

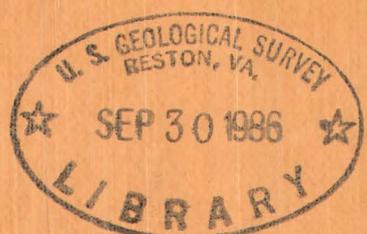
(200)
T67r
no. 495

OFFICIAL USE ONLY

W.S.M.
wsm!

Uranium in the Upper Cambrian Black Shale of Sweden

By V. E. McKelvey



Trace Elements Investigations Report 495

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

OFFICIAL USE ONLY

OFFICIAL USE ONLY

Geology and Mineralogy

This document consists of 19 pages.
Series A

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

URANIUM IN THE UPPER CAMBRIAN BLACK SHALE OF SWEDEN*

By

V. E. McKelvey

January 1955

Trace Elements Investigations Report 495

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

OFFICIAL USE ONLY

USGS - TEI-495

GEOLOGY AND MINERALOGY

<u>Distribution (Series A)</u>	<u>No. of copies</u>
Argonne National Laboratory	1
Atomic Energy Commission, Washington	1
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Butte	1
Division of Raw Materials, Casper	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Hot Springs	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, Phoenix	1
Division of Raw Materials, Richfield	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Washington	3
Exploration Division, Grand Junction Operations Office	1
Grand Junction Operations Office	1
Technical Information Service, Oak Ridge	6
Tennessee Valley Authority, Wilson Dam	1
U. S. Geological Survey:	
Fuels Branch, Washington	2
Geochemistry and Petrology Branch, Washington	2
Geophysics Branch, Washington	1
Mineral Deposits Branch, Washington	2
E. H. Bailey, Menlo Park	1
A. L. Brokaw, Grand Junction	1
N. M. Denson, Denver	1
C. E. Dutton, Madison	1
W. L. Emerick, Plant City	1
L. S. Gardner, Albuquerque	1
J. W. Huddle, Lexington	1
A. H. Koschmann, Denver	1
R. A. Laurence, Knoxville	1
J. D. Love, Laramie	1
V. E. McKelvey, Menlo Park	1
L. R. Page, Washington	1
P. C. Patton, Denver	2
J. F. Pepper, New Philadelphia	1
J. F. Powers, Salt Lake City	1
J. M. Schopf, Columbus	1
Q. D. Singewald, Beltsville	1
A. E. Weissenborn, Spokane	1
TEPCO, Denver	2
TEPCO, RPS, Washington, (Including master)	3

CONTENTS

	Page
Abstract	4
Introduction	4
Distribution and geologic setting of the alum shales	5
Stratigraphy and lithology	5
Mineralogy and composition	12
Areal variations in facies	13
Origin	13
Suggestions for prospecting	18
Literature cited	19
Unpublished report	19

ILLUSTRATIONS

Figure 1. Map of western Europe, showing margin of Upper Cambrian sea and axes of geosynclinal zones	6
2. Stratigraphic column of Paleozoic rocks of southern Sweden	7
3. Map of southern Sweden, showing margin of Upper Cambrian sea and location of areas now underlain by Upper Cambrian alum shales	8
4. Stratigraphic column of Upper Cambrian alum shale in Kvantorp district, Sweden, showing distribution of kolm lenses, limestone lenses, uranium, oil, and total calorific value.	10
5. Diagram showing relation of kolm lens to enclosing alum shale	11
6. Map of southern Sweden, showing areal variations/ ^{in thickness} of <u>Peltura scarabaeoides</u> zone of Upper Cambrian alum shale	14
7. Map of southern Sweden, showing uranium content of <u>Peltura scarabaeoides</u> zone of Upper Cambrian alum shale and area containing more than 1 cm equivalent thickness of kolm lenses.	15

ABSTRACT

The Peltura zone of the Upper Cambrian black shales of Sweden contains about 0.02 percent uranium. Maximum amounts are present in rocks deposited in an embayment in the sea and in rocks in or closely adjacent to that part of the vertical sequence that contains maximum amounts of distillable oil, total organic matter, pyrite, and a black highly uraniferous kerogen called "kolm". Available data suggest that the precipitation of uranium is favored by a low redox potential and that the uranium in the shale matrix may be in fine-grained kolm.

INTRODUCTION

One of the Upper Cambrian black shales of Sweden is remarkable because it is more uraniferous than any other marine black shale known and because it contains sizeable quantities of a uraniferous hydrocarbon called "kolm", the equivalent of which is rare in other black shales. I was privileged to visit these deposits in October 1952 under the guidance of Dr. Josef Eklund of the Swedish Geological Survey. The information gained from this visit was presented orally at a symposium on uranium in carbonaceous rocks held by the Geological Survey in December 1952. It is recorded here in the hope that it may be of interest to others engaged in the search for uraniferous shales in the United States.

Much information on alum shale is available in the literature (see particularly Munthe and others, 1938, and Westergard, 1944 a, b.), but the data and diagrams presented here are based largely on information given me by Dr. Eklund, supplemented by an unpublished report compiled by Dr. George Bain (1946).

Although I am largely responsible for the speculations on origin, the development of the ideas presented benefited greatly from stimulating discussions with Dr. Eklund and several associates on the Geological Survey, particularly H. L. James and D. E. White.

