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Summary

The diffusion of non-sorbing species in different rock materials and fissure coating materials have been studied on a laboratory scale. The non-sorbing species were iodide, Uranine and Cr-EDTA. The results show that the effective diffusivity for iodide in granites with fissure coating material is of the same magnitude or higher as the effective diffusivity for iodide in granites without fissure coating material. The results also show that it is difficult to give just one value of the diffusivity in a rock material from a certain area because of the variations in the rock material. The effective diffusivity for iodide in rock materials without fissure coating material was determined to be from $1 \cdot 10^{-14}$ m^2/s to about $7 \cdot 10^{-13}$ m^2/s.

To simulate the overpressure that exists in the bedrock at large depths, diffusion experiments with iodide in rock materials under pressure have been started. No results from these experiments can yet be presented.

Electrical resistivity measurements in salt-water-saturated rock cores which are under pressure have been performed. The resistivity is measured in the saturated core at various pressures, and in the salt solution with which the core has been saturated. The ratio between these two resistivities has a direct relation to the ratio of the effective diffusivity for a component in the rock material and the diffusivity in free water for the same component.

Results from two measurements are presented and they show that the effective diffusivity is reduced by about 60 % at 230-240 bar from the value at atmospheric pressure. More experiments must be made before any conclusions can be drawn.

Contents

1. Introduction

The present Swedish concept for a final repository for radioactive waste is to emplace the waste in deep underground repositories in crystalline rock. Radionuclides released from a repository would be transported with the moving groundwater along fissures in the rock. The fissure surfaces in old fissures, which have been in contact with moving groundwater, have a different mineral composition than the surrounding rock. This fissure coating material could be the result of weathering and alteration of the rock or precipitates and crystallization products from the groundwater.

To estimate the velocity of the moving nuclides in the fissures it is important to know the radionuclide sorption and the diffusion in micropores in both the fissure coating material and the surrounding rock. This paper describes three types of experiment on a laboratory scale to determine the diffusion of nuclides in rock materials.

- Diffusion experiments with non-sorbing species (iodide, Uranine and Cr-EDTA) in different rock materials and fissure coating materials. Experiments have been performed on a large number of rock materials from different areas of Sweden.

- Diffusion experiments with non-sorbing species in different rock materials under pressure. No experiment of this type has yet been performed. The first experiment is planned to be started in the next few weeks.

- Electrical resistivity measurements on salt water saturated rock cores which are under pressure. Two initial experiments have been performed and further measurements will be made on different rock materials.

2. Mineral composition of the rock materials

The rock materials were taken from different areas of Sweden, and at different depths in the rock matrix. The fissure coating materials were from the Stripa mine in central Sweden and from Finnsjön outside Forsmark on the east coast of Sweden. Table 1 gives the areas and depths from which the rock materials have been taken, and also a description of the materials and a notation that will be used in the presentation of the results from the diffusion experiments and the resistivity measurements.

The fissure coating materials and their description have been received from the Swedish Geological Survey (SGU) in Gothenburg (1),and that of the other rock materials from the SGU in Uppsala (2).

Area	Depth (m)	Description of the material	Notation
Finnsjön Fi 4	≈ 100	granite. quartz-granodiorite; quartz. feldspar. microcline, dark mica, hornblende	F
Stripa	≈ 340	granite, quartz-monzonite; quartz. feldspar, microcline, light and dark mica	S
Karlshamn		gneiss	KG
Vipängen		gabbro	G
Studsvik	≈ 99	migmatite, granitic origin	SV
Gideå	495-496	granite, finegrained, light grey; quartz, feldspar, light and dark mica	GA 1
Gideå	500-501	gneiss, medium-to coarsegrained, dark grey; quartz, feldspar, biotite	GA 7
Svartboberget	503-504	gneiss, fine-to medium grained; plagioclase, garnet, epidote, mica, accessoric silicate mineral	SB 1
Svartboberget	504-504.5	migmatite granite, fine-to medium grained, grey; remains of garnetholding gneiss, newly formed coarsegrained quartz-feldspar	SB 7
Svartboberget	508.7-509.2	garnetholding biotitegneiss; stripes of coarsegrained quartz-feldspar	SB 21
Fjällveden	508-509	biotite gneiss; dark stripes of quartz and biotite, light stripes of quartz and feldspar	FJ 1
Stripa	≈ 340	fissure coating material without granite	SP
Stripa	≈ 340	granite + thin layer (< 1 mm) of fissure coating material	SS 1
Stripa	≈ 340	granite + thick layer (≈ 7 mm) of fissure coating material containing quartz. chlorite. muskovite	SS 2
Finnsjön Fi 8	321.6	granite + thick layer (≈ 8 mm) of fissure coating material. calcite	Fi 81
Finnsjön Fi 8	72.0	granite + fissure coating material (≈ 4 mm) containing prehnite. chlorite and calcite	Fi 83
Finnsjön Fi 8	163.4	granite + thin layer (< 1 mm) of fissure coating material containing laumontite and zeolite minerals	Fi 85
Finnsjön Fi 4	362.1	crushed zone with fissure coating material (≈ 1 mm thick) containing calcite and laumontite	Fi 41
Finnsjön Fi 5	326	fissure coating material containing calcite and prehnite	Fi 51
Finnsjön Fi 8	294	fissure zone/crushed zone with fissure coating material (5-10 mm thick) containing calcite. prehnite and laumontite	Fi 87
Finnsjön Fi 7	321	fissure zone with fissure coating material (≈ 1 mm thick) containing calcite. prehnite and chlorite	Fi 71

Table 1. Origin of the samples.

3. Diffusion of iodide, Uranine and Cr-EDTA in rock materials

3.1 Introduction

The diffusion of iodide, Uranine and Cr-EDTA in the different rock materials and fissure coating materials described in Table 1 has been studied. Some experiments are finished some are still in progress and some more will be started. The pieces in the diffusion experiments are about 10 mm thick but have different cross sectional areas.

3.2 Porosity determination

Two different methods were used to determine the porosity of the rock pieces studied in the diffusion experiments. The first method was a "water saturation" method and this determination was made on the pieces before the diffusion experiment was started. The pieces were heated at 90° C in vacuo for three days. The dried pieces were then weighed. After that the pieces were placed above a pan of distilled water in a vacuum chamber. A pressure close to the boiling point of water (about 25 mm Hg) was maintained for several hours, and then the samples were dropped into the water. After a week the pieces were taken out from the water and weighed again, surface dry. From the difference in weight between the piece dry and the piece water-saturated the porosity was calculated.

The second method was a leaching method. The pieces were saturated with a solution of iodide, Uranine or Cr-EDTA of known concentration. The amount of component each piece contained in the saturated condition was determined by leaching out the component from the piece with a small volume of distilled water. From this information the pore volume and the porosity of the piece were determined. The porosity measurements by the second method were carried out after the diffusion experiments. The results of the porosity determination are presented together with the results of the diffusion experiments in tables 2 and 3.

3.3 Diffusion experiments

A hole, with the same dimension as the piece of rock, was made in a 10 mm thick PVC-plate. The piece of rock was fixed in the hole with silicone glue. The plate with the rock sample was then heated in a vacuum chamber and saturated with distilled water by the same method used in making the porosity measurements, the water saturation method. After saturation two chambers made of transparent PVC were fastened on to the PVC-plate, one on each side (see Fig. 1). In the experiments with Uranine and Cr-EDTA one of the chambers was filled with distilled water and the other was filled with a solution containing Uranine or Cr-EDTA. The concentrations were about 10 g/l and 8 g/l respectively. In the first experiments with iodide one chamber was filled with distilled water and the other with a solution containing 1 mol/l of sodium iodide. Later it was shown that there had been some erosion of the rock samples that had been in contact with the 1 mol/l sodium iodide solution. In all the following experiments a solution containing 0.1 mol/l sodium iodide was used instead. Also to avoid any osmotic effects the other chamber was filled with 0.1 mol sodium nitrate solution instead of destilled water, to obtain equal ionic strength on either side of the rock piece.

In an earlier investigation of the diffusion of iodide, Uranine and Cr-EDTA by the method described here (3), it was shown that there was no diffusion through the 10 mm thick PVC-plate, and that the diffusion through the silicon glue was so small as to be negligible.

Samples (10 ml) were taken from the chamber which at the outset contained of distilled water or sodium nitrate solution, and the concentration of the diffusing component was measured. The iodide concentration was measured with an ion selective electrode, the concentration of Uranine with UV-spectrophotometry and the concentration of Cr-EDTA with atomic absorption spectrometry. Each time a sample was taken out 10 ml of distilled water or sodium nitrate was added to the chamber to keep the volume in the chamber constant.

3.4 Detemination of the diffusivity

The rate of change of concentration at a point in a one-dimensional system is given by Fick´s second law

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad 1$$

D is the diffusion coefficient. In this case with diffusion in a porous material the apparent diffusion coefficient must be used to account for porosity, tortuosity and sorption effects. It can be expressed as

$$D = \frac{D_e}{\alpha} = \frac{D_p \cdot \varepsilon_p}{\varepsilon_p + K_d \cdot \rho} \qquad 2$$

where $D_e = D_p \cdot \varepsilon_p$ is the effective diffusion coefficient, D_p is the pore diffusion coefficient, ε_p is the porosity of the material, K_d is the sorption coefficient and ρ is the density of the material.

The solution of eq. 1 for the case of diffusion through a porous slab initially at zero concentration, with constant inlet concentration c_1 at $x = 0$, and outlet concentration c_2 ($c_2 \ll c_1$) at $x = \ell$ is (4)

$$\frac{c(x,t)}{c_1} = 1 - \frac{x}{\ell} - \frac{2}{\pi} \sum_{n=1}^{\infty} \sin \frac{n\pi x}{\ell} \exp \left(- \frac{D_e \cdot n^2 \cdot \pi^2 \cdot t}{\ell^2 \cdot \alpha}\right) \qquad 3$$

Eq. 3 gives the concentration distribution in the slab at different times.

The rate at which the diffusing substance emerges from a unit area of the face $x = \ell$ of the slab is given by differentiating eq. 3 and putting it into Fick´s first law.

$$N = -D_e \left.\frac{\partial c}{\partial x}\right|_{x=\ell} \qquad 4$$

By integrating eq. 4 with respect to the time t, the total amount of diffusing substance Q which had passed through the slab in time t is obtained.

$$\frac{Q}{\ell \cdot c_1} = \frac{D_e \cdot t}{\ell^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left(- \frac{D_e \cdot n^2 \cdot \pi^2 \cdot t}{\ell^2 \cdot \alpha}\right) \qquad 5$$

As $t \to \infty$ eq. 5 approaches the line

$$Q = \frac{c_1 \cdot D_e}{\ell} \cdot t - \frac{c_1 \cdot \ell \cdot \alpha}{6} \qquad 6$$

with the slope $c_1 \cdot D_e/\ell$ and an intercept on the time axis $t = \ell^2 \cdot \alpha / 6 \cdot D_e$.

If the diffusing component does not sorb on the rock material then $\alpha = \varepsilon_p$. which means that the intercept on the time axis gives the porosity of the material.

3.5 Results

Fig. 2 shows the total amount of iodide which has diffused through a piece of granite + fissure coating material from Finnsjön (Fi 83) at various times. The concentration of iodide at the high concentration side in this experiment was 1.0 mol/ℓ and the solution at the low concentration side was at the outset distilled water. After about 30 days the curve can be fitted to a straight line from which the effective diffusivity can be calculated. The intercept on the time axis gives the α-value which in this case should be the porosity of the material. For long times the experimental data no longer fits the line. No explanation could be given to this. The concentration at the low concentration side is all the time so low that it is negligible compared to the concentration at the high concentration side. In Fig. 3 the diffusion of Uranine through the same type of material from Finnsjön (Fi 83) is presented.

