APHID

A program for stoichiometric phase classification and quality analysis using least-squares and conversion to additive/exchange component.

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Introduction

APHID is a robust, automated program designed to perform phase classification and quality analysis using electron microprobe data. The source code for APHID is available in MATLAB (for users who would like to modify the program to suite their needs, and have access to MATLAB). A compiled executable is also available for Windows platforms. This manual will give a complete, practical overview of how to run APHID. Please see Steffen (2004) for a complete discussion of the theory and algorithms used in APHID.

Installation

APHID is distributed as a single folder (APHID) that has been compressed into a .zip file (APHID.zip). The folder contains this file (Manual.pdf), APHID.m, APHIDInput.txt, APHID.exe, mglinstaller.exe and four subfolders: The first folder (BackgroundFiles) contains the background files that describe the transformations required (Model data of Steffen, 2004). Any additional background files that you create or modifications to the default background file (MasterA.txt) should be incorporated into this folder. The second folder (InputData) contains example input composition files. There are three example input composition files (SingleTest.txt, ShortTest.txt, and LongTest.txt) and any additional compositional files that you would like APHID to consider should be stored in this folder. The third directory (Functions) contains all of the MATLAB functions that run APHID. These files will only be of interest to an experienced MATLAB user who would like to modify APHID. The fourth directory (Output) contains the output of the program. This folder is initially empty but APHID will store output files (LastSingle.csv, Bulk.csv, Mode.csv, and Endmembers.csv) to this location. Please note that APHID will overwrite these output files so if you would like to retain APHID output you will need to change the names or move the output files you would like to preserve. APHID.m is the MATLAB M-file that calls APHID, APHIDInput.txt is the text file that provides input information to APHID, and APHID.exe is the APHID executable for Windows platforms.

If you have access to MATLAB I suggest that you run APHID from the MATLAB prompt, however for Windows users, the executable APHID.exe is available.

If you will be using APHID.exe (Windows) the following additional installation steps are required. Execute mglinstaller.exe (included in the APHID distribution). This will open a command line window that will create two folders (bin and toolbox). Click return in this window to install these folders in the default location (the APHID distribution directory or {APHID}). The location of {APHID}/bin/win32 must be added to search path so that the dynamic linker can access the .dll files in these libraries. This can be done permanently by right clicking on the "My Computer" icon and then navigating to Properties/Advanced/Environmental Variables and adding {APHID}\bin\win32 to the system variable path. If the APHID directory is C:\APHID then you would add C:\APHID\bin\win32 to the start of the search path. Directories in the search path are seperated by semicolons. If you do not have access to the system variables (e.i. you are a NT user without root privileges) or you are not comfortable modifying the search path, then you can temporary add this directory to a command prompt session by typing "path={APHID}\bin\win32;%path%" in this case "path=C:\Aphid\bin\win32;%path%" which will append the directory to the front of the search path. If you permanently install the search path, APHID.exe can be run by simply double clicking on the APHID.exe icon. A commend prompt will open and run APHID.exe, print the results to the screen and close immediately. It is usually better to run APHID.exe from a existing command prompt by typing APHID in the command prompt from within the APHID distribution directory, which will allow you to view the results after the program is finished.

Interface

For users that are running APHID through MATLAB, APHID can be run by changing the working directory to the APHID installation directory and typing "APHID;" on the MATLAB command line. This will run the APHID.m script. The purpose of the semicolon is to suppress unnecessary output. For windows executable users, double click on the APHID.exe icon or type APHID while the command prompt is in the APHID distribution directory (see previous section for details). APHID.exe or APHID.m should not be moved from the APHID folder. The basic information required to run APHID is included in the APHIDInput.txt file. The structure of the APHIDInput.txt file, and all other input files is discussed in the following section.

Input

There are three files required to run APHID. The first is APHIDInput.txt that contains the basic information required for APHID. APHID will always look for a file with this name, located in the APHID directory. The second file is the data or composition file that is located in the InputData directory. The third file is the stoichiometric model file that is located in the BackgroundFiles directory. The structure of each of these files will be discussed in this section.

