. Entering 2's for the formats will give the alternate formats of 204/206-207/206 - 208/206 and 207/206 - 238/206. The raw-data format, however, does not change.

Enter the default disk\path for your LabData files and your raw-data files. The first time you run PBDAT, these will be the same as the PBDAT program. You can easily change the disk\path for both of these file-types while running PBDAT, so don't bother to plan ahead too much at this point.

When you're finished, enter the values with **CTRL-ENTER** and return to the Top Level screen.

You can "shell out" to DOS from the Top-Level screen by pressing **F2**. This will cause a temporary exit to DOS while keeping PBDAT in memory, so that you can perform the various DOS functions

(show a directory of files, move or delete files...) or even run another program. To return to PBDAT, type **EXIT {ENTER}**.

ENTERING DATA FROM THE KEYBOARD

First, specify a **LabData** file for the program to use by pressing **F5**. The screen will display a list of the **LabData** files present on the default drive/path. The first time you run the program, just pick any of the example-files shown. More information on **LabData** files is given in a later section.

Introduction to FORM Screens

First, press the **Pb-208 SPIKED**[1] and **U-235 SPIKED** softkeys to use for our example. Press the **KEYBOARD** key (**F10**) to start keyboard data-entry. The screen will then show:

---

[1]PBDAT will work with ^{206}Pb spikes too, because to the program, a ^{206}Pb spike is mathematically equivalent to a ^{208}Pb spike. So long as you have the correct isotope ratios in the LabData file for your 206 spike, just follow all the procedures for 208-spiked samples.

SAMPLE, SPIKE, & ALIQUOT WEIGHTS

```
                    Sample Name  ...  ??

          Sample Weight (grams) ...  1
Total-Aliquot Weight (grams)
 (enter only if appropriate) ...  --

 Pb-Unspiked Aliquot (grams) ...  0
   Pb-Spiked Aliquot (grams) ...  1

    U/Th Spiked in Total (1)
    or Pb-Spiked (2) Aliquot ...  2

  Pb-Spike delivered (grams) ...  0
   U-Spike delivered (grams) ...  0
  Th-Spike delivered (grams) ...  0
```

ENTER - Enter One CTRL-ENTER - Enter All
F1 - Help F9 - Recall one F10 - Recall All

This is a FORM screen. When it appears, the response to the **Sample Name** query will be highlighted, indicating where the response-cursor is. Type in a name for the sample whose data you're entering. The double-question marks will disappear, and your sample name will appear in its place as you type it in. Press the **ENTER** key[1] when you've finished typing in the sample name, and the cursor will move down to the next parameter with the sample name remaining where you typed it. To move the **FORM** cursor to any parameter, press the up-arrow or down-arrow keys.

To enter a value for a parameter, move the cursor to the appropriate parameter and type in the value. You can edit as you type with the usual cursor-control keys. When you're satisfied with your response, press the **ENTER** key and the value will be entered for that parameter. If you've made an obvious error, **PBDAT** will display an error-message and ask you to re-enter the value. Note that even if you type something into one of the response areas, unless you press the **ENTER** key it will disappear when you move the cursor to another parameter.

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[1]On some computers, there is no **ENTER** key; use **RETURN** instead.

When you've entered values for all the required parameters (a double question-mark in a response area indicates that a response for that parameter is required; other parameters may be optional), submit the form by pressing **CTRL-ENTER**[1]. Until you do this, none of the values that you entered will be used. If you want to escape from the FORM at any time, press the **Esc** key. Pressing **Esc** causes the program to ignore all of the values in the FORM that you might have just entered.

If you don't understand the significance of a parameter in the FORM, put the cursor on that parameter and press the **HELP** key (**F1**). A **HELP** screen will appear to give you more information on what the significance of that parameter is and what sort of response is required.

If you've already entered a set of values to the form (for a previous sample, for example), you can re-use the last values entered by pressing the **F10** key (**Recall All**) when the FORM is displayed. The last-entered values for that FORM will then appear in the current FORM. This feature is especially useful if you made an error in entering the data for a sample but didn't notice the error until after you submitted the FORM, or if you wish to "recycle" data with only slight changes.

The "Weights" Form for ^{208}Pb-Spiked Samples

The above FORM requires values for the various weights involved in a sample analysis. Their significance is as follows:

Sample Weight: -- The weight of the sample that was actually attacked and put into solution, in grams.

Total Aliquot Weight: -- The weight of the total solution of the entire sample, in grams. Enter a value here if you only put a fraction of the total solution of the sample through chemistry; if all of the solution were used (so that the Total Aliquot is just the sum of the Unspiked Aliquot and Spiked Aliquot weights), you needn't enter any value here - **PBDAT** will then assume the Total Aliquot to be the sum of the spiked and unspiked aliquots.

Pb-Unspiked Aliquot (grams): -- The weight of the solution used as the Pb-unspiked aliquot. Samples spiked with Pb before dissolution will have no Pb-unspiked aliquot, nor will blanks. In these cases, enter zero.

Pb-Spiked Aliquot (grams): -- The weight of the solution spiked with ^{208}Pb (or ^{206}Pb).

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[1]Or **CTRL-RETURN**.

U/Th-Spiked in Total (1) or Pb-spiked (2) Aliquot: -- If the sample were total-spiked (spiked before attack or before any aliquoting) for U(Th), enter a value of 1. If the U(Th) spike were added to the same aliquot as the Pb-208 spike, though, enter a value of 2. Incidentally, **PBDAT** always assumes that if a ^{230}Th spike were used, it was either mixed with the U spike or added to the same aliquot as the U spike.

Pb-Spike (U-Spike, Th-Spike) Delivered (grams): -- The amount of the Pb, U, or Th spikes delivered, in grams. If the Th spike is part of a mixed U-Th spike, then the U and Th spike weights must be the same.

The "Pb-Unspiked Ratios" Form (^{208}Pb-Spiked Samples)

After you submit the completed "WEIGHTS" FORM, the next FORM will be:

Pb-Unspiked Aliquot Ratios

(errors must be 2-sigma, in percent)

206/204 ... ??
%error ... ??

206/207 ... ??
%error ... ??

206/208 ... ??
%error ... ??

Pb-blank (nanograms) ... ??