Fig. 4 shows the total amount of iodide which has diffused through a piece of rock material (migmatite) from Studsvik (SV) at various times. The concentration of iodide at the high concentration side was 1 mol/l and at the low concentration side it was distilled water at the outset. After 130 days sodium nitrate was added to the solution at the low concentration side to obtain equal ionic strength on either side of the rock piece. The slope of the line, fitted to the experimental data, increased by about a factor of 2 when the ionic strength on the low concentration side was raised to the same level as that on the high concentration side. This means that the diffusivity increased by the same factor.

In Fig. 5, 6 and 7 the diffusion of iodide, Uranine and Cr-EDTA through pieces of migmatite from Studsvik (SV) are presented. Each figure shows two curves. One curve is the result of an experiment where the only diffusing component is iodide, Uranine or Cr-EDTA. The second curve is from an experiment where the three components were mixed together and the diffusivity of each component was measured when the other two components were present in the same solution. The concentration of iodide at the high concentration side was 1 mol/l, of Uranine ≈ 10 g/l and of Cr-EDTA ≈ 8 g/l. The solution at the low concentration side was distilled water from the beginning. All the pieces had the same diffusion area. The figures show that the presence of Uranine and Cr-EDTA does not have any effect on the concentration increase of iodide. The concentration increase of both Uranine and Cr-EDTA, however, is influenced by the presence of the other two components. Only one experiment has been performed with simultaneous diffusion of the three components, and therefore it is difficult to draw any conclusions from the result. It should be noticed, however, that the components might influence one another.

In Fig. 8 a comparison is made between two experiments with iodide diffusion in Finnsjö granite (F). One experiment was performed with 1 mol/l sodium iodide at the high concentration side and distilled water at the low concentration side (1), and the other with 0.1 mol/l sodium iodide at the high concentration side and 0.1 mol/l sodium nitrate at the low concentration side. The figure shows the relative concentration, c_2/c_1, of iodide at different times. c_2 is the concentration at the low concentration side and c_1 is the concentration at the high concentration side, which is constant with time. The two pieces had the same diffusion area. According to Fig. 8 there is no effect on the diffusivity because of the difference in ionic strength and concentration of iodide between the high and low concentration side. This result seems to contradict the results presented in Fig. 4. A difference between the experiment presented in Fig. 4 and those presented in Fig. 8 is that in the former case the same rock piece was used with a different ionic strength at the low concentration side while in the latter case two different rock pieces were used. There may have been a difference between the pieces. The change in slope in Fig. 4 may also be due to the change in diffusivity of iodide when nitrate is added.

In table 2 the determined effective diffusivities are presented together with the porosities measured by the two methods described earlier, and the α-value determined from the intercept on the time axis (see fig. 2). The table also gives the formation factor, $\varepsilon_p \cdot \delta_D/\tau^2$, which is calculated by the relation

$$\frac{D_p \cdot \varepsilon_p}{D_v} = \frac{\varepsilon_p \cdot \delta_D}{\tau^2} \qquad 7$$

where $D_p \cdot \varepsilon_p$ is the effective diffusivity (m^2/s), D_v is the diffusivity in free water (m^2/s), ε_p is the porosity, δ_D is the constrictivity and τ is the tortuosity. The diffusivity in free water, D_v, for iodide is $1.6 \cdot 10^{-9}$ m^2/s at 25° C (5) and for Uranine and Cr-EDTA $4.5 \cdot 10^{-10}$ m^2/s and $4.2 \cdot 10^{-10}$ m^2/s respectively (3).

All the effective diffusivities for iodide in table 2 are determined from experiments where the concentration of iodide at the high concentration side was 1 mol/l and the low concentration side contained distilled water.

Porosity determinations by the water saturation method (method 1) have not been made on all the pieces, shown by a line in table 2. Porosity determinations by the leaching method (method 2) have not yet been performed for most of the pieces, shown by empty spaces in the column method 2 in table 2.

Iodide, Uranine and Cr-EDTA are considered to be non-sorbing species, and in that case the α-value is equal to the porosity ε_p. The α-could then be compared with the porosity determinations made by meth. 1 and 2.

In the iodide diffusion experiments with gabbro (G) the concentration at the low concentration side was lower than the detection limit up to about 250 days and then it increased very slowly. It is hard to say if the concentration increase is because of diffusion through the rock piece or diffusion through the silicon glue. The diffusivities of Uranine and Cr-EDTA in gabbro (G) have been estimated by using the time the experiments have been running and the lowest concentration that could be measured by the analysis method. This is because the concentrations are still lower than the detection limits after about 190 days (Uranine) and 130 days (Cr-EDTA).

Table 3 is of the same type as table 2. The difference is that the iodide diffusion experiments presented in table 3 were performed with 0.1 mol/l sodium iodide at the high concentration side and 0.1 mol/l sodium nitrate at the low concentration side. The results presented in table 3, except the porosity determinations by method 1, are preliminary, because the experimental time is not enough to do a definite determination of the diffusivities.

Notation	Porosity		Effective diffusivity (m^2/s)			$\alpha=\varepsilon_p+K_d\cdot\rho$	$\frac{\varepsilon_p\cdot\delta_d}{\tau^2}$
	Method 1	Method 2	Iodide	Uranine	Cr-EDTA		
F1)	$1.8\cdot10^{-3}$ 2) $-2.1\cdot10^{-3}$	$1.3\cdot10^{-3}$ $1.1\cdot10^{-3}$ $0.6\cdot10^{-3}$ -	$8.4\cdot10^{-14}$ $7.4\cdot10^{-14}$	$2.3\cdot10^{-15}$	$6.9\cdot10^{-15}$	$5.9\cdot10^{-3}$ $4.0\cdot10^{-3}$ $0.2\cdot10^{-3}$	$4.9\cdot10^{-5}$ $5.1\cdot10^{-5}$ $0.5\cdot10^{-5}$ $1.6\cdot10^{-5}$
S1)	$3.0\cdot10^{-3}$ 2) $-3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$ $3.0\cdot10^{-3}$	$1.3\cdot10^{-13}$ $1.2\cdot10^{-13}$			$12.3\cdot10^{-3}$ $2.4\cdot10^{-3}$	$7.6\cdot10^{-5}$ $8.7\cdot10^{-5}$
KG1)	- -	$3.0\cdot10^{-3}$ $2.7\cdot10^{-3}$	$1.4\cdot10^{-13}$ $5.0\cdot10^{-14}$			$7.4\cdot10^{-3}$ $4.8\cdot10^{-3}$	$7.6\cdot10^{-5}$ $3.5\cdot10^{-5}$
G	$2.9\cdot10^{-3}$ 2) $-3.4\cdot10^{-3}$		$3.7\cdot10^{-16}$ $9.2\cdot10^{-16}$	$<4.0\cdot10^{-16}$ $<2.8\cdot10^{-16}$	$<7.5\cdot10^{-16}$ $<8.2\cdot10^{-16}$	$0.3\cdot10^{-3}$ $1.3\cdot10^{-3}$	$0.02\cdot10^{-5}$ $0.06\cdot10^{-5}$ $<0.09\cdot10^{-5}$ $<0.06\cdot10^{-5}$ $<0.18\cdot10^{-5}$ $<0.19\cdot10^{-5}$
SP	- -	$4.4\cdot10^{-3}$ $3.7\cdot10^{-3}$	$2.2\cdot10^{-15}$ $1.4\cdot10^{-14}$			$2.1\cdot10^{-3}$ $1.4\cdot10^{-3}$	$0.14\cdot10^{-5}$ $0.86\cdot10^{-5}$
SS1	-		$1.2\cdot10^{-13}$			$12.3\cdot10^{-3}$	$7.5\cdot10^{-5}$
SS2	- -	$2.7\cdot10^{-3}$	$2.1\cdot10^{-13}$	$7.6\cdot10^{-14}$		$64.2\cdot10^{-3}$ $16.7\cdot10^{-3}$	$13.1\cdot10^{-5}$ $16.9\cdot10^{-5}$
SV	$1.8\cdot10^{-3}$		$1.2\cdot10^{-13}$ 3)			$3.0\cdot10^{-3}$	$7.6\cdot10^{-5}$
			$2.0\cdot10^{-13}$				$13.0\cdot10^{-5}$
	$2.0\cdot10^{-3}$			$2.3\cdot10^{-14}$		$2.2\cdot10^{-3}$	$5.2\cdot10^{-5}$
	$1.9\cdot10^{-3}$				$9.5\cdot10^{-15}$	$0.32\cdot10^{-3}$	$2.3\cdot10^{-5}$
						$3.3\cdot10^{-3}$ 4)	$7.6\cdot10^{-5}$
	$1.8\cdot10^{-3}$		$1.2\cdot10^{-13}$	$3.4\cdot10^{-15}$	$4.9\cdot10^{-15}$	$0.04\cdot10^{-3}$	$0.75\cdot10^{-5}$
						$0.09\cdot10^{-3}$	$1.2\cdot10^{-5}$
Fi 81	$10.4\cdot10^{-3}$ $16.4\cdot10^{-3}$		$9.2\cdot10^{-14}$	$1.2\cdot10^{-14}$		$12.2\cdot10^{-3}$ $1.0\cdot10^{-3}$	$5.8\cdot10^{-5}$ $2.7\cdot10^{-5}$
Fi 83	$19.0\cdot10^{-3}$ $18.0\cdot10^{-3}$		$2.5\cdot10^{-12}$	$6.2\cdot10^{-14}$		$275\cdot10^{-3}$ $25.0\cdot10^{-3}$	$158\cdot10^{-5}$ $13.8\cdot10^{-5}$
Fi 85	$10.5\cdot10^{-3}$ $8.8\cdot10^{-3}$		$2.4\cdot10^{-11}$	$2.8\cdot10^{-14}$		$269\cdot10^{-3}$ $4.5\cdot10^{-3}$	$1500\cdot10^{-5}$ $6.2\cdot10^{-5}$
Fi 41	- - $89.6\cdot10^{-3}$ $86.6\cdot10^{-3}$	- -	$6.7\cdot10^{-11}$ $2.2\cdot10^{-11}$	$1.5\cdot10^{-11}$ $4.0\cdot10^{-11}$		$684\cdot10^{-3}$ $240\cdot10^{-3}$ $534\cdot10^{-3}$ $82.7\cdot10^{-3}$	$4188\cdot10^{-5}$ $3333\cdot10^{-5}$ $1356\cdot10^{-5}$ $8889\cdot10^{-5}$

1) These results have been presented earlier by Skagius, Neretnieks (3).

2) The porosity determinations by method 1 have not been made on the same rock pieces as the diffusivity measurements but on pieces from the same rock material.

3) The first value; distilled water at the low concentration side. The second value, 1 mol/l sodium nitrate at the low concentration side.

4) Simultaneous diffusion of iodide, Uranine and Cr-EDTA. The first value iodide, the second Uranine and the third Cr-EDTA.