APHIDInput.txt

This is the APHIDInput.txt file that is shipped with APHID:

```
ShortTest.csv %Datafile
MasterA.txt %Background File
Total   %Calculate on the basis of Ratio or total Error
20  %Error Threshold
1 %PhaseCheck
```

This file has five lines and follows MATLAB style rules for comments (everything after a "%" in a line is not read by the program). The first line of this file contains the name of the file (located in the InputData directory) that holds the compositional information that will be classified by APHID, in this case ShortTest.csv. The second line is the name of the stoichiometric mineral model file (located in the BackgroundFiles directory) that will be used by APHID, in this case MasterA.txt. The third line will contain the statement "Total" or "Ratio" to indicate if APHID should calculate the difference between the original and stoichiometric model composition as Total or Ratio. If this line equals "Total" the program will compare the stoichiometric model to the stoichiometrically perfect analysis weight (total weight will equal 100%). For example, if a sample of quartz was being analyzed and the original analysis was 99.5% SiO_2 with all other oxides being below detection, the error would be .5 % (quartz should have a composition of 100 % SiO_2). If this line equals "Ratio" then APHID compares the ratios between the oxide components and the stoichiometric components. So in this case the error of the analysis would be 0 %. Essentially, this line controls whether or not you would like to the program to consider errors in the total weight of the analysis. **APHID does not compute errors related to adding unanalyzed components (in the current version of APHID H is the only**

unanalyzed component) to the analysis. The fourth line contains the error or residual threshold for phase classification. If the error or residual (calculated as Total or Ratio) between the original and stoichiometric model composition with the lowest residual (with permissible exchange components) is above this value then the phase classification is undetermined (see Steffen, 2004). The fifth line of this file should contain a value of 0 or 1. If the value is 1, then APHID will perform the PhaseCheck process on the data (see PhaseCheck section below).

Running APHID with the supplied APHIDInput.txt should produce a clean APHID run (no errors). The output (to screen) will first indicate that PhaseCheck has been run and there are no misclassifications, followed by the results of the modal analysis and finally the bulk composition analysis.

Input Composition File

This is the input composition file SingleTest.csv that came with APHID:

```
Si,Al,Fe,Mg,Ca,Na,K,Ti,H,Mn,Zn,MineralName
40.881,16.676,19.093,7.053,10.665,1.776,0.182,0.355,0,0,0,Amphibole
```

The input file comes in the form of comma-separated variable (.csv) file. In the .csv file, commas separate the columns of data and the rows of data are separated by carriage returns. Spreadsheet programs such as OpenOffice.org's Calc or Microsoft's Excel can read and output spreadsheet data into .csv format. The first row of the input file contains the labels for the columns. In this case the labels of the columns are the element in the analysis. **Although it is impossible to analyze H on the electron microprobe all APHID input data should include a column for H that has been set to zero**. APHID also allows extra columns of data, not associated with the mineral composition to be passed into the program through the input file. In this case the column MineralName is the user supplied mineral classification that is used by PhaseCheck to determine of if the phase classification performed by APHID agrees with the user supplied phase classification. In most cases APHID will be performing phase classification on unclassified analyses and a MineralName column will not be provided. Any extra columns of data supplied in the input file (such as a column for sample name) are made available as raw output (see raw output section below) and can be used by an experienced MATLAB programmer to develop post-processing routines.

The compositions of phases should be input as weight percent oxides. **Fe should be reported as FeO for all analyses. For stoichiometric mineral models in which Fe is Fe^{+3} or**

Fe_2O_3, APHID will automatically convert the analysis to a ferric basis. APHID does not support mixed ferrous/ferric mineral models, but this does not greatly inhibit phase classification. APHID only supports multiple oxidation states for Fe at this time.

If there is a single row of data in the input file, APHID performs a realtime phase classification and error analysis. If there is more then one row of data in the file, APHID performs batch processing, which includes modal and integrated bulk composition analysis. For a discussion of these operation modes, see Steffen (2004).

