Special Report 84-27

September 1984

Deuterium diffusion in a soil-water-ice mixture

Joseph L. Oliphant and Allen R. Tice

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Special Report 84-27	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DEUTERIUM DIFFUSION IN A SOIL-WATER-ICE MIXTURE		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Joseph L. Oliphant and Allen R. Tice		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire 03755-1290		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS DA Project 4A161102AT24, Task A, Work Unit 002
11. CONTROLLING OFFICE NAME AND ADDRESS Office of the Chief of Engineers Washington, D.C. 20314		12. REPORT DATE September 1984
		13. NUMBER OF PAGES 17
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Deuterium
Frozen soil
Laboratory tests
Tracer studies
Water migration

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
An experiment was performed to determine the rate of equilibration of deuterium between the ice and liquid phases of water in partially frozen soil. The results of this experiment are consistent with a diffusion rate of deuterium in ice of 1 or 2×10^{-10} cm^2/s. A method for calculating the approximate equilibration time, given the size of the ice crystals in the system, is provided. This calculation compares well with the experimental results.

PREFACE

CONTENTS

ILLUSTRATIONS

TABLES

DEUTERIUM DIFFUSION IN A SOIL-WATER-ICE MIXTURE

by

Joseph L. Oliphant and Allen R. Tice

INTRODUCTION

It has been suggested that deuterated water could be used as a tracer in experiments aiming to clarify the mechanisms of water and ice migration in frozen soils. Arnason (1969) has shown that for summer water percolation in a temperate glacier in Iceland, equilibrium of deuterium concentrations between the ice and water is closely approximated. Arnason also showed in a 3-hour laboratory experiment with melting snow that equilibrium was approached but not reached. To use deuterium oxide as a tracer for water migration in partially frozen soil, the processes and rates of equilibration of deuterium between frozen and unfrozen phases need to be understood and quantitatively known.

The processes by which equilibration between phases containing deuterium take place include diffusive and convective movement of water containing deuterium and protium in the liquid phase and diffusive movement in the solid phase. There also may be some resistance to movement across the phase boundaries that needs to be considered. The diffusion coefficient for deuterated water in the liquid phase is on the order of 10^{-5} cm^2/s (Franks 1982) and that for deuterium in ice is about 10^{-10} cm^2/s (Franks 1972). The relatively low but finite diffusion rate in ice can cause, under some conditions, equilibrium between the ice and water but under other conditions this equilibrium will not be attained. The following experiment was designed to test the rate of equilibration of deuterated water between the ice and liquid water phases in frozen soil.

EXPERIMENTAL

Oven dry morin clay was mixed with about 7% by weight deuterium oxide (D_2O) and then compacted in stainless steel tubes of 15-mm i.d. to a thickness of about 5 mm. About 20 specimens were prepared, placed in a cold environment (-20°C) and frozen. Following freezing, each specimen or wafer

was sanded to a uniform thickness of 2.5 ± 0.1 mm with Carborundum cloth and fine sandpaper. Each sanded wafer was then stored, in a small airtight glass bottle to minimize sublimation.

Cylindrical single crystals of ice of 15-mm o.d. and about 40 mm long were prepared from deionized, distilled water by use of a dye extrusion technique. These were sawed into 5-mm thick sections, then sanded to a thickness of 2.5 ± 0.1 mm. Each ice wafer was then examined under polarized light to ensure that it was a single crystal. They were then stored like the soil-deuterium wafers until they were ready for use. We selected single crystal ice as opposed to polycrystalline ice to guard against any signal contribution from liquid films between ice grain boundaries. Nuclear Magnetic Resonance (NMR) readings were taken on samples of the single crystal ice. No NMR signal above the background reading was detected at -0.5°C.

A test tube 150 mm long and 19 mm o.d. with a rubber stopper was selected to contain and seal the samples for NMR analysis. A 16- -o.d. by 5-mm-thick plastic disk was placed in the bottom of the test tube to serve as a flat support for the samples. Next, a frozen soil-deuterium oxide wafer was added, followed by an ice wafer. This sandwiching of ice wafers between soil-deuterium oxide wafers was repeated until the complete detection region of the NMR analyzer was filled by 16 wafers (Fig. 1). Two of the layered samples were made (called sample A and sample B here), and one sample of the Morin clay mixed with 7% distilled water without any ice layers was also fashioned. The samples were prepared in the -20°C coldroom.

