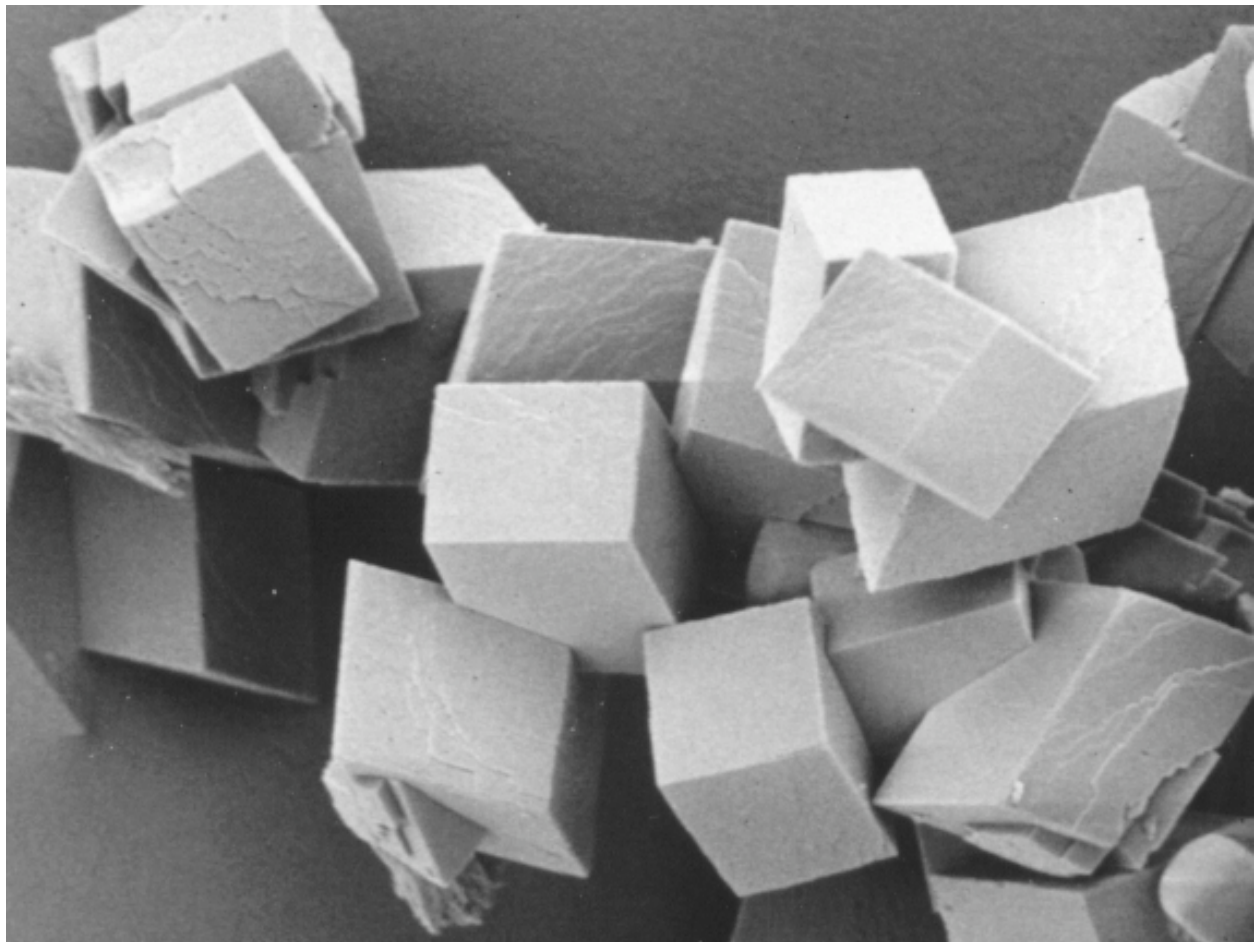# USER'S GUIDE TO GALOPER - A PROGRAM FOR SIMULATING THE SHAPES OF CRYSTAL SIZE DISTRIBUTIONS - AND ASSOCIATED PROGRAMS

U.S. Geological Survey

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Cover photo: Scanning electron micrograph (SEM) of synthetic calcite crystals that have undergone Ostwald ripening, followed by supply-controlled growth. The mean crystal diameter is 6.2 micrometers. Photo by Dan Kile, US Geological Survey.

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

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RTS-ID Number R2-0589

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And the clouds flew round with the clouds.

USER'S GUIDE TO GALOPER - A PROGRAM FOR SIMULATING THE SHAPES OF CRYSTAL SIZE DISTRIBUTIONS - AND ASSOCIATED PROGRAMS

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ABSTRACT

GALOPER is a computer program that simulates the shapes of crystal size distributions (CSDs) from crystal growth mechanisms. This manual describes how to use the program. The theory for the program's operation has been described previously (Eberl, Drits, and Środoń, 1998). CSDs that can be simulated using GALOPER include those that result from growth mechanisms operating in the open system, such as constant-rate nucleation and growth, nucleation with a decaying nucleation rate and growth, surface-controlled growth, supply-controlled growth, and constant-rate and random growth; and those that result from mechanisms operating in the closed system such as Ostwald ripening, random ripening, and crystal coalescence. In addition, CSDs for two types weathering reactions can be simulated. The operation of associated programs also is described, including two statistical programs used for comparing calculated with measured CSDs, a program used for calculating lognormal CSDs, and a program for arranging measured crystal sizes into size groupings (bins).

INTRODUCTION

GALOPER is an acronym for "Growth According to the Law of Proportionate Effect and by Ripening." The GALOPER computer program, written in Microsoft Macro language, calculates shapes for crystal size distributions (CSDs) formed by theoretical crystal growth mechanisms described in Eberl, Drits, and Środoń, 1998. Assuming that the theory is correct,

crystal growth mechanisms can be determined by comparing GALOPER calculated CSDs to those measured for natural samples.

This report describes how to obtain, install, and use GALOPER and associated programs. The section on the use of GALOPER provides descriptions and examples of calculations of various crystal-growth mechanisms in both open and closed systems. The use of associated programs is then described, followed by three simulation examples. Appendices provide summaries of inputs and results. The authors thank Alex Blum, Dana Bove, and Dan Kile for reviewing this report and the program.

An analysis starts with measurement of a sample's crystal size distribution. Such size distributions are measured by methods appropriate to the size of the crystals, methods which, for example, may include light microscopy (Kile and others, 2000), atomic force microscopy (Blum and Eberl, 1992), X-ray diffraction analysis (Eberl and others, 1996), transmission electron microscopy (Środo~ and others, 2000), or use of a simple ruler (Kile and Eberl, 1999). Generally, several hundred measurements, made in a systematic manner and by choosing the same crystallographic direction for all crystals, then are entered into the CrystalCounter computer program (CrysCntr.xls), which organizes data into group sizes (bin sizes), and calculates a size-frequency plot (CSD). The next step in the analysis is to use GALOPER to simulate the measured CSD by calculating one or more theoretical CSDs from crystal growth mechanisms that the sample may have experienced during its reaction history. The success of the simulation is determined by statistical test, either by the Kolmogorov-Smirnov test (KSTest.xls program) or by chi-square analysis (ChiSq.xls program). The measured CSD shape can reveal information about crystal growth history because the shapes of CSDs are reaction path dependent.

Computer Requirements

GALOPER will run under either IBM or Macintosh systems. Use of GALOPER requires Microsoft Excel, and an elementary knowledge of how to use the Excel program (pasting data, changing the axis on a chart, and so on). GALOPER works best on a computer having 16 megabytes or more of RAM. Ten 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 4 megabytes of disk space.

Although this program has been used by the US 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 Programs

The latest Windows and Macintosh versions of the software described in this report can be obtained by anonymous ftp from the Internet address: ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/mac_version (or .../pc_version)/GALOPER, from ddeberl@usgs.gov, or by writing D. D. Eberl, U.S. Geological Survey, 3215 Marine Street, Suite E-127, Boulder, Colorado, USA, 80303-1066.

A typical ftp session follows. Push return after each of these steps:

1. Log into your server

2. Type "ftp:// brrcrftp.cr.usgs.gov" . Do not type the quotation marks.

3. For the requested name, type "anonymous" .

4. For the password, type your e-mail address.

5. To find the PC version of GALOPER and associated materials, type "cd /pub/ddeberl/pc_version/GALOPER". To find the MAC version, type "cd /pub/ddeberl/mac_version/GALOPER". There is a space between cd and /pub...