Enter values for the three ratios (raw values from the mass-spectrometer run, NOT corrected for mass fractionation), together with their errors. The errors should be at the 2-sigma (or 95%-confidence limit) level, in percent, and should correspond to the statistical errors from the mass-spectrometer run, without including the uncertainty due to mass-fractionation.

If you entered a value of zero for the Pb-unspiked aliquot weight in the previous FORM, the above FORM will ask you for only one ratio: the estimated Pb-unspiked 206/208. You may not have any hard data for this ratio, but you'll still have to enter your best

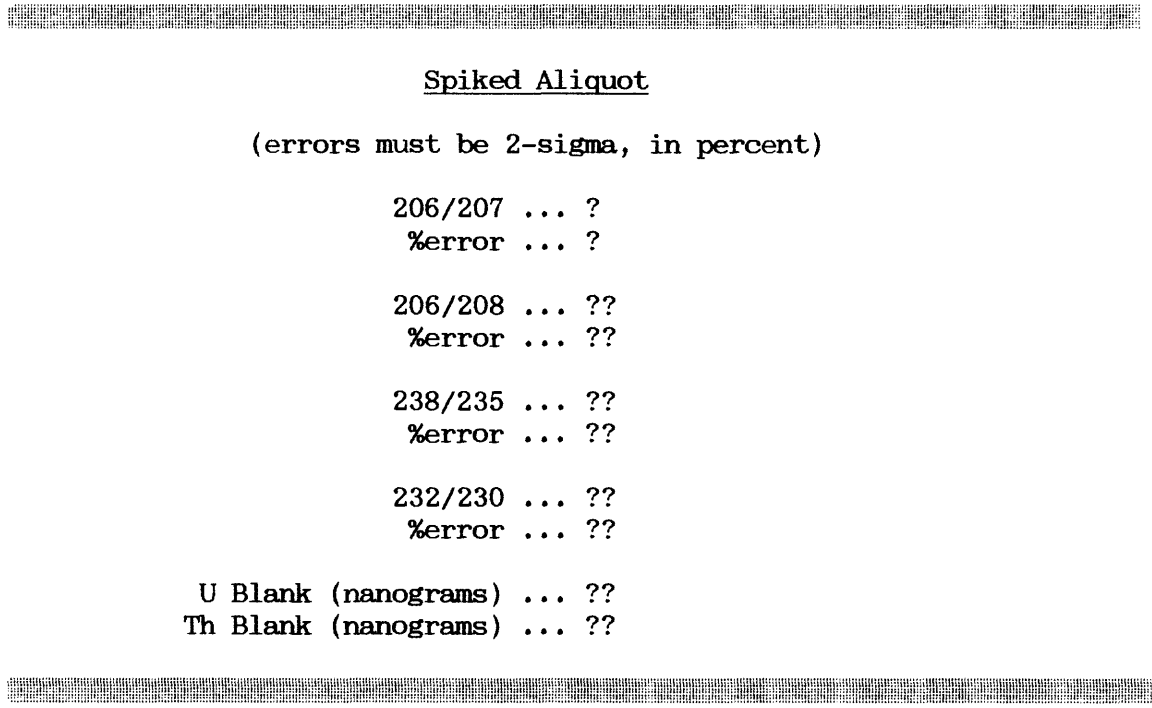
estimate in order to get any reduced Pb-data.

The **Pb-blank** is the blank that corresponds to the unspiked portion of the analysis only. So if the dissolution process alone contributed a significant amount to the overall blank, you should include only the fraction of the dissolution blank that corresponds to the Pb-unspiked aliquot.

If you didn't measure Pb-isotope ratios for the Pb-unspiked aliquot, just bypass this FORM by pressing the **Esc** key.

The "Spiked Aliquot" Form (^{208}Pb-Spiked Samples)

The next FORM requires the isotope ratios for the Pb-spiked aliquot, as shown below (assuming a U-235 uranium spike):



The 206/207 ratio for the Pb-spiked aliquot is optional -- if you don't have data for this ratio, don't enter any values for it. *If your sample contains radiogenic Pb, though, you should always include the 206/207 ratio for the Pb-spiked aliquot.* **PBDAT** can then calculate the Pb concentration more accurately, by mathematically compensating for the effect of a varying Pb-blank in the spiked aliquot.

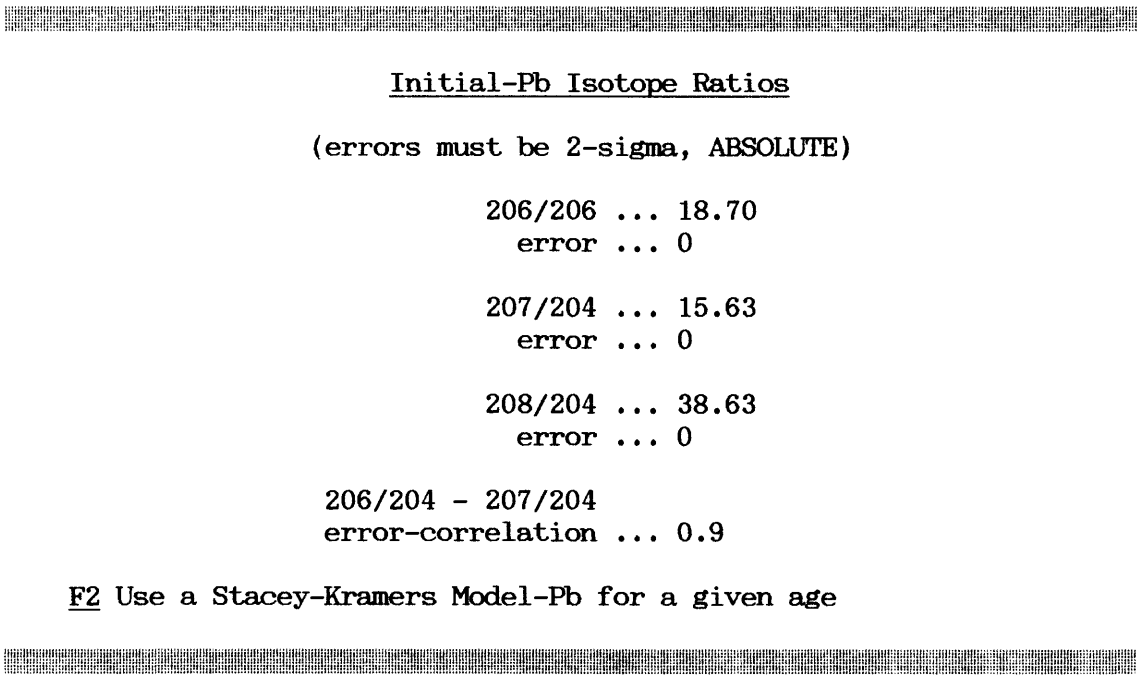
If you didn't enter any Pb-unspiked aliquot ratios, the FORM will also ask for the estimated Pb blank. Enter the Pb blank that corresponds to the Pb-spiked aliquot.