Stoichiometric Model Files

The formation of the stoichiometric model file requires some understanding of crystal chemical theory, especially as it applies to the formation of additive and exchange components and the permissible value for these components in a stoichiometric mineral analysis. If the following discussion stretches your understanding of crystal chemistry it is suggested that you review the example Model File (MasterA.txt) as well as Steffen (2004), (Spear, 1993; Thompson, 1982).

A listing of a complete stoichiometric model file is too long for inclusion in this manual. However this discussion assumes that also have the standard stoichiometric model file (MasterA.txt, located in the BackgroundFiles directory) open. MasterA.txt is best read using a basic text file viewer, such as Notepad, Emacs, MEdit (distributed with MATLAB) that allows for horizontal scrolling without word-wrap (These files will appear horribly garbled using Word). The data in this file can be separated into two sections: 1) General information that control phase classification such as: elements to consider, phases to consideration, information for transformation between weight and cation components, and definition of exchange components. 2) Model information that defines the specific information required for a stoichiometric mineral model.

General Information

The first line (K Al ….) of MasterA.txt contains the elements that APHID will expect to receive from the compositional analysis file. If all of these elements are not present in the input file then APHID will produce an error message. The sections of this datafile are divided by lines that start with an "*", line two is a division line. The input and model files can contain data for

more elements and this line provides a simple mechanism to add and remove elements from consideration.

Line three is a listing of the stoichiometric mineral models that will be compared to input compositions in order to perform phase classification. A mineral model for all of the phases listed on line 3 must be provided in the file below. If this is not the case the APHID will produce an error message. The file can contain stoichiometric models for phase not present on this line (they will be ignored by APHID) and this line provides a simple mechanism to add and remove phase from consideration for classification.

Lines five through eight contain information required to transform analysis from weight percent oxide to cations and back. Line five is the label (the element). Notice that there are two versions of Fe: Fe2 for phases FeO and Fe3 for Fe_2O_3. Line six is the atomic or gram formula weight of the oxide. Line seven is the number of cations present in the oxide. Line eight is the charge of the cation. These values should not have to be changed by the user, but additional elements may need to be added

Lines 10-29 define the additive and exchange components used in the model. The additive and exchange components are listed (additive components first) as columns and the cation and additive components (this time additive components last) are listed as rows. **In all cases additive components should have "Add" as the last three characters.** The lower left portion of this matrix is an identity matrix showing that the additive components listed as rows are equal to the additive components listed as columns. Above this portion of the matrix the relationship between the cation components (rows) and the additive components (columns) is defined. In the upper right portion of the matrix the exchange components (columns) are defined in terms of cation components. The following is a submatrix of the data in MasterA.txt showing this relationship.

SiAdd	MgAdd	AlAdd	CaAdd	DiTri	Fe-Mg	Ca-Mg	Tsch	KEden	Fe-Al	FeTsch	
1	0	0	0	0	0	0	-1	-1	0	-1	Si
0	0	1	0	2	0	0	2	1	-1	2	Al
0	0	0	0	0	1	0	0	0	1	-1	Fe
0	1	0	0	-3	-1	-1	-1	0	0	0	Mg
0	0	0	1	0	0	1	0	0	0	0	Ca
1	0	0	0	0	0	0	0	0	0	0	SiAdd
0	1	0	0	0	0	0	0	0	0	0	MgAdd
0	0	1	0	0	0	0	0	0	0	0	AlAdd
0	0	0	1	0	0	0	0	0	0	0	CaAdd

Relates additive components listed as columns to additive components listed as rows

Relates additive components listed as columns to cation components listed as rows

Definition of exchange components (rows) in the form of cation components (columns)

zero matrix (exchange components can not be defined in terms of additive components)

In APHID, all endmembers must be defined by the additive component and a single exchange component (not a combination of two or more exchange components). So although some of the exchanges present in MasterA.txt are redundant (non-independent), they are all required to uniquely define all endmembers in terms of a single exchange component. The use of a single exchange component to define each endmember greatly simplifies the determination of exchange bounds in the mineral models.

