

MEASUREMENT OF EXTREMELY LOW FLUID PERMEABILITIES OF ROCKS SIGNIFICANT TO STUDIES OF THE ORIGIN OF LIFE

> FINAL REPORT ON PROJECT SPONSORED BY NASA GRANT, NGR 05-020-331

SUBMITTED BY PROFESSOR SULLIVAN S. MARSDEN, JR. PRINCIPAL INVESTIGATOR

JUNE, 1971

DEPARTMENT OF PETROLEUM ENGINEERING SCHOOL OF EARTH SCIENCES

STANFORD UNIVERSITY, STANFORD, CALIFORNIA

SOCIETY OF PETROLEUM ENGINEERS OF AIME 6200 North Central Expressway Dallas, Texas 75206

THIS IS A PREPRINT --- SUBJECT TO CORRECTION

A Novel Liquid Permeameter for Measuring Very Low Permeability

By

S. S. Marsden, S. K. Sanval, and R. M. Pirnie, Members AIME, Stanford U.

© Copyright 1970 American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.

This paper was prepared for the 45th Annual Fall Meeting of the Society of Petroleum Engineers of AIME, to be held in Houston, Tex., Oct. 4-7, 1970. Permission to copy is restricted to an abstract of not more than 300 words. Illustrations may not be copied. The abstract should contain conspicuous acknowledgment of where and by whom the paper is presented. Publication elsewhere after publication in the JOURNAL OF PETROLEUM TECHNOLOGY or the SOCIETY OF PETROLEUM ENGINEERS JOURNAL is usually granted upon request to the Editor of the appropriate journal provided agreement to give proper credit is made.

Discussion of this paper is invited. Three copies of any discussion should be sent to the Society of Petroleum Engineers office. Such discussion may be presented at the above meeting and, with the paper, may be considered for publication in one of the two SPE magazines.

ABSTRACT

paper.

A liquid permeameter for very tight rocks is described. High upstream pressures are achieved by a "pump" based on the thermal expansion of liquid. Confining or overburden pressures of up to 10,000 psi may be maintained with a modified Hassler sleeve. Pressure is measured with a low displacement diaphragmtype transducer. Permeability is measured indirectly through pressure decline over a time period.

References and illustrations at end of

INTRODUCTION

Permeability is a solid/fluid property important not only in petroleum production engineering but also in many other branches of science and technology. Ground water hydrologists deal with it quite commonly and many geological problems are concerned with fluid flow through porous media and hence with permeability. We often look on it as a property easily measured, but while this is true in many cases, these are particular systems in which permeability measurement is very difficult. It is the purpose of this paper to describe an instrument designed and developed to measure liquid permeabilities of very tight Precambrian rocks. These are currently of great importance in the study of the origin of life.

DESIGN CONSIDERATIONS

From our other knowledge of these samples, it was evident that no other known permeameter would give reliable permeability values. There were a number of reasons for this. First, a liquid permeameter was necessary because gas might tend to dehydrate A NOVEL LIQUID PERMEAMETER FOR MEASURING VERY LOW PERMEABILITY

the chert or other minerals thus causing a shrinkage and an unnaturally high value of permeability. Second, the expected very low permeability would lead to very low flow rates even at high pressure differentials and thus ordinary pumps or fluid moving devices would seem to be unsuitable. Third, since casual examination of the samples revealed some fractures and no sign of a pore structure and since such rocks are known to have permeabilities strongly sensitive to external or overburden pressure, a method of varying this latter factor seemed desirable. Fourth, since other physical measurements might be made on the sample, a harmless, non-permanent method of sample mounting also seemed desirable.

To achieve these aims, a novel approach to permeability was decided upon. This involved both the use of a pump based on the thermal expansion of a liquid and also the use of pressure decline for the calculation of permeability.

COMPONENTS

The Pump

For samples of the usual dimensions used for permeability measurements (1" D. x 1" to $1\frac{1}{2}$ " L) and even with abnormally high pressure differentials of several hundred psi, liquid flow rates of only a small fraction of a ml/hr would be obtained when the permeability is one microdarcy. Since there is little need for such pumps in other kinds of work, they are not readily available. Thus it was decided to try to develop one based on a principle successfully used some years ago for a low rate, low pressure pump, namely the thermal expansion of a confined liquid. If a liquid is heated in a closed container, it will expand and then become compressed. When the system reaches a steady temperature, it also reaches a steady pressure which can, in theory, be estimated from a knowledge of certain physical properties of the liquid and the container. If a valve to the container is opened, the liquid will flow from it and the pressure will simultaneously decline. From a knowledge of both the volume of the liquid and its isothermal compressibility, we can calculate the amount of liquid "pumped" from the

container. In practice a more accurate liquid volume can be obtained through direct measurement because the volume of the container also decreases slightly during the process.

The pump used here consists of a liquid filled steel tank of the sort used to store compressed gases. This tank is completely immersed in a water thermostat having an adjustable, mercury-in-glass thermoregulator. The liquid used in both the pump and the sample was a heavy hydraulic oil. High pressure tubing, fittings and valves were used throughout the system shown in Figure 1.

The Sample Holder

A scale drawing of the high pressure Hassler sleeve constructed for this work is shown in Figure 2. А synthetic rubber tubing sleeve reinforced with steel wire was used to enclose the cylindrical rock sample. External pressure on the sleeve was achieved with a hand-operated hydraulic pump and measured with a 0-10,000 psi Bourdon-tube gage. By use of the tubing connection arrangement shown in Figure 1, this hydraulic pump could also be used to sweep air out of the upstream flow lines and to repressure the thermal pump as needed.

The Pressure Measuring System

The pressure measuring system needs to have both a small displacement volume and also be capable of automatic recording of pressure as a function of time. A diaphragmtype, Pace transducer kit (KP-15) with indicator (CD-25) and a Heath strip-chart recording potentiometer (EU -20B) fulfilled these needs. The 500 psi diaphragm was usually used in this work. The instrument was checked as needed with a deadweight tester.

DERIVATION OF A WORKING EQUATION

In order to arrive at a relationship between pressure decline, permeability and any other pertinent variables, a simplified model of the actual flow system is assumed. This consists of two parts with a valve in between. The first is a liquid reservoir made up of a tank, the flow lines and the transducer

chamber all containing an initial volume of liquid, V_i , at an initial pressure P_i . The second part is a flow resistance consisting only of a porous medium of length, L, crosssectional area, A, and permeability, k. A slightly compressible liquid of initial density, ρ_i and constant

viscosity, µ, is assumed to flow isothermally and under viscous flow conditions so that Darcy's law may be used. Because the reservoir volume will decrease slightly with pressure, the liquid is assumed to have an effective compressibility, C, which will not be the true one. (See appendix for a simple method of calculating effective compressibility of the liquid.)

