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Hourglass inclusions: Theory and application to the Bishop Rhyolitic Tuff

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For deposit: Appendix 1

APPENDIX 1

PHYSICAL AND MATHEMATICAL ASPECTS OF HOURGLASS EMPTYING

To a first approximation the emptying of an hourglass can be described by a first order linear differential equation. Consider a cavity partially or wholly filled with melt (Figure 4). The cavity is rigid and its volume, V, is a constant which I conveniently take to be unity. The cavity is filled with a volume of melt, M, and gas, G.

Volume within the cavity is conserved so that:

$$M + G = 1 \qquad\qquad\qquad 1)$$

$$dM = -dG \qquad\qquad\qquad 2)$$

A volatile species, H (for H_2O, for example), is distributed between the gas and the melt according to equilibrium solubility relations. Strictly these relations are complex and involve temperature and gas composition as well as pressure. Here I approximate the findings of Burnham (1979) and others and adopt a simple square root of pressure rule:

$$H1 = A * P^{(1/2)} \qquad\qquad\qquad 3)$$

where H1 is the mass fraction of volatile (eg. H_2O) in the melt and A is a constant. It is assumed that H is the only volatile present so that the gas is pure H.

Because we are dealing with an essentially volumetrical problem we need also to know the densities of the melt and especially the gas. The density of the melt, (D1), will depend on the temperature, pressure and its volatile content. However, most of these effects are small so D1 is taken to be a constant as an approximation. The density of the gas (D2) will depart from ideality slightly, but this is ignored for now and an ideal approximation is used:

$$D2 = (W * P)/(83.1*T) \qquad\qquad\qquad 4)$$

where W is the molecular weight of the gas, P is the pressure in bars, T is the

temperature in Kelvins, and 83.1 is the ideal gas constant in the appropriate physical units (cm^3 bar/(deg gfw)).

I now consider a fractional evacuation process whereby the inclusion cavity loses melt volume and volatile mass as the remaining melt and gas decompress and equilibrate within the cavity. Consider that a change in the volatile content of the inclusion is balanced by an incremental loss of volatile-containing melt from the inclusion. If we designate the total volatile content of the inclusion to be $H4$, we can write the differential equation which conserves volatile mass as:

$$dH4 = + H1*D1*dM = + A*P^{(1/2)}*D1*dM = -A*P^{(1/2)}*D1*dG \qquad 5)$$

The positive sign indicates that the amount of volatile decreases in the inclusion as a positive amount of melt leaves the inclusion. Whether the amount of melt leaving the inclusion is properly regarded to be positive can be verified by working through a discretized example, which I leave for the readers who, like myself, find this to not be intuitively obvious.

The amount of H in the inclusion consists of two parts which are changing in relative amount and concentrations: the melt part ($H5$) and the gas part ($H6$):

$$H4 = H5 + H6 \qquad 6)$$

The melt part is:

$$H5 = H1 * M * D1 = A * P^{(1/2)} * (1 - G) * D1 \qquad 7)$$

The gas part is:

$$H6 = G * D2 = G * (W * P)/(83.1*T) \qquad 8)$$

In sum we have:

$$d(H5 + H6) = - H1 * D1 * dM \qquad 9)$$

Which is, by substitution:

$$d(A * P^{(1/2)} * (1 - G) * D1 + G * (W * P)/(83.1*T)) = - A * P^{(1/2)} * D1 * dG \qquad 10)$$

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Unlike most fractionation equations, it is not possible to separate the variables (P and G) in equation 10. This is because of the square root of P rule for the solubility of H_2O in the melt. It can be rearranged into the standard form of a linear ordinary differential equation and integrated by the standard procedure of using an integrating factor. The rearranged expression is:

$$dG/dP + F1(P)*G = F2(P) \qquad \text{11)}$$

where:

$$F1(P) = 1/P - a / P^{(3/2)} \qquad \text{12)}$$

and:

$$F2(P) = - a / P^{(3/2)} \qquad \text{13)}$$

with:

$$a = 83.1 * T * A * D1 / (2 * W) \qquad \text{14)}$$

The integrated result is:

$$G=G_0*(P_0*exp(2*a/P_0^{(1/2)})/(P*exp(2*a/P^{(1/2)}) +$$
$$4*a^2*S(P,P_0)/(P*exp(2*a/P^{(1/2)}) \qquad \text{15)}$$

where:

$$S(P,P_0)=(exp(b_0))/b_0 - (exp(b))/b + (1/2)*ln(P_0/P)$$
$$+ 2*a*(1/P^{(1/2)}-1/P_0^{(1/2)}) + 4*a^2/(2*2!)*(1/P-1/P_0)$$
$$+ 8*a^3/(3*3!)*(1/P^{(3/2)}-1/P_0^{(3/2)}) + 16*a^4/(4*4!)*(1/P^2-1/P_0^2) + \;.\;.\;.\qquad \text{16)}$$

with:

$$b = 2*a/P^{(1/2)} \qquad \text{17)}$$

and:

$$b_0 = 2*a/P_0^{(1/2)} \qquad \text{18)}$$

The equations show that relations between the parameters are such that it will commonly be possible to have enough information to infer an initial volume of gas in an hourglass. The final value of G can be measured microscopically. The corresponding value of P can be determined from the remaining volatiles dissolved in the quenched glass. The initial pressure (P_0) comes from other enclosed inclusions. The only remaining unknown is G_0 which can be determined by rearranging and solving equation 15.

