

SVERIGES GEOLOGISKA UNDERSÖKNING

SER. C.

Avhandlingar och uppsatser.

N:o 509

ÅRSBOK 43 (1949) N:o 7.

THE THORIUM CONTENT
OF THE CAMBRIAN ALUM SHALES
OF SWEDEN

BY

F. F. KOCZY

Pris 1 kr.

STOCKHOLM 1949

KUNGL. BOKTRYCKERIET. P. A. NORSTEDT & SÖNER

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In the connection with the extensive investigation of the radium (uranium) content of the Swedish Cambrian alum shales it was also necessary to get at least a general idea about the thorium content of the shales.

Some of the radium determinations were made by counting the total β -radiation. The potassium content of the shales is fairly constant (4—4 $\frac{1}{2}$ %) but if the radiation of the thorium family is high or varying it might be impossible to determine the uranium content of the shale with any higher degree of accuracy. Nevertheless the low thorium content of the kolm lenses indicated that also surrounding alum shales might be low in thorium. The present investigation has also demonstrated the correctness of this assumption and also the possibilities of getting fairly accurate Ra-U-determinations by the Geiger-Müller-counter.

The Oceanographic Institute of Gothenburg is planning and has already begun some work on the geochemistry of the thorium of the ocean, and had therefore a general interest in the thorium content also of ancient marine sediments.

The emanation method of determination of Ra and Th by bubbling through a solution has been investigated and a new apparatus for such investigations has been built.

Methodics.

The most used method of determining thorium (as also radium) when a higher degree of accuracy is needed is the emanation method.

The samples to be investigated must first be converted into a water solution. This is mostly done by melting with Na-K-carbonate. Is the sample too large for the crucible, the melting must be done in parts. Instead of doing so it might be possible to solve the sample in aqua regia and transform thorium and (radiothor) by boiling into solution.

Because thoron decays much more rapidly than radon one must use a continuous current of air that bubbles through the solution and carries with it the thoron. This is transported by the air current into the ionisation chamber where part of it transforms and the rest of it is carried away by the air. The thoron decayed in percent of the total is depending on the velocity of the air current and the relation between the volume of the chamber of ionisation and the scrubber vessel containing the thorium solution as shown in the following.

Of N_0 atoms thoron with the decaying constant, λ , being in equilibrium with Th in the solution, decay on the way between the vessel containing the solution and the ionisation chamber

$$N_0 \left(1 - e^{-\frac{\lambda v}{s}} \right) \text{ atoms,}$$

if v is the total volume of the scrubber, the drying tube and the rubber hoses between the solution vessel and the ionisation chamber and S the velocity of the air current expressed in cm^3 per sec. Thus only

$$N_0 e^{-\frac{\lambda v}{s}} \text{ atoms}$$

reach the ionisation chamber if the air current is kept at $s \text{ cm}^3$ per sec.

In the ionisation chamber decay

$$N = N_0 e^{-\frac{\lambda v}{s}} \left(1 - e^{-\frac{\lambda V}{s}} \right) \text{ thoron atoms} \dots (1)$$

where $V =$ the volume of the ionisation chamber

N/N_0 is the recovery of the apparatus and has its maximum when

$$s = \frac{V}{\ln\left(\frac{v}{v} + 1\right)} \text{ cm}^3 \text{ per sec.} \dots (2)$$

Table I and fig. 1 show the relation between the volumes and the velocity of the air current at optimal recovery.

Table I.

Velocity of the air current at maximal recovery, in cm^3 per sec.

V	V/v	1	5	10	50	100
1 lit.....		17.8	6.9	5.2	3.1	2.7
2 ".....		35.7	13.9	10.3	6.3	5.4
3 ".....		53.5	20.6	15.5	9.4	8.0
5 ".....		89.2	34.6	25.8	15.8	13.4

From the equations (1) and (2) it is possible to compute the relation between the recovery and the volumes at optimal velocity of the air current

$$\frac{N}{N_0} = \left(\frac{v}{V+v} \right)^{\frac{v}{v}} \frac{V}{V+v} \dots (3)$$

The numeric relation is given in Table II

Table II.

