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Compositional variations in glauconite

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ABSTRACT. Variation in composition, Fe^{3+}/Fe^{2+} ratio, per cent mixed-layering, and *d*(060) spacing have been determined both between and within grains of glauconite from the Folkestone Beds at 286.5 m in the Tollgate bore, Sandwich, Kent. Grains extracted from the rock were classified on the basis of size into large (> 1 mm) and small (< 1 mm), and on colour into light and dark green. Large grains have a progressive increase in Fe^{3+}/Fe^{2+} ratio with increase in total iron, while small grains have variable ratios; the largest variation is in the dark grains. The effect of the range of Fe^{3+}/Fe^{2+} ratio variations on structural formula (e.g. R^{3+}) is discussed. The per cent mixed-layering is not related to colour. There is a greater variation in Al, Fe, and K contents in and between large grains than small grains. Both sizes of grains may be separated on *d*(060) spacings determined by X-ray diffraction. Glauconite from coral and gastropod casts has different *d*(060) spacings than that from bryozoan casts and variegated grains, but is similar to the small grains. Large light grains may have developed from small light grains but it is unlikely that the large dark grains developed from small dark grains. The large grains probably all formed under similar conditions, with a common origin; the small from several sources or from a single source under a variety of conditions.

THE varieties of glauconitic grains from sedimentary rocks and Recent sediments have been described by Burst (1958) and McRae (1972) and the composition of individual grains have been determined by Buckley *et al.* (1978), yet little work has been carried out on inter- and intragrain chemical variation. The latter aspect has been investigated using the electron microprobe to determine the compositions of grains, together with ferric/ferrous iron ratio (Fe^{3+}/Fe^{2+}) determinations. X-ray diffraction techniques were used to measure the amounts of mixed-layering, the *d*(060) spacings, and to detect and identify other minerals present within the grains.

Experimental methods

The material chosen for study was provided by the Institute of Geological Sciences, London, from the Tollgate bore, near Sandwich, Kent, from the Folkestone Beds at a depth of 286.5 m. The host rock is an indurated calcareous sandstone containing slightly less glauconite than the Folkestone Beds at Folkestone.

The grains were separated from the rock by gentle crushing and handpicking and have been grouped on the basis of size and colour into large (> 1 mm) and small (< 1 mm), and light- and dark-green fractions. Glauconites found inside fossil fragments, presumably in the position of formation, have been included in the small dark category, together with rare grains consisting of alternating bands of light- and dark-green mineral, referred to as variegated.

Thin sections were prepared for optical examination and electron microprobe (EMP) analysis, using a Cambridge Instruments Microscan 9. About 250 EMP analyses were made on twenty selected grains. The Fe^{3+}/Fe^{2+} ratio, which is important in the calculation of structural formulae, was determined using a variant of the spectrophotometric method of Riley and Williams (1959). The method was modified so that dissolution took place in an inert atmosphere in a platinum planchette, using weighed additions of scaled-down quantities of reagents. This permitted up to fourteen determinations to be made on a single glauconite grain; ninety-three Fe^{3+}/Fe^{2+} ratio determinations were made on another twenty grains with an estimated error in the total and ferrous iron of $\pm 3\%$.

Measurement of *d*(060) spacing, mixed-layering, and impurities were made using a Philips diffractometer with a PW 1132 generator.

Results

Optical characteristics. Examination of thin sections shows that most small glauconite grains are of the dark-green type and are penetrated by deep cracks infilled with calcite. A high proportion of the dark grains show a distinct rim of clearer material and some have similar material lining the internal cracks. The large dark grains are slightly paler than the smaller grains and usually have an ovoid outline.

The large light grains have an ovoid shape similar to the large dark grains and contain small particles of calcite and quartz scattered throughout. They do not show the rims found in the dark grains. Some light grains have a layered structure which is only apparent when the grain is broken. Small light grains are pale yellow-orange, often showing a patchy variation in colour within the grain.

Ferric/ferrous iron ratios. Since a minimum

TABLE I

SUMMARY OF Fe^{3+}/Fe^{2+} RATIO VALUES AND RANGES

	SMALL'L'	SMALL'D'	LARGE'L'	LARGE'D'
Number of grains	3	4	11	9
Number of determinations	9	10	34	42
Group average Fe^{3+}/Fe^{2+} ratio	2.16	2.46	2.73	3.33
Range of grain average values	1.3-3.5	0.4-5.0	0.9-4.4	2.3-4.2
Range of individual points	0.9-4.4	0.23-5.9	0.9-5.4	2.3-4.9

sample weight of only twenty μg is required for each analysis, many determinations are possible on divisions of a single grain. Large variations in the Fe^{3+}/Fe^{2+} ratio were found between and within grains (Table I). The relationship between the total iron and the ferric and ferrous iron contents is shown in fig. 1. Increase in total iron is accompanied by an increase in ferric iron so that at high total iron values, the Fe^{3+}/Fe^{2+} ratio is higher than at low total iron values. Since the ferric iron does not increase at the expense of the ferrous iron, there is no question of the change in the ratio being caused by subsequent oxidation. Most of the points in fig. 1*a* lie on a single set of trends, suggesting that the large grains were formed under similar conditions and have a common origin. The ferric and ferrous iron contents of the small grains do not show as clear a relationship to total iron as that shown by the large grains, but have a considerable scatter (fig. 1*b*). This suggests either derivation from a variety of sources, and/or differing conditions of formation within a single source. It would appear, therefore, that the small grains had a different origin from the large grains.