6. Type "ls" to see the exact file names (the first character of "ls" is lower case L).

7. Type "bin" .

8. Type "get GALOPER.exe" or what ever file you choose to copy after the get command. The file name is case sensitive. The programs described in this manual are GALOPER, CrysCntr, ChiSq, KSTest, and Lognor, plus a file named Examp, and this instruction manual named GalopMan.

9. Type "quit".

Alternatively, one can use, for example, Netscape to open one of the following sites: ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/pc_version/ or ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/mac_version/ . The GALOPER folder can be opened by double clicking on the program's name, and the files downloaded by dragging them on to your hard disk.

<div align="center">Installation of Programs</div>

To install the programs, copy GALOPER, KSTest, CrysCntr, ChiSq, Lognor, GalopMan, and Examp onto your hard disk, and then open them by double clicking. The copies must retain the name of the original (i.e. GALOPER.xls) to run properly. If the files are compressed, both the Mac versions of the programs (compressed with the ".sea" extension) and the IBM versions (compressed with the ".exe" extension) should decompress automatically. If one has trouble expanding the programs, the latest version of the expander software can be downloaded free from the web at: www.aladinsys.com/expander . The programs are run using Microsoft Excel. 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.

<div align="center">USE OF GALOPER</div>

The GALOPER program is capable of simulating nucleation and growth for 1001 crystals. Crystal growth mechanisms are divided into two systems, Open and Closed. The open system is defined as a system in which matter is supplied to the growing crystals by a source other than the phase under study. In other words, material is being added to the crystalline phase. As an example, the growth in a sealed capsule of a crystalline phase from an amorphous phase would be considered to be an open system with respect to the crystalline phase until the amorphous phase is consumed. In the closed system, some of the crystalline phase itself dissolves to supply material to other crystals of the same phase that are growing during a ripening process; therefore, the mass of the

mineral is conserved (see Eberl, Drits, and Środo~, 1998). Closed system growth is calculated using crystals formed previously in the open system.

Each of these systems has an Input section and a Results section. To begin a calculation, the crystal growth mechanism is chosen by entering a number for the mechanism either in cell A6 for the open system, or in cell B6 for the closed system. (The open system must be run first to give the closed system a distribution of crystals to ripen.) Then, the parameters for the chosen mechanism are entered into the cells below, the program is started by pushing the appropriate start button, and the results of the calculation appear in column C for the open system and in columns D and E for the closed system. The CSDs are displayed in graphs, and the number of crystals for each group (bin) size (for use in a statistical test) appear in columns W and BP for the open system and closed systems, respectively. By making further adjustments to input parameters, one then can grow on top of previously formed crystals using, for example, other crystal growth mechanisms. In this manner, a theoretical CSD for a sample that may have experienced several crystal growth mechanisms can be simulated.

<p align="center">Crystal Growth in Open Systems</p>

Seven crystal growth mechanisms can be designated in the open system by entering the numbers below in cell A6. After the growth mechanism has been chosen, one looks down the left side of column A to find the input cells required for that mechanism. For example, if option 1 is chosen, cells A8 through A14 must be adjusted for calculation by this option, as well as cells A28 through A53, which must be adjusted for all options. The mechanisms described below are explained more fully in Eberl, Drits, and Środo~ (1998):

1.   *Constant-rate nucleation accompanied by surface-controlled growth.* During this mechanism, crystals are continually entering the system by nucleation at the same time previously nucleated crystals are growing according to the Law of Proportionate Effect (LPE):

$$X_{J+1} = X_J + \varepsilon_J X_J, \tag{1}$$

where X_J is the linear crystal dimension after J calculation cycles, and ε_J is a random number that generally varies between 0 and 1. The slow step in the process is how fast the crystal can grow

given an ε_J that varies between 0 and 1 and an unlimited supply of reactants. Growth is not limited by the supply of reactants to the crystal surface. Therefore, the growth that accompanies the nucleation is termed surface-controlled.

The input section for the open system should be set up as is shown in Figure 1. To run option 1, set the indicated cells to the following values:

Set cell A6 = 1. This chooses constant-rate nucleation and growth as the crystal growth mechanism.

Set cell A8 = 1. This is the size of the critical nucleus, which is the size of crystals that come in to existence during nucleation. The units normally are nanometers, which are the units generally used throughout the calculations. The size of the critical nucleus could be calculated for a given mineral from a knowledge of surface energies and mineral solubilities (see Kile and others, 2000), but, generally, this input is an educated guess, variations in which do not greatly affect the calculations.

Set cell A10 = 200. This input means that 200 1-nanometer (nm) crystals will nucleate during each calculation cycle while previously nucleated crystals grow by LPE. Because there are 1001 possible crystals, there will be 1001/200 = 5 nucleation cycles.

Push the "Start" button in Column A, near cell A70. The results appear in column C, which could show for this example a mean of 2.68 nm, an alpha of 0.772, and so on. Results may differ slightly from these results because there is an essential randomness to the calculation (see equation 1). The open system graph in column C in the program shows that the CSD has the asymptotic shape (the blue curve with square symbols) typical for this growth mechanism. The solid, red curve in the chart is the theoretical lognormal curve calculated from the data. The scale for the graph can be changed by double clicking on the x-axis.

To try another calculation using Option 1, set cell A10 = 90. Push the "start" button. The mean size in cell C3 will be approximately 14, but cell C11 will indicate that not all of the crystals have been included in the calculation because the group (bin) size was not large enough (due to space limitations in the program) to collect the largest crystals into groups. With a group size of 1,

only crystal sizes <101 will be counted. It is not necessary to redo the calculation. One simply can replot the data using a larger group size. This is done by setting cell A45 = 2 to replot the data, and cell A47 = 5 to choose a group size of 5. The program now will count all crystals with sizes <505. Start the calculation: now cell C11 indicates that all of the crystals have been counted, with a mean close to 17 in cell C3. Then, reset cell A45 = 1, cell A47 = 1, and cell A10 = 200, and repeat the first calculation.

2. *Constant-rate nucleation accompanied by supply-controlled growth.* This mechanism is the same as number 1, except that the rate of LPE crystal growth is limited by the supply of reactants to the crystal surface. The $\varepsilon_J X_J$ term in equation (1) becomes $v_J \varepsilon_J X_J$, where v_J is a fraction that is a function of the volume available during each growth cycle for the growth of each crystal (see in Eberl, Drits, and Środoń, 1998). The inclusion of a small fraction, v_J, in the calculation has the mathematical effect of decreasing the range of values for ε_J.

It may be unusual to have a system that is nucleating while crystals are growing by supply-controlled rather than by surface-controlled growth. Nevertheless, this option is included in the program to complete the framework.

Set the open system input to that of figure 1. Then, for this mechanism:

Set cell A6 = 2 to choose this option;

Set cell A8 = 1 for the size of the critical nucleus;

Set cell A10 = 200; and

Set cell A24 = 5000. This cell controls how much volume is available for crystal growth during each calculation cycle, in this case 5×10^3 nm^3. The total volume for all of the crystals during the previous calculation during which 200 crystals were nucleated per cycle was, from cell C19, approximately 5.3×10^4 nm^3. Generally, cell A24 should be set to 10 times less than the total system volume. The result of the calculation gives a mean of about 1.8, smaller than that found for the similar calculation done previously using option 1.

3. *Decaying-rate nucleation accompanied by surface-controlled growth.* Here new nuclei enter the system at a decreasing rate, and then grow by surface-controlled, LPE growth.

Setup the open system input section as is shown in figure 1. Then set:

Cell A6 = 3 to choose this mechanism;

Cell A8 = 1 to set the size of the critical nucleus;

Cell A16 = 0.90 to set the probability for nucleation. This input means that approximately 90% of the possible 1001 crystals, or approximately 900 crystals, will nucleate during the first calculation cycle. During the second cycle, 90% of the remaining 101 crystals, or about 90 crystals, will nucleate, while the initial 900 crystals grow one step by LPE, and so on.

