

# Studies of Celadonite and Glauconite

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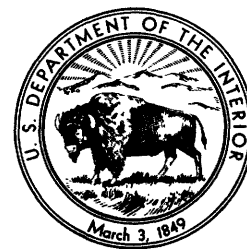
By MARGARET D. FOSTER

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 614-F

*A study of the compositional  
relations between celadonites  
and glaucosites and an interpretation  
of the composition of glaucosites*



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## CONTENTS

	Page		Page
Abstract.....	F1	Interpretation of glauconite composition.....	F13
Introduction.....	1	Relation between trivalent iron and octahedral aluminum.....	13
Selection of analyses and calculation of atomic ratios....	2	The $\text{Fe}^{+3}:\text{Fe}^{+2}$ ratio.....	13
Relation between the composition of celadonites and glauconites.....	3	Relation between iron and potassium.....	14
High potassium celadonites and glauconites.....	7	Fixation of potassium.....	14
Low potassium celadonites and glauconites.....	9	Deficiency in potassium content.....	14
Relation between Si, $\text{R}^{+2}(\text{VI})$ , $\text{Al}(\text{VI})$ , and $\text{R}^{+3}(\text{VI})$ ..	9	Relation between glauconite composition and geo- logic age.....	15
		References cited.....	17

## ILLUSTRATIONS

	Page
FIGURE 1. Chemical composition of representative celadonites and glauconites having more than 0.65 atom of potassium per half cell.....	F8
2. Relation between $\text{Si} + \text{R}^{+2}(\text{VI})$ decrease and $\text{Al}(\text{IV}) + \text{R}^{+3}(\text{VI})$ increase in high potassium- high charge celadonites and glauconites.....	10
3. Relation between decrease in Si and decrease in $\text{R}^{+2}(\text{VI})$ in high potassium-high charge celadonites and glauconites.....	10
4. Relation between increase in $\text{Al}(\text{IV})$ and increase in $\text{R}^{+3}(\text{VI})$ in high potassium-high charge celadonites and glauconites.....	10
5. Relation between excess of $\text{R}^{+2}(\text{VI})$ decrease over Si decrease and layer-charge deficiency..	13
6. Relation between $\text{Fe}^{+3}$ and $\text{Al}(\text{VI})$ in glauconites.....	13
7. Relation between total iron and potassium in glauconites.....	14
8. Extreme and average compositions of Cretaceous and Tertiary glauconites.....	16

## TABLES

	Page
TABLE 1. Chemical analyses of celadonites, together with their calculated atomic ratios.....	F4
2. Chemical analyses of glauconites having more than 0.65 potassium atom per half cell, together with their calculated atomic ratios.....	5
3. Chemical analyses of glauconites having less than 0.66 potassium atom per half cell, to- gether with their calculated atomic ratios.....	6
4. Range and median values of principal constituents in high potassium celadonites and glauconites.....	6
5. Range and median values of principal constituents in low potassium celadonites and glau- conites.....	7
6. $\text{Al}(\text{IV})\text{R}^{+3}(\text{VI})$ replacement of $\text{SiR}^{+2}(\text{VI})$ in high potassium-high charge celadonites and glauconites.....	11
7. $\text{Al}(\text{IV})\text{R}^{+3}(\text{VI})$ replacement of $\text{SiR}^{+2}(\text{VI})$ in high potassium-low charge glauconites.....	12
8. $\text{Al}(\text{IV})\text{R}^{+3}(\text{VI})$ replacement of $\text{SiR}^{+2}(\text{VI})$ in low potassium celadonites and glauconites....	12



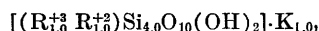
## SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

