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User's Guide to HandLens—A Computer Program that Calculates the Chemistry of Minerals in Mixtures

Open-File Report 2008-1244

U.S. Department of the Interior
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DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
Mark D. Myers, Director

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Cover: Desert rock near Moab, Utah, Photograph by the author

THE MAN WITH THE BLUE GUITAR

I

The man bent over his guitar,

A shearsman of sorts. The day was green.

They said, "You have a blue guitar,

You do not play things as they are."

The man replied, "Things as they are

Are changed upon a blue guitar."

And they said then, "But play, you must,

A tune beyond us, yet ourselves,

A tune upon a blue guitar

Of things exactly as they are."

                                        Wallace Stevens

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User's Guide to HandLens—A Computer Program that Calculates the Chemistry of Minerals in Mixtures

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Abstract

HandLens is a computer program, written in Excel macro language, that calculates the chemistry of minerals in mineral mixtures (for example, in rocks, soils and sediments) for related samples from inputs of quantitative mineralogy and chemistry. For best results, the related samples should contain minerals having the same chemical compositions; that is, the samples should differ only in the proportions of minerals present. This manual describes how to use the program, discusses the theory behind its operation, and presents test results of the program's accuracy.

Required input for HandLens includes quantitative mineralogical data, obtained, for example, by RockJock analysis of X-ray diffraction (XRD) patterns, and quantitative chemical data, obtained, for example, by X-ray florescence (XRF) analysis of the same samples. Other quantitative data, such as sample depth, temperature, surface area, also can be entered. The minerals present in the samples are selected from a list, and the program is started. The results of the calculation include: (1) a table of linear coefficients of determination (r^2's) which relate pairs of input data (for example, Si versus quartz weight percents); (2) a utility for plotting all input data, either as pairs of variables, or as sums of up to eight variables; (3) a table that presents the calculated chemical formulae for minerals in the samples; (4) a table that lists the calculated concentrations of major, minor, and trace elements in the various minerals; and (5) a table that presents chemical formulae for the minerals that have been corrected for possible systematic errors in the mineralogical and/or chemical analyses. In addition, the program contains a method for testing the assumption of constant chemistry of the minerals within a sample set.

Introduction

Rocks and sediments are composed of minerals, and minerals are defined by their crystal structure and chemical composition. In addition to these variables, mineral proportions are required to characterize a rock. Rocks have long been characterized using chemistry alone. For example, normative calculations estimate quantitative mineralogy from bulk igneous-rock chemistry by applying rules for the likely combination of elements during crystallization (for example, Cross et al., 1902; Barth, 1962). The normative method also has been applied to metamorphic and sedimentary rocks (for example, Piche and Jebrak, 2003; Tarrah and others, 2000). Geochemical modeling of the composition of natural waters has been used to predict the type and amounts of minerals that precipitate along flow paths, without necessarily analyzing for those minerals (for example, Parkhurst and Appelo, 1999). Elemental maps have been made of soil landscapes, without analyzing for the defining mineralogy (for example, Shaklette and Boerngen, 1984).

Chemistry has been emphasized over mineralogy because it was tedious and difficult to quantify minerals accurately, especially clay minerals (Moore and Reynolds, 1997), although Braun (1986) developed a method to limit the maximum and minimum amounts of a mineral in a mixture by applying linear programming to integrate X-ray diffraction and chemical data, with emphasis on the chemical data.

Recent developments have made quantitative mineral analysis much more accurate and less tedious. These methods include new developments using the Rietveld technique for modeling X-ray diffraction patterns from fundamental X-ray diffraction theory (Bish and Post, 1993; Bergmann and Kleeberg, 1998; Ufer and others, 2004), and whole-pattern fitting methods that use pure minerals as X-ray diffraction standards (Chipera and Bish, 2002; Eberl, 2003). The accuracy of such methods has been confirmed by the Reynolds Cup competition, in which sample unknowns that contained up to 17 minerals each were analyzed with excellent accuracy by at least 10 laboratories out of 37 entries worldwide (Omotoso and others, 2006).

HandLens relies on accurate mineral and chemical analyses of multiple samples and conceptually simple mathematics to calculate the chemical composition of minerals in sets of

related samples. Other methods for determining the chemistry of minerals in mixtures require mineral separations or microprobe techniques. The former method is laborious and sometimes impossible, and the latter is expensive, time intensive, and the resulting micro-chemical analyses may not be representative of the whole sample.

The samples used by HandLens must be related in that they contain minerals which, ideally, have identical chemical compositions with minerals present in different proportions. Such sample sets could be collected, for example, from the same rock formation in different locations, from rock cores at neighboring depths, or from similar samples that have been separated into different size fractions and analyzed separately.

The program calculates a correlation table for the chemical and mineralogical inputs, and plots these relations in a chart. Concentrations of major and trace elements in the minerals are determined by solving a set of simultaneous linear equations using the Solver tool in Excel. A unique mathematical solution requires that there be at least as many samples entered into the program as there are different types of minerals in the samples. In addition, HandLens calculates the major element chemistries for each mineral. This calculation applies material and charge balance constraints to mineral compositions, and a well-constrained solution to the set of linear equations requires that there be approximately as many samples entered into the program as there are variable-composition minerals in the samples. A third type of calculation allows the measured chemistry and/or mineralogy to vary within the experimental uncertainty to refine mineral chemistries. Other program features include utilities for calculating the weight percent of elements from the weight percent of elemental oxides, and the weight percent of Si by difference when this element is missing from the analyses. In addition, a table lists the formulae and most intense X-ray diffraction lines for common, rock-forming minerals. Another program, RockGenerator.xls, generates artificial sample mineralogies and chemistries, with or without random and systematic errors, from mineral compositions. Such RockGenerator data are used to test HandLens calculations. A third program, Form.xls, calculates the formula for a pure mineral from its chemical analysis.