When the valve between the two parts is opened and the liquid allowed to flow, the pressure in the reservoir decreases to some value, P_t , at time t when V_t is left in the reservoir. The pressure downstream of the flow resistance is always atmospheric pressure, P_a . Since P_t is decreasing with time, the flow rate through the porous medium

will also decrease with time. The volume of liquid upstream of the porous medium decreases from $\rm V_{i}$ to

 V_t , i.e., a volume $(V_t - V_i)$ flows through the porous medium over this

time period t. The instantaneous volumetric flow rate into the core at the upstream end (x = 0) is given by:

$$q \Big]_{x=0} = \frac{d}{dt} (V_t - V_i) = \frac{dV_t}{dt}$$
(1)

The definition of isothermal compressibility of a liquid is:

$$C = -\frac{1}{V} \left(\frac{dV}{dP}\right)_{T}$$
(2)

or:

$$V_{t} = V_{i} e^{C(P_{i}-P_{t})}$$
(3)

Therefore:

$$q \Big]_{x=0} = \frac{dV_t}{dt} = -CV_i e^{C(P_i - P_t)} \frac{dP_t}{dt}$$
(4)

The instantaneous volumetric flow rate, q, is also given by Darcy's law:

$$q = -\frac{kA}{\mu} \frac{dP}{dx}$$
(5)

Since the flow capacity of the porous medium is negligible compared to the size of the system, flow transients will be short lasting and there will be essentially steady state at any time. Hence the instantaneous weight rate of flow, W, will be the same at any cross-section and

$$W = q\rho g = \frac{kA}{\mu} \frac{dP}{dx} \rho g$$
 (6)

Separating variables

$$\int_{O}^{L} W \, dx = -\frac{k A g}{\mu} \int_{P_{t}}^{P_{a}} \rho dP \qquad (7)$$

or

$$WL = \frac{k A g}{\mu} \int_{P_a}^{P_a} \rho dP$$
 (8)

The isothermal compressibility of the liquid can also be written as:

$$C = \frac{1}{\rho} \left(\frac{d\rho}{dP} \right)_{T}$$
 (9)

or

$$\rho = \rho_a e^{C((P-P_a))}$$
(10)

Substituting into equation (8), we have:

$$W = \frac{kAg \rho_a}{\mu L} \int_{P_a}^{P_t} e^{C(P-P_a)} dP \qquad (11)$$
$$= \frac{kAg \rho_a}{\mu CL} \left[e^{C(P_t-P_a)} - 1 \right] \qquad (12)$$

From equations (4) and (6), we have:

$$W = -CV_{i}\rho_{t}ge^{C(P_{i}-P_{t})}\frac{dP_{t}}{dt}$$
(13)

Thus:

 $\frac{kA\rho_{a}}{\mu CL} \begin{bmatrix} e^{C(P_{t}-P_{a})} - 1 \end{bmatrix} = -CV_{i}\rho_{t}e^{C(P_{i}-P_{t})}\frac{dP_{t}}{dt}$ $= -CV_{i}\rho_{i}\frac{dP_{t}}{dt} \qquad (15)$

$$\frac{\mathrm{kA}}{\mu \,\mathrm{CL}} \frac{\rho_{\mathrm{a}}}{\rho_{\mathrm{i}}} t = -\mathrm{V}_{\mathrm{i}} \ln \left[1 - \mathrm{e}^{-\mathrm{C} \,(\mathrm{P}_{\mathrm{t}} - \mathrm{P}_{\mathrm{a}})}\right]_{\mathrm{P}_{\mathrm{i}}}$$
(16)

or

$$\frac{kA}{\mu CLV_{i}} e^{C(P_{a}-P_{i})} t = \ln \left[1 - e^{-C(P_{i}-P_{a})}\right]$$
(17)

$$-\ln\left[1 - e^{-C(P_t - P_a)}\right]$$

We can express:

$$e^{-C(P_i-P_a)} = 1-C(P_i-P_a) + \frac{C^2(P_i-P_a)^2}{2!} - \dots$$
 (18)

$$\approx 1 - C(P_i - P_a)$$
(19)

Thus

$$\ln C(P_{i}-P_{a}) -\ln C(P_{t}-P_{a}) =$$

$$\frac{kA}{\mu CV_{i}L} e^{C(P_{a}-P_{i})}t$$
(20)

or

$$\ln(P_t - P_a) = -\frac{kA}{\mu CV_i Le^{C(P_i - P_a)}} + \ln(P_i - P_a)$$
(21)

This is our basic relationship between pressure decline, permeability and other pertinent variables. It is apparent that the slope, m, of a semilogarithic plot of the pressure decline, $\ln (P_t-P_o)$ vs. t can be used to calculate k:

$$k = - \frac{m\mu CV_{i}Le^{C(P_{i}-P_{a})}}{At}$$
(22)

USE OF THE PERMEAMETER

The instrument can be used in a number of different ways and the results also plotted and interpreted in several ways.

Although a single liquid is used here both for flow and for confining or overburden pressure, it is quite apparent that different ones can be used for each purpose while keeping the interconnecting valve closed. For example, the aqueous or brine permeability of a rock sample can be determined while still using hydraulic oil for pressure around the sleeve.

The liquid reservoir can be used as an isothermal source of high pressure liquid by pumping oil into it with the hydraulic pump. This eliminates the need to recharge the pump by cooling off the thermostat and it speeds up the measurement for some cores.

Permeability can obviously be measured at different overburden pressures. With the present transducer, the upstream pressure is limited to 500 psi unless a precise counter-pressure such as that available from a dead weight tester is used on the other side of the transducer diaphragm.

In many cases the product $C\left(P_{1}-P_{a}\right)$ is small and so the term

$$e^{C(P_i - P_a)} \approx 1 \tag{23}$$

and

$$k = -\frac{m\mu CV_{i}L}{At}$$
(24)

For a set of cores of comparable permeability, it may be possible always to charge the reservoir to the same P_{t} and allow pressure decline to the same P_{t} . If the same liquid is used in all measurements, then most of the terms in equation (22) are fixed and

$$k = \frac{K}{t} \cdot \frac{L}{A}$$
(25)

where K is a constant. In this case it may be possible to determine automatically the time at which P_+ is

reached and then permeability measurement for even very tight cores will be greatly simplified.

NOMENCLATURE

- A = cross-sectional area of the porous medium
- g = gravitational constant

k = permeability

```
K = a constant in equation (25)
                                               APPENDIX
                                                    Because of the expansion of
L = length of the porous medium
                                               the reservoir when the liquid pres-
                                               sure is increased, the true iso-
m = slope of the ln (P_+-P_a) vs.
                                               thermal liquid compressibility is
    t plot
                                               not strictly applicable here. But
                                               we can obtain an effective compressi-
P = pressure
                                               bility as outlined below. From
q = volumetric rate of flow
                                               equation (13) and the general
                                               relationship between \rho, C and P,
t = time
                                               we may write:
                                                 W = -CV_i \rho_i g_{\overline{d+}}^{dP_t}
V = volume of liquid in reservoir
W = weight rate of flow
                                               or
x = position along porous medium
                                                 W = -CW_{i}\frac{dP_{t}}{dt}
Greek:
                                               where W_{i} is the weight of the liquid
\rho = density
                                               in the reservoir at P<sub>i</sub>. Separating
\mu = viscosity
                                               variables, integrating and rearranging
                                               we have:
Subscripts:
                                                 C = \frac{\int_{0}^{t} W dt}{W_{i} (P_{i} - P_{t})}
a = atmospheric
i = initial
                                               The compressibility can be measured
t = time of measurement
                                               before mounting the core by charging
                                               the reservoir to P, and then letting
ACKNOWLEDGEMENT
                                                the pressure decline to P<sub>+</sub> while col-
     The authors would like to
                                                lecting and weighing the oil pro-
express their sincere appreciation
                                               diced over the time interval.
to both NASA and The Petroleum
Research Fund of the American
Chemical Society for financial
support which made their work pos-
sible. We would also like to
express our appreciation to Dr.
K. A. Kvenvolden for his continued
```

encouragement and to the Ames Research Center (NASA) for the con-

struction of the cell.

