



# **USER'S GUIDE TO ROCKJOCK -- A PROGRAM FOR DETERMINING QUANTITATIVE MINERALOGY FROM POWDER X-RAY DIFFRACTION DATA**

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Open-File Report 03-78

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U.S. Department of the Interior  
U.S. Geological Survey



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By D. D. Eberl

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Cover: Teresa Dudek, Jan Srodon and Dennis Eberl atop Bow Tie Arch near Moab, Utah. Paul Nadeau is on top, but not in view. Photo by Krzysztof Mystkowski.

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THE MOTIVE FOR METAPHOR

by Wallace Stevens

You like it under the trees in autumn,  
Because everything is half dead.  
The wind moves like a cripple among the leaves  
And repeats words without meaning.

In the same way, you were happy in spring,  
With the half colors of quarter-things,  
The slightly brighter sky, the melting clouds,  
The single bird, the obscure moon—

The obscure moon lighting an obscure world  
Of things that would never be quite expressed,  
Where you yourself were never quite yourself  
And did not want nor have to be,

Desiring the exhilarations of changes:  
The motive for metaphor, shrinking from  
The weight of primary noon,  
The A B C of being,

The ruddy temper, the hammer  
Of red and blue, the hard sound—  
Steel against intimation—the sharp flash,  
The vital, arrogant, fatal, dominant X.

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# **USER'S GUIDE TO ROCKJOCK -- A PROGRAM FOR DETERMINING QUANTITATIVE MINERALOGY FROM POWDER X-RAY DIFFRACTION DATA**

*By* **D. D. Eberl**

## **ABSTRACT**

RockJock is a computer program that determines quantitative mineralogy in powdered samples by comparing the integrated X-ray diffraction (XRD) intensities of individual minerals in complex mixtures to the intensities of an internal standard. This manual discusses how to prepare and X-ray samples and standards for this type of analysis and describes the operation of the program. Carefully weighed samples containing an internal standard (zincite) are ground in a McCrone mill. Randomly oriented preparations then are X-rayed, and the X-ray data are entered into the RockJock program. Minerals likely to be present in the sample are chosen from a list of standards, and the calculation is begun. The program then fits the sum of stored XRD patterns of standard, pure minerals (the calculated pattern) to the measured pattern by varying the fraction of each standard pattern, by using the Solver function in Microsoft Excel to minimize the degree of fit parameter between the calculated and measured pattern. The calculation automatically is carried out twice for each analysis, once for the Full Pattern region (usually 20 to 65 degrees two-theta) to find integrated intensities for the non-clay minerals, and again for the Clay region (usually 58 to 65 degrees two-theta) to find intensities for the clay minerals. Integrated intensities for each mineral then are determined from the proportion of each standard pattern required to give the best fit. These integrated intensities then are compared to the integrated intensity of the internal standard, and the weight percentages of the minerals are calculated. The results are presented as a list of minerals with their corresponding weight percent. To some extent, the quality of the analysis can be checked because each mineral is analyzed independently, and, therefore, the sum of the analysis should approach 100 percent. Also, the method has been shown to give excellent results with artificial mixtures. The program

is easy to use, but does require a knowledge of mineralogy, of X-ray diffraction practice, and an elementary knowledge of the Excel program.

## SUMMARY INSTRUCTIONS FOR QUICK START

Below is a brief summary of instructions for using RockJock:

1. Very important: After copying RockJock onto your hard disk, and upon opening the program, first run the Solver option in the Full pattern and the Clay sheets. If necessary, turn on the Solver in the Visual Basic Editor. Then save the program. Do not change the program's name (RockJock.xls). Macintosh users may need to follow the more detailed installation instructions beginning on page 5 of this manual, as will non-English language users.
2. Prepare samples for analysis by adding 0.333 g ZnO to 3.000 g sample. Grind the mixture in a McCrone mill for 5 minutes with 4 ml methanol. Sieve and then side-pack the ground material into a holder to ensure random sample orientation, and X-ray from 5 to 65 degrees two-theta using Cu K-alpha radiation, with 0.02 degree steps and a count time of at least 2 seconds per step.
3. Enter the X-ray diffraction (XRD) intensities for the sample into the Input sheet, column D, with the sample name in cell D1. Select the minerals likely to be present in the sample from the list in column H. Enter option 5 in cell B18, click the Start button, and wait and wait. The Stevens poem, which may be concerned with the shadow side of quantitative analysis, is meant to be puzzled over while waiting. Weight percents of the selected minerals in the sample will appear in the Result sheet. For best results, use standards in the program that were run with your experimental setup, although adequate results may be realized from the present standards.

## INTRODUCTION

A rock is composed of atoms that are arranged in variety of mineral structures. To characterize a rock, both the elemental composition and the mineralogy should be measured quantitatively. Sometimes the elemental composition is more important, as it would be, for example, in prospecting for gold. Sometimes mineralogy is more important, for example, if a rock contains swelling clay that is cracking building foundations. Often both measurements are needed, for example, in the case of a gold ore which contains a clay mineral that may impede the refining process.

The geochemical sciences have matured and prospered because they offer precise, accurate, and routine methods for determining quantitatively the elemental compositions of natural materials. Quantitative mineralogy by XRD, however, has lagged far behind the chemical methods, mainly because the quantitative analysis of clay minerals has constituted a particularly difficult problem (Moore and Reynolds, 1997).

This report describes the RockJock computer program, and how to prepare and X-ray samples and standards for analysis by the program. RockJock offers a relatively simple and mostly automatic method for determining quantitatively the mineralogical composition of samples, including clay minerals, to within a few weight percent from powder X-ray diffraction data. The calculations are based on three previously published methods: (1) the matrix flushing technique of Chung (1974), in which integrated intensities of the unknown minerals are compared to that of an internal standard (in the case of RockJock, ZnO, zincite), thereby obviating the need for measuring the mass absorption coefficient for a sample; (2) the whole-pattern fitting routine of Smith and others (1987) for measuring integrated intensities by fitting the sum of pure mineral patterns to that of the measured XRD pattern, except that in RockJock key parts of the patterns which contain the 060 reflections for clay minerals also are fitted separately; and (3) the quantitative method of Srodon and others (2001) for sample preparation, and for the method of measuring clay mineral content from 060 reflections rather than from the more commonly used basal reflections.

RockJock is similar in its approach to the recently released Microsoft Excel-based program FULLPAT (Chipera and Bish, 2002), except that the analysis procedure in RockJock is almost entirely automatic, and that RockJock contains a special routine to analyze clay minerals. Also, RockJock finds the integrated intensity of the internal standard in an observed pattern by fitting the XRD pattern for the pure internal standard (ZnO) to the observed pattern in the same manner as it does for the other pure standard patterns. The library standards in FULLPAT contain the internal standard (Al<sub>2</sub>O<sub>3</sub>), and therefore, prior to analysis, these standards are normalized to an equal-internal standard basis so that the internal standard in each library pattern has the same integrated intensity as the internal standard in the observed pattern.