Start the calculation. The calculated mean will be about 3.2 if the program went through four calculation cycles (see cell C15). However, the mean may differ from this value if, due to the probabilistic nature of the calculation, fewer or more calculation cycles were involved. The shape of the CSD is lognormal, rather than the asymptotic shape realized by the previous constant-rate nucleation and growth options.

4.   *Decaying-rate nucleation accompanied by supply-controlled growth.* This mechanism is the same as number 3, except that the rate of crystal growth is limited by the supply of reactants to the crystal surface.

To run this option, set the inputs as shown in Figure 1. Then set:

Cell A6 = 4 to choose this option;

Cell A16 = 0.90 to give the probability for nucleation; and

Cell A24 = 5,000 to give the growth volume allowed per cycle.

Start the calculation, and if the program runs for four calculation cycles, the mean will be about 2.2, with a lognormal shape for the CSD.

5.   *Surface-controlled growth.* Surface-controlled growth occurs according to equation 1, but without simultaneous nucleation.

To run this option, set the inputs as in figure 1. Then set:

Cell A6 = 5 to choose this option;

Cell A18 = 1 to choose the starting size for all 1001 crystals;

Cell A20 = 2 to indicate that the calculation should continue to a specified mean size, rather than to a certain number of calculation cycles; and

Cell A22 = 10, which is the mean size that is specified.

Push the "start" button. The lognormal CSD that results has a mean of about 11.6.

6.   *Supply-controlled growth*. Supply-controlled growth occurs according to the modified form of the LPE discussed in number 2 above, without simultaneous nucleation.

To run this option, set the inputs as in figure 1. Then set:

Cell A6 = 6 to choose this option;

Cell A20 = 2 to calculate to an approximate mean size;

Cell A22 = 15 to specify a mean size of 15;

Cell A24 = 30,000, which is a volume available for each growth cycle that is approximately 10 times less than the total volume of the system given by the previous calculation in cell C19; and

Cell A28 = 0. Option 6 does not have a shape of its own, but rather adopts the shape of a previously formed CSD. Therefore, the crystals formed during the previous calculation for option 5 are preserved by entering a zero in this cell, and crystal growth by option 6 proceeds on top of the previously formed crystals.

Push the "start" button. The resulting mean will be about 15. Notice that growth was considerably slower than in the previous calculation (Option 5) because the volume available during each growth cycle is limited. Furthermore, the growth rate slows as the mean advances due to the cubic relation between crystal radius and volume (that is, more material is required to advance the diameter as mean size increases). If one needs to calculate a large change in mean size by this mechanism, then a minus number (for example, -10) can be entered in cell A24. The program then makes a volume available for growth during each calculation cycle that is always 10 times less than the total volume of all the crystals during the previous growth cycle. Use of a minus number speeds the calculation. If minus 100 (-100) is entered in cell A24, then the volume available is 100 times less than the total system volume.

7.   *Random growth.* Crystal growth occurs by the addition of random amounts of material to crystal surfaces, according to the formula:

$$X_{J+1} = X_J + \varepsilon_J. \tag{2}$$

If option 7 is chosen starting with crystals that are all the same size, then, according to the Central Limits Theorem, a Gaussian distribution will result (equation 2). However, option 7 is used here to grow on top of the previous distribution formed by option 6 (and 5) in the example above. Set the open system input to that of figure 1; and

Cell A6 = 7;

Cell A20 = 2 to calculate to a certain mean size;

Cell A22 = 20, which is the mean size;

Cell A28 = 0 to preserve the previous distribution of crystals upon which the currently chosen mechanism will grow. The mean size that results is about 20, but the big change is in the variance (β^2), which has decreased by one-half.

LPE weathering.   This option runs the LPE (equation 1) in reverse, subtracting $\varepsilon_J X_J$ from the previous crystal size rather than adding it. To run this option, first calculate a distribution that is to be weathered. Then set cell A6 = 5 and cell A65 = 1. The character of the weathering can be changed by decreasing system variability by setting cell A33 to 0.1, for example, rather than to

1.0. This setting has the same effect as changing the dissolution mechanism from surface-controlled to supply-controlled. One can weather the CSD calculated above by setting cell A28 = 0, cell A20 = 1 to weather for a specified number of cycles, and cell A22 = the <u>total</u> number of cycles (see cell C15 for the number of cycles already completed, and enter a larger number into cell A22).

McCabe's Law growth.   This mechanism simply adds a constant linear amount to the diameter of each crystal from a previously calculated CSD. First calculate a CSD. Then set A6 = 5, A28 = 0, and enter the desired increase in mean size in cell A67.

Proportionate growth.   This mechanism multiplies the linear dimension of each crystal by a constant. First calculate a CSD. Then set A6 = 5, A28 = 0, and enter the desired constant in cell A69.

<center>Crystal Growth in Closed Systems</center>

The closed system works on the results of the open system calculation. First calculate a CSD in the open system by using the settings in figure 1, and pushing the start button for the open system. This calculation results in a mean size of about 2.6. This is the CSD that will be ripened by closed-system calculations. Four crystal growth mechanisms can be designated by entering the following numbers in cell B6:

1. *Ostwald ripening with automatic advance of critical diameter.* During this mechanism, crystals having sizes smaller than that of the critical diameter dissolve, supplying material for the growth of crystals having sizes greater than that of the critical diameter. Crystals having the size of the critical diameter neither dissolve nor grow, but are in equilibrium with the solution. As the mean size of the sample increases, the size of the critical diameter also increases. The equation used for the change in radius (r) with number of calculation cycles (t, or time) for diffusion-controlled Ostwald ripening is:

$$\frac{dr}{dt} = \frac{K}{r}\left(\frac{1}{r*} - \frac{1}{r}\right) \tag{3}$$

where K is the rate coefficient and r* is the critical radius.

The input section for the open system should be set up as is shown in figure 2. To run option 1, set the indicated cells to the following values:

Cell B6 = 1 to choose this option;

Cell B8 = 2 to ripen to a certain mean size, rather than to a certain number of calculations cycles, or to a fraction of material passing through solution, or to a certain number of crystals remaining in the system;

Cell B10 = 5, which is the desired mean; and

Cell B12 = 1 for Ostwald ripening by diffusion control, which seems to be the prevalent mechanism, rather than by surface control.

The other important parameter is K, the rate coefficient, which needs to be set to larger values if larger crystals are ripened. If K is too large, a noisy distribution may result. In this example, since the crystals are small, set B24 = 1. The results of the calculation will show a mean of about 5.1, with about 250 crystals remaining in the system. The variance (β^2) has decreased from the starting value; the mode of the distribution has moved to the right of the theoretical lognormal curve; and about 15% of the original material has passed through solution once (see cell E5 for fraction of core volume dissolved). Some material passes through solution more than once, and cell E7 gives the fraction of the total mass that has passed through solution.

2. *Ostwald ripening to completion with a constant critical diameter.* This mechanism is the same as number 1, except that the size of the critical diameter is fixed, rather than increasing in size as the mean size increases, and all crystals having sizes smaller than this diameter eventually dissolve completely.

3. *Ostwald ripening for a fixed number of cycles at a constant critical diameter.* This mechanism is the same as number 2, except that ripening proceeds at a fixed critical diameter for a specified number of cycles. To run this options, enter 3 in cell B6, the type of ripening in cell B12, the size of the critical diameter in cell B14, and the number of calculation cycles in cell B16.

4. *Random ripening*. During this mechanism, crystals dissolve randomly with respect to size, supplying material for the growth of other crystals. The crystals that dissolve do so completely.

If the user wants to ripen the previously formed distribution (number 1 above) by random (non-Ostwald) ripening, set cell B22 = 0 to preserve the previously Ostwald ripened distribution, and then subject it to random ripening. Alternatively, the user could randomly ripen the same distribution that was Ostwald ripened, letting the same fraction of material (15%) pass through solution. To do this, set:

Cell B6 = 4 to choose random ripening;

Cell B22 = 1 to clear the old distribution and start fresh with the previously calculated open system CSD; and

Cell B18 = 0.15 to set the probability for particle dissolution. The distribution calculated previously in the open system is ripened randomly, and the results show that whereas 15% of the mass passing through solution leads to a mean of about 5 for Ostwald ripening, it leads to a mean of about 2.7 for random ripening.

