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GEOCHEMISTRY OF PELITIC ROCKS. PART III: MAJOR ELEMENTS AND GENERAL GEOCHEMISTRY

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THE
GEOLOGICAL
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GEOCHEMISTRY OF PELITIC ROCKS. PART III: MAJOR ELEMENTS AND GENERAL GEOCHEMISTRY

By Denis M. Shaw

ABSTRACT

Compilation of 155 analyses gives the following average composition of all pelitic rocks in per cent, from low to high grade (standard deviations in parentheses): SiO_2, 61.54 (4.68); TiO_2, 0.82 (0.61); Al_2O_3, 16.95 (4.21); Fe_2O_3, 2.36 (1.97); FeO, 3.90 (2.25); MgO, 2.52 (1.91); CaO, 1.76 (2.03); Na_2O, 1.84 (1.18); K_2O, 3.45 (1.32); H_2O, 3.47 (2.25); CO_2, 1.67 (2.37).

After classifying the analyses into two groups (clays, shales, and slates; phyllites, schists, and gneisses) statistical discrimination tests showed no change in composition during regional metamorphism, beyond loss of H_2O and CO_2.

The Littleton formation of New Hampshire is a series of pelitic rocks, but is not completely representative of the group, since it forms a sedimentary petrographic province. Thus, the formation is somewhat deficient in CaO, Na_2O and CO_2, contains more Al_2O_2 and possibly TiO_2, and is in a more reduced state at the low-grade level than the average pelitic rock. It is also more restricted in composition. Moreover this formation underwent minor metasomatism during metamorphism, resulting in the addition of about half a per cent of CaO and Na_2O and the loss of H_2O, as well as minor element changes.

Comparison of pelitic rocks with the average igneous rocks shows that the alkalies and alkaline earths are relatively concentrated in shales as follows: Li > K > Na; Sr > Ba > Mg > Ca. These relations cannot be explained solely on the basis of relative ionic potentials.

CONTENTS

INTRODUCTION

Statement of the Problem

In two papers (1954a, b) the writer discussed the distribution of minor elements in pelitic rocks, with particular reference to the Devonian Littleton formation of New Hampshire. This paper gives the results of a study of major elements in these and other pelitic rocks with emphasis on their behavior during regional metamorphism.

It is commonly believed by many petrologists that argillaceous sediments generally do not change in composition during metamorphism (except by loss of volatiles) although exceptions have been recognized in some areas. The meager analytical evidence supporting this view (*e.g.*, Clarke, 1924, p. 631) commonly does not allow for possible compositional variations in the original sediments and possible sampling and analytical errors. Seldom is it possible to sample a single bed in various grades of metamorphism, and even where this can be done the bed may vary laterally. The theoretical study of sampling errors by Lafitte (1953) shows that they may be large, and Fairbairn *et al.* (1951) have shown that rock analyses are not equally reliable.

On the other hand, Lapadu-Hargues (1946) presents figures to demonstrate a continual change in composition in the series shale: schist:gneiss:granite, suggesting that regional metamorphism is not isochemical.

To resolve the problem it is necessary to use a statistical approach, and the present paper attempts to meet this need. Seventeen rock analyses of the Littleton formation were made, and by working with averages the compositional variation and the sampling and analytical errors were minimized; the standard deviations express these quantities. Comparisons by the discrimination tests known as the t-test and the F-test (*see* Dixon and Massey, 1951; Shaw and Bankier, 1954) reveal the significance of differences between averages, and these methods were used throughout.

Since minor elements were previously determined on the same samples that were analyzed for major elements and modal estimates were also made, the general geochemistry and petrology of the Littleton formation is first dis-

cussed. The geology of the rocks has been described by Billings and others, and references are given in Part I (Shaw, 1954).

COMPOSITION OF THE LITTLETON FORMATION

Analyses

Sample localities, and references to geological reports on the field relations are listed in Table 1. At each locality bulk chip samples of 2 pounds or more were collected, together with hand specimens for sectioning. Further details of sampling and specimen preparation may be found in Part I of this investigation (1954, p. 1152).

The results of major element analyses made in the Rock Analysis Laboratory at the University of Minnesota and spectrochemical determinations made by the writer (taken mainly from Part I, 1954) are given in Table 2. The spectrochemical determinations of Ba were not previously published. The analyses are listed according to metamorphic grade in three groups. The low-grade rocks are fine-grained shales and slates. The medium-grade rocks are schists not containing sillimanite nor adjacent to sillimanite-bearing rocks. The high-grade rocks either contain sillimanite or are adjacent to sillimanite-bearing rocks.

The precision of the spectrochemical analyses was recorded in Part I (1954, p. 1158). The major element analyses (made under the direction of S. S. Goldich) are unlikely to have errors greater than those found by Fairbairn *et al.* (1951, Table 17) for seven replicate analyses of a granite in one laboratory, which are repro-

duced in Table 3. The errors are probably much smaller, since the writer was informed by Goldich that replicate determinations of Na_2O and

and the results agree well with the gravimetric figures. The Ba content is less than 0.1 per cent in nearly every analysis, and the earlier esti-

TABLE 1.—SAMPLE LOCALITIES

Number	Rock description	Locality	Quadrangle	Reference
L 1	Black-gray shale	⅘ mi. N Cemetery, Littleton	Littleton	Billings (1937a)
L 2	Black slate with pyrite	Slate Ledge quarry	....	....
L 3	Black slate	⅝ mi. W Walker Mt.	....	....
L 8	Black slate	Mormon Hill	....	....
L 9	Gray shale	¼ mi. E Ogontz Lake	....	....
L 10	Slate	¼ mi. E Clough Hill School	....	....
L 11	Slate	1 mi. NE Moulton Hill	....	....
L 12	Staurolite-garnet schist	E side Pearl Lake	Moosilauke	Billings (1937a)
L 29	Garnet-sillimanite gneiss	1 mi. SE West Rumney P.O.	Rumney	Fowler-Billings and Page (1942)
L 41	Sillimanite-chlorite-sericite schist	½ mi. S. Glen House	Mt. Washington	Billings *et al.* (1946)
L 49	Garnet-staurolite-sillimanite gneiss (pseudo-andalusite gneiss)	5200 ft. on Osgood trail, Mt. Madison	....	....
L 54	Sillimanite schist	Thoreau Seat, ¼ mi. E Halfway House, Mt. Monadnock	Monadnock	Fowler-Billings (1949)
L 55	Garnet-chlorite-sillimanite schist	¼ mi. NE of the east end of Dublin Lake	....	....
L 62	Staurolite schist	1 mi. S Hinsdale	Keene-Brattleboro	Moore (1949)
L 66	Staurolite-garnet schist	Spofford	....	....
L 69	Garnet-staurolite schist	2 mi. NE Alstead on Cold river	Bellow's Falls	Kruger (1946)
L 81	Sillimanite gneiss	1 mi. S West Campton	Plymouth	Moke (1946)
L 82	Garnet-staurolite schist	Summit of Garnet Hill	Moosilauke	Billings (1937a)

K_2O on four samples did not differ by more than 3.2 and 1.9 per cent respectively from the figures reported.[1]

The accuracy of the figures in Table 2 is difficult to assess, but the major element analyses are probably satisfactory. In the absence of cross-checking by other analysts the accuracy of most of the spectrochemical analyses is uncertain. The Ba figures are believed to be accurate, however. In Part I it was reported that Ba could not be determined by the spectrographic method used, but exceeded 0.1 per cent. Following this a suitable method was developed

[1] Michael Fleischer, U. S. Geological Survey (Written communication), also suggested that the errors are probably much smaller than those in the analyses reported in Table 3.

mates were too high. It does not necessarily follow that other minor element figures should be viewed with suspicion, for the first Ba determinations were qualitative, but cross-checking would be valuable. Accuracy is not involved in any of the statistical tests which follow, of course, but is relevant to the discussion of abundances.