Table 2: Results of the porosity and diffusivity determinations

Notation	Porosity		Effective diffusivity (m^2/s)			$\alpha = \varepsilon_p + K_d \cdot \rho$	$\frac{\varepsilon_p \cdot \delta_d}{\tau^2}$
	Method 1	Method 2	Iodide	Uranine	Cr-EDTA		
F	$1.9 \cdot 10^{-3}$		$7.0 \cdot 10^{-14}$			$1.8 \cdot 10^{-3}$	$4.4 \cdot 10^{-5}$
	$1.8 \cdot 10^{-3}$		$4.1 \cdot 10^{-14}$			$1.9 \cdot 10^{-3}$	$2.6 \cdot 10^{-5}$
	$2.0 \cdot 10^{-3}$			$5.8 \cdot 10^{-15}$		$0.34 \cdot 10^{-3}$	$1.3 \cdot 10^{-5}$
	$2.0 \cdot 10^{-3}$				$8.2 \cdot 10^{-15}$	$1.2 \cdot 10^{-3}$	$1.9 \cdot 10^{-5}$
GA1	$1.4 \cdot 10^{-3}$		$1.0 \cdot 10^{-13}$			$0.38 \cdot 10^{-3}$	$6.5 \cdot 10^{-5}$
	$1.4 \cdot 10^{-3}$		$9.3 \cdot 10^{-14}$			$2.0 \cdot 10^{-3}$	$5.8 \cdot 10^{-5}$
	$1.4 \cdot 10^{-3}$			$1.3 \cdot 10^{-14}$		$0.91 \cdot 10^{-3}$	$2.9 \cdot 10^{-5}$
	$1.7 \cdot 10^{-3}$			$1.3 \cdot 10^{-14}$		$0.87 \cdot 10^{-3}$	$2.8 \cdot 10^{-5}$
	$1.7 \cdot 10^{-3}$				$1.7 \cdot 10^{-14}$	$0.78 \cdot 10^{-3}$	$4.1 \cdot 10^{-5}$
	$1.6 \cdot 10^{-3}$				$2.1 \cdot 10^{-14}$	$0.22 \cdot 10^{-3}$	$5.0 \cdot 10^{-5}$
GA7	$0.58 \cdot 10^{-3}$		$1.2 \cdot 10^{-14}$			$1.6 \cdot 10^{-3}$	$0.78 \cdot 10^{-5}$
	$0.56 \cdot 10^{-3}$		$1.8 \cdot 10^{-14}$			$0.76 \cdot 10^{-3}$	$1.1 \cdot 10^{-5}$
	$0.70 \cdot 10^{-3}$			$1.6 \cdot 10^{-15}$		$0.19 \cdot 10^{-3}$	$0.35 \cdot 10^{-5}$
	$1.0 \cdot 10^{-3}$			$3.2 \cdot 10^{-15}$		$0.43 \cdot 10^{-3}$	$0.71 \cdot 10^{-5}$
	$1.3 \cdot 10^{-3}$				$<5.6 \cdot 10^{-16}$		$<0.13 \cdot 10^{-5}$
	$0.70 \cdot 10^{-3}$				$<6.6 \cdot 10^{-16}$		$<0.16 \cdot 10^{-5}$
SB 1	$0.67 \cdot 10^{-3}$		$1.8 \cdot 10^{-14}$			$0.32 \cdot 10^{-3}$	$1.1 \cdot 10^{-5}$
	$0.68 \cdot 10^{-3}$		$3.4 \cdot 10^{-14}$			$0.33 \cdot 10^{-3}$	$2.2 \cdot 10^{-5}$
	$0.70 \cdot 10^{-3}$			$8.7 \cdot 10^{-15}$		$0.48 \cdot 10^{-3}$	$1.9 \cdot 10^{-5}$
	$0.76 \cdot 10^{-3}$			$8.9 \cdot 10^{-15}$		$0.43 \cdot 10^{-3}$	$2.0 \cdot 10^{-5}$
	$0.55 \cdot 10^{-3}$				$<7.0 \cdot 10^{-16}$		$<0.17 \cdot 10^{-5}$
	$0.76 \cdot 10^{-3}$				$<7.2 \cdot 10^{-16}$		$<0.17 \cdot 10^{-5}$
FJ 1	$2.4 \cdot 10^{-3}$		$6.8 \cdot 10^{-14}$			$2.6 \cdot 10^{-3}$	$4.2 \cdot 10^{-5}$
	$2.6 \cdot 10^{-3}$		$9.1 \cdot 10^{-14}$			$5.7 \cdot 10^{-3}$	$5.7 \cdot 10^{-5}$
	$2.2 \cdot 10^{-3}$			$5.2 \cdot 10^{-15}$		$0.28 \cdot 10^{-3}$	$1.2 \cdot 10^{-5}$
	$2.2 \cdot 10^{-3}$			$5.3 \cdot 10^{-15}$		$0.28 \cdot 10^{-3}$	$1.2 \cdot 10^{-5}$
	$2.6 \cdot 10^{-3}$				$6.8 \cdot 10^{-15}$	$0.69 \cdot 10^{-3}$	$1.6 \cdot 10^{-5}$
	$2.6 \cdot 10^{-3}$				$5.5 \cdot 10^{-15}$	$0.51 \cdot 10^{-3}$	$1.3 \cdot 10^{-5}$
Fi 51	$15.3 \cdot 10^{-3}$		$1.3 \cdot 10^{-12}$			$17.1 \cdot 10^{-3}$	$78.8 \cdot 10^{-5}$
	$23.2 \cdot 10^{-3}$			$1.7 \cdot 10^{-13}$		$4.9 \cdot 10^{-3}$	$38.2 \cdot 10^{-5}$
	$33.6 \cdot 10^{-3}$				$4.2 \cdot 10^{-13}$	$23.1 \cdot 10^{-3}$	$99.5 \cdot 10^{-5}$
Fi 87	$9.1 \cdot 10^{-3}$		$<3.0 \cdot 10^{-14}$				$<1.9 \cdot 10^{-5}$
	$12.3 \cdot 10^{-3}$				$<3.1 \cdot 10^{-15}$		$<0.74 \cdot 10^{-5}$
	$10.6 \cdot 10^{-3}$						
Fi 71	$13.6 \cdot 10^{-3}$		$<1.6 \cdot 10^{-14}$				$<0.82 \cdot 10^{-5}$
	$17.2 \cdot 10^{-3}$			$1.6 \cdot 10^{-12}$		$44.3 \cdot 10^{-3}$	$351.1 \cdot 10^{-5}$
	$11.6 \cdot 10^{-3}$				$<1.7 \cdot 10^{-15}$		$<0.41 \cdot 10^{-5}$
SB 7	$1.9 \cdot 10^{-3}$		$7.0 \cdot 10^{-13}$			$19.9 \cdot 10^{-3}$	$44.1 \cdot 10^{-5}$
	$2.1 \cdot 10^{-3}$			$3.4 \cdot 10^{-14}$		$0.20 \cdot 10^{-3}$	$7.6 \cdot 10^{-5}$
	$2.8 \cdot 10^{-3}$				$<5.2 \cdot 10^{-15}$		$<1.2 \cdot 10^{-5}$
	$3.1 \cdot 10^{-3}$		$2.9 \cdot 10^{-13}$			$2.4 \cdot 10^{-3}$	$18.1 \cdot 10^{-5}$
	$2.8 \cdot 10^{-3}$						
	$2.1 \cdot 10^{-3}$						
SB 21	$2.2 \cdot 10^{-3}$						
	$2.6 \cdot 10^{-3}$						
	$2.7 \cdot 10^{-3}$						
	$2.8 \cdot 10^{-3}$						
	$2.5 \cdot 10^{-3}$						
	$2.1 \cdot 10^{-3}$						

Table 3: Preliminary results from porosity and diffusivity determinations

In Fig. 9 the determined effective diffusivities have been plotted against the porosity of the pieces, measured by the water saturation method (method 1), in a log-log diagram. Most of the pieces have a porosity of around 10^{-3} and the diffusivities vary by about one order of magnitude at this porosity value. The diffusivities for iodide are higher than for Uranine and Cr-EDTA. This is not surprising because the diffusivity for iodide in free water is higher than for Uranine and Cr-EDTA.

Fig. 10 shows a log-log diagram where the α-values have been plotted against the porosity determined by the water saturation method (method 1). For non-sorbing species the α-value should be equal to the porosity, and this case is shown by a straight line in Fig. 10. Most of the data for iodide lies beneath the line which means that the α-value is larger than the porosity. One explanation could be that the iodide sorbs on the rock material, which would give a higher α-value. Another explanation could be that the porosity as measured by the water saturation method is falsely low owing to the piece being incomletely saturated. Almost all of the data for Uranine and Cr-EDTA lies above the line in Fig. 10. This eliminates sorbing on the rock material even if the porosity values from the water saturation method are too low. Maybe not all the pore volume in the rock pieces is available for Uranine and Cr-EDTA. These results will be discussed further when the porosities of the pieces have been measured by the leaching method (method 2).

4. Diffusion experiments in different rock materials under pressure

4.1 Introduction

At great depths in the ground the rock is exposed to rather high pressures caused by the large overburden of rock. When drillcores are taken up from the ground this overburden no longer exists. As a result of this there might be an increase in the porosity of the rock samples. The effective diffusivity measured in rock samples under atmospheric pressure in the laboratory would then be higher than the effective diffusivity in the rock "in situ".

To simulate the over pressure that exists in the bedrock at large depths, diffusion experiments in rock materials under pressure have been started. The same rock materials are used as in the diffusion measurements made under atmospheric pressure and the results will be compared with one other.

4.2 Apparatus

The apparatus is shown in Fig. 11. It consists of a pressure cell, in which the rock piece is placed, a pump to raise the pressure in the cell, a pressure gauge and some valves. It also consists of two circulation systems. One will circulate a solution containing the diffusing component (high concentration side) which will be in contact with one side of the rock piece, and the other a solution that at the outset is free from the diffusing component (low concentration side), and is in contact with the other side of the rock.

Fig. 12 shows the arrangement within the pressure cell. On each side of the rock piece (ø 42 mm, ≈ 10 mm thick) a plate of stainless steel with circular channels is placed. The channels in the plates are connected with tubes, two to each plate, which lead out from the pressure cell to the two circulation systems. The solution in each circulation system flows through a tube into the centre of the plate, then circulate in the channels which are in contact with the rock piece and then out to a storage bottle via the tube connected to the periphery of the plate.

The pressure in the pressure cell is raised by filling the cell with hydraulic oil. To isolate the rock piece from the oil, the rock piece and the two plates are surrounded by a layer of polyurethane. The polyurethane is elastic and can therefore transmit the pressure from the oil to the rock piece.

During the diffusion experiment the pressure cell is placed in a water bath at a temperature of 20° C, and the pressure in the cell is up to 400 bars.

4.3 Planned experiments

Six pressure cells with equipment are available, so that six diffusion experiments can be performed simultaneously. Rock materials are taken from the same drillcores as the rock materials used in the diffusion experiments under atmospheric pressure.

5. Electrical resistivity measurements in salt-water-saturated rock cores which are under pressure

5.1 Theory

Direct measurements of diffusion in low porosity materials are very time consuming. It is therefore of interest to find a method which can reduce the experimental time. There are some indications that electrical conductivity and molecular diffusion may depend in the same way on the formation factor $\varepsilon_p \cdot \delta_D / \tau^2$ (6,3). This means that

$$\frac{D_p \cdot \varepsilon_p}{D_v} = \frac{\varepsilon_p \cdot \delta_D}{\tau^2} = \frac{R_o}{R_s} \qquad 8$$

where R_s is the resistivity of the salt-water-saturated rock sample and R_o is that of the salt water.

The concentration of the salt water solution must not be too low because then the pore surface conductivity in the rock sample might influence the results.

Electrical resistivity measurements in salt-water-saturated rock cores under atmospheric pressure have been made in an earlier investigation (3). For the same reason as the diffusion measurements under pressure were performed, it is interesting to find out if the resistivity in salt-water-saturated rock cores changes with pressure. A change in the resistivity will lead to a change of the formation factor and also to a change of the effective diffusivity according to eq. 8.

5.2 Method

The apparatus used in these experiments (see Fig. 13) is similar to the apparatus that is used in the diffusion experiments under pressure. The same type of pressure cell with a hydraulic pump, valves and pressure gauge is used. Two electrical cables are drawn from inside the pressure cell out to a conductivity meter (type Wheatstone bridge) with which the resistance is measured.

