SVERIGES GEOLOGISKA UNDERSÖKNING

SERIE C NR 818 AVHANDLINGAR OCH UPPSATSER ÅRSBOK 81 NR 4

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MINERALOGY AND MATURITY OF THE ALUM SHALES OF SOUTH-CENTRAL JÄMTLAND SWEDEN

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ABSTRACT

Snäll, S.: Mineralogy and maturity of the alum shales of south-central Jämtland, Sweden. Sveriges geologiska undersökning, Ser. C. No 118, pp. 1–46, Uppsala 1988.

The mineralogy and major elements of the alum shales of Middle and Late Cambrian age of the Caledonian front of Jämtland have been investigated. Drillcore material from Klövsjö, Myrviken and Häggenås has been used for the study, which included shales in both the autochthon and allochthon.

The Alum Shale Formation is composed of shales and subordinate stinkstones. The shale component is made up mainly of illite, quartz, organic matter and pyrite. Calcite may be present in variable amounts. Illite and quartz are the predominant silicates. Subordinate K-feldspar occurs in the Upper Cambrian and chlorite in the Middle Cambrian shales. Trace elements, including uranium, vanadium and molybdenum are also significant.

The shales show different degrees of alteration, the allochthonous units being more thermally mature than those in the autochthon. These differences were established prior to or during thrust emplacement of the allochthon.

The alteration of the silicates resulted in the illites becoming better crystallized; new polymorphs were developed. This alteration also led to an increase in the grain size of quartz. The organic matter changed in composition by reduction of the H/C ratio. Authigenic K-feldspar, formed in the main parts of the Upper Cambrian shales prior to the regional alteration, was little influenced by the latter.

The variety of methods used to investigate the maturity of the shales provides a basis for estimating the temperature of thermal alteration. However, the methods yield considerably different results. Based on illite chrystallinity a palaeotemperature between a lower limit of ca. 250–280° C and an upper limit of ca. 350–400° C is suggested for the most altered shales, which occur in the Myrviken allochthon; that is in the anchizone. Other methods suggest somewhat lower temperatures. In the case of the autochthonous Myrviken shales and the samples from Klövsjö and Häggenås, the degree of alteration probably did not exceed the upper zone of late diagenesis.

Key words: *Black alum shales, mineralogy, chemistry, maturity, diagenesis, metamorphism, Cambrian, Jämtland, central Sweden.*

INTRODUCTION

The Alum Shale Formation is dominated by organic-rich shales of Middle Cambrian to Early Ordovician age. The shales are also characterized by anomalously high contents of uranium and certain other trace elements (Eklund 1961, Armands 1972, Hessland & Armands 1978, Andersson *et al.* 1983; Andersson *et al.* 1985). The occurrence of alum shales in Sweden is shown in Fig. 1. They are thought to have been deposited in a shallow epicontinen-

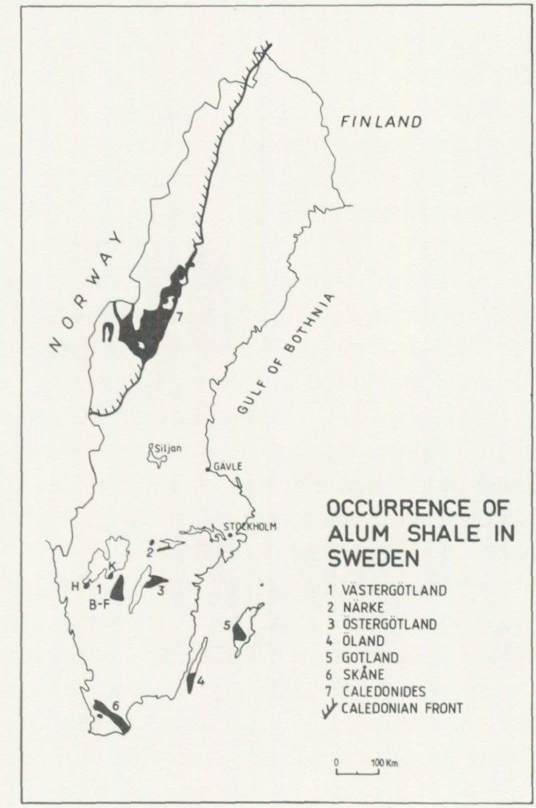


Fig. 1. Occurrence of alum shale in Sweden. The investigated area is found in the southern part of the dark screened region in the Caledonides (from Andersson *et al.* 1985).

tal sea, the bottom waters of which were reducing; strongly reducing during the Late Cambrian. It is considered that the shales originated from a calcium poor marine sapropel (Armands 1972).

These organic-rich shales are Sweden's major reserve of fossil energy and constitute the largest low-grade source of uranium in Europe (Hessland & Armands 1978; Andersson *et al.* 1983). The quantities of the shales vary from one region to another. In southern Sweden, the Alum Shale Formation is usually not thicker than 10–20 m (Westergård 1940, 1941, 1943, 1944a; Andersson *et al.* 1985) except in Skåne where the formation is ca. 80–95 m (Westergård 1944b; Andersson *et al.* 1985). In the Caledonides, however, organic carbon and trace element rich alum shales may reach a thickness of about 200 m (Asklund 1938; Andersson *et al.* 1985) by tectonic repetition of the strata. Within the formation, the organic carbon and trace element contents vary considerably; usually the Upper Cambrian shale is richest in these elements. The *Peltura* zones have the highest uranium concentrations; those in the Billingen–Falbygden area contain ca. 300 ppm over a thickness of 2–4.5 m (Andersson *et al.* 1985). The shales richest in organic matter are found in Närke; they contain as much as ca. 25 % by weight. These shales and those on Kinnekulle have been mined for oil extraction (Sundius 1941), some sections yielding, on distillation, up to 6–7 % (Fischer Assay, Westergård 1943).

The organic matter maturation in the alum shales can be related to the different stages of oil generation (Tissot & Welte 1978). In Skåne and in the Caledonides, the organic matter of the alum shales is more mature and yields no oil. The differences in the character of the organic matter has resulted from varying thermal histories. A palaeotemperature of <90° C has been estimated for the Ordovician limestone overlying the alum (oil) shales of Närke, Östergötland and Öland on the basis of conodont colour alteration (Bergström S. M. 1980). The alum shales of Billingen–Falbygden, Västergötland, are slightly more mature, having been affected thermally by dolerite intrusion. Even more altered are the shales in the eastern nappes of the Caledonides for which a palaeotemperature of about 300° C has been estimated (Bergström S. M. 1980 and Kisch 1980).

As previously mentioned, the alum shales of Jämtland are highly thermally altered and the organic matter is over-mature as regards hydrocarbon generation (Tissot & Welte 1978). The organic matter appears to be similar to that in highrank coals, although macerals (organic debris) characteristic of coals are not present. (Only primitive vegetation existed during Cambrian times.) Therefore, in the present study the maturation of the organic matter is considered equivalent to certain coal ranges. By using the terminology of coal petrology, comparison with Kisch (1980) and data in Andersson *et al.* (1985) is facilitated.

Characterizaton of organic matter in terms of coal petrology permits a subdivision into several stages, even at very high maturation levels, up to graphite. A chart correlating coal rank with hydrocarbon generation stages is given by Heroux *et al.* (1979).

Thermal alteration involved recrystallization of minerals and at least partial redistribution of trace elements. Essential to all considerations regarding the exploitation of the shales, is an understanding of the influence of the recrystallization process on the redistribution of the trace elements. In the case of uranium, the occurrence is very complex (Armands 1972 and Edling 1974); a subordinate part may be bound in the organic matter. 80–85 % of the total uranium in the Billingen shales may be extracted by acid leaching (Armands 1972); by same process about 90 % can be obtained from the Caledonian shales (ASA, unpublished report, Ch. Svemar, pers. comm.). Other trace elements also seem to be more easily extracted from the latter. The greater thermal alteration has apparently resulted in redistribution of the trace elements.

The mineralogy of the Swedish alum shales has been treated earlier by

Strahl (1958) and Bates *et al.* (1958) in their studies of black shales from various parts of the world. Their mineralogy was also studied by Assarsson & Grundulis (1961) in shales from Närke and by Armands (1972) in his thesis on the alum shales of Billingen, Västergötland.

Kisch (1980) included alum shales in his work on the incipient metamorphism of Cambro-Silurian clastic rocks from Jämtland. He measured illite crystallinity and reflectance from organic debris in the shales and was able to distinguish four zones of illite crystallinity within the lower nappes of the Scandinavian Caledonides. The crystallinity increased westwards towards the thrust front of the overlying, more highly metamorphosed allochthonous units. The reflectance measurements gave less distinct results but the easternmost illite zone was readily distinguishable. Titanium minerals differed in the various zones; in the westernmost areas only rutile was identified, while in samples from the eastern areas anatase was also present.

On the Norwegian part of the Baltic Shield, in the Oslo region, the depositional history and geochemical composition of the Lower Palaeozoic epicontinental sediments were studied by Bjørlykke (1974). This study included some information on the chemistry of the alum shale sequence.

The black alum shales of south-central Jämtland county were explored by the Geological Survey of Sweden during the latter part of the 1970s (1977–1979). An extensive drilling programme provided the basis for analysis of the regional variations of the shales, which were analysed for organic carbon content, uranium, vanadium, molybdenum, and in some cases sulphur and phosphorus. The results of these investigations have been presented in several unpublished Survey reports. In addition to the analyses referred to above, one aspect of the investigations involved study of the major element chemistry of the shales and their mineralogy (Snäll 1981). In the latter report, the research aimed at establishing the varying degrees of alteration of the shales and elucidating their mineralogical effects. Some additional laboratory work was done later which has been included in the present paper.

The geology of the study area in Jämtland (Fig. 2) has been described by Thorslund (1940) and summarized by Gee & Zachrisson (1979) and Gee & Kumpulainen (1980); it is also a part of the recent map of the Jämtland county (Lundegårdh *et al.* 1984). The study area is situated along the Caledonian thrust front, where the lower nappes are thrust over the autochthonous Cambrian to Silurian sedimentary rocks which unconformably overlie the Precambrian crystalline basement. The autochthonous sedimentary rocks dip gently (about 2°) westwards underneath the nappes.

The Middle and Upper Cambrian shales of Scandinavia have been referred to as the Alum Shale Formation (Gee 1972, Andersson *et al.* 1985). The formation contains shales from dark grey to black in colour. The autochthonous Alum Shale Formation either rests directly on the crystalline basement or is

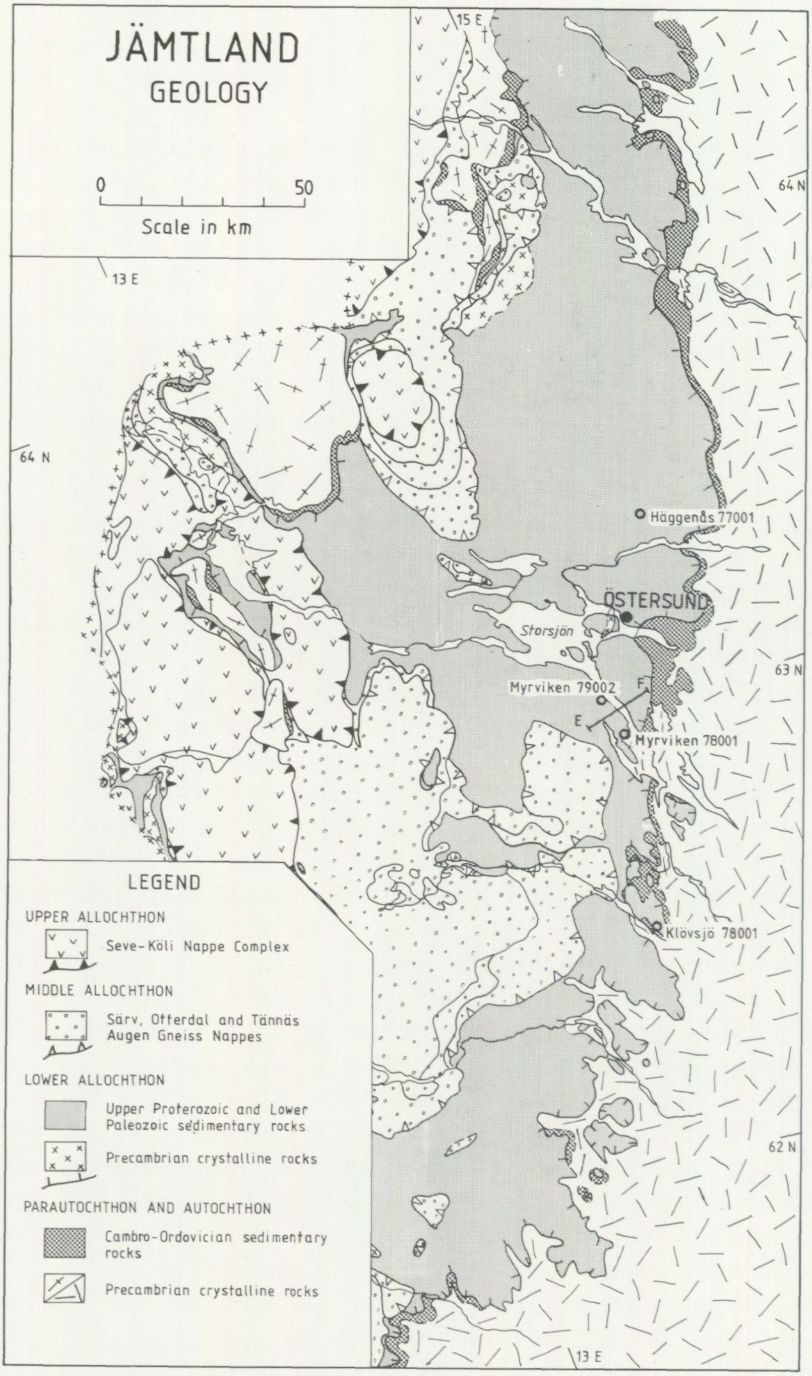


Fig. 2. Geological map of Jämtland (after Gee & Wolff 1981). The sites of the drillcores investigated in the present study are plotted on the map.

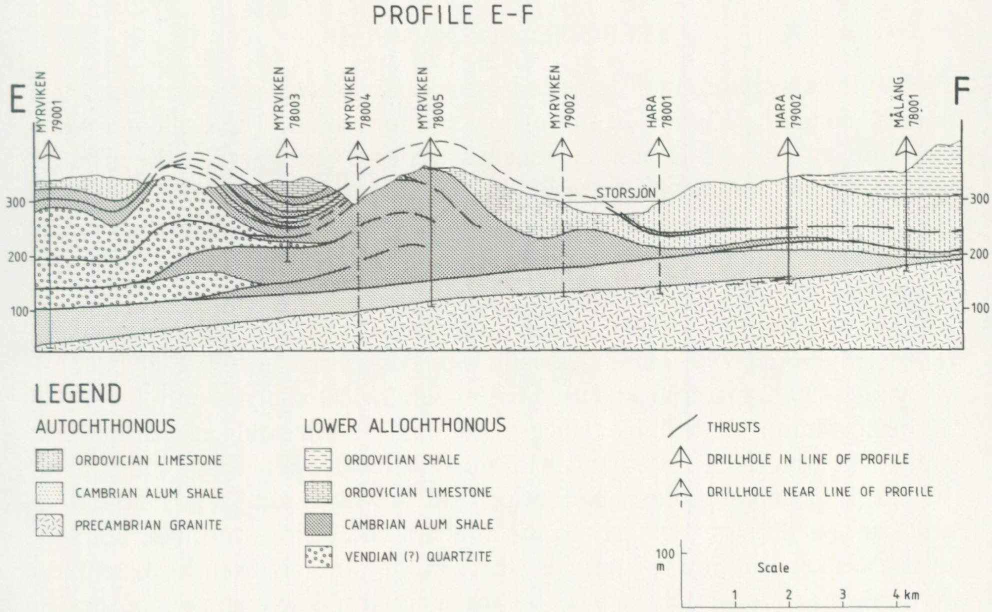


Fig. 3. Profile E–F (cf. Fig. 2) through the Caledonian front in Jämtland illustrating the development of the rocks in the investigated area (from Gee *et al.* 1982a).

underlain by a few decimetres to metres of arkosic sandstone. The allochthonous alum shales are stratigraphically underlain by several tens of metres of quartzite. At least locally, the formation contains units of Tremadoc age which are overlain by Ordovician *Ceratopyge* limestone (Bergström, J. 1980). As a result of thrusting, the Alum Shale Formation may be directly overlain /underlain by other formations comprising the nappes (Fig. 3).