5

(26)

(27)

(28)



FIG. 1 - Schematic diagram of instrument.



FIG. 2 - Scale drawing of high-pressure, Hassler sleeve cell.

STANFORD UNIVERSITY STANFORD. CALIFORNIA 94305 N71-28320 NASACR-119021

DEPARTMENT OF PETROLEUM ENGINEERING School of Earth Sciences

June 11, 1971

National Aeronautics and Space Administration Headquarters Contracts Division Washington, D. C. 20546

> RE: Measurement of Extremely Low Fluid Permeabilities of Rocks Significant to Studies of the Origin of Life

Gentlemen:

an search and the search and the second s

Several different things have been accomplished on this project and these are presented below in outline form as an introduction to the technical chapters of this report. However, first we must acknowledge the invaluable contributions made by the several people associated with the project.

Mr. R. M. Pirnie designed the high pressure sample holder and constructed parts of the flow system. But it was Mr. S. K. Sanyal who constructed, tested and used the final design of the instrument and also derived the working equation for calculating permeability from pressure decline. Some of the measurements as well as minor modifications of the instrument were made by Mr. G. O. Chen. Finally, we are deeply indebted to Dr. K. A. Kvenvolden of the Ames Research Center for his continuing interest and close collaboration on both the experimental results and interpretation of the measurements.

- I. A permeameter has been constructed, tested and used.
 - A. This instrument has measured the very low permeabilities of chert samples supplied by the Ames Research Center.
 - B. This instrument can be used to measure the liquid permeability of other low permeability rocks such as petroleum source rocks and cap rocks of oil and natural gas reservoirs.
 - C. It can also be used to study the effect of confining or overburden pressure on the permeability of the rocks described above.
 - D. With minor modifications it can be used for other experiments on fluid flow through porous media at high pressures.
- II. Two papers have been written and submitted for consideration for publication.
 - A. "A Novel Liquid Permeameter for Measuring Very Low Permeability", Sanyal, S.K., Pirnie, R.M., III, Chen, G.O., and Marsden, S.S., submitted to the Society of Petroleum Engineers of AIME in March, 1971. This paper has been tentatively accepted for publication in the Society of Petroleum Engineers' <u>Journal</u>. A revised manuscript is under preparation.

CASE

- II.
 - B. "Permeabilities of PreCambrian Onverwacht Cherts and Other Low-Permeability Rocks", Sanyal, S.K., Kvenvolden, K.A., and Marsden, S.S., submitted to Nature in June, 1971.

Copies of these papers are included as Parts II and III of this report.

- III. Papers describing the results of this project were on the programs of two meetings.
 - A. The Annual Fall Meeting of the Society of Petroleum Engineers of AIME at Houston, Texas, (October, 1970). This was an alternate paper but preprints were distributed with the preprint set.
 - B. West Coast Student Paper Contest of the Society of Petroleum Engineers of AIME at University of Southern California, (April, 1971). This paper was presented by Mr. S.K. Sanyal and he was runner-up in the Ph.D. category.

Very truly yours,

Marso Sullivan S. Marsden, Jr.

Principal Investigator

SSM:1g

PART I ORIENTATION by S. S. Marsden, Jr.

1. Introduction

The movement of fluids into and through porous or fractured solids is of significance in several branches of science and engineering. The laboratory measurement of this movement as well as the application of these measurements has long been of importance in such fields as petroleum production engineering, ground water hydrology and several branches of geology. Such measurements are frequently made on small rock samples and then the results used to predict the fluid behavior in the much larger masses of rock which exist in nature. While many instruments have been devised to make such measurements, none are universally applicable for both liquids and gases and for rocks having a wide range of fluid conductivities. It is the purpose of this report to describe such an instrument which measures the movement of a liquid through almost non-conductive rocks.

Different branches of technology use somewhat different terminology to describe this rock-fluid property. We shall use that existent in petroleum production engineering and refer to a porous or fractured solid's ability to conduct fluids as its "permeability". This is described quantitatively in terms of a well-known relationship called Darcy's law. While this law can be expressed in various ways for samples of different geometries, and different types of fluids, we shall simply use here the form appropriate for our system, i.e. the linear flow of an almost incompressible fluid (a liquid). For such a system, Darcy's law states that the volumetric rate of flow, q, (cc/sec) is directly proportional to the cross-sectional area of the rock sample, A, (cm²) and the pressure gradient, dP/dL (atm/cm) and inversely proportional to the viscosity, μ (centipoise):

$$q = \frac{kA}{\mu} \frac{dP}{dL}$$

If the units noted above are used for the various quantities in the equation, then the proportionality constant, k, which is also known as the permeability, is expressed in a unit known as the darcy. For most underground rocks of importance in petroleum engineering, this unit is too large and so the millidarcy (md.) is quite commonly used (1 darcy = 1000 md.). To give an idea of the order of magnitude of the usual numerical values for permeability, a majority of petroleum reservoir rocks fall within the range from about 100 to about 1000 md.

While it is self-evident that the existence of permeability requires some sort of fluid passage through the rock, we know from experience that these passages are primarily of two distinct types. In one case they are the interconnected, intergranular pores of the sort that exist in sandstones and in the other they are the fractures and sometimes vugs which exist in such rocks as limestones, dolomites and some shales. The former present a relatively homogeneous system and here small rock samples are generally representative of much larger ones. However, the latter are relatively heterogeneous and while we know that small rock samples are not generally representative of large masses of rock, we do not really know how large a sample is necessary to be representative. To complicate matters still further, permeability is a vector property and thus it . varies, often markedly, with direction of fluid flow. In addition, permeability may change with location and particularly with depth in a given formation. All of these factors point to the necessity of care being

taken in the selection of rock samples and in the interpretation of measurements.

Darcy's law is based on a number of assumptions, some of which will now be mentioned. In the form used here, viscous isothermal flow of an inert, incompressible, Newtonian liquid is assumed. While there is evidence that in some cases there is an interaction between some liquids (such as water) and some minerals (such as clays), we shall assume that this does not exist here. We shall further assume that there is no liquid movement through solid mineral particles and that there are no electrokinetic effects. Finally, it is assumed that only one fluid exists in the sample at the time of measurement.

Determination of the permeability of a given sample is usually made through the direct or indirect measurement of the quantities in the Darcy law expression. The flow rates at given pressure drops for samples of known dimensions are determined either gravimetrically or volumetrically over measured time periods. Temperature is measured so that viscosity can be accurately specified, either through a supplementary measurement of viscosity as a function of temperature or else from handbook data. Any primary or secondary method of pressure measurement which gives at least three and preferably four significant figures can be used. Quite commonly manometers, high-quality Bourdon gages, or various types of pressure transducers are used. The sample dimensions are obtained with vernier calipers or micrometers.

Several precautions must be taken prior to and during the measurements. While the ends of the sample are open for flow, the sides must be thoroughly sealed both to avoid loss of fluid and by-passing of fluid. Temperature must be maintained relatively constant because of its pronounced effect on viscosity. Flow rates must be kept low enough so as to be in the viscous

or non-turbulent range; this is usually checked by making a number of measurements of q at different dp and seeing that the ratio of the two quantities remains constant. While in theory any Newtonian fluid can be used, in practice it is best to use one close in properties to those existing in the natural environment from which the rock was taken and for which the data is to be applied. In this way any interaction between rock and fluid will be relatively constant in both cases. Other fluids and unnatural contaminants must be removed and excluded by cleansing the sample, the fluid and flow system carefully. Particular care must be taken to eliminate other immiscible fluids such as gases, especially air, which tends to become dissolved in liquids at the upstream or high pressure end of the sample and then come out of solution as bubbles as the absolute pressure decreases during fluid flow through the sample. To a considerable extent, these bubbles are immobile and they very effectively hinder the flow of liquid thus leading to low, incorrect values of permeability.