Rock samples were saturated with NaCl solution by the same method used for saturating rock samples with water for the porosity determination (see 3.2). The rock samples were cores (ø 42 mm, ℓ = 30 mm) and the concentration of the NaCl solution was 1 mol/l. The length of the cores and the concentration of the NaCl solution was chosen on the basis of earlier experiments (3).

On either side of the saturated rock core a stainless steel plate is placed (Fig. 14). The plates act as electrodes, and they can also, in small channels, take up the pore solution which eventually would be pressed out from the core during the experiment. Between the core and the electrodes a piece of porous foam rubber, saturated with NaCl solution, is placed. This is to ensure good electrical contact between the rock core and the electrodes. The joints between the rock core and the electrodes are covered with a narrow layer of Araldit, which is a hard epoxy-glue. The whole package with the rock core and the electrodes is then covered with polyurethane. Before this the rock core has to be surface dry. The narrow layer of Araldit is to prevent the polyurethane being pressed in between the rock core and the electrodes during the expriment.

The rock core with electrodes is then placed in the pressure cell and the electrodes are connected to the electrical cables. The pressure in the cell is raised by pumping in oil. At various pressures the resistance in the saturated rock core is measured by the conductivity meter at a frequence of 50 Hz.

5.3 Results

At the moment results from two experiments can be given. These two experiments were made on granite rock cores from Finnsjön (F). The pressure was raised in steps up to 230 and 240 bars respectively, and the resistance was measured at each level. From the resistance the resistivity can be calculated. The formation factor is then determined by eq. 8. The resistance was also measured as the pressure was lowered from 230 and 240 bars respectively down to atmospheric pressure.

In Fig. 15 the formation factor for the two rock cores at different pressures is shown. The formation factor decreases with increasing pressure. At a pressure of 230 to 240 bars the formation factor has decreased by about 60 % from the value at atmospheric pressure. According to eq. 8 this means that the diffusivity in the rock core is reduced by about 60 % at a pressure of 230-240 bars.A lowering of the pressure from 230-240 bars gives an increase in the formation factor again, however, not to the same values.

In an earlier investigation where the resistivity in saturated rock cores at atmospheric pressure was measured, the formation factor for Finnsjö granite was found to be from $8 \cdot 10^{-5}$ to $13 \cdot 10^{-5}$ (3). The two values of the formation factor at atmospheric pressure presented here are of the same magnitude.

6. Discussion and conclusions

A comparison of the diffusivity of iodide in Stripa granite (S) with the diffusivity of iodide in Stripa granite + fissure coating material (SS1, SS2) shows that the diffusivities are of the same order of magnitude. The diffusivity in fissure coating material from Stripa without any granite (SP) is, however, lower. No analysis of the mineral composition in this fissure coating material has been made. The diffusivity in pieces with fissure coating material from Finnsjõn is of the same magnitude or higher, in some cases much higher, than the diffusivity in pure Finnsjõ granite. There are two exceptions, Fi 87 and Fi 71. Still after 70-80 days the concentration at the low concentration side in the diffusion experiments with iodide in Fi 87 and Fi 71 is lower than the detection limit for the iodide electrode, which is 10^{-6} mol/l. The iodide diffusion through Finnsjõ granite (F) gave detectable concentrations after 10-20 days. The diffusion area of the Finnsjõ granite pieces is twice the diffusion area of Fi 87 and Fi 71 but that fact cannot explain the time difference required to reach detectable concentrations.

For the pieces from Finnsjõn with different fissure coating materials the porosities are higher than the porosity in pure Finnsjõ granite. Some of the pieces with fissure coating material are taken from fracture zones and crushed zones and so it is not surprising that the porosity is rather high. The other pieces with fissure coating materials are from locations in contact or near contact with a fissure. There are indications that the porosity is higher near a fissure and then decreases with distance from the fissure. The results indicate that diffusion can transport species from the moving water in fissures through the fissure coating material and into the rock matrix, and that the diffusion is higher in the rock near the fissure because of the higher porosity.

The rock materials from Gideå were fine grained granite (GÅ 1) and medium-to coarse grained gneiss (GÅ 7). The determined diffusivity in the granite is markedly higher than in the gneiss for all three diffusing components. Also the porosity of the granite, determined by the water saturation method, is higher than the porosity of the gneiss. The granite and the gneiss are taken from the same drillcore with a difference in depth of about 5 meters. This shows that it is difficult to give just one value of the diffusivity in a rock material from a certain area because of the variations in the rock material.

A comparison of the diffusivities in the rock materials from Svartboberget (SB 1 and SB 7) leads to the same conclusions. The diffusivity and the porosity of the granite (SB 7) are higher than that of the gneiss (SB 1).

The diffusivities and the porosities of the rock material from Fjällveden (FJ 1) are comparable with the diffusivities and porosities of the Finnsjö granite (F).

The formation factors presented in Table 2 and 3 should, according to eq. 7, only be dependent on the properties of the rock material and not on the diffusing component. The experiments with iodide diffusion give, however, in almost all cases a higher value for the formation factor than the experiments with Uranine and Cr-EDTA. No valid explanation could be given for this, as yet.

Too few experiments with resistivity measurements in saturated rock cores which are under pressure have been performed to draw any conclusions from the results. The formation factor at atmospheric pressure should be equal to the formation factor from the diffusion experiments for the same rock material. The two resistivity measurements made so far give, however, a larger value for the formation factor at atmospheric pressure than the iodide diffusion experiments made in the same type of granite from Finnsjön. The resistivity measurements give about 3 times higher values and this difference is of the same magnitude as earlier measurements have given (3).

KS/Ml
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Notation

c	concentration in fluid	mol/l, mg/l
c_1	concentration at the high concentration side	mol/l, mg/l
c_2	concentration at the low concentration side	mol/l, mg/l
D	apparent diffusion coefficient	m^2/s
D_e	effective diffusion coefficient	m^2/s
D_p	pore diffusion coefficient	m^2/s
D_v	diffusion coefficient in free water	m^2/s
K_d	sorption coefficient	m^3/kg
ℓ	thickness or length of a rock piece	m
N	flowrate of diffusing component	mol/m^2,s, mg/m^2,s
Q	total amount of diffusing component which had passed through the piece at time t	mol/m^2, mg/m^2
R_o	electrical resistivity in salt water	Ω m
R_s	electrical resistivity in salt water saturated rock sample	Ω m
t	time	seconds, hours, days
x	length coordinate	
α	rock capacity factor	
δ_d	constrictivity	
ε_p	porosity of the rock material	
ρ	density of the rock material	kg/m^3
τ	tortuosity	
$\frac{\varepsilon_p \cdot \delta_D}{\tau^2}$	formation factor	

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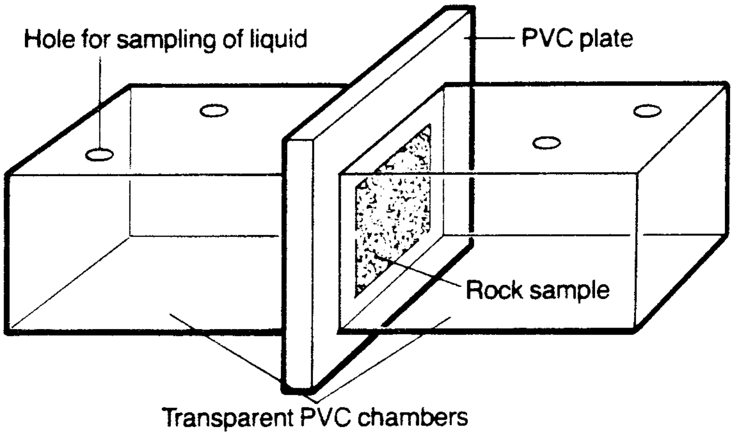

Fig 1: The diffusion cell used in the experiments with iodide, Cr-EDTA and Uranine

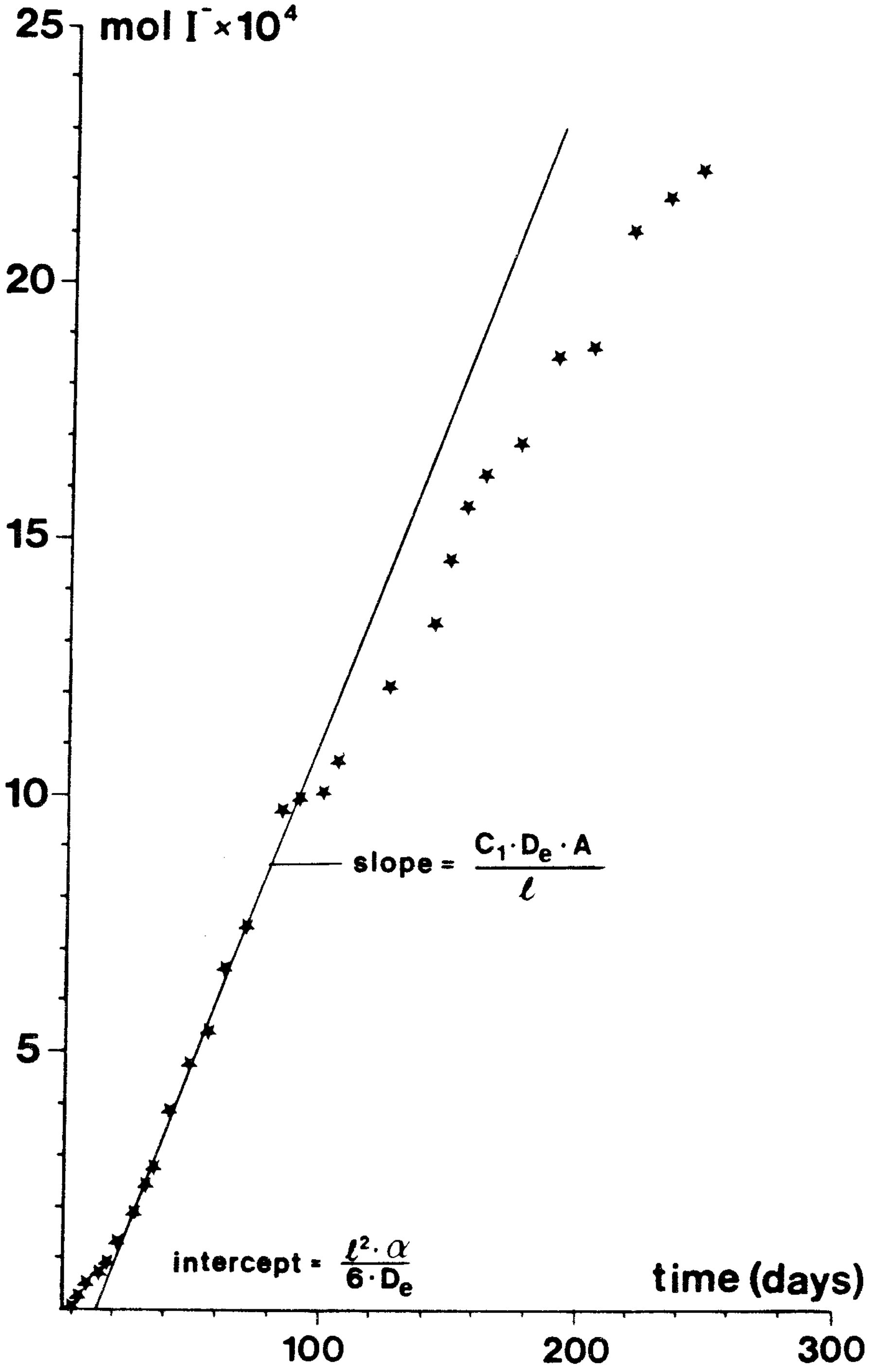

Fig 2: The diffusion of iodide through a piece of granite+fissure coating material (Fi 83)