THE JÄMTLAND INVESTIGATIONS

The regional prospecting programme provided an extensive drillcore coverage of the Alum Shale Formation in south-central Jämtland. This allowed selection of specific cores for closer study of the mineralogy and whole rock chemistry. Core material was selected to provide information on both the autochthonous and allochthonous shales.

SELECTION OF SAMPLES

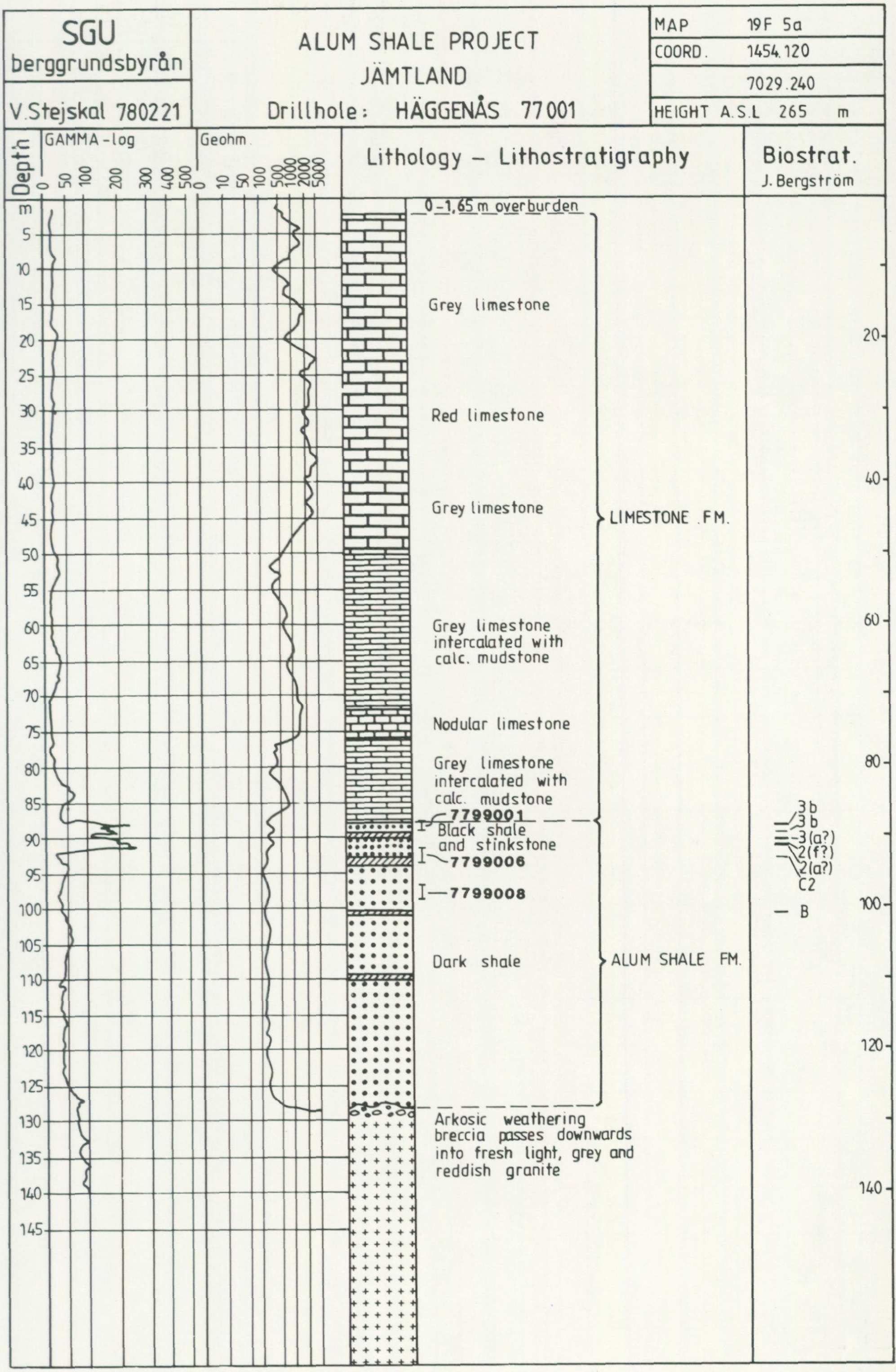
The samples were originally selected for analysis of organic carbon and the trace elements U, V and Mo throughout the formation. The drillcores were therefore cut into 1.5–2 m homogeneous sections. Carbonate in the form of stinkstones and calcite veins was eliminated as far as possible from the shales prior to analysis. This material was subsequently used for the mineralogical studies. A full description of sampling and the methods of analysis is given in Appendix I.

For the analyses, material from four drillcores (Häggenås 77001, Myrviken 78001, Myrviken 79002 and Klövsjö 78001) was chosen (cf. Fig. 2). The Myrviken 79002 material was used for mineralogical analysis only.

The northernmost drillhole (Häggenås 77001) contains only autochthonous strata. The Myrviken 79002 and Klövsjö 78001 holes penetrate both allochthonous and autochthonous formations. In the Myrviken 78001 hole, the strata analysed belong entirely to the allochthon. Sections through the rock units are shown in Fig. 4. Intervals where more minutely examined samples were taken are separately marked in the diagrams. The available biostratigraphical data are shown to the right in the diagrams, as reported by J. Bergström (Gee & Snäll 1981, Gee *et al.* 1982a, 1982b); biostratigraphical abbreviations refer to Fig. 5.

15 samples were chosen for the more detailed studies; 13 from the Upper Cambrian and two from the Middle Cambrian. Three samples were selected from the Häggenås 77001 core and also from the Klövsjö 78001 core, five from the Myrviken 78001 core and four from the Myrviken 79002 core. The Middle Cambrian shale samples were selected in the autochthon of the Häggenås 77001 core and in the allochthon of the Myrviken 78001 core (cf. Fig. 4). The samples were selected on the basis of tectonic, stratigraphical, lithological, mineralogical and trace element criteria. They were chosen to give a broad representation of the shales; thus samples with both high and with low contents of elements such as Al, Fe, U and V were selected, as well as feldspathic and non-feldspathic units. Where biostratigraphic control was available a sample was taken close above the Middle-Upper Cambrian boundary. The dominance of Upper Cambrian shales among the selected samples is due to the greater economic interest in these units.

Fig. 4. Sections with various data of the investigated cores. Intervals from which the samples were taken for mineralogical studies are marked on the diagrams (from Gee & Snäll 1981 and Gee *et al.* 1982a, 1982b).


SGU
berggrundsbyrån
V.Stejskal 780221
ALUM SHALE PROJECT
JÄMTLAND
Drillhole: HÄGGENÅS 77001
MAP 19F 5a
COORD. 1454.120
7029.240
HEIGHT A.S.L 265 m
Depth
m
GAMMA-log
0 50 100 200 300 400 500
Geohm.
0 10 50 100 500 1000 2000 5000
Lithology – Lithostratigraphy
Biostrat.
J. Bergström
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145
0–1,65 m overburden
Grey limestone
Red limestone
Grey limestone
LIMESTONE FM.
Grey limestone intercalated with calc. mudstone
Nodular limestone
Grey limestone intercalated with calc. mudstone
7799001
Black shale and stinkstone
7799006
7799008
Dark shale
ALUM SHALE FM.
Arkosic weathering breccia passes downwards into fresh light, grey and reddish granite
3 b
3 b
3 (a?)
2 (f?)
2 (a?)
C2
B
20
40
60
80
100
120
140

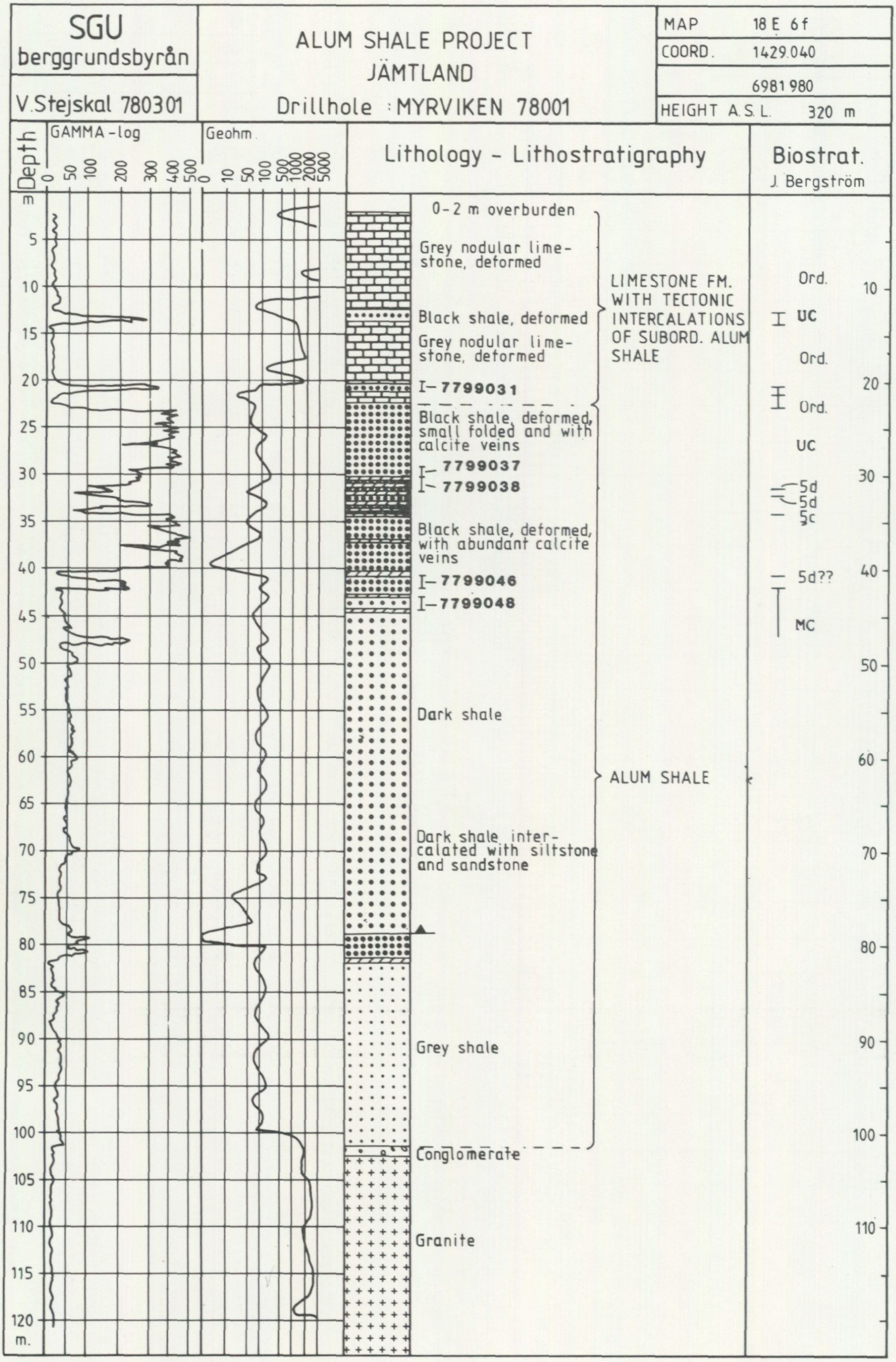

SGU
berggrundsbyrån
V.Stejskal 780301
ALUM SHALE PROJECT
JÄMTLAND
Drillhole : MYRVIKEN 78001
MAP 18 E 6f
COORD. 1429 040
6981 980
HEIGHT A.S.L. 320 m
Depth m
GAMMA-log
0 50 100 200 300 400 500
Geohm.
0 10 50 100 500 1000 2000 5000
Lithology - Lithostratigraphy
Biostrat.
J. Bergström
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 m.
0-2 m overburden
Grey nodular limestone, deformed
Black shale, deformed
Grey nodular limestone, deformed
I-7799031
Black shale, deformed, small folded and with calcite veins
I-7799037
I-7799038
Black shale, deformed, with abundant calcite veins
I-7799046
I-7799048
Dark shale
Dark shale intercalated with siltstone and sandstone
Grey shale
Conglomerate
Granite
LIMESTONE FM. WITH TECTONIC INTERCALATIONS OF SUBORD. ALUM SHALE
ALUM SHALE
Ord.
UC
Ord.
Ord.
UC
5d
5d
5c
5d??
MC
10 20 30 40 50 60 70 80 90 100 110

Fig. 4 cont.

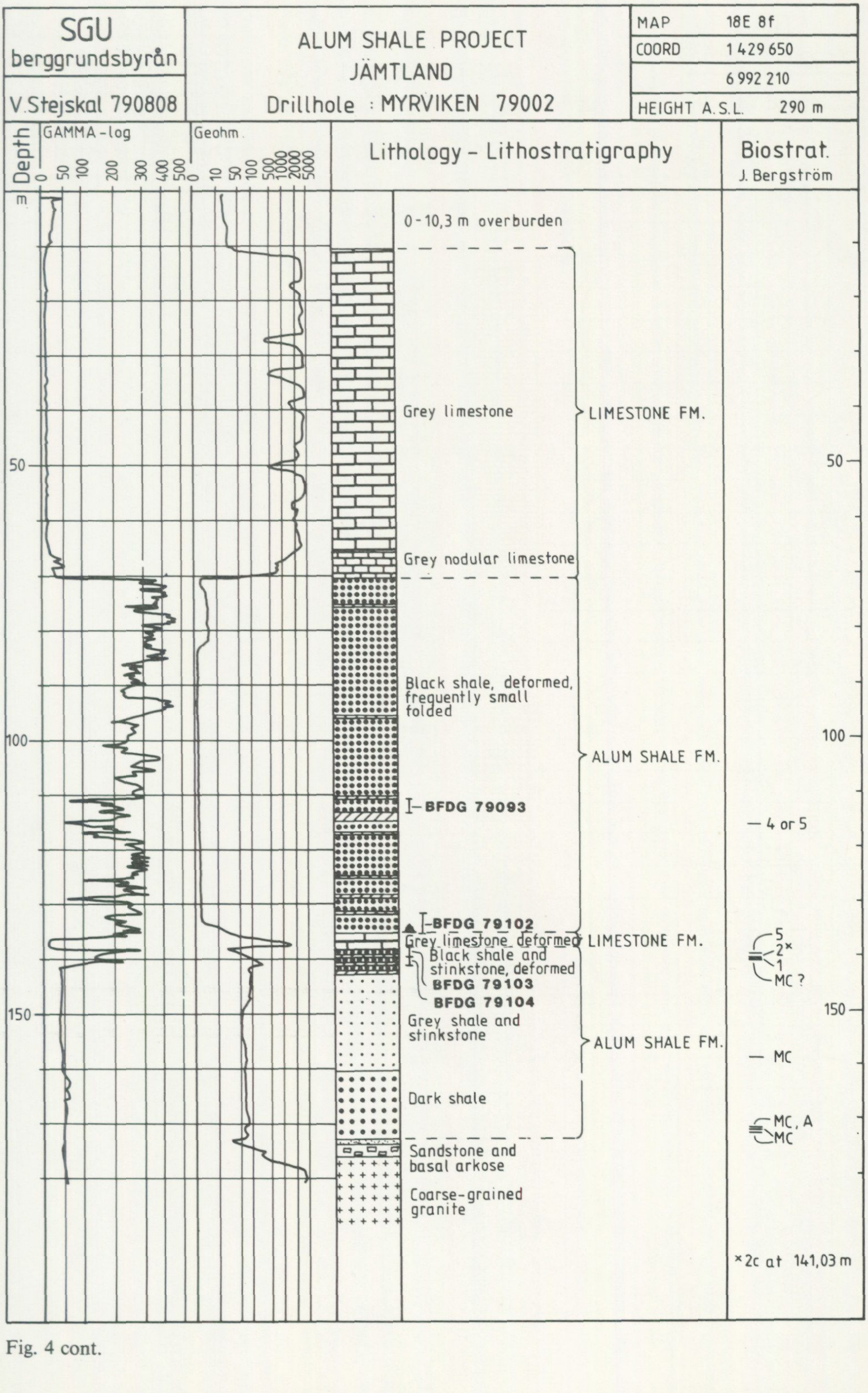

SGU
berggrundsbyrån
V.Stejskal 790808
ALUM SHALE PROJECT
JÄMTLAND
Drillhole : MYRVIKEN 79002
MAP 18E 8f
COORD 1 429 650
6 992 210
HEIGHT A.S.L. 290 m
Depth
m
GAMMA-log
0 50 100 200 300 400 500
Geohm
0 10 50 100 500 1000 2000 5000
Lithology - Lithostratigraphy
Biostrat.
J. Bergström
0-10,3 m overburden
Grey limestone
LIMESTONE FM.
Grey nodular limestone
Black shale, deformed, frequently small folded
ALUM SHALE FM.
BFDG 79093
BFDG 79102
Grey limestone deformed
LIMESTONE FM.
Black shale and stinkstone, deformed
BFDG 79103
BFDG 79104
Grey shale and stinkstone
ALUM SHALE FM.
Dark shale
Sandstone and basal arkose
Coarse-grained granite
50
100
150
4 or 5
5
2×
1
MC ?
MC
MC, A
MC
×2c at 141,03 m

Fig. 4 cont.