Finally, two more considerations must be mentioned. A dry gas will tend to dehydrate many hydrated minerals as it flows through a permeable rock and this will lead to significantly higher measured permeabilities than those obtained for aqueous solutions. Rocks existent underground are subjected to external or overburden pressures and when these pressures are removed either by natural processes or by the artificial one of taking core samples, it can often lead to significant increases in permeability. This has been attributed to natural fractures opening up when the external pressure is removed and in many or most cases, it is a reversible process. Thus permeability is generally dependent on the external pressure applied during measurement and in order to make laboratory measurements applicable to subsurface conditions, permeability should be measured as a function of

external pressure. Quite often this can be incorporated in the method used to contain the sides of the rock sample.

2. Statement of the Problem

Increasing attention has been paid over the past decade to the occurrence and distribution of discrete organic compounds in various kinds of Of particular interest to studies related to the origin of life rocks. are those organic compounds which have been found in Precambrian rocks. While there is convincing evidence that in many of these studies the reported compounds were not laboratory contaminants, there still exists the possibility that these compounds may have migrated into the rock matrix at some time subsequent to lithification. This would necessitate the rocks having a finite though possibly very small permeability to the aqueous solutions carrying these compounds or their precursors in solu-If the organic compounds were thus introduced into the rocks, then tion. the organic material would be younger than the rock by some undetermined amount and would have little to do with the biology existent at the time the rock was formed. In such a case our theories and interpretation of experimental evidence may have to be revised.

Most of these organic geochemical studies have been made on shales and cherts, two rock types which are generally considered to be (almost) impermeable unless they are fractured. However, if a permeability can be measured, then estimates can be made of the penetration of these compounds either by their solutions flowing through the rocks or else by molecular diffusion.

It was the purpose of this study to design, construct and use an instrument for measuring the expected very low liquid permeabilities of rocks important in the study of the origin of life.

3. Apparatus and Procedure

a. Design Considerations

Everything considered, it was quite apparent that no known permeameter would give reliable values of permeability for these samples of interest. There were a number of reasons for this. First, a liquid permeability rather than gas permeability was necessary because gas might remove water from the chert or shale and thus give an unnaturally high value of permeability. Second, the expected very low permeability would lead to very low flow rates even at high pressure differentials and thus ordinary pumps or liquid moving devices would seem to be unsuitable. Third, since casual physical examination of the samples revealed some fractures and no sign of a pore structure, and since such rocks are known to have permeabilities strongly sensitive to external pressure, a method of varying this latter factor seemed desirable. Fourth, since other physical measurements might be made on the sample, a harmless, non-permanent method of sample mounting or containment also seemed desirable.

To achieve these ends, a novel approach to permeability measurement was decided upon. This involved both the use of a pump based on the thermal expansion of a liquid and also the use of pressure differential decline for the calculation of flow rate and permeability. A description of the several parts of the permeameter follows.

b. The Pumps

A preliminary calculation of the flow rate required for rock samples of the usual size used in this sort of work (1" diameter x 1" to 2" long) and even with abnormally high pressure differentials of several hundred psi, shows that liquid flow rates of only a small fraction of a ml/hr are obtained when the permeability is one microdarcy. Since there is little need for such pumps in other work, they are not readily available. Thus

it was decided to try to develop one based on a principle successfully used some years ago for a low rate, low pressure pump, namely, the thermal expansion of a confined liquid.

While we are all familiar with the thermal expansion of gases, we are perhaps less familiar with the thermal expansion of liquids because it is of a lower order of magnitude. We are equally familiar with the compressibility of gases and while liquids are frequently described as being "incompressible", this is not really true since they are slightly compressible. Thus if a liquid is heated in a closed container, it will both expand and become compressed. Unless the walls of the container are strong enough, this thermal expansion of the liquid can easily rupture them. When the system reaches a steady temperature, it also reaches a steady pressure which can, in theory, be estimated from a knowledge of certain physical properties of the liquid and the container. If a valve to the container is then opened, the liquid will flow from it and the pressure will simultaneously decline. From a knowledge of both the isothermal compressibility of the liquid and the volume of the liquid, we can calculate the amount of liquid "pumped" from the container. In practice, a more accurate liquid volume can be obtained through direct measurement because the volume of the container also decreases slightly during this "depressuring".

A schematic drawing of the equipment developed is shown in Figure 1. A steel bomb of the sort used to store compressed gases was used as the container; its volume was about three liters. It was installed in a thermostat of which the temperature could be maintained within approximately \pm 0.1°C. The liquid used in both the pump and the sample was a heavy hydraulic oil. High pressure, stainless steel tubing and high pressure valves were used throughout the system. The valve-tubing arrangement shown above the thermostat was useful for filling the pump with liquid.

c. The Sample Holder

In the early part of the work, considerable effort was expended on trying to seal the samples in a low-melting, Woods-metal alloy but intolerable by-passing of the liquid between the metal and the rock surface was encountered possibly because of poor wetting of the hard, smooth rock surface by the metal. Casting the core in epoxy resin was also tried but was unsuccessful because of leaks due to the high pressures used at the upstream end. While relatively simple to use, both of these methods also have the disadvantage that they subject the sample to a relatively low and unknown external or confining pressure. Finally, a device quite commonly used in fluid flow work in petroleum engineering was used. This is known as a Hassler sleeve and a scale drawing is shown in Figure 2. The cylindrical core is held in a rubber sleeve with both ends of the core accessible for fluid flow. An external pressure on the sleeve somewhat greater than the upstream pressure prevents by-passing of the flowing liquid. The sample holder used here was designed for use up to an external pressure of 10,000 psi. This was achieved by use of a hand-operated hydraulic pump using the same oil that flowed through the core. By use of the tubing connection arrangement shown in Figure 1, this hydraulic pump could also be used to sweep air out of the upstream flow lines and to repressure the thermal pump as needed. The external pressure was read on a 0-10,000 psi Bourdon tube gage.

d. The Pressure Measuring System

Besides the usual requirements for accuracy, sensitivity and reproducibility, the pressure measuring device also needed both to have a small displacement volume with change of pressure and also to be capable of automatic recording of pressure as a function of time. A diaphragm-type Pace

transducer kit (KP-15) with indicator (CD-25) and a heath strip-chart recording potentiometer fulfilled this need. The 500 psi diaphragm was usually used in this work. The instrument was checked as needed with a dead-weight tester; this was also sometimes used as an opposing pressure on the low-pressure side of the diaphragm when data above an upstream pressure of 500 psi was desired.

PART II

A NOVEL LIQUID PERMEAMETER FOR MEASURING VERY LOW PERMEABILITY by S.K. Sanyal, R.M. Pirnie III, G.O. Chen, S.S. Marsden

ABSTRACT

A liquid permeameter for very tight rocks is described. High upstream pressures are achieved by a "pump" based on the thermal expansion of liquid. Confining or over-burden pressures of up to 10,000 psi may be maintained with a modified Hassler sleeve. Pressure is measured with a low displacement diaphragm-type transducer. Permeability is measured indirectly through pressure decline over a time period.