The blank assignments for the U- and Th-ratios should reflect only the blank for the U(Th)-spiked aliquot. You can enter zero if you're sure that the blank is negligible.

The "Initial-Pb Isotope Ratios" Form

If the Pb in the sample is radiogenic and you want to calculate Pb-U-Th isotope apparent ages, you must enter estimated values for the initial-Pb isotope ratios in this FORM. If the Pb in your sample is nonradiogenic (common), or if you're not interested in apparent ages, just escape from this FORM. The initial Pb is defined as the Pb which was present at the time the U-Pb system of interest was "born". For a mineral or rock, this will generally be the Pb present at the time of formation of the mineral or rock.

The FORM for the Initial-Pb ratios is:



The default values are those for a system with zero age on the Stacey-Kramers Pb-growth curve (Stacey and Kramers, 1975). The errors for the ratios must be entered at the 2-sigma level and in absolute values, not percent values.

NOTE: Enter nonzero errors for the initial-Pb ratios only if you have reason to believe that the actual initial-Pb isotopic composition was different from sample to sample, or if the sample is not part of a suite. If you're reducing data for several cogenetic samples and you intend to pool the data for a concordia-diagram treatment, enter zero errors even though there is some uncertainty in your estimates of the initial-Pb ratios (you'll have to estimate the effect of the initial-Pb uncertainty by reducing the data-set with different initial ratios, and performing a Yorkfit and concordia-intercept calculation for each set of reduced ratios).

If you do enter nonzero errors for the initial-Pb ratios, you'll need to enter an estimate of the correlation between the 206/204 and 207/204 errors. This value should always be nonzero-typically in the range of 0.8 to 0.95. This error correlation value is the same as the conventional correlation coefficient that you'd get if you do a linear regression of the 207/204 versus 206/204 for several samples that represent the true range of initial-Pb ratios for the system from which your samples were derived. If none of this makes much sense but you still need to enter nonzero errors, an error correlation of 0.9 is probably not too far off.

You can have PBDAT use the Stacey-Kramers growth-curve values (Stacey and Kramers, 1975) for any age by pressing **F2**, then entering the Stacey-Kramers age (in Ma). The Pb-isotope ratios defined by the Stacey-Kramers curve for that age will appear in the FORM, after which you can either edit the values, or accept them as given.

Note that much of the information that PBDAT can make use of is optional. For example, if you have only the spiked-run data for a 208-spiked Pb aliquot, enter zero for the weight of the Pb-unspiked aliquot. The program will then ask you for only the estimated 206/208 of the unspiked run and the uncertainty of that ratio. In such cases, though, you'll need to know all of the Pb ratios (including 206/204) for the spiked aliquot. You needn't enter any U or Th data, nor an estimate for the initial-Pb isotope ratios. When none of the parameters in a FORM are known or relevant, just press **Esc** when the FORM appears.

Samples Spiked with a Mixed ^{233}U-^{236}U (-^{230}Th) Spike

For samples spiked with a mixed ^{233}U-^{236}U spike instead of a ^{235}U spike, PBDAT accepts two different types of data input. The

first type is for data that is already partially reduced so that the Sample-238/Spike-233 (SAM/SPK) ratio has already been calculated. This should be the case for data from a mass spectrometer running under ANALYST (Ludwig, 1985a). The Sample-238/Spike-233 ratio is simply the ratio of moles of natural ^{238}U in the U-spiked aliquot to the moles of ^{233}U delivered as the spike. The second type is for raw $^{233}U/^{236}U$ and $^{233}U/^{238}U$ ratios. When you specify a U-233/236 spike, **PBDAT** will ask you which type of input to expect.

For the first type of data input, the FORM screen will look like this:

U-Spiked Aliquot

(errors must be 2-sigma, in percent)

Sample-238/Spike-233 ... ?
%error ... ?

232/230 ... ?
%error ... ?

U- Blank (nanograms) ... ?
Th-Blank (nanograms) ... ?

Enter the calculated ratio of the moles of ^{238}U in the U-spiked aliquot of the sample to the moles of ^{233}U that you added from the spike. The rest of the FORM is the same as for ^{235}U-spiked samples.

The second type of 233/236/238 FORM (Sample-238/Spike-233 not calculated) will look like this:

U-Spiked Aliquot

(errors must be 2-sigma, in percent)

233/236 ... ?
%error ... ?

233/238 ... ?
%error ... ?

232/230 ... ?
%error ... ?

U Blank (nanograms) ... ?
Th-Blank (nanograms) ... ?

Just enter the raw (uncorrected for fractionation) ratios and errors as usual[1].

Samples Spiked with a Mixed ^{205}Pb-U-^{230}Th Spike

For samples that were total-spiked with a mixed ^{205}Pb-U-^{230}Th spike (the U can be either 235 or 233-236), the first FORM will be:

Pb-205 Spiked Sample

Sample Name ... ??

Sample Weight (grams) ... ??

Pb-205 Spike delivered (grams) ... ??

[1]If you're using a ^{233}U spike without ^{236}U, you can still use this FORM by 1) defining the 233/236 ratio in your LabData file to be 1.000, then 2) entering a value of 1 + 3F/100 for the 233/236 ratio in the FORM, where F is the predicted mass-fractionation for your uranium runs, in percent per mass-unit.

This FORM assumes that the ^{205}Pb spike was delivered to the total sample represented by the sample weight.

The next FORM for a ^{205}Pb-spiked sample is:

Pb-Spiked Aliquot

(errors must be 2-sigma, in percent)

206/204 ... ??
%error ... ??

206/207 ... ??
%error ... ??

206/208 ... ??
%error ... ??