Stoichiometric Models for Individual Phases

Following the general section of the stoichiometric model file the stoichiometric models for individual phases are presented. The stoichiometric model files are separated by a line that starts with "*". The stoichiometric models present in MasterA.txt vary in complexity from phases such as aluminosilicate (As) and Quartz that define a fixed composition to phases such as amphibole that have large numbers of exchange vectors. In this description of the mineral modal file I will concentrate on a description of the model for plagioclase, which is relatively simple and is listed first in MasterA.txt and also below. A reference set of line numbers is added below for reference. Remember that the listing of these models follows the MATLAB comment rule (anything after "%" in a line is not read). **Use the models given as templates to create your own mineral models as required.**

		Line Number:
Plagioclase		1
6	%CationComponents	2
3	%AdditiveComponents	3
3	%ExchangeComponents	4
4	%EndMembers	5
3	%IronOxidation	6
8	%NumberOxygen_from_probe_analysis	7
8	%NumberOxygen_on_a_hydrous_basis	8
%Albite as additive		9

SiAdd	AlAdd	NaAdd	Plag	Na-K	Fe-Al				10
3.01	1.01	1.01	1.01	0.01	0.2	%upperlimit			11
2.99	0.99	0.99	-0.01	-0.20	-0.01	%lowerlimit			12
%									13
Si	Al	Na	Ca	Fe	K	SiAdd	AlAdd	NaAdd	14
1	1	0.3	1	10	10	100	100	100	15
						3	1	1	16
%									17
Anorthite		Albite	Orthoclase		Fe-Plag				18
0		1	0		0	%base			19
0		0	0		0	%SiAdd			20
0		0	0		0	%AlAdd			21
0		0	0		0	%NaAdd			22
1		-1	0		0	%Plag			23
0		1	-1		0	%Na-K			24
0		-1	0		1	%Fe-Al			25
%Si	Al	Na	Ca	Fe	K	Density			26
2	2	0	1	0	0	2.76	%Anorthite		27
3	1	1	0	0	0	2.62	%Albite		28
3	1	0	0	0	1	2.76	%Orthoclase		29
3	0	1	0	1	0	2.76	%Fe-Plag		30

The first line of the mineral model is the name of the mineral (Plagioclase). The second lines lists the number of cation components in the model (6). The third line lists the number of exchange components in the model (3). The fourth line lists the number of additive components in the model (3). The fifth line lists the number of endmembers in the model (4), this value should always be one greater then the value for the number of exchange components. The sixth line listed if oxidation state of Fe in the model (2); this value can be either 2 or 3. The seventh line lists the number of O's in the mineral formula when measured on an anhydrous basis, which is the number of O typically used when calculating the cations from a probe analysis (8). The eighth line lists the number of O present on a hydrous basis (8) or the total number of O's present. The next line is a comment line reminding you that albite will be the additive component used.

The next section (lines 10-12) defines the additive/exchange components used in the mineral model. The first line (SiAdd, AlAdd, …) lists the additive/exchange components. The additive components are listed first and the names of these components must match the names of the components listed in the general definition of additive/exchange components. The following two lines list the upper and lower bounds for these components. These values represent the

permissible bounds for the additive/exchange components given by the crystal chemistry of the phase. When these bounds are set it is best to set them to be slightly larger then theoretical considerations would dictate (e.g. the range of the Plag substitution from 1.02 to -.02 vs. a theoretical 1 to 0), which will minimize misclassification. The values of the additive bounds should bracket the additive endmember formula.