### **Computer Requirements and Disclaimer**

RockJock will run under either Windows 98 (or higher versions), or Macintosh (System X) operating systems. Calculation times are long, so the fastest computer available (>1 GHz) should be employed. One calculation can take up to half an hour or more. The more minerals that are selected to be present, the slower the calculation. The calculation is slowed further if the Auto shift option is used. Use of RockJock requires installation of Microsoft Excel 2000 (or higher versions of Excel), including the Solver option (which may not be installed in a standard installation from the original Excel disk), and an elementary knowledge the Excel program. In this report, the term “sheet” refers to a worksheet in Microsoft Excel. Cells, such as B4, designate column B and row 4. It may be necessary to use the English-language version of Excel (but see installation instructions below). RockJock works best on a computer having 100 megabytes or more of RAM. Sixty or more megabytes should be assigned to run the Excel program if the system offers an option to assign memory to a program. The program occupies about 50 megabytes of disk space.

Although this program has been used by the U. S. Geological Survey (USGS), no warranty, expressed or implied, is made by the USGS or the United States Government as to the accuracy and functioning of the program and related program material, nor shall the fact of

distribution constitute any such warranty, and no responsibility is assumed by the USGS in connection herewith.

### **How to Obtain RockJock**

The latest version of the software described in this report can be obtained by anonymous ftp from the Internet address: <ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/RockJock>, by emailing the author at [ddeberl@usgs.gov](mailto:ddeberl@usgs.gov), or by writing D. D. Eberl, U.S. Geological Survey, 3215 Marine Street, Suite E-127, Boulder, Colorado, USA, 80303-1066. The RockJock folder at the ftp site can be opened by double clicking on the folder's name (RockJock), and the files downloaded by dragging them on to your hard disk. The useful files are RockJock.xls, which is the quantitative analysis program; PkChopr.xls, which is the PeakChopper program that removes unwanted XRD peaks; RockMan.doc, which is the instruction manual for the RockJock program; and QuantExamples.xls, which is a workbook that contains some practice XRD patterns and answers. Comments or concerns about RockJock should be directed to the author.

### **Installation of RockJock**

The following instructions should be followed exactly to setup the program to run for the first time:

1. Copy the program and related files onto your hard disk. Do not change the name of the program (RockJock.xls). Double-click the files to open them. If the files are compressed (compressed with the .exe extension), they should decompress automatically under Windows when double clicked. Files with the .exe extension can be opened for the Macintosh if Aladdin expander software is used. If needed, the latest version of the expander software can be downloaded free from the web at: [www.aladdinsys.com/expander](http://www.aladdinsys.com/expander). After opening the programs,



more of the program can be viewed on the screen at one time by reducing the zoom size under the View menu.

2. After the program has been opened, go immediately to the Full Pattern sheet by clicking that tab near the bottom left of the screen. Under the Tools pull-down menu in this sheet, check to see that the Solver tool appears. If not, click the Add-ins option under the same menu and click the Solver option box. If the option does not install, then Solver has not been installed from the original Excel disk. Return to the original Excel disk and install the Solver (see the Help menu in Excel), and then repeat the steps above.

3. Next run the Solver once in the Full Pattern sheet by choosing the Solver from the Tools menu and by clicking the Solve button. This run will take a few minutes. A short cut is possible: when "Trial Solution" shows up in the lower left corner of the screen, push the Esc key on the keyboard, and halt and stop the Solver solution. Then click on the Clay tab to see the Clay sheet, and run the Solver in this sheet as well. This routine, and that described in the section below, should only have to be done once, when the program is first installed on your computer.

4. Return to the Input sheet by clicking on its tab at the bottom of the screen. Now it may be necessary to turn on the Solver in the Visual Basic Editor. If this Solver has not been turned on, the program when run will give a macro error at cell BG186 of the Input sheet. To turn on the Solver, go to the Tools menu. Under Tools, choose Macro, then Visual Basic Editor. A new Tools menu will appear. Under this menu choose References. A box will appear named Available References. A checked Solver box may appear in this box, especially for those using Windows. If so, go to paragraph 5 below. However, especially for the Macintosh, a checked box may appear that says MISSING:SOLVER.XLA. If so, click the Browse button. Twin boxes will appear. From the menus at the top of the boxes, it may be necessary to find Microsoft Excel Files in the Show menu and Add-Ins in the From menu. Choose Add-Ins in the left box, and open Solver.xla in the right box by double clicking. Click the Enable Macros button that appears. In a minute, SOLVER with a checked box should appear in the Available

References box. Click the OK button. Under the Excel Menu, click Close and Return to Microsoft Excel.

5. In the Input sheet, go to cell BG218, which will have a pink-colored font. This cell should show: =SOLVERSOLVE(TRUE). This macro statement can be seen at the top of the screen, beneath the Tools bar. If the equation cannot be seen, then under the Tools menu, click Options, and then under the View tab check the Show formula bar option. The Status bar and Windows in Taskbar options also should be checked. If cell BG218 shows only =SOLVERSOLVE(TRUE), save the program and go to the next section in this report. However, especially for the Macintosh, there may be a long string of letters after the equal sign in this macro statement indicating the address of a hard disk. If this information is present, it must be removed from this and other cells before the program will run. To remove it, copy everything that comes between the equal sign and SOLVERSOLVE(TRUE) by highlighting it, and choosing Copy from the Edit menu. Click the red X in the Formula bar to return the cell value to its original state. Under the Edit menu, choose Replace. (In some systems it may be necessary to choose Find first, and then Replace.) Paste the copied material into the Find What box. Do not enter anything into the Replace With box. Click the Replace All button. Now the unwanted material has been removed from all cells in the program. Save the program, and you are ready to start to use it. The program inputs and outputs are described in detail in Appendices 1 through 9 of this manual. Appendix 10 lists resources for quantitative analysis.

6. RockJock can run under non-English language versions of Excel if the user is willing to do some work. Most of the code is translated automatically into the non-English version, but there are a few words that must be changed manually. RockJock has been run successfully in the Spanish-language version of Excel, and the following can be used as a guide for what changes need to be made. To replace words in the program, follow the instructions in paragraph 5 above. The word Chart needs to be changed to its non-English equivalent. For example, cell Y333 in the Input sheet reads =SELECT("Chart 3"), where Chart refers to the graph that contains a plot of the X-ray pattern. The word Chart in this cell, and in all other cells in the program, should be changed to the non-English equivalent that can be found in the non-English Excel instructions. As

an example, in the Spanish language version of Excel this word is Gráfico, with the accent. Under the Edit menu Replace all Chart with Gráfico. Next, if present, clear SOLVER.Xla! from the Full Pattern and Clay sheets (replace this phrase with nothing). Then it is necessary to replace the word SOLVER with the non-English equivalent. In Spanish the word is SOLV (see Excel instructions to find the word). Finally, the solver commands need to be modified in the Full Pattern (Cells C61:C63 and D61:D63) and Clay (Cells C62:C64 and D62:D64) sheets, as follows. Go to the Full Pattern sheet. Click on cell C61 to choose it. Under the Tools menu choose Solver. Make the following changes in the Solver box that appears on the screen: under By Changing Cells, erase the current entry and type  $\$E\$6$ ; under Subject to Constraints, choose each entry and click Delete so that this box is empty. Next click on the Options button which is a part of the Solver box that is on the screen, and then click the Save Model button. Click OK, OK, and close the Solver box. Now cells C61:C63 should contain the non-English language equivalent of the English entries. It may be necessary to separate the entries in Cell C63 with slashes (/) rather than with commas or semicolons (, or ;), or maybe not. Now repeat the same procedure with cells D61:D63. When finished, change the 9<sup>th</sup> entry in cell D63 from 1 to 2 (...1,1,1... to ...1,2,1...). Now make analogous changes on the Clay sheet. If the program runs, Save it and give thanks.