INTRODUCTION

Permeability is a solid/fluid property important not only in petroleum production engineering but also in many other branches of science and technology. Ground water hydrologists deal with it quite commonly and many geological problems are concerned with fluid flow through porous media and hence with permeability. We often look on it as a property easily measured, but while this is true in many cases, these are particular systems in which permeability measurement is very difficult. It is the purpose of this paper to describe an instrument designed and developed to measure liquid permeabilities of very tight Precambrian rocks. These are currently of great importance in the study of the origin of life.¹

DESIGN CONSIDERATIONS

From our other knowledge of these samples, it was evident that no other known permeameter would give reliable permeability values. There were a number of reasons for this. First, a liquid permeameter was necessary because gas might tend to dehydrate the chert or other minerals thus causing a shrinkage and an unnaturally high value of permeability. Also, Thomas et al.² reported air and water permeabilities of very tight rocks, with the former value being always much higher than the latter. Second, the expected very low permeability would lead to very low flow rates even at high pressure differentials and thus ordinary pumps or fluid moving devices would seem to be unsuitable. Third, since casual examination of the samples revealed some fractures and no sign of a pore structure and since such rocks are known to have permeabilities strongly sensitive to external or overburden pressures, a method of varying this latter factor seemed desirable. Fourth, since other physical measurements might be made on the sample, a harmless, non-permanent method of sample mounting also seemed desirable.

To achieve these aims, a novel approach to permeability was decided upon. This involved both the use of a pump based on the thermal expansion of a liquid and also the use of pressure decline for the calculation of permeability.

COMPONENTS

The Pump

For samples of the usual dimensions used for permeability measurements (1" D x 1" to 1 1/2" L) and even with abnormally high pressure

differentials of several hundred psi, liquid flow rates of only a small fraction of a ml/hr would be obtained when the permeability is one microdarcy. Since there is little need for such pumps in other kinds of work, they are not readily available. Thus it was decided to try to develop one based on a principle successfully used some years ago for a low rate, low pressure pump, namely the thermal expansion of a confined liquid. If a liquid is heated in a closed container, it cannot expand and hence it will become compressed. When the system reaches a steady temperature, it also reaches a steady pressure which can, in theory, be estimated from a knowledge of certain physical properties of the liquid and the container. If a valve to the container is opened, the liquid will flow from it and the pressure will simultaneously decline. From a knowledge of both the volume of the liquid and its isothermal compressibility, we can calculate the amount of liquid "pumped" from the container. In practice a more accurate liquid volume can be obtained through direct measurement because the volume of the container also decreases slightly during the process.

The pump used here consists of a liquid-filled,steel tank of the sort used to store compressed gases. Its volume together with that of the flow lines upstream of the core was found to be 2856 cc. This tank is completely immersed in a water thermostat having an adjustable, mercury-in-glass thermoregulator. The liquid used in both the pump and the sample was a hydraulic oil(Pennzoil Medium, $\rho = 0.8715$ g/cc, $\mu = 70$ cp at 75°F). High pressure tubing, fittings and valves were used throughout the system shown in Figure 1. The Sample Holder

A scale drawing of the high pressure Hassler sleeve constructed for this work is shown in Figure 2. A synthetic rubber tubing sleeve reinforced

with steel wire was used to enclose the cylindrical rock sample. External pressure on the sleeve was achieved with a hand-operated hydraulic pump and measured with a 0-10,000 psi Bourdon-tube gage. By use of the tubing connection arrangement shown in Figure 1, this hydraulic pump could also be used to sweep air out of the upstream flow lines and to repressure the thermal pump as needed.

The Pressure Measuring System

The pressure measuring system needs to have both a small displacement volume and also be capable of automatic recording of pressure as a function of time. A diaphragm-type, transducer kit (Pace KP-15) with indicator (CD-25) and a Heath strip-chart recording potentiometer (EU-20B) fulfilled these needs. The 500 psi diaphragm was usually used in this work. The instrument was calibrated and checked as needed with a dead-weight tester.

DERIVATION OF A WORKING EQUATION

In order to arrive at a relationship between pressure decline, permeability and any other pertinent variables, a simplified model of the actual flow system is assumed. This consists of two parts with a valve in between. The first is a liquid reservoir made up of a tank, the flow lines and the transducer chamber all containing an initial volume of liquid, V_i , at an initial pressure p_i . The second part is a flow resistance consisting only of a porous medium of length, L, cross-sectional area, A, and permeability, k. A slightly compressible liquid of initial density, ρ_i and viscosity, μ , is assumed to flow isothermally and under viscous flow conditions so that Darcy's law may be used. Viscosity was corrected for temperature and was assumed to be independent of pressure as explained below. (Using a pressure gradient of 400 psi/inch, the maximum gradient used in these measurements,

as well as other pertinent variables, weight rate of flow through a core (1"D x 1"L) of 10^{-2} md permeability was calculated. From weight flow rate and values of other variables, the modified Reynold's Number and the Friction Factor, as defined by Cornell and Katz⁴ for rocks, were calculated. These calculated values fell on an extrapolation of the laminar flow region of the friction factor chart⁴ to a Reynold's Number of 10^{-8} . The value of the turbulence factor, β , was obtained from an extrapolation of Figure 2.37 of ref. 4 for a porosity of 2.5%. This result supports our assumption of viscous flow.) Because the reservoir volume will increase slightly with temperature and pressure, the liquid is assumed to have an effective compressibility, c, which will not be the true one. A simple method of calculating effective compressibility of the liquid is presented in the appendix. This value for the oil used was found to be $1.30 \times 10^{-4} \text{ atm}^{-1}$, while an approximate value of the true c of the oil calculated from the values of μ and ρ at 77°F. was 0.64 x 10⁻⁴ atm^{-1.8}

When the value between the two parts is opened and the liquid allowed to flow, the pressure in the reservoir decreases to some value, P_t at time t when V_t is the volume that would be occupied by a mass of oil which had a volume V_i at a pressure P_i . The pressure downstream of the flow resistance is always atmospheric pressure, P_a . Since P_t is decreasing with time, the flow rate through the porous medium will also decrease with time. The volume of liquid upstream of the porous medium increases from V_i to V_t , i.e., a volume $(V_t - V_i)$ flows through the porous medium over this time period t. The instantaneous volumetric flow rate into the core at the upstream end (x = 0) is given by:

$$q \begin{vmatrix} x=0 \\ x=0 \end{vmatrix} = \frac{d}{dt} (V_t - V_i) = \frac{dV_t}{dt}$$
(1)

From the definition of isothermal compressibility of a liquid, we get

$$V_{t} = V_{i} e^{c(p_{i}-p_{t})}$$
(2)

Here c is assumed to be independent of p. For heavy hydrocarbons the change of c with p, as given by Tait's Equation⁵ was found to be negligible. However, this error was eliminated by taking an effective c. Therefore:

$$q \bigg|_{x=0} = \frac{dV_t}{dt} = -cV_i e^{c(p_i - p_t)} \frac{dp_t}{dt}$$
(3)

The instantaneous volumetric flow rate, q, is also given by Darcy's law:

$$q = -\frac{kA}{\mu} \frac{dp}{dx}$$
(4)

Since the flow capacity of the porous medium is negligible compared to V_i , early flow transients will be of short duration and there will be essentially steady state at any particular time. Hence the instantaneous weight rate of flow, W, will be the same at any cross-section and

$$W = q\rho g = \frac{-kA}{\mu} \frac{dp}{dx} \rho g$$
 (5)