Variation in the Fe^{3+}/Fe^{2+} *ratio.* There is considerable variation in the Fe^{3+}/Fe^{2+} ratio within each group (fig. 2 and Table I). The small dark group has the largest, and the large dark group the smallest range of values; this almost precludes the large dark grains from having developed from the small dark ones. The large light grains, on the other hand, have a range of Fe^{3+}/Fe^{2+} ratios greater than the small light grains and could have developed from them.

Effect of the Fe^{3+}/Fe^{2+} *ratio.* The Fe^{3+}/Fe^{2+} ratio plays an important role in the calculation of the number of ions per half unit cell; the differences in the structural formulae calculated by using the lowest and highest grain average ratios (Table I) are illustrated by the two sets of values for each analysis of grains 8 and 9 (Tables III and IV). In grain 8, all the formulae derived using the highest grain average Fe^{3+}/Fe^{2+} ratio fit the criteria for glauconite, i.e. $\Sigma(R^{3+}+R^{2+}) \approx 2.0$, ΣR^{3+} between 1.19 and 1.49. If the lowest grain average ratio is used, none of the formulae fits the criteria; $\Sigma(R^{3+}+R^{2+})$ greatly exceeds 2.0 and ΣR^{3+} is much less than 1.19, suggesting a celadonitic composition with some trioctahedral character. Five analyses of grain 9 fit the glauconite criteria using the highest Fe^{3+}/Fe^{2+} ratio (points E, G, I, K, and Q), but none using the lowest. The average composition of grain 8 (Table II) does not fit the glauconite criteria

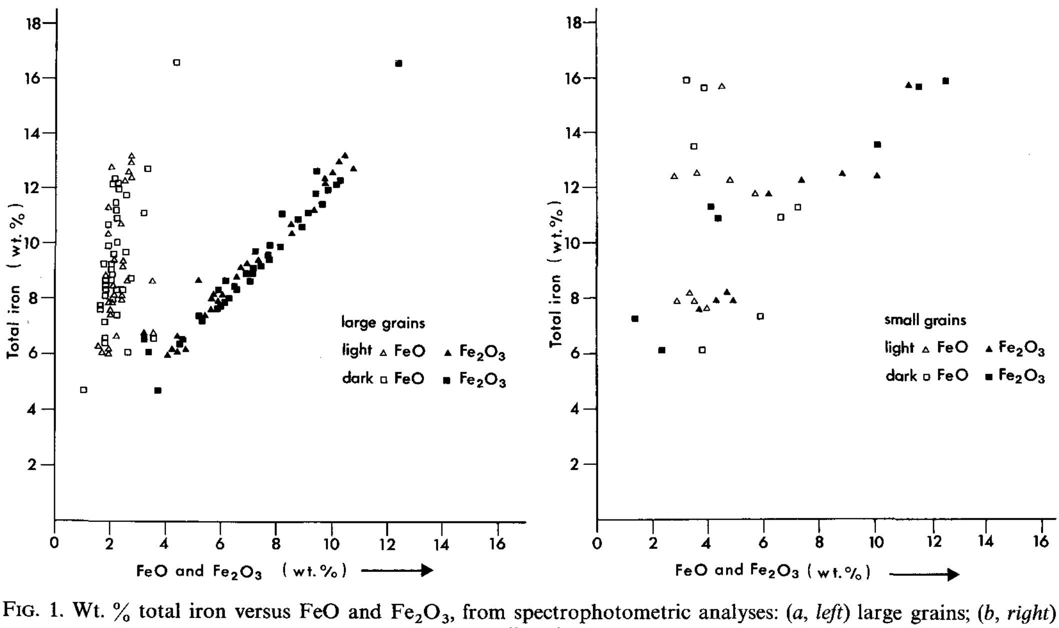

FIG. 1. Wt. % total iron versus FeO and Fe_2O_3, from spectrophotometric analyses: (*a*, *left*) large grains; (*b*, *right*) small grains.