DISTRIBUTION AND GEOLOGIC SETTING OF THE ALUM SHALES

The lower Paleozoic black shales (also called alum shales because of their content of this substance) of Sweden accumulated near the landward margin of a submerged shelf or platform that lay between two geosynclinal zones (fig. 1). The rocks that accumulated on the shelf in Sweden consist of interbedded quartz sandstone, black shale, limestone, as well as some glauconitic and phosphatic layers (fig. 2). As is typical of platform accumulations elsewhere, the deposits are thin; the entire lower Paleozoic sedimentary section is only about 225 m thick at most. The thickness of the Upper Cambrian is only 10 to 20 m.

Black shales were deposited over much of the area outlined on figure 1, but the highly uraniferous shale is found only in what were once embayments in the Upper Cambrian sea (fig. 3). The shales in Sweden are preserved now only in seven isolated patches, either in fault basins, as in the eastern part of Sweden, or under plateaus capped by a widespread diabase sill, as in the western part.

STRATIGRAPHY AND LITHOLOGY

The alum shales are a sequence of black shales of Middle Cambrian (the Paradoxides zone), Upper Cambrian (the Olenidian shale), and Ordovician (Dictyonema shale) age (fig. 2). The shale sequence is 90 m or more in thickness in westerly sections, but it thins eastward. Shale of Paradoxides age is only present in some westerly sections--elsewhere the Paradoxides beds are sandy shale or sandstone. The Dictyonema shales are also present only in westerly sections; beds of this age are absent or at least not recognized in the eastern sections. The shales are underlain by sandstone or sandy shale, locally glauconitic at the top, and overlain by the Orthoceras limestone, which is glauconitic and phosphatic at the base.

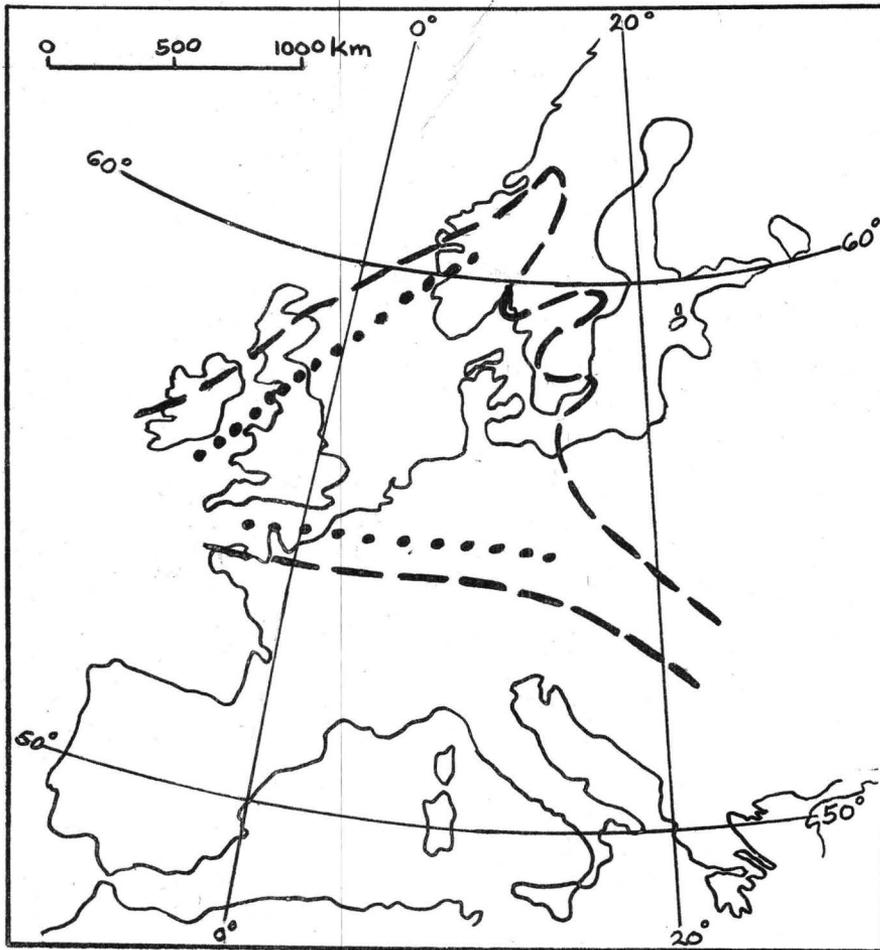


Figure 1. Map of western Europe, showing margin of Upper Cambrian sea (dashed line) and axes of geosynclinal zones (dotted lines). Sketched by J. Eklund.