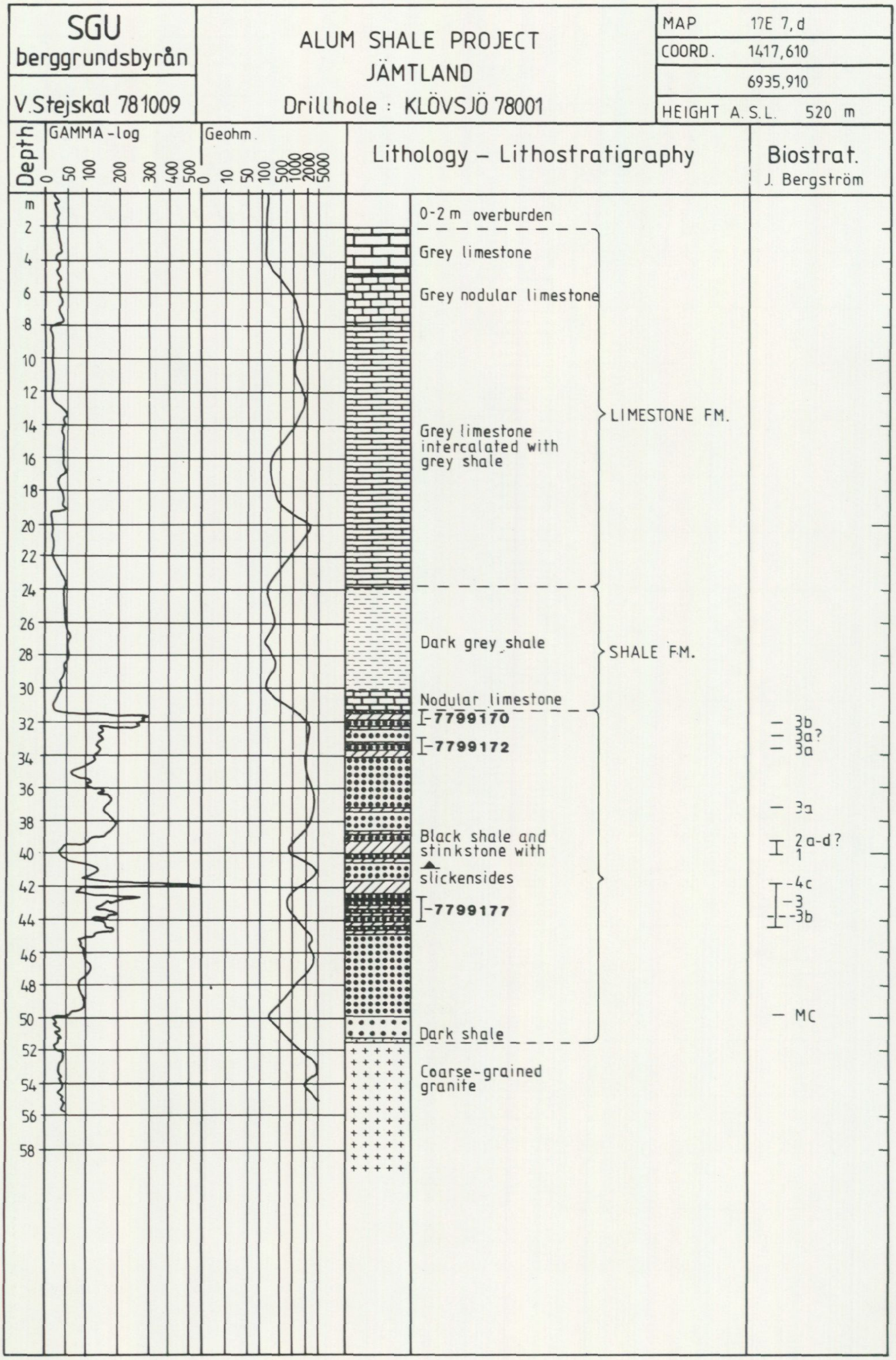
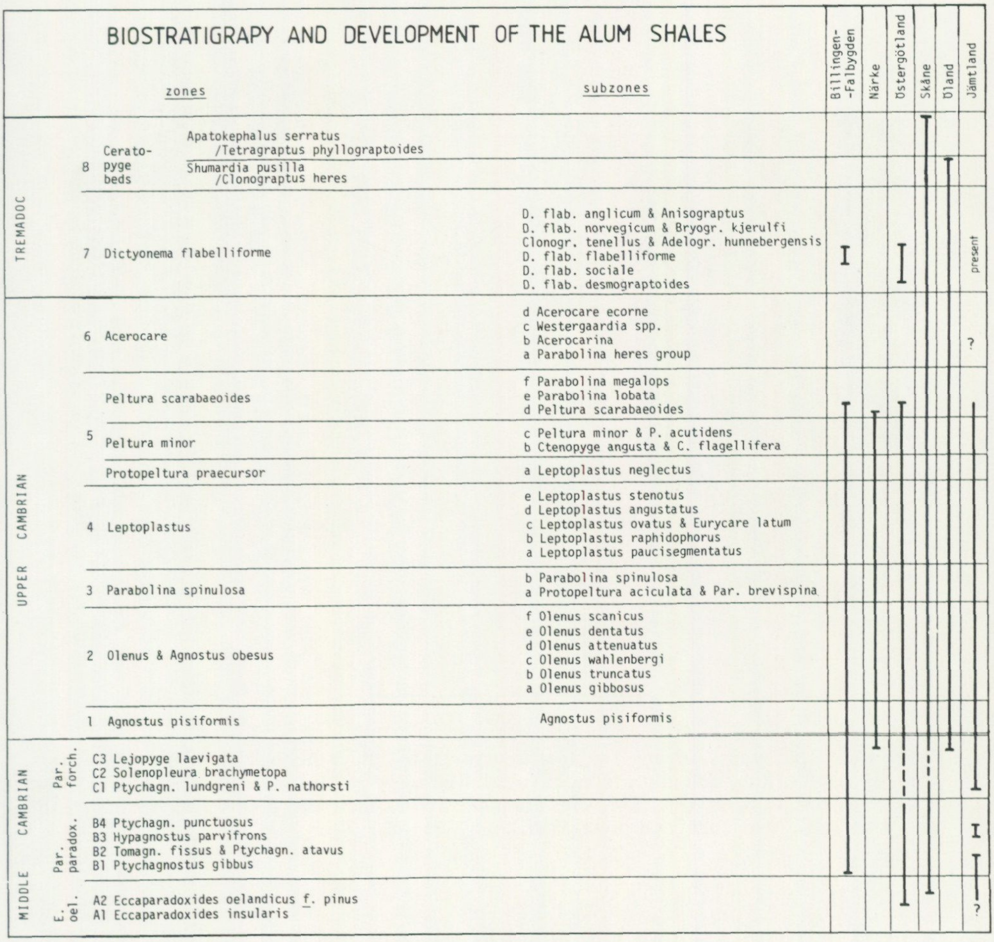

SGU
berggrundsbyrån
V.Stejskal 781009
ALUM SHALE PROJECT
JÄMTLAND
Drillhole : KLÖVSJÖ 78001
MAP 17E 7,d
COORD. 1417,610
6935,910
HEIGHT A.S.L. 520 m
Depth
GAMMA-log
0 50 100 200 300 400 500
Geohm.
0 10 50 100 500 1000 2000 5000
Lithology – Lithostratigraphy
Biostrat.
J. Bergström
m 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58
0-2 m overburden
Grey limestone
Grey nodular limestone
Grey limestone intercalated with grey shale
LIMESTONE FM.
Dark grey shale
SHALE FM.
Nodular limestone
-7799170
-7799172
Black shale and stinkstone with slickensides
-7799177
Dark shale
Coarse-grained granite
3b
3a?
3a
3a
2a-d?
1
-4c
-3
-3b
MC

Fig. 4 cont.



BIOSTRATIGRAPY AND DEVELOPMENT OF THE ALUM SHALES

		zones	subzones
TREMADOC	8	Cerato-pyge beds	Apatokephalus serratus /Tetragraptus phyllograptoides Shumardia pusilla /Clonograptus heres
	7	Dictyonema flabelliforme	D. flab. anglicum & Anisograptus D. flab. norvegicum & Bryogr. kjerulfi Clonogr. tenellus & Adelogr. hunnebergensis D. flab. flabelliforme D. flab. sociale D. flab. desmograptoides
UPPER CAMBRIAN	6	Acerocare	d Acerocare ecorne c Westergaardia spp. b Acerocarina a Parabolina heres group
	5	Peltura scarabaeoides	f Parabolina megalops e Parabolina lobata d Peltura scarabaeoides
		Peltura minor	c Peltura minor & P. acutidens b Ctenopyge angusta & C. flagellifera
		Protopeltura praecursor	a Leptoplastus neglectus
	4	Leptoplastus	e Leptoplastus stenotus d Leptoplastus angustatus c Leptoplastus ovatus & Eurycare latum b Leptoplastus raphidophorus a Leptoplastus paucisegmentatus
	3	Parabolina spinulosa	b Parabolina spinulosa a Protopeltura aciculata & Par. brevispina
	2	Olenus & Agnostus obesus	f Olenus scanicus e Olenus dentatus d Olenus attenuatus c Olenus wahlenbergi b Olenus truncatus a Olenus gibbosus
	1	Agnostus pisiformis	Agnostus pisiformis
MIDDLE CAMBRIAN	Par. forch.	C3 Lejopyge laevigata C2 Solenopleura brachymetopa C1 Ptychagn. lundgreni & P. nathorsti	
	Par. paradox.	B4 Ptychagn. punctuosus B3 Hypagnostus parvifrons B2 Tomagn. fissus & Ptychagn. atavus B1 Ptychagnostus gibbus	
	E. oel.	A2 Eccaparadoxides oelandicus f. pinus A1 Eccaparadoxides insularis	

Fig. 5. Middle and Upper Cambrian and Lower Ordovician biostratigraphy and the development of the alum shale facies in Sweden (from Bergström & Gee 1985).

DESCRIPTION OF LITHOLOGIES

Within the Alum Shale Formation of the investigated area, the following three main varieties of shale occur:

1) A grey, light to dark, frequently silty shale of Middle Cambrian age. It is found both in the allochthon and autochthon. One sample from the former (Myrviken 78001) and one from the latter (Häggenås 77001) were selected for further investigations.

2) A black, medium laminated (Potter *et al.* 1980), organic-rich shale with lenses and beds of limestone (stinkstone). In certain places, the shale contains thin veins (usually less than one millimetre in thickness) of calcite and/or

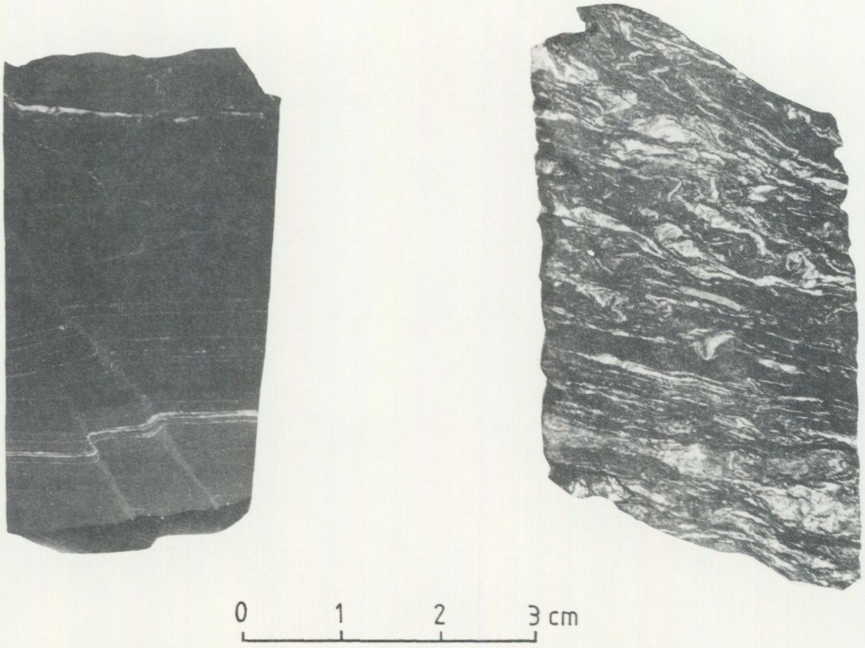


Fig. 6. Rock specimens showing the structure typical of autochthonous (left; Häggenås 77001, depth 89.10–89.18 m) and allochthonous (right; Myrviken 78001, depth 34.91–34.96 m) shale of the Southern Storsjön Area. The veins are made up of calcite and pyrite. The specimen from the allochthon is particularly carbonate-rich.

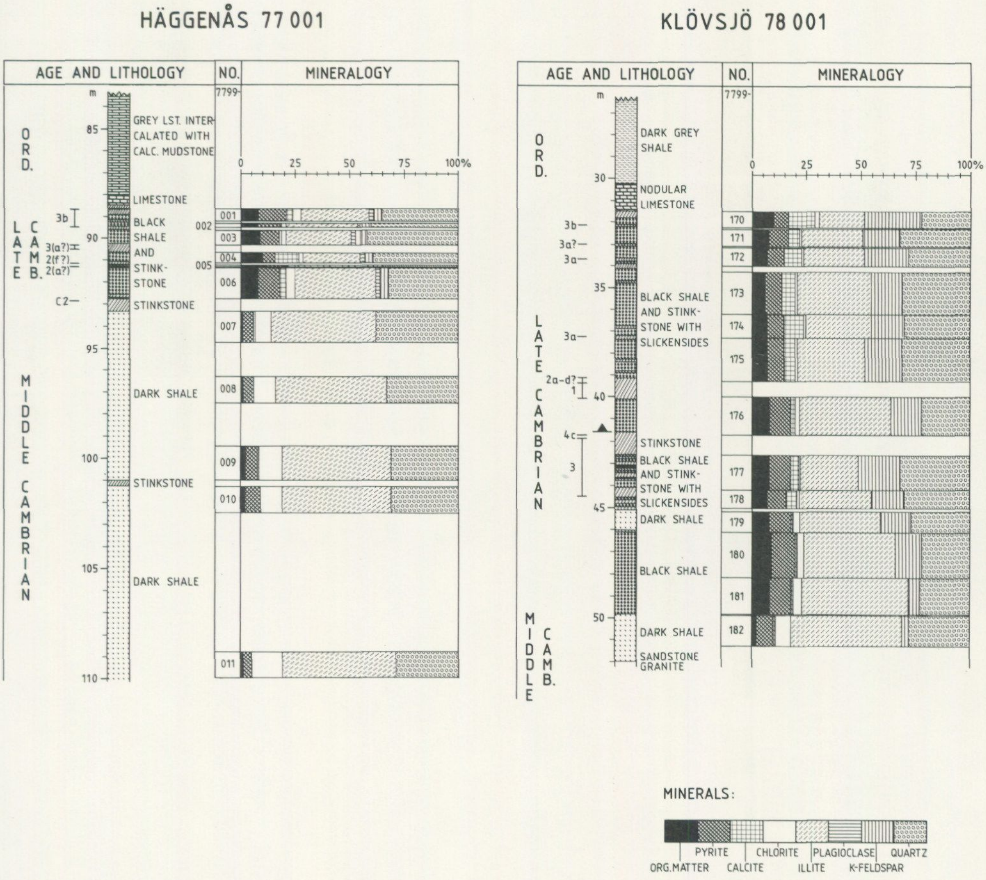
pyrite (Fig. 6, left). This shale is autochthonous and of Late Cambrian age. Samples of this type of lithology were selected from Häggenås 77001 and Myrviken 79002.