206/205 ... ??
%error ... ??

Pb-Blank (nanograms) ... ??

The Pb blank is the blank that corresponds to the complete attack, extraction (if any), and loading procedure. The rest of the data input (for ^{205}Pb-U-Th spiked samples) is the same as for ^{208}Pb-spiked samples.

Entering Data for Blank Determinations

For Pb-blanks, you usually won't have any specific data for the Pb-unspiked aliquot ratios, and you might not have any data for the Pb-spiked 206/204 ratio. So for blanks, enter the weight of the Pb-unspiked aliquot as zero (since there wasn't any unspiked aliquot). **PBDAT** will still ask you for an estimated value for the unspiked 206/208 ratio, however. Enter your best guess for this value - unless your blank is very underspiked, your guess doesn't have to be too accurate. You'll also need to enter an uncertainty in your estimate -- 5% isn't too large if you know only that the blank Pb is a "normal" common Pb (206/208 = 0.46-0.50).

The Pb-Blank value that you enter into the Pb-Spiked Aliquot Ratios FORM will depend on what type of blank-determination you are doing. For a total-blank, enter a blank-value of zero (you want to know the total contamination). For a reagent blank, though, you should enter the estimated blank for loading plus whatever handling (evaporation, weighing...) accompanied the blank procedure. It's worth noting that for blanks of very pure reagents (for example, water), the evaporation blank can easily exceed the reagent blank itself.

Entering Data for Spike-Concentration Calibrations

To calibrate the concentrations of a spike, you'll need to have (1) a standard solution or solid with known isotope ratios and concentrations, (2) an isotopic analysis of a (well mixed) mixture of the standard and the spike. Enter the data into **PBDAT** in the following way:

Sample weight:	Weight of the standard solution (or solid).
Total-aliquot weight:	Zero
Pb-Unspiked Aliquot weight:	Zero
Pb-Spiked Aliquot weight:	1
U/Th-spiked in total (1) or Pb-spiked (2) aliquot:	1
Pb, U, or Th Spike, grams delivered:	Weight of the spike delivered to the mixture.
Blank amounts:	The nanograms of Pb, U, or Th contamination that you assign to the mixing, loading, running, and (if a solid standard) dissolution procedure. But enter <u>zero</u> for the Pb-unspiked aliquot blank
Pb-isotope ratios:	For the unspiked aliquot, enter just the (accepted or known) 206/208 ratio for the <u>standard</u>. For the spiked aliquot, enter the observed ratios of the mixture.

Unless you have a combined Pb-U-Th standard, you can only reduce the data for one elemental-spike at a time, even though all three elements were combined in the mixing stage.

Examine the indicated concentration of the major spike-isotope in the **PBDAT** printout. This is the indicated concentration of that isotope in your standard using the presently-defined concentration of your spike. The percent difference in the concentration that you just obtained for the standard is the amount that you need to adjust your spike concentration; to make this adjustment, change the spike concentration in the **LabData** file by the percent difference above, but in the opposite direction.

In other words, if the spike-calibration run indicates that your standard is 1% too high compared to its accepted value, then lower the spike concentration in the **LabData** file by 1%. If the indicated standard concentration were 1% too low, then increase the spike concentration in the **LabData** file.

CREATING AND USING RAW-DATA FILES

The best method for reducing data for more than one or two samples at a time is to put the raw data in an ASCII file, so that you can edit the raw data at any time or re-reduce some of the data with new **LabData** file values without having to re-enter a lot of data. You can create these files either with LOTUS 1-2-3[1] or most other spreadsheet programs, or with any word processing program that can create ASCII files.

To be compatible with **PBDAT**, the format of your raw-data files must conform to the following certain criteria:

1) The file must be arranged in rows and columns like a spreadsheet, with different samples occupying different rows;

2) The left margin of the spreadsheet or file must be 0, and the right margin must include all 9 characters of the right-most column (so the right margin would be #columns times 9, including the 2 columns for the sample names);

3) The column-width must be 9 characters (the default setting for LOTUS);

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[1]Use the **/PF** command (PRINT FILE), which will create a ***.PRN** file.

4) The first 2 columns (A and B) must contain the sample names[1], as well as any embedded specifiers (see below);

5) The data in each column must conform to the column-headings as shown in figure 2;

6) The column-headings must directly overlie a row consisting of repeating equals-signs that extends over exactly as many columns as are in use for the raw data.

7) The first row can contain a file title of up to 80 characters.

If you use the TEMPLATE file (on the same disk as PBDAT) to start your raw-data spreadsheets, you won't have to worry about getting the format right. You can load this directly from LOTUS, or from a word-processing program by specifying the TEMPLATE.PRN file.

The TEMPLATE file (which is present as both a *.WK1 file {LOTUS} and a *.PRN {ASCII} file) contains the appropriate column-headings for both Pb-208 spiked samples and Pb-205 spiked samples, as well as U-235 or U-233/236 spiked samples. Before typing in your data, delete the rows with the column-headings for the types of spikes that you're not using, keeping only the appropriate rows. The column-headings for the various ways of spiking are indexed in figure 2.

Note that the first 2 columns (A and B) contain the sample names. You can include more information on the samples by using the rows above or below the row that contains the numeric data for the sample. Just make sure that no numeric data appears to the right of these additional comments.

If you don't have any data for one of the columns, or if that column is irrelevant (for example, thorium data when you didn't spike the sample for thorium), don't enter anything in that column. Enter all errors (uncertainties) at the 2-sigma level and in percent.

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[1]If 18 characters aren't enough, try grouping samples with similar names under a "header" name. The row containing the "header" should contain no data.

Note that the columns for uranium isotope ratios can contain either the 238/235 ratio, the Sample-238/Spike-233 ratio, or the 233/238 ratio. The program will assume one of these, depending on (1) whether the sample were spiked with a Pb-205 mixed spike, in which case the **LabData** file will specify a 235 or 233/236 U-spike, (2) whether you specified a U-235 or U-233/236 spike from the Top-Level CRT display, (3) which data-input format for U-233/U-236 spiked samples you are using, and (4) if you have embedded specifiers (see below) within the sample name columns of the raw-data spreadsheet.