All three test tubes were brought out of the coldroom and an NMR reading taken on each. The method of making the NMR readings and calculating unfrozen water contents from the readings is discussed by Tice et al. (1982). After the NMR readings were taken, each test tube was placed in a constant temperature bath held at
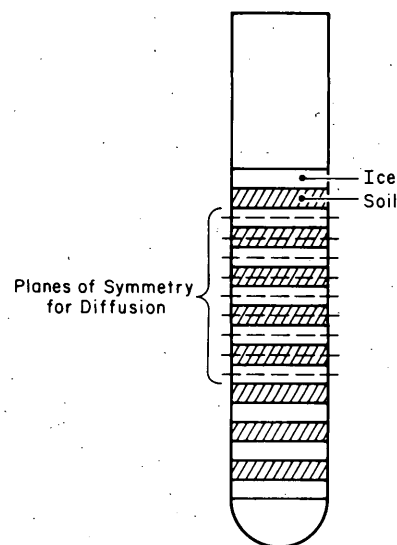
Deuterium Diffusion Experiment

Figure 1. Schematic of layered diffusion experiment showing ice and soil wafers and planes of symmetry for diffusion.

Table 1. NMR readings on layered samples and blank sample.*

Time (hr)	Sample A	Sample B	Blank	Temperature (°C)
0	29	29	51	––
0.28	33	32	71	-0.59
0.43	34	34	79	-0.51
0.83	32	35	83	-0.43
1.33	34	35	86	-0.43
1.83	34	35	89	-0.43
2.83	34	33	84	-0.48
18.3	36	36	87	-0.54
22.3	38	37	88	-0.54
26.8	35	35	87	-0.54
43.0	39	38	85	-0.54
50	41	41	84	-0.50
115	40	40	85	-0.56
120	41	40	87	-0.54
139	43	42	87	-0.51
163	44	43	87	-0.54
283	45	45	87	-0.54
308	46	47	88	-0.54
336	47	47	87	-0.54
380	47	47	88	-0.54
452	47	47	87	-0.54

*Background reading was 26.

Table 2. Deuterium content of final ice and soil samples.

Sample	Atom % Deuterium
A-Ice	5.54
A-Ice	5.44
B-Ice	4.77
B-Ice	4.75
Avg.	5.13
A-Soil	30.24
A-Soil	31.77
B-Soil	27.01
B-Soil	32.55
Avg.	30.4

-0.5°C. The test tubes were periodically removed from the bath and NMR readings taken over 19 days. The readings are given in Table 1.

After 19 days, the sample tubes were taken back into the -20°C cold-room and the layers of frozen soil and ice from the two layered samples

were separated and put into discrete sealed containers. Later, both the soil and ice layers were analyzed for the ratio of protium to deuterium they contained using an isotope ratio mass spectrometer. The details of this analysis are given by Oliphant et al. (1982). The results are shown in Table 2.

MATHEMATICAL MODEL OF DIFFUSION PROCESS

At the equilibrium temperature of $-0.5°C$, all the water in the clay disks would be in the unfrozen or liquid state (Nakano et al. 1983). As already discussed, the diffusion rate is about 5 orders of magnitude higher in the liquid state than in ice. We therefore made the assumption that in the clay the ratio of hydrogen to deuterium was a function of time but not of position in the clay disks. In the ice disks the deuterium concentration is a function of both time and the distance into the disk. In the stack of alternating ice and soil disks, each ice disk is sandwiched between two soil disks. This gives rise to a plane of symmetry at the center of each ice disk and each soil disk for the diffusion problem. To model the whole diffusion process, only one half of a soil disk and one half of an ice disk and the interface between them need to be considered, as shown in Figure 1.