3) A black, fissile and extensively slickensided shale with lustrous partings and subordinate stinkstone lenses. This shale is allochthonous and of Late Cambrian age. It is usually small-folded and penetrated by irregular veins of calcite and/or pyrite (Fig. 6, right). Samples of this type of lithology were selected from the Myrviken drillcores. The allochthonous Klövsjö units, although slickensided, are less extensively veined and small-folded than the Myrviken shales and thus, to some extent, overlap with category 2.

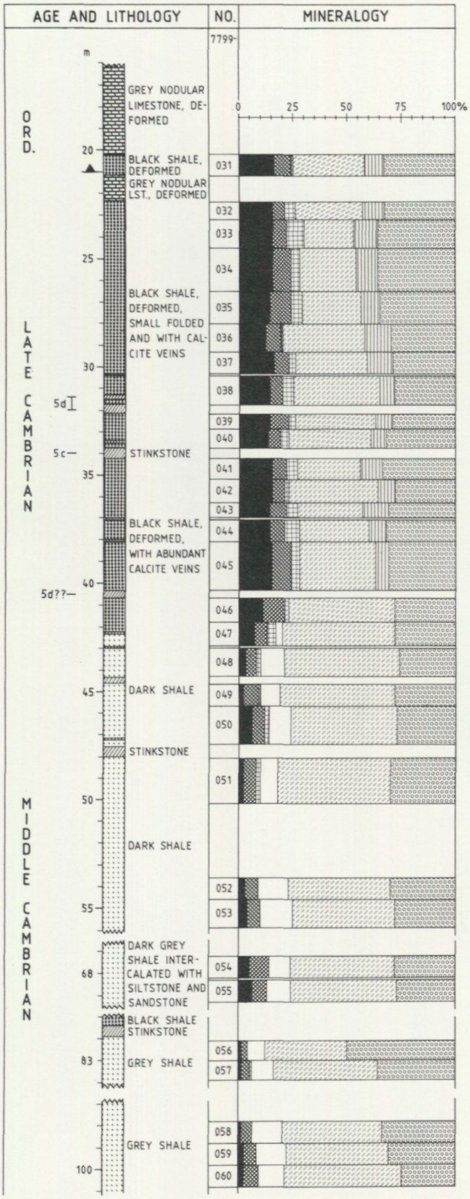
It is probable that the beds and lenses of stinkstone and disseminated carbonates originally present in the autochthonous shales have recrystallized in the allochthon, providing the source of the irregular calcite veins. Likewise, the pyrite veins apparently originated from pre-existing fine-grained disseminations in the shales.

FIGURE ELUCIDATION

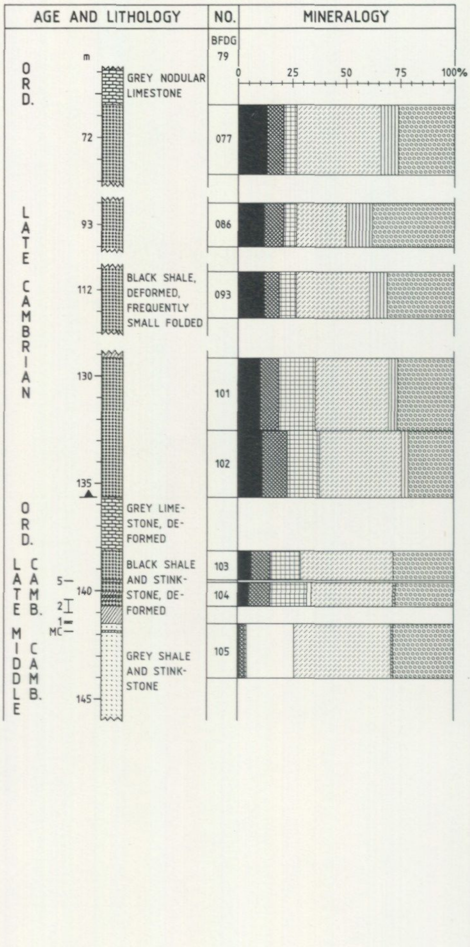
Snäll, S.: Mineralogy and maturity of alum shales.....
Due to a printing problem, Fig 7 on pages 17 and 18 is presented as a separate sheet.



MYRVIKEN 78 001



MYRVIKEN 79 002



RESULTS

WHOLE ROCK MINERALOGY AND CHEMISTRY

The results of the semi-quantitative mineral analysis (cf. Appendix I) of the whole rock samples are presented in Fig. 7. By means of XRD analysis, the following minerals were identified: quartz, feldspar, illite, chlorite, pyrite and calcite. Organic matter was obtained from the chemical analysis.

Quantitative determinations of the silicates were done in nine of the Upper Cambrian shale samples, viz. in those where major element analyses were

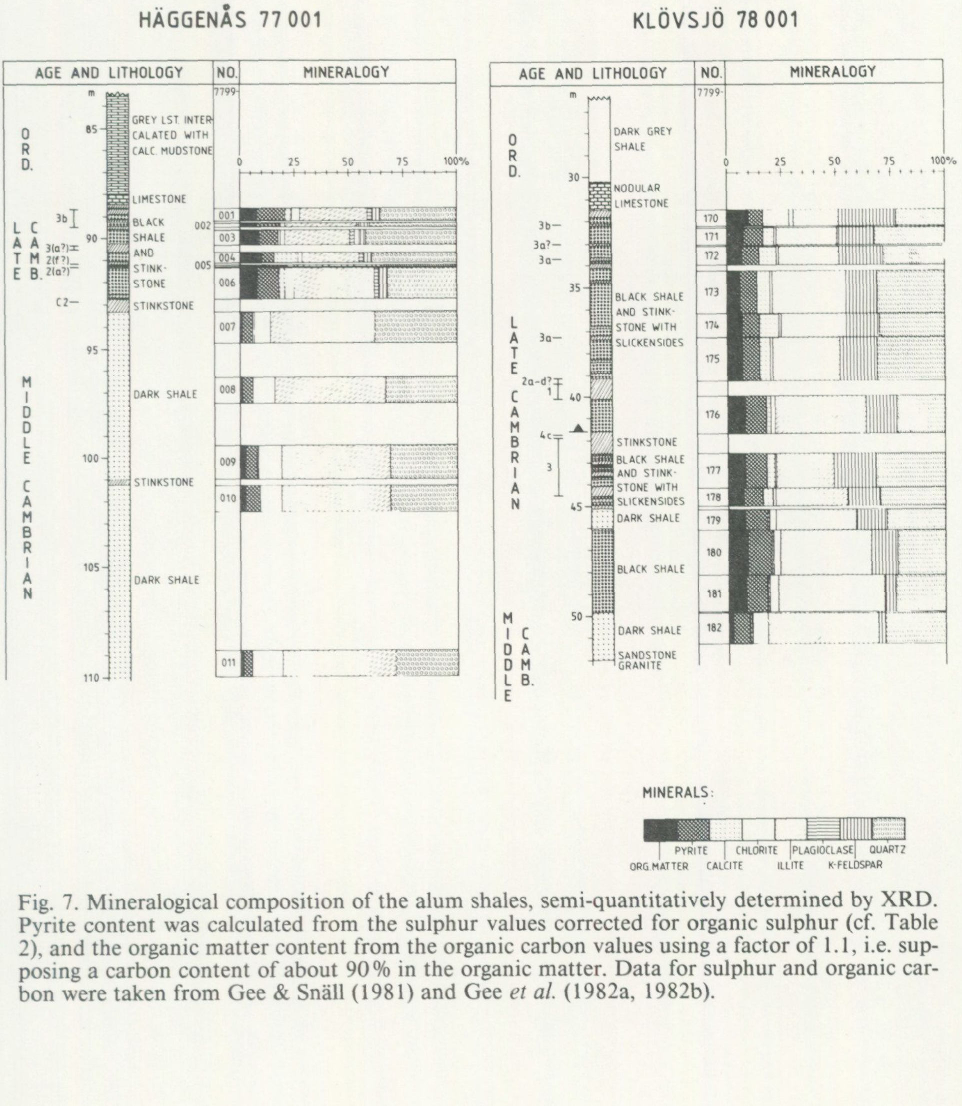


Fig. 7. Mineralogical composition of the alum shales, semi-quantitatively determined by XRD. Pyrite content was calculated from the sulphur values corrected for organic sulphur (cf. Table 2), and the organic matter content from the organic carbon values using a factor of 1.1, i.e. supposing a carbon content of about 90% in the organic matter. Data for sulphur and organic carbon were taken from Gee & Snäll (1981) and Gee *et al.* (1982a, 1982b).

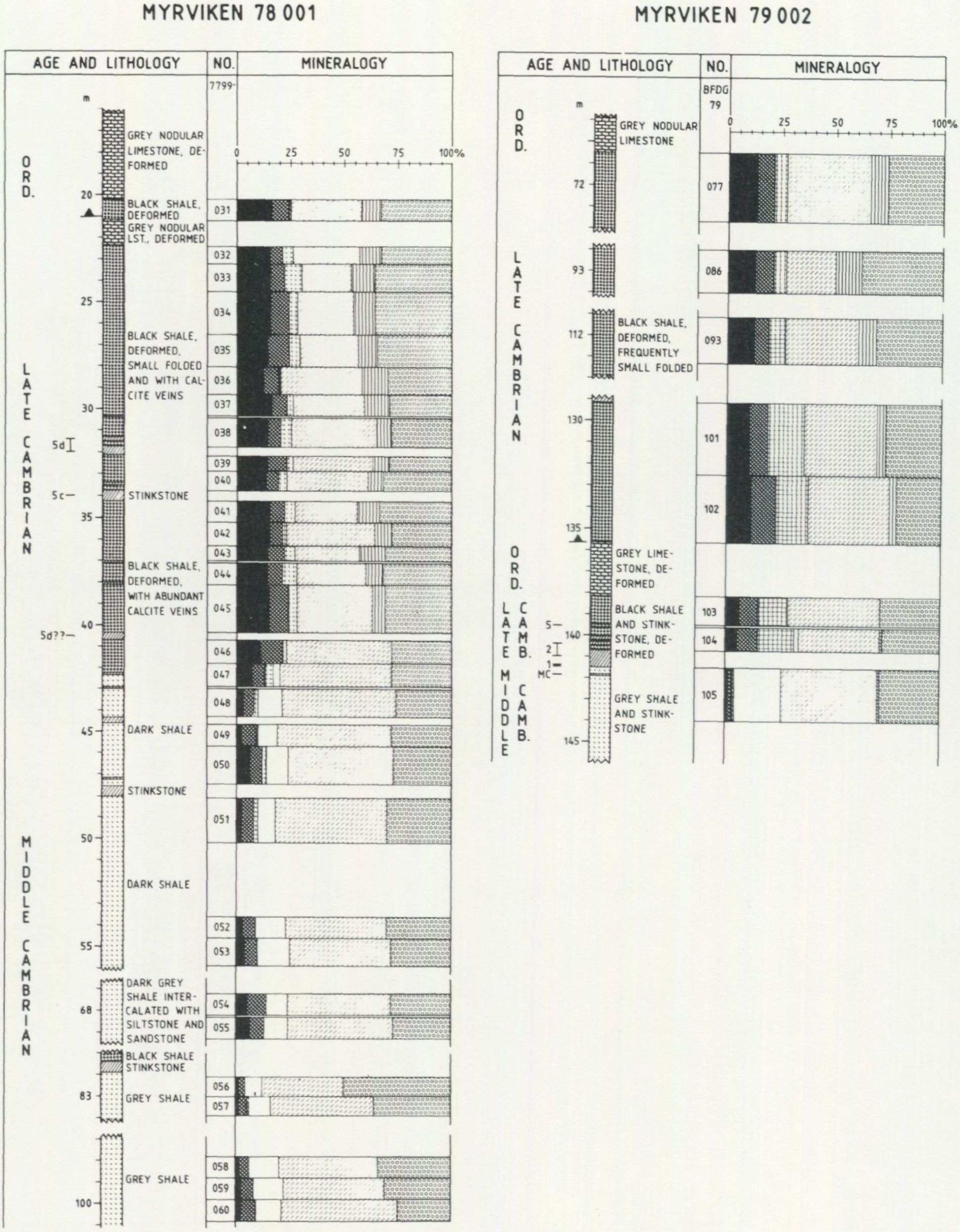

MYRVIKEN 78 001
AGE AND LITHOLOGY
NO.
MINERALOGY
7799-
m
0
25
50
75
100%
ORD.
LATE CAMBRIAN
MIDDLE CAMBRIAN
20
25
30
35
40
45
50
55
68
83
100
5d
5c
5d??
GREY NODULAR LIMESTONE, DEFORMED
BLACK SHALE, DEFORMED
GREY NODULAR LST., DEFORMED
BLACK SHALE, DEFORMED, SMALL FOLDED AND WITH CALCITE VEINS
STINKSTONE
BLACK SHALE, DEFORMED, WITH ABUNDANT CALCITE VEINS
DARK SHALE
STINKSTONE
DARK SHALE
DARK GREY SHALE INTERCALATED WITH SILTSTONE AND SANDSTONE
BLACK SHALE STINKSTONE
GREY SHALE
GREY SHALE
031
032
033
034
035
036
037
038
039
040
041
042
043
044
045
046
047
048
049
050
051
052
053
054
055
056
057
058
059
060
MYRVIKEN 79 002
AGE AND LITHOLOGY
NO.
MINERALOGY
BFDG 79
m
0
25
50
75
100%
ORD.
LATE CAMBRIAN
ORD.
LATE CAMB.
MIDDLE CAMB.
72
93
112
130
135
140
145
5
2
1
MC
GREY NODULAR LIMESTONE
BLACK SHALE, DEFORMED, FREQUENTLY SMALL FOLDED
GREY LIMESTONE, DEFORMED
BLACK SHALE AND STINKSTONE, DEFORMED
GREY SHALE AND STINKSTONE
077
086
093
101
102
103
104
105

Fig. 7 cont.

TABLE 1. Content of silicates (in wt.-%) in nine alum shale samples from Jämtland (after removal of stinkstones, carbonate- and pyrite veins), quantitatively determined (Q) from chemical analyses and semi-quantitatively by XRD. Whole rock *on silicate basis*. *) indicate that the figure also includes some chlorite.

	Quartz		K-feldspar		Plagioclase		Chlorite		Illite	
Sample no.	Q	XRD	Q	XRD	Q	XRD	Q	XRD	Q	XRD
7799001	41	46	7	5	2	2		5	50*	42
006	39	41	4	5	3	3		5	54*	46
031	41	44	13	12					46	44
037	41	39	18	16					41	45
038	36	37	9	10					64	64
170	36	31	21	21				2	43*	46
172	39	36	23	22				1	38*	41
171	38	41	23	24				0.5	39*	34

available (Table 1). For the Middle Cambrian samples, the mineral content was not calculated because of the greater complexity, due to a higher chlorite content.

Illite and quartz predominate. As shown in Fig. 7, the minerals are distributed in varying amounts in the cores. In the Upper Cambrian shales, K-feldspar is frequent, but is usually missing in the Middle Cambrian shales. Only in sections taken just above the Upper Cambrian/Middle Cambrian boundary in the Myrviken cores is feldspar absent from the Upper Cambrian shales (samples 7799046 and BFDG79103). The latter sections are allochthonous with *Peltura* species in overlying or underlying stinkstones.