TABLE II

AVERAGED ANALYSES AND STRUCTURAL FORMULAE OF TWENTY GLAUCONITE GRAINS

Grain	8	7	15	13	12	6	4	20	21	17	16	11	19	9	14	1	2	3	5	18
SiO_2	49.4	52.2	49.0	50.8	50.3	50.8	53.3	50.9	50.5	50.7	47.7	49.4	53.4	51.9	50.6	53.9	51.8	52.0	51.8	51.5
Al_2O_3	5.48	6.95	9.58	9.95	7.40	12.5	9.62	11.5	9.06	6.64	10.0	8.05	9.57	11.1	17.5	10.9	14.7	11.4	15.0	13.2
Fe_2O_3	20.8	16.7	12.8	14.2	15.2	12.0	14.4	11.2	14.4	17.7	12.8	15.9	13.5	14.0	7.94	14.4	13.8	14.4	11.2	12.2
FeO	7.49	6.84	4.63	5.11	5.49	4.91	5.20	4.59	5.20	4.84	4.27	5.32	4.49	4.68	2.65	3.93	3.77	3.93	3.73	4.08
MgO	2.83	3.27	2.77	2.89	2.95	3.08	3.10	3.15	3.07	2.92	2.60	2.58	2.54	2.81	2.63	2.90	3.29	3.00	2.51	2.72
CaO	0.82	0.20	0.50	-	0.92	0.27	0.20	0.55	0.40	-	0.47	0.50	-	0.70	-	0.20	0.21	-	0.19	0.26
Na_2O	-	0.60	-	0.79	-	0.58	0.46	0.84	0.70	0.49	0.12	-	0.58	0.60	0.83	0.44	0.59	0.21	0.48	0.64
K_2O	7.02	7.05	5.55	5.93	5.94	7.13	7.37	6.57	6.66	7.50	5.18	6.37	6.15	6.59	5.82	7.41	6.97	7.30	7.40	6.49
Total	93.84	93.81	84.83	89.67	88.20	91.27	93.65	89.30	89.99	90.79	83.14	88.12	90.23	92.38	87.97	94.08	95.13	92.24	92.31	91.09
Fe^{3+}/Fe^{2+} ratio	2.5	2.2	2.5	2.5	2.5	2.2	2.5	2.2	2.5	3.3	2.7	2.7	2.7	2.7	2.7	3.3	3.3	3.3	2.7	2.7
Si	3.68	3.79	3.81	3.77	3.83	3.69	3.80	3.76	3.76	3.80	3.78	3.78	3.89	3.74	3.67	3.79	3.60	3.74	3.68	3.71
Al	0.32	0.21	0.19	0.23	0.17	0.31	0.20	0.24	0.24	0.20	0.22	0.22	0.11	0.26	0.33	0.21	0.40	0.26	0.32	0.29
Al	0.16	0.39	0.69	0.64	0.49	0.76	0.61	0.76	0.56	0.39	0.71	0.51	0.71	0.68	1.16	0.69	0.80	0.71	0.93	0.83
Fe^{3+}	1.16	0.91	0.75	0.79	0.87	0.66	0.77	0.62	0.81	1.00	0.76	0.92	0.74	0.76	0.43	0.76	0.72	0.78	0.60	0.66
Fe^{2+}	0.47	0.42	0.30	0.32	0.35	0.30	0.31	0.28	0.32	0.30	0.28	0.34	0.27	0.28	0.16	0.23	0.22	0.24	0.22	0.25
Mg	0.31	0.35	0.32	0.32	0.33	0.33	0.33	0.35	0.34	0.33	0.31	0.29	0.28	0.30	0.28	0.30	0.34	0.32	0.27	0.29
Ca	0.13	0.03	0.08	-	0.15	0.04	0.03	0.09	0.06	-	0.08	0.08	-	0.11	-	0.03	0.03	-	0.03	0.04
Na	-	0.08	-	0.11	-	0.08	0.06	0.12	0.10	0.07	0.02	-	0.08	0.08	0.12	0.06	0.08	0.03	0.07	0.09
K	0.67	0.65	0.55	0.56	0.58	0.66	0.67	0.62	0.63	0.72	0.52	0.62	0.57	0.60	0.54	0.67	0.62	0.67	0.67	0.60
$\Sigma(R^{3+} + R^{2+})$	2.10	2.07	2.06	2.07	2.04	2.05	2.02	2.01	2.03	2.02	2.06	2.06	2.00	2.02	2.03	1.98	2.08	2.05	2.02	2.03
ΣR^{3+}	1.32	1.30	1.44	1.43	1.36	1.42	1.38	1.38	1.37	1.39	1.47	1.43	1.45	1.44	1.59	1.45	1.52	1.49	1.53	1.49
ΣA	0.80	0.76	0.63	0.67	0.73	0.78	0.76	0.83	0.79	0.79	0.62	0.70	0.65	0.79	0.66	0.76	0.73	0.70	0.77	0.73
Maximum Al_2O_3	6.4	8.1	10.9	11.8	8.2	14.3	11.2	11.9	12.3	9.0	11.6	10.7	12.6	15.5	23.4	17.5	19.3	19.1	20.5	23.0
Minimum Al_2O_3	5.1	6.3	9.1	9.1	6.9	11.6	8.3	11.0	7.4	4.9	6.6	5.0	6.4	9.0	15.5	8.8	6.3	8.3	10.5	9.2
Maximum FeO*	26.8	23.6	17.2	19.3	20.4	17.1	19.7	16.0	20.8	24.1	18.8	22.9	19.2	19.2	11.8	19.1	21.5	18.6	17.2	17.8
Minimum FeO	25.2	19.6	14.4	16.3	17.6	14.8	16.7	13.9	16.1	15.7	13.2	15.1	11.3	12.2	7.3	11.8	12.3	10.4	9.7	8.3
Maximum K_2O	7.2	7.4	5.8	5.9	6.4	7.3	8.5	7.0	6.8	7.5	5.7	6.8	7.1	7.4	7.0	7.9	7.9	8.2	8.5	8.4
Minimum K_2O	6.7	6.4	5.3	4.9	5.2	6.5	6.1	5.9	6.5	7.5	4.3	5.5	5.7	6.0	5.2	6.7	5.9	6.9	6.2	5.7
% mixed-layering	15	10–18	20–30	20–30	18–30	10–18	20	10–20	15	10	25–35	12–25	10–25	10–20	10–30	15	20	10	10–20	10–25
Number of analyses	17	11	13	6	12	4	7	3	5	4	14	16	7	17	10	6	5	9	7	10
Grain type	d	v	d	d	d	l	d	l	f	D	L	L	L	L	L	D	D	D	L	L