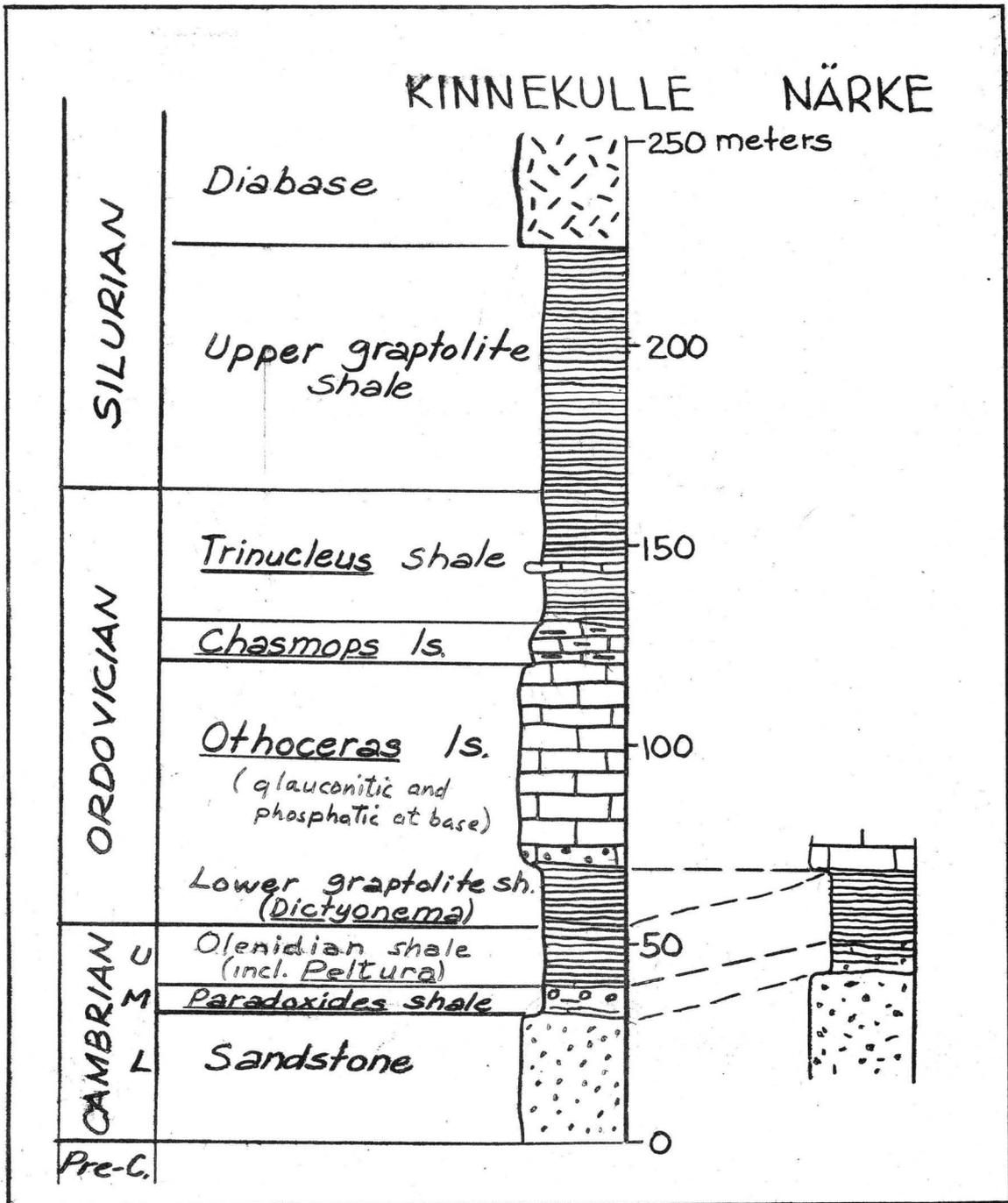


Figure 2. Stratigraphic column of Paleozoic rocks of southern Sweden.

Modified from unpublished report by G. Bain.