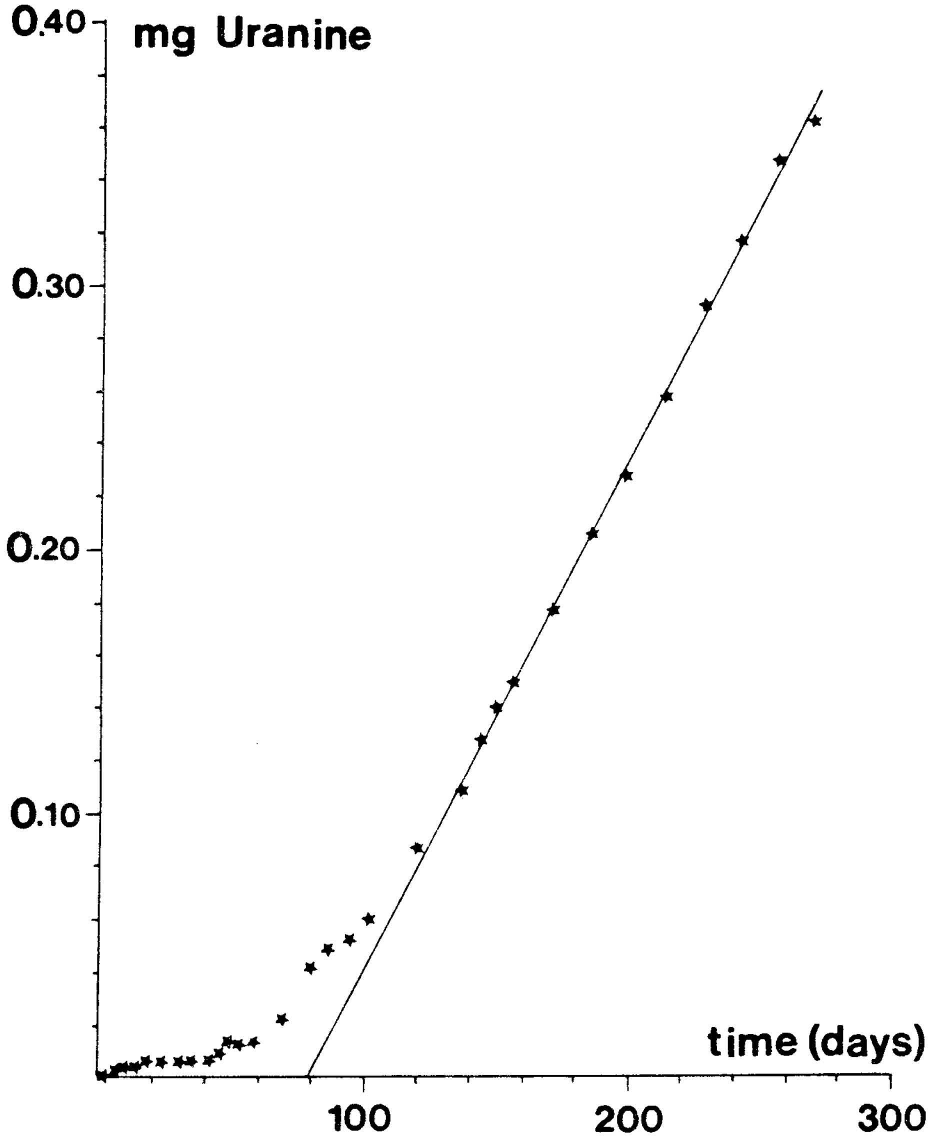

Fig 3: The diffusion of Uranine through a piece of granite+fissure coating material (Fi 83)

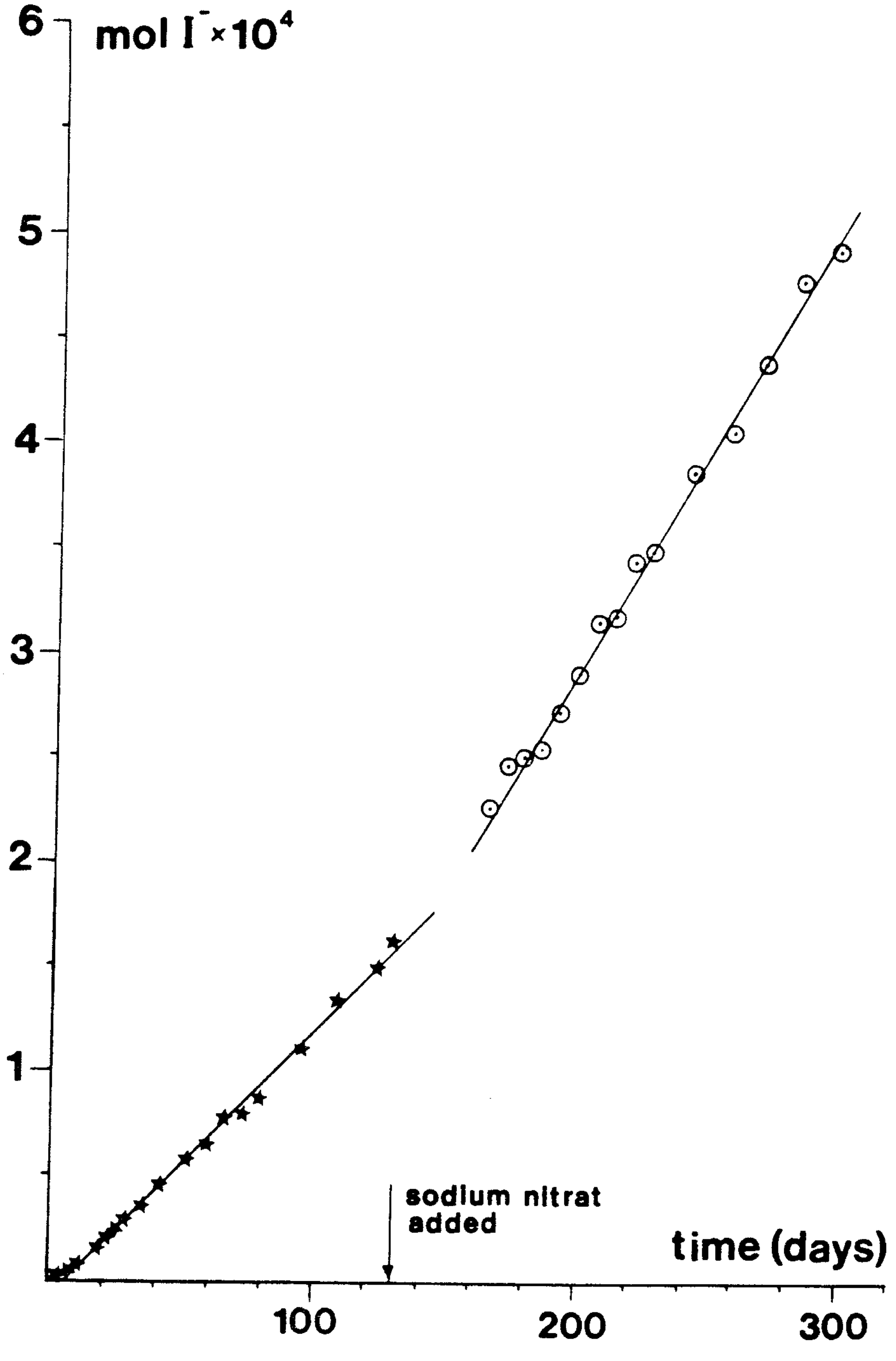

Fig 4: The diffusion of iodide through a piece of migmatite from Studsvik (SV)

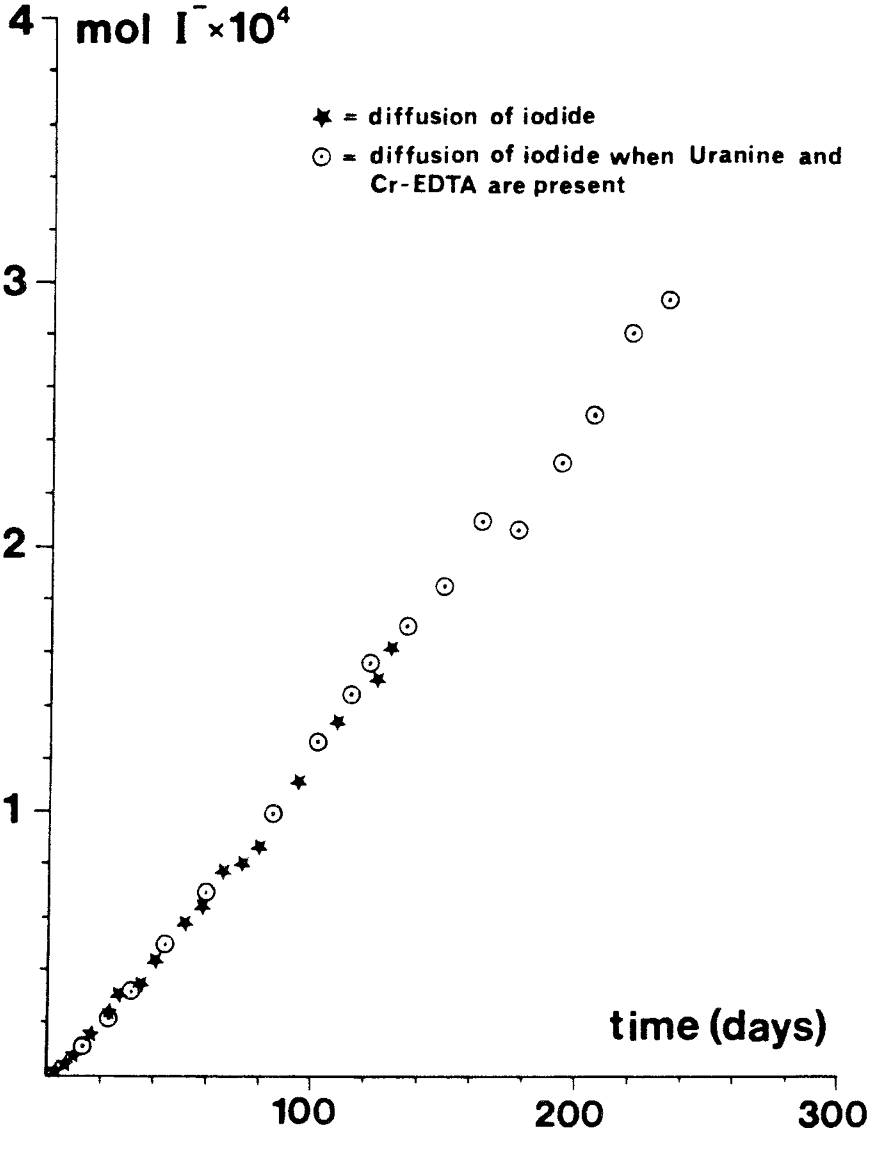

Fig 5: The diffusion of iodide through pieces of migmatite from Studsvik (SV)