Crystal coalescence option. During this mechanism crystals simply are cemented together without dissolution. Starting with the randomly ripened distribution calculated above,

Set cell B6 = 3; and

Set cell B14 = .01. A small number is entered as the critical diameter so that Ostwald ripening does not occur during the calculation. The critical diameter is fixed at a value less than that of any of the crystals, so there is no dissolution.

Set cell B16 = 2 which is the number of coalescence cycles to be calculated.

Set cell B44 = 0.5, which is the probability for coalescence.

Set cells B47 and B50 = 0. Various rules can be applied to the coalescence.

This calculation gives a mean of 5.8, with 444 particles remaining in the system.

Surface area-controlled weathering option. This option is actually an open-system process, because material leaves the system. It is included under the closed system heading for

convenience, because it is similar to Ostwald ripening. During this type of weathering, the rate of

dissolution of crystals is controlled by how far the crystal's radius differs from that of the critical

radius (see equation 3). The option is chosen by setting cell B6 = 3, B55 = 1, and B57 = 1.

Starting the program causes crystals calculated previously in the open system to be "ripened"

using a critical radius that is larger than the radius of any of the crystals, so that all of the crystals

Figure 1. Sample inputs for open system.

INPUT OPEN SYSTEM:
OPEN SYSTEM OPTIONS:
(1 = CONST-RATE NUC., SUR-CONTROLLED GROWTH; 2 = CONST-RATE NUC., SUPPLY-CONT. GROWTH; 3 = DECAYING RATE NUC., SUR-CONTROLLED GROWTH; 4 = DECAYING RATE NUC., SUPPLY-CONTROL; 5 = SURFACE-CONTROLLED GROWTH; 6 = SUPPLY-CONTROLLED GROWTH; 7 = RANDOM GROWTH)
1
OPTION 1, 2, 3 & 4:   SIZE OF CRITICAL NUCLEUS:
1
OPTION 1 & 2:   CRYSTALS TO NUCLEATE PER CYCLE (1 TO 1001):
200
NUC. ON PREV CSD? (0 = NO, OR GIVE NUMBER OF NUCLEI; 1ST RANDOMIZE USING CELL A14)
0
RANDOMIZE CRYSTAL SIZES? (0 = NO; 1 = NOW; 2 = AFTER EACH CALCULATION)
0
OPTION 3 & 4:   PROBABILITY FOR CRITICAL NUCLEUS FORMATION (0 TO 1):
0.9
OPTION 5, 6 & 7:   STARTING DIAMETER (ACTIVE IF A28 = 1)
1
CRITERIA (1 = TO NUMBER OF CYCLES; 2 = TO MEAN)
2
ENTER TOTAL NUMBER OF CYCLES OR MEAN:
10
OPTION 2, 4 & 6:   VOL TO BE ADDED/CYC (ENTER VALUE, OR -10 FOR AUTO ADVANCE)
-10
REDUCE VOL AVAILABLE BY GROWTH VOL? (0 = NO; 1 = INCLUDING NUC.; 2 = AFTER NUC.)
0
ALL OPTIONS: CLEAR OLD DATA? (1=YES):
1
TOTAL NUMBER OF CRYSTALS (1001 MAX)
1001
EPSILON VARIATION (0 TO 1):
0
1
CRYSTAL SHAPE (1 = SPHERE; 2 = CUBE; 3 = ILLITE LAYER)
2
MINERAL DENSITY (G/CM^3; FOR CALC. OF SPEC. SUR. AREA)
2.71
RATE COEFICIENT (Set at 1):
1
COLLECT OPEN FREQ? (0 = NO; OR GIVE NUMBER OF ITERATIONS; OPTIONS 1,3,5,7 ONLY)
0
UPDATE SCREEN? (1=YES):
0
PLOTTING: GIVE PLOT? (0 = NO; 1 = YES; 2 = NOW):
1
GROUP SIZE (CANNOT CHANGE FOR ITERATED CALC.):
1
CLEAR CHART? (1=YES):
1
DO NOT COUNT CRYSTALS LESS THAN: (usually 0.5)
0.5
HOW TO COLLECT DATA (0 = AT CENTER OF GROUP; 1 = AT TOP; -1 = AT BOTTOM): (use 0)
0
ITERATION OF OPEN & CLOSED SYSTEMS:
CONT. WITH CLOSED SYSTEM? (1=YES):
0
ITERATE CLOSED SYSTEM? (0 = NO; OR GIVE NUMBER OF ITERATIONS):
0
COLLECT RIPENED CRYSTALS (1 = YES):
0
PASTE RIPENED CRYSTALS INTO OPEN SYSTEM? (1=YES)
0
OTHER OPTIONS:
LPE WEATHERING? (USE OPTION 5; 1 = YES):
0
ADD CONSTANT TO DIST = MCCABE'S LAW GROWTH (0 = NO; OR GIVE CONSTANT; USE OPTION 5)
0
MULT DIST BY CONSTANT = PROPORTIONATE GROWTH (0 = NO; OR GIVE CONSTANT; USE OPTION 5)
0

Figure 2. Sample inputs for closed system.

INPUT CLOSED SYSTEM:
RIPENING OPTIONS:
(1 = OSTWALD RIPENING WITH AUTO ADVANCE OF CRITICAL DIAMETER;
2 = RIPEN TO COMPLETION AT CONSTANT CRITICAL DIAMETER;
3 = FIXED NO. CYC. AT CONSTANT CRIT. DIAM.; 4 = RANDOM RIPENING)
1
OPTION 1: RIPEN TO # OF CYC. (1), MEAN (2), FRAC (3), OR # OF CRYSTALS (4):
2
RIPEN TO THIS # OF CYCLES, MEAN, CORE FRAC. OR # CRYSTALS:
5
OPTIONS 1,2,3:   DIFFUSION (1) OR SUR. (2) CONTROLLED RIPENING? (Use 1)
1
OPTIONS 2,3:   SIZE CRITICAL DIAMETER:
0
OPTION 3:   NUMBER OF CYCLES.:
0
OPTION 4:   PROBABILITY FOR RANDOM DISSOLUTION
0.5
DISSOLVE ONLY < THIS SIZE (0 = DISSOLVE ANY SIZE)
0
ALL OPTIONS: CLEAR OLD DATA? (1=YES):
1
RATE COEFICIENT:
1
CRYSTAL SHAPE (1 = SPHERE; 2 = CUBE; 3 = LAYER)
2
FRACTION DISSOLVED PREVIOUSLY:
0
UPDATE SCREEN? (1 = YES):
0
PLOTTING: GIVE PLOT? (1 = YES; 2 = NOW)
1
GROUP SIZE (CAN NOT CHANGE FOR ITERATED CALC.)
1
CLEAR CHART? (1=YES):
1
DO NOT COUNT CRYSTALS LESS THAN: (usually 0.5)
0.5
PASTE COLLECTED CRYSTALS INTO OPEN SYSTEM?:
(O = NO, OR GIVE 1001 DATA SET = 1, 2, 3...)
0
CRYSTAL COALESCENCE: (USE OPTION 3; SET A14 TO SMALL NO.)
CRYSTAL COALESCENCE? (0 = NO; OR GIVE PROBABILITY)
0
WHAT SIZE IS INITIAL COALESCED CRYSTAL?
(0 = ANY DIAM; OR ONLY GREATER THAN ENTRY)
0
WHAT SIZE IS SECOND COALESCED CRYSTAL?
(0 = ANY DIAM; OR ONLY GREATER THAN ENTRY)
0
CRITERION FOR VOLUME MATCH (usually 10)
10
OTHER OPTIONS:
SURFACE-AREA CONTROLLED WEATHERING (1 = YES; USE OPTION 3):
0
DEGREE OF UNDERSATURATION (0<VALUE<10^6; use 1)
1

dissolve according to equation 3. The critical radius is calculated automatically as the maximum crystal size in the distribution times the degree of undersaturation, which is the value entered into cell B57. During this type of weathering, the mean size increases because the finest particles dissolve the fastest.

Iteration during Simulation of Ostwald Ripening

It was stated in the discussion of Closed System Option 1 (Ostwald ripening with automatic advance of critical diameter) that only 250 crystals remained from an initial number of 1001 crystals if 15% of the volume of the sample passed through solution once. For longer ripenings, so few crystals remain in the system that it may not be possible to calculate accurate CSDs. For these situations, the ripening calculation is iterated, starting with the open system.

