

# PETROLOGY OF ORDOVICIAN SEDIMENTS FROM WALES

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52 samples of Ordovician (Arenig-Caradoc) sediments from Wales have been analysed with respect to major elements and to certain trace elements ( $\text{Rb}_2\text{O}$ ,  $\text{SrO}$ ,  $\text{ZrO}$ ,  $\text{MnO}$  and  $\text{P}_2\text{O}_5$ ). The same samples were studied mineralogically by X-ray diffraction and in thin sections.

The correlation coefficients of the major and trace elements have been calculated. The dominant minerals are illite, mixed-layered illite/montmorillonite, chlorite, vermiculite, quartz and feldspar (plagioclase). Relatively pure potassium-bentonite beds with mixed-layered minerals are reported.

The average composition of the samples analysed shows low  $\text{MgO}$  (1.4 %) compared to published analyses from the Trondheim and Oslo Regions of Norway. This can be explained by the overall acid composition of probable Precambrian source rocks and by the fact that the Ordovician volcanism in Wales is predominantly of acid to intermediate composition. The Ordovician sediments of the Norwegian Caledonides, however, seem to be a product of more basic volcanism and larger complexes of gabbroid rocks in the Precambrian basement exposed as source rocks.

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## Introduction

The purpose of the present investigation is to provide more information on the composition of sediments of the Welsh part of the Caledonian geosyncline.

This is a part of a larger survey of the geochemistry of Lower Palaeozoic sediments along the Caledonian geosyncline undertaken by the author. Investigations on the geochemistry of the eugeosynclinal sediments from the Trondheim Region and from the foreland sediments of the Oslo Region in Norway are in progress.

The Lower Palaeozoic sediments in Wales are not considered to be typically eugeosynclinal (Boswell 1961), but this facies is also different from the foreland sedimentation on the Scandinavian Shield.

Ordovician sediments were collected from sections in 3 areas in Wales: Anglesey, Builth Wells and Llandeilo. After the analogy of the author's previous work from the Oslo Region (Bjørlykke 1965) the investigations were concentrated on Lower and Middle Ordovician (Arenig-Caradoc) sediments.

## Localization of the samples

It was difficult to find continuous sections in the selected areas, and on Anglesey and in the Builth Wells region samples had to be collected from several different sections. Samples were only collected from fossiliferous localities or other localities where the stratigraphic control was good.

Care was taken to get the samples as fresh as possible.

### LLANDEILO

At Llandeilo, samples were collected from the railway-section south of the level-crossing at Ffairfach (Williams 1953). The section consists of grit and ashy shales of Llanvirnian and Lower Llandeilian age (L20–27) with more calcareous sediments of Middle and Upper Llandeilian age (L28–29). Samples of Caradocian mudstones were collected about one mile NW of Llandeilo (L30–32).

### ANGLESEY

In Anglesey samples were collected mostly from localities described by Greenly (1919). They consist of shales and ashy shales, stratigraphically ranging from Arenigian (*D. extensus* zone) to the Caradocian (*Cl. wilsoni* zone). The author was guided in the field by Dr. D. Bates, who has recently described the Lower Palaeozoic shelly fauna of Anglesey (Bates 1968).

(N. G. R. = National Grid Reference)

- A 1. Gynfor Shales. *N. gracilis* zone. Llanbadrig. N. G. R. 378948.
- A 3. Porth Pridd Shales. *N. gracilis* zone. Porth Padrig (Cemaes Bay). N. G. R. 376944.
- A 4. Shales of Garn Formation. *N. gracilis* zone. Porth Padrig (Mynachdy). N. G. R. 305928.
- A 5. Oolitic Ironstone? Llandeilian. Bonw. N. G. R. 317897.
- A 6. Nantannog Formation. *D. murchisoni* zone. Fferam-uchaf. N. G. R. 362865.
- A 7. Shales. *Cl. peltifer* zone. Fferam-uchaf. N. G. R. 366868.
- A 8. Shales. *D. murchisoni* zone. Llanbabo. N. G. R. 378866.
- A 9. Shales of Llanbabo Formation. *N. gracilis* zone. Llanbabo. N. G. R. 378867.
- A 10. Shales. *Cl. wilsoni* zone. Llanbabo. N. G. R. 381871.
- A 11. Shales *D. bifidus* zone. Tyddyn-bach, on bank of Afon Goch. N. G. R. 444864.
- A 12. Shales. *D. bifidus* zone. Llandyfrydog. N. G. R. 443853.
- A 13. Shales. *D. hirundo* zone. Llwydiarth Esgob. N. G. R. 433844.
- A 14. Shales. *D. extensus* zone. 1.5 km WNW of Llanerchymedd. N. G. R. 404847.

- A 15. Shales. *D. hirundo* zone. 1.75 km W of Llanerchymedd. N. G. R. 400843.
- A 16. Shales. *D. bifidus* zone. 100 m N of Gwredog Farm, Rhodogeidio. N. G. R. 405863.
- A 17. (a) shales, (b) ironstone. *D. murchisoni* zone. Llangoed. N. G. R. 602796.
- A 19. Shales. *D. extensus* zone. Between the two bridges on Caernarvonshire shore. N. G. R. 552712.

#### BUILTH WELLS

The Builth inlier has been described by O. T. Jones and W. J. Pugh (1941, 1949) and G. L. Elles (1940). The area consists of highly fossiliferous shales and volcanic rocks. The spilitic lavas have been described by G. D. Nicholls (1958). The author was guided in the field by Dr. Chr. Hughes.