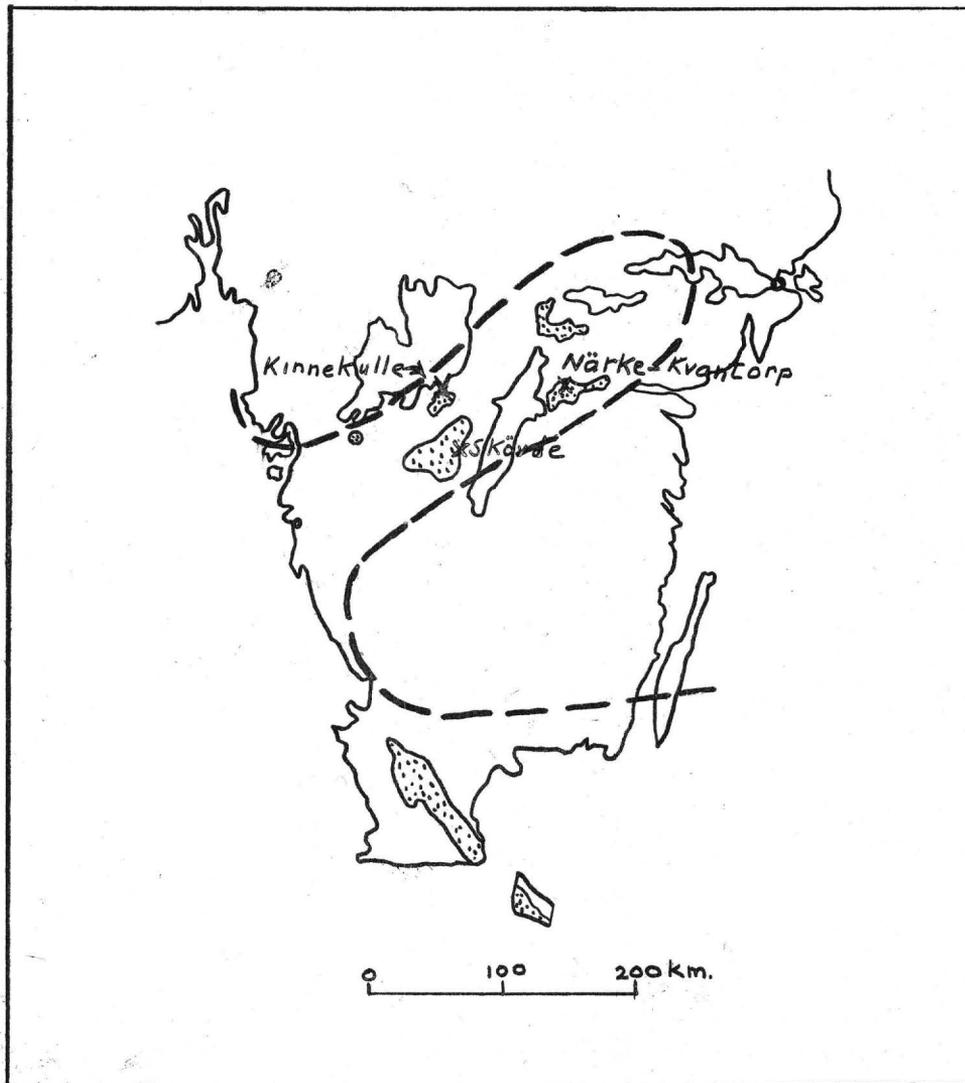


Figure 3. Map of southern Sweden, showing margin of Upper Cambrian sea (dashed line) and location of areas now underlain by Upper Cambrian alum shale (stippled). Sketched by J. Eklund.

In major aspects of lithology, the alum shales of Sweden are all black, carbonaceous, bituminous, pyritic mudstone; but they differ with respect to volumetrically minor but nevertheless important constituents. The most uraniferous part of the alum shales is the Peltura zone near the middle of the Olenidian shale. The Peltura shale ranges in thickness from about 1 or 2 m in near-shore facies to about 20 m seaward. It is divided into three zones on the basis of fossils, a lower Peltura acutidens zone, a middle Peltura minor zone and an upper Peltura scarabaeoides zone. Because the Peltura minor zone is generally thin, the uraniferous shale is divided for practical purposes into a lower Peltura acutidens and an upper Peltura scarabaeoides zone (fig. 4).

The Peltura acutidens zone and the middle part of the Peltura scarabaeoides zone are richest in oil and the lower part of the Peltura scarabaeoides is richest in uranium. The content of total carbonaceous matter (indicated in part by total calorific value on figure 4) roughly parallels that of the oil except in the upper part of the zone. Shales above and below the Peltura zone are also petroliferous and uraniferous but not as much so as the Peltura zone. The oil content and total calorific value increase rather regularly from the base of the shale sequence to a maximum in the Peltura zone and then decrease rather regularly to the top. (See, for example, Westergard, 1944b, pl. 2.) The total sulfur content of the shales varies vertically in a similar fashion, but the maximum is generally reached a few meters below the Peltura zone. The range in sulfur content is from about 2 to 10 percent in most sections and the content of the Peltura zone is around 6 to 7 percent.

The Peltura zone also contains about 0.1 percent vanadium. The highest amounts, however, are in the Dictyonema shale, which contains 0.2-0.4 percent V.

In the central part of the northern embayment (fig. 1), the most uraniferous part of the Peltura zone contains lenses of black kerogen called "kolm" which contain about 0.45 percent uranium. These lenses are as much as 10 cm in thickness and 2 m in length. Although the shale layers bend around the lenses, bedding can also be traced into them; computations of the distension of the bedding compared to the ash content of the lenses indicate that the distension is about equivalent to the hydrocarbon content of the kolm lens rather than to the full thickness of the kolm lens (fig. 5).