As an example, set up the open system input as is shown in figure 1, and calculate the open system CSD. This calculation will produce an asymptotic CSD having a mean of about 2.6. Next, ripen this distribution by setting up the closed system input as is shown in figure 2. Make the following changes to this input: ripen to a mean size of 10 by setting cell B8 = 2 and B10 = 10. Set the rate coefficient in cell B24 = 10 to speed the calculation. The calculation will yield a mean size of about 10.4, with a very "noisy" CSD shape shown in the chart. The CSD is noisy because there are only about 40 crystals left in the system.

The CSD can be made less noisy by repeating the same calculation many times. Even though the program settings for each calculation are exactly the same, the calculation is not exactly the same each time due to the randomness built into (and essential to) the open system. This randomness permits the iterative approach, during which frequencies are collected at the end of each iteration, are added together for each group size, and then are divided by the number of iterations at the end of the calculation to determine the final CSD.

To iterate the calculation:

Set cell A58 = 10 to iterate the calculation 10 times. Start the calculation. The result gives a smoother CSD that is now calculated from about 400 rather than from 40 crystals. When using

this option, the data can not be replotted using a different group size. The iterated frequencies will be plotted as long as cell A58 > 0; otherwise, the CSD for the last iteration will be plotted.

Rather than collecting only frequencies, the crystals themselves also can be collected from each iteration by setting cell A60 = 1. These collected crystals can then be pasted into the open system for plotting and/or for further growth by setting cell B41 > 1. Entering a "1" in this cell will paste the first thousand collected crystals into the open system, a "2" will paste the second thousand, and so on. In addition, the ripened crystals from the last iteration can be pasted into the open system by setting cell A62 = 1. As was discussed above, the results of the open system automatically are pasted into the closed system at the start of each closed system calculation unless the former closed system data are saved by setting cell B22 = 0.

USE OF ASSOCIATED PROGRAMS: CrysCntr, ChiSq, KSTest, Lognor, and MudMaster

The program CrystalCounter (CrysCntr.xls) organizes size measurements into groups, and calculates CSD parameters. These parameters include:

1. The mean of the sizes $= \sum Xf(X)$, where f(X) is the frequency of group size X;

2. The mean of the natural logarithms of the sizes $= \alpha = \sum \ln(X)f(X)$; and

3. The variance of the natural logarithms of the sizes $= \beta^2 = \sum (\ln X - \alpha)^2 f(X)$.

The program is run first by clearing column B in CrysCntr.xls, then by entering the raw size measurements in column B (the sample name in cell B1 and the data starting in cell B2), the group size in cell A8, and then by pushing the "start" button. Generally, a group size is chosen that just barely mitigates the noise in the data. The program will not accept measurements that are <1. Generally, all sizes should be converted to nanometers (1 nm = 10^{-9} meters) before being entered into the program. The program can accommodate up to 2000 measurements, but can be amended easily to accept more data.

The program Chi-Square Analysis (ChiSq.xls) compares GALOPER calculated distributions with measured distributions to see if they are statistically similar. First clear columns

C and D in ChiSq.xls. Then, the measured number of crystals (column E from CrystalCounter) are pasted into column C in ChiSq.xls, and the GALOPER results, either column W from the open system or column BP from the closed system, are pasted into column D in ChiSq.xls (paste with the "Paste Special", "Values" options under the "Edit" menu). Only the number of crystals, and not summation cells at the bottoms of the columns, should be included in the paste. A "0" should be entered into cell A8 if the two columns were determined independently (that is, if column D was not calculated from column C). A "1" would be entered into cell A8 if, for example, column D was a theoretical lognormal frequency distribution calculated from the numbers of crystals in column C in a test for lognormality. One can enter the starting group size and the group interval into cells A10 and A12, respectively. Cells A19 through A31 give recommendations for the analysis. In fact, it is difficult to satisfy all of these recommendations. However, it is often useful to end-sum the data if the group sizes at the end of the distribution contain less than 5 measurements each $[Np(i) < 5)]$. To end-sum the data, enter the group size at which the summing is to begin into cell A18. The level of significance in cell B9 should be >1% to indicate that the distributions being compared could be the same, that is, that they may differ only by statistical fluctuations. Due to the partially random nature of the GALOPER calculation, sometimes the same calculation can give different significance levels. The chi-square table can be found in columns U through Z.

A second statistical program, the Kologorov-Smirnov test (KSTest.xls), is included for analyses in which there are less than the 10 group size categories recommended for chi-square analysis. Also, the KS-test seems to be more lenient. First, clear columns C and D in KSTest.xls. The measured number of crystals (column E from CrystalCounter) are pasted into column C in KSTest.xls, and the GALOPER results, either column W from the open system or column BP from the closed system, are pasted into column D in KSTest.xls. Only the numbers of crystals, and not summation cells at the bottoms of the columns, should be included in the paste, and the "Paste Special", and "Values" options should be used. If one of the input columns (always column D) is in terms of frequencies rather than actual numbers of crystals, then set cell A10 = 1 for a one-

sample test. If both columns C and D are actual numbers of crystals, then set cell A10 = 2 for a

two-sample test. As an alternative, frequencies can be entered into both columns C and D, but then

the total number of crystals needs to be entered into cell A15 for a one-sample test, and also into

cell A17 for a two-sample test. The significance level is given in cells B6 and B8.

GALOPER and associated programs can be linked together to save time. For example,

column W in GALOPER can be pasted automatically into column D in KSTest.xls by entering an

equals sign (=) in cell D2 in KSTest.xls, and then by clicking cell W2 in the GALOPER program

and hitting the "enter" key. The entry in cell D2 now reads: =[GALOPER.xls]GALOPE!W2.

Remove the $ in front of the 2, so that the entry now reads: =[GALOPER.xls]GALOPE!$W2; then

copy this cell, and paste it throughout column D.

The Lognor.xls program is discussed in Example 2 below.

MudMaster.xls is a program for calculating crystal size distributions (having mean sizes

less than about 40 nm, unless there is correction for instrumental broadening, in which case larger

crystal sizes can be measured) from the shapes of X-ray diffraction peaks. The theory behind the

operation of this program is described in Drits and others (1998), and both the program and its

instruction manual (Eberl and others, 1996) are available from the same ftp site as is the GALOPER

program (see previous section on how to obtain the programs). The frequency distribution, given in

column J in Sheet 2 in the MudMaster program, can be used for comparison with GALOPER

simulations.

SIMULATION EXAMPLES

The first step in simulating the crystal growth mechanisms that may have produced a

measured CSD is to recognize the basic shape of the CSD. There are three basic shapes:

asymptotic (figure 3A), lognormal (figure 3B), and Ostwald ripened (figure 3C). These shapes are

produced by the crystal growth mechanism of constant-rate nucleation and growth (option 1 in the

open system), surface-controlled growth (or nucleation with a decaying nucleation rate; options 3

and 5 in the open system), and Ostwald ripening (option 1 in the closed system), respectively.

Next, it is necessary to recognize how the basic shape was modified by subsequent crystal growth mechanisms. Some of these modifications, discovered through GALOPER calculations, are presented in table 1.

A second aid in simulation is an $\alpha-\beta^2$ diagram, which is a plot of the mean of the natural logarithms of the sizes (α) versus the variance of the natural logarithms of the sizes (β^2). This diagram will be discussed in more detail in Example 3 below. By plotting these parameters for a CSD on this diagram, a likely reaction path for a sample can be inferred, and the CSD simulated.

Finally, chemical, geologic, isotopic and other such information about the samples can be used as an aid. For example (Folger and others, 1997), the Ar 40/Ar 39 radiometric age of an illite changed significantly (became younger) in a hydrothermal zone compared with a sample taken from the same rock that was not in the reactive zone. The chemistries of the two rocks were identical, indicating a closed system with respect to the major elements, including potassium. The illite mean crystal thicknesses and CSD shapes also were the same in the two zones, and the rock was not heated hot enough to lose Ar by bulk diffusion. In this case, one may suspect illite reaction by random ripening, during which some illite crystals dissolved and then recrystallized on other illite crystals, thereby losing Ar and becoming apparently younger. During this reaction mechanism, a significant fraction of the illite in the hydrothermal zone could have recrystallized without changing CSD shape or increasing the mean crystal thickness.