The actual situation is more complex, but equally unique. In actuality both

CO_2 and H_2O are important volatile species. The real solubility rules are more complicated. The gas is somewhat non-ideal. It takes a fair-sized routine to handle the complexities by successive approximations. The exact (but approximate) expression (eqn. 15) is useful for checking certain aspects of the computational program as well as for revealing the interrelationships between various parameters.

TREATMENT OF THE TWO VOLATILE CASE

To more closely approximate reality, I next consider the case where both CO_2 and H_2O are present. In particular, I will assume that the CO_2 and H_2O distribute themselves between gas and liquid according to equilibrium solubility relations (Silver et al., 1990, Newman et al., 1988, Blank et al., 1989). Also I will assume that the P, V, T and activity relations of H_2O and CO_2 in the gas follow modified Redlich-Kwong rules as expressed by Holloway (1977) and Flowers (1979). Given these assumptions, it is possible to calculate the amount of gas remaining in an hourglass as melt is extruded and lost (fractionated) through the neck.

The process of melt loss is approximated by: 1) assuming: a) an initial bulk composition and gas-saturation pressure within the hourglass inclusion; and b) a various fixed external pressures; and 2) in successive steps, assigning decreased pressures to the bulk composition within the hourglass and calculating equilibrium amounts (and compositions) of melt and gas. At each step in internal pressure the expanded volume of the hourglass at the decreased pressure is compared with the actual volume of the hourglass. The excess volume (equilibrium - actual) is subtracted as melt and added to a throw-away pile. The new bulk composition of gas plus melt within the hourglass volume is calculated and used as the starting composition for the next decompression step. The total and H_2O masses in the inclusion and in the accumulated throw-away pile are compared with the initial bulk mass and H_2O content of the assumed gas-free hourglass, to check that these are conserved. Given initial internal gas saturation pressure and bulk composition,

the relations between gas fraction and internal pressure are determined (Figure 5). The relations between gas fraction and internal pressure are closely similar to the exact relations calculated via the one-volatile model, as long as H_2O is the dominant volatile species. In addition the volatile composition of the melt is a unique function (except for artifacts of the discrete approximations to perfect fractionation) of the initial condition and the gas content (or equivalently the pressure within the hourglass).

THE DURATION OF HOURGLASS DECOMPRESSION

The rate at which melt will move out through a cylindrical neck is given by the Poiseuille equation which we may write as follows using the symbols presented above:

$$V*(dG/dt)=(Pi/8)*(10^6*(P-P1)/L)*(D^4/16)*(1/N) \qquad 19)$$

where V is the total volume of the hourglass, G is its volume fraction of gas, t is time, P and P1 the internal and external pressures, L and D are the length and diameter of the neck, and N is the Newtonian viscosity of the melt.

THE DIMENSIONLESS HOURGLASS NUMBER

It is helpful to consider the dimensionless quantity:

$$V/(D^4/L) = HGN \qquad 20)$$

This quantity is an attribute of the hourglass which expresses the combined effects of its total volume and its neck dimensions on the rate at which the fraction of gas in the hourglass will increase due to decompression and consequent loss of melt through the neck. I call the ratio given in 20 the Hourglass Number and label it HGN.

Using the hourglass number equation 19 may be written:

$$C*HGN*dG=(P-P1)*dt \qquad 21)$$

where C is a constant containing the viscosity, geometrical and conversion factors:

$$C = 8*16*10^{-6}/(pi*N) \tag{22}$$

P is a function of G. Similarly the viscosity N is a function of P and therefore G. If P1 is assumed to be constant, then the variables (G and t) in equation 21 can be separated and the expression integrated. The complicated functional relations between G, P and N (particularly if CO_2 as well as H_2O is present) render the analytical integration of 21 intractable. However, the equation shows that only two observable parameters (G and HGN) carry the principal information useful in evaluating the duration of time (t) and external pressure (P1) common to a set of hourglasses. For two hourglasses that formed during the same decompression history (P1 and t), there is enough information (two equations with two unknowns) to calculate both P1 and t. A useful graph (Figure 6) shows G versus HGN with contours for various combinations of P1 and t.

VISCOSITY AND EMPTYING ISOCHRONS

The curves on figure 6 depend on melt viscosity and rheology (yield stress). Melt viscosities range from 10^6 to 10^{11} poise depending on H_2O content and temperature. Reasonable uncertainties in these parameters are about 0.5 wt. % and $30^{\circ}C$ and correspond to factor of 5 uncertainties in viscosity and thus time. I adapted the results and treatment of Shaw (1972) to express the relation between viscosity, temperature (T in Kelvins) and H_2O content:

$$N=exp((3.816-23.65*H1)*(10^4/T - 1.5)-6.4) \tag{23}$$

where H1 is the mass fraction of bulk H_2O (H_2O molecular + equivalent OH) in the rhyolitic melt. The (3.816-23.65*H1) term is my linear fit to Shaw's (non-linear) slope factor S for rhyolitic melt with 2 to 6 wt. % H_2O.

The curves on figure 6 were calculated by incrementing the emptying process. The incremental computation proceeds as follows:

1) Calculate an initial gas saturation pressure corresponding to assumed initial concentrations of H_2O and CO_2 in the melt. Assume that the bulk

composition of the original hourglass is the same as that of the initial melt (neglect any initial bubble of gas). If an initial gas bubble is inferred, this can be treated subsequently.

2) As in the previous program, decrease the pressure and find the new volume of the melt + gas system as well as the new equilibrium concentration of H_2O in the melt. In the final computations I selected pressure increments that gave roughly equal increments of gas (2 percent or less) by fitting simple expressions to approximate curves of gas content versus pressure (Figure 4).

3) Find the amount of melt lost through the neck between steps 1 and 2 by subtracting the total volume of the hourglass from the expanded volume of the system figured in step 2.

