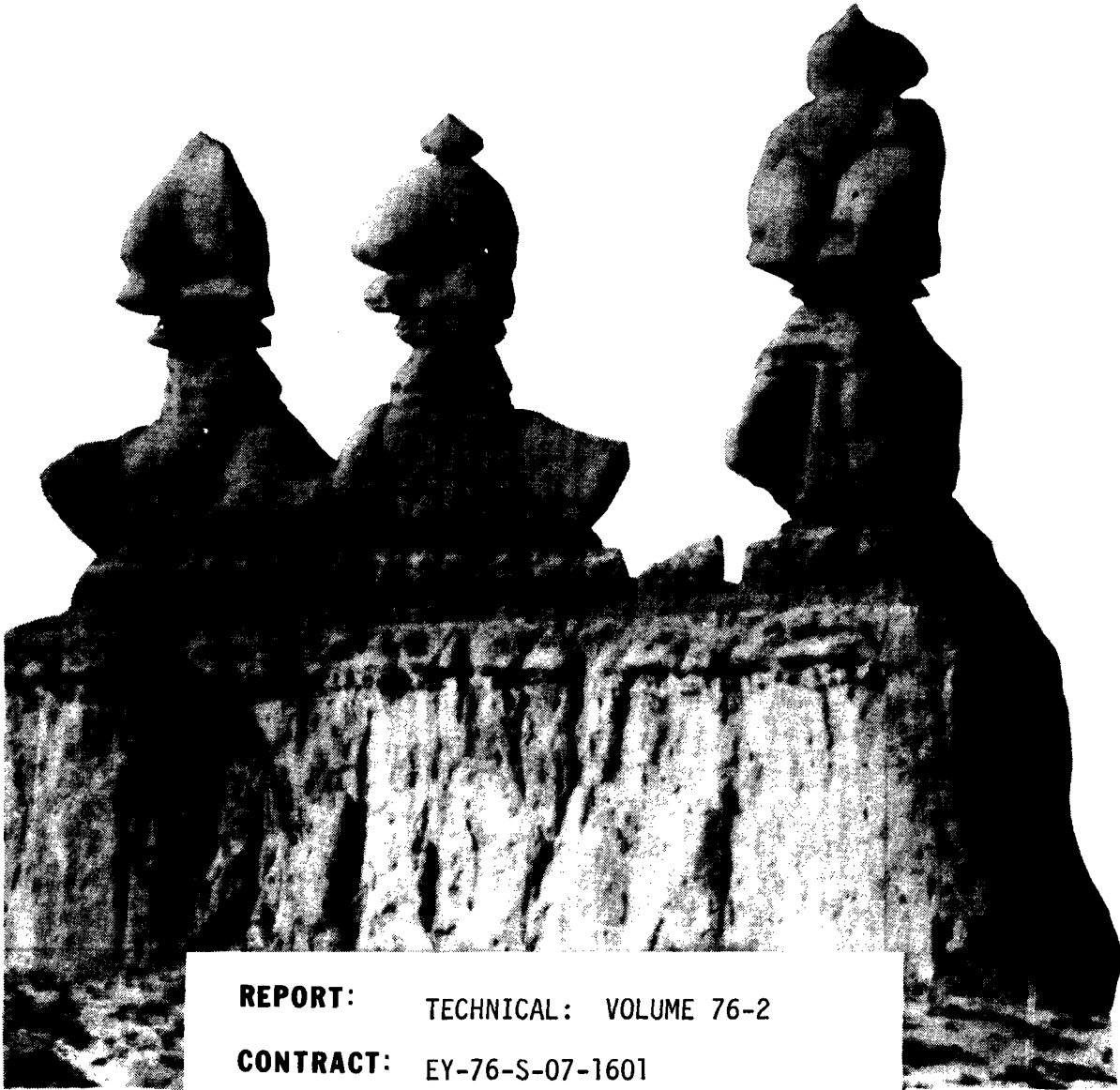


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A THERMODYNAMIC MODEL OF  
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IN ACID SULFATE SOLUTIONS

by

R. E. Dedolph and W. T. Parry

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## ABSTRACT

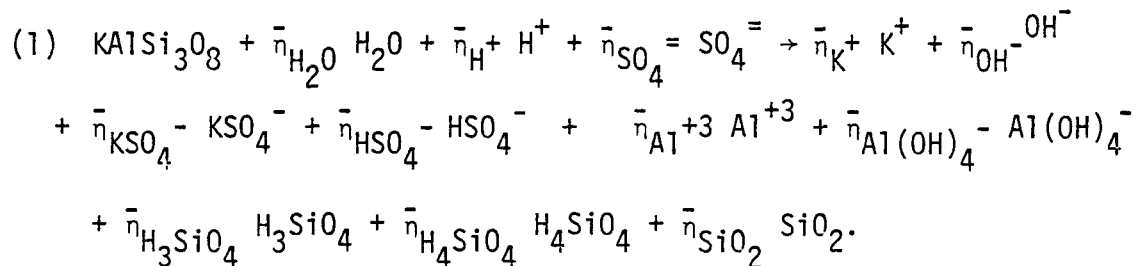
A theoretical model of the hydrolysis of microcline by a hydrothermal solution has been determined for a closed system at constant temperature. Hypothetical solution compositions and temperatures were chosen to match the known geothermal system at Roosevelt Hot Springs, Utah. The calculated reaction paths indicate that the overall reaction process is an exchange of potassium from the reactant mineral, microcline, for hydrogen from the solution. Aluminum is nearly conserved among solid phases. The amount of microcline reacted per kilogram of solution before overall equilibrium is reached is a function of temperature and initial solution pH. Since the system is closed and at constant temperature natural conditions are not reproduced well enough to apply the model as a geothermometer. The reaction paths suggest qualitative models of alteration mineral zoning patterns that are similar to zoning at Roosevelt Hot Springs, Utah; Steamboat Springs, Nevada, and Butte, Montana. The models presented view alteration zoning as a function of temperature and pH gradients within homogeneous host rocks where microcline and quartz are abundant.

## INTRODUCTION

Hydrothermal rock alteration is produced by an irreversible chemical reaction between host rock minerals and a hot aqueous solution. Helgeson (1968) outlines a thermodynamic model of hydrolysis in a closed hydrothermal system at constant temperature in which the masses of all species in the system at any point during the overall reaction progress may be calculated. The University of Utah geothermal team has been investigating the Roosevelt KGRA geothermal system in an attempt to develop geothermal exploration methods and to characterize the Roosevelt system. The Roosevelt geothermal system occurs in a Tertiary granite pluton and the geothermal reservoir is likely fractured granite. Reaction of hot geothermal fluid with minerals of the granite is of fundamental interest in resource characterization. The techniques of Helgeson (1968) have been used in the present study to model the closed-system hydrolysis of reservoir minerals. The goals of this project were: 1) to investigate the hydrolysis of microcline by a hypothetical hydrothermal solution which closely matches the Roosevelt reservoir fluid in composition and 2) to apply the calculated reaction paths and masses transferred to the development of geothermometers and chemical models of alteration, applicable to hydrothermal systems such as Roosevelt Hot Springs, Utah.

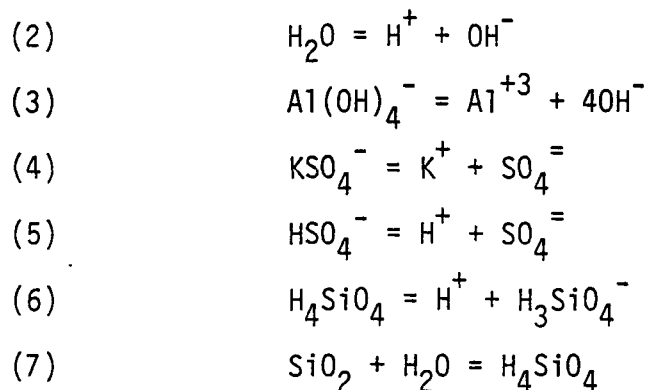
## MASS TRANSFER CALCULATIONS

The following discussion is an adaptation of the discussion presented by Helgeson (1968). The chemical reaction investigated is the reaction between microcline and a hypothetical sodium chloride hydrothermal solution. The solution has an ionic strength of 0.1 and is initially saturated only with respect to quartz. Species in solution considered are  $H^+$ ,  $OH^-$ ,  $K^+$ ,  $KSO_4^-$ ,  $HSO_4^-$ ,  $SO_4^{=}$ ,  $Al^{+3}$ ;  $Al(OH)_4^-$ ,  $H_3SiO_4^-$ , and  $H_4SiO_4$ . Other species such as  $AlOH^{+2}$  and  $AlSO_4^+$  were not considered. Considering additional solution species would increase accuracy slightly at the expense of computer time. The initial general reaction for feldspar hydrolysis can be written:

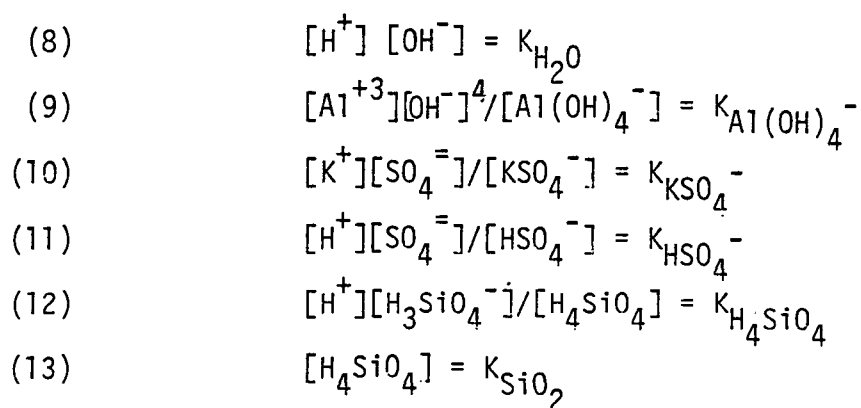


The  $\bar{n}_i$ 's are the reaction coefficients of species in solution or product mineral phases. By convention reaction coefficients of products are positive and of reactants are negative. The reaction coefficient of microcline is assumed to equal minus one. The overall reaction is irreversible, but if the overall reaction is considered in infinitely small steps each step is reversible with respect to the preceding step. The system is closed and at constant temperature. Supersaturation

and metastable phases are assumed absent. Partial equilibrium, that is equilibrium among species in solution and between product minerals and the solution is assumed. The assumption means that the following equations must simultaneously hold.



Assuming the activity of all solid phases and water to equal one, equations (2) through (7) may be rewritten as follows:



Reaction progress is a time dependent term defined as:

$$(14) \quad d\xi = \frac{dm_i}{\eta_i}$$

Where  $d\xi$  is an infinitely small increment of reaction progress and is called the reaction progress variable,  $dm_i$  is the rate of change of



the molality of species  $i$  or phase  $i$  and  $\bar{n}_i$  is the reaction coefficient of the  $i$ th species or mineral phase.  $d\xi$  is always positive and  $dm_i$  may be positive or negative. Though the reaction progress variable is a time dependent term, the relationship between time and reaction progress is not known because reaction rates in the system are not known. Taking the derivatives of equations (8) to (13) with respect to  $d\xi$  produces:

$$(15) \quad \frac{d[H^+]/d\xi}{[H^+]} + \frac{d[OH^-]/d\xi}{[OH^-]} = 0$$

$$(16) \quad \frac{d[Al^{+3}]/d\xi}{[Al^{+3}]} + \frac{4d[OH^-]/d\xi}{[OH^-]} - \frac{d[Al(OH)_4^-]/d\xi}{[Al(OH)_4^-]} = 0$$

$$(17) \quad \frac{d[K^+]/d\xi}{[K^+]} + \frac{d[SO_4^{=2-}]/d\xi}{[SO_4^{=2-}]} - \frac{d[KSO_4^-]/d\xi}{[KSO_4^-]} = 0$$

$$(18) \quad \frac{d[H^+]/d\xi}{[H^+]} + \frac{d[SO_4^{=2-}]/d\xi}{[SO_4^{=2-}]} - \frac{d[HSO_4^-]/d\xi}{[HSO_4^-]} = 0$$

$$(19) \quad \frac{d[H^+]/d\xi}{[H^+]} + \frac{d[H_3SiO_4^-]/d\xi}{[H_3SiO_4^-]} - \frac{d[H_4SiO_4]/d\xi}{[H_4SiO_4]} = 0$$

$$(20) \quad \frac{d[H_4SiO_4]/d\xi}{[H_4SiO_4]} = 0.$$

The reaction coefficient of the  $i$ th species or phase is the change of molality of the  $i$ th species or the change of number of moles produced or consumed of the  $i$ th phase with respect to change in time or reaction progress. Equation (14) may be rewritten as follows:

$$(21) \quad \bar{n}_i = \frac{dm_i}{d\xi}$$

Assuming that the solution does not change enough during the overall reaction to affect the calculated activity coefficients (8) and by substituting equation (22)

$$(22) \quad m_i = a_i / \gamma_i$$

into equation (21) we obtain:

$$(23) \quad \bar{n}_i = \frac{1}{\gamma_i} \frac{da_i}{d\xi} = \frac{dm_i}{d\xi}$$

Substituting equation (23) into equations (15) through (20) yields:

$$(24) \quad \frac{\bar{n}_{H^+}}{m_{H^+}} + \frac{\bar{n}_{OH^-}}{m_{OH^-}} = 0$$

$$(25) \quad \frac{\bar{n}_{Al^{+3}}}{m_{Al^{+3}}} + \frac{4\bar{n}_{OH^-}}{m_{OH^-}} - \frac{\bar{n}_{Al(OH)_4^-}}{m_{Al(OH)_4^-}} = 0$$

$$(26) \quad \frac{\bar{n}_{K^+}}{m_{K^+}} + \frac{\bar{n}_{SO_4^{=}}}{m_{SO_4^{=}}} - \frac{\bar{n}_{KSO_4^-}}{m_{KSO_4^-}} = 0$$

$$(27) \quad \frac{\bar{n}_{H^+}}{m_{K^+}} + \frac{\bar{n}_{SO_4^{=}}}{m_{SO_4^{=}}} - \frac{\bar{n}_{KSO_4^-}}{m_{KSO_4^-}} = 0$$

$$(28) \quad \frac{\bar{n}_{H^+}}{m_{H^+}} + \frac{\bar{n}_{H_3SiO_4^-}}{m_{H_3SiO_4^-}} - \frac{\bar{n}_{H_4SiO_4}}{m_{H_4SiO_4}} = 0$$

$$(29) \quad \frac{\bar{n}_{H_4SiO_4}}{m_{H_4SiO_4}} = 0.$$

Since the system is closed the masses of each element must be

conserved throughout the reaction. This allows writing the following mass balance equations:

$$(30) \quad \bar{n}_{\text{H}_2\text{O}} + 4\bar{n}_{\text{SO}_4^=} + 4\bar{n}_{\text{KSO}_4^-} + 4\bar{n}_{\text{HSO}_4^-} + 4\bar{n}_{\text{Al}(\text{OH})_4^-} \\ + 4\bar{n}_{\text{H}_3\text{SiO}_4^-} + 4\bar{n}_{\text{H}_4\text{SiO}_4} + 2\bar{n}_{\text{SiO}_2} = 8$$

$$(31) \quad 2\bar{n}_{\text{H}_2\text{O}} + \bar{n}_{\text{H}^+} + \bar{n}_{\text{HSO}_4^-} + 4\bar{n}_{\text{Al}(\text{OH})_4^-} + 3\bar{n}_{\text{H}_3\text{SiO}_4^-} \\ + 4\bar{n}_{\text{H}_4\text{SiO}_4} = 0$$

$$(32) \quad \bar{n}_{\text{H}_3\text{SiO}_4^-} + \bar{n}_{\text{H}_4\text{SiO}_4} + \bar{n}_{\text{SiO}_2} = 3$$

$$(33) \quad \bar{n}_{\text{Al}^{+3}} + \bar{n}_{\text{Al}(\text{OH})_4^-} = 1$$

$$(34) \quad \bar{n}_{\text{K}^+} + \bar{n}_{\text{KSO}_4^-} = 1$$

$$(35) \quad \bar{n}_{\text{SO}_4^=} + \bar{n}_{\text{HSO}_4^-} + \bar{n}_{\text{KSO}_4^-} = 0.$$

Because the initial molality of each species is known, equations (24) through (35) constitute twelve equations with twelve unknown reaction coefficients. Solving these simultaneous equations by matrix algebra produces the twelve unknown reaction coefficients. Equation (21) may be rewritten as follows:

$$(36) \quad dm_i = \bar{n}_i(d\xi).$$

This equation allows the calculation of the change of molality or number of moles of species  $i$  or phase  $i$  for an infinitely small increment in the reaction progress variable. Equation (36) may be approximated by a Taylor's expansion for a known increment of reaction progress,  $\Delta\xi$ .

$$(37) \quad \Delta m_i = \bar{n}_i \Delta \xi + \bar{n}_i' \frac{(\Delta \xi)^2}{2!} + \bar{n}_i'' \frac{(\Delta \xi)^3}{3!} + \dots$$

Where  $\bar{n}_i'$  and  $\bar{n}_i''$  are the first derivative and second derivative respectively of the reaction coefficient,  $\bar{n}_i$ . Equation (37) allows the calculation of the change of molality or number of moles to any degree of accuracy desired. If the reaction progress increment is small enough the quadratic and all subsequent terms become negligible. Due to the expense of computer time a large enough  $\Delta \xi$  must be used so that at least the quadratic term and perhaps the cubic term must be considered. Higher derivatives of the reaction coefficients may be obtained by taking the derivatives of equations (24) to (35) and solving the resulting equations simultaneously to obtain  $\bar{n}_i'$ . The second derivatives of these equations are given below.