Letting C be the mole fraction of deuterium in the ice phase and D be the diffusion coefficient in cm^2/s, we can write

$$\frac{\partial^2 C}{\partial x^2} - \frac{1}{D}\frac{\partial C}{\partial t} = 0 \tag{1}$$

for the mole fraction of deuterium in the ice phase as a function of distance into the ice x and time t. This equation holds for all values of x between the interface, $x = 0$, and the midplane of the ice disk, $x = \ell$, and for all times $t > 0$. Because of symmetry, we can also write at $x = \ell$ that

$$\frac{\partial C}{\partial x} = 0 \quad . \tag{2}$$

A mass balance for deuterium at the interface, $x = 0$, gives the equation

$$\frac{\partial C_\ell}{\partial t} = \frac{n_1}{n_2}\frac{D}{\ell}\left(\frac{\partial C}{\partial x}\right)_{x=0} \tag{3}$$

where C_ℓ is the mole fraction of deuterium in the soil disk, n_1 and n_2 are the total moles of hydrogen plus deuterium per cm^3 in the ice and soil

4

phases, respectively, and the subscript x = 0 means that this derivative should be taken at the interface. We can also write at the interface

$$n_1 D \left(\frac{\partial C}{\partial x}\right)_{x=0} + H(C_\ell - C_{x=0}) = 0 \tag{4}$$

where H has units of moles/cm^2 s and represents the rate of mass transfer across the ice disk/soil disk interface attributable to a unit concentration gradient. The higher the value for H, the lower the resistance to interphase mass transport. A lower bound for H can be estimated as follows: Assume that transport across the interface must be by diffusion through an air gap between disks with maximum thickness of 0.01 cm. The diffusion coefficient for water vapor diffusion through air is on the order of 0.1 cm^2/s. Using the ideal gas equation and the vapor pressure of water at 0°C, we can calculate that the maximum concentration of deuterium in the air would be about 4×10^{-7} moles/cm^3. We can calculate H to be

$$H = 0.1 \text{ cm}^2/\text{s} \; \frac{1}{0.01 \text{ cm}} \; \times \; 4\times10^{-7} \text{ moles/cm}^3 = 4\times10^{-6} \text{ moles/cm}^2 \text{ s.} \tag{5}$$

Smaller values for the air gap would give a higher value for H.

Equations 1 through 4, with the given boundary conditions and the initial conditions $C_\ell = C_\ell^0$ and $C = 0$, can be solved using Laplace transforms (Carslaw and Jaeger 1950). The final solution is

$$C = \frac{C_\ell^0}{1+K} + 2LC_\ell^0 \sum_{s=1}^{\infty} \frac{\alpha_s^2 - KL}{p_s \cos \alpha_s} e^{-\alpha_s^2 T} \cos \alpha_s (1-x/\ell) \tag{6}$$

and

$$C_\ell = \frac{C_\ell^0}{1+K} + 2KL^2 C_\ell^0 \sum_{s=1}^{\infty} \frac{1}{p_s} e^{-\alpha_s^2 T} \tag{7}$$

where

    L = ℓh

    h = $H/n_1 D$

    K = n_1/n_2

    T = Dt/ℓ^2

and the α_s are the positive roots of the equation

$$\tan \alpha = \frac{L\alpha}{\alpha^2 - KL} \tag{8}$$

5

and

$$p_s = \alpha_s^4 + (L^2 + L - 2KL)\alpha_s^2 + KL^2(1+K). \tag{9}$$

A computer program was written that calculates C and C_ℓ according to eq 7 and 8 for input values of H, n_1, n_2, D, ℓ, C_ℓ^0 and t. This is given in Appendix A.

RESULTS AND DISCUSSION

Although essentially pure D_2O was initially added to the Morin clay samples, the samples originally contained a small amount of water and also protons associated with the clay matrix that would equilibrate with the added deuterium. The initial concentration of hydrogen in the soil sample can be estimated as follows from the NMR data.