- B 1–B 3. Section at Garn Fawr. Upper part of *D. bifidus* zone.
- B 4–B 7. Stream section, Pendre (Elles 1940, p. 392).
  - B 4–6, Lower *D. bifidus* zone.
  - B 7, possibly Upper *D. bifidus* zone.
- B 8. Volcanic rock overlaying *D. bifidus* schist.
- B 9–B 16. Stream section, Bach-y-Graig, one mile east of Llandrindod Wells town (Elles 1940, p. 404). Length of section 140 m, 2 m from the top of the *D. murchisoni* zone up into the *Glyptograptus teretiusculus* zone. The section consists of dark graptolite shale with thin beds of feldspathic and calcareous ash.
- B 17. Bwlch-Llwyn. Shale. Top *bifidus* zone.
- B 18. Llanfawr Quarry, Middle Quarry (Elles 1940, p. 417). Shale of the *N. gracilis* zone.
- B 19. Pencerrig Lake Quarry (Elles 1940, p. 417). *G. teretiusculus* zone.

#### Preparation and analyses of the samples

The X-ray fluorescence work was carried out following the laboratory routine established at the Sedimentology Research Laboratory, Reading. The analyses were much facilitated by the use of standards and a computer programme prepared by Dr. A. Parker. The following elements were determined by X-ray fluorescence: Rb<sub>2</sub>O, SrO, ZrO and CaO. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> were determined colorimetrically on the autoanalyser at the Sedimentology Research Laboratory, Reading. Na<sub>2</sub>O and K<sub>2</sub>O were determined on a flamephotometer. Mr. J. E. Thomas was responsible for the wet analyses. Analyses of MgO (and CaO) were carried out at the Norwegian Geological Survey, Department for Geochemistry (analyst M. J. Faye) on an optical automatic quantometer.

Table 1. Geochemical composition of 52 samples of the Ordovician of Wales. A1–A19 samples from Anglesey; B2a–B19 samples from Builth Wells; L20–L32 samples from Llandello. nd = not detected.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Total Fe as Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	StrO	RbO	ZrO	K <sub>2</sub> O/ Rb <sub>2</sub> O
A1	66.5	0.55	13.16	2.73	0.06	1.60	3.20	0.19	3.75	0.444	76	100	232	375
A3	63.3	0.88	19.98	2.23	0.01	0.60	0.08	0.31	5.37	0.030	42	219	197	245
A4a	58.3	1.04	21.39	6.40	0.05	1.60	0.28	0.41	4.93	0.247	28	167	232	295
A4b	54.0	0.94	21.52	9.32	0.04	1.90	0.25	0.65	4.86	0.202	31	154	154	216
A5	62.2	0.56	12.99	15.92	0.17	2.50	0.24	0.35	0.56	0.290	44	10	208	560
A6	70.2	0.39	14.00	6.03	0.09	1.50	0.14	0.57	2.06	0.092	40	63	704	327
A7	61.1	0.91	19.00	5.74	0.04	1.60	0.09	1.20	3.90	0.133	59	156	269	250
A8	69.3	0.77	14.79	3.64	0.30	1.10	0.44	1.11	3.21	0.177	80	125	256	257
A9	65.9	0.62	14.38	7.09	0.06	1.90	0.08	0.68	2.89	0.121	33	119	208	242
A10	56.1	1.03	20.51	8.93	0.02	1.50	0.23	0.76	3.18	0.130	86	127	218	250
A11	62.3	1.02	19.57	5.20	0.03	1.90	0.24	0.71	3.26	0.102	149	143	300	228
A12	63.9	0.92	17.38	6.01	0.03	1.70	0.23	1.74	3.03	0.185	53	58	180	530
A13	60.0	0.79	16.43	14.58	0.13	2.30	0.20	5.43	1.89	0.156	85	152	290	123
A14	55.6	1.09	22.49	7.76	0.20	0.80	0.05	0.82	4.41	0.150	133	155	247	285
A15	53.2	1.08	22.12	9.44	0.76	1.50	0.09	1.03	3.02	0.200	122	115	224	263
A16	57.0	1.17	22.13	6.88	0.03	1.30	0.06	0.92	3.38	0.086	133	145	266	233
A17a	64.4	0.84	16.27	6.61	0.01	0.90	0.22	0.29	3.51	0.117	57	137	250	255
A17b	66.7	0.81	13.91	9.18	0.01	1.30	0.25	2.36	1.32	0.292	57	39	287	237
A19	60.4	1.06	15.44	6.60	0.01	1.30	0.12	0.75	4.23	0.046	97	186	259	227
Average														
A1–A19	61.6	0.87	17.76	7.38	0.13	1.51	0.35	1.07	3.30	0.168	74	125	261	267
B2a	67.1	1.02	16.78	1.69	nd	0.9	0.10	0.87	3.49	0.068	73	180	387	193
B2b	63.3	0.71	18.65	3.95	nd	0.7	0.20	4.24	1.75	0.093	113	72	495	244
B3	59.5	1.08	19.35	6.28	nd	1.1	0.24	0.87	3.44	0.135	65	141	259	244
B4	55.8	1.16	22.94	6.63	0.02	1.5	0.19	0.35	3.29	0.082	105	161	298	205
B5	56.2	1.18	22.92	6.85	0.02	1.4	0.19	0.40	3.25	0.095	104	145	290	225
B7	61.7	1.12	20.09	5.82	0.01	1.0	0.11	0.40	3.00	0.069	77	148	365	203