$$(38) \quad \frac{\bar{n}_i' \text{H}^+}{m_{\text{H}^+}} + \frac{\bar{n}_i' \text{OH}^-}{m_{\text{OH}^-}} = \frac{\bar{n}_i'' \text{H}^+}{m_{\text{H}^+}^2} + \frac{\bar{n}_i'' \text{OH}^-}{m_{\text{OH}^-}^2}$$

$$(39) \quad \frac{\bar{n}_i' \text{Al}^{+3}}{m_{\text{Al}^{+3}}} + \frac{4\bar{n}_i' \text{OH}^-}{m_{\text{OH}^-}} - \frac{\bar{n}_i' \text{Al}(\text{OH})_4^-}{m_{\text{Al}(\text{OH})_4^-}} = \frac{\bar{n}_i'' \text{Al}^{+3}}{m_{\text{Al}^{+3}}^2} + \frac{4\bar{n}_i'' \text{OH}^-}{m_{\text{OH}^-}^2} - \frac{\bar{n}_i'' \text{Al}(\text{OH})_4^-}{m_{\text{Al}(\text{OH})_4^-}^2}$$

$$(40) \quad \frac{\bar{n}_i' \text{K}^+}{m_{\text{K}^+}} + \frac{\bar{n}_i' \text{SO}_4^{=}}{m_{\text{SO}_4^{=}}} - \frac{\bar{n}_i' \text{KSO}_4^-}{m_{\text{KSO}_4^-}} = \frac{\bar{n}_i'' \text{K}^+}{m_{\text{K}^+}^2} + \frac{\bar{n}_i'' \text{SO}_4^{=}}{m_{\text{SO}_4^{=}}^2} - \frac{\bar{n}_i'' \text{KSO}_4^-}{m_{\text{KSO}_4^-}^2}$$

$$(41) \quad \frac{\bar{n}'_{H^+}}{m_{H^+}} + \frac{\bar{n}'_{SO_4^{=}}}{m_{SO_4^{=}}} - \frac{\bar{n}'_{HSO_4^-}}{m_{HSO_4^-}} = \frac{\bar{n}^{-2}_{H^+}}{m^2_{H^+}} + \frac{\bar{n}^{-2}_{SO_4^{=}}}{m^2_{SO_4^{=}}} - \frac{\bar{n}^{-2}_{HSO_4^-}}{m^2_{HSO_4^-}}$$

$$(42) \quad \frac{\bar{n}'_{H^+}}{m_{H^+}} + \frac{\bar{n}'_{H_3SiO_4^-}}{m_{H_3SiO_4^-}} - \frac{\bar{n}'_{H_4SiO_4^-}}{m_{H_4SiO_4^-}} = \frac{\bar{n}^{-2}_{H^+}}{m^2_{H^+}} + \frac{\bar{n}^{-2}_{H_3SiO_4^-}}{m^2_{H_3SiO_4^-}} - \frac{\bar{n}^{-2}_{H_4SiO_4^-}}{m^2_{H_4SiO_4^-}}$$

$$(43) \quad \frac{\bar{n}'_{H_4SiO_4^-}}{m_{H_4SiO_4^-}} = \frac{\bar{n}^{-2}_{H_4SiO_4^-}}{m^2_{H_4SiO_4^-}}$$

$$(44) \quad \bar{n}'_{H_2O} + 4\bar{n}'_{SO_4^{=}} + 4\bar{n}'_{KSO_4^-} + 4\bar{n}'_{HSO_4^-} + 4\bar{n}'_{Al(OH)_4^-} + 4\bar{n}'_{H_3SiO_4^-} + 4\bar{n}'_{H_4SiO_4^-} + 2\bar{n}'_{SiO_2} = 0$$

$$(45) \quad 2\bar{n}'_{H_2O} + \bar{n}'_{H^+} + \bar{n}'_{HSO_4^-} + 4\bar{n}'_{Al(OH)_4^-} + 3\bar{n}'_{H_3SiO_4^-} + 4\bar{n}'_{H_4SiO_4^-} = 0$$

$$(46) \quad \bar{n}'_{H_3SiO_4^-} + \bar{n}'_{H_4SiO_4^-} + \bar{n}'_{SiO_2} = 0$$

$$(47) \quad \bar{n}'_{Al^{+3}} + \bar{n}'_{Al(OH)_4^-} = 0$$

$$(48) \quad \bar{n}'_{K^+} + \bar{n}'_{KSO_4^-} = 0$$

$$(49) \quad \bar{n}'_{SO_4^{=}} + \bar{n}'_{HSO_4^-} + \bar{n}'_{KSO_4^-} = 0.$$

Assuming the reaction progress increment is small enough to ignore the cubic and all subsequent terms in equation (37) the calculation proceeds as follows. First the initial molalities are substituted into equations (24) through (35) to solve for  $\bar{n}_i$  of each species or phase. Then the initial molalities and the reaction coefficients  $\bar{n}_i$  are substituted into equations (38) to (49) to solve for each  $\bar{n}_i'$ . The reaction progress increment  $\Delta\xi$ , the reaction coefficient  $\bar{n}_i$ , and its first derivative  $\bar{n}_i'$  are placed into equation (37) to calculate the change in molality or number of moles for each species or mineral phase. This change in molality or number of moles is then added to the molality or number of moles of the preceding step. By equation (22) the activity of each species is calculated. These activities are placed into equilibrium constant expressions to test for saturation for each alteration mineral considered. If saturation is reached, then for each new phase produced a new partial equilibrium equation and appropriate terms in the mass balance equations (30) and (35) must be added. The calculation is repeated until saturation is reached with respect to the reactant mineral microcline and thus overall equilibrium is attained.

## COMPUTER PROGRAM

Originally a program to do the calculation just described was written in Flextran language (Schamber, F. H., 1975) for an NS-880, PDP-11 minicomputer. The minicomputer's 8K memory was inadequate so the program was translated to Fortran and was run on the University of Utah's Univac 1108 computer. Given a larger memory the minicomputer would be useful for these types of calculations. The following discussion is a detailed line by line description of the program used. The description proceeds with the flow of the program. The line numbers refer to the program listing given in Appendix 1 and a flow chart (Appendix 2) is provided as well. This section is not necessary for understanding the remainder of this paper. It is included only for those interested in operating this program or writing similar computer programs.

The statement on line 4 sets the largest matrix size that may be used. In the program's present form the maximum is a 15 x 16 matrix. This means that for a system with greater than 15 simultaneous equations the variable NT must be increased. Lines 5 and 6 provide for double precision on all variables that may exceed the Univac 1108's  $10^{\pm 38}$  limit of number size. Double precision increases this limit to  $10^{\pm 308}$ . Double precision must be used to avoid underflow. Inputs required are the number of complete cycles between outputs (H9), the number of simultaneous equations (N), the equilibrium constants for each

mineral whose saturation is tested for ( $EX(I)$ ), the initial molalities or number of moles for each species or mineral phase present ( $Y(I)$ ), activity coefficients for each species ( $Y3(I)$ ), and the initial ( $XS$ ). A data-file was used to make unput simpler and faster. A data-file is not required but with one, execution follows this sequence. Line 11 causes the output of "OUTPUT EVERY HOW MANY CYCLES". Line 12 then reads H9 on an I5 format and line 13 outputs H9. Line 14 outputs "HOW MANY EQUATIONS" and line 15 reads N on an I5 format and line 17 outputs N. Line 16 creates the variable NN which is used to refer to the N+1 column in matrices later on. Line 18 outputs "INPUT INITIAL MOLALITIES". Lines 19 to 22 are a loop which first reads an equilibrium constant ( $EX(I)$ ) and then tests to see if its value is zero. If  $EX(I)$  is not equal to zero the next  $EX(I)$  is read. This will be repeated for N cycles. If  $EX(I)$  equals zero then control is removed from the loop and execution proceeds downward. This method of input requires that the number of minerals whose saturation is tested for be less than N, that each equilibrium constant be on a separate line in the data-file and that the last line in the data file be blank or equal to zero. Care must be taken to see that the equilibrium constants are input in the order that the program makes its saturation tests (lines 171 and 197) and that an E10.4 format is adhered to. Line 24 reads N initial molalities and line 25 outputs these numbers. Line 26 outputs "INPUT ACTIVITY COEFFICIENTS". Line 27 reads N activity coefficients and line 28 outputs N activity coefficients. Both initial molalities and activity



coefficients are input and output on 8E10.4 formats. In the data file this means that 8 numbers in an E10.4 format will be read from each line until N numbers are found. The order of the molalities is determined by the order of the columns of the matrices. The activity coefficients must be input in the same order as the molalities. Activity coefficients for solid phases may be input with the value of any arbitrary number or zero. Line 29 outputs "INPUT INITIAL DELTA XSI". Line 30 reads (XS) and line 31 outputs (XS). XS is read and output on an 8E10.4 format. Line 32 to 35 initialize the variables H7, M9, H6 and M11. H7 is the total number of complete cycles minus one. H6 is a cycle counter which is set equal to zero each time output is made. Lines 36 to 39 form a loop which creates a matrix (E(I,J)) of size NxNN which consists of all zeros. Lines 40 to 69 place the mass balance equations ((30 to (35)) in matrix E(I,J). Lines 70 to 72 form a loop which sets the array X(I) (new molalities) equal to Y(I) (initial molalities). This is done so that lines 87 to 101 may be used to set up the initial matrix as well as all later matrices. From line 73 the program bypasses 74 to 86 to go directly to line 87. Lines 87 to 101 put equations (24) to (29) in matrix E(I,J). On the initial cycle line 102 returns execution to line 74. If output of the initial matrix is desired the following program lines should be added between line 74 and 75.

```

          DO 29 I + 1,N
          WRITE (6,101) (E (I,J), J=1,NN)
29 CONTINUE

```

From line 75 the program goes directly to line 106 where lines 106 to 109 store matrix  $(E(I,J))$  in matrix  $E1(I,J)$ . The loop from line 110 to 112 calls subroutine 40 (lines 247 to 262)  $N$  times to solve  $E(I,J)$  to produce the reaction coefficients  $\bar{n}_j$ . In this process  $E(I,J)$  is destroyed and  $\bar{n}_j$  is stored in the array  $E(I,NN)$ . The loop from 113 to 114 stores  $E(I,NN)$  and  $Y2(I)$ . Comparing equations (24) to (35) and (38) to (49) shows that the left side of both sets of equations is identical and that the terms on the right sides of all equations are constant. Therefore the same matrix used to solve for  $\bar{n}_j$  can be used to solve for  $\bar{n}_j'$  if the constant's column is changed. The loop from line 115 to 118 creates matrix  $E2(I,J)$  and fills it with zeros. The loop from lines 119 to 122 sets the  $N \times N$  portion of matrix  $E2(I,J)$  equal to  $E1(I,J)$ . Equations on lines 124 to 133 place the constant terms from equations (38) to (43) into the constants column of  $E2(I,J)$ . The loop from line 135 to 138 sets  $E(I,J)$  equal to  $E2(I,J)$ . And as before the loop from 139 to 141 calls subroutine 40 to solve  $E(I,J)$ .  $E(I,J)$  is destroyed and  $\bar{n}_j'$  is stored in  $E(I,NN)$ . The loop from 143 to 145 calculates the change in molality of each species or the change in the number of moles at each mineral phase. Line 144 has the same form as equation (37) with  $Y1(I)$ ,  $Y2(I)$ ,  $X_S$ , and  $E(I,NN)$  being  $\Delta m$ ,  $\bar{n}_j$ ,  $\Delta \xi$  and  $\bar{n}_j'$  respectively. The loop line 147 to 149 stores the molalities from the preceding cycle ( $X(I)$ ) in  $XST(I)$ . Line 150 stores total reaction progress ( $X_B$ ) in  $XBS$ . This line is meaningless on the initial cycle. The loop from 151 to 156 first adds the change in molality ( $Y1(I)$ ) to the initial, or proceeding molality ( $Y(I)$ ). Line 153 checks whether each new

molality is positive. If  $X(I)$  is positive then lines 154 and 155 are skipped and the next  $X(I)$  is calculated. This cycle repeats  $N$  times or until a negative  $X(I)$  is found. If the new molality is negative line 154 sets the reaction progress increment ( $XS$ ) equal to 90% of its previous value. Line 155 returns the program to line 143 where the cycle repeats until the reaction progress increment is small enough so that all new molalities are positive. The loop from 157 to 159 converts the new molalities  $X(I)$  to log molalities and stores them in array  $XL(I)$ . Line 160 sets the total reaction progress  $XB$  equal to the reaction progress increment  $XS$  on the initial cycle ( $H7=0$ ). Lines 161 and 162 form a loop which converts molalities to activities. Line 162 has the same form as equation (22). Line 163 adds the reaction progress increment  $XS$  to total reaction progress  $XB$  on all cycles except the initial cycle. Line 164 computes the logarithm of total reaction progress and stores this number in variable  $XBL$ . Lines 165 to 169 are equilibrium constant expression for each mineral whose saturation is tested for. The equations must be written in the same form as the equations from which the given equilibrium constants  $EX(I)$  were taken.

Line 171 to 195 are the saturation tests. All have the same form. The test for kaolinite is given below.

```

171          IF(E11 .LT. EX(I) GO TO 91
172          X2+(1.-EX(1)/E11))*100.
173          IF(X2 .GT. 0.01) GO TO 99
174          WRITE (6,207) E11
175          M9 = 1

```

If the calculated equilibrium constant  $E11$  is less than the given equilibrium constant  $EX(1)$  then lines 172 through 175 are skipped and the program proceeds to the next saturation test. If  $E11$  is greater than  $EX(1)$  then  $X2$  is calculated.  $X2$  is percentage by which  $E11$  is greater than  $EX(1)$ . If this percentage is less than or equal to 0.01% then line 174 outputs "\*\*\*KAOLINITE SATURATION\*\*" and line 175 sets  $M9$  equal to one and then the next saturation test is made. If  $X2$  is greater than 0.01% execution goes directly to line 215 where total reaction progress  $XB$  is set equal to the total reaction progress of the preceding cycle  $XBS$ . Lines 216 to 218 are "IF" statements which are executed if this portion of the program is reached on the initial cycle. This should occur if the initial solution is supersaturated or if the initial reaction progress increment was too large. This output would be seen: "INITIAL SOLUTION SATURATED, TRY AGAIN" then "CHECK FOLLOWING K OUTPUT" followed by the output of the calculated equilibrium constant values for each mineral whose saturation was tested for. After this output line 218 stops further execution. If it is not the first cycle then lines 219 to 221 reset the new molalities  $X(I)$  to equal the stored molalities from the preceding cycle  $XST(I)$ . Line 222 halves the reaction progress increment and line 223 returns execution to line 78 when the entire cycle is repeated until a small enough reaction progress increment is found so that saturation is approached slowly. This portion of the program assures that supersaturation does not exist. The 0.01% value of  $X2$  is arbitrary and may be changed depending on the accuracy desired.

After making all saturation tests line 196 checks to see if

saturation has actually been reached; that is whether M9 equals 1. If saturation has been reached line 197 calls subroutine 50 which outputs the reaction progress increment, the reaction coefficients, the log molality or logarithm of number of moles of each species or mineral phase respectively, the cycle number, and the total reaction progress. Line 198 outputs "SATURATION REACHED" and line 199 stops execution. If saturation has not been reached line 197, 198, and 199 are skipped. The loop on lines 201 to 204 checks whether the molality or number of moles of each species in solution is greater than  $10^{-32}$ . Any species or phase whose concentration is less than this value is assumed to have zero concentration. If X(I) is greater than the zero concentration level then lines 203 and 204 are bypassed. If X(I) is less than or equal to  $10^{-32}$  then line 203 sets M8 equal to 1 and line 204 outputs "ZERO CONCENTRATION". Line 206 causes lines 207 and 208 to be skipped if zero concentration has not occurred. If zero concentration is encountered then line 207 calls subroutine 50 for output and line 208 stops execution. The "IF" statement on line 209 calls subroutine 50 for output any time H6 equals zero. Line 210 increases H6 by one each complete cycle and the "IF" statement on line 211 sets H6 equal to zero when H6 equals H9. Since H6 initially equals zero the output subroutine is always called on the first cycle and every H9 cycles thereafter. For example if H9 equals 10 then output occurs on cycles 1, 11, 21, and so on. Lines 212 and 213 increase the cycle counters H7 and M11 by one each cycle. Line 214 returns execution to line 78 where the loop from line 79 to 82 sets E(I,J) equal to E1(I,J). This is done to place the mass balance

equations (24) to (28) back into  $E(I,J)$ . If the preceding cycle was the first cycle lines 105 and 106 are now executed for the first time. These lines store the molalities from the preceding cycle in  $Y(I)$ . From this point the program repeats the cycle previously described until zeroconcentration or saturation is reached. The matrix  $E(I,J)$  must be arranged so that no zeros are in its diagonal. Line 251 in subroutine 40 will cause the output of "ZEROS IN DIAGONAL, CHANGE MATRIX, START AGAIN". Then execution will be stopped. Zeros in the diagonal must be avoided because line 256 will produce division by zero. In larger matrices the execution of subroutine 40 may create zeros in the diagonal. This can be avoided by rearranging the row order of the equations. If this problem is encountered after the first cycle the preceding cycle may be repeated with a slightly different  $X_S$  value until a matrix which subroutine 40 can solve is found.

Execution is stopped each time saturation is reached. Unless this saturation represents overall equilibrium the program must be changed to account for the new phase being produced. A new partial equilibrium equation must be added, the mass balance equations must be altered and the saturation test for the new phase must be bypassed. For example if the program described reaches kaolinite saturation these changes must be made. In the datafile  $N$  must be increased by one and the molalities must be changed. In the program these lines must be added.

$$E(1,13) = 9.000$$

$$E(4,13) = 2.000$$

$$E(11,13) = 4.000$$

$$E(12,13) = 2.000$$

$$E(13,2) = -6./X(2)$$

$$E(13,3) = 2./X(3)$$

$$E(13,10) = 2./X(10)$$

$$E2(13,NN) = (2.*((Y2(3)**2)/(Y(3)**)))$$

$$+(2.*((Y2(10)**2)/(Y(10)**2)))$$

$$-(6.*((Y2(2)**2)/(Y(2)**2)))$$

and "GO TO 91" must be inserted at line 170 to bypass the saturation test for kaolinite. For each phase or species that reached zero concentration comparable equations must be removed from the program.