The blank soil column gave an NMR reading of about 87 at the equilibrium temperature. This column was made of clay mixed with distilled water that is essentially pure H_2O and contains only the natural abundance level (0.015%) of deuterium. Subtracting the background reading of 26 from 87 gives 61 counts ascribable to the hydrogen in the added water. This number must be divided by 2 to compare with the readings obtained on the A and B samples because half of the volume of these samples is made up of single crystal ice, which does not contribute to the NMR signal. Thus, a signal of 30.5 plus the background of 26, or 56.5, would correspond to 100% hydrogen in the soil disks. The final NMR readings of about 47 on samples A and B correspond to 68.8% hydrogen in the samples. This compares well with the mass spectrometer value of 69.6% hydrogen in the final soil samples as shown in Table 2 (atom % hydrogen = 100 − 30.4 = 69.6%). All the NMR readings on samples A and B can be converted to mole % hydrogen values by similar calculations. These values are shown in Figure 2. The initial values gave NMR readings of about 33. This corresponds to an initial hydrogen content of the soil disks of 23%.

The ratio n_1/n_2 used in eq 6 and 7 can be calculated from the NMR and mass spectrometer data by making hydrogen or deuterium material balances. The final amount of deuterium in the system must be equal to the initial amount in the soil disks. This leads to the equation
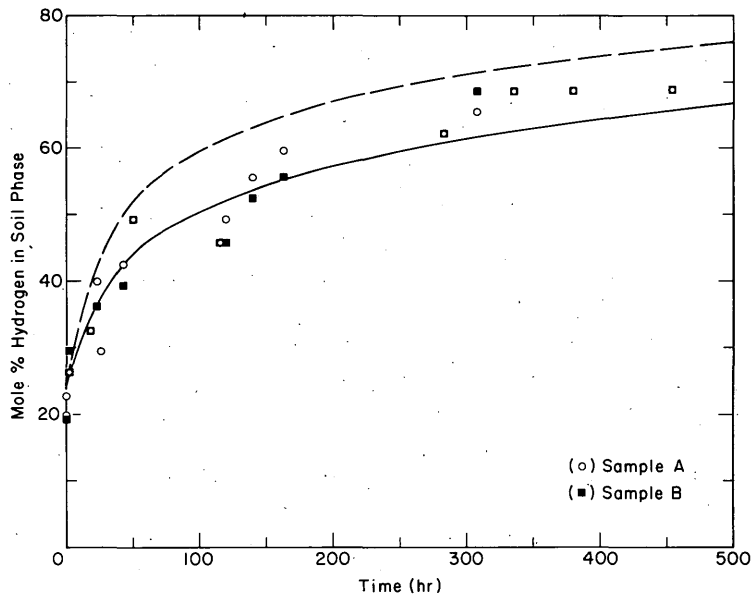
$$0.0513\ n_1 + 0.304\ n_2 = 0.77\ n_2 \tag{10}$$

Figure 2. NMR data of mole % hydrogen in the soil wafers as a function of time (dashed line represents $D = 2.5 \times 10^{-10}$ cm/s; solid line represents $D = 1 \times 10^{-10}$ cm/s).

where the two terms on the left represent the deuterium in the final soil and ice phases and the term on the right represents the deuterium in the initial soil phase. This equation gives a ratio of n_1/n_2 of 9.08. Considering the density of ice, we can calculate n_1 to have a value of 0.102 moles/cm^3, and thus n_2 has a value of 0.011 moles/cm^3.

Equations 6 and 7 were solved for values of H, n_1, n_2, ℓ and C_ℓ^0 equal to 4×10^{-6}, 0.102, 0.011, 0.125, and 0.77, respectively, and for two values of D, 1×10^{-10} cm^2/s and 2.5×10^{-10} cm^2/s. The two solutions for the mole % hydrogen in the soil phase are shown in Figure 2 as a function of time. The solution with $D = 1 \times 10^{-10}$ cm^2/s fits the data well at times less than 200 hours and the two solutions bracket the data at times from 300 to 500 hours.