Computer requirements and disclaimer

HandLens will run under either Windows 98 (or higher versions), or Macintosh (System X) operating systems. Use of HandLens requires the installation of Microsoft Excel 2000, or newer versions, but it will not run in Excel 2008 for the Macintosh because this program lacks the Solver tool. The program requires that Excel's Solver option be installed and assumes that the operator has an elementary knowledge of how to use the Excel program. In this report, the term "sheet" refers to a worksheet in Microsoft Excel. Cells, such as **B4**, designate the cell at the intersection of column B and row 4. It may be necessary to use the English-language version of Excel, but see installation step six below. The program occupies about 24 megabytes of disk space. Calculation times can be long, so the fastest computer available should be employed. On some computers, the program often crashes after a calculation is completed and subsequent data is entered into the program. The best strategy to prevent frustration if this occurs is to exit Excel at the end of a calculation (this can be done automatically), and then to open the program again.

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 HandLens

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/HandLens, by emailing the author at 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 HandLens folder at the ftp site can be opened by double clicking on the folder's name (HandLens), and the files downloaded by dragging them onto your hard disk. The useful files are HandLens.xls, which is the material balance program; RockGenerator.xls, which generates electronic sample mineralogies and chemistries that can be used to test HandLens calculations; Form.xls, which calculates mineral

formulae; and HandLens.pdf, which is this instruction manual for the program. Comments or concerns about HandLens should be directed to the author (ddeberl@usgs.gov).

Installation of HandLens

The following instructions should be followed exactly when the program is being run for the first time. Most of the instructions in this manual are written for versions of Excel prior to Excel 2007, at which time Excel underwent a major change in format, and these instructions will have to be adapted by the reader for the newer version. However, instructions are presented below for installation in either of the Excel programs.

Installation for Excel 2003

1. Copy the program and related files onto your hard disk. 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 in the Macintosh if the Aladdin expander software is used. If needed, the latest version of the expander software can be downloaded for free from at: www.aladdinsys.com/expander. After opening the program, more of the worksheet can be viewed on the screen by reducing the zoom size under the View menu.

2. After the program has been opened, go immediately to the "Material balance" sheet by clicking that tab near the bottom of the screen. The arrows at the bottom left can be used to scroll between tabs. 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 program disk and install the Solver (see the **Help** menu in Excel), and then repeat the steps above.

3. Next run Solver once in the "Material balance" sheet by choosing **Solver** from the **Tools** menu and by clicking the **Solve** button. This run will take a few minutes. A shortcut 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.

4. Return to the "Start" sheet by clicking on its tab at the bottom of the screen. Now it may be necessary to turn on Solver in the Visual Basic Editor. To turn on 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. **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 "Start" sheet, go to cell **O229**, which will have a pink font (it could be displaced from cell **O170**). 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 **O229** 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 which indicates 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 use it.

6. It may be possible to run HandLens 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. It is necessary to replace the word **SOLVER** with the non-English equivalent. In Spanish, for example, the word is **SOLV** (see Spanish Excel instructions to find the word). To replace words in the program, follow the instructions in paragraph 5 above. In addition, the **Solver** commands need to be modified in the "Material Balance" sheet (Cells **A28:A30**, **A32:A34**, **A36:A38**, **A40:A42**, and **A44:A46**). Click on cell **A28** 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 **A3**, if necessary; 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** twice, and close the **Solver** box. Now cells **A28:A30** should contain the non-English language equivalent of the English entries. It may be necessary to separate the entries in Cell **A30** with slashes (/) rather than with commas or semicolons (, or ;). Now repeat the same procedure with the other triple cells listed above. If the program runs, **Save** it and give thanks.

Installation for Excel 2007

The advantage of Excel 2007 is that it can use the additional speed of multiprocessors. Excel 2008 for the Mac will not run HandLens because this version of Excel does not contain the Solver.

The Byzantine route for converting HandLens from Excel 2003 to Excel 2007 is as follows:

1. Open Excel 2007.
2. Under the **Office Button**, open HandLens.xls.
3. Under the **Office Button**, **Save as, Excel Macro-Enabled Workbook**. The program is saved separately as HandLens.xlsm.
4. Under the **Office Button**, **Exit Excel**.
5. Open HandLens.xlsm in Excel 2007.

6. Click the **Material balance** tab at the bottom of the sheet. You may have to scroll to find it.

7. Click the **Data** tab at the top of the sheet. In the **Analysis** section (far right top), click the **Solver** tool. If there is no Solver tool, then install the Solver by following the directions given in **Excel help**. Also install the **ToolPak Add-in** (without VBA).

8. After having clicked the **Solver** tool, when the **Solver** box appears, click **Close**.

9. Click the **Start** tab at the bottom left of the sheet.

10. Click the **Home** tab at the top left of the sheet.

11. In the Editing section (far right top), click **Find & Select**, then **Replace**. Next to **Find What:** enter the word **SOLVER**. Next to **Replace with:** enter **SOLVER** again.

12. Click **Replace All**. There should be 204 replacements. Close the box.

13. Click the tab for **Manual plots** at the bottom of the sheet.

14. On the chart in this worksheet, click on the label for the x-axis, which should read **Kspar**.

15. In the formula bar near the top of the sheet, click in the formula, which should read: **='Manual plots'!D4**. This procedure somehow wakes up the chart labels.

16. Follow the same proceedure to wake up the 8 labels on the y-axis of this chart.

17. Follow the same proceedure in the **Results3** sheet to wake up the **K** label in the upper right corner of the chart.

18. Under the **Office Button**, click **Save**.

How to Run HandLens

1. If the program is being used for the first time, follow the installation instructions given above. Make a copy of the program and run the copy.

2. Enter data only in cells that contain **bold red font**! Never <u>cut</u> and paste, only <u>copy</u> and paste data values. After copying data, choose **Paste Special** under the **Edit** menu, then **Values** to paste.

3. Previous data can be erased by entering a **2** into cell **B4** and clicking the **Start** button. Before doing this the first time through, look at the input sheets to see how the data is entered, and run the program with its current data set to be sure that it works.

4. In the "Start" sheet, indicate the minerals present by entering the number **1** into the appropriate cells in column **F**. There is a 17 mineral limit.

5. Run **Mineral Setup** by entering **1** into cell **B4** and clicking the **Start** button.

6. In the "Input mineralogy" sheet, enter the sample names into column **B** and the weight percents of each mineral into the cells indicated. There is a 400 sample limit. Some of the minerals analyzed can be combined into a single category. For example, orthoclase and microcline weight percents can be added together, and the sum entered as potassium feldspar (Kspar). For best results, mineral weight percents for each sample should sum to 100 percent. The experimental uncertainty for each mineral can be entered into row **2**. For example, a ± 6 percent uncertainty is entered as **0.06**.