The initial (XS) value must be chosen so that this value is large enough to minimize the amount of computer time used but must be small enough so that masses are conserved. If XS is too large the cubic term in equation (37) becomes significant. The largest XS value used was  $10^{-6}$  and the smallest was  $10^{-10}$ .

The program is neither so elegant or complete as the PATHCALC program of Helgeson (1968) but is simpler to understand and was fun to write.

## SOLUTION COMPOSITIONS, ACTIVITY COEFFICIENTS, EQUILIBRIUM CONSTANTS

Once the reactant mineral and species to be considered are established a hypothetical initial solution composition must be chosen. This solution may represent a possible natural solution that has not yet equilibrated with the reactant mineral, microcline. Six initial solution compositions are considered. These solution compositions were chosen on the basis of known water chemistry at Roosevelt Hot Springs (Table 1b), Utah. All six hypothetical solutions, (Table 1a) have ionic strengths of 0.1. The total molalities of potassium and sulfate are equivalent to 425 ppm and 193 ppm respectively. All are saturated with respect to quartz. The solutions represent three different temperatures, 100°C, 200°C, and 300°C, and two different pH levels. In group one the pH was taken to be 1.5 pH units on the acid side of neutrality at each respective temperature and group two was chosen to have a pH 2.5 pH units on the acid side of neutrality at each respective temperature. Estimating initial pH is difficult. For natural systems activities of hydrogen may be calculated from activity diagrams like those in Figure 7 if the alteration mineralogy and the activities of potassium and sulfate ions are known. These values assume overall equilibrium. The overall process of alteration in granite rocks is controlled by the dissolution of feldspar:

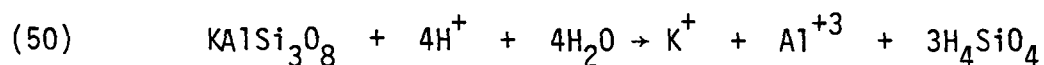




Table 1a - Assumed Initial Solution Compositions

Species	Concentration (Log Molality)					
	Group 1			Group 2		
	100 <sup>0</sup>	200 <sup>0</sup>	300 <sup>0</sup>	100 <sup>0</sup>	200 <sup>0</sup>	300 <sup>0</sup>
H <sup>+</sup>	-4.54	-4.01	-3.83	-3.54	-3.01	-2.83
Al <sup>+3</sup>	-8.89	-9.88	-10.77	-6.89	-7.38	-7.82
AlOH <sub>4</sub> <sup>-</sup>	-8.05	-6.57	-6.02	-10.05	-8.07	-7.07
K <sup>+</sup>	-1.97	-1.97	-1.97	-1.97	-1.97	-1.96
KSO <sub>4</sub> <sup>-</sup>	-3.82	-3.63	-4.23	-3.86	-4.28	-5.20
HSO <sub>4</sub> <sup>-</sup>	-4.64	-3.02	-2.65	-3.68	-2.68	-2.62
SO <sub>4</sub> <sup>=</sup>	-2.65	-2.92	-3.96	-2.68	-3.58	-4.94
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	-7.33	-7.32	-7.48	-8.33	-8.32	-8.48
H <sub>4</sub> SiO <sub>4</sub>	-3.06	-2.26	-1.57	-3.06	-2.26	-1.57
OH <sup>-</sup>	-7.50	-6.95	-6.74	-8.50	-7.95	-7.74
Concentrations (parts per million)						
K <sup>+</sup> Total	425	425	425	425	425	425
SO <sub>4</sub> <sup>=</sup> Total	193	193	193	193	193	193
SiO <sub>2</sub> Total	52	330	1617	52	330	1617

Table 1b - Roosevelt Hot Spring Water Compositions

Constituents in ppm	1	2	3	4
Na	2210	2400	2500	1840
Ca	83	9	22	122
K	425	565	488	274
SiO <sub>2</sub>	170	775	313	81
Mg	-	19	0	25
Cl	3800	4800	4240	3210
SO <sub>4</sub>	122	200	73	120

- (1) Phillips well 9-1, University of Utah
- (2) Phillips well 54-3, Chemical and Mineralogical services
- (3) Roosevelt Hot Springs, Mundorff (1970) 9-11-57
- (4) Roosevelt seep, University of Utah Analyst 6-25-75

This reaction consumes hydrogen ion. When equilibrium with feldspar is reached the overall reaction stops and the pH is at its maximum value. Therefore pH values calculated from activity diagrams represent an upper limit of pH. For hypothetical mass transfer calculations which end at overall equilibrium the initial pH must be chosen on the acid side of this upper pH limit. No reliable values for aluminum concentrations were available. Since no gibbsite is known to be present at Roosevelt Hot Springs (Parry, personal communication),  $Al^{+3}$  activity was taken to be about an order of magnitude less than that which would exist in equilibrium with gibbsite at the particular pH and temperature in question. This value was arbitrarily changed by small amounts to insure that the initial solution was undersaturated with respect to all mineral phases except quartz. The initial solution compositions and Roosevelt Hot Springs water compositions are summarized in Table 1.

Activity coefficients were calculated from the modified Debye-Hückel equation (Helgeson, 1969).

$$(51) \quad \log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a_i^0 \sqrt{I}} + \frac{0}{BI}$$

Where:  $\gamma_i$  is the activity coefficient of species  $i$ ;  $z_i$  is the valence number of species  $i$ ;  $I$  is the ionic strength;  $a_i^0$  is a parameter depending on the species;  $A$ ,  $B$ , and  $B^0$  are parameters depending on the solution and temperature.  $a_i^0$  was taken from Kharaka, et. al (1973) and  $A$ ,  $B$ ,  $B^0$  were taken from Helgeson (1969).

All equilibrium constants were taken from Kharaka, et. al 1973 except for the equilibrium constant for muscovite which was taken from

Helgeson (1969). The muscovite equilibrium constant value from Kharaka, et. al 1973 seemed unrealistic. Activity coefficients and equilibrium constant used are summarized in Table 2 and Table 3.

Table 2 - Summary of Activity Coefficients

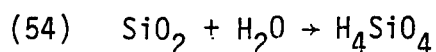
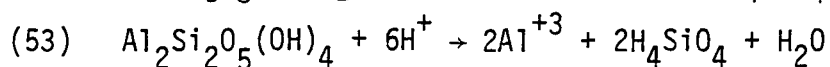
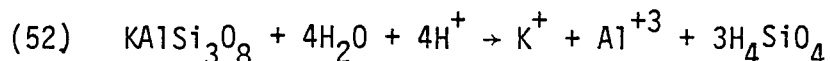
Species	Activity Coefficients (I=0.1)		
	100°C	200°C	300°C
H <sup>+</sup>	.8100	.7572	.6432
Al <sup>+3</sup>	.1380	.0742	.0188
Al(OH) <sub>4</sub> <sup>-</sup>	.7534	.6860	.5479
K <sup>+</sup>	.7363	.6644	.5197
KSO <sub>4</sub> <sup>-</sup>	.7672	.7032	.5707
HSO <sub>4</sub> <sup>-</sup>	.7534	.6860	.5479
SO <sub>4</sub> <sup>=</sup>	.3253	.2268	.0989
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	.7451	.6755	.5342
H <sub>4</sub> SiO <sub>4</sub>	1.011	1.011	1.000
OH <sup>-</sup>	.7363	.6644	.5197

Table 3 - Summary of Equilibrium Constants

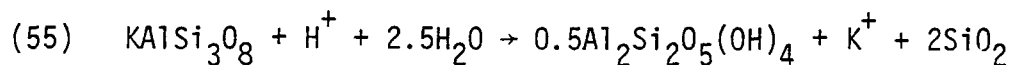
		Log Keq	
Kaol	2.29	-1.58	-3.68
K-spar	-0.33	-1.45	-2.04
musc.	7.97	0.93	-3.31
gibbsite	-31.14	-30.90	-31.61
alunite	-82.83	-84.29	-88.19
quartz	-3.06	-2.26	-1.57
$\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{=}$	-3.0	-4.51	-6.08
$\text{KSO}_4 \rightarrow \text{K}^+ + \text{SO}_4^{=}$	-1.30	-1.93	-2.75
$\text{Al(OH)}_4^- \rightarrow \text{Al}^{+3} +$ $4\text{OH}^-$	-32.10	-32.80	-34.30
$\text{H}_4\text{SiO}_4 \rightarrow \text{H}^+ +$ $\text{H}_3\text{SiO}_4^-$	-9.03	-9.36	-10.20
$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	-12.26	-11.36	-11.04
Am. silica	-2.36	-1.82	-1.48

## REACTION PATHS

Group one solutions and the 300°C group two solution all had similar reaction paths (see Figures 1, 2, 3, and 6). The following discussion applies specifically to the 200°C group one example but in general to all four reactions. The solution remains undersaturated with all phases except quartz until enough microcline dissolves to raise the  $Al^{+3}$  concentration high enough to produce kaolinite. As kaolinite precipitates the pH increases due to the net effects of equations (52), (53), and (54).



The reaction coefficient of microcline is negative one, and the reaction coefficient of kaolinite varies between 0.4999 and 0.4446. The reaction coefficient of quartz varies between 2.000 and 2.016. An estimate of the net effect can be obtained by assuming constant reaction coefficients of 0.5 and 2.0 for kaolinite and quartz respectively. After multiplying each equation by the appropriate reaction coefficient and summing, the result is:



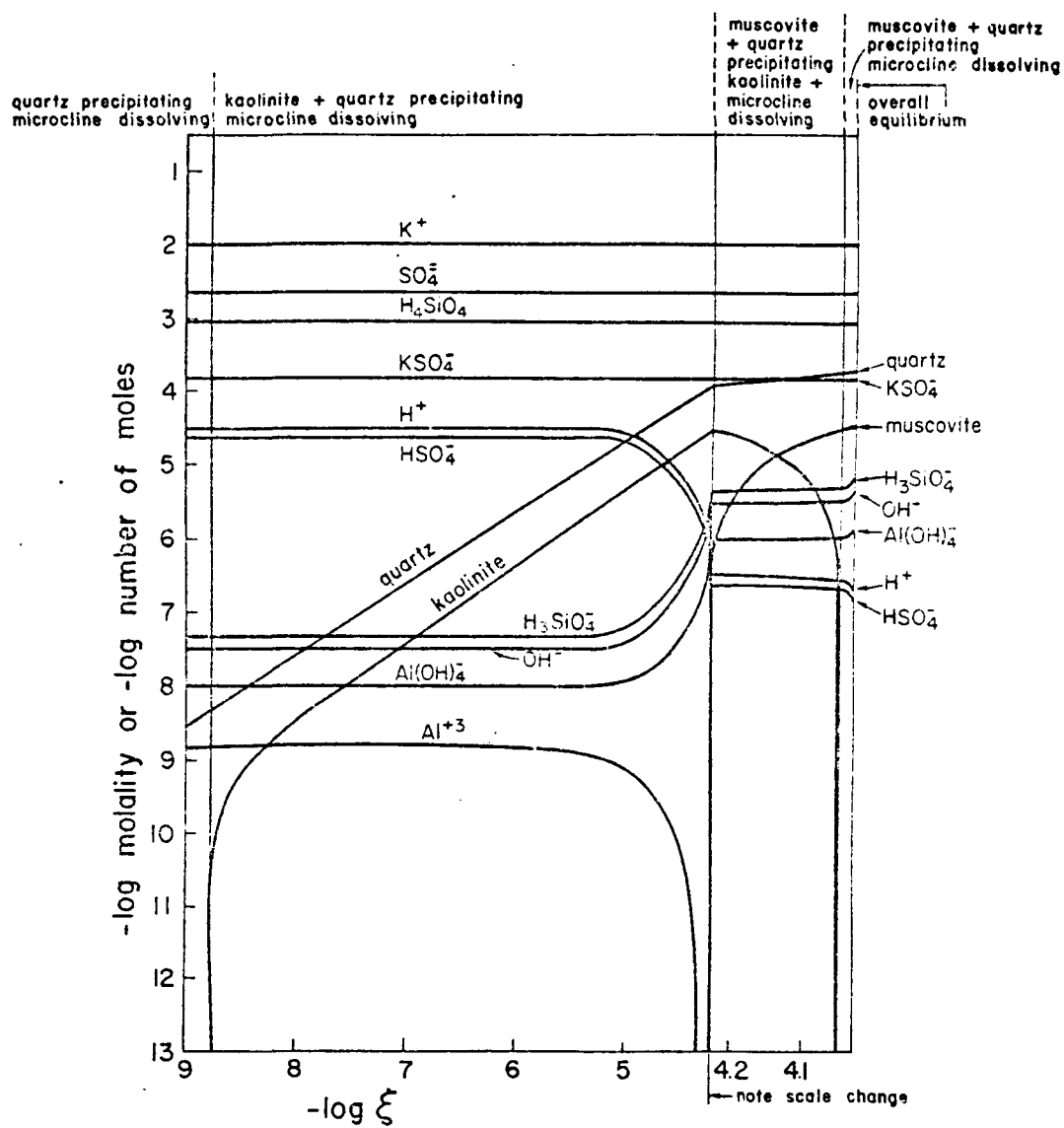


Figure 1. Group one solution at 100°C.

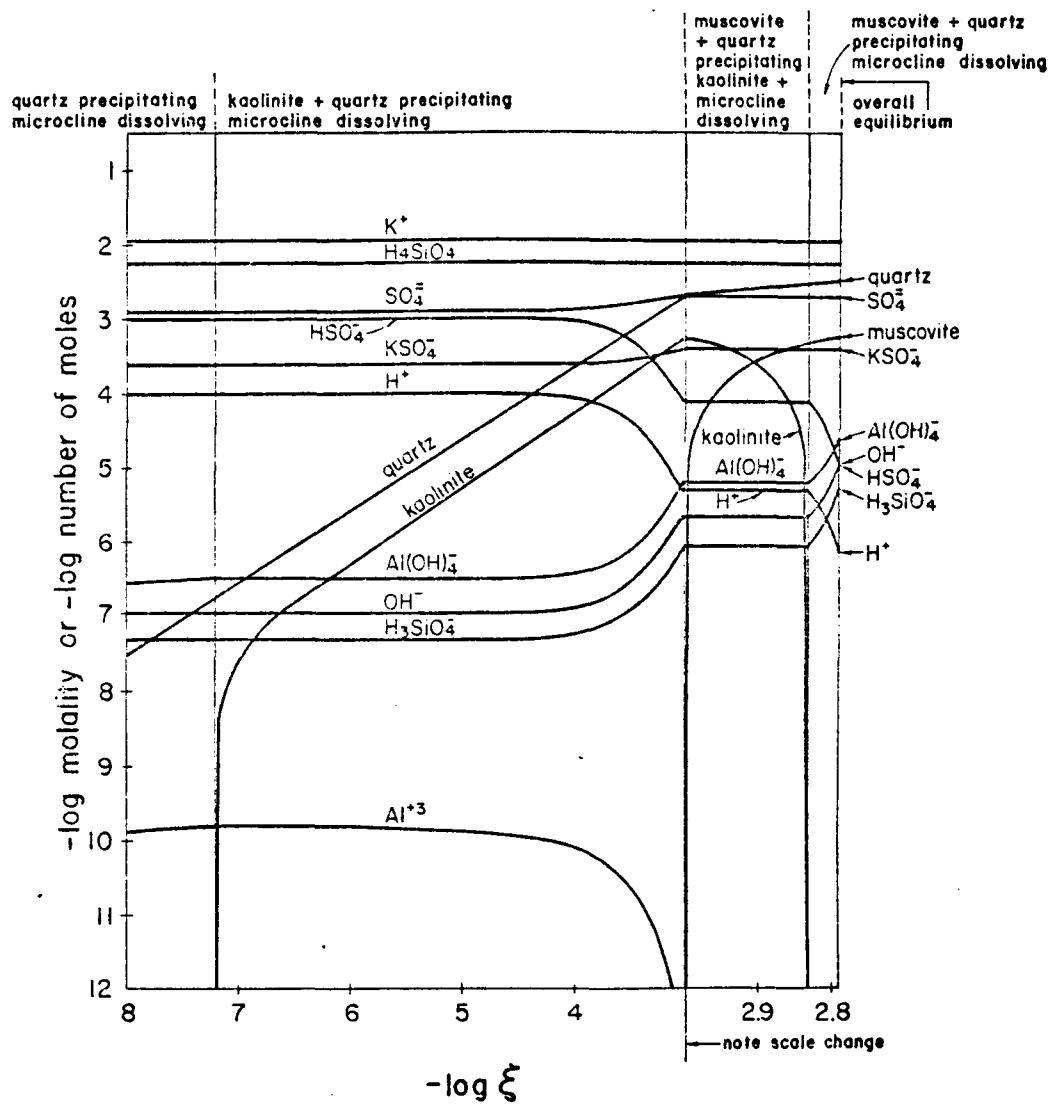
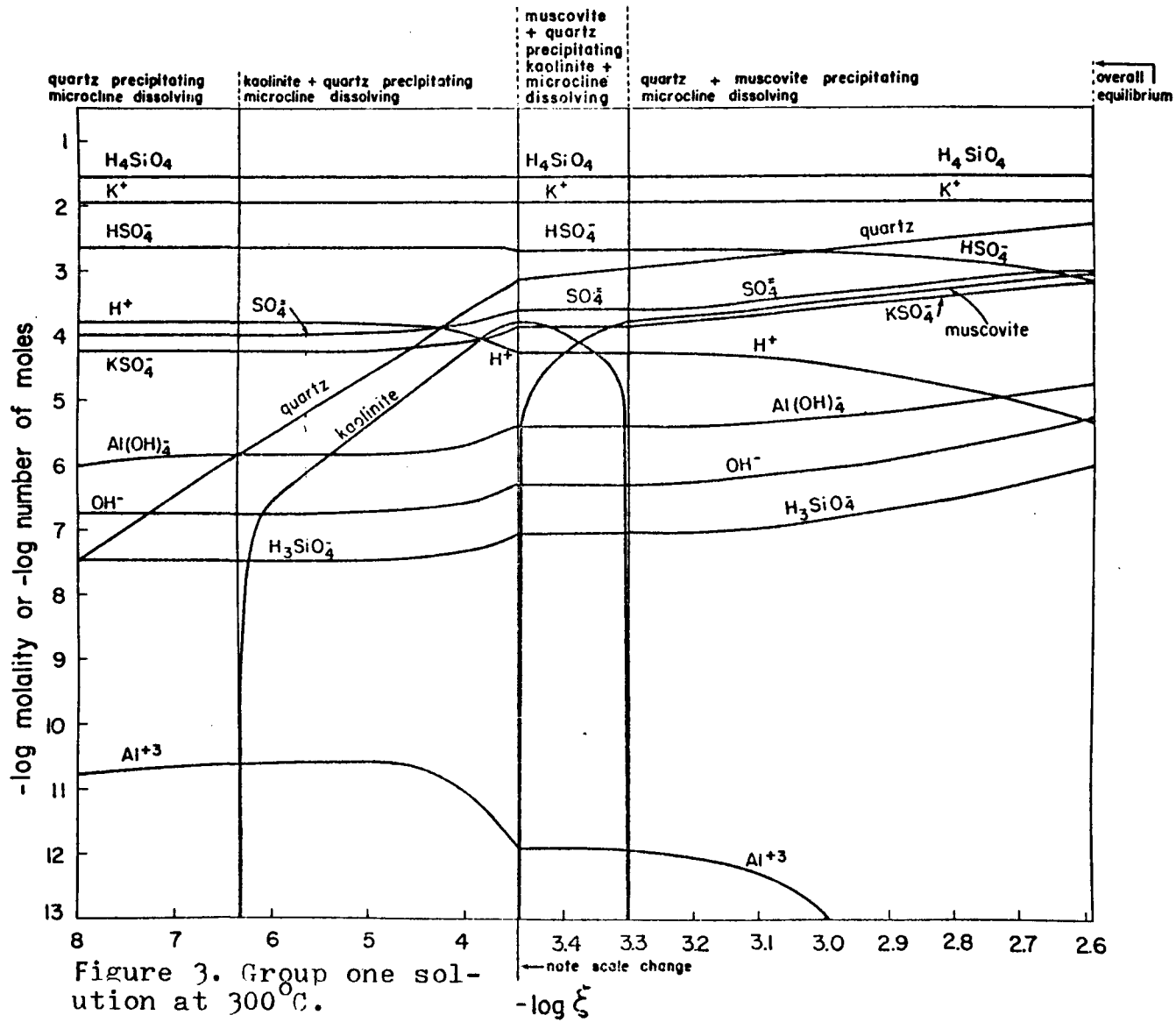