B9a	63.5	0.68	16.85	4.95	0.03	2.0	0.27	1.45	3.47	0.101	101	149	322	232
B9b	47.1	1.33	28.05	5.72	0.05	1.8	0.32	1.02	5.90	0.141	83	168	319	345
B10	64.0	0.68	16.73	4.91	0.03	2.0	0.21	1.38	3.48	0.111	148	180	340	193
B11	65.9	0.63	14.98	5.05	0.04	1.8	0.76	1.31	2.95	0.309	86	73	320	404
B12	76.9	0.43	12.14	2.49	0.16	1.0	0.29	0.65	2.90	0.088	41	77	312	375
B12b	41.6	0.20	6.34	1.16	0.62	0.5	25.20	0.65	1.19	0.132	125	28	132	520
B13	46.4	1.29	14.56	1.47	0.23	0.4	15.14	5.35	1.06	0.530	200	26	216	405
B14	51.3	1.65	29.15	2.24	nd	0.9	0.22	2.51	5.16	0.102	99	161	1178	320
B15	61.5	0.90	16.94	6.48	0.03	2.1	0.24	1.36	3.09	0.148	64	139	222	222
B16	59.0	0.95	18.43	6.69	0.03	1.9	0.22	1.53	3.33	0.188	48	132	222	252
B17	67.5	0.86	13.85	5.23	0.04	2.3	0.39	2.42	1.82	0.172	105	80	226	226
B18	68.8	0.60	11.91	4.61	nd	1.0	0.43	2.91	0.68	0.249	126	23	160	295
B19	61.0	0.87	16.89	4.63	0.03	2.3	0.46	1.87	3.14	0.486	108	136	353	232
Average B2-B19	59.89	0.91	17.76	4.57	0.08	1.40	2.82	1.66	2.97	0.140	107	117	338	281
L20	71.2	0.37	6.83	2.11	0.068	2.9	4.53	0.85	1.67	0.177	90	37	180	450
L22	70.7	0.79	14.30	2.93	nd	0.9	0.25	0.20	3.67	0.168	90	130	245	282
L23	69.6	0.65	10.16	3.05	0.129	1.8	3.10	0.83	2.97	0.380	97	61	292	488
L24a	52.0	0.45	7.70	2.57	0.035	0.8	17.46	1.19	1.46	0.590	655	33	243	441
L24b	69.6	0.37	10.51	2.12	0.028	0.8	5.27	1.11	2.18	0.347	295	52	274	422
L25	70.3	0.56	8.31	2.11	nd	0.9	6.31	1.05	1.77	0.480	530	65	350	272
L26a	61.8	0.63	10.16	3.95	0.020	0.9	8.57	0.65	2.10	0.260	450	62	241	338
L26b	46.9	0.39	6.43	2.17	0.020	0.4	22.08	0.80	2.16	0.200	870	24	202	900
L27	31.3	0.20	3.56	1.53	0.023	0.8	33.29	0.60	0.67	0.180	685	5	215	1120
L28	34.2	0.17	3.02	1.29	0.035	0.7	32.24	0.51	0.64	0.270	765	7	137	910
L29	44.5	0.31	5.49	2.04	0.023	0.9	23.34	0.65	1.14	0.230	905	28	188	407
L30	55.0	0.89	17.37	7.23	0.045	1.9	4.49	0.93	3.15	0.140	348	115	250	275
L31	57.7	1.10	19.71	8.45	0.030	2.0	0.53	1.42	3.13	0.170	115	136	254	230
L32	60.2	1.02	19.22	7.44	0.030	1.8	0.21	1.42	3.01	0.140	108	128	279	235
Average L20-L32	56.79	0.56	10.19	3.35	0.036	1.25	11.55	0.87	2.12	0.268	430	63	239	476
Average of all (52) samples:	59.68	0.80	15.73	5.31	0.08	1.40	4.10	1.23	2.86	0.188	179	105	284	339

Table 2. Table of correlation coefficients of the elemental distribution in 52 samples of Ordovician sediments from Wales. Calculations are carried out according to Chayes & Kruskal (1966).

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SrO	Rb <sub>2</sub> O	ZrO <sub>2</sub>
SiO <sub>2</sub>	1.000	0.009	0.104	0.109	-0.187	0.315	-0.735	-0.006	0.150	0.065	-0.563	0.199	0.107
TiO <sub>2</sub>	0.009	1.000	0.904	0.340	-0.083	0.129	-0.596	0.195	0.660	-0.407	-0.516	0.670	0.341
Al <sub>2</sub> O <sub>3</sub>	0.104	0.904	1.000	0.440	-0.048	0.228	-0.722	0.085	0.766	-0.438	-0.641	0.787	0.396
Fe <sub>2</sub> O <sub>3</sub>	0.109	0.339	0.440	1.000	0.088	0.555	-0.501	0.123	0.096	-0.119	-0.426	0.265	-0.098
MnO	-0.187	-0.083	-0.048	0.088	1.000	-0.080	0.142	0.029	-0.141	-0.037	-0.113	-0.164	-0.162
MgO	0.316	0.129	0.228	0.555	-0.080	1.000	0.478	0.023	0.133	0.068	-0.437	0.217	-0.103
CaO	-0.735	-0.596	-0.722	-0.501	0.142	-0.478	1.000	-0.068	-0.570	0.225	0.831	-0.648	-0.254
Na <sub>2</sub> O	-0.006	0.195	0.085	0.123	0.029	0.023	-0.068	1.000	-0.282	-0.068	-0.104	-0.128	0.183
K <sub>2</sub> O	0.150	0.660	0.766	0.096	-0.141	0.133	-0.570	-0.282	1.000	-0.300	-0.485	0.865	0.271
P <sub>2</sub> O <sub>5</sub>	0.065	-0.407	-0.438	-0.119	-0.037	0.068	0.225	-0.068	-0.300	1.000	0.357	-0.444	-0.119
SrO	-0.563	0.516	-0.641	-0.426	-0.113	-0.437	0.831	-0.104	-0.485	0.357	1.000	-0.544	-0.167
Rb <sub>2</sub> O	0.199	0.700	0.787	0.265	-0.164	0.217	-0.648	-0.128	0.865	-0.444	-0.544	1.000	0.226
ZrO <sub>2</sub>	0.107	0.341	0.396	-0.098	-0.162	-0.103	-0.254	0.183	0.271	-0.119	-0.167	0.226	1.000