Petrography

The modes of Littleton rocks of medium- or high-grade metamorphism (Table 4) were determined by the point counter and are expressed as averages of at least three determinations, each on a different slide and, where possible, from different hand specimens. The results

TABLE 2.—ANALYTICAL RESULTS

	Low grade							Medium grade					High grade					
	L1	L2c	L3	L8	L9	L10	L11	L12	L62	L66	L69	L82	L29	L41	L49	L54	L55	L81
SiO_2	65.03	58.14	64.33	62.93	59.01	67.25	61.38	62.44	58.56	59.15	62.57	63.39	62.51	60.34	58.33	61.00	49.84	64.78
TiO_2	.80	.65	1.06	.99	1.00	.97	.60	1.04	1.10	1.00	1.03	1.02	1.06	.87	1.17	.88	1.39	.94
Al_2O_3	16.52	21.00	17.98	18.95	18.93	16.42	16.81	21.29	22.30	20.27	18.22	17.65	18.91	20.90	22.55	21.32	26.17	17.43
Fe_2O_3	1.69	.33	1.41	1.80	1.27	1.76	2.95	.93	3.83	.67	1.46	1.18	.92	.78	2.09	1.12	1.49	1.02
FeO	4.36	6.32	4.80	4.34	6.03	4.29	5.36	2.71	4.42	6.41	5.23	4.58	6.08	5.20	5.84	5.86	8.33	5.78
MgO	2.45	3.41	1.19	1.32	3.08	1.05	2.73	1.25	1.87	1.83	2.16	2.37	1.66	1.90	1.87	1.68	2.36	2.28
MnO	.02	.06	.03	.02	.06	.02	.07	.08	.07	.10	.07	.05	.10	.08	.06	.12	.19	.10
CaO	.10	.32	.03	.15	.24	.05	.20	1.00	.18	.64	.30	.49	.33	.50	.25	.56	.41	1.06
Na_2O	.16	1.10	.54	.68	.77	.79	1.60	2.58	.93	1.46	1.35	2.27	1.13	1.32	.98	.88	.73	1.58
K_2O	4.26	3.85	3.49	3.44	4.42	2.81	3.47	4.01	2.88	4.19	3.54	3.27	3.94	4.27	3.62	3.58	4.49	3.13
H_2O^+	3.71	4.47	3.90	3.90	4.26	3.68	4.00	2.35	2.93	3.31	3.31	2.16	2.58	3.23	2.44	2.08	3.82	1.21
H_2O^-	.17	....	.39	.25	.17	.21	.13	.09	.16	.22	.13	.14	.12	.12	.13	.12	.09	.08
CO_2	.03	.00	.04	.02	.05	.03	.03	.03	.08	.10	.05	.03	.02	.01	.02	.01	.01	.02
P_2O_5	.09	.00	.11	.12	.14	.07	.18	.18	.15	.12	.16	.16	.10	.16	.18	.38	.10	.15
S	.03	.09	.03	.03	.02	.03	.03	.03	.03	.05	.04	.01	.03	.05	.03	.02	.02	.28
C	.32	....	.44	.76	.31	.58	.31	.09	.40	.32	.30	.82	.33	.11	.35	.48	.37	.01
Ba^a	.05	.00	.05	.04	.05	.03	.03	.08	.04	.07	.04	.05	.07	.04	.06	.03	.09	.05
Ba^b	.049	....	.062	.069	.063	.046	.066	.10	.039	.062	.035	.045	.059	.055	.044	.033	.087	.056
Ga	31	35	16	27	29	26	19	17	30	20	17	16	21	20	20	22	28	16
Cr	86	160	93	160	150	93	130	110	130	100	140	130	130	110	120	80	120	78
V	68	150	81	180	83	75	120	130	150	120	150	110	130	120	81	71	140	100
Li	tr.d	tr.d	77	85	90	83	48	76	630	58	110	100	160	69	250	120	70	65
Ni	64	110	46	99	72	68	98	38	88	60	110	73	85	67	64	54	34	52
Co	11	21	10	14	14	19	23	10	24	22	31	18	22	27	16	18	21	21
Cu	24	59	5.9	17	15	18	22	4.4	31	32	40	5.1	6.9	19	12	1.7	22	43
Sc	11	14	9.5	21	9.4	12	10	15	12	13	15	8.4	18	17	7.7	14	18	9.5
Zr	180	190	260	310	84	310	170	170	250	220	290	180	260	140	140	350	200	170
Sr	110	400	350	730	180	460	250	930	530	610	630	630	1400e	1100	360	1100	1200	730
Pb	33	—f	13	30	tr.g	16	21	64	25	39	29	31	32	31	24	29	20	33

SiO_2 to C determined gravimetrically at the University of Minnesota (L1–9, 55, 69, 81, 82 by J. A. Maxwell; L10–12, 29, 41, 49, 54, 62, 66 by D. Thaemlitz; Ba^a determined chemically by E. H. Oslund and D. Thaemlitz); Ba^b to Pb determined spectrographically at McMaster University. First group in Wt.per cent, second group in ppm

[a] Gravimetric

[b] Spectrographic

[c] Major constituents as reported by Billings (1937); spectrographic determinations on a different sample collected by the writer from the same locality

[d] Approximately 30 ppm

[e] This figure is unreliable

[f] Approximately 1 ppm

[g] Approximately 9 ppm

TABLE 3.—PRECISION OF DETERMINATIONS IN REPLICATE ROCK ANALYSES*

	C†
SiO₂	0.31
TiO₂	11.2
Al₂O₃	1.22
Fe₂O₃	19.3
FeO	5.72
MnO	30.5
MgO	9.90
CaO	6.53
Na₂O**	6.23
K₂O*	3.83
H₂O⁺	26.7
P₂O₅	23.4

* Fairbairn *et al.*, 1951, taken from Table 17.
† Relative deviation for 7 replicate analyses of a granite, *i.e.*, standard deviation × 100/mean.
** Includes three flame photometer determinations.

(iron oxides, sulfides, and graphite are present), it is pointless to attempt to recalculate the modes to weight per cent. The fractions in Table 4 are meaningful only for minor constituents. Brief petrographic descriptions of the rocks follow.