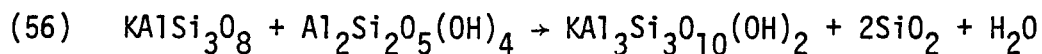
Figure 2. Group one solution at 200°C.





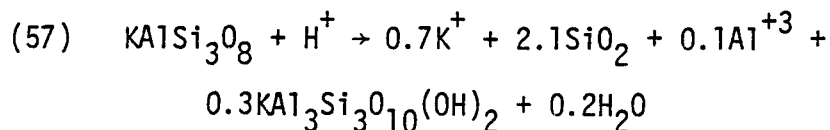
This estimate indicates an increase in potassium ion, and pH. Note that  $Al^{+3}$  is essentially conserved by equation (55) but since the reaction coefficient of kaolinite is slightly less than 0.5 some small amount of aluminum is added to the solution. An increase in pH causes a decline in the activities of  $Al^{+3}$  and  $HSO_4^-$  and an increase in the activities of  $H_3SiO_4^-$ ,  $K^+$ ,  $KSO_4^-$ ,  $OH^-$  and  $Al(OH)_4^-$ .

When pH and potassium ion concentration have increased sufficiently muscovite saturation is reached. At this point kaolinite begins to dissolve and muscovite begins to precipitate according to this reaction.



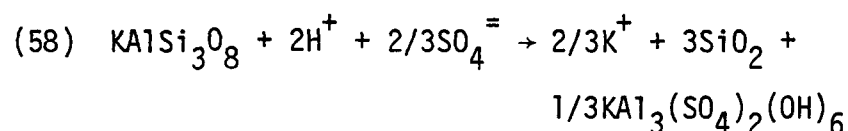
The reaction coefficients shown above are constant during this segment of the overall reaction. Also since the pH is constant the reaction coefficients of all aqueous species are zero and the solution composition is unchanged.

After all kaolinite has dissolved, muscovite continues to precipitate until overall equilibrium is reached. During this last step of reaction progress the reaction coefficient of muscovite varies between 0.32 and 0.27 and the reaction coefficient of quartz varies between 2.0 and 2.1. Assuming constant reaction coefficients of 0.3 and 2.1 for muscovite and quartz produces the following estimate of the net reaction.



Again, though this reaction is only an approximation it shows the continuing increase of pH and potassium ion concentration. A small amount of aluminum is added to solution and quartz is produced at a slightly higher rate. Equation (57) indicates an increase of  $Al^{+3}$  concentration but Figure 2 shows  $Al^{+3}$  to be decreasing.  $Al^{+3}$  decreases due to the effect of increasing pH on equation (3). The total molality of aluminum increases because of equation (57).

The 100°C and 200°C group two solutions encountered alunite saturation first. Kaolinite saturation was then reached. After saturation with respect to kaolinite all alunite dissolved. From this point on the reaction path was similar to that of the other solutions. The following description applies specifically to the 200°C group two solution but may be applied to the 100°C group two solution as well. The precipitation of alunite is approximated by this equation:



During this segment of the reaction the reaction coefficient of quartz is constant and the reaction coefficient of alunite is nearly constant. The nearly constant reaction coefficient of alunite indicates almost complete conservation of aluminum among solid phases. The molality of sulfate ion decreases and pH and potassium ion concentration increase. Alunite precipitates until kaolinite saturation occurs. At this time alunite dissolves and kaolinite precipitates. During this reaction the reaction coefficient of alunite

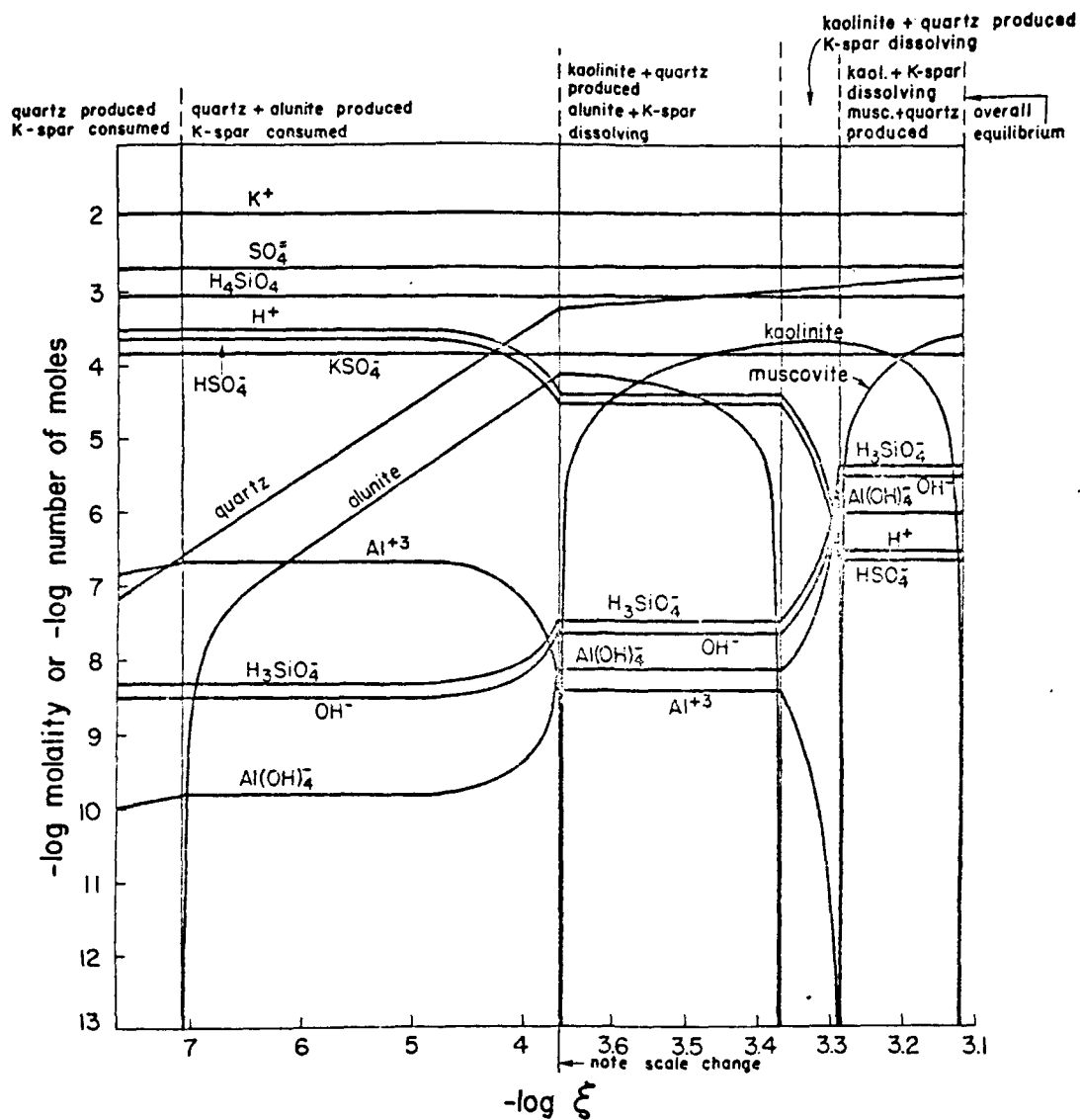
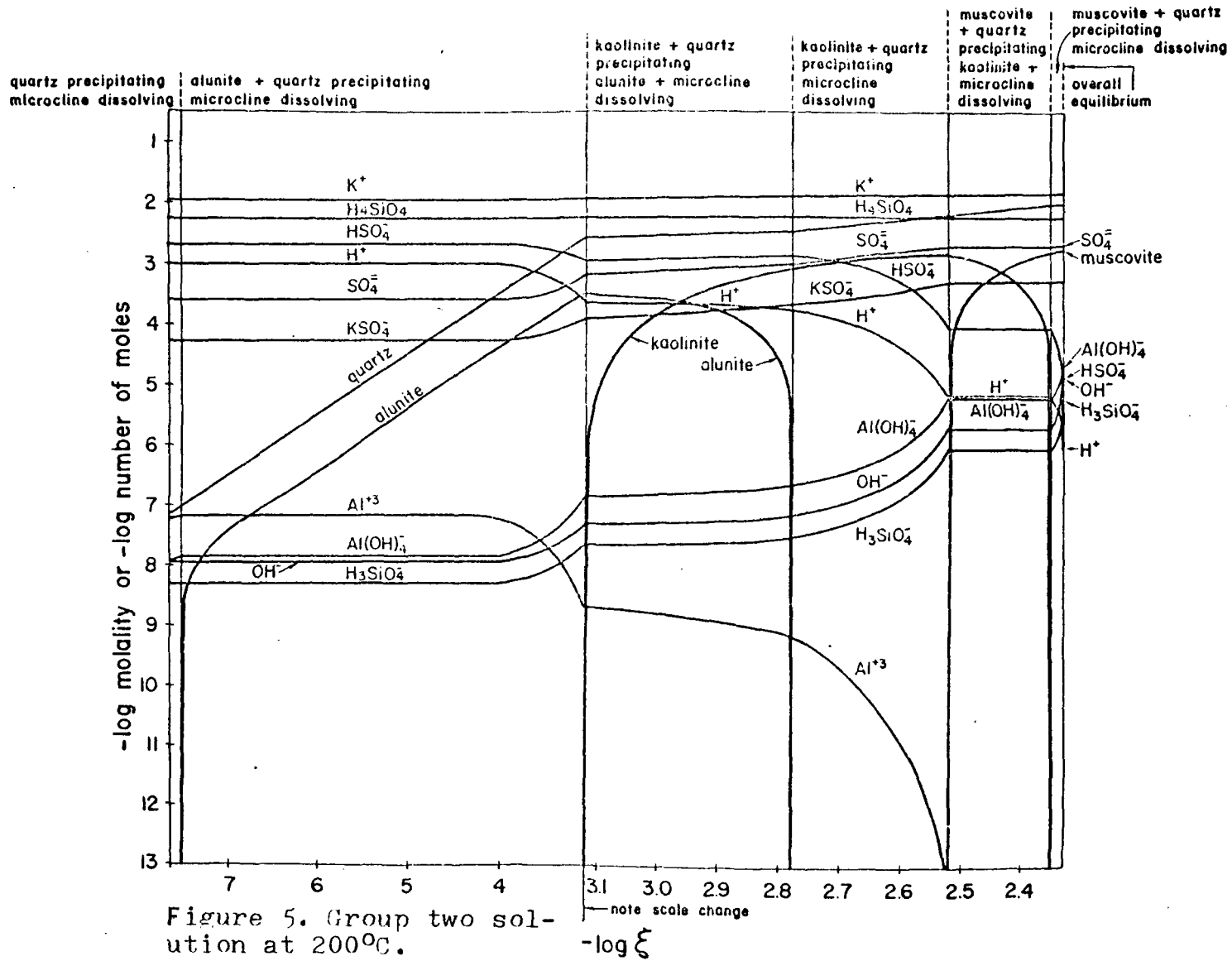


Figure 4. Group two solution at 100°C.



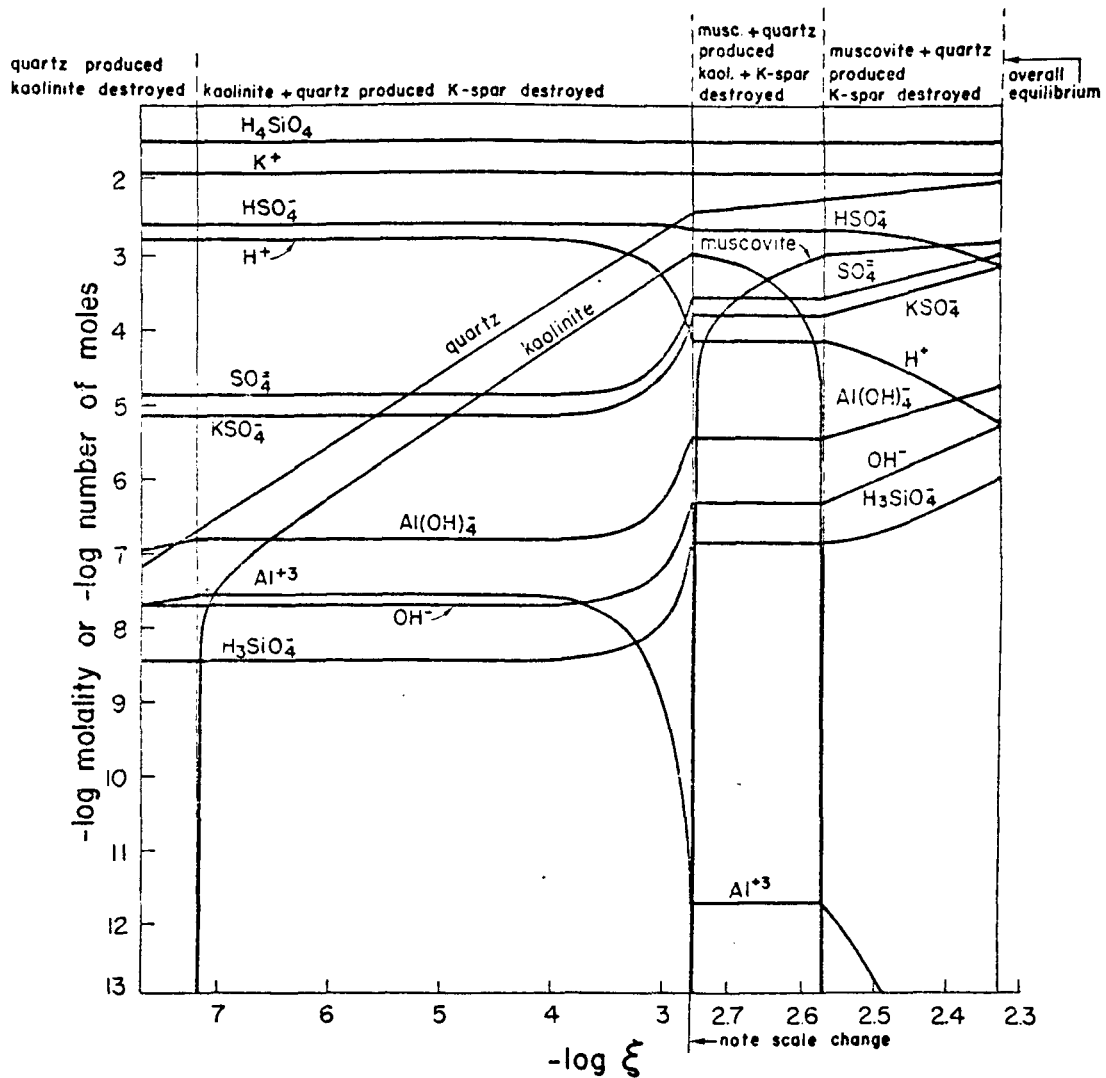


Figure 6. Group two solution at 300°C.