7. In the "Input major chem" sheet, enter weight-percent elements (not elemental oxides) where indicated. They do not sum to 100 percent because the anions are missing. Experimental-measurement error can be entered into row **2** as is described above. If the chemical data comes in the form of weight-percent elemental oxides rather than as elements, then these values can be converted into weight-percent elements in the "Oxide conversion" sheet. If the element Si is missing from the analyses, it can be calculated automatically by difference in the "Si calc" sheet by entering the weight-percent major elements into columns **D** through **K**. The weight-percent Si will appear in column **C**.

8. In the "Input trace chem" sheet, enter the element symbols into row **4**, and the ppm values for the trace elements into the cells below.

9. In the "Input other" sheet, enter other data for the samples, such as depth, temperature, latitude, surface area, cation exchange capacity. Enter the name of the type of other data into row **4**, and the data itself into the cells below.

10. In the "Start" sheet, enter the number for the analysis option into cell **B10**, and the number of samples to be analyzed simultaneously into cell **B15**. Indicate whether or not major elements are to be analyzed with the trace elements (for example, without constraints) in cell **B17**, whether Fe^{2+} should be a part of the Solver solution in cell **B20**, and how many times to iterate the calculation in cell **B22**. Explanations for these inputs will be given below, and the other inputs are self explanatory.

11. Click the **Start** button. Column **A** in the "Start" sheet lists where the answers will appear.

Analysis Options

Option 1: Analyze data for correlation table & plots

Start the calculation by entering number **1** in cell **B10** of the "Start" sheet, and by clicking the **Start** button. When the calculation is complete, open the "Correlation table" sheet by clicking its tab at the bottom of the screen. The table gives the coefficient of determination (r^2) for all paired variables, and highlights the best correlations in bold green font. The threshold for being highlighted can be changed prior to the calculation by changing the value in cell **A7** from a minimum of zero to a maximum of 1. The coefficients of determination can be multiplied by 100 to find the percent of variance in common between the paired variables.

The next sheet, "Manual plots", is a utility for plotting the input data, and can be activated by entering the reference number (from column **A**, with reference to column **B**) into cell **D3** for the material to appear on the X axis, and the reference numbers for the Y axis into cells **E3:L3**. The values for columns **E** through **L** are added together when plotted.

Option 2: Calculate mineral formulae

Start this calculation by entering **2** into cell **B10** of the "Start" sheet, and by clicking the **Start** button. Option 1 also will be calculated. Option 2 calculates the formulae for minerals in the samples by solving a series of simultaneous equations, as will be described in a later section of this report, and is based on the assumption that each mineral has the same chemical composition in all samples. There should be as many equations in the calculation as there are unknowns. Therefore, it is safest to have at least as many samples in the calculation as there are minerals that have variable compositions, although, due to complexities in the mathematics, it may be possible to use fewer samples for some calculations. The number of samples and variable minerals in the calculation are displayed on column **A** on the "Start" sheet after running **Mineral setup**. The range of compositional variation of each mineral is set in the "Input formulae" sheet, as will be discussed in a later section of this report.

The number of samples to be solved simultaneously can be set in cell **B15** of the Start sheet. Enter "**All**" to analyze all samples simultaneously. For a 10 sample set, for example, entering a **5** into this cell will cause the first 5 samples to be analyzed simultaneously, and then the next 5. The results for these two calculations will be reported separately in the "Results2" sheet. By entering a negative number, for example **-5**, the samples will be analyzed 5 samples at a time as a moving average. Samples 1 to 5 will be analyzed, followed by samples 2 though 6, and so forth, and the results will be reported separately. One needs to run enough samples simultaneously to find a unique solution, but not so many as to stretch the assumption of a constant chemistry for each mineral.

Many chemical analyses report total iron rather than ferric and ferrous iron separately. HandLens will calculate ferrous iron from total iron when **1** or **2** is entered into cell **B20**, by making the ferrous/ferric ratio a part of the Solver solution. There is a 30 or 64 sample limit, depending on which option is chosen. The 64 sample limit excludes Ti and H_2O+ from the calculation. Samples that contain minerals that have a fixed ferrous iron content (for example, pyrite) can be calculated without turning on this option (for example, enter **0** into cell **B20**).

Cell **B22** indicates how many times the calculation will be iterated to find the correct formula weights for the minerals. The first iteration uses the formula weights for the mineral compositions entered into the "Input formulae" sheet. This weight is then refined as the calculation proceeds and the mineral compositions are adjusted. Generally two or three iterations are sufficient to converge on a formula weight.

The results for Option 2 are presented in the "Results2" sheet, starting in column **AC**. The upper table (rows 1 through 20) reports initial mineral chemistries (from the "Input formulae" sheet) before the calculation began, and the tables below report results for the calculations. Structural formulae can be written from the atomic distributions given in the tables for each mineral. Moving to the left in this spreadsheet, by entering a reference number in cell **F2** (reference is to the table in columns **B** and **C**), minerals of the same type from multiple solutions can be compared. Cell **A9** gives the Solver status at the end of the calculation, and will read **0** or **1** if the calculation is valid. If Solver encounters an error, you may be attempting an impossible calculation, so cell **A9** should be checked to insure that Solver found a valid solution. Moving to the right in the spreadsheet, by entering a reference number in cell **BI2** (reference to table in cells **BE3:BF12**), the calculated versus the measured weight percent of an element can be compared for the entire sample set. Ideally, the regression line should have a slope of 1 and an intercept of 0. Deviation from this ideal indicates how well the assumption of equivalent chemistries for minerals of a given type is obeyed in all samples.

Option 3: Distribute elements among minerals

Start this calculation by entering **3** into cell **B10** of the "Start" sheet, and by clicking the **Start** button. If **0** has been entered into cell **B17**, then the concentrations of all analyzed elements in the minerals will be calculated. If the number **1** has been entered into cell **B17**, then concentrations for the trace elements only will be calculated. This calculation is accomplished without assuming any constraints for mineral compositions by solving a series of linear equations simultaneously. There must be at least as many samples in the calculation as there are different types of minerals in the samples for the calculation to be mathematically constrained. As with previous calculations, it is assumed that elemental concentrations are constant for each mineral type.