MEDIUM-GRADE ROCKS

L 12 Staurolite-garnet schist
Abundant idioblastic porphyroblasts of staurolite and red garnet in a fine-grained, light-brown schist. The staurolite shows sieve-texture, and is full of quartz inclusions. The matrix is a quartz-biotite-muscovite aggregate, with minor iron oxides, chlorite, apatite, and tourmaline. Grade: staurolite zone.

L 62 Staurolite schist
A silvery crumpled schist. Porphyroblasts of staurolite, with quartz-graphite inclusions, and of occasional garnets, in a matrix of quartz, muscovite, and biotite, with crumpled schistosity planes. Staurolite crystals have

TABLE 4.—MODAL ANALYSES

	Medium grade					High grade					
	L12	L62	L66	L69	L82	L29	L41	L49	L54	L55	L81
Quartz	27.3	30.8	41.5	37.8	32.3	34.4	28.4	31.8	37.0	7.3	41.5
Muscovite	18.4	17.6	28.7	27.9	7.5	28.0	26.7	18.8	9.7	{47.2	6.8
Sericite	...	..	...	6.4	..	...	17.0	...	..		...
Biotite	27.0	19.8	{14.7	17.5	18.3	20.0	6.2	28.9	20.6	...	27.9
Chlorite	.3	..		.1	..	.8	10.7	.7	.3	11.1	...
Staurolite	18.7	15.0	2.2	1.6	22.4	...	..	5.3	...	...	...
Sillimanite	...	..	.5	...	..	10.9	2.4	11.3	30.5	23.2	11.1
Garnet	6.9	1.1	3.7	.7	1.1	3.3	..	1.3	..	6.3	1.0
Opaques	1.4	13.2	4.0	4.6	18.3	1.9	4.2	1.7	1.3	5.0	1.4
Feldspar	...	2.3	4.3	3.2	..	.2	4.3	.1	.3	...	10.2
Tourmaline	...	..	...	...	..	.6	..	...	..	...	...
Apatite	.1	..	...	.1	..	...	..	.1	.2	...	.2
Zircon	...	..	.3	.1	..	...	..	...	..	...	...
Calcite	...	..	...	.1	..	...	..	...	..	...	...
Sphene	...	.1	...	...	..	...	..	...	..	...	...
	100.1	99.9	99.9	100.1	99.9	100.1	99.9	100.0	99.9	100.1	100.1

varied considerably from slide to slide, because of the presence of porphyroblasts and the inhomogeneity of the rocks. The determination of the mode of a schist or gneiss with reasonable precision is almost impossible; the problem has been discussed elsewhere (Shaw and Harrison, 1955). In view of this and of the uncertainty of the relative proportions of the opaque minerals

been fragmented by shearing along micaceous foliae. Principal opaque mineral is graphite, but iron oxides are also present. Minor feldspar and sphene. Grade: staurolite zone.

L 66 Staurolite-garnet schist
Silvery schistose rock. Porphyroblasts of staurolite and garnet in a fine-grained matrix of muscovite, biotite-chlorite aggregates, and quartz. Poikiloblastic staurolite-muscovite

aggregates. Feldspar is largely microcline, but some oligoclase is present. Minor sillimanite in one section. Opaque minerals include sulfides, graphite, and iron oxides. Grade: upper staurolite zone.

L 69 Garnet-staurolite schist

Dark crumpled schist. Porphyroblasts of largely sericitized staurolite and partially altered garnet (chlorite-sericite rims) in a groundmass of muscovite, quartz, and biotite, exhibiting sinuous and crumpled schistosity. Minor microcline, iron oxides, sulfides, zircon, apatite, chlorite, and carbonate. Grade: staurolite zone.

L 82 Garnet-staurolite schist

Gray fine-grained rock with conspicuous biotite grains and sporadic porphyroblasts of staurolite and garnet. Fine-grained matrix of quartz, mica, and graphite. Minor muscovite, iron oxides, chlorite. It is unlikely that the modal content of graphite is as high as shown in Table 4, since the analysis (Table 2) revealed only 0.82 per cent C. Being soft, the graphite has probably been smeared over the slide during grinding. Grade: staurolite zone.

HIGH-GRADE ROCKS

L 29 Garnet-sillimanite gneiss

A light-brown gneissic rock with sporadic porphyroblasts of garnet and aggregates of fibrolite. The matrix of the rock is a quartz-muscovite-biotite aggregate, with interstitial and included needles of sillimanite throughout. Accessory iron oxides, chlorite, tourmaline, apatite, and oligoclase. Grade: sillimanite zone.

L 41 Sillimanite-chlorite-sericite schist

A light-colored rock of even schistosity and medium grain size. Poikiloblastic muscovite grains enclose quartz and feldspar, and are partially altered to sericite and also to sillimanite, the former appearing to be later. Chlorite-iron oxide aggregates partially pseudomorph biotite. The feldspar is oligoclase. Grade: sillimanite zone, but partially retrogressive to chlorite zone.

L 49 Garnet-staurolite-sillimanite gneiss

A dark, coarse-grained rock with irregular schistosity. The bulk of the rock consists of quartz, biotite, and muscovite, with significant amounts of staurolite and sillimanite. Also present are garnet, chlorite, iron oxides, graphite, plagioclase, tourmaline, and apatite. Textural relations are very complex, and the rock has undergone repeated metamorphism.

L 54 Sillimanite schist

A gray schist with abundant biotite and large porphyroblasts of sillimanite which consist of sheaves of fibrolite needles. The matrix consists of quartz, sillimanite, biotite, and muscovite, with minor iron oxides, graphite,

TABLE 5.—AVERAGE COMPOSITION
OF LITTLETON ROCKS

	Low grade		Medium and high grade	
	m	s.d.	m	s.d.
SiO_2	62.58	3.29	60.26	4.03
TiO_2	0.87	0.18	1.05	0.14
Al_2O_3	18.09	1.67	20.64	2.57
Fe_2O_3	1.60	0.78	1.41	0.90
FeO	5.07	0.85	5.49	1.39
MgO	2.18	0.97	1.93	0.34
CaO	0.16	0.10	0.52	0.29
Na_2O	0.81	0.45	1.38	0.58
K_2O	3.68	0.55	3.72	0.51
H_2O	4.18	0.24	2.80	0.75
CO_2	.03	.03	.03	.02

oligoclase, chlorite, zircon, and apatite. Grade: sillimanite zone.

L 55 Garnet-chlorite-sillimanite schist

A hard silvery schist with conspicuous garnet porphyroblasts. Sillimanite porphyroblasts appear in thin section, much intergrown with white mica and with fibrolite needles. The remainder of the rock is a fine-grained schistose aggregate of muscovite, quartz, chlorite, and iron oxides. The last two appear to be alteration products from biotite. Grade: sillimanite zone, retrogressed to chlorite zone.