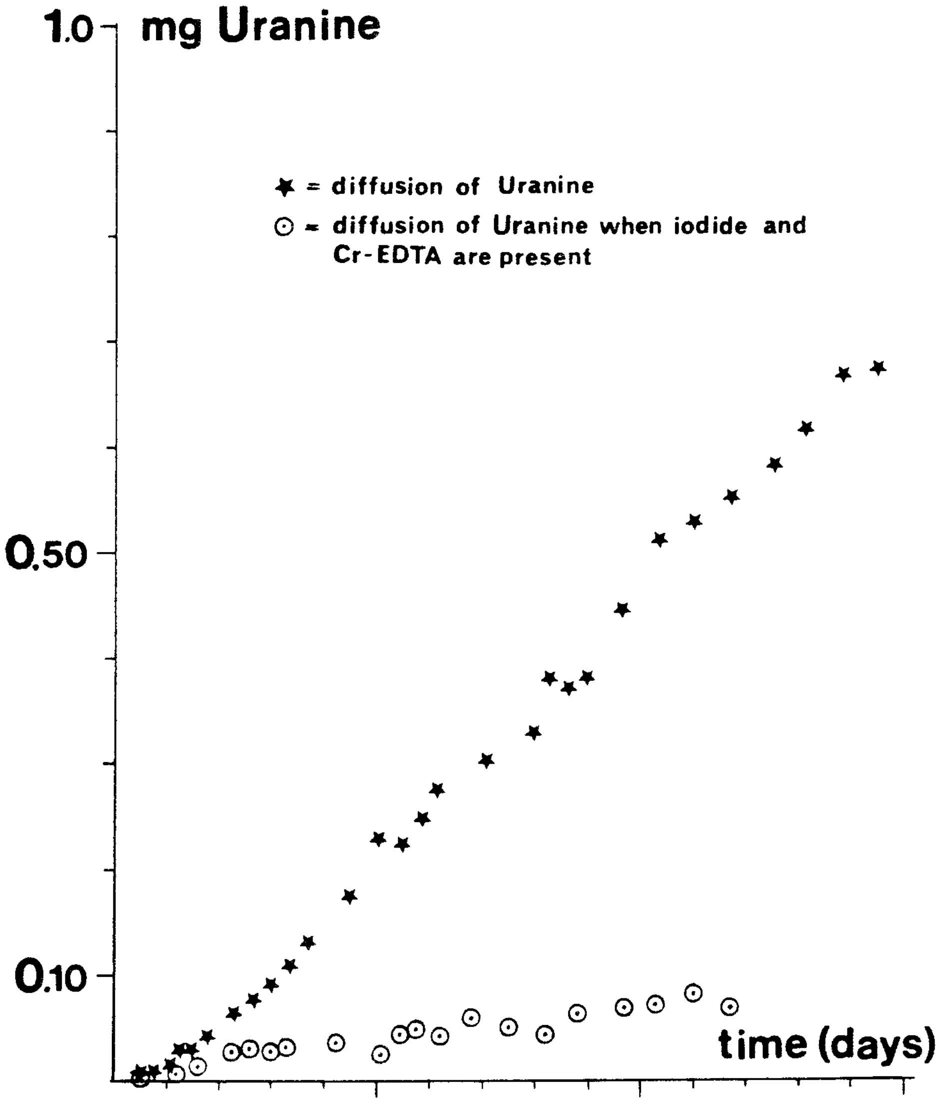

Fig 6: The diffusion of Uranine through pieces of migmatite from Studsvik (SV)

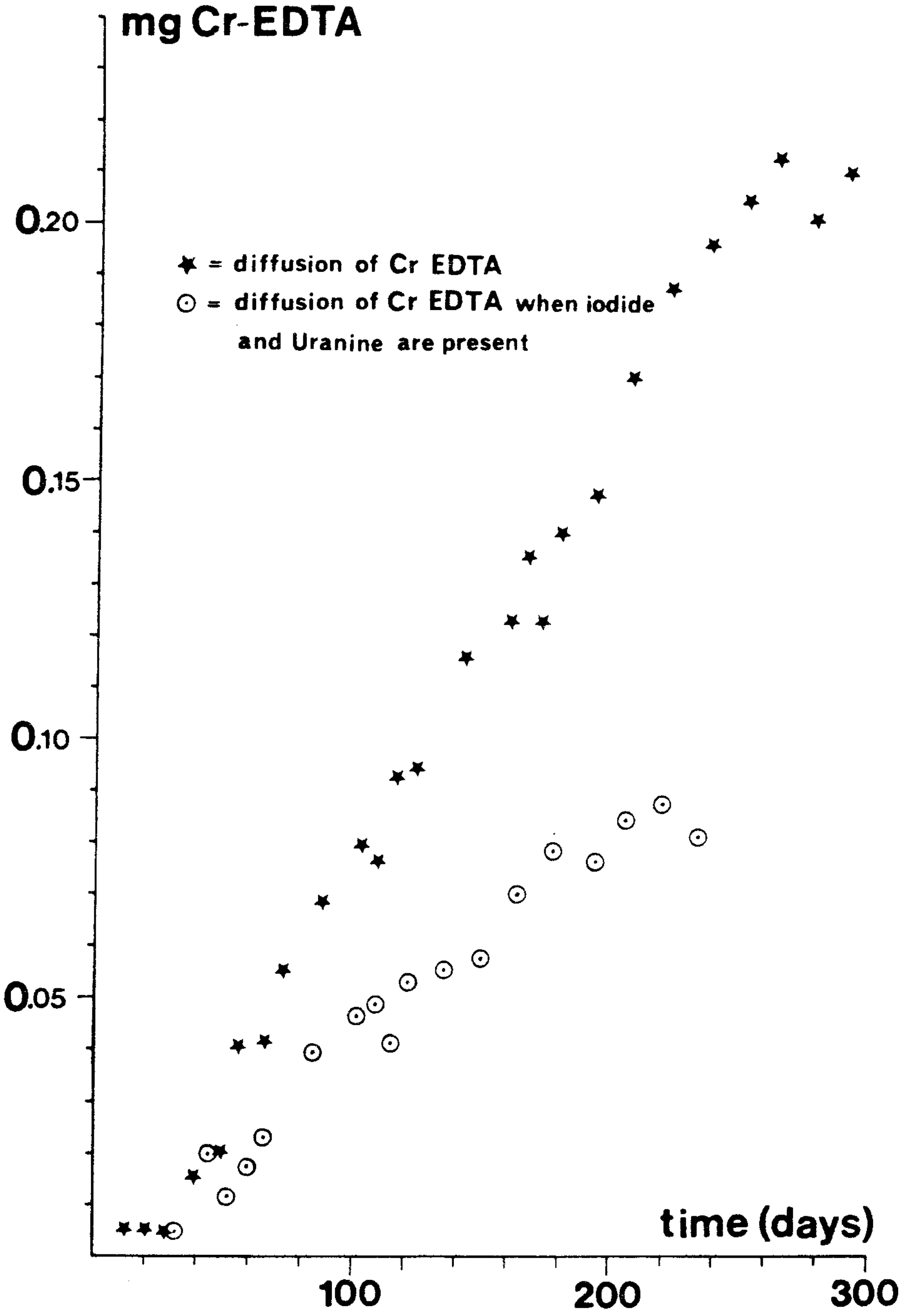

Fig 7: The diffusion of Cr-EDTA through pieces of migmatite from Studsvik (SV)

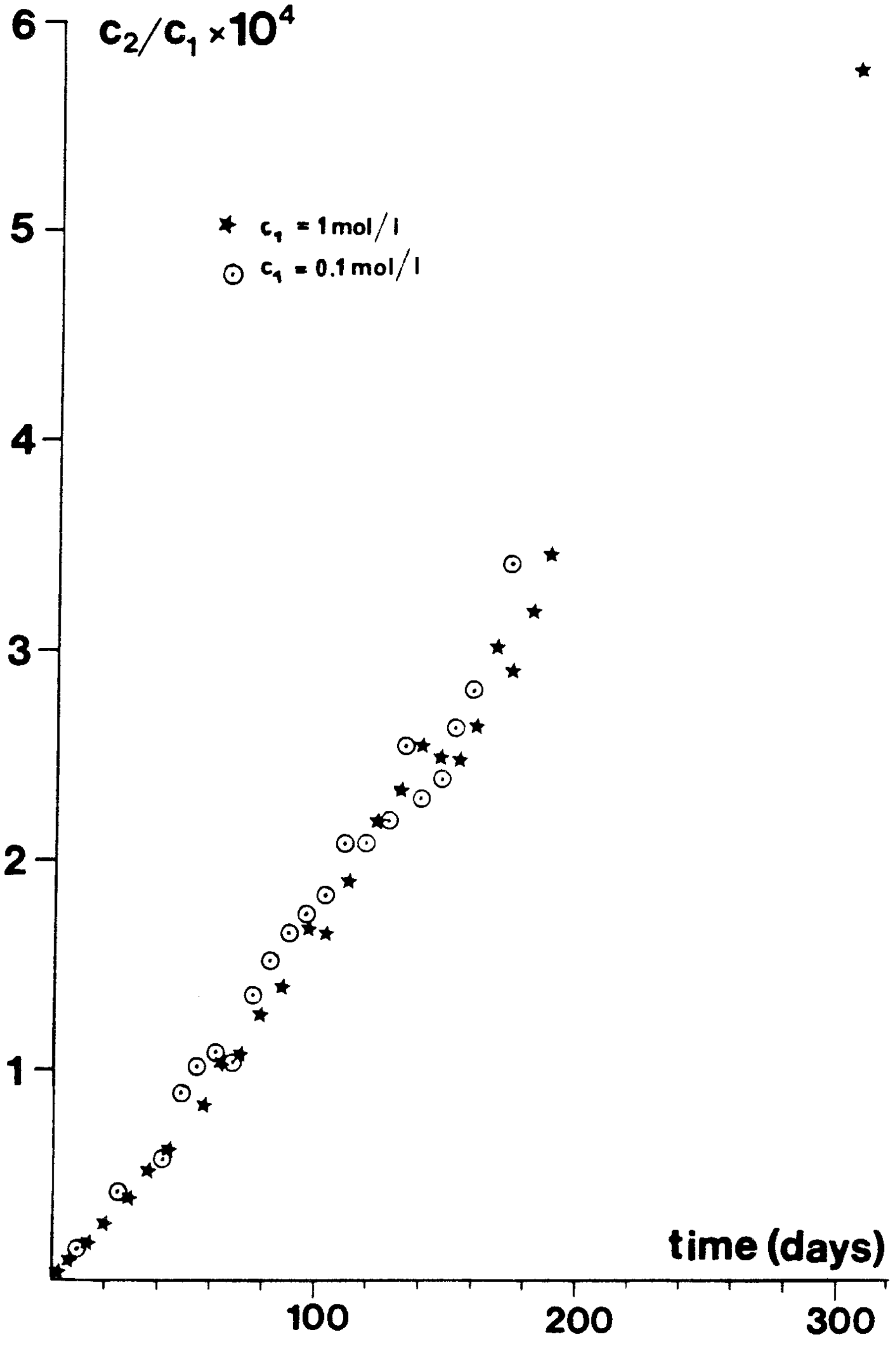

Fig 8: A comparison between two iodide diffusion experiments in Finnsjö granite (F), with different iodide concentration at the high concentration side