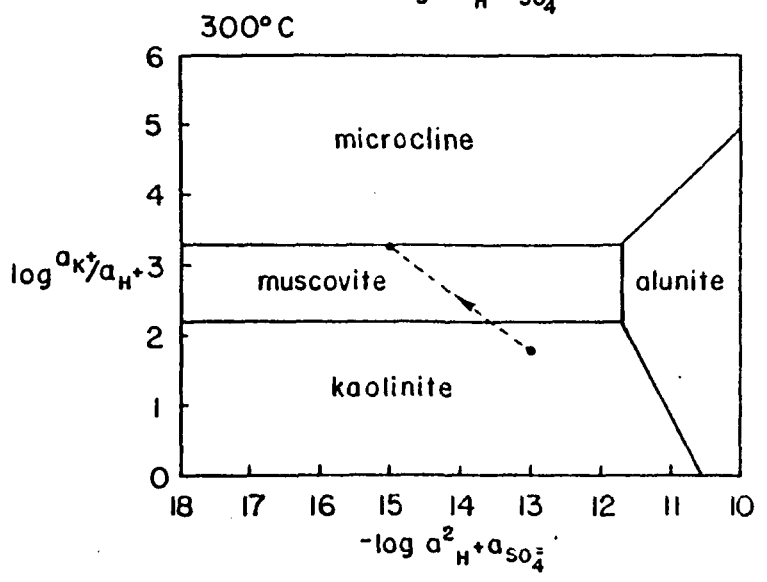
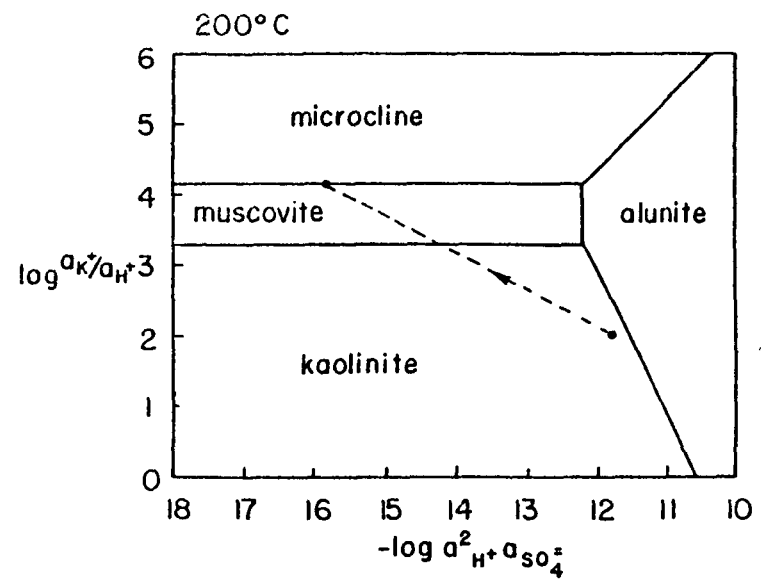
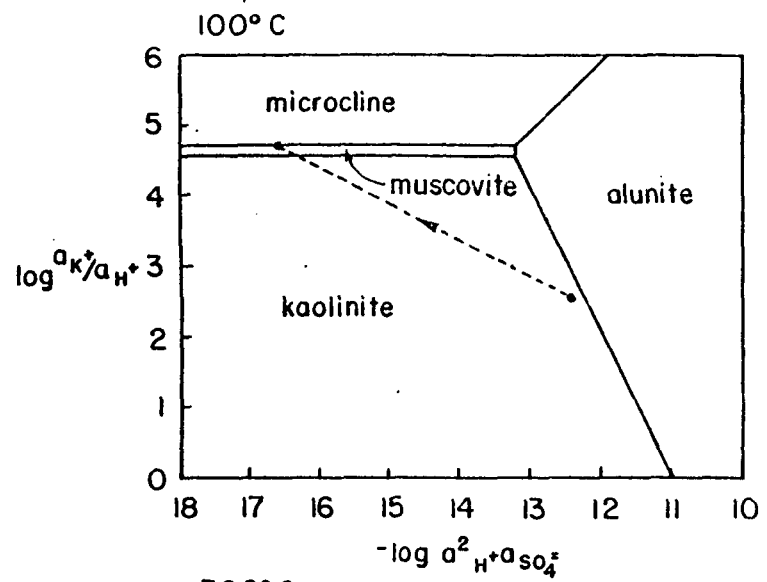


Figure 7. Activity diagrams for the system  $K_2O-Al_2O_3-S_2O_3-SiO_2-H_2O$ . Quartz saturation and unit activity of water are assumed. Group one reaction paths are shown.

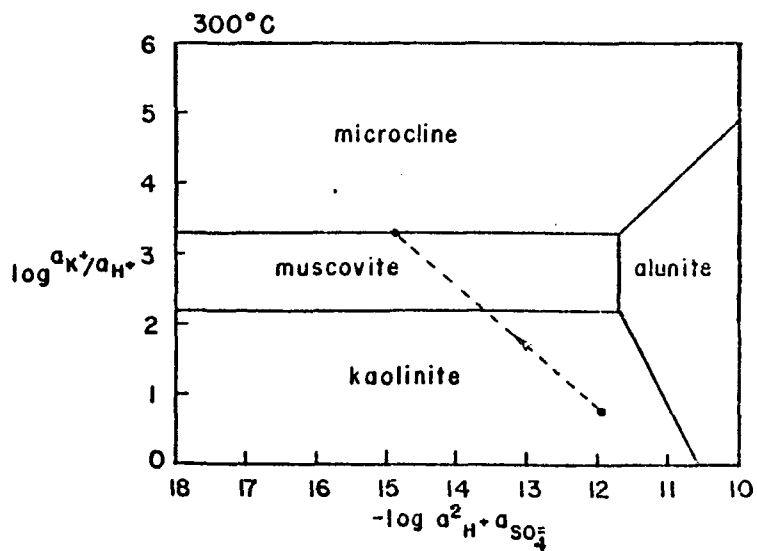
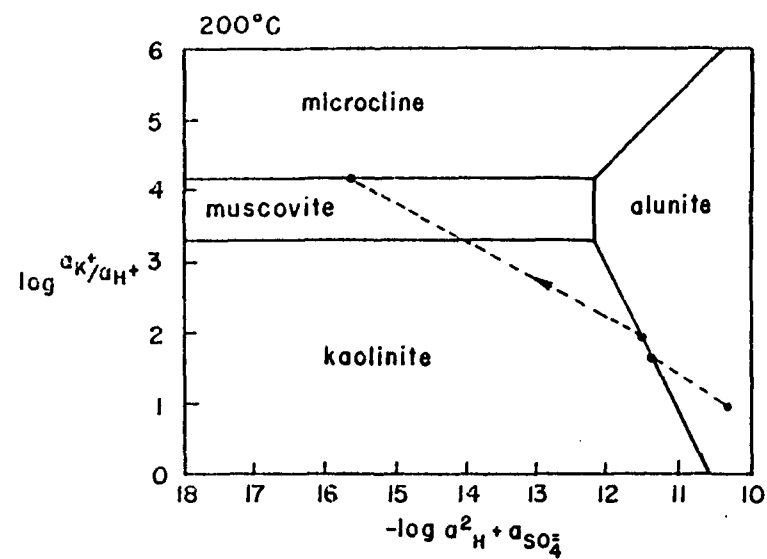
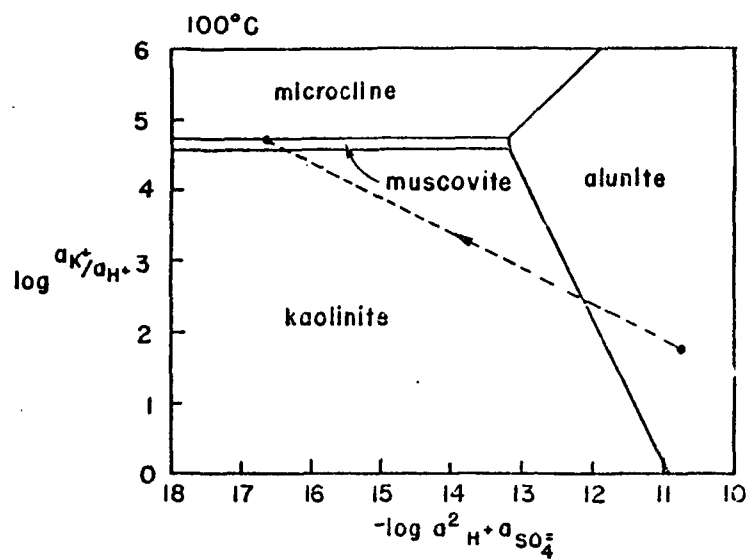
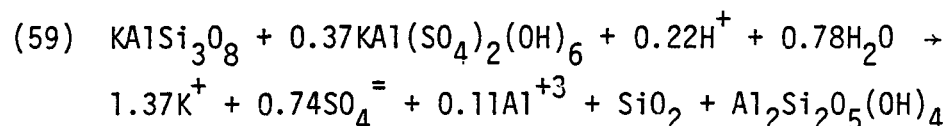


Figure 8. Activity diagrams for the system  $K_2O-Al_2O_3-S_2O_3-SiO_2-H_2O$ . Quartz saturation and unit activity of water are assumed. Group two reaction paths are shown.



varies between -0.36 and -0.37. The reaction coefficient of quartz varies between 0.90 and 0.89 and the reaction coefficient of kaolinite remains approximately constant at 1.05. Assuming constant reaction coefficients of -0.37, 0.90 and 1.0 for alunite, quartz, and kaolinite the following reaction can be written.



This reaction unlike the reaction producing muscovite from kaolinite (equation (56)) does change the solution composition. The production of  $\text{SO}_4^{=2}$  causes the pH to increase as shown by equation (6). Total aluminum molality in solution increases as is indicated by equation (59) but the molality of  $\text{Al}^{+3}$  ion decreases due to the effect of increasing pH. From this point on all solutions followed similar reaction paths.

The 300°C group two solution never became saturated with respect to alunite because of the effect of temperature on equations (5), (11) and (2). The equilibrium constant in equation (11) is  $10^{-3}$  at 100°C and  $10^{-6.08}$  at 300°C. Therefore with constant pH much more sulfate exists as  $\text{HSO}_4^-$  than at higher temperatures. This shift effectively prevents there being enough sulfate as  $\text{SO}_4^{=2}$  ion at higher temperatures to produce alunite. Also at higher temperatures the neutral point shifts to higher activities of hydrogen. Therefore, for solutions at different temperatures that are equally acid in terms of pH units from neutrality the solution at the higher temperature will have a higher activity of hydrogen ion. From

equation (11) it is evident that higher activities of hydrogen depress sulfate ion concentration.

Comparison of equations (55), (56), (58) and (59) shows that though small amounts of aluminum are added to the solution very little aluminum is transferred in comparison to other elements. This approximate conservation of aluminum is significant because activity diagrams such as Figure 7 are based on reactions which conserve aluminum. Also, since little aluminum was transferred, the uncertainty of the value of aluminum concentration in solution probably introduces very little error. In all reactions except equation (56) potassium ion is produced and hydrogen ion is consumed. The concentration of hydrogen ion controls the distribution of species in solution. The most evident change in the solution was the decrease in hydrogen ion concentration. The overall effect of each reaction was to remove hydrogen and produce potassium until microcline saturation was reached. This process is comparable to hydrogen metasomatism as described by Hemley and Jones (1964). Hydrogen ion is removed from solution by precipitating hydrated minerals. The hydrogen ion is replaced by potassium ion to maintain the electrical neutrality of the solution. Whenever the amount of potassium produced is less than the amount of hydrogen consumed, small amounts of aluminum are transferred to the solution to maintain electrical neutrality. Typically only small amounts of aluminum are involved. This effect is shown in equation (57) and (59). The alteration minerals are produced in order of decreasing hydrogen content and increasing silica content.

## MASSES TRANSFERRED

Summaries of the masses transferred for each reaction are given in Tables 4 and 5. The total amount of microcline destroyed is a function of temperature, pH and reaction path. The initial solution composition would, of course, have an effect but all six solutions have comparable compositions. With increasing temperature and decreasing pH more microcline is consumed. The effect of reaction path can be seen by noting that the 200°C and 300°C group two solutions consumed the same amount of microcline. Apparently encountering more phases lengthens the reaction path and so consumes more microcline. The amount of muscovite produced is strictly a function of the amount of microcline consumed. One-third mole of muscovite is produced for each mole of microcline destroyed. About two moles of quartz is produced for each mole of microcline destroyed. This is due to the stipulation of quartz saturation and aluminum conservation. Producing 1/3 mole of muscovite from one mole of microcline produces two moles of quartz. In each solution the total molality of K, Si, and Al increase. The change in the distribution of species in solution is chiefly a function of pH.  $H^+$ ,  $Al^{+3}$ , and  $HSO_4^-$  always decrease and  $OH^-$ ,  $Al(OH)_4^-$ ,  $H_3SiO_4^-$ ,  $KSO_4^-$  and  $K^+$  always increase.  $H_4SiO_4$  remains constant due to quartz saturation.

Table 4 - Group One Solutions  
 Mass Transfer Summary  
 all in log molality or log number of moles

	<u>100<sup>o</sup>C</u>		<u>200<sup>o</sup>C</u>		<u>300<sup>o</sup>C</u>	
	<u>initial</u>	<u>final</u>	<u>initial</u>	<u>final</u>	<u>initial</u>	<u>final</u>
H <sup>+</sup>	-4.54	-6.65	-4.01	-6.13	-3.83	-5.32
Al <sup>+3</sup>	-8.89	-15.16	-9.88	-16.44	-10.77	-15.44
Al(OH) <sub>4</sub> <sup>-</sup>	-8.05	-5.87	-6.57	-4.63	-6.02	-4.72
K <sup>+</sup>	-1.97	-1.97	-1.97	-1.94	-1.97	-1.92
KSO <sub>4</sub> <sup>-</sup>	-3.82	-3.82	-3.63	-3.38	-4.23	-3.19
HSO <sub>4</sub> <sup>-</sup>	-4.64	-6.75	-3.02	-4.93	-2.65	-3.15
SO <sub>4</sub> <sup>=</sup>	-2.65	-2.65	-2.92	-2.70	-3.96	-2.97
H <sub>3</sub> SiO <sub>4</sub>	-7.33	-5.21	-7.21	-5.20	-7.48	-5.99
H <sub>4</sub> SiO <sub>4</sub>	-3.06	-3.06	-2.26	-2.26	-1.57	-1.57
OH <sup>-</sup>	-7.50	-5.38	-6.95	-4.83	-6.74	-5.24
	<u>produced</u>	<u>destroyed</u>	<u>produced</u>	<u>destroyed</u>	<u>produced</u>	<u>destroyed</u>
microcline	-	-4.03	-	-2.79	-	-2.59
quartz	-3.74	-	-2.48	-	-2.29	-
kaolinite	-4.53	-4.53	-3.31	-3.31	-3.78	-3.78
muscovite	-4.51	-	-3.27	-	-3.07	-

Table 5 - Group Two Solutions  
 Mass Transfer Summary  
 all in log molality or log number of moles

	<u>100°C</u>		<u>200°C</u>		<u>300°C</u>	
	<u>initial</u>	<u>final</u>	<u>initial</u>	<u>final</u>	<u>initial</u>	<u>final</u>
H <sup>+</sup>	-3.54	-6.67	-3.01	-6.07	-2.83	-5.27
Al <sup>+3</sup>	-6.89	-15.29	-7.38	-16.24	-7.82	-15.30
Al(OH) <sub>4</sub> <sup>-</sup>	-10.05	-5.89	-8.07	-4.70	-7.07	-4.77
K <sup>+</sup>	-1.97	-1.95	-1.97	-1.87	-1.96	-1.87
KSO <sub>4</sub> <sup>-</sup>	-3.86	-3.80	-4.28	-3.32	-5.20	-3.17
HSO <sub>4</sub> <sup>-</sup>	-3.68	-6.78	-2.68	-4.87	-2.62	-3.14
SO <sub>4</sub> <sup>=</sup>	-2.68	-2.65	-3.58	-2.71	-4.94	-3.00
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	-8.33	-5.19	-8.32	-5.26	-8.48	-6.03
H <sub>4</sub> SiO <sub>4</sub>	-3.06	-3.06	-2.26	-2.26	-1.57	-1.57
OH <sup>-</sup>	-8.50	-5.36	-7.95	-4.90	-7.74	-5.29
	<u>produced</u>	<u>destroyed</u>	<u>produced</u>	<u>destroyed</u>	<u>produced</u>	<u>destroyed</u>
microcline	-	-3.12	-	-2.33	-	-2.33
quartz	-2.82	-	-2.03	-	-2.03	-
kaolinite	-3.60	-3.60	-2.83	-2.83	-3.05	-3.05
muscovite	-3.59	-	-2.81	-	-2.81	-
alunite	-4.15	-4.15	-3.54	-3.54	-	-

## GEOOTHERMOMETERS

One of the major objectives of this project was to investigate the use of mass transfer calculations in the development of geothermometers for use in hydrothermal systems. Examination of Figure 7 shows that the stability field of muscovite increases as temperature increases. Originally this was thought to indicate that with increasing temperatures more muscovite would be produced relative to the amount of microcline consumed. This idea is incorrect because aluminum is essentially conserved among solid phases. One third mole of muscovite will be produced for each mole of microcline destroyed regardless of the size of the stability field of muscovite. As stated previously the amount of microcline consumed is a function of initial pH, reaction path and temperature. Initial pH, reaction path and temperature are not independent of one another. Comparison of the reaction paths of the 300°C and 200°C group two solutions shows that reaction path is dependent on temperature. Comparison of the group one and group two 200°C solutions indicates that reaction path is dependent on initial pH as well. If one could estimate initial pH and reaction path without knowing the temperature it should be possible to calculate the temperature from the mass of muscovite present assuming the following conditions exist. Microcline must be the only reactant mineral present. Most natural systems of course have more than one mineral as a hostrock. Musco-

vite must be precipitated at the site where the microcline is dissolved. Since hydrothermal systems have ascending solutions this condition is clearly not met. Overall equilibrium must have been reached. As is indicated by dissolved silica and Na-K-Ca geothermometers equilibrium with respect to quartz and feldspar is reached only in small portions of natural hot springs. Also hydrothermal solutions must not be supersaturated with respect to quartz. Many natural systems are supersaturated with respect to quartz. Comparison of the activity diagrams in Figure 9 indicates that muscovite may not be a stable phase at temperatures less than 200°C if saturation with respect to opal rather than quartz exists. The mass transfer model used in this report does not reproduce natural systems well enough to be used as a geothermometer.