The results appear in the "Results3" sheet, starting in column **EX**, and are presented in concentration units of weight percent for the major elements, and ppm for the trace elements. As an example, Si should have a concentration in quartz of 46.7 weight percent (100 x atomic weight of Si/molecular weight of quartz = 100 x 28.09/60.09).

Plots of measured versus calculated elemental data can be viewed near column **E** by entering an element's reference number (see columns **B** and **C**) into cell **F2**. The points should fall on a regression line that has a slope of 1 and an intercept of zero if the assumption of a constant chemistry is obeyed.

The results of the Option 3 calculation indicate only that a particular element accompanies a particular mineral, not that it is a part of the mineral's structure. One can speculate, for example, that Ba and Zr may accompany quartz, but may be present in trace amounts of barite and zircon that were not detected by X-ray diffraction, rather than being present in the quartz structure. The Ba, and Zr may correlate with quartz because they occur in resistant minerals that were concentrated together by weathering.

Option 4: Calculate mineral formulae within uncertainty limits

Start the calculation by entering **4** into cell **B10** of the "Start" sheet, and by clicking the **Start** button. This option will calculate mineral formulae using Option 2 first, and then calculate

the formulae by assuming that the mineralogy and/or major element chemistry can vary within the uncertainty limits set in the "Input mineralogy" and "Input major chem" sheets. The results will appear in the "Results4" sheet, starting in column **AC**. The uppermost table gives the initial formulae that were entered into the "Input formulae" sheet, to be discussed below. The mineral and element multipliers used to correct the data can be read in the tables. As in Option 2, the chemistry for minerals of a given type can be compared for separate simultaneous calculations by entering the mineral's reference number (see columns **B** and **C**) into cell **F2**.

Option 5: Run all of the above options

Start the calculation by entering **5** into cell **B10** of the "Start" sheet, and by clicking the **Start** button. This option will calculate Options 1 through 4 with one click of the button.

Option 6: Enter new standard into the Input formulae sheet

Start the calculation by entering **6** into cell **B10** of the "Start" sheet, and by clicking the **Start** button. This option will enter a new or revised standard mineral formula into the program, after the formula has been added or revised in a table in the "Input formulae" sheet, as will be discussed in the next section of this report.

How To Enter A New Mineral Formula Into HandLens

Mineral chemistries calculated by Options 2 and 4 are restricted by material and charge-balance constraints. To enter new minerals into the program, or to revise chemistries for minerals that are already in the program, mineral formulae and constraints must be entered into the "Input formulae" sheet, and then introduced into the program by running Option 6 from the "Start" sheet.

To enter a new mineral, go to the "Start" sheet. Enter the mineral's name after the last mineral name in column **E**. Note the number, given in column **D**, of the new mineral. In column **G**, opposite the new mineral's name, indicate whether it has a fixed (**0**) or variable (**1**) composition. Go to the "Input formulae" sheet, and enter the mineral's number into cell **E8**, and its name into cell **F8** in the **Formula Editing Table**.

Next enter the mineral's starting composition and the upper and lower limits for its chemistry in cells **G8:AS8**. Models for this input can be followed in the **Chem Substitution Input Table** below the **Formula Editing Table**. Using calcite ($CaCO_3$, with the possibility for 0.3 atoms of Mg substitution for Ca) as an example, enter zeros in all cells in the range **G8:AS8**, except for the following cells. Enter the simplest formula for calcite first, by entering **1** into cell **S8**, thereby indicating 1 atom of Ca, and **1** into cell **AN8**, thereby indicating 1 molecule of CO_3. This is the starting formula for calcite that will be used in the material and charge balance calculations for Options 2 and 4. Check to see that the mineral is electrically balanced by consulting cells **F5** or **AU8**, which should read zero.   Since there is a range of Mg substitution in this mineral (up to 0.3 atoms per Ca position), enter the upper limit for Ca (**1.0**) into cell **S8**, and the lower limit (1.0 – 0.3 = **0.7**) into cell **U8**. Enter similar information for Mg, by entering **0.0**, **0.3** and **0.0** into cells **P8:R8**.

Next enter the constraint equations and constraint constants into rows **31** and **32**, starting in cells **G31** and **G32**. The constraint equations refer to the atoms and numbers of atoms listed in cells **G9:P11**, and not to those listed in row **8**. A constraint equation for calcite would be, for example, **=J11+K11**, which would be entered into cell **G31**. The constraint constant is 1, because the sum of Mg and Ca atoms for this mineral must equal 1; so the number **1** should be

entered directly below the constraint equation, into cell **G32**. Another constraint equation and constant for calcite would be: **=2*(J11+K11)-2** entered into cell **H31**, and the constant **0** entered into cell **H32**, which describes charge balance (the valences of Mg and Ca times the number of atoms of each, minus the charge of 1 molecule of CO_3 equals zero). One can enter less than or equal to constraints and constants, or greater than or equal to constraints and constants in a similar manner into cells **O31:R32**.

In order to enter this formula into the program, it now is important to go to the "Start" sheet, run Option 6, and save the program. Option 6 will paste the number of atoms for the mineral into the correct position in the **Chem Substitution Input Table** found in rows **41:144**, and the constraint equations and constants into the correct position in the table found in rows **147:347**.

To alter the equations for a mineral that already is entered into the program, please follow these directions exactly. Using illite as an example, highlight and copy cells **E64:AS64**. Select cell **E8** by clicking on it, and under the **Edit** menu choose **Paste Special**, **Values**. Next copy cells **G186:R187**. Select cell **G31**, and under the Edit menu choose **Paste Special**, **Formulas**. Edit the mineral's formula and constraints as desired. Then go to the "Start" sheet, run Option 6, and save the program.

Typical chemical formulae for common minerals are listed in the "Mineral index" sheet. Ranges for mineral compositions can be found, for example, in Deer and others, 1992. Formulae in the "Input formulae" sheet should be checked prior to calculation to insure that they have not been altered by someone during previous calculations.