V/v	Recovery %
100.....	94.5
20.....	81.8
5.....	59.6
1.....	25.0

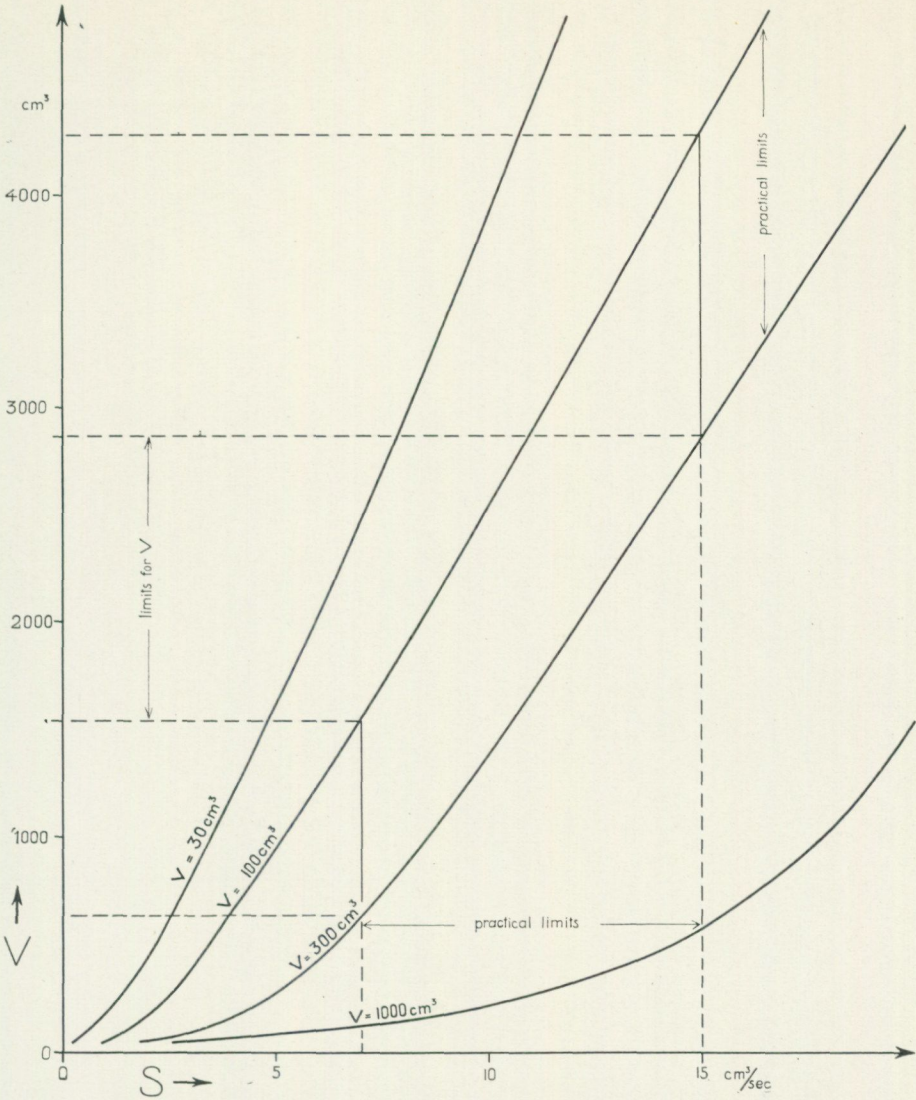


Fig. 1. The relationship between the volume of the ionisation chamber (V) and the air current (s cm³ per sec) at optimal recovery at different volumes of the scrubber (v).

The volume v varies between 100 cm³ and 300 cm³, depending mostly on the scrubber because the drying tube contains only 30 cm³ and the volume of the rubber hoses is small. The velocity of the air current may not exceed 15 cm³ per sec, else the differences in pressure become too large. If the velocity drops below 7 cm³ per sec the emanation is suspected not to be completely exhausted. The practical limits of the variables v and s are especially marked in fig. 1. The graph shows that the optimal volume of the ionisation chamber is between 1.6 and 2.8 litres or about 2 litres.