### **Acknowledgments**

The author thanks Alex Blum, Dan Kile, Cathy Rubin, and Howard Taylor for reviewing this manual. This program was partly developed under a Cooperative Research and Development Agreement (CRADA) between Texaco (now Chevron-Texaco) and the USGS.

## RUNNING ROCKJOCK

After saving the newly installed program, paste an XRD pattern (5 to 65 degrees two-theta with 0.02 steps and at least 2 seconds count time per step) for a sample into column D in the Input sheet. The intensities should start in cell D2, with the sample name in cell D1. For practice, use a pattern in the workbook, QuantExamples.xls, or use the pattern that currently is in column D.

In order to use intensities from an X-ray diffractometer, the intensities must be converted into an Excel worksheet format. For instruments using Jade software, the X-ray files are converted into text files using Jade, and then the text files are opened using Microsoft Excel by choosing Open from the Excel File menu, and then by choosing the text file that is to be opened. The Text Import Wizard box then appears. Choose the Delimited option; click Next; choose the Delimiter Space; and then click Finish. The intensities, which should start at 5 degrees two-theta, now can be copied and pasted into RockJock.

Select whether the mineral is present or not by entering a 1 or a 0 into column H next to the mineral's name on the Input sheet. A limit of 20 non-clays plus 20 clays may be selected to analyze at one time. It also is possible to select where the mineral is to be analyzed by changing the settings in column I (for the Full Pattern region enter 2; for the Clay region enter 3; or for a single XRD peak analysis enter 1), and how the mineral will be reported by changing the values in column J (for a non-clay enter 2; for a clay enter 3; or for no report enter 1). These two columns already have been optimized for the standard minerals listed. Check on the Full Pattern sheet that cells B4 through B9 read 20, 65, 0, 0, 0, 0, respectively, and that cells C5 to C26 and G6 to G25 are set to zero. On the Clay sheet, cells B4 and B5 should be set to 58 and 65, respectively, and cells C7 to C26 and cells G6 to G25 should be zero. The appropriate cells in columns C and G, which shift the standard patterns in degrees two-theta, can be set to zero automatically by entering -1 in cell B14 of the Input sheet, and starting the program (enter the number for any option in cell B18, and click the Start button).

To analyze a single sample, set cells B11 to 0, B14 to 0, and B18 to 5. Press the Start button. The weight percents will appear automatically in the Result sheet at the end of the

calculation. The total may differ from 100 percent by plus or minus 5 percent or more, because each mineral is analyzed separately, and there are small, unavoidable inaccuracies due to sample preparation and variability in the chemistry and microstructure of the minerals.

After the calculation, check the graphs in both the Full Pattern and Clay sheets to see the goodness of fit between the calculated and measured X-ray intensities. The red, calculated pattern should match the blue, measured pattern. If some peaks are not accounted for, more minerals may have to be entered into the calculation in column H of the Input sheet, or the intensities of one or more of the standard XRD patterns may have to be shifted (discussed in the following paragraph). The last worksheet in the program, Common Lines (Brown and Brindley, 1980), is helpful for identifying XRD peaks for common minerals. A calculation of Bragg's Law for converting two-theta angles into d-spacings, and vice versa, can be found in column A of the Result sheet.

Due to isomorphous substitutions, peak positions may vary for the same mineral between the standard mineral and the mineral in the sample. Peak positions for individual minerals can be shifted right or left by entering a plus or a minus whole number into the cells with the red zeros (in columns C and G in the Full Pattern and Clay sheets), which are adjacent to the minerals to be adjusted. Once the peak positions have been adjusted, the program can be run again. This shift also can be accomplished automatically by entering a whole number greater than 0 in cell B14. Before running a new sample, be sure to check that all of the shift cells in the Full Pattern sheet and the Clay sheet (in columns C and G) have been returned to zero (enter -1 in cell B14, and plot the pattern by entering 1 in cell B18). Generally, the degree of fit should be less than 0.100 for both the Full Pattern and for the Clay regions at the end of the calculation (cells C52 and C53 in the Result sheet).

X-ray patterns of artificial mixtures that were used in an international quantitative analysis competition, The Reynolds Cup, are included with the program (see the Auto XRD sheet). The Reynolds Cup samples require peak shifts, +12 for siderite because the sample contains a

phosphosiderite rather than the carbonate siderite used as a standard, and +5 for dolomite because the standard dolomite has iron substitution, whereas the dolomite in the sample does not. This shift can be done automatically, but it takes three iterations of the Solver solution (enter a 3 in cell B14), and substantially slows the calculation. Also note that the 1M illite should be used for the Reynolds Cup samples.

### **SAMPLE PREPARATION**

Samples and standards should be prepared according to the instructions found in Srodon and others (2001). It is important that these instructions be followed closely. A sample amount of 3.000 g is mixed with 0.333 g of ZnO and ground with about 4 ml of methanol in a McCrone micronizing mill (Appendix 10) for 5 minutes. The mixture then is dried at 85 ° C, sieved (500 micrometer sieve, or finer), and, to insure sample randomness, side packed into an XRD holder against frosted glass (obtained from Ward's Natural Science; Appendix 10) by tapping the holder on a hard surface. Samples should be X-rayed from 5 to 65 degrees two-theta using Cu K-alpha radiation, with a step size of 0.02 degrees two theta, and a count time of at least two seconds per step when using a scintillation counter. The program can be adapted to use other radiation wavelengths, but the author should be contacted for advice before making this adaptation.

## ENTERING NEW STANDARDS INTO THE PROGRAM

The standards that are now in the program have been run on a Siemens D-500 X-ray diffractometer with the following experimental setup: X-ray tube (Cu), 1 degree slit, 1 degree slit, soller slit, sample, 0.6 degree slit, graphite monochromator, 0.15 degree slit, scintillation detector. For the most accurate determinations a separate set of standards should be developed by the user; however, the current setup provides an immediate opportunity for practice.

Good results have been obtained thus far, based on limited data, by analyzing samples X-rayed on different machines (Nicolet and Bruker) using the Siemens-generated intensities for standards that are currently stored in the program (table 1). The biases given at the bottom of table 1 is a measure of the accuracy of the determination. Bias is defined as the sum of the absolute differences between the weight percent of each mineral used in the artificial mixture (columns labeled 0 in table 1) and the weight percent determined by the RockJock program. The best determinations were those that used standards that were X-rayed with the same instrument that performed the measurement (Siemens D500; columns labeled "1" in table 1), yielding a total bias of 29.7 for the three samples. Diffractometers labeled 2 and 3 gave total biases of 34.6, and 54.2, respectively, indicating that, although it would be best to develop individualized standards, acceptable analyses may be made with the standard set that is presently in the program. Diffractometer 3 used a different type of detector than that employed for diffractometers 1 and 2. It may be necessary to use a slit system (i.e., one degree) that is similar to the experimental setup described in the first paragraph of this section.