4) Calculate an average melt viscosity from the average concentration of H_2O figured for the melts in steps 1 and 2.

5) Using the average internal pressure (from successive steps) and the average viscosity calculate the time necessary for the amount of melt (calculated in 3) to flow out through the neck. Use this and successively calculated time increments to form an accumulated total duration of time.

6) Continue this process by updating the current bulk composition of the hourglass and repeating steps 2 through 6 until the desired gas content is attained.

7) The gas fraction was plotted by hand versus time for a specified hourglass number and shifted in time by factors of ten which is equivalent to calculating the times for 10 fold changes in hourglass number. This allowed a curve to be drawn for gas fraction as a function of time that could be inverted and drawn as isochrons for gas fraction versus hourglass number. These are the lines on figure 6.

COMMENTS ON HOURGLASS PROGRAM: HGLSSN.RV9

SEPT. 23, 1990

To whomever it may ever concern!

This program (in BASICA for IBM PC) is expanded from the first program I ever wrote and it doesn't work very well, but it does what I needed. Those who are experienced at programming will find it quicker to write their own program, no doubt. Those who just want to do a few computations may find it useful (you can trick it into providing a variety of outputs involving pressure, temperature and gas composition), and may be helped by the following explanatory comments.

INPUTS   The program will prompt you for various inputs, mostly in specified units - be careful with fractions and percents, bars vs kilobars, Kelvins etc.

210: minus delta P per increment. This is now overridden by line 215, but you may modify the program to get it back. Compare lines 822 - 900 in HGLSSN.RV9 with the same interval in HGLSSN.CP7. As written the program decreases the nominal pressure in the system (the hourglass) by the positive amount that you enter here: if you enter (+) 50, each successive computation is performed at 50 bars less than the preceeding one.

215: here you are to specify the gas fraction per increment. Each computation calculates first a new pressure at which the amount of gas in the system will be increased by your specified amount. This is only a rough approximation, because this is what the program is calculating exactly. Lines 832 and 880 contain the rules that are useful for a system with an initial melt having 4.3 % H_2O and 600 ppm CO_2. For other compositions you will need to write your own rules. Alternatively you can go back to using the pressure decrement (line 210 with appropriate modifications in the 800-900 lines).

220: Initial internal pressure. It helps to guess this value somewhat less than the gas saturation pressure (by 100 bars or so). Some guesses may get the program hung up. The program calculates the gas saturation pressure and uses it as the first pressure, so the value that you enter here is eventually ignored.

240: Initial external pressure. This must be less than the gas saturation pressure. Zero will work.

242: This is the temperature that the program will use to calculate the viscosity. The temperature used to calculate the gas saturation pressure is different and depends on the equilibrium P,T,X melting relations for albite adjusted by a constant factor (0.891 = KT see line 444) to get the Bishop rhyolite compositions to yield temperatures in agreement with Hildreth. You may prefer another rule. Just fix the value of KT so that the temperature TI gives you what you want. The temperature does affect the distribution of H_2O and CO^2 between melt and gas. As it stands the current program keeps the temperature constant at that calculated for the initial gas saturation condition. If you want to allow the temperature to float at the equilibrium condition for the purpose of calculating the gas/melt partitioning, you will have to study the program and make the necessary changes.

245: Increment for external pressure. Entering a positive number of bars here will result in decreasing the external pressure for a next set of computations.

250: The hourglass number. In view of the reciprocal relation between time and hourglass number, it is not too important what you enter here. You will find it easiest to enter some power of ten like 10,000 so that you get printouts of time that are 1 sec or more (as now printed <1 sec is buried). There really is no point in having the program calculate for more than 1 value of the hourglass number. I just haven't made that adjustment in the code.

270: This value is unimportant, but I think it is still necessary because of the way some of the equations are written. I use 10^{-6}.

280: Not sure if this is needed. I usually enter 0.5
300: This title will be printed to identify your computation.
310: and 320: Here you enter wt fractions: 0.043 = 4.3 wt. % etc. For some values that yield very low gas saturation pressures, the program bombs. Also 0 CO_2 will bomb.