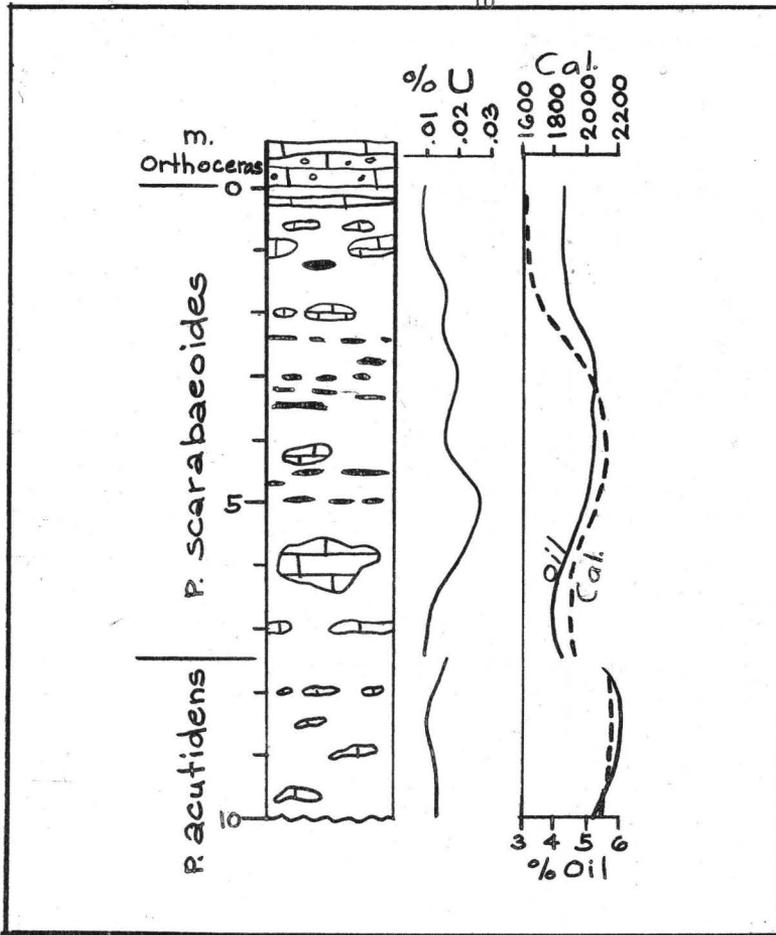


Figure 4. Stratigraphic column of Upper Cambrian alum shale in Kvantorp district, Sweden, showing distribution of kolm lenses (solid black), limestone lenses, uranium, oil, and total calorific value (in kilogram-calories per kilogram). After J. Eklund.

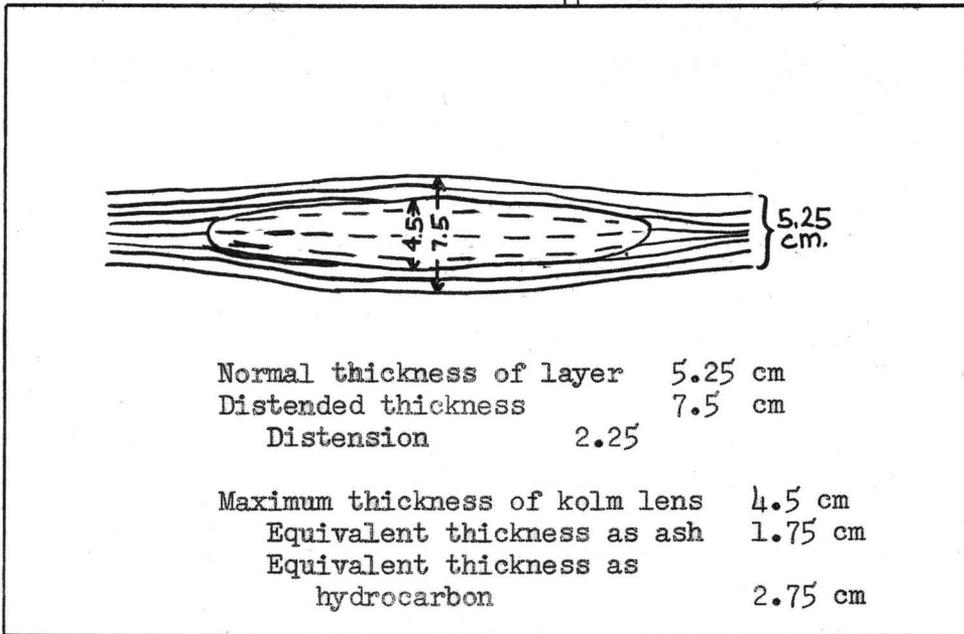


Figure 5. Diagram showing relation of kolm lens to enclosing alum shale.

After G. Bain.

In the vicinity of Skövde (fig. 3), where the shale underlies the diabase sill, petroleum coke--presumably a shale oil distillate--is found as cross-cutting veinlets and discontinuous layers in the shale and Orthoceras limestone. The coke contains much vanadium but no uranium.

The alum shale contains lenses of bituminous limestone, as much as 1 m in thickness and 25 m or more in length. They are less abundant in the kolm-bearing zone than in beds above and below and are more abundant in shoreward than seaward facies. The shale bedding bends around the limestone lenses but the lenses contain fine laminations of argillaceous matter.

MINERALOGY AND COMPOSITION

The Peltura shale consists of about 60-65 percent insoluble matter, 12 percent pyrite, and 20-25 percent carbonaceous matter. About 30 percent of the insoluble matter is quartz, 65 percent is muscovite (including 5 or 6 percent phlogopite), and about 5 percent authigenic alkali feldspar. Some of the pyrite is in visible nodules, lenses, and laminae, but most of it occurs as microscopic spherical bodies, similar to those found in many other black shales. Less than 1 to more than 6 percent of the shale is distillable oil. Some, perhaps most, of the remaining carbonaceous matter is kerogen of two types, one a yellowish translucent variety, the other a dark type similar in appearance to the megascopic kolm. The fine-grained varieties of kerogen have been separated from the shale and from each other by flotation but not much is known of their composition.

The limestone lenses are about 80 percent CaCO_3 and 20 percent shale component. They make up 15 to 20 percent of the whole volume of the Peltura zone in much of the northern embayment. The shale itself contains less than 1 percent CaCO_3 .

The mineral form of the uranium and vanadium is unknown. Eklund believes, however, that vanadium is present as the sulfide, patronite, and he suspects that uranium occurs as the oxides or possibly is carried by the fine-grained kolm. The total volume of the megascopic kolm lenses in the central part of the northern embayment is equivalent to a continuous layer as much as 7 or 8 cm in thickness but, despite their high uranium content, they contain no more than 10 percent of the total uranium in the Peltura zone.

AREAL VARIATIONS IN FACIES

The thickness of the P. scarabaeoides zone reaches a maximum in the center of northern embayment (fig. 6). Along the fringe of the basin the shale component decreases, becomes more calcareous, and finally disappears altogether so that the section, in the few places where it can be seen, consists only of limestone. Chert is present in the fringe carbonate sections, though not as a major component.