Table 3. Table of 'Null values' (Chayes & Kruskal 1966). The correlation coefficients above are calculated to estimate the 'closed system' effect in chemical analyses. A strong increase in the concentration of one major element will tend to be associated with a decrease in a number of other elements giving a negative correlation coefficient.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SrO	Rb <sub>2</sub> O	ZrO <sub>2</sub>
SiO <sub>2</sub>	-1.638	-0.041	-0.427	-0.217	-0.096	-0.055	-0.596	-0.082	-0.092	-0.089	-0.152	-0.051	-0.113
TiO <sub>2</sub>	-0.041	0.216	-0.084	0.074	0.012	0.197	-0.187	0.069	0.175	0.110	0.016	0.153	0.123
Al <sub>2</sub> O <sub>3</sub>	-0.427	0.084	-0.070	-0.022	-0.019	0.073	-0.231	0.010	0.053	0.026	-0.031	0.054	0.026
Fe <sub>2</sub> O <sub>3</sub>	-0.217	0.074	0.022	0.000	-0.007	0.066	-0.142	0.015	0.053	0.029	-0.013	0.050	0.031
MnO	-0.096	0.012	-0.019	-0.007	-0.005	0.010	-0.046	0.000	0.006	0.002	-0.008	0.007	0.002
MgO	-0.055	0.197	0.073	-0.066	0.010	0.180	-0.178	0.063	0.159	0.100	0.013	0.139	0.111
CaO	-0.596	-0.187	-0.231	-0.142	-0.046	-0.178	-0.080	-0.087	-0.174	-0.122	-0.071	-0.141	-0.141
Na <sub>2</sub> O	-0.082	0.069	0.010	0.015	0.000	0.063	-0.087	0.019	0.054	0.033	-0.001	0.048	0.036
K <sub>2</sub> O	-0.092	0.175	0.053	0.053	0.006	0.159	-0.174	0.054	0.139	0.087	0.007	0.123	0.096
P <sub>2</sub> O <sub>5</sub>	-0.089	0.110	0.026	0.029	0.002	0.100	-0.122	0.033	0.087	0.053	0.002	0.077	0.059
SrO	-0.152	0.016	-0.031	-0.013	-0.008	0.013	-0.071	-0.001	0.007	0.002	-0.012	0.009	0.001
Rb <sub>2</sub> O	-0.051	0.153	0.054	0.050	0.007	0.139	-0.141	0.048	0.123	0.077	0.009	0.108	0.086
ZrO <sub>2</sub>	-0.113	0.123	0.026	0.031	0.002	0.111	-0.141	0.036	0.096	0.059	0.001	0.086	0.065

## X-ray diffraction

### Methods

Samples for X-ray diffraction were taken from the samples prepared for X-ray fluorescence analyses.

For each sample five X-ray examinations were made after different sets of treatment.

1. Unorientated sample.

Rock powder was spread over a glass slide coated with vaseline.

2. Orientated sample.

An orientation of the clay minerals was obtained by pipetting suspended clay onto glass slides and letting it dry.

3. Glycolation.

The samples were placed in a dessicator with ethylene glycol for 24 hours.

4. Heat treatments to 400 °C.

5. Heat treatments to 550 °C.

Diagnostic criteria are the same as used by Bjørlykke (1965). Semiquantitative calculations were based on unorientated samples. The intensity of the following reflections characteristic of the main minerals was measured: 10–14Å (mixed-layered illite/montmorillonite), 10Å (illite), 7Å (chlorite), 4.26Å (quartz), 3.18–3.20Å (feldspar), 3.03Å (calcite) and 2.88Å (dolomite). The intensity of a reflection ( $I_o$ ) was measured as the height of the peak ( $h$ ) times the width at half height ( $w$ ), following Norrish & Taylor (1962). This intensity  $I_o$  of each reflection was recalculated into percentages of the total intensity of the reflections from these minerals. The relative intensity ( $I_x$ ) from a mineral  $x$  is thus:

$$I_x = \frac{I_o \cdot 100}{I_{10-14\text{\AA}} + I_{10\text{\AA}} + I_{7\text{\AA}} + I_{4.26\text{\AA}} + I_{3.03\text{\AA}} + I_{2.88\text{\AA}}}$$

### Mineralogy

*Illite* is present as a major mineral constituent in all samples analysed. The dominant illite is dioctahedral with a relatively low ratio between the intensity of the 10Å and 5Å reflections ( $I_{10\text{\AA}}/I_{5\text{\AA}}$  3–4), and a (060) reflection at 1.49Å (Maxwell & Hower 1967). The sharpness of the 10Å reflection ( $I_{10\text{\AA}}/I_{10.5\text{\AA}}$ ) (Weaver 1962) varies from 4 to 6 for the relatively well crystallized illites to more degraded illites and mixed-layered illite/montmorillonite minerals. In the bentonites (sample B14) a trioctahedral illite (degraded biotite) is found along with the common octahedral illite (Fig. 1).

*Chlorite* was identified in all samples except a few rich in volcanic material or carbonates. In most samples the ratio between the intensities of the 7Å and 14Å reflections is larger than 2, suggesting that the chlorite is relatively



iron-rich (Grim 1968). This is supported by the generally low MgO content in the bulk analyses of the samples. The iron-rich sediments of the oolitic iron ores of Anglesey (A5) contain chamositic chlorite (Fig.2).

A randomly mixed-layered *illite/montmorillonite* is found in many of the samples (Fig. 3) and is present in all three areas. All samples containing mixed-layered minerals also contain detectable amounts of feldspar. Mixed-layered minerals are mostly found in samples containing volcanic ash and lava fragments and are present in about 50% of the samples from Builth Wells.