OUTPUTS

815-820: These lines specify the output. You can specify whatever you want, fugacities, melt compositions, viscosities, equilibrium temperatures etc. But you have to look through the code to see what the variables are designated. Lines 5990-5992, 6622-6624, 6626-6628 may help. You can get these printed by letting SH = 0 in line 444. An obvious thing to do is to set this up for output files or graphics. I just haven't gotten that far yet, and I have no graphics capability on my machine - only a daisy wheel typewriter.
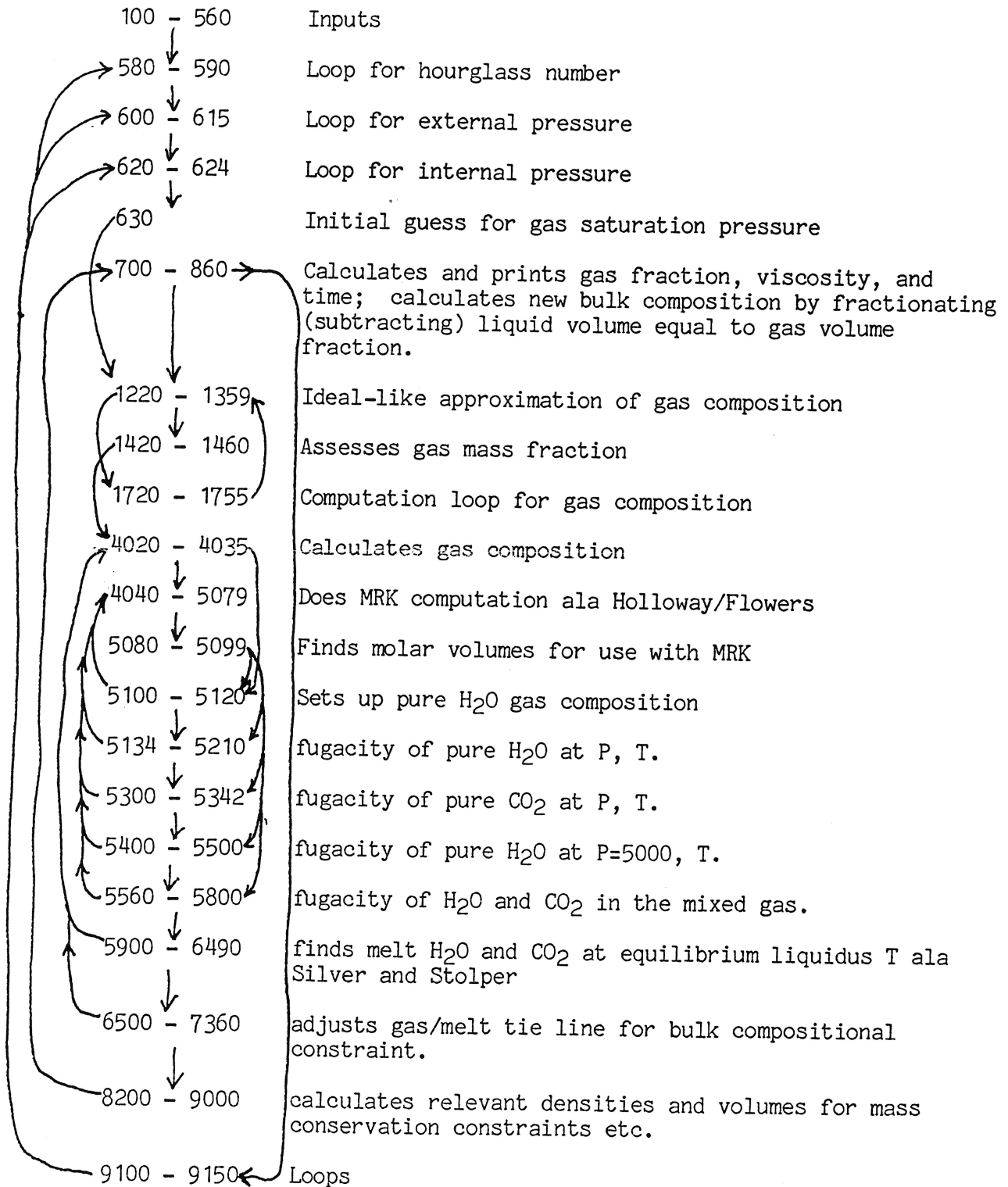
The program takes a long time on my PC to find the first solution for the gas saturation pressure - about 15 minutes. After that about one computation per minute. In the first case the program is finding both the temperature and the pressure of gas saturation by incrementally increasing the pressure until the amount of gas in the system is less than a few ppm. Afterwards, the temperature is held constant, so things go faster.

SOURCES AND LIMITATIONS

Program HGLSSN.RV9 uses a viscosity function (lines 778-780) based on Shaw, 1972, adapted for high-silica rhyolite. The H_2O solubility follows the speciation model of Silver et al. (1990) for rhyolite (lines 6100-6490). The CO_2 solubility follows Newman et al., 1988 but uses the solubility reported by Blank et al. (1989) (lines 6500-6504).

In view of these factors, **it is only appropriate to use the program as it now stands for high-silica rhyolite + H_2O + CO_2.** The program is reasonably well adapted to pressures ranging between several hundred and several thousand bars.

ORGANIZATION OF HOURGLASS PROGRAM: HGLSSN.CP7

100 – 560   Inputs

580 – 590   Loop for hourglass number

600 – 615   Loop for external pressure

620 – 624   Loop for internal pressure

630   Initial guess for gas saturation pressure

700 – 860   Calculates and prints gas fraction, viscosity, and time; calculates new bulk composition by fractionating (subtracting) liquid volume equal to gas volume fraction.

1220 – 1359   Ideal-like approximation of gas composition

1420 – 1460   Assesses gas mass fraction

1720 – 1755   Computation loop for gas composition

4020 – 4035   Calculates gas composition

4040 – 5079   Does MRK computation ala Holloway/Flowers

5080 – 5099   Finds molar volumes for use with MRK

5100 – 5120   Sets up pure H_2O gas composition

5134 – 5210   fugacity of pure H_2O at P, T.

5300 – 5342   fugacity of pure CO_2 at P, T.

5400 – 5500   fugacity of pure H_2O at P=5000, T.

5560 – 5800   fugacity of H_2O and CO_2 in the mixed gas.

5900 – 6490   finds melt H_2O and CO_2 at equilibrium liquidus T ala Silver and Stolper

6500 – 7360   adjusts gas/melt tie line for bulk compositional constraint.

8200 – 9000   calculates relevant densities and volumes for mass conservation constraints etc.