The distribution of chlorite is reciprocal to that of K-feldspar i.e. there is a very low content of chlorite (if any) in the Upper Cambrian shales and up to 15% in the Middle Cambrian shales. One sample (BFDG 79105) from the Myrviken 79002 core contains 22% chlorite (Fig. 7). The Upper Cambrian shales have a higher quartz to clay mineral ratio than the Middle Cambrian shales. The relative increase of clay mineral content from the Upper Cambrian to the Middle Cambrian shales is not only indicated by XRD analyses, but also by the high potassium content of the Middle Cambrian whole rock samples (cf. Table 2).

The content of quartz is usually 30–40% in the shales but may vary from 20 to 50%. Illite shows a very large variation, from 25 to 55%. Relatively high feldspar content (around 15%) is found in the shales from the Klövsjö 78001 core. In the Myrviken cores (78001 and 79002), the feldspar content usually is around 10% in the Upper Cambrian. However, there are sections in the lower parts of the allochthonous sequence which have a lower feldspar content (3–4%) and, as mentionend above, the feldspar is absent in two sections (cf. Fig. 7). In the Häggenås 77001 core, it is 4–7% in the Upper Cambrian sequence. Monoclinic potassium feldspar (XRD-determinations) is the predominant feldspar mineral. Plagioclase was found only in the Häg-

TABLE 2. Major elements of the alum shales in Jämtland. Some trace elements are also given. Figures are in wt.-% (for trace elements ppm) and refer to air dry material. Sample 7799046E is identical with 7799046, but with organic matter and sulphides removed. UC and MC are Upper and Middle Cambrian, respectively. *) means that the determination was done after removal of organic matter and sulphides. **)indicates that the volatile matter (V. M.) of the organic matter is not included.

		Häggenås 77001			Myrviken 78001						Klövsjö 78001		
		7799001 UC	7799006 UC	7799008 MC	7799031 UC	7799037 UC	7799038 UC	7799046 UC	7799046E* UC	7799048 MC	7799170 UC	7799172 UC	7799177 UC
SiO_2	%	51.2	51.3	55.9	50.9	50.1	45.4	50.4	67.4	54.6	45.5	51.3	52.7
TiO_2	%	0.68	0.74	0.88	0.75	0.70	0.65	0.74	0.95	0.90	0.60	0.62	0.69
Al_2O	%	12.0	13.5	18.4	12.4	12.2	12.1	12.9	17.2	18.2	11.2	12.4	12.8
Fe_2O_3	%	10.3	9.1	8.0	6.9	5.4	5.2	8.6	2.0	8.1	6.7	7.3	8.2
MnO	%	0.02	0.03	0.02	0.02	0.06	0.08	0.03	0.01	0.06	0.04	0.03	0.03
CaO	%	2.4	2.0	0.2	0.9	1.8	6.7	1.6	0.4	1.4	7.1	4.5	2.3
MgO	%	1.22	1.34	1.7	0.92	0.98	0.93	1.09	1.51	1.9	1.24	1.18	1.10
Na_2O	%	0.2	0.3	0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.1	0.2	0.2	0.2
K_2O	%	4.1	4.4	5.2	4.2	4.4	3.9	4.0	5.1	4.9	4.7	5.2	5.4
H_2O+	%	1.6*	2.1*	3.4*	2.0*	2.1*	2.1*	2.1*	2.6	3.2*	1.1*	1.1*	1.3*
H_2O-	%	0.7	0.7	0.8	0.7	0.5	0.5	0.6	0.4	0.6	0.5	0.6	0.6
P_2O_5	%	0.31	0.35	0.04	0.21	0.20	0.62	0.20		0.05	0.42	0.52	0.34
CO_2	%	1.4	1.1	0.02	0.38	1.1	2.3	0.67		0.70	5.2	3.4	1.7
F	%	0.12	0.14	0.11	0.10	0.09	0.14	0.10		0.11	0.14	0.14	0.13
S	%	6.8	5.2	2.9	4.8	4.2	3.6	5.7		2.6	3.9	4.3	5.2
BaO	%	0.06	0.08	0.06	0.09	0.11	0.10	0.07	0.05	0.07	0.05	0.06	0.06
$C_{org.}$	%	5.9	6.7	1.2	12.3	12.5	11.1	8.5		2.5	7.6	4.1	5.5
U	ppm	90	112	5	163	225	135	120		12	152	75	91
V	ppm	600	500	200	700	2000	900	800		300	900	400	600
Mo	ppm	249	219	62	521	453	347	283		83	462	174	240
Total**		99.10	99.16	98.96	97.71	96.71	95.56	97.32	95.02	98.93	96.34	97.01	98.34
Corr. for F and S (S as FeS_2)		2.53	1.95	1.12	1.72	1.48	1.28	2.06		0.99	1.45	1.61	1.94
Corr. total**		96.57	97.21	97.84	95.99	94.23	94.28	95.26		97.94	94.89	95.40	96.40
SiO_2/Al_2O_3 (molar ratio)		7.2	6.4	5.2	7.0	7.0	6.4	6.6	6.6	5.1	6.9	7.0	7.0
$Fe_{tot.}$-Fe_{pyrite} (expressed as Fe_2O_3)		2.0	2.8	4.4	1.3	0.6	1.1	1.8		5.0	2.1	2.1	1.9

genås 77001 core and in the autochthonous parts of the Myrviken 79002 core.

The pyrite content of the shales is usually around 8–10 %. The calcite content varies considerably. Values within the interval 5–8 % are common. As mentioned previously, pyrite and calcite are frequently found as thin irregular veins in the shales. The content of calcite, and in many samples also of pyrite, is lower in the Middle Cambrian than in the Upper Cambrian shales.

The whole rock chemical analyses of the shales are shown in Table 2 (for methods of analysis see Appendix I). The variations in organic carbon content are obvious. The samples of the Upper Cambrian shales have a higher carbon content than those of the Middle Cambrian. The highest content of organic carbon is found in the allochthonous shales of the Myrviken 78001 core. Large variations in the aluminium content of Upper and Middle Cambrian shales also occur. The chlorite-bearing (cf. Fig. 7) Middle Cambrian shales are much richer in aluminium than the Upper Cambrian shales within which chlorite is absent or occurs only in small amounts.

Total iron as Fe_2O_3 shows variations from 5 to 10 %. As most of the iron is present as pyrite, sulphur shows similar variations. However, considering the iron content after subtraction of pyrite bound iron (at the very bottom of Table 2) there is a regularity in the values. The most altered of the allochthonous Upper Cambrian shales, viz. those from the Myrviken 78001 core, show the lowest iron content, 2–3 times lower than in the Upper Cambrian autochthon. Presence of chlorite in the Middle Cambrian shales (7799008 and -048) is responsible for the highest iron and crystal water content recorded, in both the autochthonous and allochthonous formations. The non-pyrite bound iron of the shales is thought to be exclusively located in the clay mineral lattices as no iron-bearing carbonate mineral or oxide has been identified.

GRAIN SIZE OF THE SILICATES

Alteration of the shales is accompanied by recrystallization and grain size changes. The latter have been investigated by conventional hydrometric methods.

Grain size analyses of the shales after removal of organic matter and sulphides are given in Fig. 8. It is apparent that the samples of the Upper Cambrian autochthon (7799001 and -006 from the Häggenås 77001 core) are the most fine-grained with 95 % of the grains smaller than 15 μm and 45 % smaller than 2 μm. Larger grain sizes are found in the allochthonous shales, the largest in the most altered shales (samples 7799037 and -038 from Myrviken 78001 core). But the Middle Cambrian shales are the most coarse-grained (Fig. 8, samples 7799008 and -048 from Häggenås 77001 core and Myrviken 78001 core) irrespective of whether they are autochthonous or allochthonous. In these shales the silicates occur in aggregates. Dispersion of

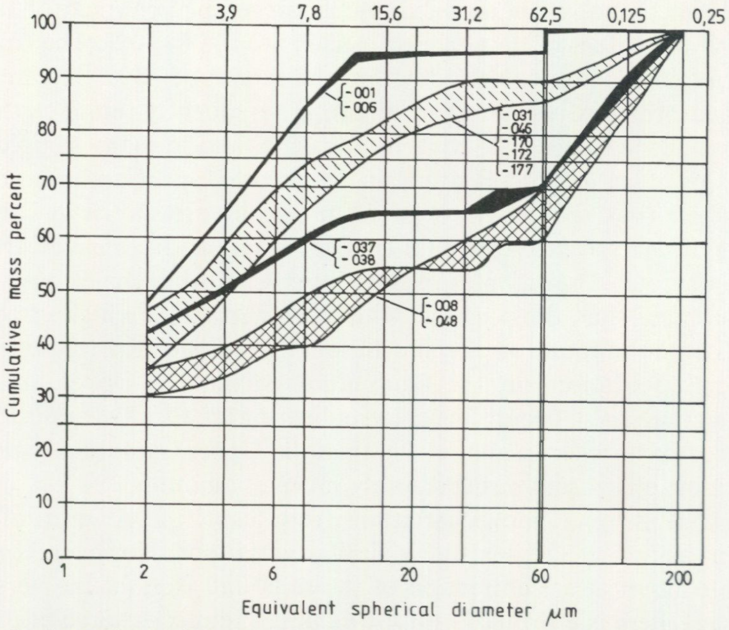


Fig. 8. Grain size analyses of the silicates after removal of organic matter and sulphides. Minor amounts of calcite may remain among the silicates. -008, -048 etc. refers to sample no. 7799008 and 7799048, respectively. Closely spaced curves are not shown separately, they are integrated into the shaded zones in the diagram.

organic matter in the major component, viz. in the silicate phase, was less developed in these shales, reflecting different textures.

The minerals are differently distributed in the various grain size fractions. In the finest fractions there is no feldspar, and quartz is present only in small amounts. Table 3 gives the quartz content of the <1 µm fraction. On the other hand, the fraction coarser than 30 µm shows a dominance of quartz.

There are variations in quartz content of the <1 µm fraction between shale samples from the autochthon and the allochthon. The samples of the autochthonous Upper Cambrian (7799001, -006 and -177) have a higher quartz content (8–10 %) than the samples of the most altered allochthonous shales (7799037 and -038, 1–3 %). This indicates a growth of quartz during the alteration, increasingly so with higher alteration.

CLAY MINERALS

Clay minerals and organic matter are sensitive indicators of variations in their environment of deposition and subsequent alteration and were therefore studied more comprehensively.

TABLE 3. Quartz content of the < 1 µm fraction of the alum shale samples from Jämtland.

Sample no.	Drillcore	Strata	Quartz content wt.-%
7799001	Häggenås 77001	Upper Cambrian, autochthon	10
006	”	” ” ”	8
008	”	Middle ” ”	6
031	Myrviken 78001	Upper Cambrian, allochthon	7
037	”	” ” ”	3
038	”	” ” ”	1
046	”	” ” ”	3
048	”	Middle ” ”	<1
170	Klövsjö 78001	Upper Cambrian, allochthon	3
172	”	” ” ”	10
177	”	” ” autochthon	10

By X-ray diffraction (XRD) analysis, structural and compositional variations of the clay minerals were indicated. In the whole rock chemical compositions (Table 2), such variations were not very pronounced. To obtain clay minerals as pure as possible, the <1 µm fraction was separated from all of the samples. In this fraction the clay mineral concentrate was contaminated with small amounts of quartz and, in the case of the Middle Cambrian samples (7799008 and -048), by minor chlorite. Chemical analyses of the <1 µm fraction are shown in Table 4, and the percentage of quartz contamination in Table 3. Structural formulae of the illites, after correction for the quartz component, are shown in Table 5.

As expected for illites, the potassium content of all samples is high, 7.1–8.1 % K_2O. Magnesium content varies very little and lies between 2.1 and 2.7 % MgO. Calcium shows large variation from 0.1 to 1.3 % CaO, apparently being all bound in illite, as no calcite has been identified by XRD methods in the <1 µm fractions.

The largest differences between the samples are found in the distribution of iron and aluminium (Table 4). As also indicated in the whole rock analysis, the iron content is lowest in the samples from the most altered shales, viz. the Upper Cambrian, allochthonous units of the Myrviken 78001 core (no. 7799031, -037, -038 and -046). Even within the latter, however, there are significant differences between samples from different allochthonous units. Aluminium shows a reciprocal relationship to iron, the most altered allochthonous shales having the highest aluminium contents (7799037 and 7799038). These compositional variations which result from increasing thermal alteration of the shales can be illustrated (Table 4, very bottom) by comparing the molar ratios SiO_2/Al_2O_3 and $SiO_2+Fe_2O_3+MgO/Al_2O_3$ (Foscolos *et al.* 1976). The lowest values occur in the allochthonous Myrviken 78001 samples and the highest in the Klövsjö 78001 samples.

TABLE 4. Chemical analysis of the < 1 µm fraction of the alum shale samples from Jämtland (wt.-%). Organic matter and sulphides have been removed before grain size fractioning.

		Häggenås 77001 (autochthon)			Myrviken 78001 (allochthon)					Klövsjö 78001 (autochthon and allochthon)		
		7799001 UC	7799006 UC	7799008 MC	7799031 UC	7799037 UC	7799038 UC	7799046 UC	7799048 MC	7799170 UC	7799172 UC	7799177 UC
SiO_2	%	54.2	52.0	48.0	53.8	51.6	51.1	52.0	48.9	52.1	55.8	55.7
TiO_2	%	0.94	1.00	0.85	1.06	0.71	0.69	0.92	0.81	1.15	1.01	1.06
Al_2O_3	%	23.4	25.1	26.5	26.0	27.3	28.3	27.0	28.1	22.9	22.7	22.5
Fe_2O_3	%	3.2	3.1	4.9	2.1	1.0	1.1	2.0	4.6	3.8	2.9	2.6
MnO	%	0.02	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.01
CaO	%	0.9	1.1	0.1	0.2	0.1	0.4	<0.1	<0.1	1.3	1.1	0.8
MgO	%	2.2	2.4	2.2	2.3	2.7	2.4	2.4	2.5	2.7	2.1	2.1
Na_2O	%	0.1	<0.1	0.4	0.1	<0.1	<0.1	0.1	0.2	<0.1	<0.1	<0.1
K_2O	%	7.4	7.6	7.5	7.6	7.9	7.7	8.1	7.4	7.5	7.1	7.1
H_2O+	%	4.5	4.2	4.3	4.2	5.0	4.5	4.0	3.9	4.3	4.0	4.0
H_2O-	%	1.6	1.6	1.7	1.0	0.7	0.9	0.9	1.1	2.2	2.0	1.5
BaO	%	0.07	0.08	0.06	0.09	0.09	0.09	0.08	0.08	0.06	0.05	0.04
Total		98.33	98.20	96.53	98.46	97.12	97.20	97.51	97.61	98.03	98.78	97.41
SiO_2/Al_2O_3 (molar ratio)		3.9	3.5	3.1	3.5	3.2	3.1	3.3	3.0	3.9	4.2	4.2
$SiO_2+Fe_2O_3$ $+MgO/Al_2O_3$ (molar ratio)		4.2	3.8	3.4	3.8	3.5	3.3	3.5	3.3	4.3	4.5	4.5

Illite crystallinity

One of the most convenient methods for characterizing the varying degree of alteration of shales involves the determination of illite polymorphs and crystallinity. The principal changes of these properties in illite during diagenesis and low-grade metamorphism have been compiled by Dunoyer de Segonzac (1970) (Fig. 9). Measured parameters (XRD characteristics) are summarized in Table 6.