Averaged EMP analyses and structural formulae of twenty glauconitic grains. Analyst H.A.Buckley. Maximum and minimum values of Al_2O_3, total iron as FeO* and K_2O are listed; amount of mixed-layering estimated from K_2O. Grains arranged in increasing variability left to right. Grain types; d=small dark, l=small light, D=large dark, L=large light, v=variegated, f=fossil.

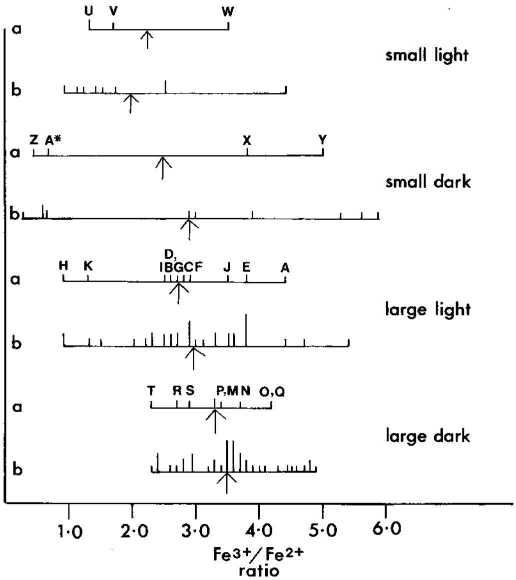

FIG. 2. Range of Fe^{3+}/Fe^{2+} values for the four grain groups: (*a*) grain averages; letter identifies different grains; (*b*) positions of individual analyses; coincident points are stacked. Arrow in (*a*) group average ratio; (*b*) group mean ratio.

when the average small dark grain ratio of 2.5 : 1 is used, whilst that of grain 9 does using the average large light grain ratio of 2.7 : 1. This is unexpected when the variability of grain 9 is compared with the almost constant composition of grain 8.

A low Fe^{3+}/Fe^{2+} ratio can cause the octahedral Al^{3+} content to appear anomalously high; some grains do, however, have a high Al content (e.g. grains 5 and 14, fig. 3). These Al-rich grains contain similar amounts of mixed-layering to the iron-rich grains and, unless the mixed-layer mineral present has a widely varying composition, the Al content is believed to be original.

Electron microprobe analyses. EMP analyses were made on twenty glauconite grains with up to seventeen determinations on traverses of some of the larger grains. The results are listed in Table II, in order of increasing variation in Al, Fe, and K. The average composition of each of the twenty grains is given in Table II along with the structural formulae calculated using the respective group average Fe^{3+}/Fe^{2+} ratio (Table I) and the amount of mixed-layering estimated from the curve of Manghnani and Hower (1964). The twenty grains used in the EMP analyses were not the same twenty grains as were used for the iron determinations.

Inter-grain chemical variations. The amount of Al, Fe, and K varies considerably between some grains (Table II), giving a range of composition from aluminous (grain 14, fig. 3) to iron-rich (grain 8, fig. 3) glauconites. The range of octahedral Al^{3+}–Fe^{3+} interchangeability (the areas enclosed within dashed and dotted lines, fig. 3), shows the differences between grains and between points in

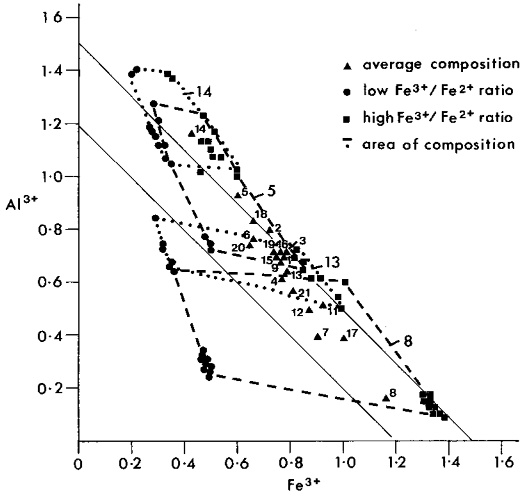

FIG. 3. Trivalent octahedral ion contents (R^{3+}) of half unit cell; triangles indicate R^{3+} composition calculated from average grain composition (Table II) and relevant grain average Fe^{3+}/Fe^{2+} ratio (Table I). Circles indicate R^{3+} composition of individual points in grains 14, 5, 13, and 8 using the lowest grain average Fe^{3+}/Fe^{2+} ratio; squares indicate R^{3+} composition using highest grain average Fe^{3+}/Fe^{2+} ratio. Area of compositional variation for grains 5 and 8 enclosed by dashed lines, 14 and 13 by dotted lines. Solid lines indicate limits of glauconite R^{3+} content (Buckley *et al.* 1978).

the same grain. Areas of compositional overlap were found between some grains of different average octahedral contents, e.g. 14 and 5, 5 and 13, 13 and 8, in fig. 3.