9100 – 9150   Loops

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100   : LPRINT "HOURGLASS HG# HGLSSN.RV8 2/27/90 REV ALA NEWMAN STOLPER 4050-70;
SILVER ETC H20 AND BLANK CO2 (1990) NEW VISCOSITY (SHAW 1972) NEW TRIP FOR P NEA
R PEXT MOD 9/14/90"
105   : LPRINT "XOHM <= 0 SEE 6240 "
110   : LET D1=2.321: LET E=3.76: LET D2=2.605
120   : LET R=83.12: LET T=1000
210   : INPUT "-DELTA P PER INCREMENT BARS=YP";YP
215   : INPUT "+DELTA GAS FRACT PER INCREMENT";DGF
220   : INPUT "INITIAL INTERNAL P BARS = PINT";PINT
240   : INPUT "INITIAL EXTERNAL P BARS = PEXT";PEXT
242   : INPUT "T K FOR VISCOSITY COMP";TIK
245   : INPUT "INCREMENT FOR EXTERNAL P=";XP
246   : INPUT "NO OF INCREMENTS FOR EXT P=Q6";Q6
250   : INPUT "HOURGLASS NUMBER = HGNI";HGNI
270   : INPUT "VOLUME OF INCLUSION = V (CM 3)";V
280   : INPUT "VOL FRACT GAS OBSERVED=GI";GI
300   : INPUT "INCLUSION TITLE =T$";T$
310   : INPUT "WT FRACT H20 IN GL = H4 =?";H4
320   : INPUT "WT FRACT CO2 IN GL = C4 =?";C4
444   : LET U1=10: LET KT=.891: LET SH=1: LET SN=0: LET T=1060
500   : LPRINT "DATE        TIME        ";DATE$;TIME$
502   : LPRINT "INCLUSION TITLE ";T$
505   : LPRINT "BULK MASS FRACT H20, CO2";H4;C4
508   : LPRINT "T(RHYOLITE)/T(ALBITE) = ";KT
510   : LPRINT "INITIAL INTERNAL P BARS ";PINT
512   : LPRINT "INITIAL EXTERNAL P BARS ";PEXT
520   : LPRINT "INITIAL HOURGLASS NUMBER";HGNI
560   : LET HI=H4: LET CI=C4
580   : FOR HGE=1 TO 4 STEP 1
582   : LET HGN=HGNI*10^(1-HGE)
590   : LPRINT "HOURGLASS NUMBER = ";HGN
600   : FOR Q5=1 TO Q6 STEP 1
602   : LET Q=1: LET GP=0
603   : LET Q7=50
605   : LET TTOT=0: LET G=0: LET G1=0: LET G2=0: LET G3=0
608   : LET MT=MTI: LET MEX=0: LET HEX=0: LET MTOT=0
610   : LET P5=PEXT+(Q5-1)*XP
612   : LPRINT "PEXTERNAL =   ";P5
615   : LET H4=HI: LET C4=CI
620   : FOR Q=1 TO Q7 STEP 1
621   : IF Q>1 THEN 700
622   : LET P1=.9*((H4/.001426)^2+(C4/.0000005))
624   : LET DP=.08*P1
630   : LET P=P1: GOTO 1220
700   : LET VG=M3*MT/D3
702   : LET VM=M1*MT/D1
704   : LET FV=VG+VM-V
706   : LET FM=FV*D1
710   : LET H4=(H1*(M1*MT-FM)+H3*(M3*MT))/(MT-FM)
720   : LET C4=(C1*(M1*MT-FM)+C3*(M3*MT))/(MT-FM)
730   : LET MT=MT-FM
740   : LET MEX=MEX+FM: LET MTOT=MT+MEX: LET HEX=HEX+H1*FM
742   : LET HT=H1*(VM*D1-FM)+H3*VG*D3+HEX
746   : LET CKH=HT/MTOT: LET CKM=MTI/MTOT
760   : LET G2=V3/(V3+V1)
770   : LET G3=G2-G1
778   : LET SV=3.816-23.65*H1
780   : LET VIS=EXP(SV*10000/TIK-1.5*SV-6.4)
790   : LET TM=8*16*VIS*G3*HGN/(1000000!*3.14159*(P-P5))
795   : IF TM<0 THEN 9150
800   : LET TTOT=TTOT+TM
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800  : LET TTOT=TTOT+TM
807  : LET Q7=INT(GI/DGF)+5
810  : LET G=G+G3: LET G1=G2
812  : IF Q>2 THEN 820
815  : LPRINT "P/1000 T(C)/1000 VIS/10^6 GAS%   t/10^3   % H20   PMCO2/10   C3
XH"
820  : LPRINT USING "###.### ";P/1000;(TI-273)/1000;VIS/1000000!;G*100;TTOT/1000
!;100*H1;100000!*C1;C3;XH
822  : IF P<(1+10^(-4))*P5 THEN 9100
825  : LET GP=DGF*Q
827  : IF GP>=.174 THEN 880
830  : LET PW=P
832  : LET P=EXP(-.2278*LOG(GP)+6.15)
835  : PRINT "PW, P, P1, DP, G3, N3";PW,P,P1,DP,G3,N3
860  : GOTO 1220
880  : LET P=EXP(-.588*LOG(GP)+5.52): GOTO 1220
900  : LET P=(P+P5)/2
1220 : LET C=1
1222 : LET H1=(1-.000001)*.001426*P^.5
1230 : GOSUB 1720
1270 : IF M5>M3 THEN 1274
1272 : IF M5<M3 THEN 1284
1274 : LET H1=H1-.0001*C
1275 : GOSUB 1720
1277 : IF M5<M3 THEN 1310
1279 : GOTO 1274
1284 : LET H1=H1-.0001*C
1285 : GOSUB 1720
1287 : IF M5>M3 THEN 1340
1289 : GOTO 1284
1310 : LET H1=H1+.00001*C
1312 : GOSUB 1720
1314 : IF M5>M3 THEN 1330
1315 : GOTO 1310
1330 : LET H1=H1-.000001*C
1332 : GOSUB 1720
1334 : IF M5<M3 THEN 1336
1335 : GOTO 1330
1336 : LET H1=H1+.0000001*C
1337 : GOSUB 1720
1338 : IF M5<M3 THEN 1420
1339 : GOTO 1336
1340 : LET H1=H1+.00001*C
1342 : GOSUB 1720
1344 : IF M5<M3 THEN 1350
1346 : GOTO 1340
1350 : LET H1=H1-.000001*C
1352 : GOSUB 1720
1354 : IF M5>M3 THEN 1356
1355 : GOTO 1350
1356 : LET H1=H1+.0000001*C
1357 : GOSUB 1720
1358 : IF M5<M3 THEN 1420
1359 : GOTO 1356
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```
1420 : LET H3=((-H1^2)/44)/((H1^2)/18-(H1^2)/44-(P*(.001426)^2)/18)
1430 : LET XH=(H3/18)/(H3/18+(1-H3)/44)
1438 : LET C1=.0000005*P*(1-XH)
1440 : LET M3=(C4*(1+F)-C1)/((1-H3)*(1+F)-C1)
1450 : LET M5=(H1-(1+F)*H4)/(H1-(1+F)*H3)
1460 : GOTO 4020
1720 : LET H3=((-H1^2)/44)/((H1^2)/18-(H1^2)/44-(P*(.001426)^2)/18)
1730 : LET XH=(H3/18)/(H3/18+(1-H3)/44)
1738 : LET C1=.0000005*P*(1-XH)
1740 : LET M3=(C4*(1+F)-C1)/((1-H3)*(1+F)-C1)
1750 : LET M5=(H1-(1+F)*H4)/(H1-(1+F)*H3)
1755 : RETURN
1780 : LET C=.1
1790 : GOTO 1222
1846 : LET H3=0: LET M3=0: LET M5=0: LET H1=H4*(1+F): LET XH=0
1860 : LET C1=C4*(1+F): LET V3=0:
1862 : GOTO 8220
4020 : LET H9=H3
4022 : LET P9=P
4024 : LET C3=1-H3
4026 : LET XH=(H3/18)/((H3/18)+(C3/44))
4028 : LET XC=1-XH
4030 : LET P=P9
4035 : GOTO 5100
4040 : LET V8=.7*R*T/P: LET N=1: LET CL=1
4042 : LET T2=T-273
4044 : LET C3=1-H3
4046 : LET XH=(H3/18)/((H3/18)+(C3/44))
4048 : LET XC=1-XH
4050 : LET AH=(1.668E+08-193080!*T2+186.4*T2^2-.071288*T2^3)*1.01325
4060 : LET AC=(7.303E+07-71400!*T2+21.57*T2^2)*1.01325
4061 : LET AK=EXP(-11.07+5953/T-2746000!/T^2+4.646E+08/T^3)
4062 : LET AR=((3.5E+07*4.6E+07)^.5+R^2*T^2.5*AK/(2*1.02668))*1.01325
4070 : LET A5=2*XC*XH*AR+XH^2*AH+XC^2*AC
4071 : LET AT=A5/(R*R*T^2.5)
4072 : LET BH=14.6
4074 : LET BC=29.7
4076 : LET B5=XC*BC+XH*BH
4078 : LET BT=B5/(R*T)
5042 : LET V8=R*T/P: GOTO 5080
5070 : LET V8=1.05*V8: GOTO 5080
5079 : RETURN
5080 : LET P8=83.12*T/(V8-B5)-A5/((V8^2+B5*V8)*(T^.5))
5082 : IF ABS (P8-P)<.001*P THEN 5079
5083 : LET VN=V8+1: LET PN=83.12*T/(VN-B5)-A5/((VN^2+B5*VN)*(T^.5))
5084 : LET VM=V8+(VN-V8)/(P8-PN)*.8*(P8-P): LET PM=R*T/(VM-B5)-A5/((VM^2+B5*VM)*
(T^.5))
5090 : LET VX=VM+(VM-V8)/(P8-PM)*.8*(PM-P): LET PX=R*T/(VX-B5)-A5/((VX^2+B5*VX)*
(T^.5))
5093 : LET N=N+1
5094 : LET VN=VX: LET PN=PX: LET V8=VM: LET P8=PM
5095 : IF P8<0 THEN 5070
5098 : IF ABS (P8-P)<.001*P THEN 5079
5099 : GOTO 5084
5100 : LET P=P9
5110 : LET H3=1
5112 : LET CL=1
5120 : GOSUB 4040
5134 : LET V9=V8
5150 : LET Z=P*V9/(R*T)
5200 : LET I=EXP(LOG(V9/(V9-B5))+BH/(V9-B5)-2*(AH*XH+AR*XC)/(B5*R*T^1.5)*LOG((V9
+B5)/V9)+A5*BH/(B5^2*R*T^1.5)*(LOG((V9+B5)/V9)-B5/(V9+B5))-LOG(P*V9/(R*T)))
```