Separating variables and integrating, we have

$$WL = \frac{k A g}{\mu} \int_{p_a}^{p_t} \rho dp$$
(6)

From the definition of isothermal compressibility of liquid, we can write

$$\rho = \rho_a e^{c(p-p_a)} \tag{7}$$

Substituting this relation into equation (6) and integrating, we have:

$$W = \frac{kAg \rho_{a}}{\mu cL} [e^{c(p_{t}-p_{a})}-1]$$
 (8)

From equations (3) and (5), we have:

$$W = -cV_{i}\rho_{t}ge^{c(p_{i}-p_{t})}\frac{dp_{t}}{dt}$$
(9)

$$= -c V_{i} \rho_{i} g \frac{dP_{t}}{dt}$$
(10)

Thus:

٠

$$\frac{kA\rho_a}{\mu cL} \left[e^{c(p_t - p_a)} - 1 \right] = - cV_i \rho_i \frac{dp_t}{dt}$$
(11)

Separating variables, integrating and simplifying:

$$\frac{kA}{\mu cLV_{i}} e^{c(p_{a}-p_{i})} t = \ln[1-e^{-c(p_{i}-p_{a})}]$$
(12)
$$-\ln[1-e^{-c(p_{t}-p_{a})}]$$

Since $c(p_i - p_a)$ is small, we can write

$$e^{-c(p_i - p_a)} \approx 1 - c(p_i - p_a)$$
 (13)

Thus

$$\frac{\ln[c(p_{i}-p_{a})]-\ln[c(p_{t}-p_{a})]}{\frac{kA}{\mu c V_{i}L}} e^{c(p_{a}-p_{i})t}$$
(14)

or

$$\ln[\frac{p_{t} - p_{a}}{p_{i} - p_{a}}] = -\frac{kA}{\mu c V_{i} L e^{c(p_{i} - p_{a})}} t$$
(15)

This is our basic relationship between pressure decline, permeability and other pertinent variables. It is apparent that the slope, m, of a semi-logarithic plot of the pressure decline, $\ln[c(p_t-p_a)]$ vs. t or $\ln[\frac{p_t-p_a}{p_1-p_a}]$ vs. t (both plots having same slope) can be used to calculate k:

$$k = -\frac{m\mu cV_{i}Le^{c(p_{i}-p_{a})}}{A}$$
(16)

(17)

In many cases the product $c(p_i - p_a)$ is small and so the term $e^{c(p_i - p_a)} \approx 1$ and

$$k = -\frac{m\mu c V_{i}L}{A}$$
(18)

EXPERIMENTAL PROCEDURE

After measurement with micrometer calipers, the cylindrical core was saturated under vacuum with oil and inserted in the Hassler sleeve. Then the entire core-holder was assembled and the confining pressure applied. With the valve just upstream of the core closed, the hydraulic oil reservoir was heated to a predetermined temperature in order to achieve a desired P_i . When thermal and pressure equilibrium were achieved, the aforementioned valve was opened quickly and pressure decline with time was continuously recorded. Data from this chart was used to prepare plots of $\ln \frac{P_t - P_a}{P_i - P_a}$ vs. t similar to those shown in Figure 3-5. Measured slopes from these were used with the other data required by Eq. (16) to calculate k.

The μ values were corrected for temperature by referring to a μ versus temperature plot for the oil, prepared by using a Fisher Electroviscometer. For this temperature range (75° to 85°F), change in μ of mineral oils is negligible for a pressure increase of 400 psi, which is the maximum p_i we have used.^{6,7} Within the 0-400 psi range, an increase in p increases μ and decreases c slightly, the actual change in the value of ' μ c' being negligible. To check for any leakage through the core-sleeve, a solid steel cylinder of the same dimensions as the cores used, was installed in sleeve, an overburden pressure of 100 atm. applied, and the oil upstream

of the cylinder raised to an equilibrium pressure of 400 psig. The valve upstream of the sleeve was opened and no pressure decline was noticed over 2 hours, indicating absence of any leak.

RESULTS AND DISCUSSION

Figure 3 gives the results for two runs on a sandstone and demonstrates the repeatability of measurements. The lower curve shows the total run and the upper plot was a replot of the pressure decline data using the pressure at 8 minutes as the p_i . These were carried down to a p_t of 4 psig which we considered to be the lower limit for the 500 psig diaphragm. For samples with this magnitude of permeability (20 md), lower pressure diaphragms (100 psig or 25 psig) should be used for more accuracy. For this measurement as well as the others reported here, the confining pressure was 100 atmospheres.

Figure 4 presents the results for a chert sample having no measureable pressure decline after the transient period, that is, essentially zero permeability. If we assume, however, that there is a pressure decline corresponding to the sensitivity of the pressure reading at the end of the experiment and use this to establish a slope, then we can say that this sample has a permeability of 1.16×10^{-3} md. This gives an estimate of the lower limit of measurement for a time period of about 3.6 hours, but longer time periods can be used to establish even lower ones. The time needed per run may be reduced by using a liquid which gives a lower value of the quantity (µc) in Eq. (15).

Figure 5 shows results for a sample of Precambrian chert having a permeability of 91.7 x 10^{-3} md. Results for other samples of this sort

are to be presented elsewhere.

The model on which the derivation is based is a simplification which evidently does not include all pertinent factors since it accounts for only the linear pressure decline on the semi-log plot and not the initial transient behavior which is always observed. This would appear to be due to the compression of oil in the tubing between the valve and the sample as well as the gradual compression of fluid within the void structure of the rock. Generally 1 to 2 hours were needed to reach the linear portion of the decline curve. An analysis of this early transient effect may shed more light on the nature of the void structure.

USE OF THE PERMEAMETER

The instrument can be used in a number of different ways and the results also plotted and calculated in serveral ways.

Although a single liquid was used here for both flow and confining pressure, different ones could be used for each purpose while keeping the interconnecting valve closed. For example, the aqueous or brine permeability of a rock sample can be determined while still using hydraulic oil for pressure around the sleeve.

The liquid reservoir can be used as an isothermal source of high pressure liquid by pumping oil into it with the hydraulic pump. This eliminates the need to recharge the pump by cooling off the thermostat and it speeds up the measurement.

Permeability can obviously be measured at different overburden pressures. With the present transducer, the upstream pressure is limited to 500 psi unless a precise counter-pressure, such as that available from a

dead weight tester, is used on the other side of the transducer diaphragm. For more accuracy, a second transducer with a 25 psi plate in series with the main one and separable from the flow lines by a valve can be used to record lower pressures.

For a set of cores of comparable permeability, it may be possible always to charge the reservoir to the same p_i and allow pressure decline to the same P_t . If the same liquid is used in all measurements, then most of the terms in equation (15) are fixed and

$$k = \frac{K}{t} \cdot \frac{L}{A}$$
(19)

where K is a constant. In this case it may be possible to determine automatically the time at which P_t is reached and then permeability measurement for even very tight cores will be greatly simplified.

REFERENCES

- Nagy, B., Nagy, L. A., Bitz, M. C., Engel, C. G. and Engel, A. E. J.: "Investigations of the Precambrian Onverwacht sedimentary rocks in South Africa", Abstracts, 4th International Meeting on Organic Geochemistry, Amsterdam, Holland (1968), 23.
- Thomas, L. K., Katz, D. L. and Tek, M. R.: "Threshold Pressure Phenomena in Porous Media", <u>Trans.</u>, AIME (1968), <u>243</u>, II-174.
- 3. Vairogs, Juris, Hearn, C. L., Dareing, D. W. and Rhoades, V. W.: "Effect of Rock Stress on Gas Production from Tight Reservoirs, SPE paper 3001, Houston, Texas (Oct. 4-7, 1970).