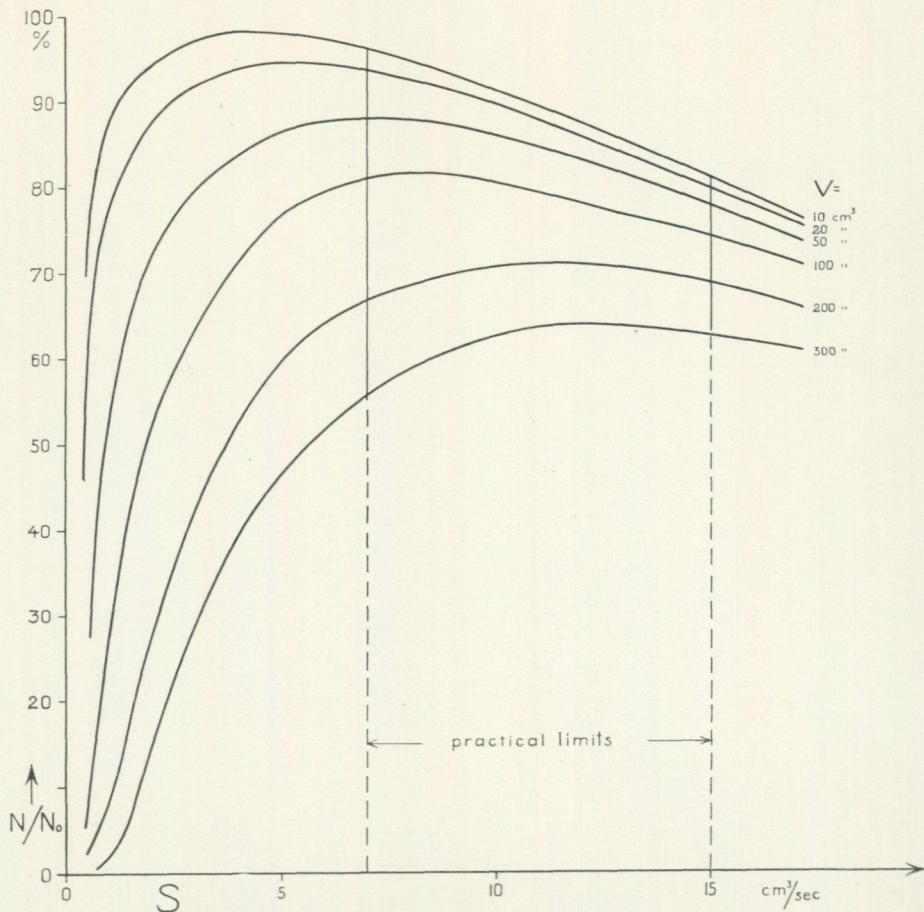


Fig. 2. The relation between the recovery of emanation (N/N_0) and the air current (s) at different volumes of the scrubber (v), the volume of the ionisation chamber being 2 litres.

Graph 2 shows the relation between the volume v and the velocity of the air current through the apparatus the volume of the ion chamber being 2 litres. The practical limits are indicated in the graph. It shows that — the volume v being 200 cm^3 — the optimal velocity of the air is about 10 cm^3 per sec and the recovery will then be 71.5 %. For $v = 50 \text{ cm}^3$, the optimal velocity is 7 cm^3 per sec and the recovery increases to 88 %. The recovery depends less on the air velocity, if the volume v is kept between 100 and 200 cm^3 .

The apparatus was constructed according to these theoretical principles. The ion chamber has a volume of about 2.2 litres. The volume v including the scrubber (50, 100 or 250 cm^3), the rubber hoses, the drying tube (30 cm^3) varies between 100 and 300 cm^3 . The ion chamber was of about the same type as that used by G. Halledauer (1924) for the measurement of the radium emanation. In order to increase the sensitivity of the apparatus the electrical capacity of

the ion chamber was made small by using big cylinders (diam. = 14 cm, length = 15 cm) and small electrodes (diam. = 2 mm). The diameter of the electrostatic protecting tubes round the electrical connections was great (about 6 cm) and the connections were as short as possible. The potential on the chambers was kept at ± 100 volts, the same potential being used for the Wulf string electrometer which was adjusted for a sensitivity of 25 scale units per volt. The potential was produced by a power supply with a stabilizing penthode able to reduce variations of 30 percent in the main current down to 1 percent.