### STUDIES OF CELADONITE AND GLAUCONITE

By MARGARET D. FOSTER

#### ABSTRACT

A study based on 10 analyses of celadonites and 19 analyses of glauconites having high contents of potassium (more than 0.65 ion per half cell) shows that both range widely in content of trivalent iron and octahedral aluminum, which seem to bear a reciprocal relation to each other. The relations among Si,  $R^{+3}(VI)$ , Al(IV), and  $R^{+3}(VI)$  indicate that these micas belong to an isomorphous replacement series that starts with the generalized theoretical tetrasilicic dioctahedral end-member,



and that is characterized by coupled replacement of Si and  $R^{+2}(VI)$  by Al(IV) and  $R^{+3}(VI)$ . In this series, celadonites, with Si ranging from 4.00 to 3.75, stand closest to the end-member, and represent lesser degrees of replacement than the glauconites, in which Si ranges from 3.80 to 3.55. Celadonites and glauconites having fewer than 0.66 potassium ion per half cell belong to the same replacement series, and are similar in layer composition to the high potassium celadonites and glauconites. Because celadonites and glauconites have the same crystal structure, are very similar in chemical composition, and are near members of the same replacement series, optical, X-ray, and thermal data at present contribute little to their differentiation.

In many celadonites and glauconites the decrease in  $R^{+2}(VI)$ , compared to the theoretical end-member, is greater than the decrease in Si, and the increase in  $R^{+3}(VI)$  is greater than the increase in Al(IV). The fact that the excess of  $R^{+3}(VI)$  decrease over Si decrease usually agrees closely with the excess of  $R^{+3}(VI)$  increase over Al(IV) increase strongly suggests oxidation of bivalent iron to trivalent. The further fact that the excess of  $R^{+3}(VI)$  decrease over Si decrease also agrees closely with the layer charge deficiency, as compared with a charge of  $-1.00$  per half cell (the layer charge of the theoretical end-member) seems to suggest that originally all these celadonites and glauconites had layer charges close to  $-1.00$ , but that oxidation has reduced the layer charge by an amount equivalent to the bivalent iron oxidized.

The lack of correlation between iron and potassium in glauconites suggests that glauconitization is made up of two separate, unrelated processes, incorporation of iron into the octahedral layer, and fixation of potassium in interlayer positions, with incorporation of iron preceding complete fixation of potassium. According to this concept, the amount of iron incorporated into the glauconite structure is dependent on the iron concentration

of the specific environment, with the iron content of the glauconite reflecting the degree of iron richness of the environment. A low potassium content may indicate immaturity, or lack of time for more complete fixation of potassium, if it is accompanied by high layer charge; or it may indicate degeneration, oxidation with attendant loss of layer charge and interlayer cations, if the layer charge is relatively low.

The great range in composition of Cretaceous and Tertiary glauconites suggests that factors such as specific environment of development, opportunity for potassium fixation, and exposure to oxidation are of greater importance in determining the composition of a glauconite than the geologic age in which it was formed.

#### INTRODUCTION

The relation between celadonite and glauconite is a subject of continuing controversy. A comparative study of 10 analyses of celadonite and 40 analyses of glauconite by Hendricks and Ross (1941) confirmed the close compositional relationship between the two minerals. However, they recommended (p. 708), retention of both names, as "the well established term 'glauconite' is used for a mineral of characteristic sedimentary origin whereas the term 'celadonite' is used for a mineral of quite different occurrence and paragenesis." Later workers, on the basis of optical, X-ray, and thermal data, as well as chemical analyses, have maintained that these minerals are identical. Schüller and Wohlmann (1951), on the basis of a single analysis of a celadonite, concluded that the composition of celadonite was near that of glauconite, except that silicon is partially replaced by trivalent iron in celadonite and by aluminum in glauconite. As their X-ray spacings were similar, they suggested their identity. A study of minerals from Karadagh, Crimea, convinced Savich-Zablotsky (1954) that the names "celadonite" and "glauconite" refer to the same mineral, their only difference being mode of origin. Malkova (1956), after electron-microscope and thermal studies of one sample of celadonite, and comparison of its chemical composition with that of seven other celadonites and glauconites, concluded that cela-

donite and glauconite are identical and suggested that the name "celadonite" be reserved for ferruginous varieties, and that aluminous varieties be called skolite, discarding the term "glauconite" entirely. Lazarenko (1956) also considered celadonite and glauconite identical, and, on the basis of electron micrographs, and X-ray, optical, and thermal data, placed glauconite, celadonite, and skolite in the hydromica group.