As is shown on figure 7, the uranium content of the P. scarabaeoides zone increases in the same direction as the thickness, and kolm is present only where the shale is of maximum thickness and uranium content.

According to Eklund, the uranium content decreases sharply with small increases in CaCO_3 in the shale, just as we have observed in this country. The zone containing 0.02 percent uranium in the non-calcareous rocks in the heart of the field contains only 0.005 percent along the margin where the CaCO_3 content rises to about 1 percent, and the uranium drops to 0.002 percent as the CaCO_3 increases to 4 percent.

ORIGIN

The facts of the occurrence of uranium in the alum shale cited above suggest some speculations as to the environment of deposition of the shale, the factors influencing precipitation of uranium, and its present mode of occurrence in the shale. These speculations are presented here not as well documented conclusions but as ideas that may be worth testing in the study of uraniferous black shales.

The vertical sequence of rocks in the Cambrian and Lower Ordovician of Sweden is, from oldest to youngest, sandstone, glauconitic sandstone, black shales, chert (thin and not everywhere present), phosphatic and glauconitic beds, and limestone. Not as much is known of the lateral sequence but the Peltura shale at least passes into carbonatic and cherty beds laterally. This is roughly the same vertical and lateral sequence that is associated with many other black shale formations over the world (in southeastern Idaho, for example, the vertical sequence associated with the Phosphoria is sandstone, limestone, cherty limestone, phosphorite, carbonaceous mudstone, phosphorite, chert and limestone; the vertical sequence

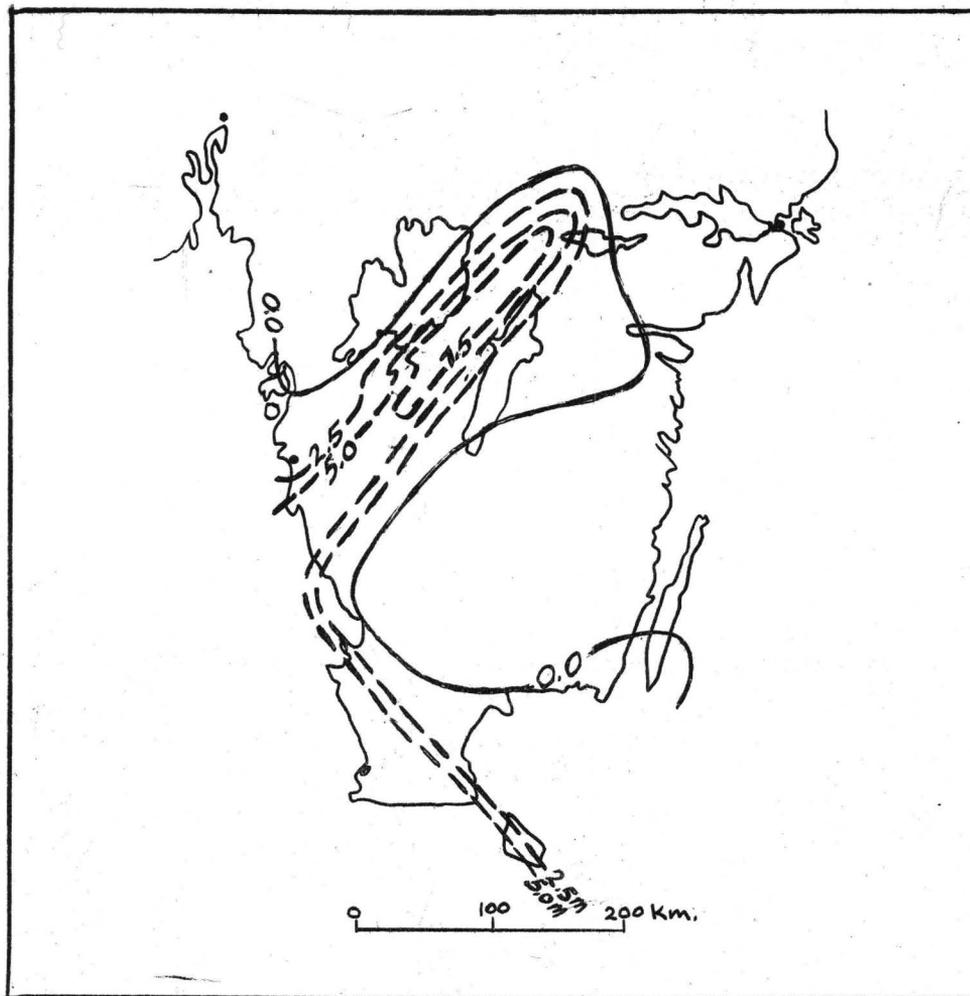


Figure 6. Map of southern Sweden showing areal variations in thickness of Peltura scarabaeoides zone of Upper Cambrian alum shale. The 0.0 line is from a sketch by Eklund; the 2.5 m and 5 m lines are after Bain.