L 81 Sillimanite gneiss

Coarse-grained, dark gneiss with irregular schistosity and banding. Occasional porphyroblasts of garnet occur in a matrix of rounded quartz and oligoclase grains, with interstitial biotite, fibrolite, and muscovite. Accessory sulfides, iron oxides, and apatite. Grade: sillimanite zone.

Behavior During Metamorphism

In order to test whether any significant composition changes occurred during the metamorphism of the Littleton shales and slates, the average compositions (m) and standard deviations (s.d.) were calculated for the more important constituents (Table 5). Medium- and high-grade rocks were grouped together, and their means refer to the 11 analyses in Table 2.

The means of the low-grade rocks refer to the 7 analyses in Table 2. Using the data of Tables 2 and 5 discrimination tests were applied, as in Part I (1954), to judge whether the differences between the means in Table 5 were significant.

TABLE 6.—AVERAGE COMPOSITION OF LITTLETON ROCKS, EXCLUDING WATER AND CARBON DIOXIDE

	Low grade		Medium and high grade	
	m	s.d.	m	s.d.
SiO_2	65.47	3.27	62.14	3.88
TiO_2	.91	0.19	1.08	0.15
Al_2O_3	18.93	1.80	21.29	2.74
Fe_2O_3	1.67	0.81	1.45	0.93
FeO	5.31	0.90	5.67	1.46
MgO	2.28	1.02	1.99	0.36
CaO	0.16	0.11	0.54	0.33
Na_2O	0.84	0.47	1.42	0.59
K_2O	3.85	0.58	3.84	0.54

The results indicated a significant difference at the 95-per-cent probability level for TiO_2, Al_2O_3, CaO, Na_2O, and H_2O, and a significant difference at the 99-per-cent level for CaO and H_2O.

The largest change was for H_2O, as would be expected. This decrease of water content during metamorphism might be large enough to confuse the position for other elements, so the m and s.d. values were again computed after each analysis in Table 2 had been recalculated to 100 per cent after excluding total H_2O and CO_2. The resulting figures are presented in Table 6. Discrimination tests were again applied; the results show that the apparent changes in TiO_2 and Al_2O_3 were illusory. CaO and Na_2O showed significant differences at the 95-per-cent level, and only CaO at the 99-per-cent level.

These results may be interpreted as indicating that the schists and gneisses contain less H_2O and more CaO than the sedimentary rocks, with a probability of 99 to 1. Similarly, there is a probability of 19 to 1 that they contain more Na_2O. Other oxides show no significant differences. As stated in Part I (1954) Li and Pb showed an increase in the high-grade rocks at the 99-per-cent level, whereas Cu and Ni showed a decrease with a probability of 95 to 99 per cent.

Before accepting these figures as indicating

definite compositional changes during metamorphism, it is necessary to consider the possible influence of other factors. The principal factor might be a collecting bias, arising from the small grain size of the shales and slates, which might obscure chemical properties. Thus a shale could contain perhaps 15 per cent carbonates without thereby losing its shaly characteristics. This would tend to overemphasize the CaO, CO_2, and MgO content of shales. However, the facts reveal a deficiency of CaO in shales with respect to their metamorphosed equivalents, which is the reverse of what might be expected. Moreover, this kind of bias could not be applied in the case of Na_2O. It is therefore concluded that there is a strong probability that for the Littleton formation both CaO and Na_2O increased by about 0.5 per cent during metamorphism. The only other acceptable explanation would be that the schists and gneisses are not the metamorphosed equivalents of the shales and slates, i.e., there was a facies change in the original sediments. In view of the fairly extensive area from which samples were taken, and in the absence of supporting evidence, this hypothesis is at present rejected. The change in both oxides is much larger than the probable analytical errors listed in Table 3.

In the course of metamorphism water was expelled, probably carrying small amounts of Ni and possibly Cu. It seems likely that this took place at an early stage, since the medium-grade rocks have a lower H_2O content than the shales and slates. Ca and Na were added, together with some Li and Pb, from some exterior source, perhaps magmatic. Although these two opposing directions of flow seem contradictory, it must be remembered that metamorphism is a process of stewing which may have continued for a long time, and only the final results can be studied by analyses.

There was apparently no appreciable change in K, although Billings (1937b) has recorded instances of potash metasomatism in these rocks in the proximity of granitic masses.

COMPOSITION OF PELITIC ROCKS

Compilation of Analyses

For many years Clarke's (1924) average composition of shales has been used as a reference

by sedimentologists. Unfortunately, Clarke's figures comprise only two analyses, each of a composite sample (containing 51 and 27 rocks their face value, except where a clay was obviously a carbonate rock with minor amounts of silica and clay minerals. With coarser rocks the

TABLE 7.—REFERENCES FOR ANALYSES OF CLAYS, SHALES, AND SLATES

Reference	Analyses	Average or composite
Barth, T. F. W., 1936, Geol. Soc. America Bull., v. 47, p. 775–850	nos. 1, 2, 3	. . . .
Bastin, E. S., 1909, Jour. Geology, v. 17, p. 445–472	p. 456	Average of 79
Clarke, F. W., 1915, U. S. Geol. Survey Bull. 591	p. 70; N, O: p. 250; A, B, C, E, G, H: p. 251; G, K, B, D, E, F: p. 253; D, A, B: p. 255; A: p. 256; A, B (N.M.), A, B (Ariz.): p. 257; J, (B.C.): p. 265; F	. . . .
Clarke, F. W., 1924, U. S. Geol. Survey Bull. 770	p. 518; B	Composite of 52
	p. 518; A	Composite of 51 red clays
	p. 552; A	Composite of 51 shales
	p. 552; B	Composite of 27
	p. 552; G: p. 554; A, B, C, D, E, F	. . . .
	p. 631; A	Average of 12
	p. 631; B	Average of 2 composites, listed on p. 552
Dale, T. N., 1906, U. S. Geol. Survey Bull. 275	pp. 34–35; I, II, III, IV, VI, IX, X, XI, XII, XIII, XIV	. . . .
Eckel, E. C., 1904, Jour. Geology, v. 12, p. 25–29	p. 26	Average of 36
Grout, F. F., 1919, U. S. Geol. Survey Bull. 678	p. 229	Average of 3
Niggli, P., 1952, Gesteine und Minerallagerstätten, v. II	p. 308; 2: p. 310; 8, 11, 12: p. 311; 16, 17: p. 313; 41	. . . .
Simonen, A, 1953, Comm. géol. Finlande Bull., no. 160	p. 32–33; 1, 2, 3, 4, 5, 6, 8, 9, 10, 11	. . . .
Van Hise, C. R., 1904, U. S. Geol. Survey Mon. 47	p. 895	Average of 9
	p. 896; C	Average of 22
Wells, R. C., 1937, U. S. Geol. Survey, Bull. 878	p. 11; A: p. 23; R: p. 28; E, F: p. 40; F, G	. . . .

respectively), and there is no information on the range in composition. Analysis errors may therefore be significant.