If your data is for ^{233}U-^{236}U spiked samples with raw 233/236 and 233/238 ratios, the 233/236 ratios and errors must occupy the last two columns of the spreadsheet (AB and AC for 208-spiked samples, T and U for Pb-205 spiked samples).

Using Embedded Specifiers within the Raw-Data File

The raw-data spreadsheet can contain all of the necessary information to tell the program how the data is to be reduced, including which **LabData** file to use, whether spiked with Pb-208 or Pb-205, U-235 or U-233/236, whether the U-Th was spiked in the total aliquot or the Pb-spiked aliquot, and what initial-Pb ratios to use. These specifiers can change from sample to sample, so that a large raw-data spreadsheet can contain data reduced at various times (or by various laboratories), with different spikes and procedures, yet the whole file can be reduced in a single request that creates a single reduced-data file.

Embedded specifiers consist of a few characters enclosed in asterisks, and must occur within the sample name columns (A and B). The specifiers affect how data for samples below the specifiers are reduced. The types of embedded specifiers that you can use are shown below:

SPECIFIER	SIGNIFICANCE
L	The characters following the specifier indicate the name of the **LabData** file to be used (for example, *L* C:\PBDAT\NEWLAB).
205	Samples were spiked with a mixed 205Pb/U/Th spike (the **LabData** file for the spike determines whether a ^{235}U or ^{233}U-^{236}U spike is assumed.
208	Samples were spiked with a ^{208}Pb or ^{206}Pb spike.
235	Samples were spiked with a ^{235}U spike (208-spiked samples only).

233 Samples were spiked with a mixed ^{233}U-^{236}U-spike (208-spiked samples only).

TU Samples were total-spiked with U(Th).

PU Samples were spiked for U(Th) in the Pb-spiked aliquot.

SAMSPK Raw data for any ^{233}U-^{236}U spiked samples will be in the form of Sample-238/Spike-233 ratios rather than the raw 233/236 and 233/238 ratios.

368 Raw data for any ^{233}U-^{236}U spiked samples will be in the form of raw 233/236 and 233/238 ratios.

INIT Use the values in this row as the initial-Pb ratios and uncertainties. From columns C to I, respectively, the cells in this row will contain values for the initial-Pb 206/204, 6/4-error, 207/204, 7/4-error, 208/204, 8/4-error, and 206/204-207/204 error-correlation. See below, however, for obtaining Stacey-Kramers Pb ratios in a simpler way.

SK Use the number following this specifier to calculate a Stacey-Kramers single-stage Pb[1] to use for the initial-Pb ratios (for example, ***SK* 1750**). The uncertainty in these ratios will be set to zero.

*Note that if you want to reduce just part of the data in a raw-data file, you must include the row numbers of the appropriate embedded specifiers in the sample numbers that you request. Otherwise, **PBDAT** will never access the embedded specifiers to be able to do what you want.* So if the embedded specifiers of interest occur in, say, row 13 of the raw-data spreadsheet followed by the actual data in rows 14 through 20, you would have to include the "sample number" for row 13 for the embedded specifiers to work (see example below). You'll be able to tell which "sample number" to use from the printout or display when you access the raw-data file from PBDAT.

Reducing Data from a Raw-Data File

To reduce data from a raw-data file, press the **DATAFILE** key (**F6**) from the Top-Level screen. The screen will show:

---

[1]Stacey and Kramers, 1975.

DATA REDUCTION FROM A RAW-DATA DATAFILE

Press F5 for ALL datafile sets in memory, F6 to access NEW file.

Printer: OFF LabData file: ZIRCLAB

Screen: FAST Raw-Data file: HENRYMTS.PRN

ENTER SAMPLE NUMBERS TO BE REDUCED: *

Separate first and last sample-numbers of a continuous sequence with a comma, different continuous sequences or individual samples with a semicolon; for example, 1,5;12,15;21. Be sure to include rows with embedded specifiers.

F1 HELP	F2 FAST SCREEN	F3 SLOW SCREEN	F4 NO SCREEN	F5 ALL SETS
F6 NEW FILE	F7 PRINTER?	F8	F9	F10

Select a raw-data file with the F6 key. The screen will display all files with the .PRN extension in the current disk and directory. Change the disk or path to search with the F2 key if the file you want isn't shown. Once you've selected a file, the screen will show the file's title and sample names as they are accessed from the disk, as well as a few of the isotope ratios for the samples. A typical display might look like this:

East Dakota Zircons, 1440 Ma initial

#	NAME	Wt (g)	206/204	206/207	206/208
1:	*L* C:\PB\OLDLAB	---	---	---	---
2:	*208* *TU*	---	---	---	---
3:	*INIT*	16.162	---	---	---
4:	84/TL 1043 -200	.05432	1012.2	10.113	14.125
5:	84/TL 1043 -100+150	.03156	734.24	8.2361	10.113
6:	84/TL K-feldspar	.1043	16.129	1.0458	.465211
7:	*PU*				
8:	88/ZE 53A -400 1.7nm	.0835	15421	15.663	18.943

The top line of the screen shows the title of the raw-data file that you put in the top row of the raw-data spreadsheet. Note the embedded specifiers.

Specify the output of the reduced data with the following keys:

F2 screen output continuously scrolls as the results are calculated,

F3 screen pauses when full to allow you to examine the results for each sample,

F4 except for sample names, the screen output is suppressed (gives fastest data-reduction),

F7 toggles the printer on or off; cancels screen display if printer is toggled on.

You can now reduce the data in the raw-data file. If you want to reduce data for all of the samples in the raw-data file, just press the **ALL** key (**F5**). If you want to reduce only part of the data, indicate the sample-numbers of continuous sequences of data by entering the first and last number of the sequence separated by a comma, and indicate discrete sample-numbers or the start of a different continuous sequence by a semicolon. So to specify that sample numbers 1 though 6, then 9, then 12 through 15 be reduced, you would enter **1,6;9;12,15**.

Remember to include rows containing any embedded specifiers if you want those embedded specifiers to take effect. Remember also that once an embedded specifier is acted upon, it remains in effect until specifically cancelled by either another embedded specifier or by softkey-commands from the Top-Level Screen.

After you've specified which samples in the datafile to reduce, the program will display the Initial-Pb Ratios FORM. Enter the initial-Pb ratios as discussed earlier (or press **Esc** if you don't want apparent ages to be calculated for any of the samples, or if the initial-Pb ratios are specified in the raw-data file itself). The data will then be reduced.