Theory Behind the Operation of HandLens

The calculation of Option 3 in HandLens, an option that distributes elements among minerals without material-balance or charge-balance constraints, is based on the definition for concentration. As an example, the concentration ($ppmBa_{Sample}$) of the trace element Ba in a sample containing potassium feldspar (Kspar) as the exclusive Ba-containing source is represented:

$$ppmBa_{Sample} = \%Kspar_{Sample} \times ppmBa_{Kspar} \times 10^{-2}. \tag{1}$$

It is trivial to calculate the concentration of an element in a mineral for a sample that contains only one mineral, or in a sample that is known to contain the element in just one mineral. The concentration of Ba in the sample ($ppmBa_{Sample}$) can be analyzed, for example, by inductively coupled plasma mass spectrometry (ICP-MS), and the weight percent of potassium feldspar in the sample ($\%Kspar_{Sample}$) can be determined by quantitative X-ray diffraction (for example, RockJock program; Eberl, 2003). If there are two Ba-containing minerals (for example, Kspar and muscovite, Musc) in a sample, however, then there no longer is a unique solution to the problem, because there are two unknowns (the concentrations of Ba in Kspar and in muscovite), but just one equation:

$$ppmBa_{Sample} = \left(\%Kspar_{Sample} \times ppmBa_{Kspar} + \%Musc_{Sample} \times ppmBa_{Musc} \right) \times 10^{-2}. \tag{2}$$

A second equation is added by analyzing a second sample that has the same concentration of Ba for each mineral, but that has different proportions of Kspar and muscovite. By extension, at least as many samples are required as there are different types of minerals in the samples to find a unique concentration for each element in each mineral.

The simultaneous equations could be solved by linear programming (for example, Braun, 1986), but in HandLens they are solved by using Excel's powerful Solver tool in the Material balance sheet. Using Equation (2) as an example, but applying the equation to at least two samples simultaneously, with $ppmBa_{Sample}$, $\% Kspar_{Sample,}$ and $\%Musc_{Sample}$ known from the

analysis of each sample, the ppm of Ba in Kspar and muscovite are varied by the Solver until the difference in the sum of the R^2's between the measured $ppmBa_{Sample}$ and those calculated from equations similar to (2) are minimized for all samples simultaneously, where:

$$\sum_{Sample1}^{SampleN} R^2 = \sum \left[Measured(ppmBa)_{SampleN} - Calculated(ppmBa_{SampleN}) \right]^2. \qquad (3)$$

HandLens will solve for concentrations of an element in up to 17 minerals and 400 samples simultaneously.

A similar approach is used for calculating the major element composition of each mineral (Option 2), but in this case the variability of the major elements can be constrained in Solver by the known compositional variability of each mineral, and by charge balance considerations. For this option, HandLens solves equations analogous to Equations 2 and 3 for all major elements in all minerals simultaneously, with the solutions being limited in Solver by constraints that have been entered into the Input formulae sheet.

Option 4 starts with mineral compositions calculated by Option 2, and then also varies the weight percents of the minerals and/or the elements, within the ranges given by the error values entered into the Input mineralogy and Input major chem sheets, to minimize the sum of the R^2's.

Tests of HandLens Using RockGenerator

The program RockGenerator.xls generates chemical compositions for imaginary or real samples from inputs of mineral chemical formulae and weight percent minerals. Weight percents for the minerals in each sample can be entered manually, or can be calculated automatically by assuming a random distribution of quantitative mineralogy for each sample. Trace element concentrations for each mineral also are entered either manually or automatically. The program's output of artificial sample chemistries then can be used to test the HandLens program, and to back calculate HandLens solutions for real samples. RockGenerator also will generate error,

either random (Gaussian), systematic, or both, for quantitative mineralogy and chemistry to further test HandLens. Instructions for using RockGenerator are included in the "Start" sheet of the RockGenerator program. Be sure to turn on the **Analysis ToolPaks** under the **Tools** menu in RockGenerator.

Tests of Option 1: analysis of data for the correlation table and plots

Option 1 does not require extensive testing, because it simply plots the input quantitative mineralogy, chemistry, and other data against itself. One should be aware that the correlations in the "Correlation Table" sheet may have a positive or negative slope, because the sign of the slope is not expressed in r^2. Regression equations in the "Manual plots" sheet can reveal chemical information concerning pure phases by extrapolating the linear regression to the pure mineral at 100 percent.

Tests of Option 3: assigning trace elements to the minerals

Ten minerals were chosen for analysis. Mineral-weight percents in each sample and trace-element ppm for each mineral were generated randomly and automatically in RockGenerator. The mineral weight percents and the overall concentrations of the trace elements for each sample then were entered into HandLens, which calculated the trace element concentrations for each mineral. These values then were compared with those that had been used in RockGenerator.

The first test was whether or not Option 3 in HandLens can calculate accurately concentrations of elements in minerals under ideal conditions. These conditions included the presence of as many samples (10) as minerals in the calculation, a random distribution of mineral weight percents among samples, no random or systematic error in chemical or mineralogical data, and constant compositions for the minerals. HandLens performed nearly perfectly under these conditions ($r^2 = 1.00$, with an intercept close to 0, and a slope of 1.00; fig. 1A). The same calculation was performed with 20 samples, with identical results; but with 9 samples, one less

than the minimum number required for a mathematically unique solution, the solution is somewhat degraded, with $r^2 = 0.94$, an intercept of 2.69, and a slope of 0.94 (fig. 1B).

The next test was to introduce ±10 percent Gaussian-distributed random error (0.10 is one standard deviation) into the ppm trace elements assigned to each sample. This error could be both measurement uncertainty and error in the assumption of a constant composition for each mineral. With 10 samples included in the calculation, the solution no longer is accurate ($r^2 = 0.35$; fig. 2A). For the same calculation, but with 20 samples, the accuracy improves considerably, with $r^2 = 0.84$ (Fig. 2B). The same calculation, with 20 samples having a 5 percent rather than a 10 percent error, gave essentially the same r^2 (0.85), indicating that the number of samples used in the calculation may be more significant than uncertainty in the measurement.