The next section (14-16) lists the cation and additive components (the additive components should be listed last and in the same order as they were listed on line 10) the weights assigned to these components (line 15) and the value of the additive components (line 16). In the least-squares process weighting controls how the residual or error is distributed between the elements. The additive components should be weighted relatively strongly (approximately 100 times more strongly then the cation components). This strong weighting will enforce stoichiometry additive/exchange components. Cation components should be weighted relative to their relative uncertainty but be aware that the least-squares process assigns error in an absolute sense. This can lead to very large relative changes for elements present in trace quantities. Therefore trace cations should be weighted strongly, perhaps even more strongly then the additive components in order to decrease the trace components relative error. H (not HAdd) should be weighted very weakly (suggest .001) in order to allow the least squares solution to fix the value of H to that defined in the mineral model. Line 16 defines the value of the endmember in terms of additive components, this value should match the chemical formula of the endmember.

The next section (lines 18-25) defines the endmembers in terms of the exchange components. The first line (18) lists the name of the endmembers while the next line (19) defines which endmember is the additive component. The column with a 1 marks the additive component. The following rows represent the additive and exchange components (in the same order as they were listed on line 10) and how the endmember proportions are defined in terms of the additive/exchange components. The rows that correspond to the additive components will typically be all zeros. If we look at the line for the Plag exchange (23), we can see that the value of the anorthite endmember is equal to the value of the Plag exchange while the value of additive endmember albite is decreased by the value of the Plag exchange.

The final section of the mineral model lines (26-30) defines the endmembers (rows) in terms of cations (columns). Note that the row and column labels are commented out and not

read by the computer. The cations should be listed in the same order given on line 14, and the endmembers should be listed in the same order as given on line 18. There is an additional column in this table that indicates the density (typically taken at STP) for each endmember. APHID must compute have the density of each phase in order to calculate the integrated bulk composition. For endmembers that are fictive (not present in nature), I suggest that you estimate the density using the density of the other endmembers. APHID calculates the density of solid solution phase assuming ideal volume mixing. Ideal mixing and possible errors in fictive endmembers still provide sufficient accuracy for calculation of the integrated bulk composition.

Output

The output of APHID depends on the mode under which APHID was run. If the input file contains data for a single analysis (e.g. SingleTest.csv) then APHID runs in realtime analysis mode and performs phase classification and error analysis. If the input file contains more then one analysis (ShortTest.csv, LongTest.csv) then APHID runs in batch processing mode and performs a model and a bulk composition analysis on the dataset.

Realtime Classification and Error Analysis

The purpose of realtime analysis is to confirm the phase analysis (most interactive microprobe users know the phase they are analyzing) and more importantly to provide information about the quality of the analysis. This allows the operator to determine if additional standardization or analysis is required. Realtime analysis occurs when there is a single analyzed composition present in the input file. The following is an example of realtime data that is output to the screen (Realtime results are also saved to LastSingle.csv in the Output directory). The results have been reformatted slightly to fit on the screen.

Phase Identified as:
Amphibole

K	Al	Si	Mg	Fe2	Ca	H	Na	Ti	Mn	Total	Total – H	
0.18	16.67	40.88	7.05	19.09	10.66	0	1.77	0.35	0	96.68	96.68	Original Weight
0.18	16.64	40.73	7.09	19.15	10.71	1.97	1.76	0.35	0.00	98.61	96.64	Model Weight
0.18	16.87	41.30	7.19	19.42	10.86	1.99	1.78	0.35	0.00	100.0	98.00	Perfect Weight
0.00	-0.03	-0.14	0.03	0.06	0.053	1.97	-0.01	0.00	0.00	2.31	0.34	Error Model
0.00	0.203	0.42	0.13	0.33	0.203	1.99	0.01	0.00	0.00	3.31	1.32	Error Perfect
0.03	2.98	6.20	1.59	2.42	1.7	0	0.52	0.04	0	15.54	15.54	Original Cations

0.03	2.98	6.19	1.60	2.43	1.74	1.99	0.51	0.04	0.00	17.55	15.55	Model Cations

The realtime analysis prints out information for all of the input elements, the calculated element H, the total of the analysis with H, and the total analysis without H. The seven rows are 1) The original composition, as input into APHID. 2) The model weight: The total of the model analysis minus H will equal the original analysis if the phase is anhydrous or the phase has a perfect total analysis weight. Otherwise this value will be slightly different then the original analysis total. This difference will be proportional to error in the total analysis weight. 3) The perfect weight (The total of the perfect weight always equals 100) as calculated using Total. 4) The error, residual, or difference between the original analysis and the model analysis. 5) The error, residual, or difference between the original analysis and the perfect weight analysis. 6) The values of the cations calculated from the original analysis. 7) The values of the cations calculated from the stoichiometric model (This value is same if calculated from either the model or perfect weight composition). This information provides the user with all the data required to evaluate the stoichiometric quality of the analysis.