If there are problems with background (for example, if the background from your instrument is different than the background for the stored standards) one can let the background be a part of the Solver solution by setting cell Y17 in the Input sheet to 1. If your zincite pattern is subtly different from the stored pattern, artificial mixtures (e.g., 1.5 g each of kaolinite and quartz, plus 0.333 g ZnO) can be analyzed to test the zincite standard. If the RockJock values are consistently different from 100 percent, then the ZnO correction factor can be adjusted in the Result sheet, cell F3. For example, if you always have a total around 93% (46.5 % quartz + 46.5

% kaolinite) rather than 100 percent, then cell F3 in the Result sheet can be set to 1.075 (100/93 = 1.075).

If new standards are to be developed:

1. First enter a pattern (5 to 65 degrees two-theta with 0.02 degree steps and at least 5 seconds count time per step) for pure ZnO (obtained from the J. T. Baker Co.; 3 g ground in a McCrone mill with 4 ml of methanol) into the Full Pattern sheet, column P. This pattern should be shifted so that the XRD peaks have “true” positions when compared with published values (e.g., the 110 reflection maximum should be at 56.60 degrees two-theta for Cu K<sub>a</sub> radiation). The same shifted ZnO pattern, but from 51 to 65 degrees two-theta, should be pasted into column H in the Shifter sheet, and into column P in the Clay sheet. Use exactly this same ZnO chemical in all analyses.

2. Next determine the ZnO integrated intensities in two regions of the pattern (the Full Pattern region and the Clay region), as follows. Enter the position-corrected ZnO pattern into column D on the Input sheet, with intensities starting at 5 degrees two-theta in cell D2. Set cells C4 = 20, C6 = 65, and cells C8, C10, and C13 to 0. Set cell B18 to 1, click the Start button, and record the integrated intensity for the Full Pattern region (cell A15 in the Input sheet). Next set cells C4 = 55 and C6 = 65. Click the Start button, and record the calculated integrated intensities for the standard for the Clay region found in cell A15. Enter these integrated intensities into the Standards sheet, cells D3 and F3, respectively, and save the program.

3. According to the instructions in Srodon and others (2001), two X-ray patterns (with at least 5 seconds count time per step) are prepared for each standard, one for the pure mineral (3 g), and the other for a mixture of the pure mineral (1.2 g) with either a clay (1.2 g pure kaolinite) if the mineral is a non-clay, or with a non-clay (1.2 g pure quartz) if the mineral is a clay, plus the internal standard (0.6 g of ZnO from the J. T. Baker Co.). The mixture is ground in a McCrone mill for at least 5 minutes in 4 ml of methanol, except for pure clay standards, which should be ground for 20 minutes in 4 ml of hexane to ensure random orientation.



**TABLE 1.** Comparison between weight percent minerals found for artificial mixtures<sup>1</sup> using three different powder diffractometers to collect the data, and Siemens-generated XRD standards to analyze the data in RockJock. The diffractometer codes are: 0 = weight percents used in the artificial mixtures; 1 = Siemens; 2 = Nicolet; 3 = Bruker.

Sample:	RC-AR1				RC-AR2				RC-AR3			
Diffractometer:	<b>0</b>	1	2	3	<b>0</b>	1	2	3	<b>0</b>	1	2	3
Microcline	<b>8.0</b>	8.5	7.7	9.1	<b>10.0</b>	12.3	11.7	13.3	<b>2.0</b>	1.8	1.9	3.5
Albite	<b>8.0</b>	9.5	10.1	9.9	<b>10.0</b>	10.7	11.9	12.0	<b>2.0</b>	2.8	3.9	4.4
Calcite	<b>5.0</b>	4.9	5.1	4.8	<b>3.0</b>	2.5	2.6	2.9	<b>17.0</b>	15.4	16.4	18.6
Dolomite	<b>3.0</b>	3.4	3.3	3.3	<b>2.0</b>	2.3	1.8	2.7	<b>5.0</b>	4.9	5.6	5.8
Halite	<b>3.0</b>	3.3	2.4	2.9	<b>2.0</b>	1.1	0.5	2.0	<b>5.0</b>	2.0	2.0	2.6
Pyrite	<b>2.0</b>	1.5	1.7	1.9	<b>3.0</b>	2.5	2.7	2.3	<b>2.0</b>	1.4	1.9	1.9
Siderite	<b>3.0</b>	2.6	2.0	2.5	<b>2.0</b>	1.8	1.7	1.9	<b>5.0</b>	4.1	3.6	5.4
Barite	<b>2.0</b>	1.8	2.4	1.9	<b>2.0</b>	2.0	2.2	2.0	<b>2.0</b>	2.8	2.3	2.1
Quartz	<b>20.0</b>	20.0	19.7	19.3	<b>40.0</b>	40.3	38.1	40.1	<b>15.0</b>	14.8	12.8	16.1
Gypsum	<b>0.0</b>	0.0	0.0	0.0	<b>0.0</b>	0.0	0.0	0.0	<b>5.0</b>	2.8	5.2	1.7
Kaolinite	<b>9.0</b>	8.1	9.7	10.3	<b>7.0</b>	6.2	8.3	7.7	<b>10.0</b>	7.3	9.4	8.6
Fe-smectite	<b>7.0</b>	6.7	7.2	5.6	<b>6.0</b>	6.5	5.6	7.3	<b>5.0</b>	5.7	4.4	9.5
Illite	<b>25.0</b>	23.6	25.2	20.4	<b>9.0</b>	6.5	10.5	5.5	<b>28.0</b>	25.7	31.2	20.4
Chlorite	<b>5.0</b>	5.3	3.7	6.4	<b>4.0</b>	4.2	4.0	5.4	<b>0.0</b>	0.7	0.0	1.2
Total	100.0	99.2	100.2	98.3	100.0	98.9	101.6	105.1	100.0	91.1	100.6	101.8
Bias	0.0	6.8	7.8	13.7	0.0	9.6	15.0	13.9	0.0	13.3	11.8	26.6

<sup>1</sup>Reynolds Cup samples prepared by D. McCarty, Chevron-Texaco.