Seven of the analysed grains (1, 3, 4, 15, 16, 17, and 21) fit the glauconite criteria of Buckley *et al.* (1978), using their respective group average iron ratios, whilst in six of the remainder (2, 5, 6, 14, 18, and 20) octahedral Al^{3+} exceeds Fe^{3+}. The latter are all light grains, with the exception of grain 2. The compositional differences between grains in the present sample are greater than those previously recorded between samples from different localities by Buckley *et al.* (1978). The average composition of all the glauconite grains from the Tollgate bore sample (between points 9 and 13 in fig. 3) is different from that recorded for grains from beds of similar age at Folkestone (Buckley *et al.* 1978, anals. 1, 5, and 9). The average composition of the

TABLE III

CHEMICAL ANALYSES AND STRUCTURAL FORMULAE OF GRAIN 8

	A		B		C		D		E		F		G		H		I	
SiO_2	49.7		50.1		48.4		49.8		49.6		48.8		49.1		49.3		50.2	
Al_2O_3	5.60		5.38		6.35		5.91		5.44		5.09		12.6		5.40		5.62	
FeO	25.8		26.5		25.5		26.5		26.0		26.1		20.2		25.2		26.5	
MgO	2.86		2.88		2.67		2.76		2.85		2.82		2.37		2.84		2.85	
CaO	0.92		0.79		0.79		0.79		0.79		0.78		0.79		0.96		0.72	
Na_2O	-		-		-		-		-		-		-		-		-	
K_2O	6.98		7.04		6.96		6.99		7.02		6.91		6.92		6.66		7.09	
Total	91.86		92.69		09.67		92.75		91.70		90.50		91.98		90.36		92.98	
Numbers of ions on the basis of 22 (O,OH,F)																		
Si	3.81	3.66	3.81	3.66	3.76	3.61	3.78	3.63	3.81	3.66	3.81	3.65	3.64	3.53	3.83	3.68	3.80	3.65
Al	0.19	0.34	0.19	0.34	0.24	0.39	0.22	0.37	0.19	0.34	0.19	0.35	0.36	0.47	0.17	0.32	0.20	0.35
Al	0.32	0.15	0.29	0.12	0.34	0.17	0.31	0.14	0.30	0.13	0.28	0.10	0.64	0.60	0.32	0.15	0.30	0.13
Fe^{3+}	0.47	1.32	0.48	1.35	0.47	1.32	0.48	1.34	0.48	1.33	0.49	1.36	0.36	1.01	0.47	1.31	0.48	1.34
Fe^{2+}	1.18	0.26	1.20	0.27	1.18	0.27	1.20	0.27	1.19	0.27	1.22	0.27	0.89	0.20	1.17	0.26	1.20	0.27
Mg	0.33	0.31	0.33	0.31	0.31	0.30	0.31	0.30	0.33	0.31	0.33	0.32	0.26	0.25	0.33	0.32	0.32	0.31
Ca	0.15	0.14	0.13	0.12	0.13	0.13	0.13	0.12	0.13	0.12	0.13	0.13	0.13	0.12	0.16	0.15	0.12	0.11
Na	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K	0.68	0.65	0.68	0.66	0.69	0.66	0.68	0.65	0.69	0.66	0.69	0.66	0.65	0.63	0.66	0.63	0.69	0.66
$\Sigma(R^{3+} + R^{2+})$	2.30	2.04	2.30	2.05	2.30	2.06	2.30	2.05	2.30	2.04	2.32	2.05	2.15	2.06	2.29	2.04	2.30	2.05
ΣR^{3+}	0.79	1.47	0.77	1.47	0.81	1.49	0.79	1.48	0.78	1.46	0.77	1.46	1.00	1.61	0.79	1.46	0.78	1.47
ΣA	0.73	0.79	0.81	0.78	0.82	0.79	0.81	0.77	0.82	0.78	0.82	0.79	0.78	0.75	0.82	0.78	0.81	0.77