We show in Figure 3 the calculated mole fraction of hydrogen as a function of position in the soil and ice phases at several different times for $D = 1 \times 10^{-10}$. It can be seen that the change in concentration across the interface is negligible even though a lower bound for the value of H was used in the calculation. Thus, interfacial resistance to diffusion appears to be negligible for this system. It can also be seen that times on the order of 1000 hours or more are necessary for significant approaches to equilibrium in the ice disks.
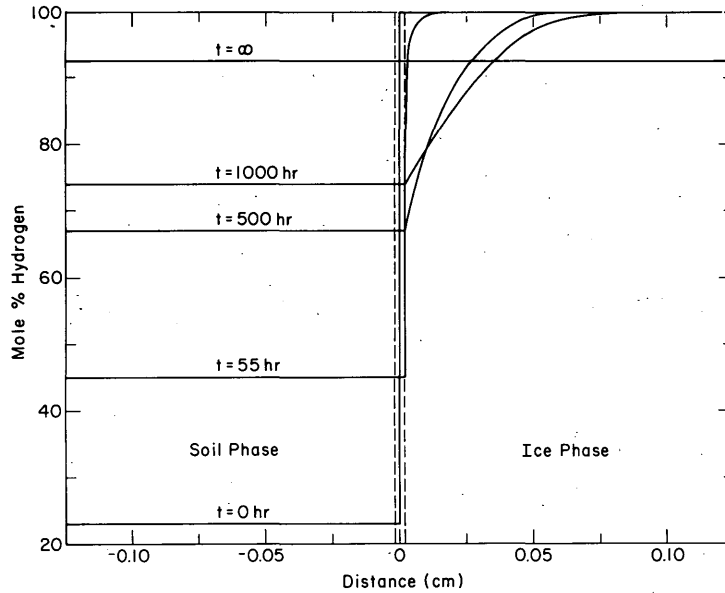
7

Figure 3. Calculated concentration of hydrogen in the ice and soil wafers as a function of position at several times.
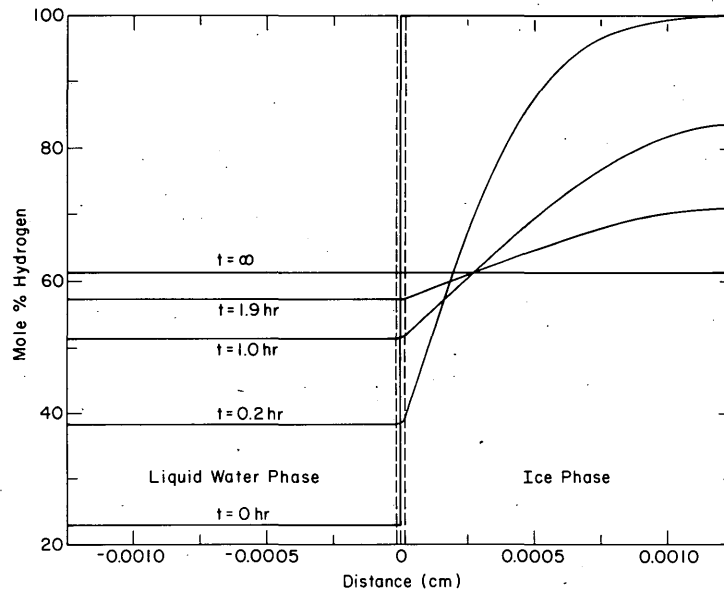

Figure 4. Calculated concentration of hydrogen in water and ice phases for a hypothetical experiment using ice crystals 0.0025 cm thick.

In Figure 4 is shown the mole fraction of hydrogen as a function of position at several times for ice pieces 2.5×10^{-3} cm thick, which is probably closer to the size of ice crystals that form in rapidly frozen soils. For this calculation, n_1 and n_2 were set equal to 0.102 moles/cm^3 and ℓ was set equal to 0.00125 cm. All other parameters were the same as for the

calculation shown in Figure 3. The interfacial resistance is still negligible compared to the resistance to diffusion in the ice phase. Most importantly, at this size for the ice crystals, equilibrium is approached after only a few hours.

CONCLUSIONS

We found that using a value for the diffusivity D of deuterium in ice of 1×10^{-10} cm^2/s in an analytical model of an experimental diffusion process gave a good fit to both NMR and mass spectrometer data obtained for the experiment. We also showed that for ice having a thickness of 0.25 cm, a time of several thousand hours was required for equilibration of deuterium and hydrogen isotopes between the ice phase and surrounding liquid water. For ice thicknesses on the order of 2.5×10^{-3} cm, only a couple of hours is required.