One can determine the accuracy of an Option 3 calculation by consulting the chart in the "Results3" sheet, which is near column **F**. This graph plots the measured concentration of an element for each sample versus the sample concentration calculated by summing the calculated concentrations of that element in all minerals for each sample. If a trace element's concentration varies widely for a given mineral, there will be considerable scatter in this regression for that element.

Figure 1. Tests of Option 3 using errorless chemistry (RockGenerator data) for 15 trace elements, for a 10 or 20 sample solution (A), and a 9 sample solution (B).
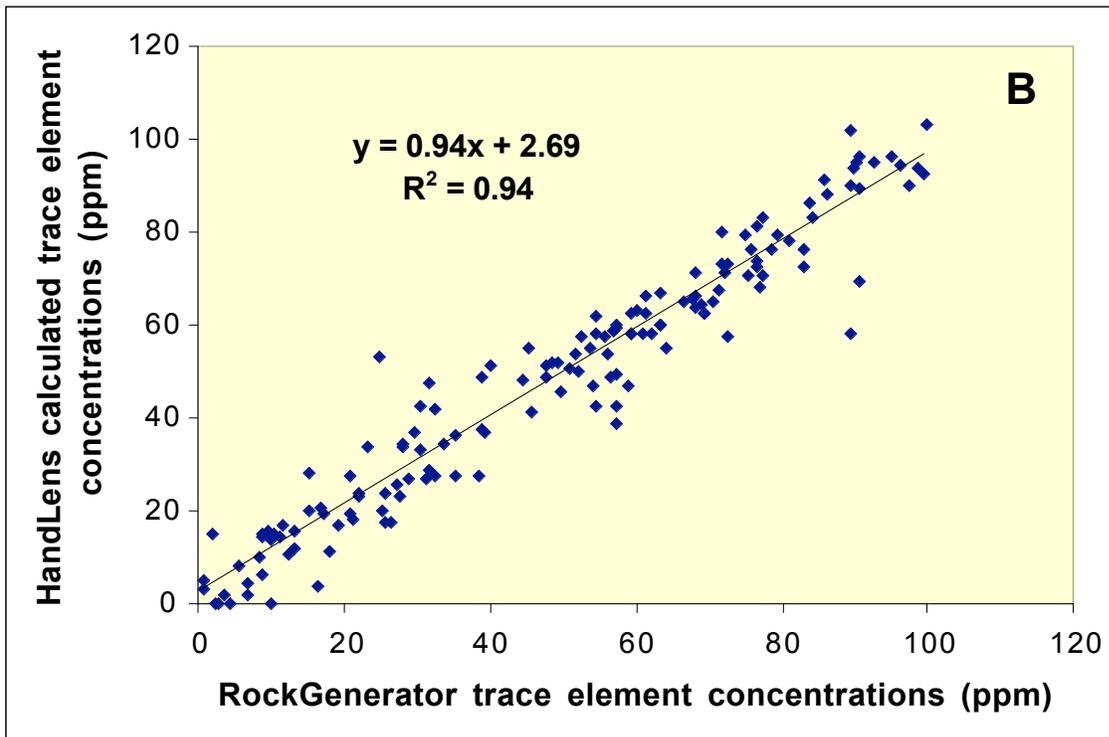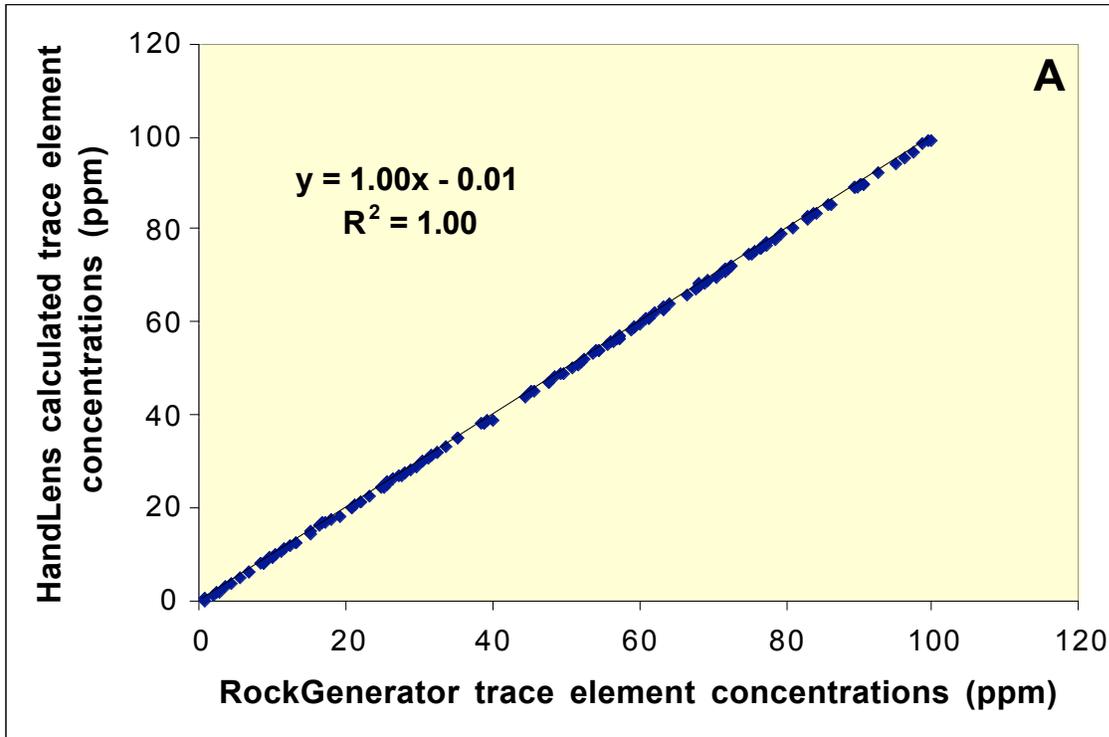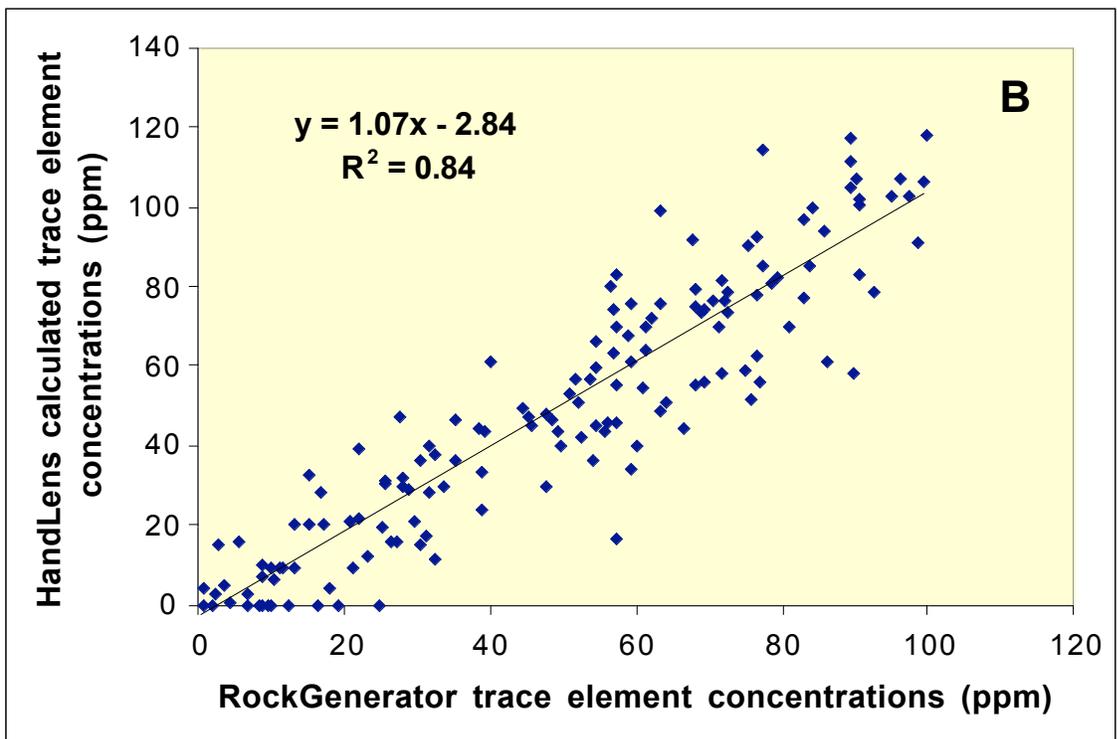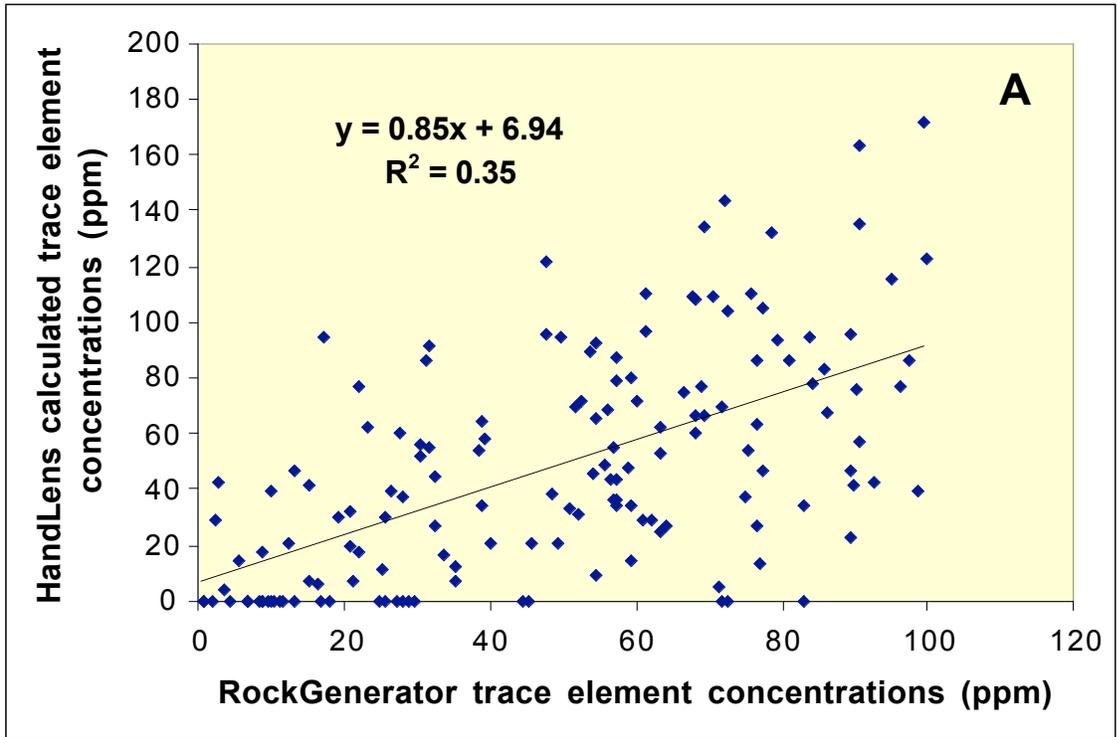
Figure 2. Tests of Option 3 for input trace element chemistries having 10 percent random (Gaussian) error for (A) a 10 sample solution, and (B) a 20 sample solution.