After all the samples in the datafile have been reduced (unless you've only reduced data for one or two samples), the screen will ask you to specify a name for the reduced-data file (a simple ASCII file in the form of a spreadsheet). The screen will show you the default path and extension (always .PRN, for **ISOPLOT** compatibility). If you want a different disk\path or extension, include them in the file name.

PBDAT will now ask you for the format of the reduced-data file: "Zircon", "Whole-Rock", or "Complete." If you store all of the reduced-data ratios and errors that PBDAT calculates ("Complete" format -- see Figure 3) you won't be able to access the file from either LOTUS or most word-processing programs, because it will be too wide (**ISOPLOT** won't have any problems with the file, though). If you want to store just a subset of the calculated data, in order to maintain compatibility with LOTUS or another program, or just to keep the file compact, specify either 'Zircon' or "Whole-Rock' format.

The "Zircon" format will contain all of the parameters listed in Figure 3 except: $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$ ratios & errors, the thorium-concentration error, and the $^{238}U/^{204}Pb$-$^{235}U/^{204}Pb$-$^{232}Th/^{204}Pb$ ratios or errors.

The "Whole-Rock" format will contain all of the parameters listed in Figure 3 except: any of the radiogenic-isotope ratios or errors, and the common-Pb concentration & error.

When you've specified the file format, **PBDAT** will ask for a file-title. This title will occupy the first row of the reduced-data file, and will appear when you access the file from **ISOPLOT**.

USING LabData FILES

LabData files contain the data for a laboratory's spikes, typical blank compositions, and typical mass-discriminations of isotope-ratio measurements (figure 4). If necessary, you can define several **LabData** files for the various spikes or other variables that might be used by your lab.

To access the **LabData** screen, press the **LabData** key (**F5**) from the Top-Level screen. The display (using ZIRCLAB as an example of a LabData-file name) will then be:

LabData Files

N Define a New LabData File

L Load another LabData File into memory
(or see a catalog of all LabData Files)

E Erase a LabData File from disk

D Display LabData File "ZIRCLAB"

P Print " " "

- press F2 - F10 to edit or view data for ZIRCLAB -

F1 HELP	F2 U233 Spike	F3 Pb208 Spike	F4 Pb205 Spike	F5 U235 Spike
F6 Th230Spike	F7 Mass Discr	F8 Blanks	F9 Store File	F10 New Name

Defining a New Labdata File

To define a new **LabData** file, press the N key from the **LabData** screen. The computer will ask you which spikes you wish to define, and present you with a FORM for each spike. The spike FORMs will require the concentrations (in moles per gram) of the major spike-isotope, the ratios of the isotopes in the spike (these must have already been corrected for mass-discrimination bias), and the uncertainties of the concentrations. If most of your data reduction is for suites of samples (where the relative concentration-uncertainty is of more relevance than the absolute uncertainty), you should assign concentration uncertainties of zero, unless you have significant random errors (such as weighing errors) in your spike delivery.

After you've defined the spikes for the new **LabData** file, PBDAT will display FORMs for blanks and for mass discrimination. The BLANKS FORM will require you to enter typical uncertainties (in percent of the amount) for any assigned Pb, U, and Th blanks, as well as the Pb-isotope ratios of the Pb-blank, the uncertainty (absolute this time, not percent) in these ratios, and the correlations of the ratio-uncertainties.

Realistic uncertainties in the blank amounts are typically very high -- 30% to 100% for Pb, and 100% or more for very low U and Th blanks. Also, the correlation between the uncertainties of the Pb-blank 206/204 and 207/204 ratios is generally rather high (0.7-.9), as common leads from random ore deposits (whence comes, ultimately, most of your Pb-blank) in general will have highly correlated 206/204 and 207/204 ratios. This is true also for the 206/204-208/204 uncertainty correlation, but to a lesser degree (due to the effect of variable Th/U ratios for the sources of base-metal ore deposits).

The mass-discrimination FORM requires estimates of typical mass-discrimination (arising during measurement in the mass spectrometer) for your Pb, U, and Th runs, in percent per mass-unit[1]. You'll also need to assign uncertainties in your estimates, in absolute values. So if your typical mass-discrimination for Pb runs is 0.11% per mass unit with a possible range (2-sigma) of from 0.06% to 0.16%, you would enter the uncertainty as 0.05.

Other LabData File Operations

You can use the softkeys of the **LabData** screen to edit the values for the spikes, mass-discriminations, or blanks of the **LabData** file in memory. If you want to store your changes on a disk, remember to press the Store File key (**F9**) before you return to the Top-Level screen. Use the **New Name** KEY (**F10**) to either rename a LabData file in memory, or to store a modified version under a different name.

---

[1]Positive values indicate enrichment of the lighter isotopes during analysis.

To switch from one **LabData** file to another, press the L key from the **LabData** screen. You can inspect the values for any **LabData** file by pressing the D key, or change the name of a **LabData** file in memory with F10 (remember to store the changed file back on the disk, though).

COMMON ERRORS IN USING PBDAT

There are several common mistakes that users make in using PBDAT, usually because of a misunderstanding about exactly what sort of errors should be entered for the various parameters. Some of the more-common errors are:

1) **Using over-optimistic uncertainties for the blank amounts and Blank-Pb isotope ratios.**

   It is not at all uncommon for Pb blanks to vary by 50% or more, especially if the procedure or reagents vary over time. The only time a small value, such as 10%, is justified is when that value is the 2-sigma variation of many (say 5 or more) blanks on an unchanging procedure. The same comments hold for the isotope ratios of the blank. For blanks which are typically very small and difficult to measure (such as for U and Th), the uncertainty can be even larger (a factor of 2 or more).

2) **Using fractionation-uncertainties derived from replicate runs of standards and applying these uncertainties to samples.**

   Fractionation uncertainties derived from pure standards (which have not seen any chemistry) generally constrain only the minimum fractionation range, as such runs are commonly done in a more-reproducible manner than actual samples. For example, the samples have seen a chemical purification (which, to the extent that it is not perfect, can affect the running behavior of the filament-load); the samples may vary widely in size, whereas the standard runs are generally for a relatively constant amount - thus the standard runs may have been taken at a much more restricted range of filament temperatures than the samples.