The writer has therefore compiled from the literature numerous analyses under the headings of clay, shale, argillite, slate, phyllite, schist, and gneiss. These terms have rather vague meanings in many cases, reflecting unsatisfactory terminology and diversity in the rocks. In fine-grained rocks wide variations in CaO, CO_2, and SiO_2 are found in rocks labeled clay, shale, argillite, and slate. In selecting analyses, however, these names were taken at

terms schist and gneiss may be meaningless unless further qualified, and analyses were taken only where the name or mode indicated a rock of pelitic affinities, i.e., presence of micas, aluminium silicates, staurolite, garnet, or chloritoid and absence of basic plagioclase, amphibole, and pyroxene.

Analyses were taken only where there were determinations of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, and H_2O. If the presence of CO_2 figures had been stipulated, many analyses would have been rejected.

Of the 155 analyses compiled, 85 were low

grade and 70 high grade; 43 of the former and 18 of the latter included CO_2 determinations. The analyses would occupy too much space to list individually, but complete references are

ing 0.78 per cent is divided among minor constituents, using the averages presented later for the Littleton formation, as follows: C, 0.37 per cent; P_2O_5, 0.14 per cent; MnO, 0.07 per cent;

TABLE 8.—REFERENCES FOR ANALYSES OF PHYLLITES, SCHISTS, AND GNEISSES

Reference	Analyses	Average or composite
Barth, T. F. W., 1936, Geol. Soc. America Bull., v. 47, p. 775–850	nos. 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 19	. . . .
Bastin, E. S., 1909, Jour. Geology, v. 17, p. 445–472	p. 456	Average of 30
Clarke, F. W., 1915, U. S. Geol. Survey Bull. 591	p. 29; O: p. 36; O (2): p. 43; B: p. 44; E: p. 50; F, G: p. 55; C: p. 62; G, C: p. 73; O: p. 121; Y: p. 144; T: p. 154; E, F: p. 191; Q, S, T: p. 216; A	. . . .
Clarke, F. W., 1924, U. S. Geol. Survey Bull. 770	p. 625; C, D, F, G, H:	. . . .
	p. 626; F	. . . .
	p. 631; D	Average of 5
Goldschmidt, V. M., 1921, Norske Vid. Akad. i Oslo, Skrifter I, Mat.-naturv. Klasse, no. 10	p. 58	Composite of 18
	p. 72	Composite of 6
	p. 75	Composite of 4
	p. 70, 79	. . . .
	p. 84	Composite of 6
	p. 93, 96	. . . .
Goldschmidt, V. M., 1933, Fortschr. Mineral. Krist. Petrog., v. 17, p. 112-156	p. 130	Composite of 8
Pitcher, W. S., 1953, Geol. Soc. London Quart. Jour., v. 58, p. 413–446	nos. 1, 2	. . . .
Simonen, A., 1953, Comm. géol. Finlande Bull., no. 160	p. 50–52; nos. 47–68	. . . .

given in Tables 7 and 8. Each was given equal weight, although many were either averages or analyses of composites. Care was taken to avoid recording any analysis twice, but after all computations were completed it was found that Clarke's average had been used twice, once as published and once in the form of the two constituent composites (*see* Table 7).

The mean and standard deviation of each major constituent were calculated independently by different persons, and the results for each group are presented in Table 9. Totals are not shown, partly because CO_2 was not recorded in every analysis and partly because other constituents such as P_2O_5, S, and C were not included in the compilation. The final average and s.d. obtained when the low- and high-grade rocks are combined are shown in columns 1 and 2 of Table 10. In column 3 the average has been recalculated to total 99.22 per cent. The remain-

Sr, 0.07 per cent; Ba, 0.06 per cent; S, 0.05 per cent; Zr, 0.02 per cent. Column 4 gives the composition in terms of the nine major metallic oxides only, and column 5 shows Clarke's average for comparison.

Range in Composition

In order to demonstrate the range in composition of the analyses used in the compilation, histograms have been drawn for the nine major element oxides (Fig. 1). Most of the oxides have a unimodal distribution. While this does not prove that each oxide is normally distributed (which is assumed for the statistical tests following), it suggests that the departures from normality are not serious. For CaO, Fe_2O_3, and FeO, the distribution patterns are less regular, however. With lime it seems likely that one peak is due to chance, and would be eliminated

TABLE 9.—COMPARISON OF AVERAGE LOW- AND HIGH-GRADE PELITIC ROCKS

	Low grade (85)		High grade (70)	
	m	s.d.	m	s.d.
SiO_2	59.93	6.33	63.51	8.94
TiO_2	.85	.57	.79	.67
Al_2O_3	16.62	3.33	17.35	5.08
Fe_2O_3	3.03	2.08	2.00	1.66
FeO	3.18	1.84	4.71	2.44
MgO	2.63	1.98	2.31	1.82
CaO	2.18	2.54	1.24	.92
Na_2O	1.73	1.27	1.96	1.06
K_2O	3.54	1.33	3.35	1.31
H_2O	4.34	2.38	2.42	1.53
CO_2	2.31*	2.60	.22†	.22

* Determined in only 43 analyses
† Determined in only 19 analyses

TABLE 10.—AVERAGE COMPOSITION OF PELITIC ROCKS

	Pelitic rocks* (155)		Adjusted average from column 1	Average from column 1 excluding water and carbon dioxide	Clarke's average shale (78)
	m	s.d.			
SiO_2	61.54	4.68	60.76	64.10	58.38
TiO_2	.82	.61	.81	.86	.65
Al_2O_3	16.95	4.21	16.73	17.70	15.47
Fe_2O_3	2.56	1.97	2.53	2.70	4.03
FeO	3.90	2.25	3.85	4.05	2.46
MgO	2.52	1.91	2.49	2.65	2.45
CaO	1.76	2.03	1.74	1.88	3.12
Na_2O	1.84	1.18	1.82	1.91	1.31
K_2O	3.45	1.32	3.41	3.60	3.25
H_2O	3.47	2.25	3.43	...	5.02
CO_2	1.67	2.37	1.65	...	2.64
Total	100.48		99.22†	99.45	98.78

* Only 62 figures for CO_2
† Remainder comprises C, P, Mn, Sr, Ba, S, Zr

if the interval were doubled. Moreover, the histogram suggests that the distribution is closer to a log-normal pattern. In the case of the iron oxides, the irregularities seem to reflect the fact that the oxidation state is seldom of genetical significance in low-grade rocks, depending rather on diagenetic and weathering processes. Recalculation to total iron in either oxidation state would give a unimodal distribution.