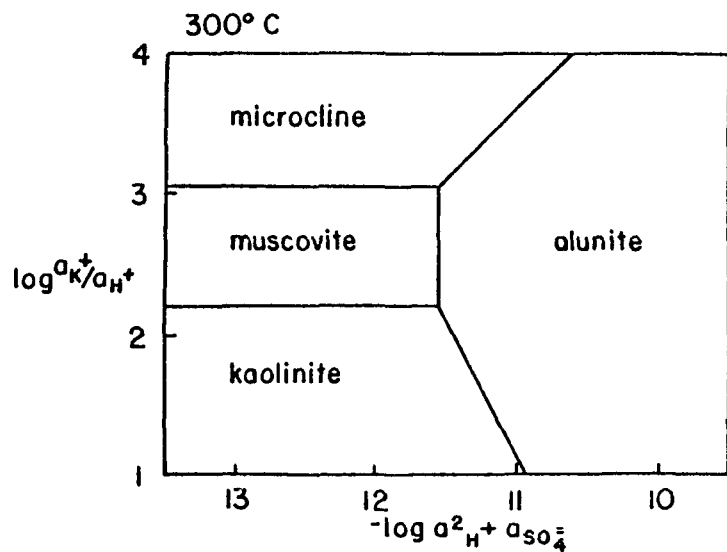
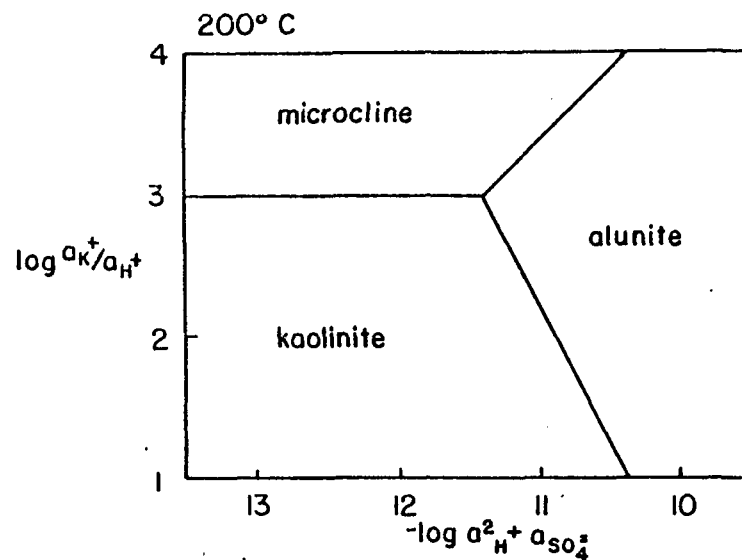
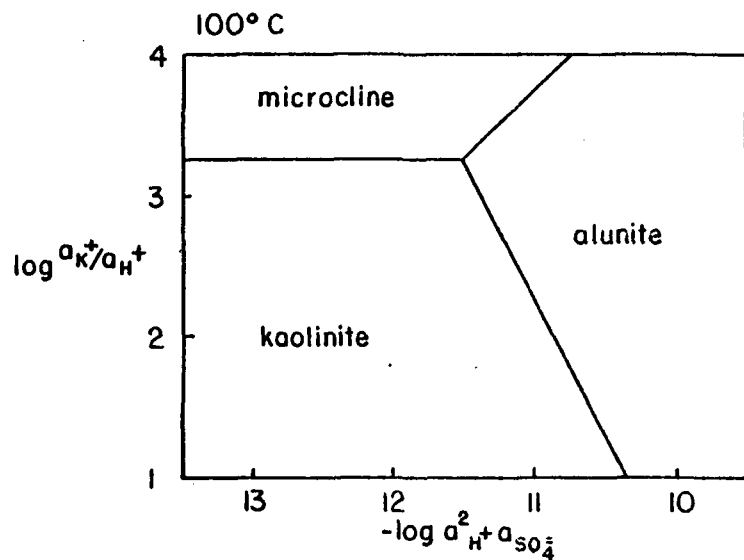


Figure 9. Activity diagrams for the system  $K_2O-Al_2O_3-S_2O_3-SiO_2-H_2O$ . Opal saturation and unit activity of water are assumed.



## CHEMICAL MODELS

From the reaction paths calculated the following model of a hypothetical geothermal system may be developed. These assumptions are made: (1) The system is within a homogeneous microcline-quartz host rock. (2) Solutions flow by convection in a vertical fracture. (3) The fracture is unobstructed and extends from a heat and solution reservoir at depth to the surface. (4) The temperature of last fluid-wall rock equilibration is 300°C. (5) The solution has an ionic strength of 0.1 and its composition at 300°C is the same as the final composition of the 300°C group two solution given in Table 5. (6) The solution is abundant enough and circulates rapidly enough so that the solution composition is not altered by chemical reactions. This assumption means that pH and the molalities of the other species in solution remain fairly constant. The fact that the Na-Ca-K geothermometer of Fournier and Truesdell (1972) is successful in many geothermal systems partially justifies this assumption. This geothermometer is based on the assumption that the potassium concentration is a function of the temperature of the last fluid-wall rock equilibration rather than depth. Equations 55, 56, and 57 indicate that the potassium ion and hydrogen ion concentrations are interdependent. If potassium ion concentration is independent of depth then hydrogen ion concentration should be independent of depth also. (7) The solution is assumed to be just at the boiling point through-

out the system. (8) Vapor may be present though vapor is assumed not to affect the density of the fluid. (9) The solution issues at the surface. These last three assumptions allow estimation of temperature as a function of depth by use of a boiling point reference curve such as Figure 10. As the weight percent sodium chloride in Roosevelt Hot Springs waters is less than 1% the curve for pure water was used. (10) The vertical thermal gradient of the area surrounding the fracture is  $100^{\circ}\text{C}/\text{Km}$ . (11) The solutions diffuse upward and outward into the wall rock during ascent. The horizontal thermal gradient is a function of the rate of outward diffusion and is not known. (12) Supersaturation is assumed not to exist.

Given these assumptions Figure 11 can be drawn. The alteration zoning is a function of temperature. Two alteration zoning patterns are evident. The vertical sequence of surface, kaolinite + quartz, kaolinite + muscovite + quartz, muscovite + quartz, and stable microcline + muscovite + quartz is seen. A similar horizontal zoning pattern exists. The horizontal pattern is dependent on depth but for most of the system has the sequence fracture, quartz + muscovite, quartz + muscovite + kaolinite, kaolinite + quartz, fresh rock. Note that Figure 11 has no horizontal scale because the rate of flow of hot water outward from the fracture is not known.

Due to the stipulation of constant pH and wall rock-fluid equilibration only at  $300^{\circ}\text{C}$  the above model implicitly assumes that alteration occurs in pulses of maximum flow separated by periods of absolute quiescence. The constant pH assumption also requires that atmospheric oxygen does not react with the ascending fluid in

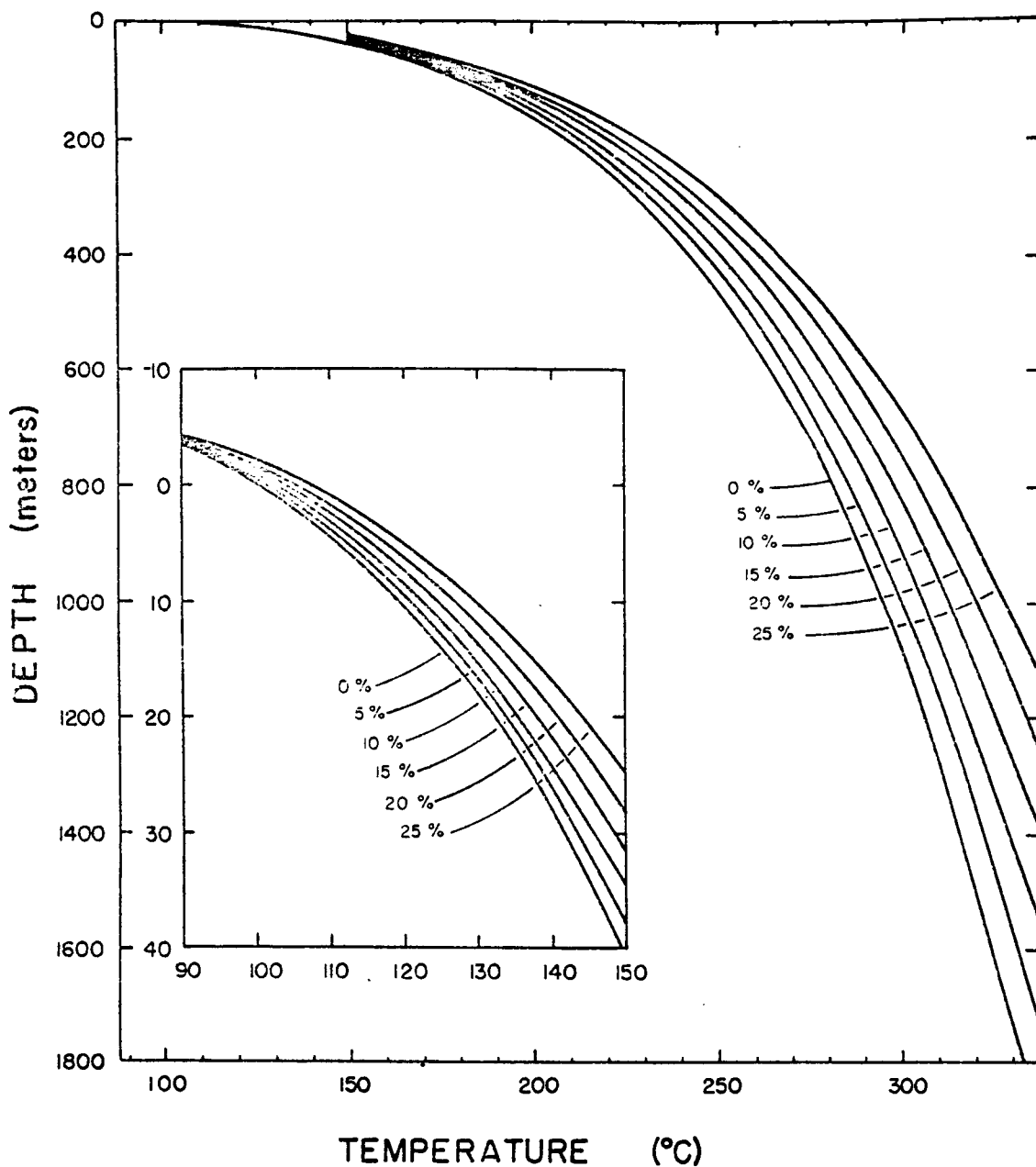


Figure 10.  
 Boiling-point curves for  $H_2O$  liquid (0 wt percent) and for brine of constant composition given in wt percent NaCl. Insert expands the relations between  $100^{\circ}$  and  $150^{\circ}C$ . The temperature at 0 meters of each curve is the boiling point for the liquid at 1.013 bars (1.0 atm) load pressure which is equivalent to the atmospheric pressure at sea level. The uncertainty is contained within the width of the lines. Taken from Haas 1971.

- (1) microcline(stable)+muscovite+quartz
- (2) muscovite+quartz
- (3) muscovite+kaolinite+quartz
- (4) kaolinite+quartz
- (5) fresh rock

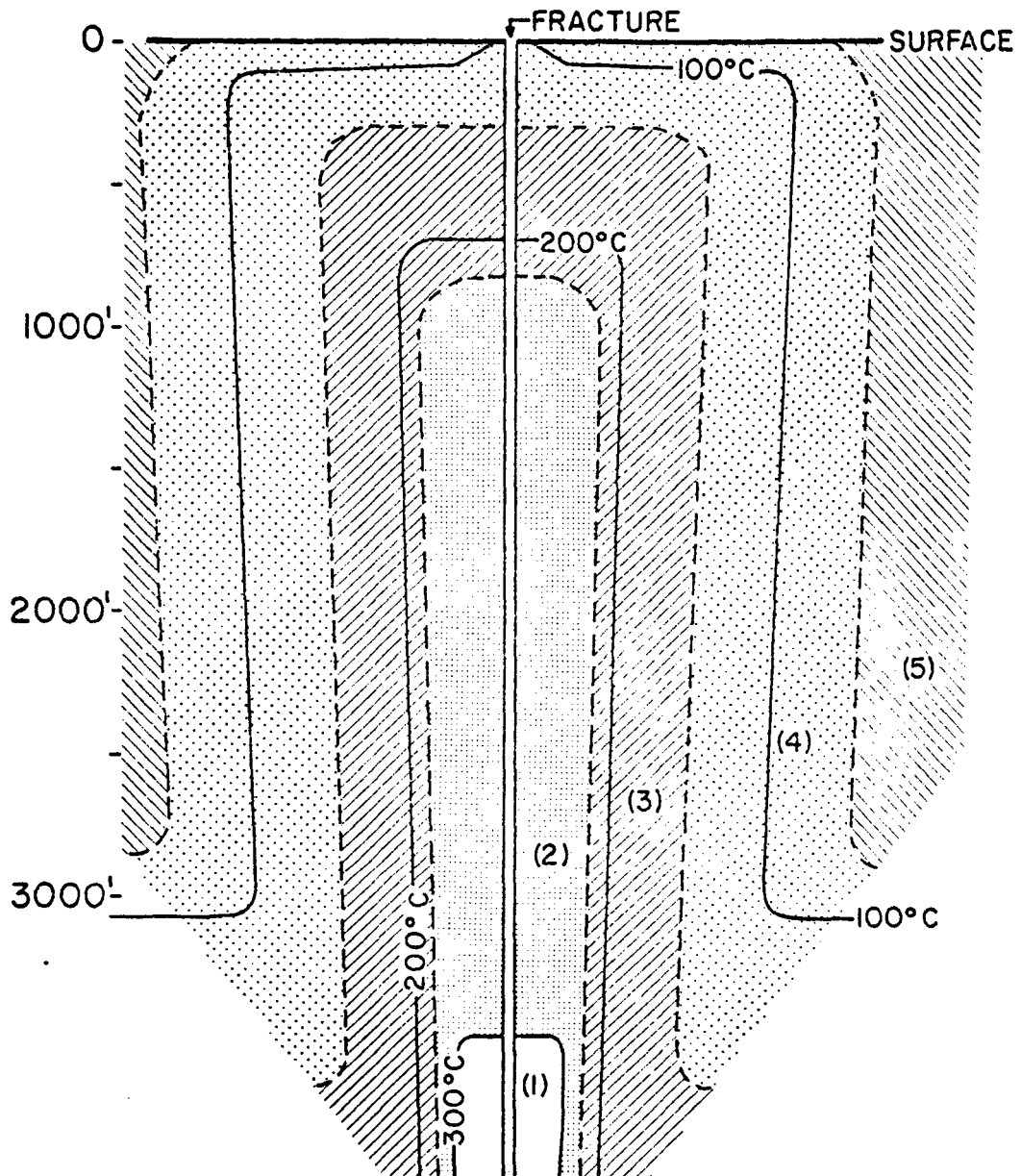


Figure 11. Maximum flow, constant pH model. pH=5.27

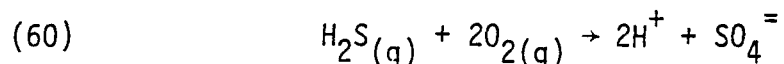
the near-surface portion of the system. In natural systems alteration probably occurs in pulses of peak flow separated by periods of lesser flow.

During peak flow diffusion of the fluid into the wall rock is at a maximum and so the alteration halo reaches its greatest extent. Due to the rapid introduction of new solution from below, the constant pH assumption is met best at this time and so alteration zoning is mostly a function of temperature. Pulses following the initial pulse diffuse into previously altered rock. If each succeeding pulse is of the same magnitude and the permeability of the wallrock remains constant the alteration should become more complete. More host-rock microcline is consumed. Since the permeability and flow remain the same the horizontal thermal gradient remains constant and thus the size and sequence of the alteration zones would not change. If alteration increases the permeability or the flow is greater than before, the alteration zones expand outward but not upward if constant pH is maintained. There would be no upward expansion of alteration zoning because the vertical thermal gradient is a function of the boiling point of the solution.

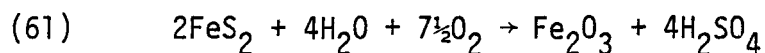
Between pulses, the flow may not be adequate to maintain constant pH. As shown by the reaction paths in Figures 1, 2, 3, 4, 5, and 6 if no new fluid is introduced the pH will increase. So, during lesser flow alteration zoning becomes a function of pH as well as temperature. Overall equilibrium is reached in a greater portion of the system and so the microcline (stable) + muscovite + quartz assemblage extends to much shallower depths in the system than shown

in the constant pH model of Figure 11. Since diffusion is less, the lateral thermal gradient is steeper and so, a narrower alteration zoning pattern is superimposed on the more extensive alteration zones shown in Figure 11. This narrower zoning would have the same sequence of alteration minerals as before.