The measurements were carried out in the following way. Compressed air from tubes stored for one month was blown at the optimal velocity through the solution containing thorium. The air containing the thorium emanation is dried effectively by silica gel before it enters into the ion chamber. The ionisation is repeatedly measured *i. e.* the time for charging the electrode up to 0.4 volts. The apparatus was standardized by means of a thorium solution prepared from twenty years old thorium nitrate, which was delivered from the Auer-gesellschaft, Berlin.

The thorium content was computed according to the formula

$$A = k (S_a - S_z)$$

where S_a = scale units per half an hour by measuring the sample

S_z = » » » » » » » » the leakage

k = apparatus constant or sensitivity expressed in gram Th per scale units per half an hour obtained at the standardisation:

$$k = \frac{E}{S_e - S_z}$$

where S_e = scale units per half an hour at the standardisation

E = thorium content of the solution used for the standardisation.

The mean error is computed according to the formula

$$M_a = \frac{E}{(S_e - S_z)^2} \sqrt{(S_e - S_z)^2 m_a^2 + (S_a - S_z)^2 m_e^2 + (S_a - S_e)^2 m_z^2}$$

m_a, m_z, m_e being the mean errors at the measurement of the sample, of the leakage and at the stabilization respectively.

M_a being the mean error at the computation of the thorium-content.

Provided that the mean error is proportional to the deflection during half an hour $m_e = m_e' S_e, m_a = m_a' S_a, m_z = m_z' S_z$

and that the proportionality factors are equal $m_z' = m_a' = m_e'$

and that $S_e = e S_z$ and $S_a = a S_z$

the formula is transformed to

$$M_a = \frac{m_a' E}{(e - 1)^2} \sqrt{a^2 (e - 1)^2 + e^2 (a - 1)^2 + (a - e)^2}$$