Behavior During Metamorphism

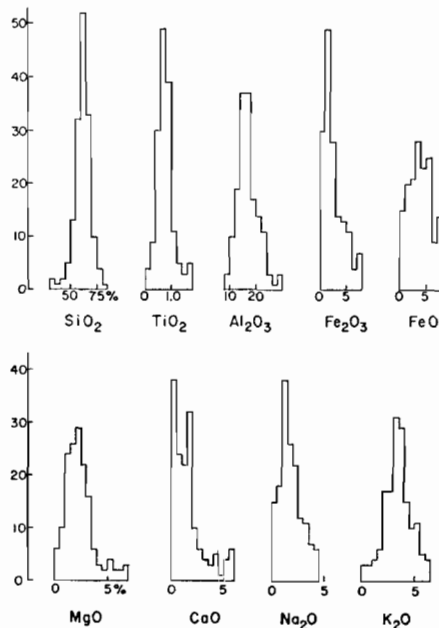In Table 9 the low-grade average of several oxides appears significantly different from the

FIGURE 1.—HISTOGRAMS FOR MAJOR ELEMENT OXIDES IN PELITIC ROCKS
Intervals as follows: SiO_2, 5 per cent; TiO_2, 0.2 per cent; Al_2O_3, 2 per cent; Fe_2O_3, 1 per cent; FeO, 1 per cent; MgO, CaO, Na_2O, K_2O, 0.5 per cent. Ordinate, frequency per cent.

high-grade one. The t-tests were applied only in the case of H_2O, initially, and show that there is at least 99-per-cent probability that the difference is real. For CO_2 it was undesirable to apply the test in view of the uncertain magnitude of experimental error, but the averages show a clear difference. Taken together, the difference in volatile content amounts to about 4 per cent. Since this might confuse the situation in respect of other constituents, the m and s.d. figures were again computed, after each analysis had been recalculated to 100 per cent, excluding H_2O and CO_2 (Table 11).

The averages in Table 11 seem similar, but close examination shows some possible real differences. Applying t-tests as before, it appears that the mean values for Fe_2O_3, FeO, and CaO differ significantly at the 99-per-cent probability level, but for no other oxide is there

any significant difference. Summing up, H_2O, CO_2, Fe_2O_3, and CaO decrease and FeO increases, going from low- to high-grade rocks.

The behavior of H_2O is clearly due to progressive dehydration during metamorphism.

TABLE 11.—COMPARISON OF AVERAGE LOW- AND
HIGH-GRADE PELITIC ROCKS, EXCLUDING
WATER AND CARBON DIOXIDE

| | Low grade (85) | | High grade (70) | |
	m	s.d.	m	s.d.
SiO_2	63.34	5.37	65.01	8.59
TiO_2	.90	.62	.82	.72
Al_2O_3	17.59	3.51	17.84	5.44
Fe_2O_3	3.23	2.26	2.06	1.73
FeO	3.40	1.92	4.84	2.52
MgO	2.88	2.28	2.38	1.92
CaO	2.39	2.98	1.27	.94
Na_2O	1.83	1.34	2.00	1.06
K_2O	3.73	1.36	3.43	1.34

The changes in iron oxides suggest a change in oxidation state, or progressive reduction, as is well known from various metamorphic regions. This is confirmed by calculating the total iron as FeO from Table 11, which gives 6.31 per cent (low grade) and 6.69 per cent (high grade), about the same in each group. There is a slight decrease in oxygen (0.03 per cent) accompanying this reduction.

In considering the behavior of CaO it must be recalled that the low-grade rocks were collected by many persons and are from many different geological environments. Fine-grained rocks are difficult to identify, and it seems probable that the decrease of CaO represents a collecting bias. In other words, many of the low-grade rocks contained carbonates in fair quantity: the same rocks after metamorphism would have revealed their CaO content by the presence of calcium silicates and would therefore have been excluded from the compilation. This view is supported by the marked decrease in CO_2, whose abundance in the low-grade rocks is adequate to satisfy all the CaO and part of the MgO.

The evidence of the collected analyses therefore suggests that the regional metamorphism of pelitic sediments is accompanied by no bulk changes in composition, beyond the partial loss

TABLE 12.—COMPARISON OF LOW-GRADE
LITTLETON ROCKS WITH THE AVERAGE
LOW-GRADE PELITIC ROCK

| | Littleton formation | | Low-grade rocks | |
	m	s.d.	m	s.d.
SiO_2	62.58	3.29	59.93	6.33
TiO_2	.87	.18	.85	.57
Al_2O_3	18.09	1.67	16.62	3.33
Fe_2O_3	1.60	.78	3.03	2.08
FeO	5.07	.85	3.18	1.84
MgO	2.18	.97	2.63	1.98
CaO	.16	.10	2.18	2.54
Na_2O	.81	.45	1.73	1.27
K_2O	3.68	.55	3.54	1.33
H_2O	4.18	.24	4.34	2.38
CO_2	.03	.03	2.31	2.60

TABLE 13.—COMPARISON OF MEDIUM- AND
AND HIGH-GRADE LITTLETON ROCKS WITH THE
AVERAGE MEDIUM- AND HIGH-GRADE PELITIC
ROCK

| | Littleton formation | | Medium- and high-grade rocks | |
	m	s.d.	m	s.d.
SiO_2	60.26	4.03	63.51	8.94
TiO_2	1.05	.14	.79	.67
Al_2O_3	20.64	2.57	17.35	5.08
Fe_2O_3	1.41	.90	2.00	1.66
FeO	5.49	1.39	4.71	2.44
MgO	1.93	.34.	2.31	1.82
CaO	0.52	.29	1.24	.92
Na_2O	1.38	.58	1.96	1.06
K_2O	3.72	.51	3.35	1.31
H_2O	2.80	.75	2.42	1.53
CO_2	.03	.02	.22	.22

of water and carbon dioxide and a slight loss in oxygen caused by the change in the oxidation state of iron. The behavior of CaO, however, is obscured by the difficulty of estimating the lime content of normal pelitic sediments.

Metamorphism of the Littleton Formation

The results expressed in the preceding paragraph differ radically from conclusions on a previous page regarding the metamorphism of the Littleton formation, and the two must be reconciled.

Tables 12 and 13 permit comparison of the

two groups of low-grade and high-grade rocks. It should first be noted that the s. d. values for the Littleton analyses are much smaller than for the other group (referred to in the following as the average pelitic rock), even though the number of Littleton analyses was much smaller. This is due partly to the lower experimental errors which can be expected for a series of similar rocks being analyzed in the same laboratory at about the same time. But chiefly this shows the homogeneous composition of the formation, contrasting with the wider variations among all pelitic rocks.

Using discrimination tests as before, it transpires that in the low-grade groups there is a 99-per-cent probability of a real difference between means for Fe_2O_3, FeO, CaO, Na_2O, and CO_2. The last, however, was not tested. For iron, it is apparent that the differences in Fe_2O_3 and FeO signify that the Littleton rocks are in a less oxidized state than the average pelitic rock. With respect to the others, it appears that the Littleton rocks are more free of calcite than the average and contain less Na_2O. The apparent difference in alumina is nearly significant at the 95-per-cent level, but no other oxides show a change. The low-grade Littleton formation therefore contains perhaps more Al_2O_3 and less CaO, Na_2O, and CO_2 than the average pelitic sediment, and is in a more reduced state. These differences are characteristic of the sediments as originally laid down (with the possible exception of the oxidation state), and inasmuch as the formation seems rather homogeneous in composition it could be considered a sedimentary petrographic province.