Below are some examples of CSD simulations for minerals from a variety of sources. The data are in the file Examp.xls that accompanies GALOPER.
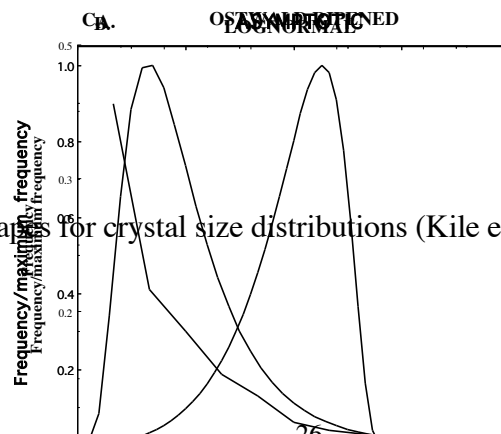

Figure 3: Three basic shapes for crystal size distributions (Kile et al., 2000).

Example 1: Nucleation with a decaying rate, followed by supply-controlled growth

Sample CCNG-40 is a synthetic calcite described by Kile and others (2000). Copy the raw size measurements for this sample from column A in the file Examp.xls into CrysCntr.xls, and, using a group size of 1000 nm, calculate the CSD shape. The CSD has a mean size of 6200 nm, with $\beta^2 = 0.158$, and a lognormal shape, which indicates that the crystals must have undergone surface-controlled growth (either option 3 or option 5 in the GALOPER program).

The calculation strategy is first to simulate the shape of the CSD, then its mean. In GALOPER, set the open system input to that shown in figure 1. Then set cell A6 = 3 for nucleation with a decaying nucleation rate; set A8 = 3, which is a likely size for the calcite critical nucleus (see Kile and others, 2000); and set cell A16 = 0.9 for the nucleation probability. Start the calculation, and repeat the calculation until it runs for four cycles (cell C15 = 4). Due to the random nature of the calculation, sometimes the calculation may take more or fewer cycles to complete, but four cycles approximately matches the simulated β^2 to that measured. Next the mean size is matched by subjecting the crystals to supply-controlled growth. Set A6 = 6 to choose this mechanism, cell A20 = 2 to react to a certain mean size, cell A22 = 6000, which is the mean size chosen (slightly smaller than the measured mean of 6200 because the calculation may overshoot), cell A28 = 0 to grow on top of the previous crystals, and cell A47 = 1000, which is the same group size as that used in CrystalCounter. Then, set A24 = -20, which means that the volume of material available for growth during each calculation cycle will be 20 times less than the total volume of the crystals. This option is an approximation used to speed calculation. It may be more realistic to enter a small, positive, constant value into cell A24, which would tend to keep β^2 constant during the calculation, as is to be expected for supply-controlled growth. Keying the volume available to the total volume causes β^2 to increase slightly as the mean advances, particularly if the mean advances to large sizes.

Table 1. How subsequent crystal growth mechanisms may change the initial shapes of crystal size distributions (CSDs).

Scenario No.	Initial shape	Subsequent growth Mechanism	Final result
1	Any shape	Supply-controlled or random ripening	Preserves the initial relative shape of the CSD. β^2 remains constant.
2	Asymptotic	Surface-controlled	Transforms the asymptotic CSD shape into a lognormal shape, sometimes leaving a pointed hat (circumflex) above the mode of the theoretical lognormal distribution.
3	Lognormal	Ostwald ripening	Moves the mode of the CSD to the right of the theoretical lognormal curve, makes the CSD more symmetrical (β^2 decreases), and finally skews the CSD to the left.
4	Lognormal	McCabe's Law or random growth	Shifts the mode to the left of that of the theoretical lognormal curve. Decreases β^2 as the mean increases.
5	Ostwald	McCabe's Law or random growth	Decreases β^2 as the CSD becomes narrower than the universal steady-state curve, and the mode shifts to the left of the universal steady-state curve for Ostwald ripening.

Following completion of the calculation and after clearing the appropriate columns in ChiSq.xls, paste the values from column W in GALOPER into column D in ChiSq.xls, and the values from column E in CrysCntr.xls into column C in ChiSq.xls. The level of significance for the chi-square test is >20%, which is considered to be a match The KS-test also gives a high level of significance (>10%).

Example 2:   Surface-controlled growth, followed by Ostwald ripening, with use of Lognor.xls

A sample of sphene was studied by Kretz (1966). The data, from Kretz (1966, Table 8) are given in Examp.xls. The data already are grouped into sizes, so CrystalCounter is not needed. Paste the data from column D in this file into column C (after C has been cleared) in the program Lognor.xls. Set the initial size in cell A6 = 25,000, and the group size in cell A8 to 50,000. The Lognor.xls program then plots the data and compares it to a theoretical lognormal curve calculated from the same data. The KS-test can be used to test if the CSD has a lognormal distribution shape by pasting the sphene crystal numbers into column C of KSTest.xls, and the theoretical lognormal frequency from column Q in Lognor.xls into column D of KSTest.xls, and setting cell A10 = 1. The test shows that the data are not lognormally distributed. Although the CSD at first looks lognormal, a closer inspection reveals that its mode is shifted to the right of the theoretical lognormal mode, which is typical for Ostwald ripening (scenario number 3 in table 1).

To simulate this process, calculate a lognormal CSD using option 5 in the open system in GALOPER. Option 5 is used, rather than option 3, as an approximation, because the results of option 5 are easier to control. Set the starting diameter size in cell A18 = 2 nm (a guess), and let the program run for 7 cycles (cells A20 and A22), using a group size of 5 (cell A47). β^2 for the resulting distribution (0.28) is slightly larger than that of the measured distribution (0.23), but β^2 should decrease during ripening. Next, ripen this distribution in the closed system by setting B6 = 1, and ripen to a mean size of 36 (cells B8 and B10), with a rate coefficient of 10 (cell B24) and a group size of 5 (cell B34). Results of the ripening show a small shift in the mode of the calculated CSD to the right of the lognormal mode, with about 1% of the mass having passed through solution.

The calculation can be continued by using supply-controlled growth to preserve the shape and β^2 of the CSD as the mean size increases. This can be done by pasting the ripened CSD into the open system (set cell A62 = 1 and start the calculation); then start supply-controlled growth to a mean of 212,000 nm. However, because it is known that β^2 will remain constant during this simulation, it is easier to model this last mechanism rather than to simulate it. The last mechanism can be modeled by multiplying the distribution by a constant (proportionate growth option in cell A69). The constant to be used is the sample mean divided by the ripened mean, or 21,2487 ÷ 36 = 5,902. To carry out this procedure, first paste the ripened system into the open system (set cell A62 = 1 and start). Next set cells A6 = 5, A28 = 0, A47 = 25,000, A62 = 0, and A69 = 5,902. Run the calculation for one cycle (done automatically if cells A20 and A22 were not changed from the previous calculation). By combining groups in the GALOPER calculation using a separate worksheet, so that the GALOPER size categories match those given by Kretz (1966), the KS-test indicates that the calculated and measured distributions are the same at the 5-10 % level of significance. The calculation shows that even a very small amount of ripening can be detected in the CSD shape.

Example 3: A second nucleation, and use of an $\alpha-\beta^2$ diagram

An an $\alpha-\beta^2$ diagram is shown in figure 4, on which have been plotted parameters for a hydrothermal illite collected from a bore hole in Red Mountain, Lake County, Colorado. This diagram was constructed using GALOPER calculations; the crystal thickness distribution for the sample was measured by X-ray diffraction (XRD) using the MudMaster computer program (Eberl and others, 1996) and the PVP-10 intercalation technique to remove the effects of swelling from XRD peak broadening (Eberl, Nüesch, and others, 1998). Curve A-B is calculated for the evolution of β^2 with α for constant-rate nucleation and growth (option 1 in the open system), starting with a 2-nm thick critical nucleus (the thickness of an elementary illite particle). The numbered pluses on this curve are the number of nucleation cycles. The shapes of the CSDs formed along this curve are expected to be asymptotic. Curve A-C was calculated for surface-controlled growth (option 5) with a 2-nm thick starting diameter. The ticks on this curve also refer to the number of calculation

cycles for this mechanism, and the CSDs are lognormal. The curves that are above and parallel to A-C are reaction paths for surface-controlled growth, but these calculations started with clay thickness distributions formed by constant-rate nucleation and growth.