as

$$A = E \frac{S_a - S_z}{S_e - S_z} = E \frac{a - 1}{e - 1}$$

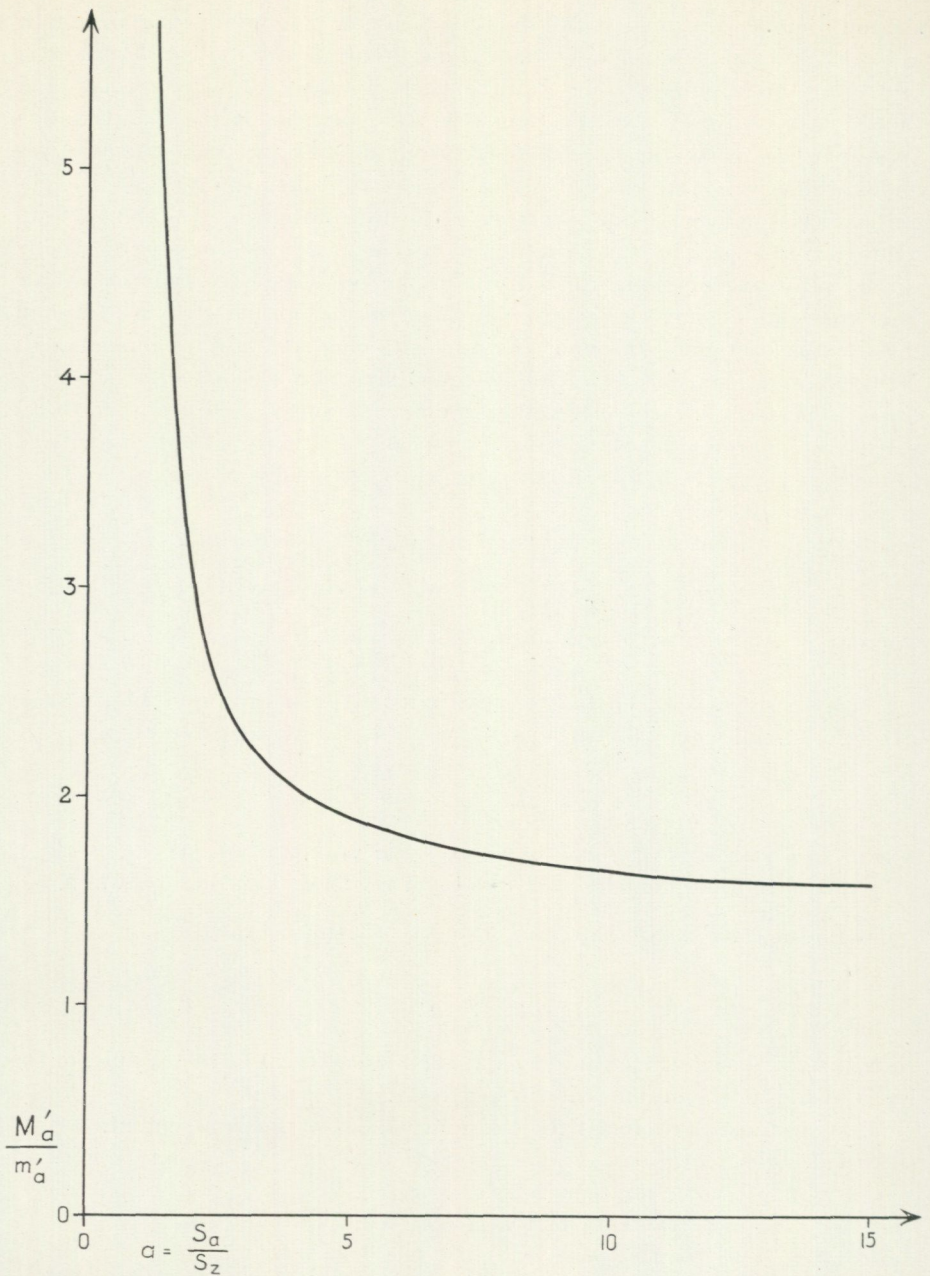


Fig. 3. The relation between the ratio of the mean error of thorium computation (M'_a) and the mean error of the determination of the electrometer deflection (m'_a) and the ratio of the electrometer deflection by measuring the sample and the leakage $\left(\frac{S_a}{S_z}\right)$.

the formula becomes

$$M_a = \frac{m_a' A}{(a - 1)(e - 1)} \sqrt{a^2(e - 1)^2 + e^2(a - 1)^2 + (a - e)^2}$$

Considering that $e \gg 1$ and as in the radical quantity the term a^2e^2 is great compared to the other values, the formula can be simplified

$$M_a \leq \frac{m_a' a A \sqrt{3}}{a - 1}$$

The mean error in per cent is written

$$M_a' = m_a' \frac{1.5 a}{a - 1}$$

and this formula *approximately* expresses the relation between the mean error of the thorium determination and that of the electrometer deflections (Graph 3).

This formula enables us to discuss the lower limit for an accurate measurement. The sensitivity of the apparatus was found to be one scale unit per half an hour corresponding to a thorium content of 1.9×10^{-6} g. As the leakage normally causes a deflection of 4 scale units ($S_z = 4$) and the mean error of the deflections during the measurement is about 2.5 per cent ($m_a' = 0.025$), the lower limit is 4.6×10^{-6} g Th, if we require a mean error of the determination not exceeding 10 per cent ($M_a' = 0.1$). For this investigation 10 g of alum shales was used and so the thorium content could be measured down to about $5 \times 10^{-7} \pm 5 \times 10^{-8}$ g Th per g.