Comparing the high-grade groups (Table 13), significant differences at the 99-per-cent level are found for TiO_2, Al_2O_3, CaO, and CO_2. The last was again not tested. For CaO, the increase of this oxide during metamorphism of the Littleton rocks has not eliminated the original deficiency in lime. The evidence confirms the tentative conclusion that the Littleton formation is more aluminous than the average. The difference in TiO_2 was unexpected, but it is not considered a result of experimental errors. It is possible that the same depositional processes which led to above average Al_2O_3 also concentrated TiO_2 slightly. If this is true, the similarity of means for TiO_2 in the low-grade rocks is

accidental. For Na_2O, the increase during metamorphism has brought the Littleton formation closer to the average.

This formation is a homogeneous group of rocks whose composition is relatively constant in each grade, and is characterized by certain compositional chemical features. In a well-defined group with a narrow compositional range any changes in composition are more readily detectable than in a heterogeneous group. The latter, comprising the average pelitic rock, is made up of samples from different series such as the Littleton formation. Each series may or may not show changes in composition when considered alone, but when averaged such changes will cancel out or merge in the much wider range of composition. It is concluded, therefore, that there is no contradiction in saying that although the average pelitic sediment does not change its content of metallic oxides during metamorphism the Littleton pelitic formation does.

Metasomatic Metamorphism According to Lapadu-Hargues

In a study of the composition of metamorphic rocks Lapadu-Hargues (1946) presented evidence based on the compilation of analyses from which he concludes that there is a progressive change in composition during the metamorphism of pelitic sediments leading ultimately to rocks of granitic composition. He assembled 302 analyses from the literature, and divided them into seven groups, as follows:

I, schistes sedimentaire; II, schistes à sericite et micaschistes à muscovite seule; III, micaschistes à deux micas; IV, gneiss à deux micas et formes feldspathisées des micaschistes; V, gneiss profonds et gneiss granitoïdes; VI, granites francs; VII, granulites.

The analyses were recalculated to molecular per cent, and each group averaged. The averages for some constituents are listed in Table 14; these figures show a progressive change. However, the writer contends that the basis of classification of analyses was not entirely relevant to pelitic rocks because:

(1) Some of the classification groups do not correspond to grades of metamorphism. For example, a *"micaschiste à deux micas"* (Group III), consisting of muscovite, biotite, quartz,

and small amounts of other minerals, could be a stable assemblage in any of Harker's biotite, garnet, or staurolite-kyanite zones, and, in places, in the sillimanite zone. Also, the two groups of gneisses (IV and V) could include rocks of the same grade of metamorphism.

TABLE 14.—OXIDE AVERAGES IN PELITIC ROCKS
AS CALCULATED BY LAPADU-HARGUES

	I	II	III	IV	V	VI	VII
Na$_2$O + K$_2$O	4	4.25	4.75	5.50	6.25	7.0	7.75
Al$_2$O$_3$	15.5	13.5	11.75	10.25	9.5	8.75	8.24

(2) A feldspathic gneiss is not necessarily a metamorphosed pelitic rock. It could be a pelitic rock injected by magmatic material, or partially granitized, or partially assimilated, or it may be the result of simple metamorphism of a nonpelitic sediment such as a graywacke, arkose, or marl. In the face of abundant evidence that pelitic rocks can undergo metamorphism of high degree with no changes other than mineralogical, there seems to be no good reason for considering rocks which are clearly nonpelitic, unless it is equally clear that they were once argillaceous. This is not to say that pelitic rocks in some regions have not been granitized but rather that they are not necessarily granitized during regional metamorphism.

The view that pelitic rocks usually undergo a far-reaching change in composition during regional metamorphism can therefore not be accepted. This conflicts in no way with the possibility that individual rock series such as the Littleton formation may undergo metasomatism of various kinds.

GEOCHEMISTRY OF PELITIC ROCKS

Minor Elements

The analyses in Table 2 are generally so similar that it is difficult to detect any correlation between the abundance of major and minor elements. In the following, individual minor elements will be discussed, chiefly in relation to the mineralogy of the recrystallized rocks. Genetic aspects have been partially covered in Part II of this investigation (1954), and will be referred to later.

GALLIUM: There is no sign here of the sympathetic variation of Ga and Al so frequently recorded for igneous rocks and minerals. Ga probably replaces Al in mica, chlorite, staurolite, sillimanite, garnet, feldspar, and tourmaline.

CHROMIUM, VANADIUM, NICKEL, COBALT: These elements vary sympathetically but do not correlate with Fe or Mg, as might be expected, or any other major elements. They are probably located in Mg and Fe minerals such as biotite, chlorite, staurolite, garnet, iron oxides, and tourmaline. Some V may also replace P in apatite.

LITHIUM: No apparent correlation with any major element. Presumably Li replaces Mg in micas and chlorite, and may also occur in tourmaline. Some specimens of sillimanite, Kyanite, and andalusite analyzed by G. R. Pearson (1955, McMaster Univ. M.Sc. thesis) show unusually high Li content.

COPPER: This element would be expected to correlate well with S, but only in L 81 is this apparent. Probably located chiefly in accessory sulfides, with small amounts in the silicates.

MANGANESE: Since in geochemical properties Mn resembles both Fe and Ca, it may be expected to occur principally in garnet, staurolite, biotite, iron oxides, and apatite. No correlation with other elements apparent.

SCANDIUM: The small quantities of Sc present are probably located principally in the Mg-Fe minerals biotite and chlorite.

ZIRCONIUM: Almost entirely in zircon, with small amounts replacing Mg and Fe in other silicates.

STRONTIUM: This element resembles both Ca and K, but no correlation is apparent with either. Probably occurs in micas, feldspars, apatite, and calcite.

LEAD: Rather similar in behavior to Ca and K (especially the latter) with affinity also for S. Probably is located chiefly in micas, sulfides, and possibly apatite.

BARIUM: Owing to its large size Ba most closely resembles K and will replace it in micas and feldspars. No close correlation, however. Special care was taken with both gravimetric and spectrographic determinations of this ele-

TABLE 15.—AVERAGE PELITIC ROCK AND LITTLETON FORMATION COMPARED WITH CRUSTAL ABUNDANCES

	Average Littleton rock per cent	Volatile-free Littleton average (a) per cent	Average igneous rock* (b) per cent	Enrichment factor (a/b)	Volatile-free average pelitic rock (c)	Enrichment factor (c/b)
SiO₂	61.17	63.31	62.90	1.01	64.10	1.02
TiO₂	0.98	1.01	0.80	1.26	0.86	1.08
Al₂O₃	19.65	20.34	15.22	1.34	17.70	1.16
Fe₂O₃	1.48	1.53	1.96	0.78	2.70	1.38
FeO	5.33	5.52	4.43	1.25	4.05	0.91
MgO	2.03	2.10	3.08	0.68	2.65	0.86
MnO	0.07	0.07	0.13	0.54	....	....
CaO	0.38	0.39	5.40	0.07	1.88	0.35
Na₂O	1.16	1.20	3.22	0.37	1.91	0.59
K₂O	3.70	3.83	2.65	1.45	3.60	1.36
H₂O⁺	3.19	....	....	....	....	....
H₂O⁻	0.16	....	....	....	....	....
CO₂	0.03	....	....	....	....	....
P₂O₅	0.14	0.14	0.23	0.61	....	....
S	0.05	0.05	0.052	1.00	....	....
C	0.37	0.38	....	....	....	....
Ba†	0.05	0.05	....	....	....	....
Total	99.94	99.92	100.072	....	....	....
Ba**	0.057	....	0.055	1.0	....	....
Ga	19 ppm	....	20 ppm	1.0	....	....
Cr	110	....	100	1.1	....	....
V	120	....	100	1.2	....	....
Li	55	....	20	2.8	....	....
Ni	64	....	80	0.8	....	....
Co	18	....	23	0.8	....	....
Cu	18	....	70	0.3	....	....
Sc	14	....	15	0.9	....	....
Zr	200	....	220	0.9	....	....
Sr	710	....	300	2.4	....	....
Pb	16	....	10	1.6	....	....