	J		K		L		N		O		P		Q	
SiO_2	49.5		49.9		48.1		49.1		48.9		49.9		50.4	
Al_2O_3	5.30		5.28		5.34		5.14		5.13		5.74		5.51	
FeO	26.2		26.4		25.6		26.8		26.2		25.8		25.7	
MgO	2.89		2.94		2.79		2.86		2.83		2.84		2.83	
CaO	0.77		0.79		1.09		0.69		0.77		0.94		0.75	
Na_2O	-		-		-		-		-		-		-	
K_2O	7.06		7.00		6.97		7.12		7.28		7.17		6.99	
Total	91.72		92.31		89.89		91.71		91.11		92.39		92.18	
Numbers of ions on the basis of 22 (O,OH,F)														
Si	3.81	3.66	3.81	3.66	3.78	3.63	3.79	3.64	3.80	3.65	3.80	3.65	3.84	3.69
Al	0.19	0.34	0.19	0.34	0.22	0.37	0.21	0.36	0.20	0.35	0.20	0.35	0.16	0.31
Al	0.29	0.12	0.29	0.12	0.28	0.11	0.26	0.09	0.27	0.10	0.32	0.15	0.33	0.17
Fe^{3+}	0.48	1.35	0.48	1.35	0.48	1.34	0.49	1.38	0.49	1.36	0.47	1.31	0.47	1.31
Fe^{2+}	1.20	0.27	1.20	0.27	1.20	0.27	1.24	0.28	1.22	0.27	1.17	0.26	1.17	0.26
Mg	0.33	0.32	0.33	0.32	0.33	0.31	0.33	0.32	0.33	0.31	0.32	0.31	0.32	0.31
Ca	0.13	0.12	0.13	0.12	0.18	0.18	0.11	0.11	0.13	0.12	0.15	0.15	0.12	0.12
Na	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K	0.69	0.66	0.68	0.65	0.70	0.67	0.70	0.67	0.72	0.69	0.70	0.67	0.68	0.65
$\Sigma(R^{3+} + R^{2+})$	2.30	2.06	2.30	2.06	2.29	2.03	2.32	2.07	2.31	2.04	2.28	2.03	2.29	2.05
ΣR^{3+}	0.77	1.47	0.77	1.47	0.76	1.45	0.75	1.47	0.76	1.46	0.79	1.46	0.80	1.48
ΣA	0.82	0.78	0.81	0.77	0.88	0.85	0.81	0.78	0.85	0.81	0.85	0.82	0.80	0.77

EMP analyses and structural formulae of sixteen points on grain 8 (small 'D' type). Structural formulae in pairs: on left using low (0.4:1) Fe^{3+}/Fe^{2+} ratio, on right using high (5.0:1) ratio. Analyst H.A.Buckley.

dark grains in the current work is, however, similar to that of the earlier analyses.

Intragrain variations. The amount of intragrain variation ranges from grains of almost constant composition (homogeneous) to grains with widely varying compositions (heterogeneous); the analysed grains are listed in Table II in order of increasing major element variability. In general, the small grains are less variable than the large, which is surprising in view of the wide range of Fe^{3+}/Fe^{2+} values recorded in the small dark grain category (Table I).

At high total iron values, the effect of variations in the Fe^{3+}/Fe^{2+} ratio (changing from the lowest to the highest grain average) on the R^{3+} content is greater than that caused by the variations in the chemical composition.

X-ray diffraction. X-ray diffraction was used to measure the *d*(060) spacing, to check the amount of mixed-layering and any impurities in the various grain types (Table V). In addition to the light and dark grains, glauconitic material found inside fossil gastropods, corals, and cyclostome bryozoans was examined after being released by treatment with dilute acetic acid.

The *d*(060) spacing, when used in conjunction with the Fe^{3+} content, can be diagnostic in clay mineral identification. Only the large grains plot within the suggested glauconite field of Buckley *et al.* (1978) while most of the small grains fall outside it (fig. 4). All the 'fossil' grains were initially grouped in the small dark category because of their size and colour. Glauconites from the coral and gastropod casts have spacings similar to the small light and dark grains, whilst the bryozoan and variegated grains have two distinct spacings, possibly indicative of different origins. The separation of the grains into the various groups on the

TABLE IV

CHEMICAL ANALYSES AND STRUCTURAL FORMULAE OF GRAIN 9

	A	B	C	D	E	F	G	H	I
SiO_2	52.4	51.6	51.7	49.9	55.2	50.5	51.9	52.2	53.8
Al_2O_3	10.3	12.1	11.7	13.3	9.08	11.0	8.89	9.97	9.56
FeO	19.0	16.2	18.4	15.5	15.3	16.4	17.8	16.7	16.4
MgO	2.74	2.69	2.76	2.62	2.62	2.95	3.01	2.99	2.87
CaO	0.21	0.24	0.21	0.32	0.10	0.07	0.16	0.10	0.29
Na_2O	0.56	0.62	0.61	0.81	0.63	0.71	0.61	0.84	0.51
K_2O	6.40	7.00	6.93	7.00	6.05	6.25	6.59	6.00	6.23
Total	91.14	90.45	92.31	89.45	88.98	87.88	88.16	88.80	89.66
Numbers of ions on the basis of 22 (O,OH,F)									
Si	3.80 3.74	3.77 3.71	3.73 3.67	3.69 3.64	4.03 3.97	3.79 3.73	3.87 3.81	3.87 3.81	3.93 3.87
Al	0.20 0.26	0.23 0.29	0.27 0.33	0.31 0.36	- 0.03	0.21 0.27	0.13 0.19	0.13 0.19	0.07 0.13
Al	0.68 0.61	0.81 0.74	0.73 0.65	0.85 0.78	0.78 0.74	0.76 0.69	0.65 0.58	0.74 0.67	0.75 0.68
Fe^{3+}	0.55 0.92	0.47 0.79	0.53 0.89	0.45 0.77	0.44 0.75	0.49 0.82	0.53 0.89	0.49 0.83	0.47 0.80
Fe^{2+}	0.61 0.21	0.52 0.18	0.58 0.20	0.50 0.18	0.49 0.17	0.54 0.19	0.59 0.20	0.54 0.19	0.53 0.18
Mg	0.30 0.29	0.29 0.29	0.30 0.29	0.29 0.28	0.29 0.28	0.33 0.33	0.34 0.33	0.33 0.33	0.31 0.31
Ca	0.03 0.03	0.04 0.04	0.03 0.03	0.05 0.05	0.02 0.02	0.01 0.01	0.03 0.03	0.02 0.02	0.05 0.05
Na	0.08 0.08	0.09 0.09	0.09 0.08	0.12 0.11	0.09 0.09	0.10 0.10	0.09 0.09	0.12 0.12	0.07 0.07
K	0.59 0.58	0.65 0.64	0.64 0.63	0.66 0.65	0.56 0.55	0.60 0.59	0.63 0.62	0.57 0.56	0.58 0.57
$\Sigma(R^{3+} + R^{2+})$	2.14 2.03	2.09 2.00	2.14 2.03	2.09 2.01	2.00 1.94	2.12 2.03	2.11 2.03	2.10 2.02	2.06 1.97
ΣR^{3+}	1.23 1.53	1.28 1.53	1.26 1.54	1.30 1.55	1.22 1.49	1.25 1.51	1.18 1.47	1.23 1.50	1.22 1.48
ΣA	0.70 0.69	0.78 0.77	0.76 0.74	0.83 0.81	0.67 0.66	0.71 0.70	0.75 0.74	0.71 0.70	0.70 0.69