Modal Analysis

Modal analysis is a post-processing technique applied to the raw APHID data that determines the number of analysis that were classified for each phase model, the modal percentage of each phase, and also returns the a list of analysis (row index into the input data) that were classified as each phase. The list is suppressed in the screen output but is available in the file output (Mode.csv) as well as the raw data output. Modal analysis is only preformed under batch processing mode (when there is more then one analysis in the input data).

Bulk Composition Analysis

Bulk composition analysis is a post processing technique applied to the raw APHID data that determines an integrated bulk composition for the analysis and also determines how elements are partitioned between the phases. Bulk composition analysis is automatically performed every time APHID is run in batch processing mode (more then one analysis in the input file). Bulk composition analysis output is sent to the screen, printed to the file Bulk.csv in

the Output directory, and is also available as raw data output. An example of bulk composition analysis output (using ShortTest.csv as input). The results have been reformatted slightly to better fit on the page.

K	Al	Si	Mg	Fe	Ca	H	Na	Ti	Mn	Zn	
0.78	19.60	33.51	3.33	16.59	4.25	2.06	1.24	18.21	0.43	0.00	Bulk Composition
0.00	0.00	21.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Quartz
0.00	11.92	12.32	9.49	21.48	12.95	0.00	0.00	0.00	24.36	0.00	Garnet
0.62	9.06	12.77	0.00	0.07	11.13	0.00	45.11	0.00	0.00	0.00	Plagioclase
0.00	27.88	7.90	4.95	7.54	0.00	10.39	0.00	0.26	38.13	100.0	Staurolite
13.82	15.74	10.59	-0.13	0.23	1.73	17.46	41.07	0.04	-0.01	0.00	WhiteMica
0.00	7.59	5.48	36.39	9.99	0.00	39.41	0.00	0.02	0.00	0.00	Chlorite
2.05	7.51	10.74	18.80	10.21	22.29	8.44	12.59	0.17	0.00	0.00	Amphibole
0.00	12.10	10.65	0.08	6.23	51.91	8.65	0.00	0.05	4.18	0.00	Epidote
83.51	8.20	8.54	30.28	8.63	0.00	15.65	1.22	0.51	4.36	0.00	Biotite
0.00	0.00	0.00	0.14	35.62	0.00	0.00	0.00	36.89	28.98	0.00	Ilmenite
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	62.06	0.00	0.00	Rutile

The first row of the data is the integrated bulk composition for this set of analyses. The subsequent rows depict how the elements are partitioned among the phases. There are some negative values present in this chart indicating that there are some negative compositions present in the data. The least squares technique does not specifically prohibit negative values and in all of the negative cases the original data was zero and the least squares transformation changed the compositions to negative values. The magnitude of these negative values can be decreased by weighting these components strongly. These negative values can be removed entirely by removing these cation and associated exchange components from the mineral models (e.g. example removing Mn and the MnTsch components from the WhiteMica model)