- 4. Cornell, D. and Katz, D. L.: "Flow of Gases through Consolidated Porous Media", Ind. Eng. Chem., (1953), 45, 2145.
- 5. Weast, R. C., Editor-in-Chief: <u>Handbook of Chemistry and Physics</u>, The Chemical Rubber Co., Cleveland, Ohio (1964), F.9.
- Perry, J. H., Editor: <u>Chemical Engineer's Handbook</u>, McGraw Hill Book.
 Co. Inc., New York (1941), 2nd Edition, 798.
- 7. Amyx, J. W., Bass, D. M. and Whiting, R. L.: <u>Petroleum Reservoir Engine-</u> ering, McGraw Hill Book Co. Inc., New York (1960), 302,312.
- Hayward, A. T. J.: "Generalizations for Isentropic and Isothermal Compressibility of Hydraulic Mineral Oils", Jour. Inst. Pet., London (1970), Vol. 56, No. 547.

NOMENCLATURE

- A = cross-sectional area of the porous medium
- c = isothermal compressibility of liquid
- D = diameter of the core
- g = gravitational constant
- k = permeability
- K = a constant in equation (19)
- L = length of the porous medium
- m = slope of the $\ln[c(p_t-p_a)]$ vs. t or $\ln[\frac{p_t-p_a}{p_i-p_a}]$ vs. t plot.
- P = pressure
- q = volumetric flow rate
- t = time
- V = volume of liquid in reservoir
- W = weight rate of flow

x = position along porous medium Greek: β = turbulence factor in Ref. 4 ρ = density μ = viscosity Subscripts: a = atmospheric i = initial t = time of measurement

ACKNOWLEDGEMENT

The authors would like to express their sincere appreciation to both NASA and The Petroleum Research Fund of the American Chemical Society for financial support which made their work possible. We would also like to express our appreciation to Dr. K. A. Kvenvolden for his continued encouragement and to the Ames Research Center (NASA) for the construction of the cell.

APPENDIX

Because of the expansion of the reservoir when the liquid pressure and temperature are increased, the true isothermal liquid compressibility is not strictly applicable here. But we can obtain an effective compressibility as outlined below. From equation (10) and the general relationship between ρ , ς and p, we may write:

$$W = -cV_{i}\rho_{i}g \frac{dP_{t}}{dt}$$
 (A-1)

or

1

$$W = -cW_{i} \frac{dP_{t}}{dt}$$
 (A-2)

where W_i is the weight of the liquid in the reservoir at p_i . Separating variables, integrating and rearranging, we have:

$$c = \frac{\int_{0}^{t} W \, dt}{W_{i}(P_{i}-P_{t})}$$
(A-3)

The compressibility can be measured before mounting the core by charging the reservoir to P_i and then letting the pressure decline to P_t while collecting and weighing the oil produced over the time interval.



FIGURE 1. SCHEMATIC DIAGRAM OF THE INSTRUMENT (Capillary Tube Shown Was Used Only in Early Tests.)



)

FIGURE 2. SCALE DRAWING OF THE HIGH PRESSURE HASSLER SLEEVE

.



(``

FIGURE 3. PRESSURE DECLINE CURVES FOR A SANDSTONE SAMPLE





)

 \sum



)

 \bigcirc

FIGURE 5. PRESSURE DECLINE CURVE FOR A CHERT SAMPLE

24E

PART III

PERMEABILITIES OF PRECAMBRIAN ONVERWACHT CHERTS AND OTHER LOW-PERMEABILITY ROCKS by S. K. Sanyal, K. A. Kvenvolden and S. S. Marsden

Permeability is the rock property that permits the passage of a fluid through the interconnecting pores of a rock. Quantitative estimates of this property are of importance in any branch of science or engineering where flow of fluids through rocks is considered. While much permeability data exist for rocks having relatively high permeabilities (exceeding one millidarcy), very little data are available for rocks such as shales, cherts, dense carbonates, and evaporites which may have permeabilities of less than one millidarcy. Permeability measurements on Precambrian cherts are of interest in attempting to decipher results of organic geochemical studies made on these ancient rocks.

The quest for geologic evidence concerning the origin and evolution of life on earth has led to detailed examinations for morphological and molecular fossils in Early Precambrian sedimentary rocks, most of which have extremely low permeabilities.^{1,2} The oldest rocks thus far considered are the Onverwacht Group of the Swaziland Sequence exposed in the Eastern Transvaal of South Africa. The age of this group is at least 3.2×10^9 years. Fossil-like microstructures as well as polymeric organic matter (commonly called kerogen) have been found in carbonaceous cherts of the Onverwacht Group,³ but the biogenic nature of the microstructures is uncertain.⁴ Also, several kinds of molecular fossils (<u>n</u>-alkanes, isoprenoid hydrocarbons, fatty acids, porphyrins, amino acids) have been reported to be present in these rocks.^{5,6,7} The significance of these microstructures and molecular fossils relative to the origin and evolution of life on earth remains in question. Recently, Nagy⁸ determined that the permeability and porosity of a single sample of Onverwacht chert were 5.7×10^{-7} millidarcy and 0.5 percent respectively. He showed that even at this extremely low permeability the possibility exists for contamination of these rocks with organic compounds dissolved in fluids flowing through these rocks for billions of years. This finding has wide implications regarding the significance of organic compounds found in small concentrations in low-permeability rocks of all geologic ages.

In January of 1968 we began the development of a novel liquid permeameter for measuring very low permeabilities in rocks. Permeabilities and porosities of four samples of chert from four different formations of the Onverwacht Group were measured. For comparison the same measurements were made on a sample of Precambrian Keewatin chert from Canada, a sample of Precambrian Bitter Springs limestone from Australia, and samples of Castile gypsum, Rustler dolomite, and Bone Spring limestone from West Texas.

Permeabilities of the samples studied here were determined by a new technique described in detail elsewhere.⁹ The sample is held in a Hassler sleeve capable of being maintained at confining pressures as high as 10,000 psi by means of a hydraulic pump. Upstream pressures are maintained by a 'thermal pump' which utilizes the thermal expansion of a liquid to create pressures as high as 1000 psi. Pressures are measured with a low-displacement, diaphragm-type transducer. Permeabilities are measured indirectly through pressure decline over a period of time.

For the permeability measurements reported here, hydraulic oil was used in both the hydraulic and thermal pumps. This choice of fluid contrasts with that chosen by Nagy⁸ who used a 2000 ppm NaCl brine. Theoretically, permeability of a rock is independent of the flowing fluid. In reality this independence is not strictly true.¹⁰ Extremely low-permeability

rocks like the ones studied here have a higher permeability to air than to water.¹¹ This difference may be due to dehydration of minerals in contact with flowing air causing an increase in permeability, or the swelling of clay minerals in contact with flowing water causing a decrease in permeability. This latter effect can be minimized by use of strong brine or a non-interacting fluid such as hydraulic oil. Permeability measurements were made at confining pressures of between 1500 and 1800 psi. An increase in confining pressure on a rock generally reduces its permeability,^{10,12,13} and this effect is particularly evident for rocks of very low permeability.¹⁴ Nagy⁸ did not specify the confining pressures he used. This limits to some extent a comparison of the results. Permeabilities were measured at various orientations to bedding because in the presence of small-scale structures (laminations, banding, fractures, solution channels, etc.), rock permeability depends markedly on the directions in which fluid flow takes place.