The investigated samples show a very low thorium content but a high radium content. It is obvious that a high radium content could cause a considerable error in the determined thorium value. So we have to take account of this effect. The smallest amount of thorium which can be observed, produces 28 α -particles during half an hour of which 70 percent decay in the ion chamber *i. e.* 20 particles. If the radium content is permitted to change the total ionization by 1 %, the radium emanation passing the chamber does not produce more than 0.2 α -particles per half an hour. The computation according to formula (1) indicates that 50×10^{-5} % of the radium emanation in equilibrium with the solution's radium content decays in the chamber. If the solution's radium content is 6×10^{-10} g, about 0.2 α -particles are produced per half an hour, and as we have seen this will effect the thorium value by only 1 %.

Results.

Core samples from three drilling holes were investigated, Four samples from different levels at Per Mångård, from the highest and lowest level at Tornby, a sample with a high radium content from Norrtorp was studied. Values of the kerogene, pyrite and clay content in Table III was taken from A. H. Westergård (1940, 1941, 1944).

Table III.

Sample	Depth m	10^{-6} g Th/g	10^{-6} g U/g	Kerogene %	Pyrite %	Clay %	Th/U
Per Mångård I	1—2	0.6	110	13	8	79	0.0054
» » II	3—4	1.0	160	14	11	75	0.0063
» » IV	10—12	1.3	40	12	13	75	0.033
» » VI	15—17	1.9	20	6	8	86	0.095
Tornby I	1—3	1.6	190	14	6	80	0.0084
» IV	11—12	1.8	10	3	5	92	0.18
Norrortorp I	1—5	0.6	200	17	13	70	0.003

It is evident that the thorium content is very low in these samples, and shows very small variations. Joly (1910) and Fletcher (1912) report a thorium content of 13×10^{-6} g per g in clay, and in sandstone 6×10^{-6} g per g. Evans and Goodman found 4.4×10^{-6} g Th per g in acid and intermediate rocks, and 3.9×10^{-6} g Th per g in alkaline rocks from measurements of the total α -radiation and the radium content. Evans and Reitt could compute the thorium content, and found 1.1×10^{-6} g Th per g in limestone and 3.33×10^{-6} g Th per g in sandstone. I. Lahner (1939) has observed 1.5 to 3.4×10^{-6} g Th per g in limestone and dolomite from the Alps, and 1.8 and 4.6×10^{-6} g Th per g in two pieces of coral.

These investigations indicate that the content of thorium or radio-thorium in Swedish alum shales is so low that it is possible to use the G-M counter for the radium determination in the shales. The error will be less than 1 percent according to the following consideration. 1 g uranium in equilibrium with its decay products produces about the same number of β -particles and γ -quanta as 4 to 6 g Thorium in equilibrium with its decay products. As the thorium content of the shales does not exceed 2 g per ton, and the uranium content is not below 10 g per ton, less than 3 percent of the counted particles originates from thorium. The thorium content being fairly constant, the mean error caused by thorium is found to be below 1 percent.

Discussion.

This investigation was carried out in 1943, but it was not possible to procure the paper on the radioactivity in ancient sediments by R. Beer and Clark Goodman until after the war. Studying the total α - and β -radiation, determining the potassium and radium content, they obtained data for computing the thorium content. These American sediments was found to contain up to 60 g uranium per ton. A relationship between the content of carbon and uranium was established, similar to that found by us for the amount of kerogene and uranium in the Swedish black shales. But we found that the relationship does not hold true for the Dictyonema shales, which show a higher uranium content. Beer and Goodman also found a relationship between the content of thorium and uranium as is illustrated in fig 11 in their paper. Provided the linear equation holds true, the uranium-thorium ratio should be 9 for a uranium value