In natural geothermal systems where the hydrothermal fluid reaches the surface there is interaction between the fluid and atmospheric oxygen. As seen at Steamboat Springs, Nevada by Schoen, White and Hemley (1973) oxidation of ascending  $H_2S$  gas may lower pH in the upper portions of active hot springs according to equation (60).



At Steamboat Springs this reaction was described for areas where  $H_2S$  gas but no hot water was reaching the surface. The hydrogen ion and sulfate ion were carried downward by descending groundwater thus producing a very acid environment in the upper portion of the system. This process should occur to some extent in any geothermal system where  $H_2S$  gas is a component of the solution. The acid environment should have lowest pH at the surface. The depth of this environment depends on the depth of the water table and the magnitude of upward flow of ascending solutions. Maximum depth occurs when flow is not sufficient to reach the surface and minimum depth occurs with maximum surface flow. Similarly if sulfides such as pyrite are present near the surface, reactions such as equation (61) should contribute to a surface acid-sulfate environment.



Presumably the sulfide minerals would have been produced during periods of high flow when the near surface pH was quite high. Examination of the reaction path of the group two 100°C solution (Figure 4) indicates that as the pH is lowered the minerals produced change from kaolinite + quartz at the assumed constant pH of 5.27 to kaolinite + alunite + quartz to alunite + quartz to quartz alone. This surficial zoning pattern was found by Schoen, White, and Hemley (1973) at Steamboat Springs. Assuming a surface pH of 3 the vertical zoning pattern should now be quartz, alunite + quartz, alunite + kaolinite + quartz, kaolinite + muscovite + quartz, muscovite + quartz, microcline (stable) + muscovite + quartz. Given the correction of a changing pH model for periods of low flow and interaction with atmospheric oxygen in the upper portion of the system, Figure 12 can be drawn from Figure 11. The exact position of the alteration zones and water table is arbitrary. Again there is no horizontal scale. A natural system is best represented by various combinations of the constant pH model of Figure 11 and the changing pH model of Figure 12 with each superimposed on the other.

Solution compositions chosen were based on waters found at Roosevelt Hot Springs, Utah (see Table 1). At Roosevelt Hot Springs the host rock is composed of a Tertiary granite (quartz monzonite?) and a Precambrian gneiss. The rocks have abundant quartz and potassium feldspar. Only the alteration assemblages of surface outcrops and the upper 200' of the system have been studied. According

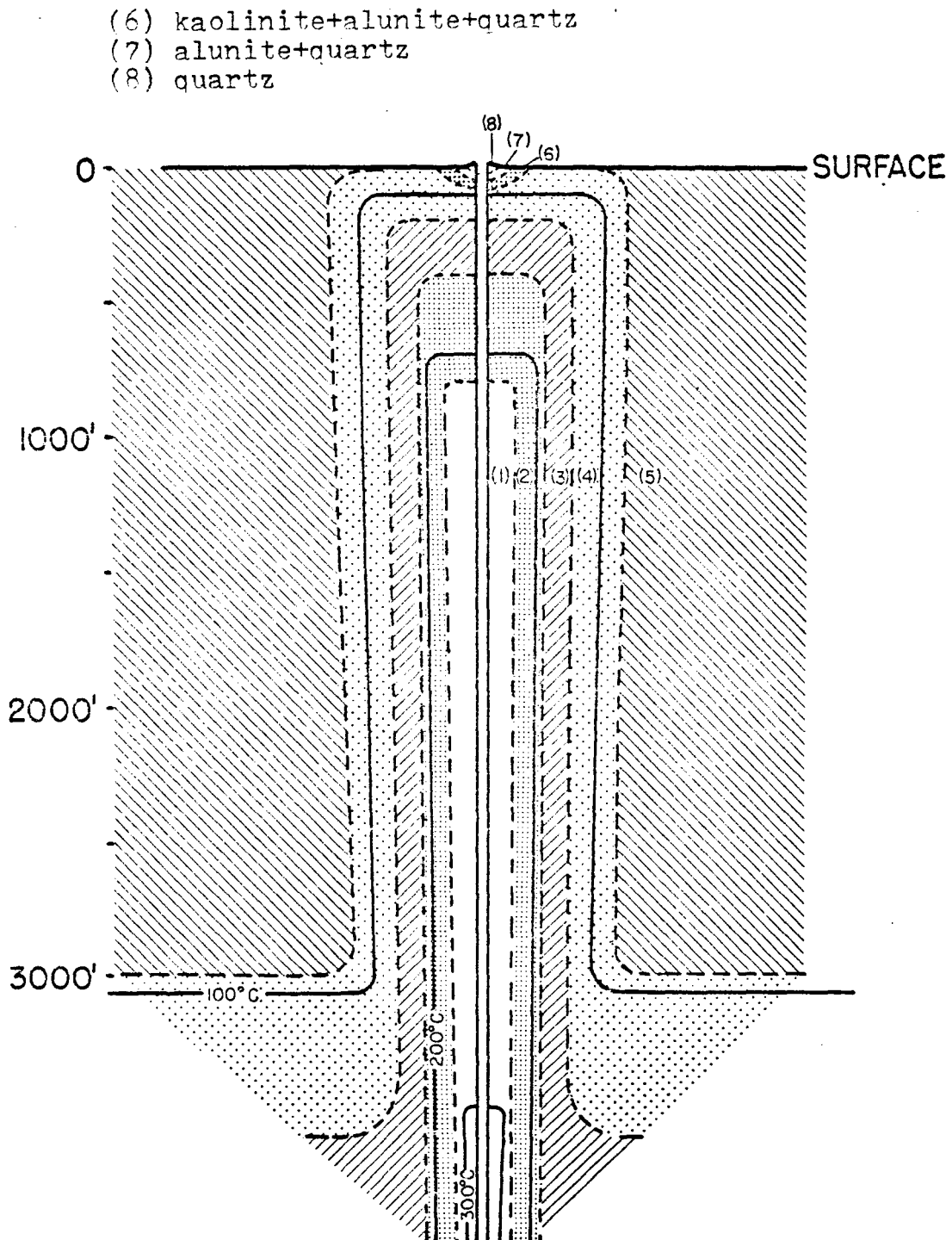


Figure 12. Minimum flow model. See figure 11 for key for zones (1) through (5).



to Parry, Benson, and Miller (1976) the following general zonal alteration is found. Outward from the fracture is: 1) an alunite-quartz zone 2) an argillic zone containing a potassium mica-montmorillonite subzone 3) a propylitic zone. Ignoring montmorillonite which was not considered in the theoretical model, comparison of the near surface portion of Figure 12 with this observed zoning shows the two patterns to be identical. This similarity allows alteration zoning seen at Roosevelt Hot Springs to be explained as a function of temperature and pH gradient.

Steamboat Springs, Nevada is a well known presently active geothermal system. The thermal waters flow in a steep easterly dipping north-south fracture zone. The host rocks are mainly granodiorite with some andesite. Although plagioclase is dominant, orthoclase and quartz are abundant. At Steamboat Springs the U.S.G.S. has drilled eight core drill holes. On the main terrace in drill holes GS-3 and GS-4 Schoen and White (1965) describe the following distinct zoning pattern with respect to fractures. Near the fracture there is a sericitic zone in which sericite, quartz and pyrite appear to be stable alteration minerals. Enveloping the sericite zone is a less intensely altered argillic zone in which montmorillonite, illite and chlorite are present. Comparison of this zoning with the lateral zoning of Figure 11 show a general similarity. At Steamboat Springs the sodium and calcium content of the water and host rock would tend to make montmorillonite a stable phase in the argillic zone at the expense of kaolinite. If the ratio of the activity of sodium ion to hydrogen ion is greater

than 5.5 then sodium montmorillonite replaces kaolinite in Figure 7.

According to Sales and Meyer, (1948) at Butte, Montana successive zones of sericitized and argillized quartz monzonite occur around every ore-bearing fracture regardless of size, attitude or relative age. The two types of alteration always occupy the same relative positions; sericite adjacent to the ore-bearing vein, clay minerals always between the sericitized rock and fresh quartz monzonite. This lateral zoning pattern is exactly that shown in Figure 11. The argillic zone of Sales and Meyer (1948) is composed of two subzones, a kaolinite subzone near the fracture and a montmorillonite subzone away from the fracture. This is not shown in Figure 11 as montmorillonite was not considered. Since the observed zoning at Butte corresponds to Figure 11 this zoning may be viewed as a function of temperature.

#### ACKNOWLEDGEMENTS

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APPENDIX ONE

MASS TRANSFER PROGRAM LISTING

```

000001
000002 MASS TRANSFER PROGRAM
000003
000004 PARAMETER NT = 15, NNT=NT+1
000005 DOUBLE PRECISION E11,E22,E3,E4,E5,E,E1,E2,X,Y,Y1,Y2,Y3,Y4,X5,XB
000006 DOUBLE PRECISION XL,XBL,XST,XBS,EX
000007 INTEGER N9,N7,N6,M9
000008 DIMENSION E(NT,NNT),EX(NT),E1(NT,NNT),E2(NT,NNT),XST(NT)
000009 DIMENSION X(NT),Y(NT),Y1(NT),Y2(NT),Y3(NT),Y4(NT),XL(NT)
000010
000011 WRITE(6,200)
000012 READ(5,100) M9
000013 WRITE(6,100) M9
000014 WRITE(6,201)
000015 READ(5,100) N
000016 N1 = N+1
000017 WRITE(6,100) N
000018 WRITE(6,203)
000019 DO 40 I=1,N
000020 READ(5,101) EX(I)
000021 IF(EX(I).EQ.0.)GO TO 41
000022 40 CONTINUE
000023 41 CONTINUE
000024 READ(5,101) (Y(I),I=1,M)
000025 WRITE(6,101) (Y(I),I=1,M)
000026 WRITE(6,204)
000027 READ(5,101) (Y3(I),I=1,M)
000028 WRITE(6,101) (Y3(I),I=1,M)
000029 WRITE(6,205)
000030 READ(5,101) X5
000031 WRITE(6,101) X5
000032 H7 = 0
000033 M9 = 0
000034 H6 = 0
000035 M11 = 0
000036 DO 29 I=1,N
000037 DO 29 J=1,N
000038 E(I,J) = 0.000
000039 29 CONTINUE
000040 E(1,1) = 1.000
000041 E(1,4) = 4.000
000042 E(1,6) = 4.000
000043 E(1,7) = 4.000
000044 E(1,8) = 4.000
000045 E(1,9) = 4.000
000046 E(1,10) = 4.000
000047 E(1,11) = 1.000
000048 E(1,12) = 2.000
000049 E(1,NN) = 8.000
000050 E(4,3) = 1.000
000051 E(4,4) = 1.000
000052 E(4,NN) = 1.000
000053 E(5,5) = 1.000
000054 E(5,6) = 1.000
000055 E(5,NN) = 1.000
000056 E(6,6) = 1.000
000057 E(6,7) = 1.000
000058 E(6,8) = 1.000
000059 E(11,1) = 2.000
000060 E(11,2) = 1.000
000061 E(11,4) = 4.000
000062 E(11,7) = 1.000
000063 E(11,9) = 3.000
000064 E(11,10) = 4.000
000065 E(11,11) = 1.000
000066 E(12,9) = 1.000
000067 E(12,10) = 1.000
000068 E(12,12) = 1.000
000069 E(12,NN) = 3.000
000070 DO 30 I=1,N
000071 X(I) = Y(I)
000072 30 CONTINUE
000073 GO TO 51
000074 31 CONTINUE
000075 GO TO 37
000076 095 WRITE(6,206)
000077 STOP
000078 015 CONTINUE
000079 DO 11 I=1,N
000080 DO 11 J=1,NNT
000081 E(I,J) = 1/(I,J)
000082 11 CONTINUE
000083
000084 E(1,1) = 1.000
000085 E(1,1) = 1.000
000086 E(1,1) = 1.000
000087 51 E(2,2) = 1./X(2)
000088 E(2,11) = 1./X(11)
000089 E(3,3) = 1./X(3)
000090 E(3,4) = -1./X(4)
000091 E(3,11) = 4./X(11)
000092 E(7,2) = 1./X(2)
000093 E(7,7) = -1./X(7)
000094 E(7,6) = 1./X(6)
000095 E(6,5) = 1./X(5)
000096 E(6,6) = -1./X(6)
000097 E(6,8) = 1./X(8)
000098 E(9,2) = 1./X(2)
000099 E(9,9) = 1./X(9)
000100 E(9,10) = -1./X(10)
000101 E(10,10) = 1./X(10)
000102 IF(M11.EQ.0) GO TO 31
000103
000104 DO 12 I=1,N
000105 12 Y(I) = X(I)
000106 37 DO 13 I=1,N
000107 DO 13 J=1,NN
000108 E1(I,J) = E(I,J)
000109 13 CONTINUE
000110 DO 14 I=1,N
000111 CALL SUB40(E,N,NN,1095,I,NT,NNT)
000112 14 CONTINUE

```

```

000113      DO 15 I=1,N
000114      15 Y2(I) = E(I,M)
000115      DO 16 I=1,N
000116      DO 16 J=1,M
000117      E2(I,J) = 0.000
000118      16 CONTINUE
000119      DO 17 I=1,N
000120      DO 17 J=1,M
000121      E2(I,J) = E1(I,J)
000122      17 CONTINUE
000123
000124      E2(2,M) = ((Y2(2)**2)/(Y(2)**2)) + ((Y2(11)**2)/(Y(11)**2))
000125      E2(3,M) = ((Y2(3)**2)/(Y(3)**2)) + (4.*((Y2(11)**2)/(Y(11)**2))
000126      "      - ((Y2(4)**2)/(Y(4)**2))
000127      E2(7,M) = ((Y2(2)**2)/(Y(2)**2)) - ((Y2(7)**2)/(Y(7)**2))
000128      "      + ((Y2(8)**2)/(Y(8)**2))
000129      E2(8,M) = ((Y2(5)**2)/(Y(5)**2)) - ((Y2(6)**2)/(Y(6)**2))
000130      "      + ((Y2(8)**2)/(Y(8)**2))
000131      E2(9,M) = ((Y2(2)**2)/(Y(2)**2)) + ((Y2(9)**2)/(Y(9)**2))
000132      "      - ((Y2(10)**2)/(Y(10)**2))
000133      E2(10,M) = ((Y2(10)**2)/(Y(10)**2))
000134
000135      DO 16 I=1,N
000136      DO 16 J=1,M
000137      E(I,J) = E2(I,J)
000138      16 CONTINUE
000139      DO 19 I=1,N
000140      CALL SUB40(I,M,N,$1095,I,T,NT)
000141      19 CONTINUE
000142
000143      5 DO 21 I=1,N
000144      Y1(I) = (Y2(I)*YS) + ((E(I,M))*((XS)**2))/2)
000145      21 CONTINUE
000146
000147      DO 36 I=1,N
000148      XS(I) = X(I)
000149      36 CONTINUE
000150      X05 = X5
000151      DO 23 I=1,N
000152      X(I) = Y(I) + Y1(I)
000153      IF(X(I).GT.0.0) GO TO 23
000154      X5 = 0.9*X5
000155      GO TO 45
000156      23 CONTINUE
000157      DO 28 I=1,N
000158      XL(I) = DLOG10(X(I))
000159      28 CONTINUE
000160      IF(M7.EQ.0) X8 = X5
000161      DO 24 I=1,N
000162      24 Y4(I) = Y3(I)*X(I)
000163      IF(M7.NE.0) X0 = X8+X5
000164      X0L = DLOG10(X0)
000165      E11 = ((Y4(3)**2)*(Y4(10)**2))/(Y4(2)**6)
000166      E22 = ((Y4(3))*(Y4(10)**3)*(Y4(5)))/(Y4(2)**4)
000167      E3 = ((Y4(5))*(Y4(3)**3)*(Y4(10)**3))/(Y4(2)**10)
000168      E4 = Y4(3)*(Y4(11)**3)
000169      E5 = (Y4(5))*(Y4(3)**3)*(Y4(8)**2)*(Y4(11)**6)