4. The pattern of the pure mineral needs to be justified in two-theta space with respect to the pattern that contains the ZnO internal standard. To do this, paste the XRD pattern for the ZnO-containing standard mineral into column D in the Input sheet. The sample name should be in cell D1, followed by the intensities starting at 5 degrees two-theta, and ending at 65 degrees. Enter 1 into cell B18 and click the Start button. This operation will plot the XRD pattern shifted against the position of the ZnO internal standard. Choose a mineral XRD peak (not a ZnO peak), and determine its position by entering angles that are on either side of the peak into cells C4 and C6. Push the start button again. The two-theta peak position for this peak will be shown in cell A4. Note this position. Now enter the X-ray intensities for the pure mineral into column D. Set cell B18 to 0 and click the Start button. (the number 1 is not entered into this cell because the pure mineral does not have an internal ZnO standard against which to shift the pattern.) The peak position for the pure mineral now appears in cell A4. This position should be the same as the angle noted for the ZnO-containing sample. If it is not the same, then manually shift the pattern of the pure mineral in a separate Excel worksheet by the number of steps necessary to make the peak position found for the pure mineral the same as that found for the ZnO-containing sample. Remove or insert intensities, having approximately the same value as adjacent intensities, at the top or bottom of the data in order to have the shifted pattern vary from 5 to 65 degrees.

5. Next measure the integrated XRD intensities for the pure mineral in two regions of the pattern (the Full Pattern region and the Clay region), as was done for the ZnO pattern, and as is repeated here. Paste the shifted XRD pattern for the pure mineral into column D on the Input sheet. Set cells C4, C6, C8, C10, and C13 to 20, 65, 0, 0, and 0, respectively. Click the Start button, and record the integrated intensity for the Full Pattern region (cell A15). Next, set cells C4 and C6 to 55 and 65, respectively. Click the Start button, and record the integrated intensities for the standard for the Clay region found in cell A15 .

6. The shifted pattern for the pure mineral and the integrated intensities now must be entered into the Standards sheet. Click the tab for this sheet. Enter the mineral name into column

C, the integrated intensity for the Full Pattern region into column D, and the integrated intensity for the Clay region into column F. Enter the shifted XRD pattern for the pure standard mineral into the correct column, starting in column M. Note that the position of the mineral in the Standards table is keyed to the position of the mineral's pattern starting in column M. When the program is run, the name of the new standard will appear automatically in column G of the Input sheet.

7. Next measure the mineral intensity factor (MIF), which compares the integrated intensity of the mineral to that of the internal standard. MIF is defined as:

$$MIF = \frac{I_m(\%S)}{I_s(\%M)}, \quad (1)$$

where  $I_m$  and  $I_s$  are the integrated intensities of the mineral and the ZnO standard, respectively, and %S and %M are the weight percents of the ZnO standard (20 percent) and the mineral (usually 40 percent). The term MIF is defined exactly the same as the reference intensity ratio (RIR) of earlier literature (Snyder and Bish, 1989); but the acronym MIF is preferred here because it is easier to pronounce. To measure the MIFs, set the "Present?" values in column H of the Input sheet to 1 for the mineral and for the material that the mineral is mixed with (a disordered kaolinite, such as KGa2, for a non-clay standard, and quartz for a clay standard). All other settings in column H should be zero. Set the values in columns I and J as indicated at the tops of the columns. The cell in column I should be set either to 2, in which case the mineral is a non-clay to be analyzed in the Full Pattern region, or to 3, in which case it is a clay mineral to be analyzed in the Clay region. The cells in column J are set either to 2, for reporting the mineral as a non-clay, or to 3 for reporting it as a clay. Now set cell B18 to 5. Click the Start button.

When the calculation is complete, the MIF for the Full Pattern region can be calculated, using equation 1, from the value in the Full Pattern sheet in cell E31 for the ZnO integrated intensity, and from the value either in cell E32 or in cell I6 for either the non-clay or the clay mineral.

Similarly, the MIF for the Clay region can be solved using analogous cells in the Clay sheet. The MIF solutions also are presented automatically in cells hidden behind the top graph of the Full Pattern sheet. Be sure to pick the correct solution (either for a non-clay or a clay) from this

automatic solution. Solve for kaolinite and quartz standards first, because these minerals are used in subsequent calculations. The MIF values now should be entered in columns E and G in the Standards sheet in the appropriate cells.

Impure standards also can be used. If, for example, a clay standard contains a quartz impurity, the peaks for quartz in the “pure” pattern can be removed electronically using the PeakChopper program that accompanies the RockJock program. Its corrected X-ray pattern and integrated intensities then are entered into the Standards sheet as described above. The ZnO + quartz spiked clay sample then is run as described above, except that cell H2 in the Result sheet is set to 0.20 for the ZnO/sample ratio used in the standards [ $0.20 = 0.6 \text{ g ZnO} / (3.0 \text{ g sample} + \text{zincite})$ ]. After the calculation, the amount of quartz in the sample can be read in the Result sheet. For example, if the results of the calculation is 48 percent, then the amount of quartz in the original clay sample was 8 percent (48 percent minus the 40 percent quartz added to the clay). In solving for the MIFs in equation 1,  $\%M = 32$  percent. Do not use the automatic solutions found behind the graph in the Full Pattern sheet in this case. Other impurities can be handled in a similar manner. Be sure to return cell H2 in the Result sheet to its original value [ $0.111 = \text{g ZnO} / (\text{g sample})$ ] before running more samples.

## USING THE AUTOMATIC MODE

RockJock can analyze a group of similar XRD patterns in one continuous run of the program, using a single set of standards. Although analysis time for each pattern may be long, the program can run for about 9 hours (32,000 seconds, which is the maximum time allowable in the Solver) without further input, at which time a Continue button may have to be clicked to continue the analysis.

Enter the XRD patterns into the Auto XRD sheet in the columns that are indicated in this sheet. In the Input sheet, set cell B11 to the number of XRD patterns to be analyzed; set the minerals present in column H; set cell B18 to 5; and click the Start button . At the end of the calculation, the results are saved automatically (see cell Y19 in the Input sheet), and the results themselves are in the Auto Results sheet. Graphs for the Full Pattern and Clay regions for each sample can be studied in the Auto Graph sheet by entering the analysis number of the pattern (1, 2, 3, etc.) into cell A2. The analysis number of the patterns can be found in the top row of the Auto Analysis sheet.

The Auto Graph sheet can be copied and saved separately as a record of the analyses. To do this, click on the Auto Graph tab near the bottom of the screen to select this sheet. Under the Edit menu, select Move or Copy Sheet. Under To Book select (New Book), and check the Create a Copy box. Click the OK button. When the new worksheet is ready, under the File menu, choose Save as, and give the worksheet a name with an *.xls* extension (e.g., Yukon.xls).

## USEFUL TIPS

To stop the calculation at any time, press the Escape (Esc) key. This key also can be pressed to study calculation progress during the Solver solutions. To update the graphs during the Solver calculation, press the Esc key, and then click the Continue button that comes on the screen.

Pointing to a pattern in the graphs will bring up the mineral name associated with that pattern and the two-theta angle.

If a chart is selected on a sheet subsequent to the Input sheet, the program will not run, and a Macro error message will appear. To fix this problem, go to the sheet, click on any cell to unselect the chart, and start the program again.

Use 1Md illite for aluminous, dioctahedral smectite and illite. Do not use the other Al-rich smectites unless you are analyzing bentonites. Illites and Al-rich smectites have nearly the same pattern of reflections in the 060 region. Therefore they can not be distinguished from each other, and should be reported together. Another technique has been developed (PVP surface area technique; Blum and Eberl, written communication) to distinguish between smectite and illite with the aid of RockJock calculations.