	J	K	L	M	N	O	P	Q
SiO_2	57.6	51.8	51.6	50.5	49.4	50.9	50.5	52.0
Al_2O_3	14.9	9.53	10.3	15.6	11.1	15.6	10.5	10.3
FeO	12.2	19.2	18.2	14.6	18.0	18.2	17.7	18.0
MgO	2.30	2.96	2.96	2.88	2.94	2.82	2.85	2.92
CaO	0.20	0.34	0.27	0.06	0.16	0.15	0.20	0.12
Na_2O	0.47	0.58	0.58	0.59	0.65	0.61	0.63	0.54
K_2O	7.18	6.27	6.49	7.39	6.37	6.59	6.47	6.93
Total	94.85	90.68	90.40	91.62	88.62	89.37	88.85	90.81
Numbers of ions on the basis of 22 (O,OH,F)								
Si	3.89 3.85	3.81 3.74	3.79 3.73	3.62 3.58	3.72 3.65	3.79 3.73	3.78 3.71	3.81 3.74
Al	0.11 0.15	0.19 0.26	0.21 0.27	0.38 0.42	0.28 0.35	0.21 0.27	0.22 0.29	0.19 0.26
Al	1.08 1.02	0.64 0.55	0.68 0.61	0.94 0.88	0.70 0.62	0.68 0.60	0.71 0.62	0.70 0.61
Fe^{3+}	0.33 0.56	0.56 0.94	0.53 0.90	0.41 0.70	0.54 0.91	0.54 0.91	0.52 0.89	0.52 0.88
Fe^{2+}	0.36 0.13	0.62 0.22	0.59 0.20	0.46 0.16	0.60 0.21	0.60 0.21	0.58 0.20	0.58 0.20
Mg	0.23 0.23	0.32 0.32	0.32 0.32	0.31 0.30	0.33 0.32	0.31 0.31	0.32 0.31	0.32 0.31
Ca	0.03 0.03	0.05 0.05	0.04 0.04	0.01 0.01	0.03 0.03	0.02 0.02	0.03 0.03	0.02 0.02
Na	0.06 0.06	0.08 0.08	0.08 0.08	0.08 0.08	0.10 0.09	0.09 0.09	0.09 0.09	0.08 0.08
K	0.62 0.61	0.59 0.58	0.61 0.60	0.68 0.67	0.61 0.60	0.63 0.62	0.62 0.61	0.65 0.64
$\Sigma(R^{3+} + R2+)$	2.00 1.94	2.14 2.03	2.12 2.03	2.12 2.04	2.17 2.06	2.13 2.03	2.13 2.02	2.12 2.00
ΣR^{3+}	1.41 1.58	1.20 1.49	1.21 1.51	1.35 1.58	1.24 1.53	1.22 1.51	1.23 1.51	1.22 1.49
ΣA	0.71 0.70	0.72 0.71	0.73 0.72	0.77 0.76	0.74 0.72	0.74 0.73	0.74 0.73	0.75 0.74

EMP analyses and structural formulae of seventeen points on grain 9 (large 'L' type). Structural formulae in pairs, on left using low (0.9:1) Fe^{3+}/Fe^{2+} ratio, on right using high (4.4:1) ratio. Analyst H.A.Buckley.