Figure 4. An $\alpha-\beta^2$ diagram on which has been plotted a reaction path for illite sample number 1916 from Red Mountain, Lake County, Colorado (Eberl and others, 2000).
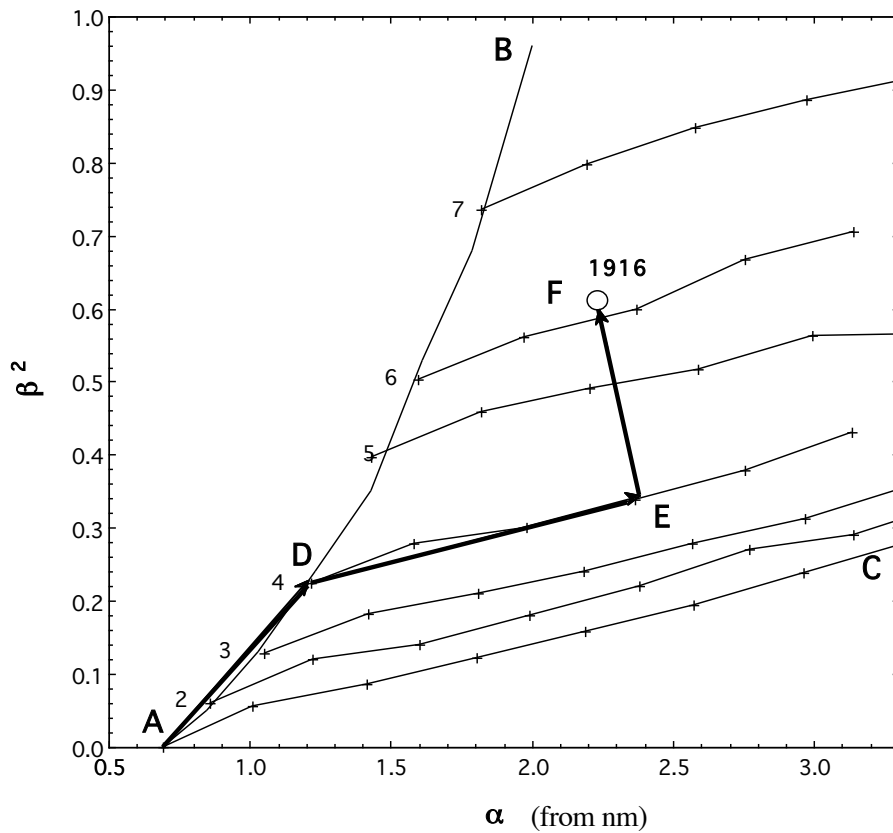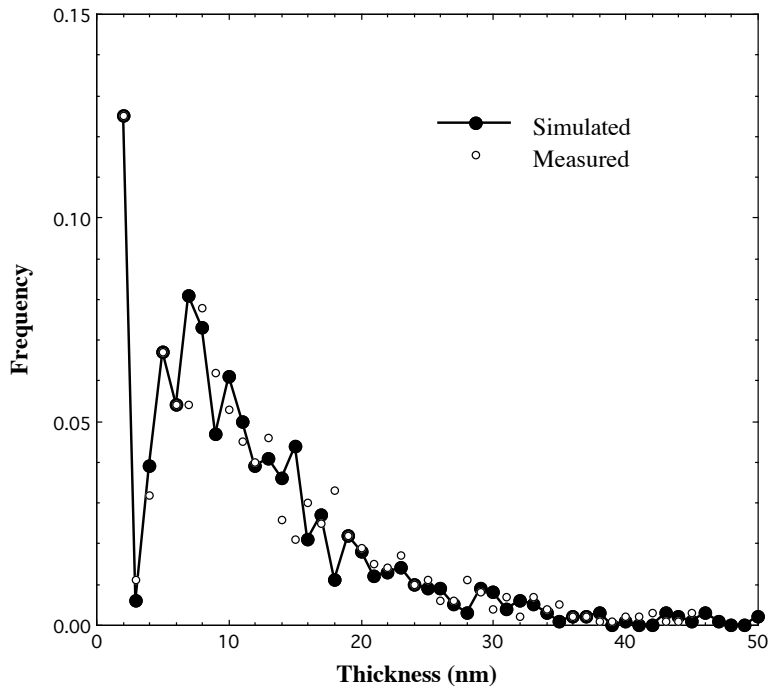
Figure 5. Simulated and measured crystallite thickness distribution for illite sample number 1916 (Eberl and others, 2000).

The α and β^2 values for sample 1916 are plotted in figure 4, and the sample's measured CSD is given in figure 5 (open circles). The CSD would appear to be lognormal, except that it is bimodal and has a second peak at 2 nm, as though there was a second nucleation event. The thickness distribution, which is given in the file Examp.xls, was modeled by trial and error. The reaction path through the α - β^2 diagram that best simulates the CSD shape is: (1) path A-D (figure 4) with nucleation and growth for 4 cycles (option 1 with 250 nuclei per cycle), followed by (2) path D-E with surface-controlled growth without nucleation for 3 cycles (option 5), followed by (3) path E-F with a second nucleation event that nucleated 125 additional 2-nm thick crystals. When this exact path is followed, the simulated and measured distributions are significantly correlated (>10% by the KS-test).

The last stage in the simulation, during which new nuclei were added to the lognormal-like CSD formed along path A-D-E, was accomplished by setting cell A6 = 1, cell A14 = 1, and cell A28 = 0, then starting the program. This calculation randomizes crystal sizes in the column in which they are stored to insure that they are not sorted with respect to size. Next, by setting cell A12 = 125 and cell A14 = 0, 125 new 2-nm thick crystals are added to the distribution, resulting in the calculated CSD shown in figure 5. In the simulation, the secondary nuclei replace crystals already stored in the program, which is a calculation trick. Of course, the additional nuclei in nature would be added to crystals already present, without replacing them. But this trick was used because the program has room for only 1001 crystals. The results are nearly equivalent if the preexisting crystals are replaced randomly with respect to size.

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APPENDIX 1: SUMMARY OF INPUTS FOR THE OPEN SYSTEM.

Input	Cell	Value	Comments
Open system option	A6	1 to 7	Choose the crystal growth mechanism. To grow on top of previously formed crystals, set A28 = 0.
Size of critical nucleus	A8	>0	For options 1-4, this is the size of the crystals that appear during nucleation. Usually this value this is a guess that is several unit cell sizes.
Particles to nucleate per cycle	A10	1 to 1001	Input for options 1 & 2. The number of nucleation cycles = A30/A10.
Nucleate on previous CSD?	A12	0 = no; or give number of new nuclei	Cell A6 must = 1. These nuclei replace crystals formed previously, which should not be sorted with respect to size. Therefore, the stored crystal sizes should be randomized first (see cell A14).
Randomize crystal sizes?	A14	0 to 2	Stored crystal sizes should be randomized before calculating a second nucleation event (cell A12) in order to randomly replace previously formed crystals.
Probability for critical nucleus formation	A16	A fraction ranging from >0 to <1.	For option 3, the probability that a crystal will nucleate during each calculation cycle. Nucleation ceases when a maximum of 1001 crystals have nucleated.
Starting diameter	A18	>0	For options 5 – 7, the starting diameter for all of the crystals prior to growth. Active if A28 = 1.
Criteria for growth	A20	1 or 2	For options 5 –7, entering "1" will grow to designated mean size, "2" to number of cycles.

Appendix 1 (continued)

Total number of cycles or mean	A22	>0	For options 5-7, enter number of calculations cycles (A20 = 1) or mean size (A20 = 2) to be attained during calculation.
Volume to be added per cycle	A24	Positive or negative number	For options 2, 4 and 6, the volume that is added to the crystals during each growth cycle. A negative number adds a fraction of the current total volume (e.g. –10 adds 0.1 x total volume for each calculation cycle; -100 adds .01 x total volume, etc.).
Reduce volume available by growth volume	A26	0, 1, or 2	For options 2, 4 and 6, entering "1" or "2" reduces the volume in cell A24 by the volume used during growth cycles.
Clear old data?	A28	0 = no; 1 = yes	If A28 = 1, crystal growth starts fresh; if = 0, growth is on top of previously formed crystals. Set to 0 for supply-controlled growth (options 2,4, and 6).
Total number of crystals	A30	1 to 1001	Number of crystals that nucleate and/or grow during the calculation.
Epsilon variation	A32 & A33	Range of values, usually 0 to 1.	The range allowed for the random number used in the Law of Proportionate Effect (equation 1).
Crystal shape	A35	1 or 2	Calculates either spheres (1) or cubes (2). Relative answers will not change; only absolute volumes change.
Mineral density	A37	Give density, in g/cm^3	Used for calculating the specific surface area of a mineral.