A relatively pure mixed-layered *illite/montmorillonite* is found in the bentonites (B14). Its 10–15Å reflection expands partly after glycol treatment, and heat treatment causes a collapse to 10Å (Fig. 1). Chemical analyses of this sample (B14) show high alumina content (29%  $\text{Al}_2\text{O}_3$ ) and a potassium content of 5%. A sodium content of 2% is due mostly to the plagioclase content. These bentonites are mineralogically and chemically similar to the potassium bentonites of the Oslo region (Hagemann & Spjeldnæs 1955 and Jørgensen 1964) and to equivalent beds in Kinnekulle, Sweden (Byström

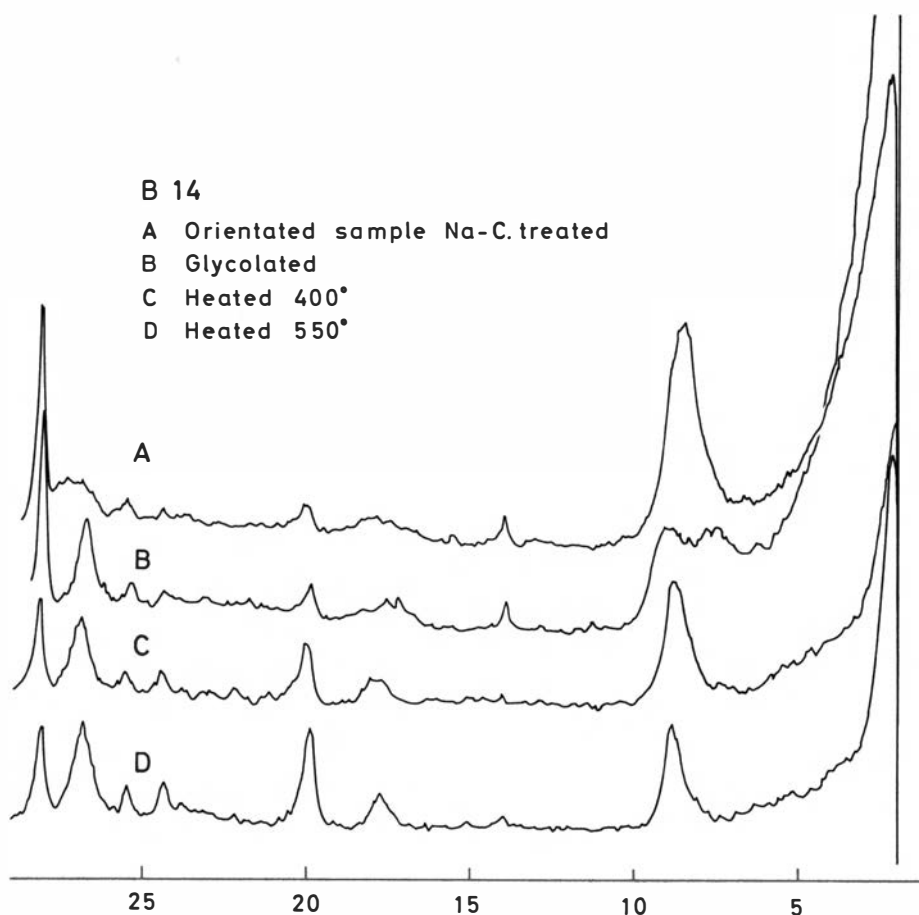


Fig. 1. X-ray diffraction diagrams of potassium bentonite from Builth Wells (B14).

1956). The present bentonites however have a distinctively higher content of aluminium and titanium than values reported from the Palaeozoic bentonites in Norway and Sweden.

The pure bentonite (B14) has an anomalously high  $\text{ZrO}_2$  concentration (1178 p. p. m.), and by separation with heavy liquids, zircon crystals, both euhedral and anhedral, were found to be abundant in the heavy liquid fraction. Zircon crystals have also been reported from bentonites of the Oslo region by Hagemann & Spjeldnæs (1955), and from K-bentonites in Pennsylvania by Weaver (1953).