* Elements expressed in per cent from Wickman (1954, Table 6, no. 2), except S and Ba (Clarke, 1924, p. 29)

  † Gravimetric

  ** Spectrographic

ment, with the object of comparing the results; Table 2 shows that agreement is generally excellent.

Genetic Consideration

Table 15 has been compiled to assist in considering the chemical features of the origin of pelitic rocks. These rocks formed as the result of gradational processes acting on the crust of the earth, whose composition is believed to approximate the average igneous rock. The latter has recently been recalculated by Wickman (1954), whose figures for major elements are shown in column 3. Figures relating to minor elements (except Ba) are taken from Part II (1954, Table 14). Since Wickman's figures are expressed on a volatile-free basis, the average Littleton rock and the average pelitic rock have been recalculated in the same way. The enrichment factors indicate the degree to which an element or oxide has been concentrated during the formation of pelitic rocks. In the Littleton average (column 1), the figures for

major elements (and Ba) were derived from the analyses in Table 2; those for minor elements are taken from Part I. Assuming that iron is transported principally in the ferric state, the iron in the average volatile-free Littleton rock, pelitic rock, and igneous rock has been recalculated as Fe_2O_3, giving 7.66 per cent, 7.20 per cent, and 6.88 per cent, respectively. The enrichment factors, then, are 1.11 and 1.05, respectively.

On the basis of the enrichment factors the elements may be divided into three groups; equal to, greater than, and less than 1.0. The first group, comprising Si, Ti, Fe, S, Ba, Ga, and possibly Cr, Sc, Zr, shows no concentration in normal argillaceous rocks—*i.e.*, these elements are not quantitatively enriched in any other sedimentary facies of chemical origin. Si may be concentrated in sandstones and cherts, but the former are not of chemical origin and the latter are not quantitatively important. Neither are sedimentary iron ores quantitatively important.

The second group, comprising Al, K, Li, Sr, Pb, and possibly V, is concentrated to varying degrees in the normal pelitic rock. For Al, this is due to its relative abundance in clay minerals, which are either formed during weathering and subsequently transported beyond the limits of normal clastic deposition, or are formed as a result of the flocculation of Al and Si hydrosols. Si is not concentrated to the same degree, because of the survival of some quartz during weathering and its accumulation as a resistate. Fe also might be expected to concentrate to a degree comparable with Al, but accumulates also in small quantities in oxidate deposits. Ti would behave in a manner similar to Al, but may also accumulate in resistates as ilmenite. In the Littleton formation Ti has been somewhat concentrated; this, no doubt, was accompanied by a lack of Ti in contemporaneous resistates. The ionic potentials of Si, Ti, Al, V, and Fe would all suggest the accumulation of these elements in hydrolyzate or pelitic sediments, if other factors did not intervene.

The ionic potentials of K, Li, Sr, Pb are low, and their enrichment is due principally to sorption.

The elements with enrichment factors less than 1.0 are Mg, Mn, Ca, Na, P, Cu, and prob-

ably Ni and Co. Mn, Ni, and Co have ionic potentials suggesting that they would be transported as sparingly soluble hydroxides to accumulate in argillaceous rocks. Clearly Mn does not accumulate in this way (at any event, not in the Littleton formation) and was most likely precipitated from solution under strong oxidizing conditions before reaching the locale of deposition of Al and Si. This removal of manganese during gradation is well known (*see* Rankama and Sahama, 1950, p. 647–650). Mg, Ca, Na, and Cu will go into solution as cations during weathering, and P as a complex anion; they will be distributed principally between pelitic sediments and the ocean waters, occurring in the former as a result of sorption (Mg, Ca, Na, Cu), precipitation as carbonate (Ca, Mg), and precipitation by other factors (P, Cu).
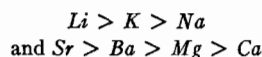
Sorption

The more electropositive metal ions are readily attracted to colloidal and finely crystalline clay minerals, and may be adsorbed or absorbed. These processes are important in the formation of argillaceous sediments. Goldschmidt (1937) relates the sorptive effects to ionic potential, so that in a series of elements of the same charge, those of lowest ionic potential (highest radius) should be the most adsorbed, and thereby removed from solution. The order of increasing ionic potential among some of the alkalies is

$$K < Na < Li$$
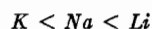
and with some alkali earths is

$$Ba < Sr < Ca < Mg$$

Enrichment factors show the following relations:

$$Li > K > Na$$
$$\text{and } Sr > Ba > Mg > Ca$$

If the ionic potential relation holds, sorption is only one factor influencing the occurrence of these elements in pelitic rocks. Thus Mg is concentrated more than Ca because it is an essential constituent in several clay minerals (*e.g.*, illite). A similar explanation may partially account for the enrichment in Li, since lithium-bearing clay minerals are known.

The familiar characteristics of pelitic rocks, that $MgO > CaO$ and $K_2O > Na_2O$, are no doubt principally due to sorptive action.

Conclusions

The Littleton formation is a series of pelitic rocks that shows the general chemical characters of all pelitic rocks. It is atypical, however, inasmuch as it shows certain chemical singularities and a rather narrow range of composition not characteristic of the group. The formation is somewhat deficient in CaO, Na_2O, and CO_2, contains more Al_2O_3 and possibly TiO_2, and is in a more reduced state at the low-grade level than the average pelite. Moreover, this formation underwent a minor metasomatism during metamorphism, resulting in the addition of Ca, Na, Li, and Pb, together with a loss of water, Ni, and possibly Cu. This again is not typical of the average pelitic rock, at least as far as major metallic oxides are concerned. The evidence suggests that the only usual change in composition during the regional metamorphism of shales is the loss of water and carbon dioxide.

Comparison of the pelitic series with the average igneous rock suggests that the abundance of the alkalies and alkaline earths in argillaceous rocks cannot be explained solely on the basis of relative ionic potentials.

The new figures for the average and range in composition of pelitic rocks show that the group is rather broad and stresses again the necessity for studying the homogeneity of rock types in quantitative geochemistry.

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