Appendix 1 (continued)

Rate coefficient	A39	Generally use 1	Input can be used to tweak the calculation so that it

			approaches a desired mean. Best to leave at 1, or change very slightly.
Collect open frequency?	A41	0 = no; or give iterations	Open system can be iterated several times so that the frequency distribution can be plotted more accurately, using more than 1001 crystals. These frequencies are stored in column AK. For use only with options 1, 3, 5, and 7. Data can not be re-plotted.
Update screen	A43	1 = yes	Set at "1" to watch the calculation happen. Otherwise, screen updates automatically at end of calculation.
Give plot?	A45	0, 1, or 2	Calculation can be terminated by pressing escape key, and the results plotted by setting this cell to 2.
Group size	A47	integer	Bin size for the calculation. Results can be replotted with different size by changing A45 and this cell.
Clear chart?	A49	1 = yes	Keep former chart to compare calculations.
Do not count particles less than:	A51	Positive number or zero	Plotting and results will ignore crystals smaller than this value.
How to collect data	A53	0, -1, 1	Should data be collected into bins starting from center, beginning, or end of group size? Always use 0.
Continue with closed system?	A56	1 = yes	Calculation will continue with closed-system calculation after open-system calculation is complete.

Appendix 1 (continued)

Iterate closed system?	A58	0 = no; or enter number of iterations	Open and closed systems are iterated to create less noisy CSDs for long ripenings.
Collect ripened particles?	A60	1 = yes	Crystals that remain from each ripening iteration are collected in column DB. They can be pasted into open system using cell B41.
Paste ripened into open system?	A62	1 = yes	Crystals from closed system are pasted into open system. Use cell B41 to paste crystals collected during ripening iterations into open system.
LPE weathering?	A65	1 = yes	Use option 5; set epsilon to a smaller variation (A33) to induce supply-controlled weathering.
McCabe's Law growth	A67	0 = no; or give size increase	Constant linear amount added to each crystal. Use option 5 (cell A6) and save old data (set A28 = 0).
Proportionate growth	A69	0 = no; or give multiplier	Each crystal size is multiplied by a constant. Use option 5 (cell A6) and save old data (set A28 = 0).

APPENDIX 2: SUMMARY OF INPUTS FOR CLOSED SYSTEM

Input	Cell	Value	Comments
Ripening options	B6	1 to 4	Choose ripening mechanism.
Ripen to number of cycles, mean, fraction or number of particles	B8	1 to 4	For option 1, one can choose to ripen to a certain number of cycles (1), to a mean size (2), to a fraction of material passing through solution (3), or to a number of crystals remaining in the system (4).
Ripen to this number	B10	Number or fraction	For option 1, choose how far to ripen, given the entry in cell B8.
Diffusion or surface-controlled ripening?	B12	1 or 2	For options 1, 2, or 3, choose ripening mechanism. Diffusion-controlled ripening seems to be the common one (enter 1).
Size of critical diameter	B14	Enter size	For options 2 and 3, the critical radius for ripening (see equation 3) will be fixed at this value/2.
Number of cycles	B16	Enter number	For option 3, the number of ripening cycles using equation 3 and the fixed critical radius (B14).
Probability for random dissolution	B18	Fraction from 0-1	For option 4, probability that a crystal will dissolve without respect to size (random ripening).
Dissolve only < this size	B20	Enter size	For option 4, only crystals less than this size have a probability to dissolve.
Clear old data?	B22	1 = yes	Set to "0" to ripen previously ripened distribution.
Rate coefficient	B24	Positive number	Increase number to increase ripening rate.

Appendix 2 (continued)

Crystal shape	B26	1 = sphere 2 = cube	Shape should be the same as in open system.
Fraction dissolved previously	B28	Fraction from 0 to 1	This amount will be added to the fraction dissolved during ripening (cell E5).
Update screen?	B30	1 = yes	Enter "1" to watch calculation.
Give plot?	B32	1 or 2	Give plot at end of calculation (1) or now (2).
Group size	B34	Enter class size	Bin size for the calculations and plot.
Clear chart?	B36	1 = yes	Enter zero to compare plot with next calculation.
Do not count particles less than:	B38	Enter size	Crystals < this size will not be included in the plot or in the calculations.
Paste collected particles into open system?	B41	0 = no, or give data set	Crystals remaining in the system after ripening iterations (collected using cell A60) are pasted into open system, 1001 at a time. 1 = first 1001 collected crystals; 2 = next 1001, and so on.
Crystal coalescence?	B44	0 = no, or give probability	Coalescence probability for crystals. Entry >0 activates this option.
What size are the initial and second coalesced crystals?	B47 & B50	Enter sizes	Sets rules for coalescence if entries are >0. Crystals < these sizes will not coalesce.

Appendix 2 (continued)

Criterion for volume match	B52	Enter volume (usually 10)	During a ripening cycle, the volume dissolved from the disappearing crystals must equal the growth volume. This entry indicates how much they may differ. If the calculation does not converge, use a number >10.
Surface-area controlled weathering	B55	1 = yes	Use option 3 in cell B6.
Degree of undersaturation	B57	$<10^6$	Entry is multiplied by the largest crystal size to determine critical diameter size during weathering (see equation 3). Generally enter "1".

APPENDIX 3: SUMMARY OF RESULTS FOR OPEN SYSTEM

Result	Cell	Comments
Mean diameter	C3	$\overline{X} = \sum Xf(X)$, where f(X) is the frequency of diameter X.
Alpha	C5	$\alpha = \sum \ln(X)f(X)$.
Beta^2	C7	$\beta^2 = \sum (\ln X - \alpha)^2 f(X)$.
Number of particles	C9	Number of crystals in the system.
Number of particles not counted	C11	Crystal sizes that fall outside of the end of the calculated distribution. To include these crystals, replot (set cell A45 = 2) with larger group size (A47).
Diameter of largest particle	C13	Size of largest crystal in distribution.
Total number of cycles	C15	Total number of cycles in the calculation.
Total surface area	C17	Total surface area for spherical or cubic crystals (set shape in cell A35).
Total volume	C19	Total volume for spherical or cubic crystals (set shape in cell A35).
Specific surface area	C21	Uses density in cell A37 to calculate specific surface area in square meters per gram.

APPENDIX 4: SUMMARY OF RESULTS FOR CLOSED SYSTEM

Result	Cell	Comments
Mean diameter	D3	$\overline{X} = \sum Xf(X)$, where f(X) is the frequency of diameter X.
Alpha	D5	$\alpha = \sum \ln(X)f(X)$.
Beta^2	D7	$\beta^2 = \sum (\ln X - \alpha)^2 f(X)$.
Number of particles	D9	Number of crystals in the system.
Number of particles not counted	D11	Crystals that fall outside of the end of the calculated distribution. To include these crystals, replot (set cell B32 = 2) with larger group size (B34).
Diameter of largest particle	D13	Size of largest crystal in distribution.
Diameter of smallest particle	D15	Size of smallest crystal in distribution.
Number of cycles	D17	Number of cycles in the calculation.
Number of iterations	D19	Number of times ripening calculation was repeated starting with open system (see cell A58).
Units of diameter dissolved	E3	Sum of the length of crystals dissolved during previous calculation cycle.
Fraction of core volume dissolved	E5	Fraction of original material that has passed through solution once during the ripening process.

Appendix 4 (continued)

Fraction total volume dissolved	E7	Fraction of the original material that has passed through solution. Some material may pass through solution more than once because the size of the critical diameter increases as the mean size increases.
Volume core dissolved (this run)	E9	Volume of material not previously dissolved that has dissolved during this calculation.
Total volume of system	E11	Total volume calculated for spherical or cubic crystals (set shape in cell A35).
Critical diameter	E13	Diameter used to calculate dissolution during ripening (equation 3).
L (Scherrer equation)	E15	Volume-weighted mean size.