```
5210 : LET F7=I*P
5300 : LET P=P9
5310 : LET H3=0
5312 : LET CL=1
5320 : GOSUB 4040
5330 : LET V6=V8
5340 : LET I6=EXP(LOG(V6/(V6-B5))+BC/(V6-B5)-2*(AC*XC+AR*XH)/(B5*R*T^1.5)*LOG((V
6+B5)/V6)+A5*BC/(B5^2*R*T^1.5)*(LOG((V6+B5)/V6)-B5/(V6+B5))-LOG(P*V6/(R*T)))
5342 : LET F6=I6*P
5400 : LET P=5000: LET P3=5000: LET H3=1: LET CL=1
5410 : GOSUB 4040
5470 : LET V1=V8
5480 : LET Z=P*V1/(R*T)
5490 : LET I2=EXP(LOG(V1/(V1-B5))+BH/(V1-B5)-2*(AH*XH+AR*XC)/(B5*R*T^1.5)*LOG((V
1+B5)/V1)+A5*BH/(B5^2*R*T^1.5)*(LOG((V1+B5)/V1)-B5/(V1+B5))-LOG(P*V1/(R*T)))
5500 : LET F8=I2*P
5560 : LET P=P9
5600 : LET VM=16.4*(1+.00002*P)^(-1/4)
5610 : LET K1=.17
5612 : LET HR=.15251
5613 : LET K=(K1-4)/K1
5614 : LET KR=HR-(1/2-(1/4-K*(HR-HR^2))^(1/2))/K
5620 : LET K3=LOG(KR)+LOG(F7/F8)-200000!*16.4*((1+.00002*P)^(3/4)-(1+.00002*P3)^
(3/4))/(3*R*T)
5630 : LET K2=EXP(K3)
5660 : LET H3=H9
5662 : LET P=P9
5670 : LET CL=1
5672 : GOTO 5700
5700 : GOSUB 4040
5710 : LET V7=V8
5780 : LET Z=P*V7/(R*T)
5790 : LET I3=EXP(LOG(V7/(V7-B5))+BH/(V7-B5)-2*(AH*XH+AR*XC)/(B5*R*T^1.5)*LOG((V
7+B5)/V7)+A5*BH/(B5^2*R*T^1.5)*(LOG((V7+B5)/V7)-B5/(V7+B5))-LOG(P*V7/(R*T)))
5795 : LET I4=EXP(LOG(V7/(V7-B5))+BC/(V7-B5)-2*(AC*XC+AR*XH)/(B5*R*T^1.5)*LOG((V
7+B5)/V7)+A5*BC/(B5^2*R*T^1.5)*(LOG((V7+B5)/V7)-B5/(V7+B5))-LOG(P*V7/(R*T)))
5797 : LET F4=I4*XC*P
5800 : LET F9=I3*XH*P
5900 : LET HX=F9/F7
5910 : LET XD=K2*HX+(1/4)*(-K1*K2*HX+((K1*K2*HX)^2-4*K1*(K2*HX)^2+4*K1*K2*HX)^(1
/2))
5920 : LET TM=1373+.0095*P: LET T=T/KT
5934 : LET K4=(455.9+72.27*LOG(1373)-.03506*1373-379300!*1373^(-2))
5935 : LET K5=3812*1373^(-1/2)+4.3725E-06*1373^2-6.93E-06*(P-1)
5936 : LET K6=(K4+K5)*(T-TM)
5937 : LET K7=-72.27*((T*LOG(T)-T)-(TM*LOG(TM)-TM))+.01753*(T^2-TM^2)
5938 : LET K8=-379300!*(1/T-1/TM)-7624*(T^(1/2)-TM^(1/2))-1.4575E-06*(T^3-TM^3)
5939 : LET SS=K6+K7+K8
5940 : LET XO=EXP(SS/(8*R*T))
5945 : LET K=(K1-4)/K1
5950 : LET XB=1-XO+.25*(K1*XO-((K1*XO)^2+4*K1*XO-4*K1*XO^2)^.5)
5960 : LET H5=(XB*18)/((XB*18)+(1-XB)*32.5)
5962 : LET H6=(XD*18)/((XD*18)+(1-XD)*32.5)
5964 : IF ABS (H5-H6)<.0002 THEN 5980
5965 : IF XB>XD THEN 6300
5966 : GOTO 6400
5980 : LET N6=0: LET T=T*KT
5982 : IF SH=1 THEN 6010
5990 : LPRINT "LIQ T(K)        P(BARS)        VoCO2        VoH2O        V MIX
    X H2O ";T
5992 : LPRINT USING "##.###^^^^    ";T;P;V6;V9;V7;XH
5995 : LET T=T*KT: GOTO 6500
```