```

```

000170
000171      IF(E11.LT.EX(1)) GO TO 91
000172      X2 = (1.-(EX(1)/E11))*100.
000173      IF(X2.GT. 0.01) GO TO 99
000174      WRITE(6,207) E11
000175      M9 = 1
000176      91 IF(E22.LT.LX(2)) GO TO 92
000177      X3 = (1.-(LX(2)/E22))*100.
000178      IF(X3.GT. 0.01) GO TO 99
000179      WRITE(6,208) E22
000180      M9 = 1
000181      92 IF(E3.LT. FX(3)) GO TO 93
000182      X4 = (1.-(LX(3)/E3))*100.
000183      IF(X4.GT. 0.01) GO TO 99
000184      WRITE(6,209) E3
000185      M9 = 1
000186      93 IF(E4.LT. EX(4)) GO TO 94
000187      X5 = (1.-(LX(4)/E4))*100.
000188      IF(X5.GT. 0.01) GO TO 99
000189      WRITE(6,210) E4
000190      M9 = 1
000191      94 IF(E5.LT. EX(5)) GO TO 95
000192      X6 = (1.-(LX(5)/E5))*100.
000193      IF(X6.GT. 0.01) GO TO 99
000194      WRITE(6,211) E5
000195      M9 = 1
000196      95 IF(M9.EQ.0) GO TO 96
000197      CALL SUB50(X5,Y2,N,X,X8,M7,NT,XL,X0L,E3)
000198      WRITE(6,212)
000199      STOP
000200      96 NA = I-1
000201      DO 25 I=1,N
000202      IF(X(I).GT. 0.1E-31) GO TO 25
000203      M8 = 1
000204      WRITE(6,213)
000205      25 CONTINUE
000206      IF(M8.EQ. 0) GO TO 97
000207      CALL SUB50(X5,Y2,N,X,X8,M7,NT,XL,X0L,E3)
000208      STOP
000209      97 IF(M6.EQ. 0) CALL SUB50(X5,Y2,N,X,X8,M7,NT,XL,X0L,E3)
000210      M6 = M6 + 1
000211      IF(M6.EQ.M9) M6 = 0
000212      M7 = M7 + 1
000213      M11 = M11 + 1
000214      GO TO 2015
000215      99 X0 = X05
000216      IF(M7.EQ. 0)WRITE(6,103)
000217      IF(M7.EQ. 0)WRITE(6,104) E11,E22,E3,E4,E5
000218      IF(M7.EQ. 0)STOP
000219      DO 39 I=1,N
000220      X(I) = X5T(I)
000221      39 CONTINUE
000222      X5 = 0.5*X5
000223      M11 = M11 + 1
000224      GO TO 2015
000225
000226      **FORMATS**

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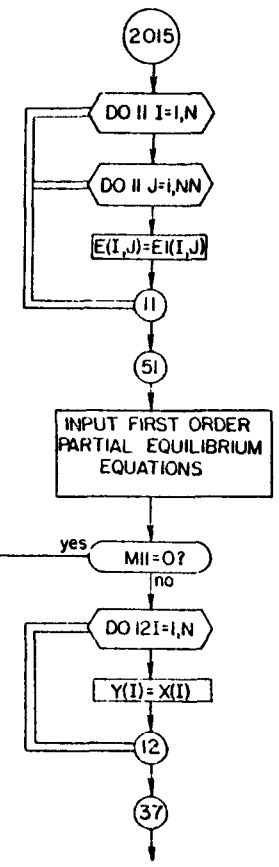
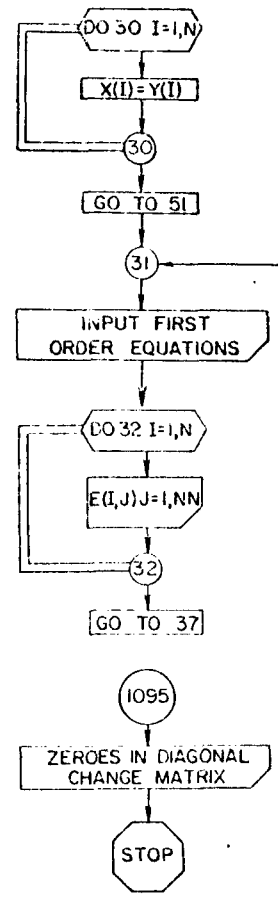
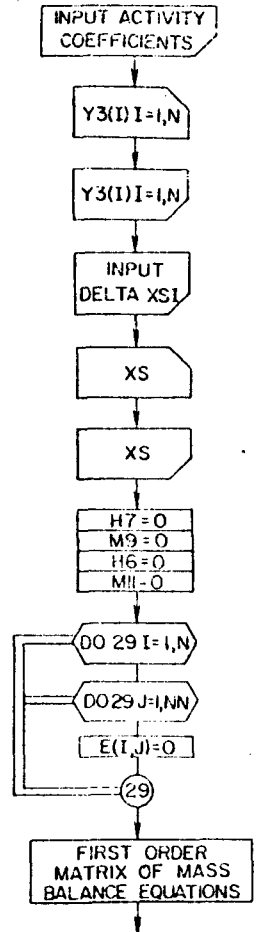
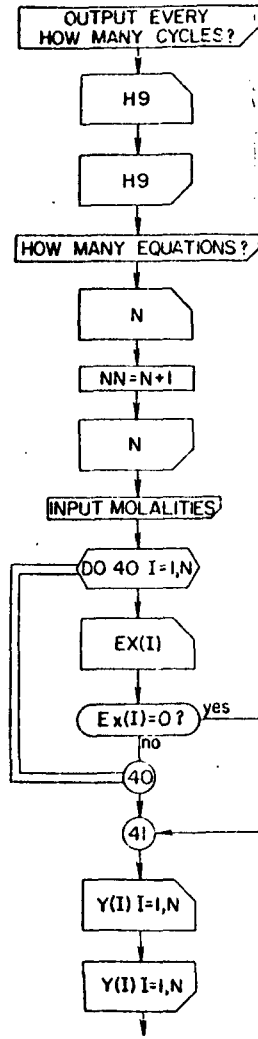
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000227
000228 100 FORMAT(I5)
000229 101 FORMAT(8E16.4)
000230 103 FORMAT(1X,'INITIAL SOLUTION SATURATED, TRY AGAIN')
000231 104 FORMAT(1X,'CHECK FOLLOWING K OUTPUT',5D10.4)
000232 200 FORMAT(1X,'OUTPUT EVERY HOW MANY CYCLES?')
000233 201 FORMAT(1X,'HOW MANY EQUATIONS?')
000234 202 FORMAT(1X,'INPUT 1ST ORDER EQUATIONS')
000235 203 FORMAT(1X,'INPUT MOLALITIES')
000236 204 FORMAT(1X,'INPUT ACTIVITY COEFFICIENTS')
000237 205 FORMAT(1X,'INPUT INITIAL DELTA XSI')
000238 206 FORMAT(1X,'ZEROS IN DIAGONAL, CHANGE MATRIX, START AGAIN')
000239 207 FORMAT(1X,'** NAOLITE SATURATION ** K=',E13.4)
000240 208 FORMAT(1X,'** N-SPAN SATURATION ** K=',E13.4)
000241 209 FORMAT(1X,'** MUSCOVITE SATURATION ** K=',E13.4)
000242 210 FORMAT(1X,'** JIBSITE SATURATION ** K=',E13.4)
000243 211 FORMAT(1X,'** ALUNITE SATURATION ** K=',E13.4)
000244 212 FORMAT(1X,'SATURATION REACHED END ALL')
000245 213 FORMAT(1X,'ZERO CONCENTRATION')
000246
000247 SUBROUTINE SUB44 (E,F,INT,5,INT,INT)
000248 DOUBLE PRECISION E,F
000249 DIMENSION E(NT,INT)
000250 F = E(I,I)
000251 IF (F.EQ.0.0D0) RETURN 4
000252 DO 3 J=1,INT
000253 E(I,J) = E(I,J)/F
000254 3 CONTINUE
000255 DO 4 J=1,INT
000256 IF (I.EQ.J) GO TO 4
000257 F = E(J,I)
000258 DO 5 K=1,INT
000259 E(J,K) = E(J,K) - F*E(I,K)
000260 5 CONTINUE
000261 4 CONTINUE
000262 RETURN
000263
000264 SUBROUTINE SUB50 (XS,Y2,P,X,XB,H7,NT,XL,XPL,F3)
000265 DOUBLE PRECISION XS,Y2,XB,X,XL,XBL
000266 INTEGER H7,H7P1
000267 DIMENSION Y(NT),X(NT),XL(NT)
000268 WRITE(6,200) XS
000269 DO 6 I=1,NT
000270 WRITE(6,201) I,Y2(I)
000271 6 CONTINUE
000272 WRITE(6,202)
000273 DO 7 J=1,NT
000274 WRITE(6,204) J,XL(J)
000275 7 CONTINUE
000276 H7P1 = H7 + 1
000277 WRITE(6,203) XBL,H7P1
000278
000279 199 FORMAT(E13.4)
000280 200 FORMAT(1X,'XS=',E13.4,'//1X,'APPROX. REACTION COEFFICIENTS',/)
000281 201 FORMAT(3X,I3,3H = ,E13.4)
000282 202 FORMAT(1X,'NEW LOG MOLALITIES',/)
000283 203 FORMAT(1X,'REACTION PROGRESS =',F10.4,3HXS(1//1X,'END OF CYCLE',/
000284 H 16,/)
000285 204 FORMAT(3X,I3,3H = ,F10.4)
000286 RETURN
000287 ENU

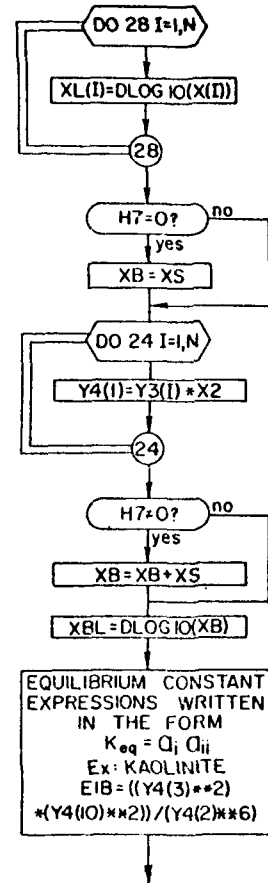
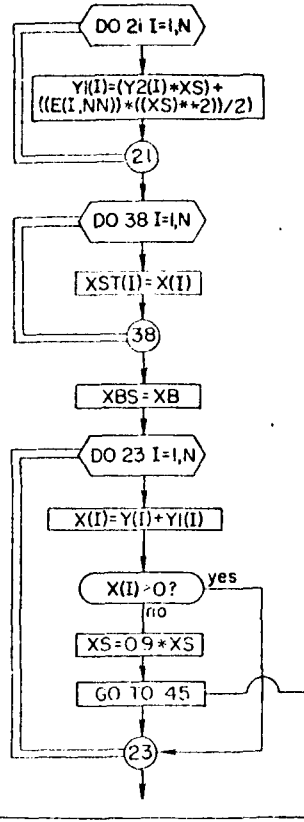
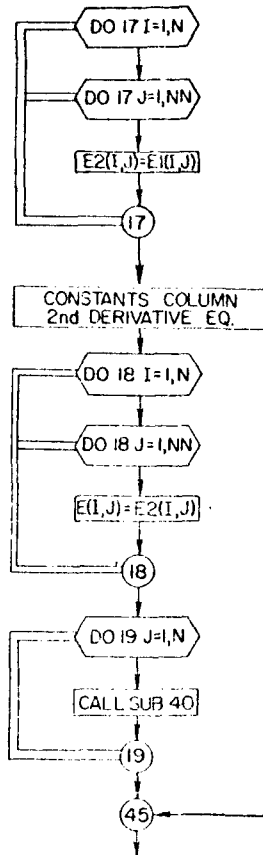
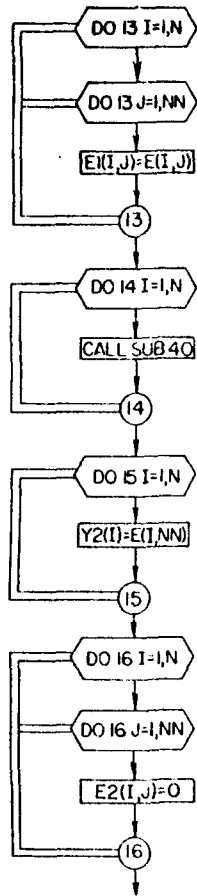
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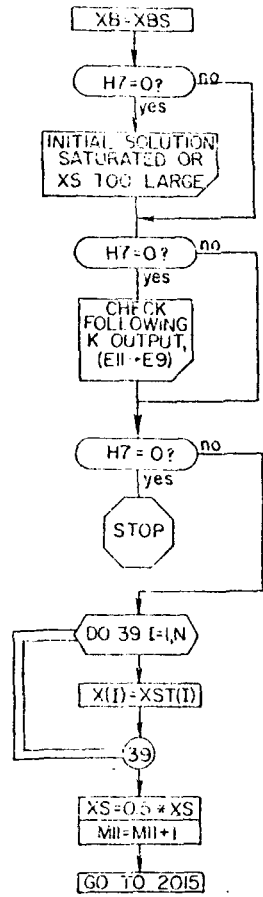
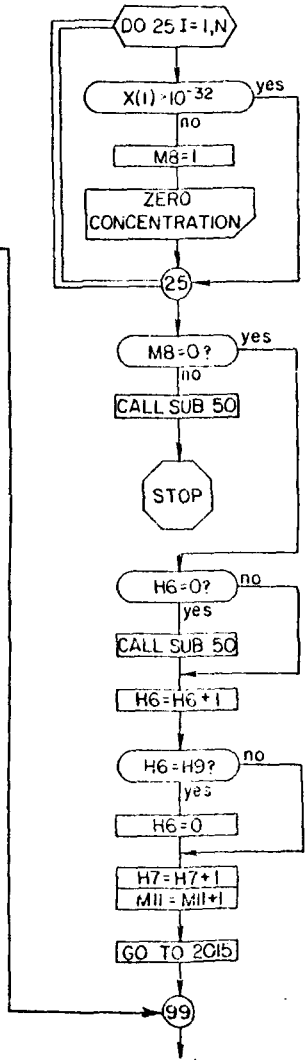
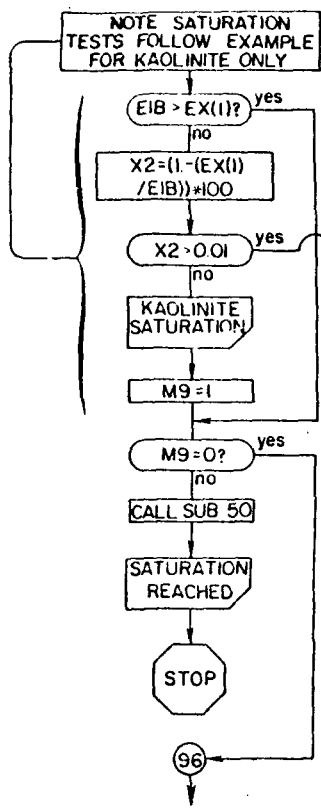
APPENDIX TWO

MASS TRANSFER PROGRAM FLOW CHART

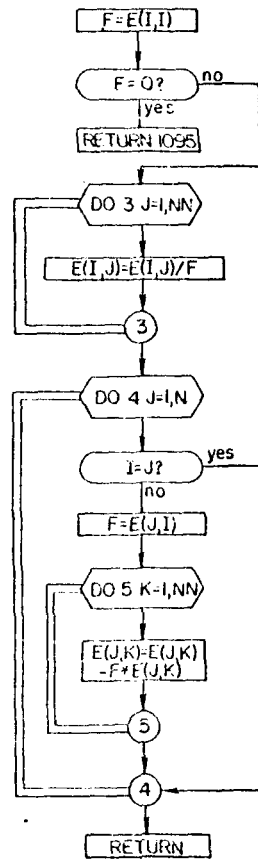




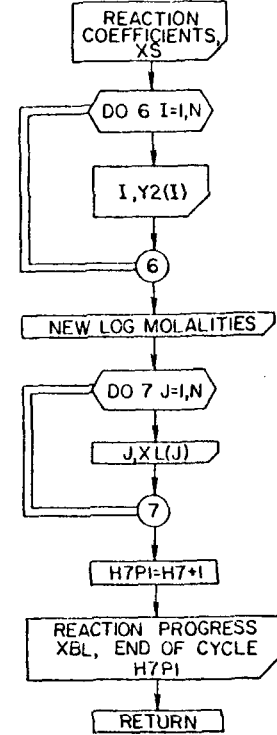




SUB 40



SUB 50



## REFERENCES

- Fournier, R. O. and Truesdell, A. H., 1972, An empirical Na-K-Ca geothermometer for natural waters: *Geochimica et Cosmochimica Acta*, v. 37, p. 1255-1275.
- Haas, J. L., Jr., 1971, The effect of salinity on the maximum thermal gradient of a hydrothermal system at hydrostatic pressure: *Econ. Geol.*, v. 66, p. 940-946.
- Helgeson, H. C., 1968, Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions - I. Thermodynamic relations: *Geochimica et Cosmochimica Acta*, v. 32, p. 853-877.
- \_\_\_\_\_, 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: *Am. Jour. Sci.*, v. 267, p. 729-804.
- Hemley, J. J., and Jones, W. R., 1964, Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism: *Econ. Geol.*, v. 59, p. 538-569.
- Kharaka, Y. K., and Barnes, I., 1973, Solution-mineral equilibria computations: U.S. Geol. Survey Computer Contribution available from National Technical Information Service, U.S. Department of Commerce; Springfield, V.A. 22151, pub. no. 215-899.
- Parry, W. T., Benson, N. L., and Miller, C. D., 1976, Geochemistry and hydrothermal alteration at selected Utah hot springs: v. 3, final report for National Science Foundation, pub. by Dept. of Geol. and Geophysics, Univ. of Utah.
- Sales, R. H. and Meyer, C., 1948, Wall rock alteration at Butte, Montana: *Am. Inst. of Mining and Met. Engrs. Trans.*, v. 178, p. 9-35.
- Schamber, F. H., 1975, Flextran: Instruction and programming manual: available from Tracor Northern; 2551 Beltline Highway; Middleton, Wisconsin, 53 .
- Schoen, R. and White, D. E., 1965, Hydrothermal alteration in GS-3 and GS-4 drill holes, main terrace, Steamboat Springs, Nevada: *Econ. Geol.*, v. 60, p. 1411-1421.

- Schoen, R., White, D. E., and Hemley, J. J., 1973, Argillization by descending acid at Steamboat Springs, Nevada: Clays and Clay Minerals, v. 22, p. 1-22.
- Sigvaldason, G. E. and White, D. E., 1961, Hydrothermal alteration of rocks in two drill holes at Steamboat Springs, Washoe County, Nevada: Art. 331 in U.S. Geol. Survey Prof. Paper 424-D, p. D116-D122.
- Truesdell, A. H. and Jones, B. F., 1973, Wateq. A computer program for calculating chemical equilibria of natural waters: U.S. Geol. Survey available from National Technical Information Service, U.S. Dept. of Commerce; Springfield, V.A. 22151, pub. number 220-464.
- White D. E., 1968, Hydrology, activity, and heat flow of the Steamboat Springs thermal system, Washoe County, Nevada: U.S. Geol. Survey Prof. Paper 458-C.