A mathematical model was given for the isotope equilibration process that will allow an estimate of the required equilibration time if the thickness of ice crystals in the system is known. This can be used to help design any tracer experiments using deuterium in frozen soils.

LITERATURE CITED

Arnason, B. (1969) The exchange of hydrogen isotopes between ice and water in temperate glaciers. Earth and Planetary Science Letters, 6:423–430.

Carslaw, H.S. and J.C. Jaeger (1950) Conduction of Heat in Solids. London: Oxford University Press, p. 258–259.

Franks, F. (1972) Water, A Comprehensive Treatise. Vol. 1. New York: Plenum Press, p. 140–141.

Franks, F. (1982) Water, A Comprehensive Treatise. Vol. 7. New York: Plenum Press, p. 42–43.

Nakano, Y., A.R. Tice, J.L. Oliphant and T.F. Jenkins (1983) Transport of water in frozen soil. I. Experimental determination of soil-water diffusivity under isothermal conditions. USA Cold Regions Research and Engineering Laboratory, CRREL Report 83-22.

Oliphant, J.L., T.F. Jenkins and A.R. Tice (1982) Method for measuring enriched levels of deuterium in soil water. USA Cold Regions Research and Engineering Laboratory, Special Report 82-25.

Tice, A.R., J.L. Oliphant, Y. Nakano and T.F. Jenkins (1982) Relationship
between the ice and unfrozen water phase in frozen soil as determined
by pulsed nuclear magnetic resonance and physical desorption data.
USA Cold Regions Research and Engineering Laboratory, CRREL Report
82-15.

APPENDIX A. COMPUTER PROGRAM THAT CALCULATES C AND C_ℓ.

```
100  PRINT "INPUT H,N1,N2,D,L1,C0"
110  INPUT H,N1,N2,D,L1,C0
115  PRINT @41:H,N1,N2,D,L1,C0
120  H1=H/N1/D
130  L=L1*H1
140  K=N1/N2
150  FUZZ 10,1.0E-10
160  DIM A(150),P(150)
170  FOR I=1 TO 150
180  N=I
190  A1=PI*(N+1/2.00000001)
200  A2=PI*(N-1/2.0000001)
210  A3=(A1+A2)/2
220  R1=TAN(A1)-L*A1/(A1*A1-K*L)
230  R2=TAN(A2)-L*A2/(A2*A2-K*L)
240  R3=TAN(A3)-L*A3/(A3*A3-K*L)
250  IF R3=0 THEN 310
255  IF A3=A2 THEN 310
260  IF SGN(R2)=SGN(R3) THEN 290
270  A1=A3
280  GO TO 210
290  A2=A3
300  GO TO 210
310  A(I)=A3
315  PAGE
320  PRINT A3,R3
330  NEXT I
340  DIM X(51),C2(51)
350  FOR J=1 TO 20
360  T=(J-1)*200000
370  T1=D*T/L1/L1
380  S1=0
390  FOR I=1 TO 150
400  P(I)=A(I)^4+(L*L+L-2*K*L)*A(I)^2+K*L*L*(1+K)
405  IF A(I)^2*T1>230 THEN 420
410  S1=S1+1/P(I)*EXP(-(A(I)^2)*T1)
420  NEXT I
430  C1=C0/(1+K)+2*K*L*L*C0*S1
440  PRINT @41:T/3600,C1,1-C1
450  FOR Q=1 TO 6
460  S2=0
470  X(Q)=(Q-1)*L1/5
480  FOR I=1 TO 150
485  IF A(I)^2*T1>230 THEN 510
490  S3=EXP(-(A(I)^2)*T1)*COS(A(I)*(1-X(Q)/L1))
500  S2=S2+(A(I)^2-K*L)/(P(I)*COS(A(I)))*S3
510  NEXT I
520  C2(Q)=C0/(1+K)-2*L*C0*S2
530  PRINT @41:X(Q),C2(Q),1-C2(Q)
540  NEXT Q
550  NEXT J
```

11