Do not use 1M and 2M<sub>1</sub> illite unless you are specifically analyzing for these polytypes, and then analyze for them in the Full Pattern region (enter 2 in column I in the Input sheet). Likewise, use disordered kaolinite for all kaolinites (except for halloysite), unless you are specifically interested in the polytype, in which case, analyze for it in the Full Pattern region.

Fe-smectite is a common phase in sediments, but it can give a false-positive reading in RockJock. Be sure that your sample contains smectite before selecting this mineral by studying the low-angle region of the pattern. Treating oriented samples with ethylene glycol is especially helpful for uncovering the presence of smectite.

Check the pattern's low angle region to see if minerals that have peaks in this region should be included in the analysis. Some of these minerals are: smectite (6 to 8 degrees two theta), illite and mica (8.8 degrees), chlorite (6.2 degrees), amphibole (10.5 degrees), gypsum

(11.6 degrees), bassanite (14.8 degrees), alunite (17.9 degrees), etc. If these peaks are not found, then the mineral should not be included in the analysis.

All minerals are solved for weight percents in both the Full Pattern and the Clay regions, but the solutions are only reported for the selected region (region is selected in column I of the Input sheet). One can compare the solutions found for a given mineral in the two regions by studying columns F through H of the Result sheet. The solutions may not be exactly the same, because, for example, intensities for non-clays may be very small in the Clay region, and, therefore, the solution for non-clays in the Clay region is inaccurate. However, the possibility that RockJock may find different weight percents for the same mineral analyzed in the two regions is a potential weakness of the approach. Generally, however, the effect of such differences on the final result has been found to be insignificant. There was an attempt to solve this problem by iteration and by constraining the solutions in the two regions (discussed later), but these types of analyses proved to be not as accurate as allowing mineral standards in both regions to vary freely during the Solver solution. After an initial run of a sample, the solution for a mineral can be manually fixed in a given region by constraining (in the Solver) the value for the cell for the factor in column F by making it equal to the value for the factor in column K. Then the Solver is run within the same sheet. The final results then are collected by running option 6 in the Input sheet.

If there is a question as to which feldspar is in a sample, select all of the feldspars the first time through, and then eliminate those that are less than 1 weight percent for the final calculation. The same strategy works with chlorite.

Several different regions for analysis can be set in the Full Pattern sheet, cells B4 through B9. This option is useful if a mineral has a distinctive peak outside the normal analysis range of 20 to 65 degrees. For example, gypsum has a strong peak at 11.6 degrees two-theta (Cu radiation). In this case, cells B4 and B5 can be set to the normal values of 20 and 65, and cells B6 and B7 can be set to 11 and 12 to include this gypsum peak in the analysis. Low-angle clay peaks, especially those for illite and chlorite, are too variable to be useful in this type of approach.

It sometimes is beneficial to fix the solution for the quartz peak, found in the Full Pattern region, in the Clay region. This approach is particularly useful when analyzing for biotite, the peaks for which lie beneath the quartz reflection in the Clay region. Therefore, the biotite peak tends to “eat” the quartz reflection, unless quartz is fixed. To fix the quartz peak in the Clay region, set cell Y21 in the Input sheet to 1.

For faster calculation, select a shorter two-theta angle range in the Full Pattern sheet (for example, enter 21 to 38 degrees in cells B4 and B5, rather than 20 to 65 degrees two theta).

After an initial solution for a sample, the answer can sometimes be improved by shifting the standards with respect to two-theta to minimize the degree of fit value in cell E29 in the Full Pattern and Clay sheets. Standards can be shifted manually by entering positive or negative whole numbers into the appropriate cells in columns C and G in these sheets. The shifting also can be automated by entering the number of Solver iterations into cell B14 of the Input sheet. The number of iterations required to lead to accurate, automatic standards peak shifts is determined by experimentation. Calculations that include automatic shifts are slow, and therefore it might be better to shift manually, when required.

The 060 reflections for clay minerals generally shift towards smaller two-theta angles with increasing iron content. Similarly, the dominant dolomite peak shifts to smaller angles with increasing iron content. Increasing magnesium content causes the most intense calcite peak to shift towards larger angles.

Do not run different polytypes of the same mineral in different regions for a given analysis. For example, if 2M1 illite is analyzed in the Full Pattern region, and 1Md in the clay region, then illite may be counted twice in the final analysis.

If you develop your own standards, be sure to purchase a large quantity of ZnO, all from the same chemical lot, to use as a constant internal standard through the years.

Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) may be converted into bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) during grinding in alcohol. To prepare a gypsum standard, grind selenite crystals, which may not convert. To prepare a bassanite standard, heat gypsum to 150 C overnight, and it will convert to bassanite.



If your sample contains a lot of quartz, it is sometimes necessary to exclude the strongest quartz peak (at 26.64 degrees two theta) from the Solver analysis, because it may dominate the analysis in the full pattern region. To do this, in the Full Pattern sheet, set cells B4 to B7 to 20.0, 26.2, 27.0 and 65.0, respectively, prior to analysis.

## MANUAL MODE

The Input sheet in RockJock can be used to find XRD peak positions, integrated peak intensities, and integral peak breadths. To do this, enter the XRD pattern into Column D in the Input sheet. Set the start angle, step size, and radiation wavelength in cells B5, B7 and B9. Set cell B18 to either 0 or 1, depending on whether the sample has a ZnO internal standard. Next set the angles in cells C4 and C6 to bracket the minimums of the peak to be measured. Set cells C8 and C10 to either 0 or 1. If zeros are entered, the peak will be picked between the values entered into cells C4 and C6. If ones are entered, the peak will be picked from minimum intensities on either side of the peak. Next set the background removal option in cell C13. Entering a 0 does not remove background, and this is the option selected automatically during quantitative analysis. Entering 1 or 2 causes the background to be picked from the minimum on the left or right side of the peak, respectively. Entering 3 causes the background to be picked from a line drawn between the minimums on the left and right sides of the peaks. Entering 4 causes the background to be selected from a minimum in the 50-degree region that is present in XRD patterns of most sediment samples. After either 0 or 1 is entered into cell B18 and the program is started, the manner in which the background was determined is indicated on the chart on the Input sheet. The results, which include the position of the peak's maximum intensity, the analytical range for the peak, the peak's maximum intensity, the positions of the peak's minimums, the peak's integrated intensity, and the peak's integral peak breadth, appear in column A.

## DESUETUDE ROCKJOCK

RockJock originally followed the analytical scheme proposed by Srodon and others (2001), which integrated single, key XRD peaks for each phase, and then corrected these integrated peaks for interference by other peaks. This scheme still can be used in the RockJock program by setting cell B18 to 2 on the input sheet and by setting the cells in column I to 1 (single peak analysis) for the minerals present. After option 2 has been run, integrated intensities for the phases can be found in column Q of the Input sheet. To find weight percents, the Clay region also must be run (set cell B18 in the Input sheet to 4) to find the integrated intensity for ZnO, and then option 6 should be run to collect the final results. The peaks to be analyzed for each phase, the type of background removal, and the MIFs are set in the Single Peak table in the Input sheet in columns K through R, and the interference corrections are set in the Result sheet, column AP. However, this method of analysis has proven to be unwieldy for complex samples, and it is less accurate than pattern fitting. Single peak analysis can be used together with pattern fitting simply by entering a 1 in column I for the selected mineral in the Input sheet, and then using analysis option 5. However, the single peak parameters for the selected mineral must be entered into the Single Peak table on the Input sheet (columns K through R).