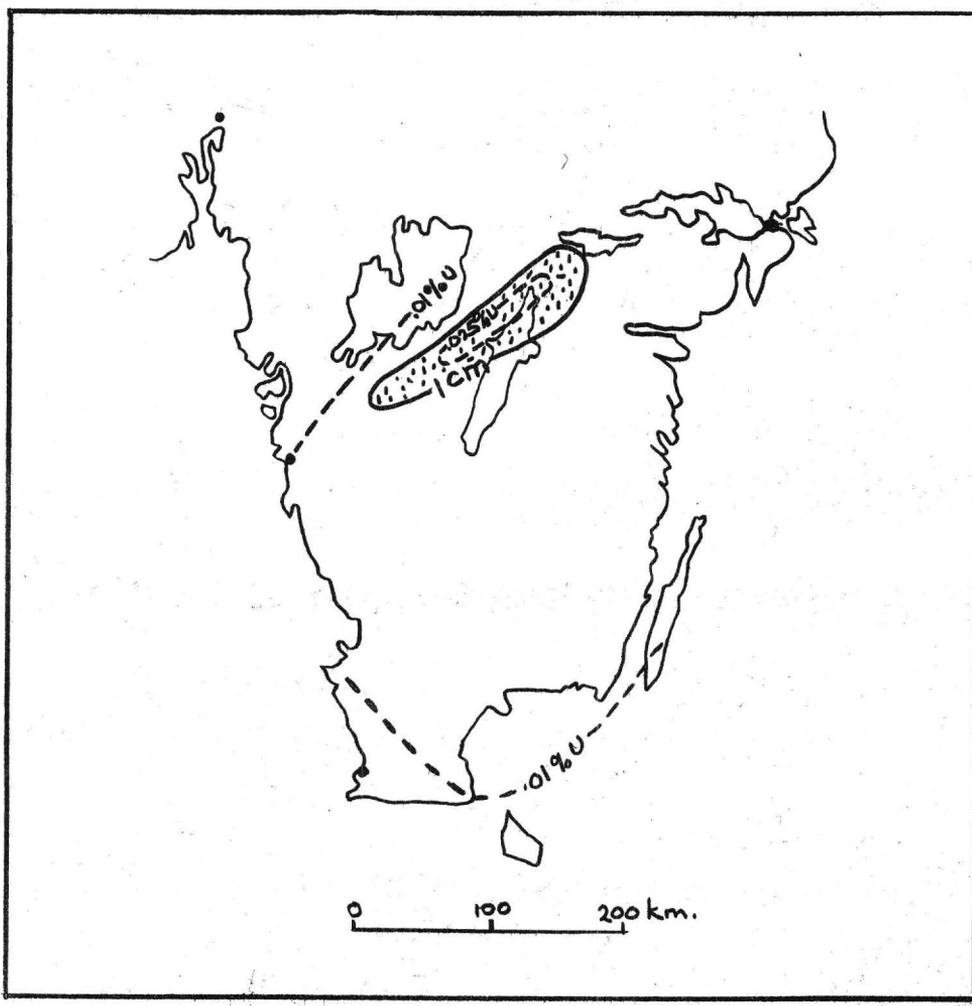


Figure 7. Map of southern Sweden showing uranium content (dashed line) of *Peltura scarabaeoides* zone of Upper Cambrian alum shale and area (stippled) containing more than 1 cm equivalent thickness of kolm lenses. Data on the uranium content are from Bain, those on the kolm content are from Eklund.

associated with the Chattanooga in parts of Tennessee is phosphatic sandstone, black shale, glauconitic phosphorite, and cherty limestone). The progressive lateral introduction of bioclastics, clastics, redbeds, and salines in the Phosphoria show clearly that the carbonaceous shale there is the deepest water facies. It seems likely that this is also true of the alum shale. The vertical sequence thus records a progressive depression of the sea bottom, followed by a gradual elevation of it. Just what range in depth this sequence represents is difficult to appraise. The range probably was different in different areas because of differences in the temperature, rate of circulation, and so forth. Nevertheless, comparisons with modern environments where such sediments are being deposited suggest that the shale accumulated at depths of 50 meters or more. (See, for example, papers by Gripenberg, Strøm, Trask and others in Recent Marine Sediments, Trask, 1939.)

The fact that the oil, total calorific value, sulfur, and uranium contents reach their maxima fairly close together near the middle of the shale sequence indicates they owe their origin to some common factors and that conditions favoring these factors ranged toward and then away from some optimum. Several physical and chemical factors, probably closely related as to cause, may have been involved but two may be singled out as important 1) depth of water and 2) low redox potential. Judging from the vertical and lateral sequence of rock types already discussed, it seems likely that the greatest concentrations of the above named constituents were deposited when the Upper Cambrian sea was at or near its greatest depth. All other conditions--e. g. the production of organic matter in the upper waters of the sea--being equal, the redox potential would decrease with increasing depth of water so that the two go hand in hand. But regardless of how reducing conditions were brought about--whether by increased depth of water or by increased production of plankton in the upper waters of the sea--the increase in the amount of hydrocarbons (see Brongersma-Sanders, 1948, 1951; Smith, 1952), total organic matter, and sulfides all suggest that the sediments of and closely adjacent to the Peltura zone were deposited under the most extreme reducing conditions of any in the sequence. Because uranium also is most concentrated in this zone, it may be concluded that its concentration is also favored by reducing conditions. Very likely this is not the only factor that controls or affects precipitation of uranium (e. g., many pyritic shales do not contain appreciable amounts of uranium) but that a low redox potential is an important factor seems clearly indicated by the position of uranium and its association with other substances in the sequence.

The concentration of uranium within the Peltura zone is highest in the northern embayment. This also suggests that its precipitation is effected by reducing conditions, for the bottom waters of such an embayment might well be restricted in their circulation, much as are those of the fiords in the same part of the world today.