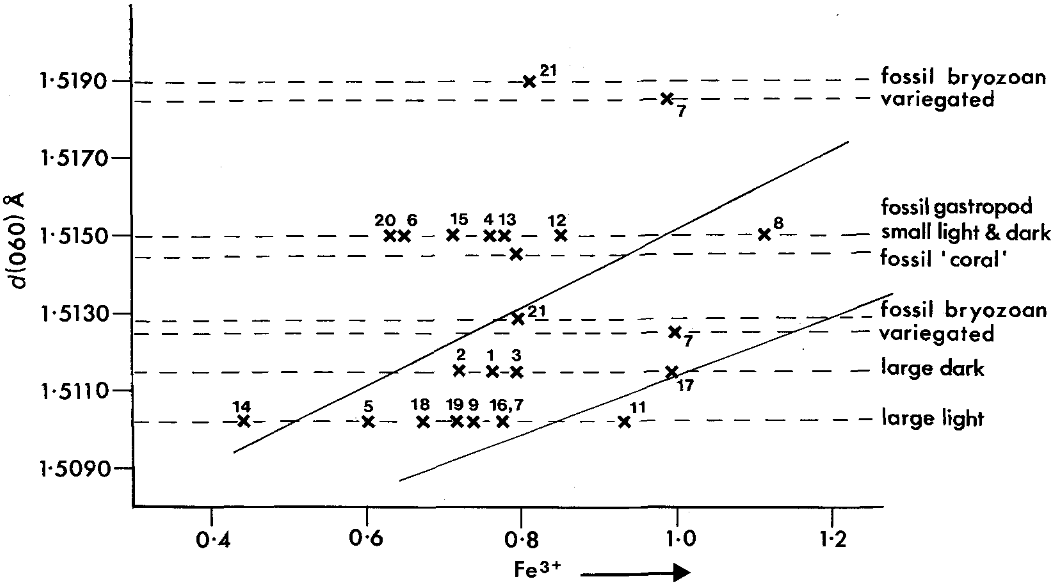

FIG. 4. Fe^{3+} versus *d*(060) spacing: dashed lines indicate positions of measured spacings; solid lines indicate approximate limits of glauconite (Buckley *et al.*, 1978).

basis of their Fe^{3+}-*d*(060) spacing (fig. 4) supports the earlier proposal that large and small grains in the sample have different origins.

Discussion

A wider range of chemical variation than has been previously described has been found between and within glauconite grains from the Tollgate bore sample. The classification of the grains into large and small, and light-and dark-green categories, is supported by the chemical and X-ray results. Small grains have, on average, less compositional variation and lower Fe^{3+}/Fe^{2+} ratios than the large grains; the positive relationship between total iron and the Fe^{3+}/Fe^{2+} ratio was observed only in the large grain group. The small dark group has the largest range of Fe^{3+}/Fe^{2+} values, and the large dark group the smallest, making it most unlikely that the former developed into the latter. The dark grains have more total Fe and less Al than the light grains and the octahedral contents of the latter usually plot outside the glauconite field (fig. 3). The amount of mixed-layering in the grains does not appear to be related to the colour, to compositional variation other than interlayer potassium, or to any specific type of grain.

The Fe^{3+}/Fe^{2+} data and the X-ray results suggest strongly that all the large grains formed under similar conditions and probably have a common origin. The small grains appear to derive from several sources or from a single source under a variety of conditions. The 'fossil' grains can be divided into those with *d*(060) spacings similar to the small light and dark grains, and those with different spacings; some of the former probably developed into small dark grains. Large light grains may have developed from small light grains but this is unlikely in the case of the large dark grains.

TABLE V

X-RAY DIFFRACTION ANALYSES AND d(060) SPACINGS OF GLAUCONITE GRAINS

grain type	d(060) Å spacing	XRD analysis
large 'D'	1.5115	g, m-l, q, ch, ka
large 'L'	1.5102	g, m-l, ch, ca
small 'L & D'	1.5150	g, m-l, q, ch, ca
variegated	1.5125,1.5185	g, much m-l, q, ca
fossil casts		
'bryozoan'	1.5128,1.5190	g, m-l, q
'coral'	1.5145	g, m-l
'gastropod'	1.5150	g, m-l

g = glauconite, m-l = mixed-layer clays, q = quartz, ch = chlorite, ka = kaolinite, ca = calcite. Analyst L.R.Johnson.

There is considerable intragrain chemical variation from grains of almost constant composition to those with widely varying compositions; no completely homogeneous grains were found in the

Tollgate bore sample. The difference in chemical composition between the large and small grains is greater than that between light and dark grains of similar size.

Only six of the twenty grains analysed (1, 3, 9, 16, 17, 21) fulfil all the chemical and Fe^{3+}-*d*(060) requirements of the mineral glauconite. Only two grains, 5 and 16, contain less than 10% of mixed-layering; in all the grains from the Tollgate bore sample, the glauconite is neither as pure nor as crystalline as that reported from the Folkestone Beds in the Folkestone area (Buckley *et al.* 1978).

The Folkestone Beds have been shown to contain glauconitic material from a variety of sources. This supports the sedimentary model of Middlemiss (1975) and Allen (1982) for Folkestone Bed times, of a broad shallow strait connecting northern and southern seas in which considerable sediment transport occurred. It is most unlikely that any of the glauconitic material in the Folkestone Beds at the Tollgate locality could have formed in such an active environment. It is considered to have been incorporated into the sediment by reworking from contemporary and pre-existing glauconitic sediments.

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