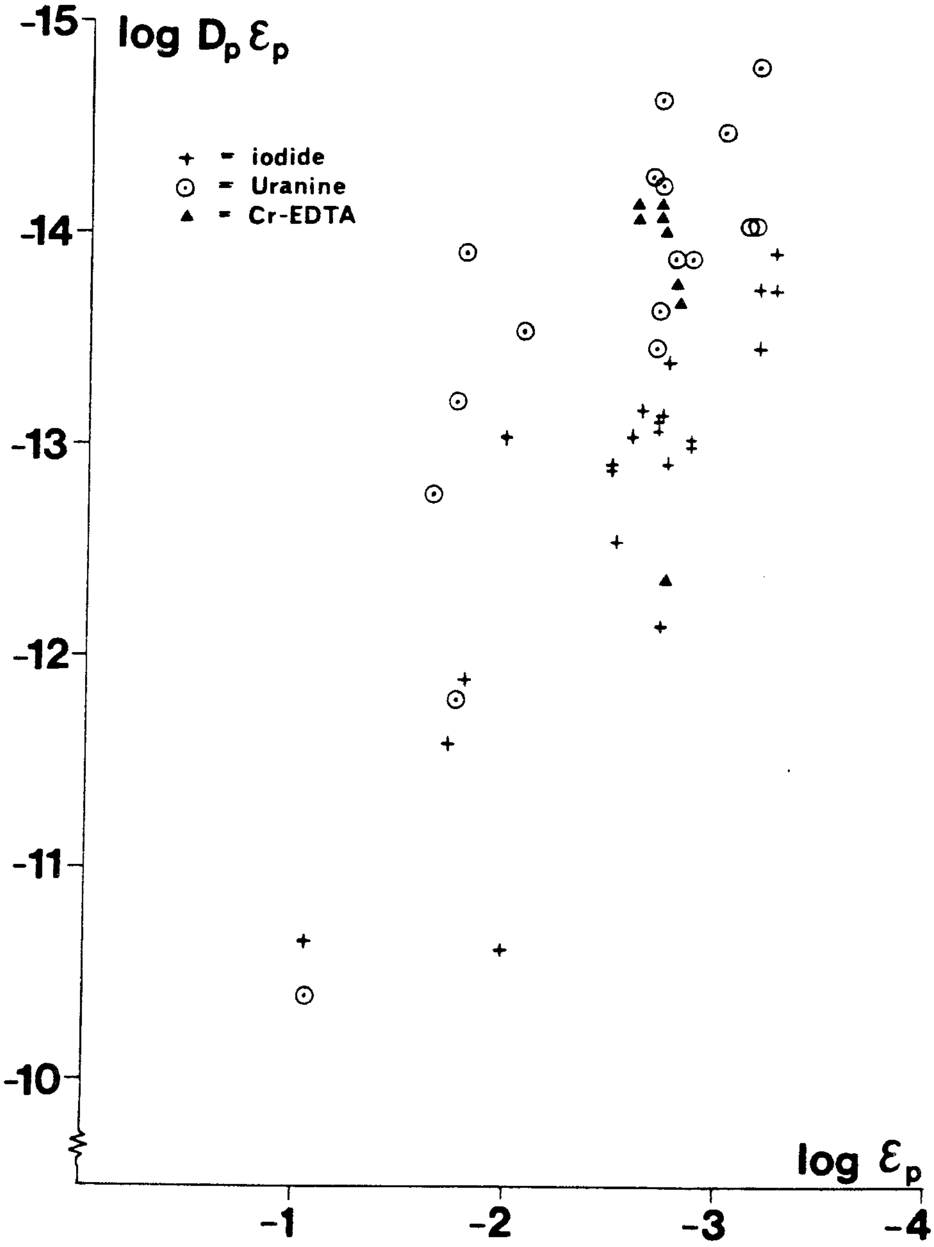

Fig 9: The effective diffusivities versus the porosity of the pieces determined by method 1

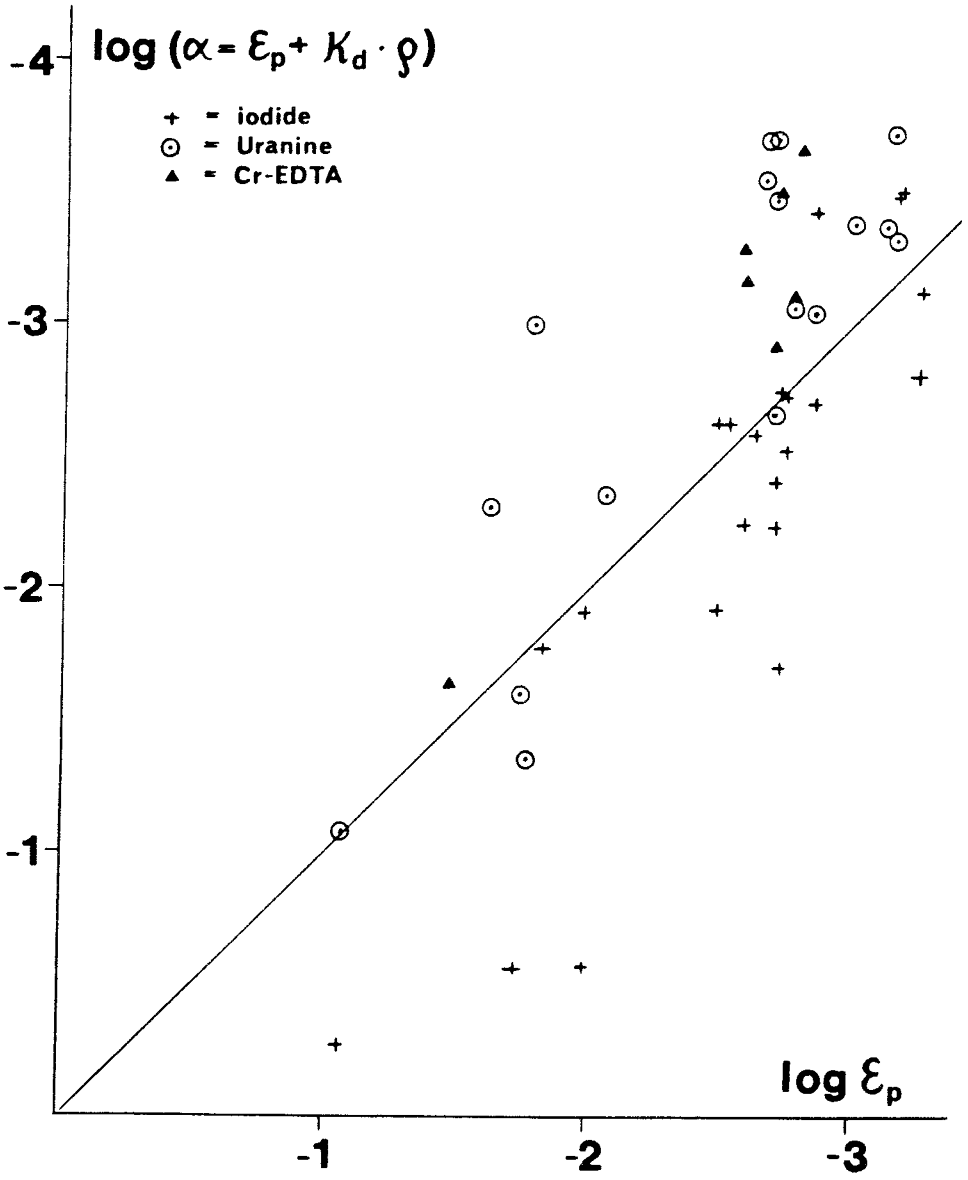

Fig 10: The α-values versus the porosity of the pieces determined by method 1

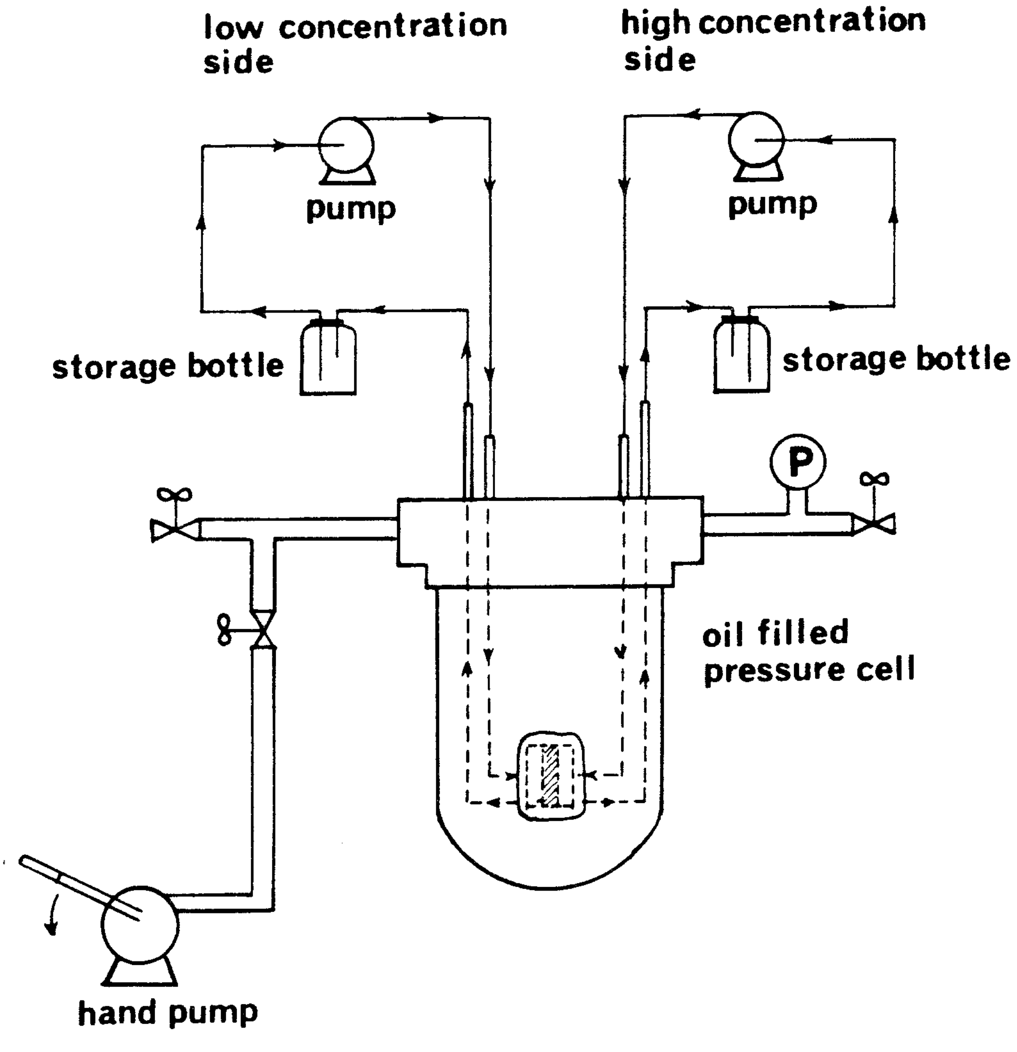

Fig 11: The apparatus used in the diffusion experiments in rockmaterials under pressure