```
5995 : LET T=T*KT: GOTO 6500
6010 : LET XOHM=.46*H1^(.5)-.22*H1
6020 : LET DELFN=.5
6030 : LET N9=0
6100 : LET XH2OM=XH*.033*(F7/712.2)*EXP(-10*(P-799)/(41.84*1.9872*T)+4300/1.9872
*(1/T-1/1123.16))
6110 : LET AOH=-LOG(((XOHM)^2)/((XH2OM)*(1-XH2OM-XOHM)))
6120 : LET BOH=1.093+16.858*XOHM+7.892*XH2OM
6130 : LET N9=N9+1
6150 : LET XB=.5*XOHM+XH2OM
6160 : IF ABS(BOH-AOH)<.001*BOH THEN 6500
6190 : IF N9=1 THEN 6220
6200 : LET DELFN=(XOHMY-XOHM)/((BOHY-AOHY)-(BOH-AOH))
6220 : LET XOHMY=XOHM
6225 : IF N9>1 THEN 6230
6228 : LET XOHM=.8*XOHM: GOTO 6235
6230 : LET XOHM=XOHM-DELFN*(BOH-AOH)/2
6235 : LET BOHY=BOH: LET AOHY=AOH
6240 : IF XOHM<=0 THEN 105
6250 : GOTO 6110
6300 : LET N6=N6+1
6310 : IF N6=1 THEN 6330
6320 : GOTO 6350
6330 : LET T5=20
6340 : GOTO 6360
6350 : LET T5=-.8*(T4-T)/(XS-(XB-XD))*(XB-XD)
6360 : LET T4=T: LET T=T+T5
6390 : LET XS=XB-XD: LET T=T*KT: GOTO 5100
6400 : LET N6=N6+1
6410 : IF N6=1 THEN 6430
6420 : GOTO 6450
6430 : LET T5=-20
6440 : GOTO 6460
6450 : LET T5=-.8*(T4-T)/(XS-(XB-XD))*(XB-XD)
6460 : LET T4=T: LET T=T+T5
6490 : LET XS=XB-XD: LET T=T*KT: GOTO 5100
6500 : LET KC=EXP(LOG(.000221)+LOG(F6/563.4)-28.6*(P9-500)/(83.144*T)+4130/1.987
2*(1/T-1/1123.16))
6502 : LET YC=KC*XC
6503 : LET H6=XB*18.015/(XB*18.015+(1-XB-YC)*32.5+YC*44)
6504 : LET C6=(YC*44)/(YC*44+XB*18+32.5*(1-YC-XB))
6505 : IF C6<0 THEN 6660
6506 : IF YC>1 THEN 6670
6510 : LET C1=C6
6520 : LET H1=H6
6550 : IF H3<=0 THEN 6650
6620 : IF SH=1 THEN 6900
6622 : LPRINT "H2O SOLIDUS  X H2O GAS  T=(T-2)*.917  XO            XB           X
D  "
6624 : LPRINT USING "##.###^^^^  ";H5;XH;T;XO;XB;XD
6626 : LPRINT "  F CO2      Fo CO2        Fo H2O        FR H2O        F H2O        H2O MELT
(XD)   CO2 MELT"
6628 : LPRINT USING "##.###^^^^  ";F4;F6;F7;F8;F9;H6;C6
6900 : LET Q6=(H3-H6)/(1-H3-C6)
6902 : LET X6=(Q6*(1-C4)+H4)/(1+Q6)
6903 : IF SH=1 THEN 6916
6905 : LPRINT "H2O LAST GAS      H2O NEW GAS           FRACT XLS"
6906 : LPRINT USING "##.###^^^^          ";XH;X6;F/(1+F)
```