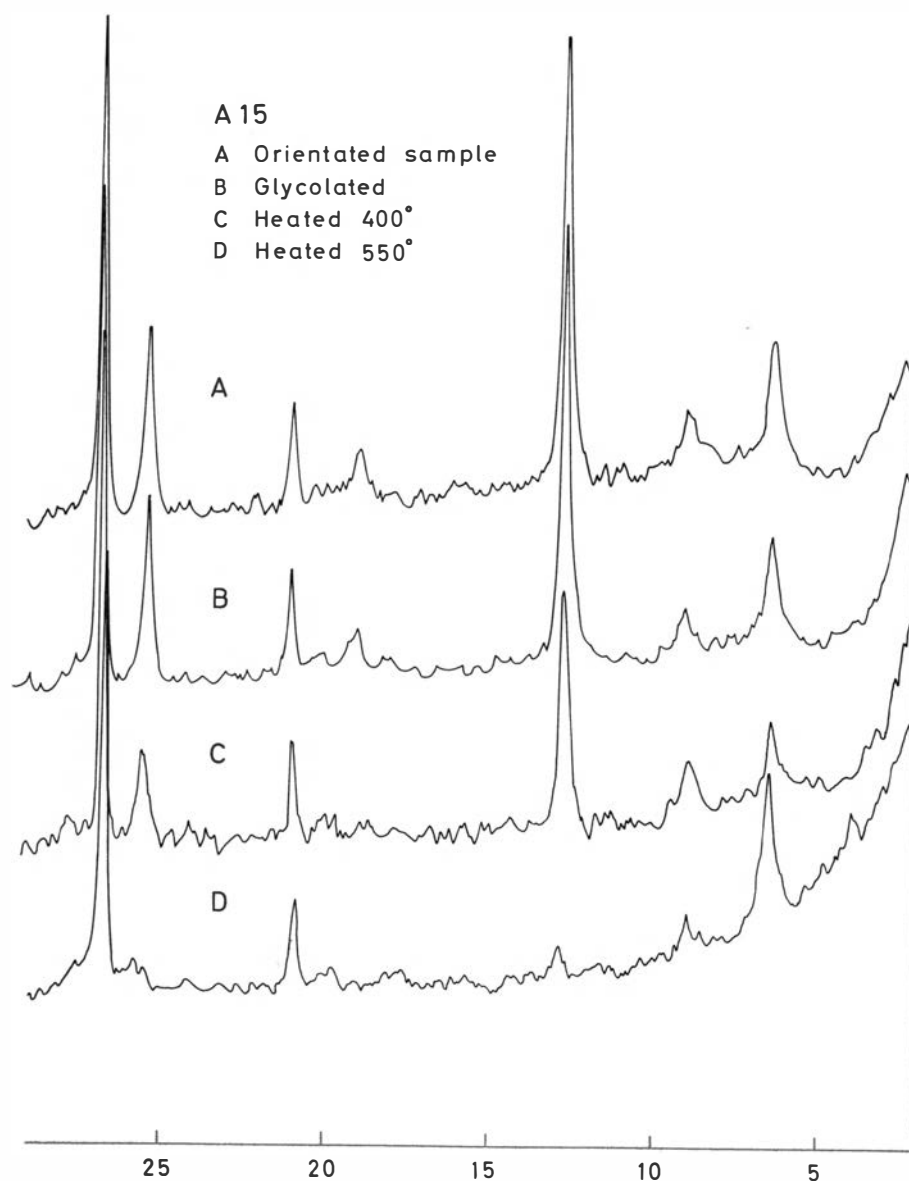


Fig. 2. X-ray diffraction diagram of oolitic ironstone from Anglesey (A15).

*Vermiculite* was identified by a collapse of the (001) reflection from 14Å to 10Å after heat treatment. It was found to be present in the Caradocian mudstones of the Llandeilo district and in three samples from Anglesey. It seems most likely that the vermiculite in these sediments was formed by relatively recent weathering of the mudstones.

*Feldspar* is a major mineral component in most samples analysed (Fig. 3). Particularly high feldspar contents are found in the sediments rich in volcanic ash and lava fragments. A few mature shales have feldspar contents below the detection limit. The dominant feldspar is plagioclase (oligoclase) with (040) reflection at 3.18Å.

### Correlation of major and minor elements

The correlations between the analysed elements were calculated according to Chayes & Kruskal (1966). The calculations were carried out on the computer at the University of Oslo, taking advantage of a programme prepared for this purpose by Dr. O. H. J. Christie.

The correlation coefficients listed in Table 2 are partly a result of the fact that chemical analyses represent a closed system (totalling 100%). This effect is shown in Table 3 which is based on the assumption that no correlation between elements exists (Chayes & Kruskal 1966). The correlation coefficients in this table are therefore solely a consequence of the closed system (null values). It is evident that  $\text{SiO}_2$  is negatively correlated with most other elements because an increase in the  $\text{SiO}_2$  content will be at the expense of most other major elements. By subtracting the 'null values' in Table 3 from the correlation coefficients in Table 2, one will obtain more significant figures of the correlations between the elements.

It can be seen from the table that a strong correlation exists between  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  (0.904) and that this is partly a result of the closed system giving a null value of 0.216. However, even if one allows for this, a significant correlation remains (0.688). It can also be seen that the correlation between  $\text{CaO}$  and  $\text{SrO}$  (0.831) with a null value -0.071 and between  $\text{Rb}_2\text{O}$  and  $\text{K}_2\text{O}$  (0.865) with null value 0.123 is stronger than that between  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ .

### DISTRIBUTION OF ALKALI METALS

Analyses of sodium, potassium and rubidium are given in Table 1. The sodium content of the sediments analysed is generally moderate (average 1.23%  $\text{Na}_2\text{O}$ ) except in beds with a high plagioclase content. The potassium content is relatively high, with maximum values found in the potassium bentonites. The average  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio of all samples is 2.53 which is somewhat lower than the  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio of an average Palaeozoic shale (2.80, Clarke 1924). The lowest average  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio (1.79) is found in the Builth Wells area, where andesitic (spilitic) volcanism has deposited ash beds rich in sodium.