XRD patterns of the significant interval for determination of polymorphs (23–26° 2θ) of the <1 μm fraction of the samples are shown in Fig. 10. The 1 M and 2 M illite peaks are fairly well resolved in the allochthonous samples of the Myrviken 78001 core, the uppermost samples (7799031, -037 and -038)

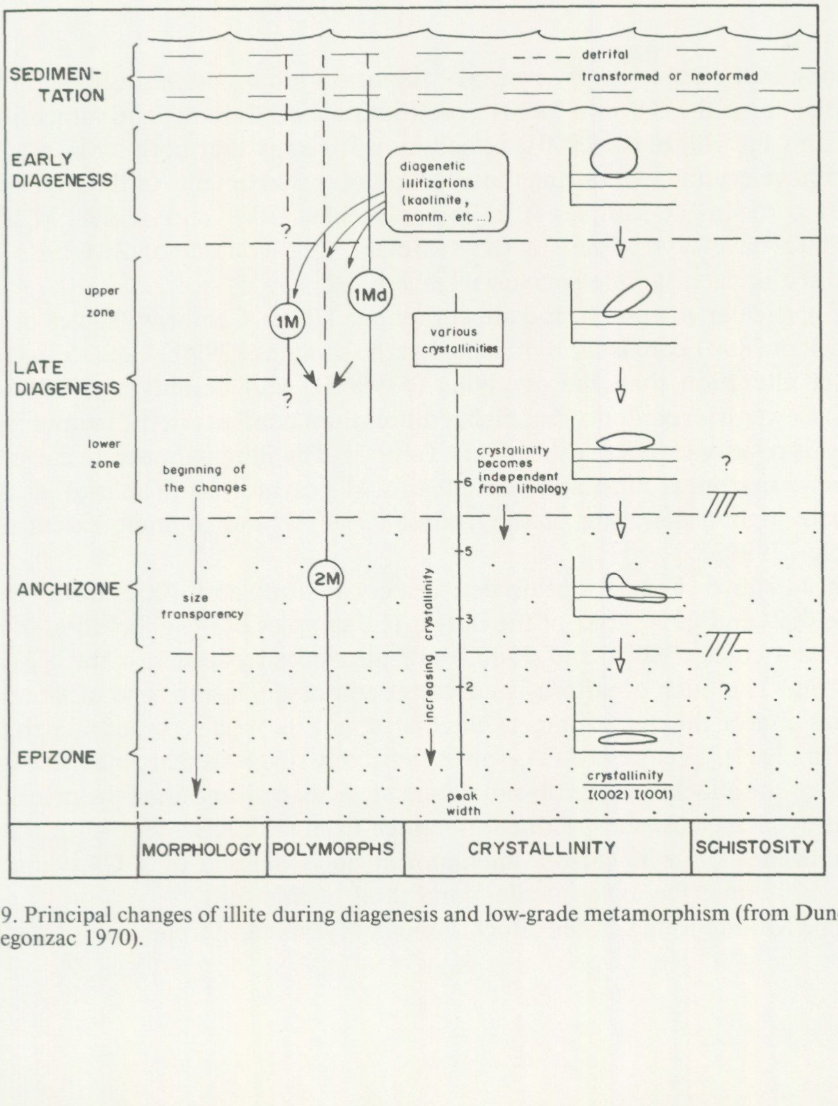


Fig. 9. Principal changes of illite during diagenesis and low-grade metamorphism (from Dunoyer de Segonzac 1970).

TABLE 5. Structural formulae of illites in the <1 µm fraction of the alum shale samples from Jämtland. Chemical data of Table 4 corrected for quartz admixture (Table 3) have been used for calculations.

Sample no.	Formula				
7799001	$K_{0.73}$	$Na_{0.01}$	$Ca_{0.07}$	$(Al_{1.56}Fe_{0.19}Mg_{0.25})^{VI}$	$(Si_{3.43}Al_{0.57})^{IV}O_{10}(OH)_2$
006	$K_{0.73}$		$Ca_{0.09}$	$(Al_{1.56}Fe_{0.18}Mg_{0.27})^{VI}$	$(Si_{3.34}Al_{0.67})^{IV}O_{10}(OH)_2$
031	$K_{0.71}$	$Na_{0.01}$	$Ca_{0.02}$	$(Al_{1.66}Fe_{0.12}Mg_{0.25})^{VI}$	$(Si_{3.43}Al_{0.57})^{IV}O_{10}(OH)_2$
037	$K_{0.71}$		$Ca_{0.01}$	$(Al_{1.71}Fe_{0.05}Mg_{0.28})^{VI}$	$(Si_{3.44}Al_{0.56})^{IV}O_{10}(OH)_2$
038	$K_{0.67}$		$Ca_{0.03}$	$(Al_{1.72}Fe_{0.06}Mg_{0.25})^{VI}$	$(Si_{3.44}Al_{0.56})^{IV}O_{10}(OH)_2$
046	$K_{0.072}$	$Na_{0.01}$		$(Al_{1.67}Fe_{0.11}Mg_{0.25})^{VI}$	$(Si_{3.44}Al_{0.56})^{IV}O_{10}(OH)_2$
170	$K_{0.69}$		$Ca_{0.10}$	$(Al_{1.46}Fe_{0.21}Mg_{0.29})^{VI}$	$(Si_{3.53}Al_{0.47})^{IV}O_{10}(OH)_2$
172	$K_{0.69}$		$Ca_{0.09}$	$(Al_{1.55}Fe_{0.17}Mg_{0.24})^{VI}$	$(Si_{3.51}Al_{0.49})^{IV}O_{10}(OH)_2$
177	$K_{0.69}$		$Ca_{0.07}$	$(Al_{1.57}Fe_{0.15}Mg_{0.24})^{VI}$	$(Si_{3.54}Al_{0.46})^{IV}O_{10}(OH)_2$

showing best resolution. By contrast, the peaks are broad and diffuse in the samples from the Klövsjö 78001 core (both autochthonous and allochthonous) and the Häggenås 77001 autochthon. It seems that both 1 M and 2 M illites have crystallized during the altertion of the sediments of the Myrviken 78001 core. In the samples from the Häggenås 77001 core, only 1 M illite seems to have crystallized in the sediment. The content of 2 M illite determined in each sample is given i Table 6.

Of particular interest in the allochthonous Upper Cambrian shales of the Myrviken 78001 core is the evidence that the samples 7799037 and -038 show greater alteration than the overlying (7799031) and underlying (7799046) units. Lower iron contents and higher aluminium contents in the former indicate this relationship (cf. Table 4 and Table 5). The illite parameters, i.e. crystallinity, sharpness ratio and content of 2 M polymorphs (Table 6), clearly indicate higher alteration of the sample 7799037 and to some extent also sample 7799038.

Fig. 11 shows the relationship between crystallinity and I(002)/I(001) ratio of the 002- and 001- peaks of the illites. The samples of the allochthon of the Myrviken cores (78001 and 79002) are distributed parallel to the I_{002}/I_{001} axis (Fig. 11). Such a pattern is characteristic of the lower zone of late diagenesis and of the anchizone, as elucidated in Fig. 9 (cf. crystallinity to the right in Fig. 9). The present C.I.-values definitely suggest anchizone metamorphism of the allochthonous Myrviken shales. After calibration of the measurements by means of slate specimens obtained from H. J. Kisch, transition from late diagenesis into anchizone metamorphism is defined by a C.I.-value of $0.45^\circ\ \Delta 2\theta$ under the experimental conditions of this study.

The 2 M illite found in the allochthonous Myrviken samples is expected in

TABLE 6. Mineralogical characteristics of illite of the alum shale samples from Jämtland. The <2 µm fraction was used for crystallinity (Kisch 1980) and sharpness ratio (Weaver 1960) determinations; the <1 µm fraction was employed for the determination of the percentage of the 2 M polymorphs (Velde & Hower 1963). In the case of the latter, determination below 25 % was not possible.

Sample no.	Drillcore	Strata	Crystallinity peak width °Δ2θ	Sharpness ratio	$\frac{2M}{2M+1M+1Md}\times 100$
7799001	Häggenås 77001	Upper Cambrian, autochthon	0.50	2.3	<25
006	”	” ” ”	0.49	2.2	30
008	”	Middle ” ”	0.65	1.8	–
031	Myrviken 78001	Upper Cambrian, allochthon	0.36	4.0	52
037	”	” ” ”	0.33	5.2	66
038	”	” ” ”	0.36	4.6	58
046	”	” ” ”	0.35	4.4	54
048	”	Middle ” ”	0.40	3.5	45
170	Klövsjö 78001	Upper Cambrian, allochthon	0.98	1.4	<25
172	”	” ” ”	0.71	1.8	<25
177	”	” ” autochthon	0.68	1.8	<25
BFDG79093	Myrviken 79002	Upper Cambrian, allochthon	0.35	4.8	–
102	”	” ” ”	0.35	4.1	–
103	”	” ” autochthon	0.46	2.8	–
104	”	” ” ”	0.48	2.6	–

anchizone shales (Fig. 9) and it is evident from Fig. 10 that 1 M illite has not broken down. According to Weaver & Broekstra (1984), crystallization of 2 M illite is characteristic of the anchizone; starting with 0 % 2 M illite at the lower border and ending with 100 % at the border to the epizone. Also by this definition, all the allochthonous shales in the Myrviken 78001 core (cf. Table 6) fall within the anchizone.

The illites in the samples of the autochthon of the Myrviken area are not so well crystallized. They group together with the illites from the Häggenås 77001 core, also in autochthonous strata (cf. Fig. 11). The least crystallized illites occur in the Klövsjö shales, where the differences between the autochthonous and allochthonous units are probably related to primary clay mineral composition. (The illite in the Klövsjö sample 7799170 with the C.I. value 0.98 is from the allochthon. It is possible that the glauconite observed in this sample is present also in the clay fraction and affects the crystallinity parameters).

The distributional pattern in Fig. 11 and the presence of 1 M illite in the Häggenås shales indicate the upper zone of late diagenesis for these shales (cf. Fig. 9). The Klövsjö shales have a lower degree of alteration as defined by the illite crystallinity. They might possibly be placed in the uppermost part of the upper zone of late diagenesis.

ORGANIC MATTER

Geochemistry and degree of organic metamorphism

Maturation of organic matter in sedimentary rocks with increasing degree of metamorphism can be recognized by changes in geochemistry and petrology of the organic matter (Héroux *et al.* 1979). Kerogen becomes more aromatic and less aliphatic, and the atomic H/C ratio decreases. In terms of coal petrology, rank increases (cf. Héroux *et al.* 1979).

Only Upper Cambrian samples were used for studies of maturation. (Sample 7799005 was substituted for 7799006 because of loss of material from the latter). Enrichement of the organic matter (see Appendix I) of the shales involved removal of carbonates and most of the silicates. After enrichment, the concentrate of organic matter contained sulphides, oxides and minor amounts of silicates (heavy minerals and traces of quartz). Carbon, hydrogen, nitrogen and sulphur were determined (Table 7) in air dry samples. The moisture (110° C), pyrite content of residue, ash values and the content of volatile matter are also listed in Table 7. Because of the variable ash content only the H/C ratios and the values of volatile matter are of interest for direct comparison.

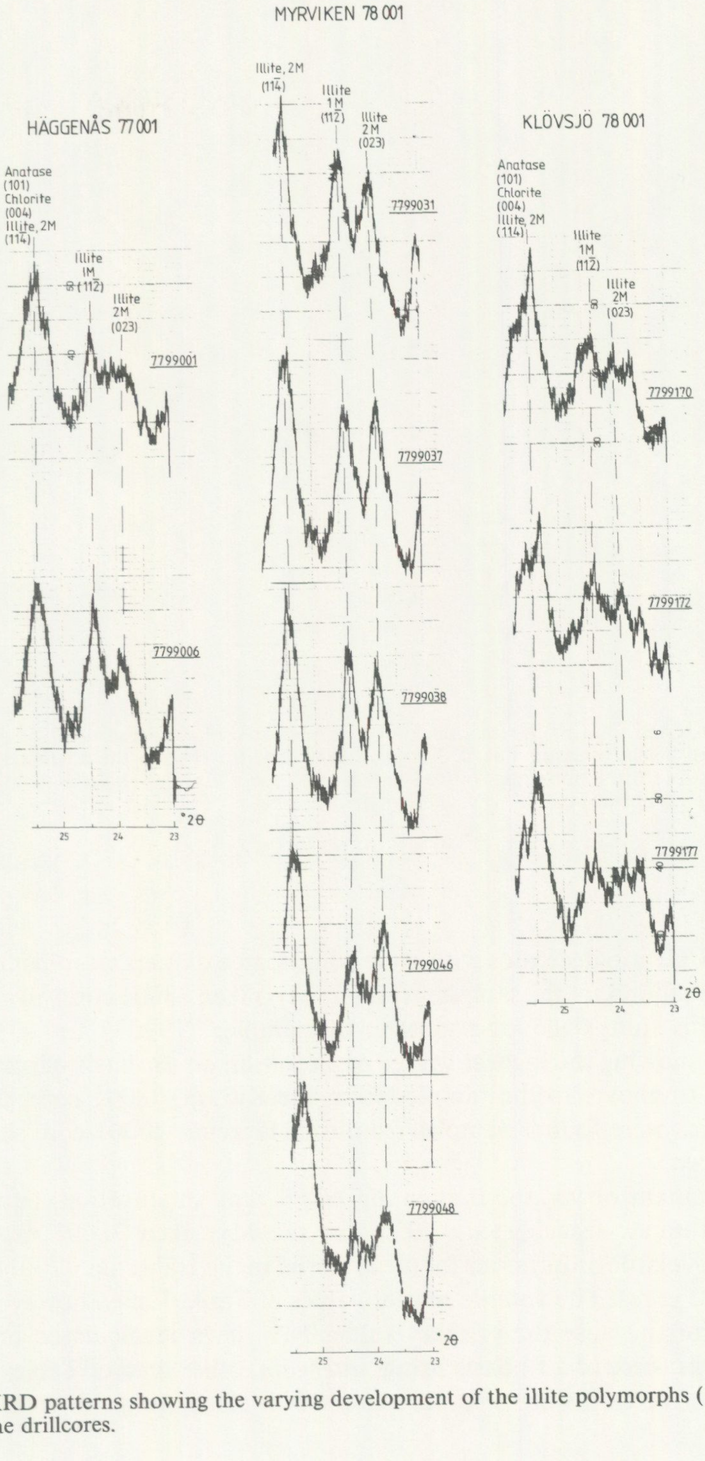


Fig. 10. XRD patterns showing the varying development of the illite polymorphs (< 1 μm fraction) in the drillcores.

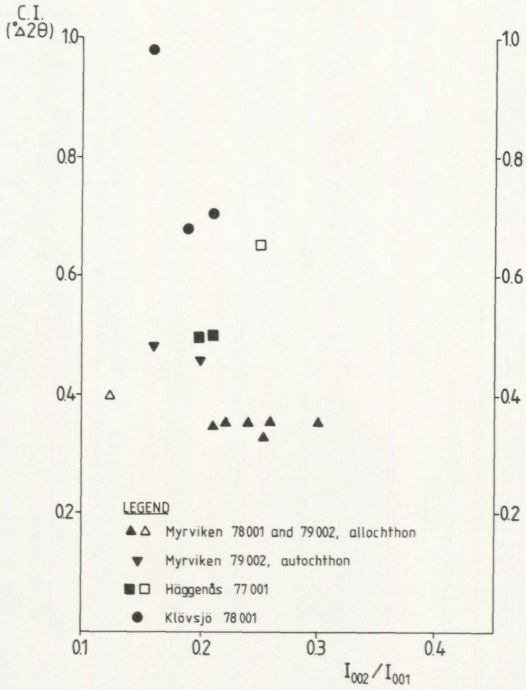


Fig. 11. Diagram showing the relationship between crystallinity, i.e. the width of the illite 10 Å peak at half height (measured as °Δ 2θ, Kisch 1980) and the ratio of the intensities of the illite (002) and (001) diffraction peaks. Filled symbols are Upper Cambrian shales and unfilled symbols are Middle Cambrian shales.

The H/C ratio decreases with increasing degree of metamorphism. Very low values are found for the samples from the Myrviken 78001 core (all allochthonous in this study), the lowermost in the samples 7799037 and -038, i.e. the samples showing the highest degree of alteration on the basis of other criteria referred to above. In the samples from the Klövsjö 78001 core, the highest H/C ratios were found. Samples from the Häggenås 77001 core show values in between.