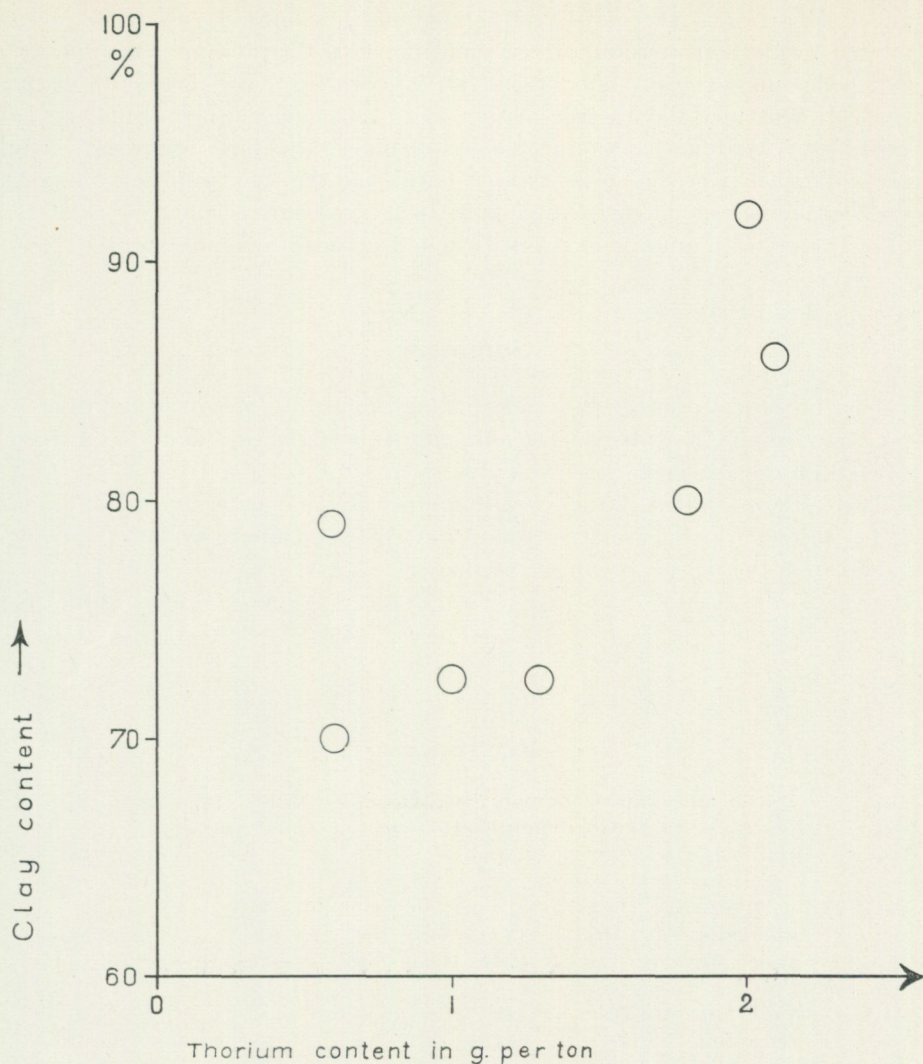


Fig. 4. The relation between clay and thorium content of the samples measured.

of 37 g per ton, and consequently the thorium content 330 g per ton. Compared to this our values are far too low to support Goodmans hypothesis that petroleum sources show a high Th/U ratio. In contrary we found a reversal proportionality between the karogene and thorium and further a direct proportionality between the clay and the thorium (Fig. 4). So the Dictyonema shales show the highest amount of uranium but the lowest of thorium.

Deep sea sediment have a low thorium content as well as sea water, the amount of which could be estimated only from the thorium-radium ratio in marine sediments (Koczy 1949). The thorium content of marine sediments can be derived from thorium precipitated chemically or from thorium present in

minerals carried to the sea. Here the thorium in solution seems to be precipitated by the seawater almost very quickly. Or, if the thorium is transported as a compound of heavy minerals, it settles down here near the mouth of the river. In this way the absence of thorium in most marine sediments can be explained. The alum shales forms a marine sediment and have been very slowly precipitated in a nearly closed basin. Considering the slow sedimentation and the high kerogene content it is probable that no river has mouthed near the bay. Therefore thorium is likely to be found in small amounts only.

Summary.

The theoretical principles for determining thorium by means of the emanation method are considered. The optimal volume relation and the optimal velocity of the air current are computed.

The thorium content of the Swedish alum shales was determined and found to be between 0.6 to 2 gram per ton. An attempt is made to explain these low values from the marine origin of the shales.

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