3) **Assigning a concentration-uncertainty to the spikes that reflects the absolute uncertainty in concentration, rather than the random, sample-to-sample error.**

   To repeat what I've said earlier in this documentation: If most of your data reduction is for suites of samples (where the relative concentration-uncertainty is of more relevance than the absolute uncertainty), you should assign concen-

tration uncertainties of zero, except for weighing errors in your spike delivery. If you really want to know the effect of the true spike-concentration uncertainty for an isochron or concordia-intercept age, you'll have to vary the spike concentrations by what you think the true error might be, re-reduce the suite of data, and re-calculate the regression line for the suite.

4) **Assigning nonzero isotope-ratio uncertainties for the initial-Pb of a suite of samples that probably shared the same initial-Pb.**

This topic is discussed in a note under the discussion of the "Initial-Pb Isotope Ratios" Form.

UTILITY FUNCTION FOR CALCULATING RADIOGENIC $^{207}Pb/^{206}Pb$ AGES

You can use **PBDAT** as a quick tool for calculating radiogenic $^{207}Pb/^{206}Pb$ ages by pressing **R** from the top-level screen. Enter the radiogenic $^{207}Pb/^{206}Pb$ ratio together with the percent error in the ratio (optional) and the time that radiogenic Pb-isotope growth ended (also optional). If the second optional value is not entered, a value of zero is assumed (yielding the usual radiogenic 207/206 age).

UTILITY FUNCTION FOR CALCULATION OF STACEY-KRAMERS SINGLE-STAGE EVOLUTION MODEL AGES

To use **PBDAT** as a tool for the calculation of Stacey-Kramers (Stacey and Kramers, 1975) single-stage Pb evolution ages and Mu-values[1], press **M** from the top-level screen. Enter the $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios of interest. **PBDAT** will calculate the model age and Mu for the specified ratios.

---

[1]Ratio of $^{238}U/^{204}Pb$ normalized for U-decay to the present day.

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FIGURE CAPTIONS

Figure 1: Example printout of the raw and reduced data for a single sample, spiked with Pb-208 and U-235/Th-230.

Figure 2: Key to types of data in the columns of a raw-data file. A) for Pb-208 spiked samples; B) for Pb-205 spiked samples.

Figure 3: Key to column-headings for "Complete" format reduced-data files created by **PBDAT**.

Figure 4: Example of a **LabData** printout.

INDEX

Figure 1

```
SAMPLE# 1 : Reduced-Data Printout
          206/204   %err        206/207   %err        206/208   %err
UNSPKD    7356.3    1.67        10.254    .0043       14.325    .0054
SPIKED    --        --          10.225    .012        2.3446    .0031
SPIKE     17.89                 .42583                1.4411E-04

BLANK:  6/4=18.9+/-2     7/4=15.55+/-.2     8/4=37.9+/-1.8

 .04432  g Pb208 IV       spiked, @ 5.9285E-09 +/-.05%     moles 208/g
 .03321  g U235 III       spiked, @ 5.9419E-08 +/-.05%     moles 235/g
 .03321  g Th230 II       spiked, @ 7.981E-08 +/-.15%      moles 230/g

     SAMPLE WT.      TOTAL-AL.    Pb-UNSPIKED AL.   Pb-SPIKED AL.
      .01234          .74559         .53214            .21345            grams
-------------------------------------------------------------------------------
       Pb-Unspiked Aliquot, Corrected for  .065+/- .039 nG Pb-Blank,
            and  .11+/- .05 % per a.m.u. Mass-Discrimination
  206/207         206/208        206/204         207/204         208/204
  10.246          14.311         7501.1          732.1           524.15
 +/-.054%        +/-.125%       +/-2.01%        +/-2%           +/-1.98%

 Error-Correls:  207/204-206/204= .999643     208/204-206/204= .99816

                        Moles Pb per gram:
    206             207             208             204             TOTAL
  2.0823E-07      2.0323E-08      1.4551E-08      2.776E-11       2.4313E-07
 +/-.131%

 3.4  nG Common-Pb in Unspkd Al. ---- ( .389 PPM)

PPM Total Pb = 50.129          Pb-Spiked Aliquot Blank = .16 nG
-------------------------------------------------------------------------------
238/235 = 5.4376 +/- .014%                 232/230= .75374 +/- .032%
 .005 nG U-Blank,      .008 nG Th-Blank          U-Th Spiked Al.= .74559 Grams
                        238              235              232
Moles per Gram:     9.1365E-07       6.6264E-09       1.6259E-07
    219.06    PPM Uranium        (+/-.453%)
    37.73     PPM Thorium        (+/-.62%)              Th/U= .1722

238/204= 32912                    235/204= 238.7     (+/-2.06%)
232/204= 5857                                        (+/-2.11%)
Rho(U/4-6/4)= .97225        Rho(U/4-7/4)= .95687        Rho(Th/4-8/4)= .95687
-------------------------------------------------------------------------------
Radiogenic-Pb         206*             207*             208*
Moles per Gram:    2.0779E-07       1.9897E-08       1.3565E-08

Initial-Pb:    206/204= 15.862 +/- 0          207/204= 15.341 +/- 0
               208/204= 35.497 +/- 0          Rho(6/4-7/4) = 0

                206/238          207/235          207/206       208/232
 RATIOS:        .227432          3.00274          .0957557      .083434
 ERRORS:         .472%            .476%            .0609%        .655%
 AGES (Ma):     1321             1408.3           1543          1619.7

Rho (207/235-206/238) = .991779      207/206 Age-Error = 1.1 m.y.
```

Figure 2A

Index to LOTUS Column-Positions of Raw-Data Datafile Parameters For ^{208}Pb or ^{206}Pb - spiked samples