Different analytical schemes were tried and rejected, but this software is still available in the RockJock program for experimentation. For example, it is possible to constrain the values found for the minerals in the Full Pattern region when solving for the Clay region, and vice versa. Also, it is possible to iterate the calculation between these regions and to let the background be part of the Solver solution. These options are set in cells Y12 through Y17 of the Input sheet. However, it was found by analysis of artificial mixtures of known composition that constraint of the solutions from one region to the other, iteration, and background fitting do not improve the final results.

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## APPENDIX 1: INPUT SHEET INPUTS AND OUTPUTS

### Summary of inputs for the Input sheet.

<u>Input</u>	<u>Cell</u>	<u>Value</u>	<u>Comments</u>
Sample name and XRD intensities	D1 and following	Name and intensities	Enter sample name in cell D1, and sample XRD intensities in cells D2 through D3002.
Sample name	B3	None	<u>Do not enter a name.</u> Name is entered automatically from cell D1 when program is run.
Starting angle for X-ray intensities	B5	Usually 5 degrees	Should be 5 degrees or smaller for quantitative analysis.
Step size	B7	0.02	Must use 0.02 for quantitative analysis unless all of the standards are changed to a different step size.
Radiation wavelength	B9	1.5418	Program is currently set up for Cu K-alpha radiation. Some changes in the program will have to be made to use other wavelengths.
Auto analysis?	B11	0 or positive whole number	Enter the number of patterns that were entered into the Auto XRD sheet. A zero leads to analysis of the single pattern that was entered into column D of the Input sheet.

Auto shift standard patterns?	B13	-1 = set all to zero; 0 = keep present shifts; or give number of iterations.	Shifts the standard patterns with respect to two-theta during the Solver solution to account for isomorphous substitutions, etc. Substantially slows the calculation, so that shifts might better be done manually.
Type of analysis	B18	0 through 6	Performs the type of action indicated on the Input sheet in cells B15 and B16. 0 = plots sample XRD pattern with no shift; 1 = plots pattern with shift against internal standard (type of standard is set in Shifter sheet); 2 = single peak analysis, for peaks entered in columns K through R, with integrated intensities given in column Q; 3 = runs only Full Pattern region part of analysis; 4 = runs only Clay region part of analysis; 5 = runs full analysis, including both regions and results; 6 = collects all data from single peak, Full Pattern and Clay analyses, and enters them into Result sheet.
Start angle	C4	Angle	Starting angle for manual peak analysis
End angle	C6	Angle >C4	Ending angle for manual peak analysis.
Auto pick left background?	C8	0 = no; 1 = yes	If 1, finds minimum on left side of peak. Otherwise the value used is that entered in cell C4.
Auto pick right	C10	0 = no;	If 1, finds minimum on right side of peak.

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background?		1 = yes	Otherwise, the value used is that entered in cell C6.
Background correction type	C13	0 through 4.	Removes background according to description in cells B11 and B12.
Watch calculation?	Y9	1 = yes	Turns on screen during calculation. Slows calculation.
Smooth Power	Y11	Enter whole number	Smooths measured XRD pattern, with larger number causing more smoothing. Enter 1.
Number of iterations	Y13	Enter whole number.	Causes the calculation to iterated between the Full pattern and Clay regions. Generally does not improve calculation results. Enter 1.
Constrain when?	Y15	Enter whole number	Constrains the Solver solution for the non-clays in the Clay region, and the solution for the clays in the Full pattern region during interation. Enter 0.
Auto background correction?	Y17	1 = yes	Causes the background to be a part of the Solver solution. Enter 0.
Auto save after auto analysis?	Y19	0 = no; 1 = yes	Saves the program after all patterns have been run on auto analysis. Guards against loss of data.
Constrain quartz analysis in Clay	Y21	0 = no; 1 = yes	Constrains shape of quartz peak in Clay region so that it is determined by solution found for quartz in

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region?

the Full Pattern region. In other words, the Solver does not vary quartz in the solution for the Clay region.

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### Summary of outputs for Input sheet.

<u>Output</u>	<u>Cell</u>	<u>Value</u>	<u>Comments</u>
Position of XRD peak maximum	A4 and A5	Gives two-theta value and d-spacing of chosen peak	Peak is chosen as the maximum intensity between the two-theta values entered into cells C4 and C6.
Analysis range	A7 and A8	Chosen two-theta values for peak analysis	Gives the analysis range chosen for the peak in cells C4 and C6.
Maximum intensity of peak	A10	Intensity	Gives maximum intensity of chosen XRD peak.
Angles for tail minimums	A12 and A13	2-theta for left and right sides of peak	If cells C8 and C10 = 1, then the two theta values are the minimum values for the peak. Otherwise, they are the values entered into cells C4 and C6.
Integrated intensity	A15	Integrated XRD peak intensity	Integrated intensity between angles given in cells A12 and A13.
Integral peak breadth	A17	Integrated intensity/maximum intensity	Peak intensities are integrated between two-theta values found in cells A12 and A13.



## APPENDIX 2: SHIFTER SHEET INPUTS AND OUTPUTS

<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Start and stop analysis angle	B7 and B8	Two-theta angles used to find maximum of position standard	Normally use 56 and 57 degrees to find top of 110 ZnO peak. Sometimes the sample will interfere with this peak (especially true for pyrite standard), in which case, another ZnO peak should be used (62 to 64 degrees).
Standard number for position analysis	B10	Enter 1 through 5, depending on the position standard chosen.	Always enter 1 to use the ZnO standard. The other position standards, except for quartz, are not installed.
Turn off shifter?	B18	1 = yes; enter 0.	Use this option to turn off the Shifter option, in which case the pattern in the Input sheet will not be corrected in two-theta position against an internal standard when options 1 through 5 are entered into cell B18 in the Input sheet.
Steps for shifting sample	B18	Positive or negative whole number	This cell automatically adjusts when program is run. However, the pattern also can be shifted manually by entering a positive or negative whole number into this cell.