The content of volatile matter suggests a rank (maturation) equivalent to semi-anthracite (Stach *et al.* 1975) for the Myrviken 78001 material and medium volatile bituminous for the material in the Häggenås 77001 and Klövsjö 78001 cores. The volatile matter values of Table 7 may, however, contain large errors because the primary values have been recalculated on a 100° C dry and ash-free (d.a.f.) basis using, *inter alia*, other data of Table 7. A number of corrections were also necessary when calculating the volatile matter

TABLE 7. Elementary analysis of Upper Cambrian alum shale residues after extraction of carbonates and silicates. Pyrite, moisture, ash and volatile matter are also given. The high sulphur values include sulphur in pyrite as well as in organic matter. Air dry samples. Wt.-%. D.a.f. = dry (110 °C) ash-free. (For accuracy of the element determinations, see Snäll 1981.)

Sample no.	Drillcore	C %	H (moisture included) %	N %	S_{tot} %	H/C (d.a.f.) %	Moisture 110°C %	Pyrite %	Ash %	Volatile matter (d.a.f.) %
7799001	Häggenås 77001	26.9	1.2	1.2	31.1	0.36	4.0	50.1	42.0	44
005	”	17.6	0.8	0.6	12.9	0.38	2.1	24.6	67.2	31
031	Myrviken 78001	36.7	1.2	1.1	14.9	0.32	2.0	26.1	47.1	12
037	”	55.5	1.7	1.4	15.7	0.31	2.3	27.9	24.0	14
038	”	50.0	1.6	1.2	16.5	0.31	2.6	28.6	30.0	14
046	”	28.7	1.2	0.7	22.3	0.39	2.4	40.2	48.8	13
170	Klövsjö 78001	44.4	2.2	1.9	20.0	0.51	2.8	33.8	30.5	26
172	”	20.0	1.2	0.9	20.5	0.55	2.5	36.1	59.0	29
177	”	14.2	1.0	0.9	14.3	0.68	1.8	24.8	70.0	27

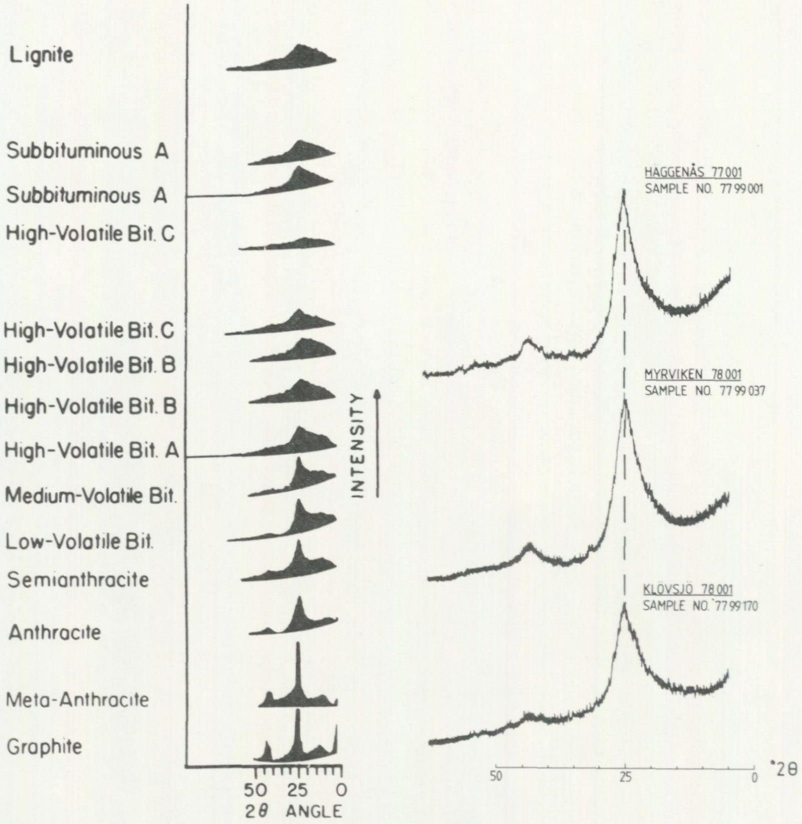


Fig. 12. XRD patterns of the organic matter isolated from the shales (right). For comparison, data have been taken from Griffin (1967) (left in figure).

values, including those required for transformation of pyrite into hematite (taking place during heating for ash determination) and for pyrite transformation into pyrrhotite (taking place during the volatile matter determinations).

Reflectance studies

Kisch (1980) demonstrated that significant variations in "vitrinite" reflectance occur in the Jämtland shales. An attempt was therefore made to compare the reflectance of the organic matter in the shales of the present study with his data. Thin sections of shales were prepared as well as polished briquettes. The measurements were made by Svenskt Stål AB (SSAB, Oxelösund). No systematic variation between the samples was detected.

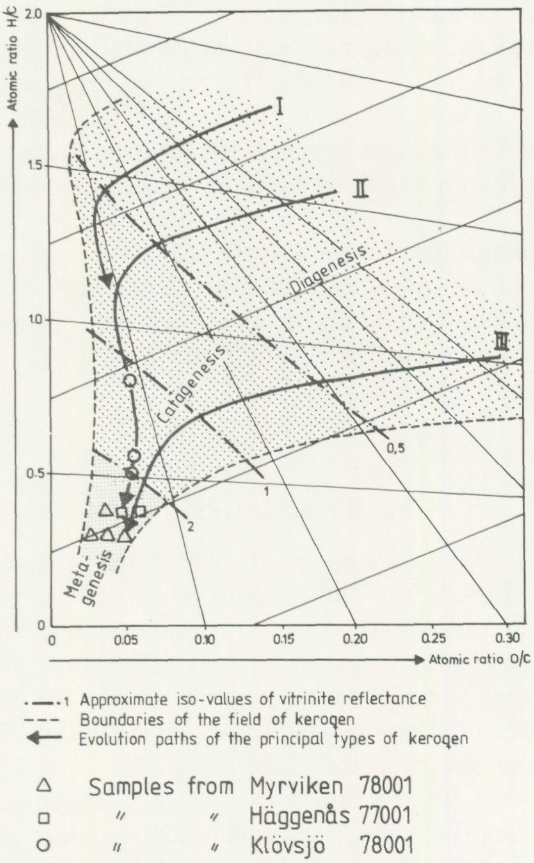


Fig. 13. General scheme of kerogen evolution from diagenesis to metagenesis in the van Krevelen (1961) diagram (from Tissot & Welte 1978). The Jämtland alum shales are plotted along path I in the diagram on the basis of the atomic H/C ratios in Table 7.

XRD STUDIES

XRD patterns of coals of the different maturity stages have been given by Griffin (1967). For comparison of patterns three samples, one from each core, were analysed. Results are shown in Fig. 12. It is evident that the patterns of the Myrviken 78001 and Häggenås 77001 material are most similar to the XRD pattern of anthracite given by Griffin, and that of the Klövsjö 78001 material is more similar to that of semi-anthracite.

STAGES OF KEROGEN EVOLUTION

When relating maturity of organic matter in the alum shales to stages of petroleum and gas generation, the van Krevelen (1961) diagram taken from Tissot & Welte (1978, Fig. 13) is applicable. Assuming an algal source for the organic matter in the alum shales as indicated by Rock-Eval analyses (J.R. Dyni, U.S. Geological Survey, pers. comm. 1986), the maturation pathway, represented by atomic ratios H/C and O/C will be along path I (Fig. 13), i.e. parallel to the H/C axis. A plot of the H/C ratios from Table 7 in Fig. 13 indicates metagenesis for the Myrviken and Häggenås samples and late catagenesis for the Klövsjö samples, all being in the zone of gas formation (cf. Tissot 1984).

The zones of maturation for kerogen in Fig. 13 cannot, however, be correlated directly with the zones for clay minerals in Fig. 9. Within the zone of late diagenesis of Dunoyer de Segonzac (1970), parts of both the zones of metagenesis and catagenesis (Fig. 13) of Tissot & Welte (1978) are probably included.

SUMMARY AND DISCUSSION

From visual examination, it is apparent that the shales have been subject to different degrees of alteration. This is confirmed by the chemical and mineralogical data and by investigations of the organic matter. All these methods suggest that the allochthonous shales in the Myrviken cores (78001 and 79002) are the most altered. The autochthonous shales in the Myrviken 79002 core show a lower degree of alteration (cf. Table 6 and Fig. 11), similar to that of the authochthonous shales in the Häggenås 77001 core. The shales of the Klövsjö 78001 core, both allochthonous and autochthonous, are less altered than all other shales (including the autochthonous shales in the Häggenås 77001 and Myrviken 79002 cores). It is therefore probable that the cover, both autochthonous and allochthonous, always has been less at the site of the Klövsjö 78001 core than in the case of the Myrviken and Häggenås cores, and that the allochthonous Klövsjö units have not been transported more than a few kilometers (cf. Gee *et al.* 1982b).

Proximity to the thrust zones does not seem to have influenced the clay minerals. Samples from the sections just above a thrust zone (cf. Fig. 4, drillcore Myrviken 79002) or below it do not differ from the samples taken at a larger distance from these zones. The fact that the allochthonous shales are more altered than underlying autochthonous shales in the Myrviken 79002 core, and that this metamorphic difference is not gradual, means that alteration of the shales must have taken place in some other geological environment prior to thrust emplacement on the autochthon.

The presence of K-feldspar in the shales bears no relation to the degree of their alteration. K-feldspar is most frequent in the least altered shales, viz. the shales in the Klövsjö 78001 core. In the allochthonous shales of the Myrviken cores, the content of K-feldspar varies greatly, this mineral being absent in some units. Pore water composition in the local sedimentary basins may have been the governing factor controlling crystallization of K-feldspar.

The various methods applied to quantify the grades of alteration have yielded correlatable results. Thus, illite crystallinity and the presence of 2 M illite polymorphs suggest anchizone metamorphism, as does research in coal petrology. H. J. Kisch (pers. comm. 1986) has found that the onset of the anchizone is associated with anthracite with approximately 2.5–3% Ro (vitrine reflectance).

Alteration of the sediments caused an enrichment of aluminium and a decrease of iron in the illites. Fine-grained quartz has recrystallized and is now found as coarser grains in the silt fraction. The latter is evident from the grain size analyses (Fig. 8) when comparing curves of the most altered material (samples 7799037 and -038) with the less altered (e.g. samples 7799001 and -006) and from the determinations of the quartz content in the $<1\mu m$ fraction (Table 3). Also, in the Middle Cambrian shales, the quartz content in the $<1\ \mu m$ fraction is lower (Table 3) in the samples from the allochthonous, more altered shale (sample 7799048) than in the sample from the autochthonous shale (sample 7799008).

PALAEOTEMPERATURE OF THE SHALES

Maturation (rank) of organic matter is controlled by pressure, heat and duration of application of these parameters. This has been demonstrated for coal (Hacquebard 1977) and is expected also to apply for the organic matter of probable algal origin in the alum shales. Heat is the most important of these factors; by comparison, pressure is probably subordinate (Tissot & Welte 1978, p. 196). Pressure is thought to be significant only in the early stages of diagenesis and results mainly in a loss of water due to compaction (Hacquebard 1977). The time factor (duration of heating) is also important. Application of the Arrhenius rate equation suggests that, in the process of maturation, the time factor is linear and the temperature factor exponential (Waples & Connan 1976).

The relationship between maturation, temperature and duration of metamorphism is given diagrammatically in Fig. 14. This diagram indicates that even a temperature of about 90° C, maintained since the time of deposition, will alter organic matter of Cambrian age to anthracite. Shorter periods of heat application need higher temperatures to reach the corresponding rank.

In the case of the alum shales, temperatures higher than 90° C are indicated by other criteria. Plotting the results (atomic H/C ratios and rank of the organic matter) of this study in a composite diagram compiled by Wassojewitz *et al.* (1969) gives palaeotemperatures around 200° C for the most altered

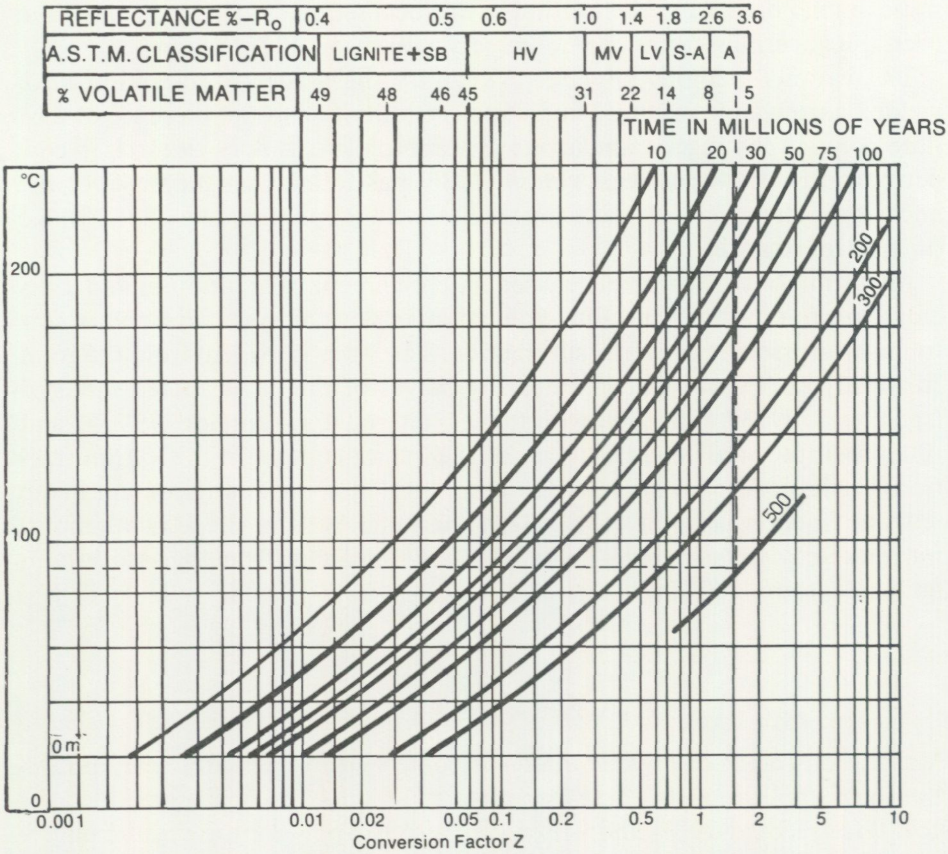


Fig. 14. Relationship between rank, temperature and time of coalification (from Karweil 1956 and Haquebard & Donaldson 1970). Here the isogrades have been extrapolated to 500 millions of years to facilitate a representation of the Late Cambrian alum shales.

Jämtland shales. Wassojewitz *et al.* (1969) diagram is based on literature data from coal bearing units of various ages (younger than Cambrian) on the European Platform.

Higher temperatures are suggested also by the mineral fraction, viz. by the illite polymorphs. Anchizone metamorphism is indicated by the presence of 2 M illite polymorphs in the allochthonous shales of the Myrviken cores. In the case of the anchizone, a temperature between a lower limit of ca. 250–280° C and an upper limit of ca. 350–400° C has been suggested (cf. Weaver & Broekstra 1984). For the shales not altered to anchizone, i.e. the autochthonous shales, palaeotemperatures below ca. 250–280° C are therefore indicated.

SHALE OVERBURDEN

In the Caledonides of Jämtland, Kisch (1980) found that both illite chrystallinity and "vitrinite" reflectance of the organic matter in the Cambro-Silurian shales increased from east to west towards the more central parts of the mountain range, i.e. higher in the tectonostratigraphy of the lower nappes. The present study has shown that there is a variation vertically in the degree of alteration within the alum shale sequences in the drillholes in the Caledonian front; allochthonous shales are more altered than autochthonous; furthermore the degree of alteration varies in the thrust sheets. This was demonstrated by the atomic H/C ratio of the organic matter as well as the illite chemistry, crystallinity and polymorphs. Within the separate thrust sheets maturity of the organic matter varies very little. This is shown by the atomic H/C ratios (illite parameters vary somewhat more than the H/C ratios of the organic matter). This indicates that maturation was not the result of frictional heating. Similar results were obtained by Hacquebard & Donaldson (1974) in a study of coal maturation in the Rocky Mountains in Canada. They found that the rank of coal was very little influenced by tectonic movements of the strata and concluded that the determining factor for maturation was the original thickness of overburden before folding and thrusting.