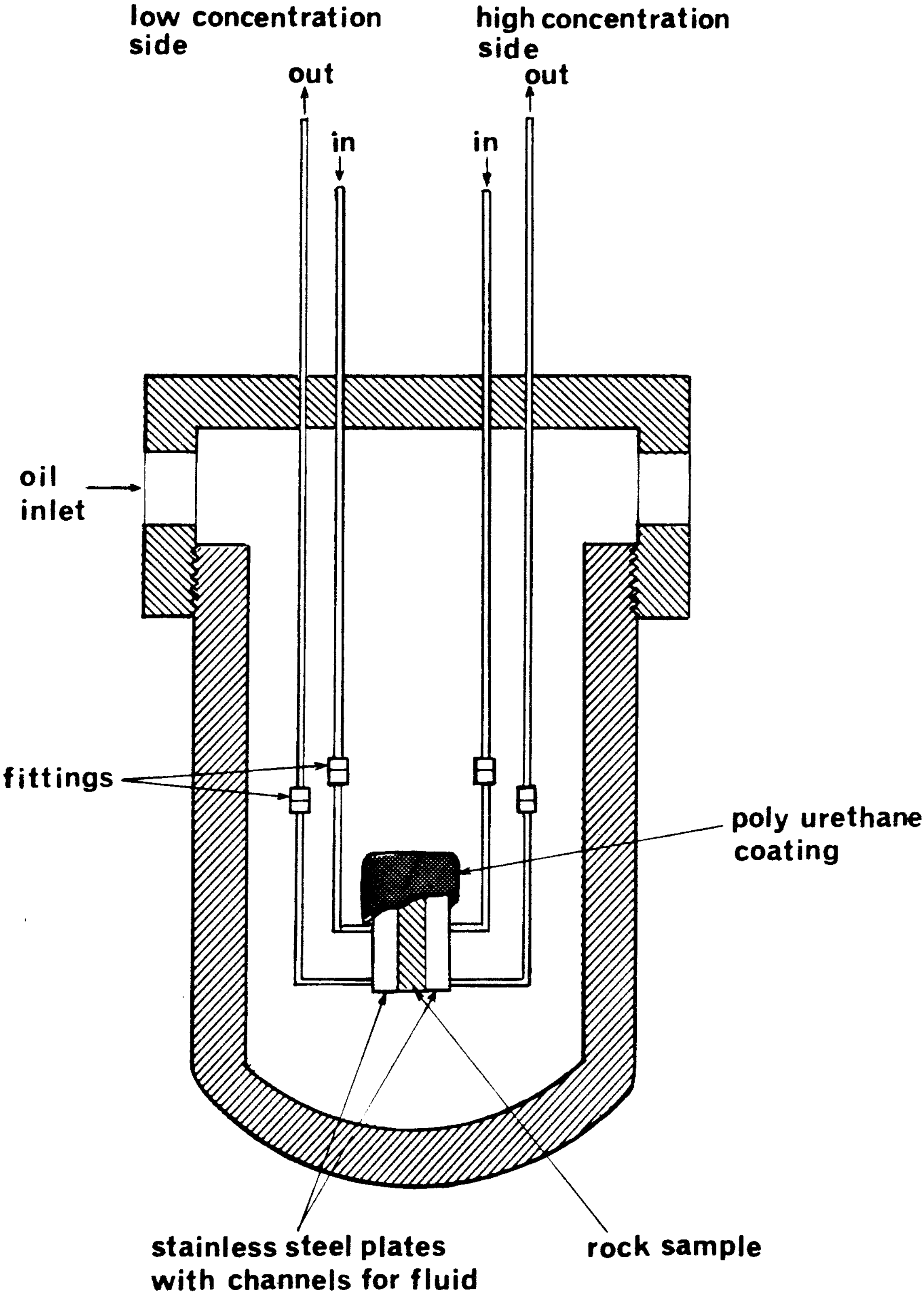

Fig 12: The pressure cell

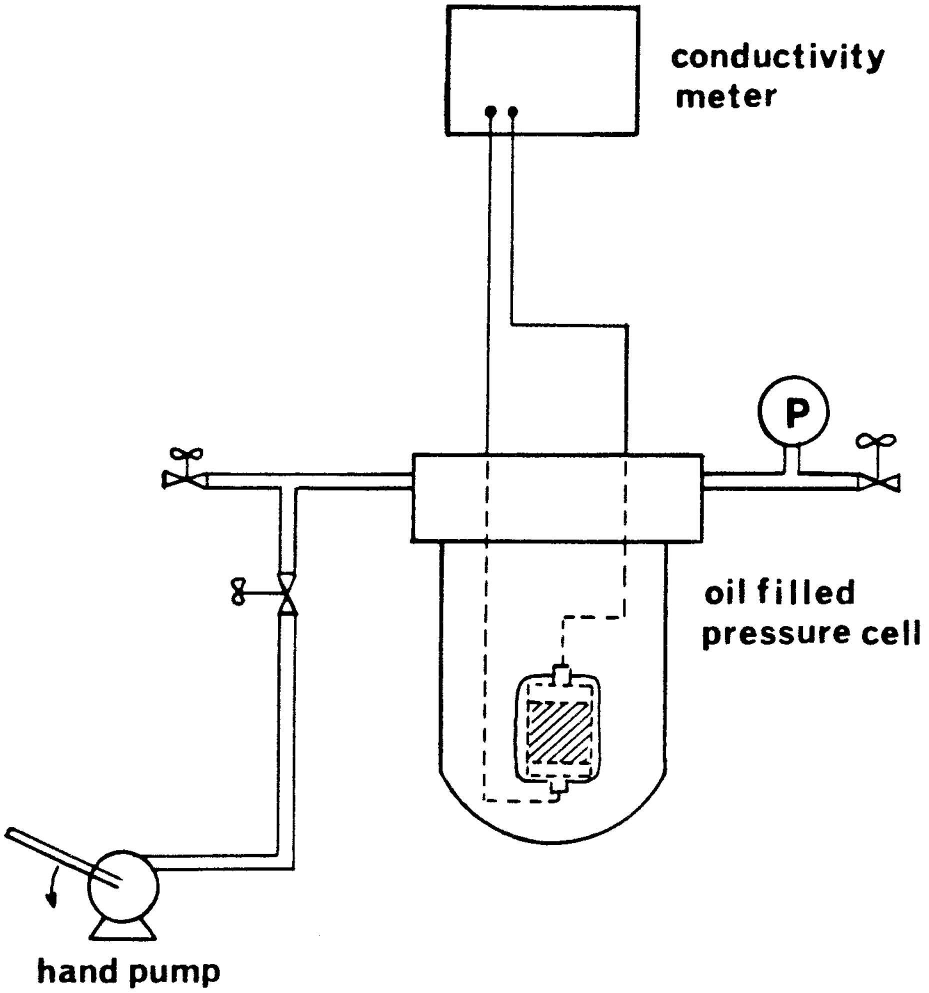

Fig 13: The apparatus used when measuring the electrical resistivity in salt-water-saturated rock cores which are under pressure

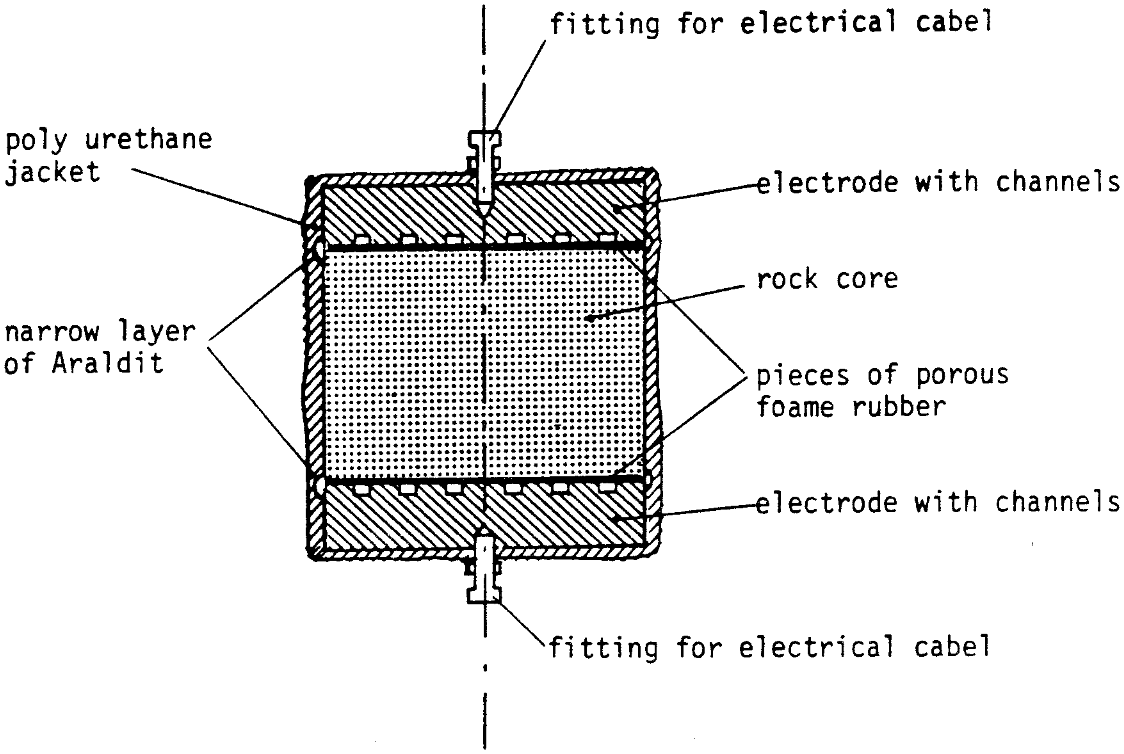

Fig 14: The rock core with electrodes covered with polyurethane

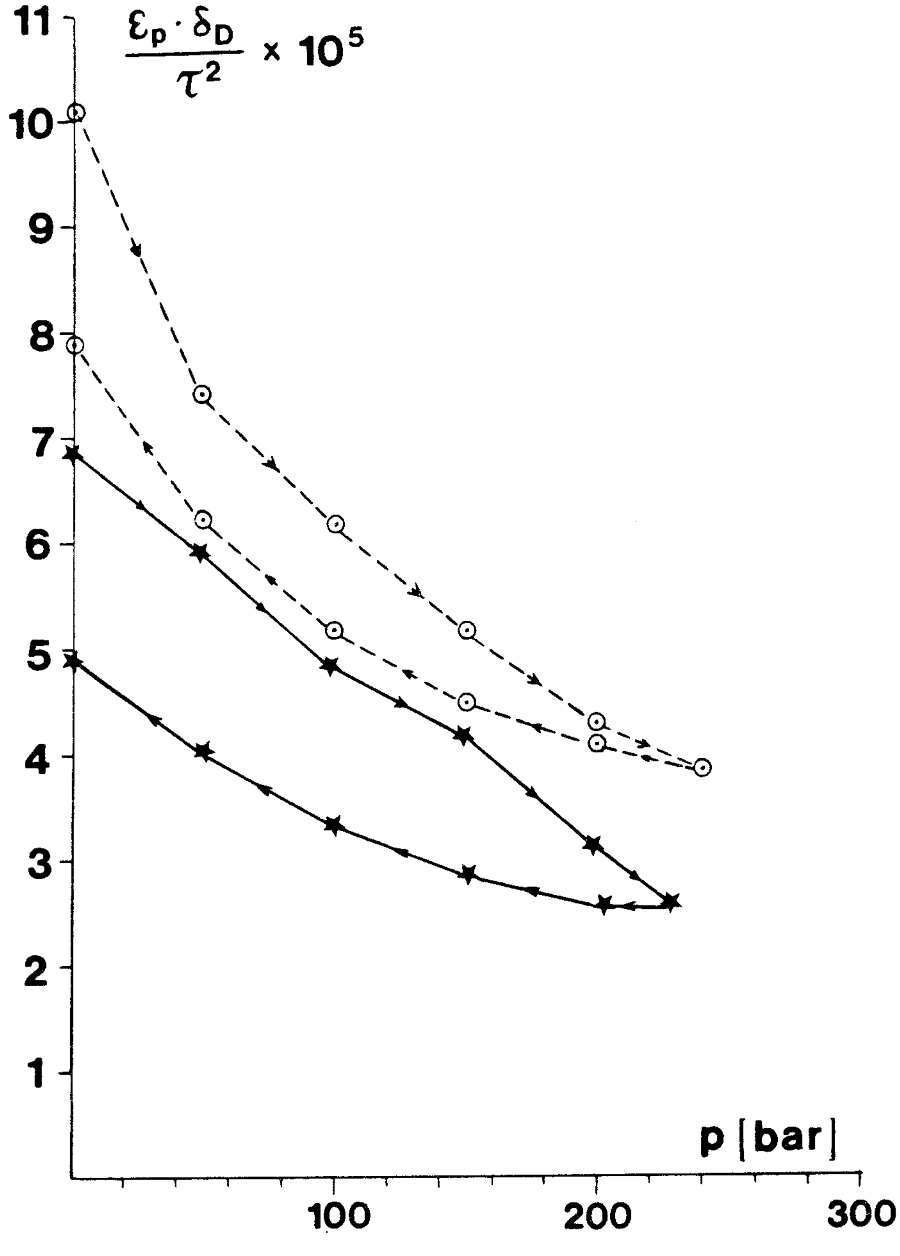

Fig 15: The formation factor versus the pressure for two granite cores from Finnsjön (F)

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