PhaseCheck

The purpose of PhaseCheck to provide the user with a mechanism to check the stoichiometric mineral models used for phase classification by comparing the phase as identified by the user with that calculated by APHID. PhaseCheck must be turned off when APHID is classifying unknown phases. PhaseCheck is turned off and on by changing the value of the fifth and final line of APHIDInput.txt (1 for ON, 0 for OFF). In order to run PhaseCheck the user must supply an additional column in the composition input file (MineralName) that contains the name of the phase. If the name of the phase for each analysis matches the classification

calculated by APHID for every analysis then PhaseCheck runs nearly silently, just printing to the screen that no misidentifications were discovered. If the calculated and user supplied phase classifications do not agree then PhaseCheck prints out information about the phase identified by the user and the phase identified by APHID. In the following example the MineralName column of SingleTest.csv was changed to "Plagioclase". PhaseCheck determined that the user supplied phase (Plagioclase) did not agree with the calculated phase (Amphibole) and printed out the following information. The information has been slightly reformatted to fit on the page.

```
----------Analysis 1----------
Calculated Phase is Amphibole
K     Al     Si     Mg    Fe2    Ca     H     Na   Ti    Mn  Total
0.18  16.67  40.88  7.05  19.09  10.66  0     1.77  0.35  0   96.68      Original
0.18  16.87  41.30  7.19  19.42  10.86  1.99   1.78 0.35  0   100.0000   Perfect
0.18  16.64  40.73  7.09  19.15  10.71  1.97   1.76 0.35  0   98.61      Model

SiAdd  MgAdd  CaAdd  HAdd  Fe-Mg  KEden  NaEden  Ca-Mg  Ti-Si  Mn-Mg Tsch   Components
8.10   5.10   2.10   2.10   7.10   1.10   1.10    0.10   2      2     1.75    UpperLimit
7.90   4.90   1.90   1.90  -0.10  -0.10  -0.10   -2.10  -0.10  -0.10 -0.50   LowerLimit
 8.00  5.00   2.00   1.99   2.43   0.035  0.51    -0.25   0.040 0     1.21    Value

User Phase is Plagioclase
K     Al     Si     Fe3    Ca     Na    Total
0.18  16.67  40.88  19.09  10.66  1.77  89.27   Original
0.1   16.60  44.96  21.46  14.51  2.26  100.00  Perfect
0.17  16.05  43.47  20.75  14.035 2.18  96.68   Model

SiAdd'  AlAdd  NaAdd  Plag  Na-K  Fe-Al  Components
3.10    1.10   1.10   1.02  0.02   0.20  UpperLimit
2.90    0.90   0.90  -0.02 -0.22  -0.02  LowerLimit
3.00    1.00   1.00   0.77 -0.01   0.80  Value
```

For misidentified analyses, PhaseCheck prints out the original, perfect (calculated by Total), and model (calculated by Ratio) values for the calculated and user supplied phase. PhaseCheck also prints out the values for the additive and exchange components as well as limits for these components. This information will help the user identify if the phase is misidentified due to errors in the stoichiometric mineral models (typically incorrect values for the additive/exchange limits) or if the user made a mistake classifying the phase. When PhaseCheck is run in batch mode it will print out this information for every misidentified analysis, but will allow APHID to continue execution.

Raw Output

The raw output of APHID is only available when the program is run using MATLAB (not using winAPHID.exe). **The use of the raw output of APHID requires a good understanding of MATLAB programming techniques**, especially an understanding of MATLAB cell arrays, MATLAB's abstraction of pointers. The use of raw output allows an experienced user to create postproccessing functions. The following is the output list APHID:

[data, mode, MineralList, ExtraData, ExtraLabel, BulkComposition]

"data" is the raw data output. data is a cell vector that will have a length that is equal to the number of analyses provided as input into APHID. Each index in this cell vector contains another cell structure (the analysis data structure) that holds all of the raw data available for that analysis. MineralList is a array of structures (one structure for each stoichiometric model that was identified in the analyses) that contains the key (location of useful information) into the data structure. Here is MineralList created during by a call to APHID in which SingleTest.csv was input:

```
MineralName: 'Amphibole'
     MineralNameLocation: 1
         ErrorLocation: 2
   CationOriginalLocation: 4
     CationOriginalOrder: {'K'  'Al'  'Si'  'Mg'  'Fe2'  'Ca'  'H'  'Na'  'Ti'  'Mn'}
   WeightOriginalLocation: 3
     WeightOriginalOrder: {'K'  'Al'  'Si'  'Mg'  'Fe2'  'Ca'  'H'  'Na'  'Ti'  'Mn'}
    WeightPerfectLocation: 8
      WeightPerfectOrder: {'K'  'Al'  'Si'  'Mg'  'Fe2'  'Ca'  'H'  'Na'  'Ti'  'Mn'}
        CationLocation: 6
          CationOrder: {'K'  'Al'  'Si'  'Mg'  'Fe2'  'Ca'  'H'  'Na'  'Ti'  'Mn'}
       AdditiveLocation: 9
         AdditiveOrder: {1x11 cell}
      EndMemberLocation: 5
        EndMemberOrder: {1x8 cell}
        WeightLocation: 7
```