The high thermal maturity of the shales indicates a considerable overburden. S. M. Bergström (1980) suggested 4–7 km on the basis of his CAI studies. Assuming a thermal gradient of ca. 25° C/km and a palaeotemperture of 90° C, an overburden of nearly 4 km, existing for several hundred million years, is required for the alteration of the autochthonous Myrviken and Häggenås shales. Such a thickness may have been of primary origin, related to deposition of a thick Old Red Sandstone succession; alternatively, it might be the result of the tectonic emplacement of the Caledonian nappes. Present-day thermal gradients of ca. 15° C/km (cf. Parasnis 1975) suggest that the overburden may have been greatly in excess of 4 km, indicating that nappe emplacement probably played a significant role. It seems unlikely that overburden thicknesses of over 4 km existed for very long periods after orogenic uplift; this would imply that much thicker sequences existed over a shorter period (a few tens of millions of years).

The greater alteration of the allochthonous shales clearly indicates that they were metamorphosed prior to thrust emplacement on the autochthon. This early metamorphism may have been related to stratigraphic variations prior to orogenesis (thicker successions in the west) or to the development of an early tectonic overburden, perhaps with emplacement of higher temperature units on the shales.

In the allochthonous units of the Myrviken 78001 core, the most altered shales (7799037 and -038) are overlain and underlain by somewhat less altered units (7799031 and -046, respectively). Tectonic contacts separate the more altered from the less altered shales. The amount of movement along these internal thrust contacts in the allochthon is not known. If great, the units might be derived from different parts of the depositional basin and experienced different post-depositional histories.

Studies on conodont colour alteration (Bergström S.M. 1980) indicated that the allochthonous successions in the Southern Storsjön Area were slightly more altered than the autochthonous units, but the evidence is ambiguous. A conodont colour index of 5 (indicative of 300° C+, Epstein *et al.* 1977) was obtained for the allochthon and 4.5–5 for the autochthon. Somewhat lower values (3.5–4) were obtained from the Brunflo autochthon. These values suggest temperatures higher than those indicated by the present study for the autochthonous shales but similar to those for the allochthon. The different temperatures obtained for the autochthon might be attributed to low accuracy of the methods involved in both studies. However, even if high thermal gradients (ca. 30° C/km) are assumed, an overburden of several kilometres is necessary to produce the alteration of even the autochthonous shales. Bergström S.M. (1980), discussed the possibility of a thick allochthonous cover, but favoured an alternative hypothesis involving a particularly high thermal gradient caused by ”hot spots” as an explanation for high palaeotemperatures for the autochthon. The fact that the autochthonous shales are less altered than those in the allochthon eliminates this possibility of a ”hot spot”. The present study indicates similar thicknesses of overburden at the sites of both the Myrviken and Häggenås drillholes. This would support the idea of a large cover of nappes reaching far to the east.

COMPARISON WITH OTHER ALUM SHALES

The mineralogy of the shales can be compared only with the alum shales of Närke and Billingen because of lack of data from other areas. The general mineralogical composition of the Upper Cambrian shales from these three areas is similar. As in Billingen (Armands 1972), the major minerals of the Upper Cambrian shales in Jämtland are quartz, illite, K-feldspar and pyrite. Calcite and minor amounts of chlorite are also present. Kaolinite, which has been identified in Närke (Strahl 1958 and Assarsson & Grundulis 1961) and in Billingen shales (Armands 1972), has not been recorded in Jämtland. If it ever was present it would have been broken down by the intense alteration (cf. Dunoyer de Segonzac 1970). There are, however, other differences between the shales in the various areas. The shales in Jämtland generally have a lower content of pyrite and a higher content of calcite than the shales in

Närke and Billingen. The relatively high calcite content of the Jämtland shales, especially of the allochthonous shales, is explained by the occurrence of this mineral in irregular veins probably derived from stinkstone layers or from the calcite in the matrix. It was not possible to completely eliminate the calcite veins when sampling the shales.

The thermal maturity of the organic matter in the Jämtland alum shales is generally greater than that of the alum shales in southern Sweden. Only in the Skåne shales does the degree of metamorphism reach such high levels as in Jämtland (cf. Andersson *et al.* 1985). In the Billingen shales, the organic matter is of bituminous rank; its atomic H/C ratio is 0.8–0.9. Even higher H/C-ratios, ca. 1.2, have been found in the shales from Närke (Andersson *et al.* 1983). These ratios should be compared with the values given in Table 7. In the most altered of the investigated shales in Jämtland (from the Myrviken 78001 allochthon), the H/C-ratio of the organic matter is only 0.3–0.4 (on a d.a.f. basis). In the least altered units (from both the Klövsjö 78001 autochthon and allochthon), the H/C-ratio is 0.5–0.7.

CONCLUSIONS

The mineralogical composition of the Upper Cambrian alum shales in Jämtland is, in general, similar to that of correlative units in southern Sweden. However, the Jämtland shales contain somewhat less pyrite and more calcite. The allochthonous black shales in Jämtland differ from alum shales elsewhere in Sweden by being more deformed, recrystallized, folded and penetrated by thin irregular calcite and/or, in some cases, pyrite veins.

All the alum shales in Jämtland (in both autochthonous and allochthonous strata) differ from the shales in southern Sweden (if Skåne alum shales are excepted) by being more mature. Alteration of the Jämtland shales has resulted in a higher degree of organic matter maturation. The silicates were affected by the varying alteration of the Jämtland shales, as illustrated by the changes in crystallinity, polymorphs and chemical compositon of illite.

Both illite parameters and maturity of the organic matter show that the allochthonous Myrviken shales have been most altered and Klövsjö shales (allochthonous and autochthonous) least altered. The autochthonous shales of Myrviken area and the Häggenås shales (also autochthonous) were intermediately affected, i.e. more altered than the Klövsjö shales but less than the allochthonous Myrviken shales.

Varying degrees of alteration of the different tectonic units were observed also within the same drillcore (Myrviken 78001), more altered units are underlain as well as overlain by less altered units.

Alteration of the shales resulted in an enrichment of aluminium and decrease of iron content in the illites. Iron content of the illites in the most altered shales is 2–3 times lower than in illite from less altered shales. Very fine-grained quartz present in the <1 µm fraction of the least altered Jämtland shales recrystallized to coarser particles in the more altered units. Crystallinity of illite increases with increasing degree of alteration and also the development of the 1 M and especially 2 M polymorphs.

The K-feldspar occurring in large sections of the Upper Cambrian strata has been formed in local diagenetic environments with favourable pore water chemistry. Its abundance has not been influenced by the degree of alteration of the shale.

Based on illite crystallinity, peak ratios and polymorph criteria, the degree of alteration of the most altered shales, viz. the Myrviken allochthonous shales, is in the anchizone (cf. Fig. 9). A palaeotemperature between a lower limit of ca. 250–280° C and an upper limit of ca. 350–400°C is suggested for these shales on the basis of the clay mineralogy. The degree of alteration of the Häggenås, Klövsjö and autochthonous Myrviken shales seems not to have exceeded the upper zone of late diagenesis (<ca. 250–280° C).

Alteration of the allochthonous shales either took place in widely separated parts of the depositional basins prior to Caledonian deformation or occurred during emplacement of the Caledonian nappes due to build up of a tectonic overburden.

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APPENDIX I

SAMPLE PREPARATION AND ANALYSIS

Preparation of whole rock samples

When sampling, the drillcores usually were cut into 1.5–2 m sections. The cores (23 mm in diameter) were split lengthwise into two parts, one part for analysis and one part for reference. When sectioning the cores, interlayered stinkstones were, if possible, removed from the analysed shale sections. However, in some cases it was not possible to completely separate very thin limestone lenses and calcite veins in the shales.

The samples (0.5–1.5 kg) were crushed and divided into 200–300 g portions. These portions were ground for 3 minutes (100 g each time) in a swing mill (1000 Upm). The powder obtained was used for the whole rock chemical and mineralogical analyses.

Sample preparation for special studies of the silicates

From the portions of crushed pieces about 100 g (for each sample) were taken. In a mill (IKA Analytical Mill, with a rotating knife which cuts down the rock pieces) grain sizes were brought down to pass a 800 µm sieve. The material was split again. 50 g was wet oxidized to destroy the organic matter and the sulphides (Cassidy & Mankin 1960); thereby the silicates are dispersed. As oxidizing agent, $NaClO_4$ was used (Cassidy & Mankin 1960). The samples were treated at 70° C for a couple of days. Successively oxidized material was decanted. After treatment was completed, all the pyrite had been transformed into oxides. The samples were then washed in distilled water. The iron oxides were removed following a method described by Mehra & Jackson (1960). The samples were freeze-dried. A part of the dried material was used for grain size analyses, another part for grain size fractioning, e.g. the separation of the <1 µm and <2 µm fractions. Grain size fractioning was done by means of a centrifuge.

Sample preparation for special studies of the organic matter

Whole rock material ground for 3 minutes (cf. above) was used. 15 g were taken. It was treated for 33 hours in 1 N HCl to extract the carbonates. Released Ca-ions were washed out with distilled water. The silicates were broken down by treatment in 40 % HF (200 ml) at room temperature during 20 hours. Precipitated fluorides were extracted in saturated $AlCl_3$-solution (cf.

Kisch 1980). Then the samples were treated for four hours in 1 M HCl and again washed with distilled water. Finally the samples were washed in 96% ethyl alcohol. After drying C, H, N, S and Fe were determined in the samples.

CHEMICAL ANALYSIS

Major elements Si, Al, Ti, Fe, Ca, Mg, K and also Mn and Ba were determined by means of X-ray fluorescence, Na by atomic absorption spectrophotometry. Before analysis, the shales were ignited at 950° C and isoformed in a lithium borate melt. However, all concentrations reported refer to natural shale.

C_{tot} was determined in a LECO high frequency oven equipped with an IR detector. CO_2 was determined gravimetrically and organic carbon obtained by subtraction of C in CO_2 from C_{tot}. For the P determinations, the samples were extracted in 3 M HNO_3. Determination of P was then done in extract solution according to Asklund *et al.* (1966). For S determination, the samples were ignited at 1300° C in an airstream. The sulphur oxides formed were further oxidized to H_2SO_4 in 3% H_2O_2. The acid was titrated against NaOH.

A modified Penfield method was used to determine crystal water (H_2O^+). The determinations were done on the inorganic sulphide-free fraction, i.e. the silicate fraction, to avoid interference from volatiles in the organic matter. Volatiles in the organic matter were determined separately by SSAB, Oxelösund, according to international standard (ISO 562, 1974). During heating in the unoxidized atmosphere pyrite is transformed into pyrrhotite. The V.M. values were corrected for this. Loss on ignition was determined at 1050° C.

Determination of C, H, N and S in the samples enriched in organic matter and pyrite was done by a Carlo Erba elemental analyser at the Institute of Chemistry, Swedish University of Agricultural Sciences.

MINERALOGICAL ANALYSIS

INSTRUMENTAL

Mainly X-ray diffraction (XRD) methods were applied. A Philips diffractometer (PW 1730 generator) with an AMR X-ray focussing monochromator was used. The radiation (CuK_α) was generated at 40 kilovolts and 30 milliamperes for the whole rock analyses and at 40 kilovolts and 25 milliamperes when illite polymorphs, crystallinity and sharpness ratio were determined. In the first case, a 1° divergence and a 0.2° receiving slit were used, and in the latter case 1° slits both in receiving and diverging sites.

Analyses of the whole rock samples were performed with goniometer scanning rate 1° 2θ/min., chart rate 10 mm/min. and TC 4 on the scale 200 c/s. Spectra covering the interval 2°–65° 2θ were recorded.

Analyses of the <1 µm fractions for illite polymorph determination were performed with scanning rate 0.25° 2θ min., chart rate 5 mm/min. and TC 10 on the scale 200 c/s.

Analyses of the <2 µm fractions for illite crystallinity and sharpness ratio determinations were performed with a scanning rate of 0.5° 2θ/min., chart rate 20 mm/min. and TC 1 mostly on the scale 4×10^3 c/s (cf. Kisch 1980). All the determinations were done twice. (Calibration was performed against polished slates specimens provided by H. J. Kisch.)

QUANTITATIVE DEMTERMINATIONS

Whole rock. – Organic matter, calcite and pyrite were quantitatively determined (Fig. 7) in all samples using the data of C_{org}, CO_2 and S from the chemical analyses of the samples. A factor of 1.1 (based on known carbon content of coal of semi-anthracitic–anthracitic rank) was used to calculate the organic matter content from the organic carbon values. This factor may be slightly low for the shales from the Häggenås 77001 core, the Klövsjö 78001 core and for the autochthonous parts of the Myrviken 79002 core.

The quantities of minerals (figures under headline Q in Table 1) were calculated from the chemical composition of the shales (Table 2) using the ideal K-feldspar and quartz formulae and composition of illite according to Table 5. The chemical formulae of the illites in Table 5 were calculated from data in Table 4 after correction for quartz (Table 3). They accordingly represent the true composition of the illite (<1 µm fraction) in every sample.

The semi-quantitative determinations of the silicates in Fig. 7 (and figures under headline XRD in Table 1) were done from XRD data only. To find a simple and accurate way of mineral representation on the basis of XRD data, reference black shale samples were made with quartz and illite in six different proportions. Various parameters were tried to obtain the best representation of the minerals. The best fit to a reference line was obtained by the ratio: $x = (I_{\text{quartz }50^\circ} + I_{\text{quartz }60^\circ})/(I_{\text{illite }35^\circ} + I_{\text{ilite }62^\circ})$ where e.g. $I_{\text{quartz }50^\circ}$ means intensity of the quartz peak at $2\theta = 50^\circ$. Scattering of calculated percentages was ±5 % (absolute) with 95 % confidence for the reference samples.

A fixed proportion is defined by $y = c \cdot x$ where c is a constant. However, variations in illite intensities are low as compared to variations in quartz intensities. Illite, in practice, is acting as an internal standard for quartz determination. K-felsdspar content was determined from the intensity ratios of the K-feldspar peaks at 27.5° 2θ and the illite peaks.

The content of plagioclase was estimated on the basis of the peak intensity ratios $I_{\text{plagioclase } 22^\circ}/I_{\text{quartz } 50^\circ}+I_{\text{quartz } 60^\circ}$. The chlorite content was estimated from the intensity ratio $I_{\text{chlorite } 12.5^\circ\ (7\text{Å})}/I_{\text{illite } 9^\circ\ (10\text{Å})}$ based on Augedahl's (1978) documentation that equal concentrations of illite and chlorite yield chlorite 7Å-peaks which are double the strength of the illite 10Å-peaks.

< 1 μm fraction. – Quartz content of the < 1 μm fraction was determined by means of DTA by comparison with XRD patterns with known quartz admixtures. The DTA analyses were performed at the laboratory of Engineering Geology, Norwegian Institute of Technology, Trondheim. Control measurements were not done, but errors of the DTA determinations are estimated to ±30 % (relatively) for quartz content around 10 % and ±50 % (relatively) for the lowest concentrations (1–3 %).

SPECIAL CLAY MINERAL ANALYSES

The silicate < 2 μm fraction (organic matter and pyrite removed) was used for illite crystallinity (Kubler 1967, 1968, Dunoyer de Segonzac 1969 and Kisch 1980) and sharpness ratio determinations (Weaver 1960). The samples were prepared according to Drever (1973). Thickness of specimen was 11–14 mg/cm^2. The samples were Na saturated and air dried when analysed. The relative humidity was 60 %.

The silicate < 1 μm fraction was used for illite polymorph and quantitative 2 M determinations (Velde & Hower 1963). For the latter determinations the ratio 023-peak 2 M illite/the combined illite peak at 35° 2θ was measured. Pure muscovite (2 M) was used as reference. Background values were obtained from analysis of pure phlogopite (1 M). Mixtures of muscovite and phlogopite were analysed for comparison with the XRD patterns of the shale fractions. Grain size of all the minerals was < 1 μm.

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