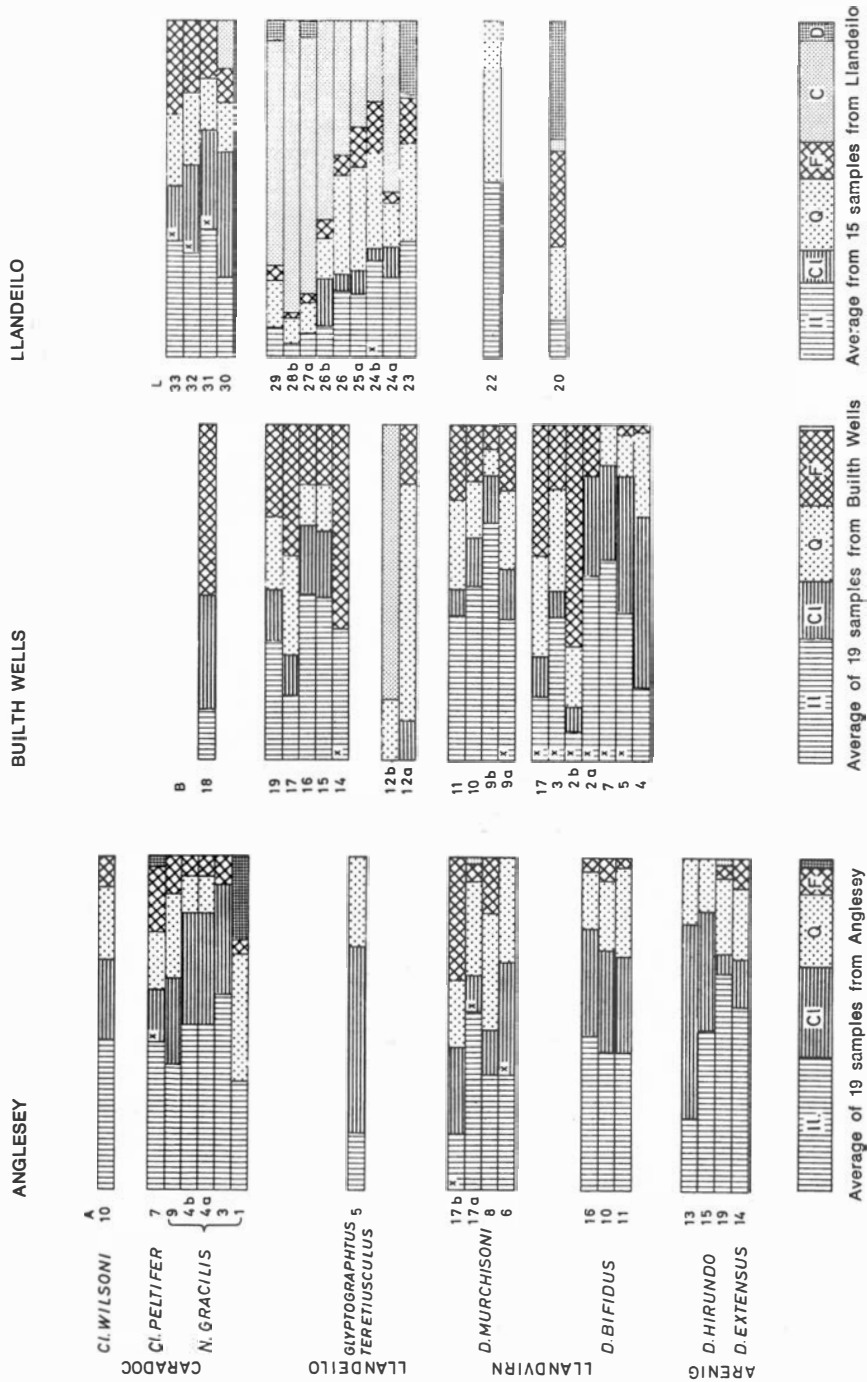


Fig. 3. Semiquantitative mineral composition of 53 samples of the Ordovician of Wales.

The average potassium/rubidium ratio in the Llandeilo area ( $K_2O/Rb_2O = 476$ ) is significantly higher than in Anglesey ( $K_2O/Rb_2O = 267$ ) and Builth Wells ( $K_2O/Rb_2O = 281$ ). Within each area higher  $K_2O/Rb_2O$  ratios are found in the bentonite samples and in samples containing some volcanic ash (B9b, B11, B12, B13, B14, A12, L23, L24, L26) and in the limestones. Low  $Rb_2O$  values (10 p. p. m.) and high  $K_2O/Rb_2O$  ratios are found in the oolitic iron ores and in the limestones.

The correlation coefficient between the  $K_2O$  content and  $Rb_2O$  content in the present material was found to be 0.86, which agrees well with the values obtained by Landergren (1948, p. 72) from iron ores and associated rocks from the Precambrian of Sweden (correlation coefficient 0.84). The present material shows higher  $K_2O/Rb_2O$  ratios in the samples rich in relatively unaltered volcanic debris than in the more mature shales with lower feldspar content. This is in accordance with general theories on the distribution of alkali metals (Heier & Adams 1963). The mean value of the present 52 samples from the Ordovician of Wales is 339, which is considerably higher than the values cited for mature shales ( $K_2O/Rb_2O = 150$ ) by Heier & Adams (1963).

#### *MnO, $P_2O_5$ , CaO, SrO and $ZrO_2$*

MnO values are generally low, showing little systematic variation and no significant positive correlation with other elements. The  $P_2O_5$  content shows only weak correlations with other elements, the strongest being with calcium (0.357). SrO is well correlated with CaO (correlation coefficient 0.831) and is negatively correlated with other elements except  $P_2O_5$ . The CaO/SrO ratios of the samples from Builth Wells and Llandeilo are between 260 and 270, while a lower average value (CaO/SrO = 47) is found in the less calcareous sediments of Anglesey, where SrO must be assumed to be present mainly in silicate minerals.

The  $ZrO_2$  content shows few significant variations, but is enriched in one of the bentonite samples (B14) in which zircons have been found (see page 132).

#### *$SiO_2$ , $TiO_2$ , $Al_2O_3$ and $Fe_2O_3$*

The  $SiO_2$  content varies between 55% and 66% in most noncarbonaceous samples, the silica content in the relatively pure bentonite being as low as 51.30 (B14). The average  $Al_2O_3$  content is 17–18% both in Anglesey and in the Builth Wells area, while the alumina content in the Llandeilo area is significantly lower (10.19%  $Al_2O_3$ ). Even after allowing for the admixture of carbonaceous matrix, the average  $Al_2O_3$  values of the Llandeilo samples is only 12.8%. This reflects the low maturity of the pre-Caradocian ashy grits in Llandeilo.

The  $TiO_2$  content is well correlated with  $Al_2O_3$  (correlation coefficient 0.904) and shows a clear positive correlation with  $K_2O$  (0.660),  $Rb_2O$  (0.700) and  $Na_2O$  (0.600). This suggests that  $TiO_2$  is mainly present in illite and

mixed-layered minerals, and this is supported by the high  $\text{TiO}_2$  content in the bentonites (1.65%  $\text{TiO}_2$  in B14). High iron contents are largely due to the presence of iron-rich chlorites, most typically developed in the samples from the oolitic ironstones.