WeightOrder: {'K' 'Al' 'Si' 'Mg' 'Fe2' 'Ca' 'H' 'Na' 'Ti' 'Mn'}

The length of MineralList structure array equals the number of different phases that were identified by APHID. In this case a single phase was identified (there was only 1 analysis) and MineralList only contains a single structure. MineralList provides the key into the data, the raw output. MineralList contains fields that end with location, this provides the location of that data in the analysis data structure. In this case typing the following command provides information about the model (stoichiometrically perfect) cations values for this analysis:

data{1}(MineralList(1).CationLocation)

Creates the result:

0.0352 2.9815 6.1913 1.6070 2.4343 1.7453 1.9998 0.5196 0.0405 0.0000

The following command can be used to display the order of the cations

MineralList(1).CationOrder

Creates the result:

'K' 'Al' 'Si' 'Mg' 'Fe2' 'Ca' 'H' 'Na' 'Ti' 'Mn'

Through the use of data and the MineralList data, APHID provides the raw data required for an experienced MATLAB user to develop postproccessing routine on the raw data created by APHID. For case where multiple phases are identified the data provided by mode can be used to find the indexes into the raw data that identify analysis that were classified as a particular phase.

A summary of data provided by MineralList:

MineralName: The name of stoichiometric model phase
MineralNameLocation: Location of mineral name in raw data
ErrorLocation: Location of sum of residual (calculated using Total or Ratio)
CationOriginalLocation: Location of original cation values
CationOriginalOrder: Order of original cation values
WeightOriginalLocation: Location of original weights (same in input)

WeightOriginalOrder: Order of Original weights
WeightPerfectLocation: Location of weights calculated by “Total”
WeightPerfectOrder: Location of weights calculated by “Total”
CationLocation: Location of stoichiometrically perfect cation values
CationOrder: Location of stoichiometrically perfect cation values
AdditiveLocation: Location of additive/exchange component values
AdditiveOrder: Order of additive/exchange component values
EndMemberLocation: Location of endmember proportion data
EndMemberOrder: Order of endmember proportion data
WeightLocation: Location of weights calculated by “Ratio”
WeightOrder: Order of weights calculated by “Ratio”

“mode” is the cell array that contains the same data that was output into Mode.csv, it is the output of the modal analysis. “mode” will be empty if APHID was run in realtime mode (there was only one analysis supplied in the input file). BulkComposition is a cell array that contains the same information that was output to Bulk.csv, and the description of the data is can be found in the previous bulk composition analysis section. BulkComposition will also be empty if APHID was run in realtime mode.

ExtraLabel is a cell array of strings that contains the column labels of any column supplied in the input file that were not explicitly used by APHID. ExtraData is a cell array of the data in these columns. The data supplied in ExtraLabel and ExtraData allow the user to pass information into the input file that can be used to postprocess the raw data. A good example of this would be the use of this data to separate the raw data based on sample name or sample location.

References

Spear, F. S., 1993. *Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*. Mineralogical Society of America, Washington.

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Thompson, J. B., 1982. Composition space: an algebraic and geometric approach. In: *Characterization of Metamorphism Through Phase Equilibria* (ed Ferry, J. M.) *Reviews in Mineralogy*, pp. 1-31, Mineralogical Society of America, Washington.