Column	Parameter
C	sample-weight, in grams - actually dissolved
D	weight of solution of dissolved sample before aliquoting
E	weight of Pb-unspiked liquid aliquot of dissolved sample
F	weight of Pb-spiked liquid aliquot " " "
G	grams Pb-spike delivered to F
H	grams uranium spike delivered either to C, D, or F
I	" thorium " " " " " " "
J	unspiked-aliquot 206/204 (OR spiked-aliquot 206/204, if the unspiked 206/207 is unknown and assigned a value of zero)
K	% uncertainty in J (not including mass-discrimination error)
L	unspiked-aliquot 206/207
M	% uncertainty in L (not including mass-discrimination error)
N	unspiked-aliquot 206/208
O	% uncertainty in N (not including mass-discrimination error)
P	Pb-spiked aliquot 206/207
Q	% uncertainty in P (not including mass-discrimination error)
R	Pb-spiked aliquot 206/208
S	% uncertainty in R (not including mass-discrimination error)
T	238/235 of U-spiked aliquot (if spiked with U-235), OR
"	Sample-238/Spike-233 of U-spiked aliquot (if spiked with U-233/236 and SAM/SPK ratio is used), OR
"	233/238 of U-spiked aliquot (if spiked with U-233/236 and SAM/SPK ratio is <u>not</u> used)
U	% uncertainty in T (not including mass-discrimination error)
V	232/230 of Th-spiked aliquot
W	% uncertainty in V (not including mass-discrimination error)
X	Pb blank of Pb-unspiked aliquot, in nanograms
Y	U blank of U-spiked aliquot, in nanograms
Z	Th blank of Th-spiked aliquot, in nanograms
AA	233/236 of U-spiked aliquot (<u>only if</u> SAM/SPK ratio not used)
AB	% uncertainty in 233/236 (" " " " " ")

Figure 2B

Index to LOTUS Column-Positions of Raw-Data Datafile Parameters
For mixed $^{205}Pb/U/^{230}Th$ - spiked samples

Column	Parameter
C	sample weight, in grams
D	weight (g) of mixed $^{205}Pb-^{235}U-^{230}Th$ or $^{205}Pb-^{233}U-^{236}U-^{230}Th$ spike delivered
E	observed 206/204 (not including mass-discrimination error)
F	% uncertainty in E (not including mass-discrimination error)
G	observed 206/207
H	% uncertainty in G (not including mass-discrimination error)
I	observed 206/208
J	% uncertainty in I (not including mass-discrimination error)
K	observed 206/205
L	% uncertainty in K (not including mass-discrimination error)
M	observed 238/235 ratio (U-spike isotope is 235), OR
"	Sample238/Spike233 ratio (U-spike isotopes are 233-236 and SAM/SPK is known), OR
"	observed 233/238 ratio (U-spike isotopes are 233-236 but SAM/SPK is not known)
N	% uncertainty in M
O	observed 232/230
P	% uncertainty in O (not including mass-discrimination error)
Q	Pb blank for Pb run, in nanograms
R	U blank for U run, in nanograms
S	Th blank for Th run, in nanograms
T	233/236 of U-spiked aliquot (<u>only if</u> U-spike isotopes are 233-236 and SAM/SPK ratio is not known)
U	% uncertainty in T (if relevant)
V-AB	-- not used for Pb-205 spiked samples

Figure 3

Column Headings of Reduced-Data Files ("Complete" Format)

Column#	Heading
1	Sample weight (grams)
2	ppm U
3	ppm Th
4	ppm Pb
5	ppm common-Pb
6	Nanomoles ^{206}Pb per gram
7	Raw (observed) 206/204 of Pb-unspiked aliquot
8	Blank & mass-discr. corrected sample 206/204 (or 204/206)
9	" " " " 207/204 (or 207/206)
10	" " " " 208/204 (or 208/206)
11	Radiogenic Pb-206/U-238 (or U-238/Pb-206)
12	Radiogenic Pb-207/U-235
13	Radiogenic Pb-207/Pb-206
14	Radiogenic Pb-208/Th-232
15	206/238 age (Ma)
16	207/235 " "
17	207/206 " "
18	208/232 " "
19	Mu (238/204)
20	Nu (235/204)
21	232/204
22	% uncertainty in U concentration
23	" Th "
24	" Pb-204 "
25	" Pb-206 "
26	" Alpha (206/204) [or 204/206]
27	" Beta (207/204) [or 207/206]
28	" Gamma (208/204) [or 208/206]
29	Error-correlation for Alpha-Beta [or 204/206-207/206]
30	" Alpha-Gamma [or 204/206-208/206]
31	% uncertainty in radiogenic 206/238 [or 238/206]
32	" " 207/235
33	" " 207/206
34	Error-correlation for 206/238-207/235 [or 207/206-238/206]
35	% uncertainty in radiogenic 208/232
35	% uncertainty in Mu and Nu (238/204 and 235/204)
37	% uncertainty in 232/204
38	Error-correlation for Alpha-Mu (206/204-238/204)
38	" Beta-Nu (207/204-235/204)
40	" Gamma-232/204 (208/204-232/204)

Figure 4

```
--------------------------------------------------------------------------------
DATA FROM LABDATA FILE  "OLDLAB3.LBD":


Pb-208 Spike  (Pb208 IV):

[208] = 5.9285E-09 +\- .05  % moles/g
(not a mixed Pb/U spike)
206/204= 17.89        206/207= .42583        206/208= 1.4411E-04

Pb-205 mixed spike   (Pb205a):

[205] = 3.9485E-11 +\- .5  % moles/g
[235] = 1.7055E-09 +\- .5  % moles/g
[230] = 1.2744E-09 +\- .5  % moles/g

206/205 = .001128                238/235 = 0
206/204 = 20.3                   232/230 = .000392
206/207 = 1.21
206/208 = .4846

U-235 spike  (U235 III):

[235] = 5.9419E-08 +\- .05  % moles/g
238/235 = 4.1841E-04

Mixed U-233/U-236 spike  (U233a):

[233] = 4.9584E-09 +\- .1  % moles/g
233/236 = 2534         233/238 = 1.0172

Th-230 spike  (Th230 II):

[230] = 7.981E-08 +\- .15  % moles/g
233/230 = .001292

Average mass-discrimination during mass-spectrometer runs, in %/a.m.u. --

Pb:   .11 +/- .05       U:  .3 +/- .15           Th:  .3 +/- .3

Average Blanks:

Uncertainty in assigned amount:  Pb - 60%      U - 100%       Th - 100%

Pb blank ratios and uncertainties:
206/204 = 18.9+/-2       207/204 = 15.55+/-.2      208/204 = 37.9+/-1.8
Error-Correlations: 206/204-207/204= .7     206/204-208/204= .7
--------------------------------------------------------------------------------

208/204 = 15.55+/-1.8
```