#### ANGLESEY

The shale samples from Anglesey contain illite as the dominant mineral with varying amounts of chlorite, quartz and feldspar. The present data suggests no systematic change in the composition of the sediments from Arenigian to Caradocian time. Oolitic iron ores, particularly of Llandeilian age, are common in Anglesey (Greenly 1919), and ordinary looking shales from other stratigraphical horizons are also relatively iron-rich. The average iron content of the samples from Anglesey is 7.38%, which is considerably higher than in Llandeilo or Builth Wells. A sample from an oolitic iron ore of Llandeilian age (A5) contains iron-rich chlorites (chamosite) and only a small amount of illite. Most samples contain minor amounts of feldspar (oligoclase) which at least partly represent admixtures of volcanic ash. Sample 17b contains feldspar as a major constituent, together with mixed-layered illite/montmorillonite, chlorite and quartz. This represents a layer rich in volcanic ash compared to sample 17a taken at the same locality (Fig. 3).

#### BUILTH WELLS

In the Builth Wells-Llandrindod area the Middle Ordovician sediments have a strong admixture of volcanic ash and lava fragments. The feldspar content is higher than in the Anglesey and the Llandeilo areas, and the 'illites' are mostly mixed-layered illite/montmorillonite. These mixed-layered minerals are probably formed by alteration of volcanic ash and lava detritus. The chlorite content (and MgO content) is lower than in the Anglesey area. The average  $\text{Na}_2\text{O}$  content is high (1.66%) due to the high feldspar content. Sample B14 represents a pure potassium bentonite which contains mixed-layered illite/montmorillonite and fragments of feldspar. In thin-section this bentonite shows brown spots of altered biotite surrounding altered feldspar. Sample B17 contains fragments of volcanic lava similar to the type one finds *in situ* in the area (Nicolls 1958). A sample from a lava of Llanvirnian age (B8) contains 6.40% sodium, and thin-section analysis reveals that the high sodium contents of samples B2b and B13 are due to a large amount of lava fragments.

#### LLANDEILO

In the Llandeilo area (Ffairfach section) the Llanvirnian and Llandeilian sediments consist of ashy shales and grits of relatively acid composition. Besides quartz and feldspar these sediments contain illite and only small amounts of chlorite. Both dolomite and calcite are present in the carbonaceous beds (Fig. 3).

The *N. gracilis* shales following the Lower Bala regional transgression (Williams 1953, p. 203) consist of chlorite-rich mudstones with a high iron and alumina content. The composition of these sediments indicates clearly a higher maturity than that of the underlying Caradocian sediments, and probably also a different source. The  $K_2O/Rb_2O$  ratio is also significantly lower in the Caradocian sediments, indicating a higher maturity (see p. 135).

#### LOW MAGNESIUM SHALES

The analysed Ordovician shales from Wales are characterized by a low average content of magnesium ( $MgO = 1.4\%$ ) compared to the average content of 51 Palaeozoic shales from different parts of the world ( $MgO = 2.32\%$ , Clarke 1924). The  $MgO$  content of the larger part of the Caledonian sediments of the Trondheim Region is substantially higher, mostly between 4% and 6% (Vogt 1927, 1945), and the Middle Ordovician shales of the Oslo Region have magnesium contents of the same order (Bjørlykke 1965). The Lower Ordovician sediments of the Oslo Region, however, have significantly lower magnesium contents, probably because they have been derived from a more acid source (Bjørlykke 1965).

The sources of the Ordovician shales in Wales are volcanic ash and lava fragments and Precambrian basement rocks. In Anglesey the admixture of volcanic rocks is less than in the Llandeilo and Builth Wells areas. The main source of the Ordovician sediments in Anglesey is the Mona complex, as all recognized members of the Mona complex are found as fragments in Ordovician conglomerates (Greenly 1919, p. 404). The overall composition of the Mona complex seems to be relatively acid, and even the Gwna-greenschist has  $MgO$  values only between 1% and 3% (Greenly 1919, p. 70). Hornblende schists and other gabbroid rocks of the Mona complex are quantitatively of less importance. The Precambrian basement to the south-east of Wales (the Longmynd and Malvern axis) also consists of a wide range of rock types, but contains no large gabbroid rock complexes (Andersen 1965).

The Ordovician volcanism in Wales is also mostly of acid to intermediate composition, in contrast to the Trondheim Region where basic lavas prevail in a large part of the Ordovician sequence. In the Oslo Region the post-Arenigian sediments are chlorite-rich (Bjørlykke 1965) probably because gabbroic Precambrian rocks were the main source, together with basic volcanics of the Trondheim Region.

The evidence presented above suggests that the  $MgO$  content in geosynclinal sediments is controlled by the composition of the basement rock and admixtures of volcanic material, and that uptake of  $Mg^{++}$  from sea-water is quantitatively less important.

#### Conclusion

From the geochemical and mineralogical data presented in Fig. 3 and Table 1, there is little evidence of any extensive stratigraphically conditioned varia-

tion of the geochemical and mineralogical composition of the sediments in the three areas studied. This is to be expected, as it has been pointed out by Jones (1938) and Black (1957) that the Welsh geosyncline developed as a series of almost separate basins with their own histories of sedimentation. In contrast to the shelf sedimentation of the Oslo Region, where lithologic units are very extensive, the Welsh sediments mostly reflect the local conditions in each area of sedimentation.

In Llandeilo there is a marked increase in the chlorite content (and MgO content) in the Lower Caradocian mudstones compared to the underlying Llandeilian and Llanvirnian sediments which are made up of volcanic ashes and grit. Corresponding variations were not found in the other areas studied.

The Welsh sediments are characterized by a high average feldspar content and high  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  and  $\text{K}_2\text{O}/\text{Rb}_2\text{O}$  ratios indicating a generally low maturity. The  $\text{Na}_2\text{O}$  content is particularly high in the Builth Wells area, where the andesitic volcanism was most intense.

A low average MgO content (1.4%) of all samples analysed reflects the overall acid to intermediate composition of the Precambrian basement and of the volcanic ashes and lavas.

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December 1969

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