### APPENDIX 3: FULL PATTERN SHEET INPUTS AND OUTPUTS

<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Choose two-theta regions for Solver analysis	B4 to B9	Usually 20-65 degrees.	By changing cells B6 to B9, other two-theta regions also can be entered into the analysis. For example, low-angle peaks can be included in the analysis, or certain peaks can be excluded if they are too intense, .
Shift standard non-clay patterns	C4 to C26	Positive or negative whole number	Shifts standard patterns with respect to two-theta. After initial Solver solution, shift patterns manually using these cells to minimize the degree of fit value in cell E29. Then run the program again. Cells C4 and C5 shift the measured pattern and the ZnO pattern, and, therefore, should always be set at 0.
Shift standard clay patterns	G6 to G25	Positive or negative whole number	Shifts standard patterns with respect to two-theta. After initial Solver solution, shift patterns manually using these cells to minimize the degree of fit value in cell E29. Then run the program again.
Full Pattern and Clay factors	E6 to F26	Decimal	These cells are varied automatically during the Solver solution, and are multiplied by the intensities of the stored standard XRD patterns. But they also can be manipulated manually to change the proportions of the standard patterns in the graphs.
Calculated MIFs (hidden)	B11	Values for	Gives values for non-clay and clay MIFs when

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beneath upper graph)	to	standards	standards are prepared and run properly.
	B14		
Bragg's Law	D53	Enter d-	To calculate XRD peak positions or spacings.
	to	spacing or	
	D57	two-theta	
Solver model	C61	Solver	Controls Solver settings for Full Pattern region.
	to	setup	
	C63		

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#### APPENDIX 4: CLAY SHEET INPUTS AND OUTPUTS

<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Choose two-theta region for Solver analysis	B4 and B5	Usually 58 to 65 degrees.	The range can be expanded to as far as 51 to 65 degrees two theta.
Shift standard clay patterns	C7 to C26	Positive or negative whole number	Shifts standard patterns with respect to two-theta. After initial Solver solution, shift patterns manually using these cells to minimize the degree of fit value in cell E29. Then run the analysis again.
Shift standard non-clay patterns	G6 to G25	Positive or negative whole number	Shifts standard patterns with respect to two-theta. After initial Solver solution, shift patterns manually using these cells to minimize the degree of fit value in cell E29. Then run the analysis again.
Full Pattern and Clay factors	E6 to F26	Decimal	These cells are varied automatically during the Solver solution, but also can be manipulated manually to change the proportions of the patterns in the graph.
Bragg's Law	D55 to D59	Enter d or two-theta	To calculate XRD peak positions or spacings.
Solver model	C62 to	Solver setup	Controls Solver settings for Clay region.

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C64

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## APPENDIX 5: RESULT SHEET INPUTS AND OUTPUTS

<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Calculation time	A1 to A6	Time and date	Gives calculation time.
Bragg's Law calculation	A10 to A17	Input d or two-theta	Calculates d-spacing or two-theta angle.
Weight percent minerals	Col B to C	Weight percent	The total should be approximately 100 percent.
Warnings	Col D	Normally hidden text	Warns about non-standard settings in the program.
ZnO sample ratio	H2	Normally 0.111	(Weight ZnO)/(weight sample + zincite). Change to 0.20 when analyzing impure standards for mineral content.
ZnO correction factor	F3	Set to 1.	Untested method for correcting results when using different sources of ZnO.
Corrected ZnO/sample ratio	H3	Equals 2 x F3	Untested. It is an output, so do not change it.
Weight percent comparison	Col E to H	Wt. percents	Table compares weight percents calculated for the same mineral in the Full Pattern and Clay regions.
Interference corrections	Col	Correction	Used for single peak analysis, and is now obsolete.



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AP factors

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**APPENDIX 6: STANDARDS SHEET INPUTS**

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<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Standards table	Col B to Col H	Enter information for standards	Enter information about the standards, as is described in the text, including sample name, integrated intensities for Full Pattern (20-65 degrees) and Clay (55 to 65 degrees) regions, MIFs for each region, and sample descriptions.
Intensities for pure standards	Start in Col M	XRD intensities for standards	Start at 5 degrees and use 0.02 degree steps. Do not remove background. Note that column in which intensities are entered is related to position in Standards table (see above).

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## APPENDIX 7: AUTO XRD SHEET INPUTS

<u>Input</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Intensities for samples to be analyzed in series of analyses.	Start in Col C	XRD intensities	Start at 5 degrees and use 0.02 degree steps. Put the sample name in the first row, followed by intensities. Set value of cell B11 in the Input sheet to the number of patterns to be analyzed that are contained in the Auto XRD sheet.

## APPENDIX 8: AUTO RESULTS SHEET OUTPUTS

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<u>Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Time for calculation	A1 to A6	Time and dates	Gives starting and ending times, and dates for automatic calculation.
Results of Auto calculation	Start in Col C	Weight percents	Pattern number is used to identify result in Auto Graph sheet. Results are completely erased if new Auto calculation is started.

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## APPENDIX 9: AUTO GRAPH SHEET INPUTS

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<u>Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Pattern number	A2	Whole number	Entering pattern number produces graphs and weight percents for each auto analysis. Pattern number corresponds with number for result shown in Auto Results sheet. This page can be saved separately, as is described in the ‘Using the Automatic Mode’ section.

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## APPENDIX 10: RESOURCES FOR QUANTITATIVE MINERAL ANALYSIS

### Sources of standard minerals:

Source Clay Minerals Repository  
Purdue University  
1150 LILY Hall  
West Lafayette, IN 47907-1150 USA  
Voice: (765) 494 4258 FAX: (765) 496 2926  
E-mail: [sourceclays@purdue.edu](mailto:sourceclays@purdue.edu)  
Web: <http://cms.lanl.gov> (follow links to Source Clays Project)

Ward's Natural Science  
5100 West Henrietta Road  
P.O. Box 92912  
Rochester, NY 14692-9012 USA  
Voice: 1-800-962-2660 FAX: 716-334-6174  
International calls: 716-334-6174  
Web: [http://www.wardsci.com/online\\_catalog/](http://www.wardsci.com/online_catalog/)

Excalibur Mineral Corp.  
1000 North Division Street  
Peekskill, NY 10566 USA  
Phone: (914) 739-1134  
Email: [info@excaliburmineral.com](mailto:info@excaliburmineral.com)

Trinity Mineral Company  
John Veevaert  
P.O. Box 2182 Weaverville, California 96093-2182 USA  
Phone: (530) 623-2040; (888)-689-8402 (Toll Free)  
Email: [john@trinityminerals.com](mailto:john@trinityminerals.com)

David Shannon Minerals  
6649 East Rustic Drive  
Mesa, Arizona 85215 USA  
Phone: (480) 985-0557.

Mineralogical Research Co.  
15840 East Alta Vista Way  
San Jose, California 95127-1737 USA  
Phone: (408) 923-6800

Minerals Research  
31 Sherwood Drive  
Brockport, NY 14420 USA  
phone: (585) 637-4915; FAX: (585) 395-2416  
email: fmumpton@frontiernet.net

McCrone Micronising Mill:

McCrone Associates  
850 Pasquinelli Drive  
Westmont, IL 60559 USA  
Voice: 800-622-8122; Fax: 630-887-7764  
Web: <http://www.mccrone.com/mac/home2.html>

Jade XRD search-match software:

Materials Data  
1224 Concannon Blvd.  
Livermore, CA 94550 USA  
Voice: 925-449-1084; FAX: 925-373-1659  
Web: <http://www.materialsdata.com>

Information concerning the Solver:

Frontline Systems Incorporated  
Voice: 775-831-0300  
Web site: <http://www.solver.com>

Microsoft Excel:

Web site: <http://www.microsoft.com/office/excel/default.asp>