```
6916 : LET C7=1-X6
6918 : LET M9=M5: LET M7=M3
6920 : LET M5=(H4-H6/(1+F))/(X6-H6/(1+F))
6922 : LET M3=(C4-C6/(1+F))/(C7-C6/(1+F))
6944 : IF ABS (M5-M3)<.04*M5 THEN 8200
6950 : LET C3=(C4-C6*((1-M5)/(1+F)))/M5
6951 : IF C3>1 THEN 6990
6952 : IF C3>(1-H3) THEN 7200
6954 : IF C3<(1-H3) THEN 7300
6960 : IF C3>1 THEN 6990
6962 : LET H3=1-C3
6980 : GOTO 4020
6990 : LET C3=1: GOTO 6962
7200 : LET N7=N7+1
7210 : IF N7=1 THEN 7230
7220 : LET MF=(C5-C7)/(MD-(M5-M3))
7225 : GOTO 7240
7230 : LET C3=(1-H3)+.1*(C3-(1-H3))
7235 : GOTO 7250
7240 : LET C3=(1-H3)-.5*(M5-M3)*MF
7250 : LET MD=(M5-M3): LET C5=C7
7260 : GOTO 6960
7300 : LET N7=N7+1
7310 : IF N7=1 THEN 7230
7320 : LET MF=(C5-C7)/(MD-(M5-M3))
7325 : GOTO 7340
7330 : LET C3=(1-H3)-.1*(C3-(1-H3))
7335 : GOTO 7350
7340 : LET C3=(1-H3)-.5*(M5-M3)*MF
7350 : LET MD=(M5-M3): LET C5=C7
7360 : GOTO 6960
8200 : LET XH=(H3/18)/((H3/18)+(1-H3)/44): LET N7=0
8205 : LET H9=H3
8206 : IF M3<=0 THEN 640: IF M5<=0 THEN 640
8208 : GOSUB 4040
8210 : LET D3=(XH*18+(1-XH)*44)/V8
8211 : LET M3=(H1-(1+F)*H4)/(H1-(1+F)*H3)
8212 : LET V3=M3/D3
8220 : LET D4=2.313/(1+.0000406*(T-1063)-1.67E-06*(P-1))
8230 : LET VH=24.7+.007*(T-1173)-1.5*(P/1000)+.084*(P/1000)^2-.0014*(P/1000)^3
8240 : LET DH=18/VH
8250 : LET D1=1/(((1-H1)/D4)+(H1/DH))
8258 : LET M1=(1-M3)/(1+F)
8260 : LET V1=M1/D1
8270 : LET V2=M1*F/D2
8300 : LET D=1/(V1+V2+V3)
8590 : LET T=T/KT
8591 : IF Q>1 THEN 9000
8592 : IF M3*C3<.01*C4 THEN 8900
8593 : LET N3=N3+1
8594 : IF N3=1 THEN 8599
8595 : LET DP=P-PW: LET DM=M3-MW: LET PW=P: LET MW=M3: LET P=P-.8*DP*M3/DM: GOTO
     1220
8599 : LET W3=M3*C3: LET PW=P: LET MW=M3: LET P=P+DP: GOTO 1220
8900 : LET P4=P: LET W8=H3: LET N3=0: LET TI=T*KT
8910 : LET MMI=D1*V*V1/(V1+V3): LET MGI=D3*V*V3/(V1+V3): LET MTI=MMI+MGI
8920 : LET MT=MTI
8940 : LPRINT "INITIAL PSAT (BARS) =";P4
9000 : NEXT Q
9100 : NEXT Q5
9150 : NEXT HGE
9200 : END
```