The importance of reducing conditions in the precipitation of uranium in black shales was anticipated by Goldschmidt, who said (1954, p. 566): "Precipitation of uranium, however, might result from a reduction of hexivalent uranium to the quadrivalent stage by the action of hydrogen sulfide in stagnant bottom waters. . . . There is every reason to believe that the origin of the uranium in Swedish kolm is to be sought in the uranium content of sea water, precipitated under reducing conditions. . . . We may therefore expect the accumulation of the solute uranium from sea water by re-precipitation in areas where strongly reducing conditions prevail."

The fact that zones and areas of high concentrations of uranium and vanadium in the shales do not coincide indicates a significant difference in the chemistry of their precipitation. The mode of occurrence of high vanadium concentrations suggests precipitation at a higher redox potential than that favoring the precipitation of uranium; it is possible also that the difference may reflect pH control over the solubilities of salts of the two metals. Further analysis of the vertical sequence and association of these and other elements in this and similar sections might make it possible to assign quantitative values to pH, redox potential, and other factors controlling precipitation of various compounds.

The abundance of the highly-uraniferous kolm in the areas of maximum concentration of uranium and its rarity or absence elsewhere suggests that the uranium is carried by the dark kolm-like substance in the matrix. The fact that bedding can be traced into the kolm lenses indicates that the latter were formed shortly after the deposition of the enclosing rocks. It seems likely that the lenses may represent the aggregation of smaller, dispersed globules of the substance, possibly under the stimulus of compaction of the enclosing sediment. The abundance of megascopic lenses may thus reflect an abundance of similar particles too small to be seen by the unaided eye. And, since the large lenses of kolm contain 0.45 percent

uranium, it is easy to imagine that similar amounts of uranium in smaller, dispersed particles of the same substance might account for the remainder of the uranium in the shale. Only about 4 percent of the matrix would need to be kolm to account for the uranium content of the shale.

The exact form in which the uranium is present in the kolm or how it got there is unknown. Gott and Erickson (1952) have suggested that uranium and other metals are held in organic compounds, possibly like the porphyrins, and may thus be transported as a part of hydrocarbon compounds. (See also Goldschmidt, 1954, p. 497.) Possibly the uranium was concentrated in the parent compounds of the kolm particles during the life of the organisms that produced them or possibly the uranium was extracted from the matrix by the kolm itself during the process of its migration from the matrix to the lenses in which it is now found. Plainly the heart of this problem is the kolm itself--what is it, how does it differ from the yellow kerogen, and how did it originate. Whatever the origin, the presence of uranium in the kolm and its absence in the natural petroleum coke, which is rich in vanadium, shows a difference in the affinity uranium and vanadium bear for different types of hydrocarbons.

SUGGESTIONS FOR PROSPECTING

The uranium in the alum shales of Sweden was most concentrated in an embayment of the Upper Cambrian sea. The association of the maximum concentration of uranium with maxima of oil and total organic matter in the vertical sequence and with a near maximum of pyrite indicates that, among the factors that control the precipitation of uranium, low redox potential in the seabottom environment may be of particular importance.

It would seem appropriate, therefore, to search for and test portions of black shales in this country that might have been deposited under conditions of very low redox potential, as judged both by paleogeographic relationships and the sequence of rocks and component constituents in vertical sections. It is well to recall, in such a search, that the highly uraniferous part of the Peltura shale in Sweden occupies an area only about 100 miles long and 20 miles in maximum width and that the highly uraniferous beds are only a few feet thick. Zones of this thickness and areal extent could be easily overlooked in some of our black shale formations.

LITERATURE CITED

- Brongersma-Sanders, M., 1948, The importance of upwelling water to vertebrate paleontology and oil geology: *Verhandelingen der Koninklijke-Nederlandsche Akademie van Wetenschappen*, Afd. Natuurkunde, Tweede Sectie, Deel XLV, no. 4.
- _____, 1951, On conditions favouring the preservation of chlorophyll in marine sediments: *Third World Petroleum Cong.*, v. 1, p. 401-414.
- Goldschmidt, V. M., 1954, *Geochemistry*: Clarendon Press, Oxford.
- Gott, G. B., and Erickson, R. E., 1952, Reconnaissance of uranium and copper deposits in parts of New Mexico, Colorado, Utah, Idaho, and Wyoming: *U. S. Geol. Survey Circ.* 219.
- Munthe, H., Westergard, A. H., and Lundquist, G., 1938, Beskrivning till Karbladet Skövde, Sveriges Geol. Undersökning, Ser. As Karblad i skalan 1:50,000 med Beskrivningar no. 121.
- Smith, P. U., Jr., 1952, The occurrence of hydrocarbons in recent sediments from the Gulf of Mexico: *Science*, v. 116, p. 437-439.
- Trask, P. D., 1939, *Recent marine sediments*: Am. Assoc. Petroleum Geologists, Tulsa, Oklahoma.
- Westergard, A. H., 1944a, Borringar genom Skaves alunskiffer 1941-1942: *Sveriges Geol. Undersökning, ser. c.*, no. 459.
- _____, 1944b, Borringar genom alunskiffer-lagret på Oland och i Ostergötland 1943: *Sveriges Geol. Undersökning, ser. c.*, no. 463.

UNPUBLISHED REPORT

- Bain, George, 1946, Uranium distribution in Sweden: *U. S. Atomic Energy Comm.* RMO-663.