Tests of Option 2: calculation of mineral formulae

Ten minerals were chosen for analysis, eight of which had variable compositions (table 1). Ten sample chemical compositions were calculated by the RockGenerator program for randomly chosen proportions of the minerals. The sample chemistries and quantitative mineralogies were entered into HandLens to test whether the original mineral chemistries could be recovered accurately. Mineral chemistries are compared quantitatively by calculating bias, which is defined as the sum of the absolute difference in stoichiometry between input and output mineral chemistries. The number of atoms for each mineral was converted into structural formulae for presentation here. HandLens gave mineral chemistries that were identical to those entered into RockGenerator, with a bias sum of zero (table 1), demonstrating that Option 2 in HandLens works perfectly for errorless data.

Table 1. Test of HandLens Option 2 for a 10 mineral and 10 sample data set.

Mineral	RockGenerator Input & HandLens output formulae are identical	Bias
Quartz	SiO_2	0.00
Kspar	$K_{0.95}Na_{0.05}AlSi_3O_8$	0.00
Plagioclase	$Na_{0.85}Ca_{0.15}Al_{1.15}Si_{2.85}O_8$	0.00
Calcite	$Ca_{0.95}Mg_{0.05}CO_3$	0.00
Pyrite	FeS_2	0.00
Smectite	$(Al_{1.60}Mg_{0.30}Fe^{2+}_{0.10})(Si_{3.90}Al_{0.10})O_{10}(OH)_2(Ca_{0.20}K_{0.10})$	0.00
Illite	$(Al_{1.20}Fe^{3+}_{0.50}Mg_{0.10}Fe^{2+}_{0.20})(Si_{3.50}Al_{0.50})O_{10}(OH)_2(K_{0.80})$	0.00
Muscovite	$(Al_{1.80}Fe^{3+}_{0.20})(Si_{3.00}Al_{1.00})O_{10}(OH)_2(K_{1.00})$	0.00
Biotite	$(Fe^{3+}_{0.50}Mg_{0.50}Fe^{2+}_{2.00})(Si_{2.50}Al_{1.50})O_{10}(OH)_2(K_{1.00})$	0.00
Chlorite	$(Mg_{4.00}Fe^{3+}_{1.00}Fe^{2+}_{1.00})(Si_{3.00}Al_{1.00})O_{10}(OH)_8$	0.00
	TOTAL BIAS	0.00

The same calculation was made, but with 20 samples having a 6 percent random error (Gaussian distribution of random error with one standard deviation of 0.06) in both mineralogy and chemistry. The results of this calculation (table 2) were not perfect (bias = 1.93), but the chemical formulae for the minerals are close to the input values. The same calculation made with 10 samples gave almost double the bias (3.60).

Table 2. Test of HandLens Option 2 for a 10 mineral and 20 sample data set, having 6 percent random error for mineral and chemical data. Input formulae are in Table 1.

Mineral	HandLens output formulae (see table 1 for input formulae)	Bias
Quartz	SiO_2	0.00
Kspar	$K_{0.92}Na_{0.08}AlSi_3O_8$	0.06
Plagioclase	$Na_{0.80}Ca_{0.17}K_{0.03}Al_{1.17}Si_{2.83}O_8$	0.13
Calcite	$Ca_{0.93}Mg_{0.07}CO_3$	0.03
Pyrite	FeS_2	0.00
Smectite	$(Al_{1.69}Mg_{0.31}Fe^{2+}_{0.10})(Si_{3.71}Al_{0.29})O_{10}(OH)_2(Ca_{0.22}\ K_{0.16})$	0.65
Illite	$(Al_{1.05}Fe^{3+}_{0.49}Mg_{0.12}Fe^{2+}_{0.33})(Si_{3.57}Al_{0.43})O_{10}(OH)_2(K_{0.80}Ca_{0.04})$	0.49
Muscovite	$(Al_{1.72}Fe^{3+}_{0.28})(Si_{3.00}Al_{1.00})O_{10}(OH)_2(K_{0.90}\ Na_{0.10})$	0.36
Biotite	$(Fe^{3+}_{0.48}Mg_{0.43}Fe^{2+}_{2.07}\ Al_{0.02})(Si_{2.50}Al_{1.50})O_{10}(OH)_2(K_{1.00})$	0.17
Chlorite	$(Mg_{4.02}\ Fe^{3+}_{1.00}\ Fe^{2+}_{0.98})(Si_{3.00}Al_{1.00})O_{10}(OH)_8$	0.03
	TOTAL BIAS	1.93

Tests of Option 4: correction of systematic measurement errors for formulae

Ten minerals and 20 samples were chosen for analysis as above, but for this calculation a systematic error of 6 percent (true Si value x 1.06) was introduced in the weight-percent Si values to determine if this error could be corrected using Option 4. In this option, one or more of the chemical or mineralogical inputs is included in the Solver calculation and is varied within uncertainty limits set in the Input mineralogy and Input major chem sheets. Uncertainty limits for all minerals and elements were set to zero, except for Si, which was set to 0.10. Such a calculation could be used, for example, to correct inaccurate Si values that had not been measured directly, but calculated by difference. The calculation gave a bias from Option 2 of 2.28 for the uncorrected data, and a bias from Option 4 of 0.24 for the corrected data, indicating that the Option 4 was successful in this limited test.

Tests of Fe^{2+} calculation from total iron

Often chemical analyses do not distinguish between Fe^{3+} and Fe^{2+}, but instead report total iron as Fe^{3+}. HandLens offers the option of calculating Fe^{2+} from total iron as a part of the

Solver solution. This was attempted with 20 samples and the same mineral data set as was used above, except ferrous and ferric iron were added together and entered into the "Input major chem" sheet as Fe^{3+}. Cell **B20** was set to **1**. The resulting mineral formulae had a total bias of 3.44, and Fe^{2+} was not accurately assigned to the variable, Fe^{2+}-containing minerals. On the other hand, the same calculation, but with this option turned off (cell **B20** set to **0**), gave a bias of 16.4.

It was determined that the previous calculation was too complex because it contained 5 minerals that had variable amounts of Fe^{2+} (table 1). The calculation was simplified by removing smectite and illite. In this case, the assignment of Fe^{2+} was accurate, with a total chemical bias for the minerals of 0.28. With only illite removed, the bias was 0.69, and the Fe^{2+} assignment was accurate, except that the calculation missed the 0.10 atoms of Fe^{2+} in the smectite structure (table 1).

Other tests of HandLens

There is much more testing that could be done, but it is left to the reader's innovation to test HandLens solutions according to their particular analytical needs.

Applications of HandLens

With this program, the large amounts of chemical data that are being generated by multi-element analysis techniques can be put into a mineralogical context, and used to solve geological and environmental problems. We have used it, for example, to find the origin of arsenic in the Mancos shale (pyrite in our shale samples contains about 300 ppm As), of cadmium and zinc in soils from Nome, Alaska (these elements occur with muscovite, and therefore are not likely to be readily available for uptake by plants), and of arsenic in river sediments from New Jersey (arsenic is in the clay fraction, and therefore is less concentrated in stream sediments where the water runs fast and washes out the clay). If used intelligently and with discretion with excellent data, HandLens is an accurate and convenient tool for integrating chemistry and mineralogy.

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