Porosity, ϕ , of a sample was calculated from its bulk volume, $V_B^{}$, its dry weight, $W_O^{}$, and its weight after it was saturated with oil under vacuum, $W_E^{}$, by means of the relation

$$\phi = \frac{W_{s} - W_{o}}{\rho_{o} V_{B}}$$

where ρ_{0} is the density of the oil.

Permeability and porosity values of the samples studied as well as directions of permeability measurements and confining pressures are listed in Table 1. For Onverwacht cherts, permeabilities vary from a value immeasureably small by our technique (i.e., less than 10^{-6} millidarcy) to 2.09 x 10^{-2} millidarcy, and porosities vary from 0.03 to 0.72 percent. The chert sample from the Hooggenoeg Formation had a very low permeability

which probably approaches the value obtained by Nagy⁸ of 5.7 x 10^{-7} milli-The other Onverwacht chert samples had permeabilities greater by darcy. several orders of magnitude. The Keewatin chert from Canada had a permeability of 1.1×10^{-4} millidarcy which is similar to the chert permeability listed by Davis¹⁵ of 1.9 x 10^{-4} . Permeabilities to air of two Precambrian cherts have been obtained by Smith, et al;¹⁶ Gunflint chert from Canada had air-permeabilities of 1.9 x 10^{-1} and 2.0 x 10^{-2} millidarcy and porosities of 0.44 and 0.55 percent; Bitter Springs chert had values of 2.2 x 10^{-1} and 1.7 x 10^{-1} millidarcy and 0.62 and 1.15 percent. Thomas, et al.,²² have shown that air permeabilities generally are slightly higher than liquid permeabilities in tight rocks. Therefore, Gunflint and Bitter Springs cherts appear to be about as permeable as the most permeable Onverwacht cherts. Bitter Springs limestone, with a liquid-permeability of 4.0 x 10^{-2} millidarcy and a porosity of 0.24 percent, is about as permeable and porous as samples of chert from the same formation.

Although attempts were made to measure permeabilities at various orientations to bandings or laminations, too few measurements were obtained to determine if any relationship existed between permeabilities and direction of flow within the rocks with one exception. Castile gypsum had permeabilities two to three orders of magnitude higher parallel to the laminations than perpendicular to the laminations.

Three out of four samples of Onverwacht chert had measured permeabilities much higher than the single value reported by Nagy.⁸ The relationship between measured permeabilities and true permeabilities during geologic time is not known. Cementation, compaction and metamorphism may have caused significant reduction in permeabilities during the geologic past. On the other hand, earth movements may have increased the effective,

in-situ permeabilities of these rocks by inducing fracturing which may not be evident in small laboratory samples.

It is quite likely that fluids have been able to flow through these rocks by means of both intergranular and fracture channels. Our data suggest that that flow of fluids in these rocks may have been even higher than estimated by Nagy,⁸ and consequently, many of the Onverwacht cherts may have been host-rocks rather than source-rocks for some of the organic compounds they now contain.

S. K. Sanyal

Department of Petroleum Engineering Stanford University Stanford, California 94305

K. A. Kvenvolden

Exobiology Division NASA - Ames Research Center Moffett Field, California 94035

S. S. Marsden, Jr.

Department of Petroleum Engineering Stanford University Stanford, California 94305

REFERENCES

1.	Barghoorn,	E.S.,	and	Schopf,	J.W.,	Science,	152,	758	(1966).
						Contraction of the second s			

- 2. Schopf, J.W., and Barghoorn, E.S., Science, 156, 508 (1967).
- 3. Engel, A.E.J., Nagy, B, Nagy, L.A., Engel, C.G., Kremp, G.O.W., and Drew, C.M., Science, 161, 1005 (1968).
- 4. Nagy, B., and Nagy, L.A., Nature, 223, 1226 (1969).
- 5. MacLeod, W.D., Jr., Jour. Gas Chrom., 6, 591 (1968).

- 6. Han, J., and Calvin, M., Nature, 224, 576 (1969).
- 7. Kvenvolden, K.A., and Hodgson, G.W., <u>Geochim. Cosmochim. Acta</u>, 33, 1195 (1969).
- 8. Nagy, B., Geochim. Cosmochim. Acta, 34, 525 (1970).
- 9. Sanyal, S.K., Pirnie, R.M., III, Chen, G.O., and Marsden, S.S., Jr., paper submitted to Soc. Petrol. Engr. Journal (1971).
- 10. Afinogenov, Yu. S., Sniiggims, Novosibirsk, 6, 34 (1969).
- 11. Thomas, L.K., Katz, D.L., and Tek, M.R., <u>Trans. AIME</u>, 243, II-174, (1968).
- 12. McLatchie, A.S., Hemstock, R.A., and Young, J.W., <u>Trans. AIME</u>, 213, 386 (1958).
- 13. Fatt, I., and Davis, D.H., Trans. AIME, 195, 329 (1952).
- 14. Vairogs, J., Hearn, C.L., Dareing, D.W., and Rhoades, V.W., paper presented at the 45th Annual Fall Meeting of Soc. Petrol. Engineers of AIME (1970).
- 15. Davis, S.N., Flow through Porous Media, 53, Academic Press, New York (1969).
- Smith, J.W., Schopf, J.W., and Kaplan, I.R., <u>Geochim. Cosmochim. Acta</u>, 34, 659 (1970).

				TABLE 1			
Sample	No.	Name	Age	Porosity (%)	Permeability (Millidarcy)	Direction of Permeability	Confining Pressure (psi)
Onverwacht Cherts						•	
5-6		Theespruit Formation	PreCamb.	0.72	2.09×10^{-2}	perpendicular to laminations	1500
5-10	0	Hooggenoeg Formation	PreCamb.	0.03	< 10 ⁻⁶	no specific orientation	1700
5-18	m	Kromberg Formation	PreCamb.	0.12	1.16×10^{-3}	parallel to laminations	1600
5-23	~	Swartkoppic Formation	PreCamb.	0.44	1.23×10^{-2}	50° to Laminations	1600
	} 1		1		 	1 	
20		Keewatin Chert	PreCamb.	0.10	1.1×10^{-4}	no specific orientation	1600
8-9		Bitter Springs Limestone	PreCamb.	0.24	4.05 x 10 ⁻²	no specific orientation	1400
3-2-1	(Y)	Castile Gypsum	Permian	4.80	1.3 x 10 ⁻⁴	perpendicular to laminations	1600
3-2-2	(Y)	Castile Gypsum	Permian	3.42	1.6×10^{-4}	perpendicular to laminations	1500
3-2-1	(B)	Castile Gypsum	Permian	6.43	9.17 x 10 ⁻²	parallel to laminations	1800
3-2-2	(B)	Castile Gypsum	Permian	4.60	3.10×10^{-2}	parallel to laminations	1600
3-1-1		Rustler Dolomite	Permian	1.37	4.39 x 10 ⁻²	parallel to laminations	1500
3-1-2		Rustler Dolomite	Permian	0.41	9.35×10^{-2}	parallel to laminations	1500
3-4		Bone Springs Limestone	Permian	0.44	4.9 x 10 ⁻⁴	no specific orientation	1400

-

 \bigcirc