In correlating dioctahedral potassium micas on the basis of their charge relations, Foster (1956) found that the  $\text{Si}_4$  end of the trisilicic-tetrasilicic dioctahedral micas was represented by a celadonite from near Reno, Nev. In this celadonite, silicon exactly and completely filled the four cation positions (per half cell) of the tetrahedral layer. In another celadonite, silicon filled 3.88 of the 4.00 tetrahedral cation positions, with aluminum occupying only 0.12 positions. In two glauconites included in the study, silicon occupied only 3.62 and 3.67 tetrahedral positions, respectively. A similar relation between silicon occupancy in celadonites and glauconites is found in atomic ratios calculated from the analyses compiled by Hendricks and Ross (1941), with the atomic ratios per silicon ranging from 3.78 to 4.00 in the celadonites and from 3.44 to 3.84 in the glauconites. This difference in silicon occupancy in materials so closely related compositionally suggests the possibility that celadonites and glauconites are members of an isomorphic series.

Some of the confusion as to the relation between celadonites and glauconites may be attributed to the kind of specimens that have been compared. In previous studies of these minerals the importance of the potassium content was not realized, and the chemical composition of specimens containing 8–10 percent  $\text{K}_2\text{O}$  were compared with others containing only 3 or 4 percent  $\text{K}_2\text{O}$ , which are often interlayered, most commonly with montmorillonite, hydrous mica, or chlorite, or contain impurities like quartz, calcite, or apatite. In the present study many of the same analyses are used as were used in previous studies, but they are herein grouped for comparison according to potassium content and interlayer charge, in order to minimize as far as possible the disturbing effects of interlayering or contaminants.

#### SELECTION OF ANALYSES AND CALCULATION OF ATOMIC RATIOS

Most of the analyses used to study the compositional relationship between celadonites and glauconites having more than 0.65 potassium ion per half cell (that is, more than 7.0 percent  $\text{K}_2\text{O}$ ) were taken from the compilation of Hendricks and Ross (1941), although a few were taken from Smulikowski's (1954) compilation and

a few from more recent literature. These analyses made by classical methods are considered more reliable for a study of this kind than analyses made on very small samples (less than 50 mg) by a combination of microchemical, spectrochemical, and colorimetric methods. The inaccuracy of the later analyses is indicated by their totals ranging, for example, from 98.78 to 102.34 in Burst's (1958) eight analyses, and from 98.56 to 102.50 in the nine analyses of Bantor and Kastner (1965). Recalculating such analyses to obtain totals of 100.00, as Bantor and Kastner have done, only compounds the errors. In such a recalculation it is assumed that all the values found for the different constituents are equally in error, and the same correction is applied to all. However, it is more probable that only one or two values are in error, as some of the analytical techniques used are much more accurate than others. A slight error in the value obtained by one of the less reliable techniques is multiplied many times because of the very small samples used (less than 0.50 mg in some instances), and the very large factor required to convert the amount found to percent per gram. Analyses made by classical methods are usually made on much larger samples, thus avoiding such multiplication of error.

The samples analyzed by the longer classical methods were and are generally very carefully prepared by magnetic separation, heavy liquids, and handpicking, and examined under a petrographic microscope for impurities.

Under the conditions of occurrence of glauconite, calcite or apatite may be present, and their complete removal may be difficult. Consequently, any  $\text{CO}_2$  or  $\text{P}_2\text{O}_5$  reported in an analysis used in this study was presumed to indicate calcite or apatite present as impurities, and their  $\text{CaO}$  equivalent was deducted from the  $\text{CaO}$  reported in the analysis before calculating the atomic ratios of the various constituents. Determination of  $\text{CO}_2$  and  $\text{P}_2\text{O}_5$  is desirable in all analyses of glauconite, for proper allocation of the  $\text{CaO}$  reported in an analysis of glauconite. If not determined,  $\text{CO}_2$  and  $\text{P}_2\text{O}_5$  would escape detection in the course of the analysis, as  $\text{CO}_2$  would be driven off during the determination of inherent water, and any  $\text{P}_2\text{O}_5$  present would be included in the value reported for  $\text{Al}_2\text{O}_3$ .

In calculating formulas for celadonites and glauconites, Hendricks and Ross (1941) followed the usual custom of assigning all the  $\text{MgO}$  to the octahedral layer. In their formulas the number of octahedral positions occupied ranged from 1.94 to 2.17 per half cell in the glauconites and from 2.01 to 2.24 in the celadonites. As the two celadonites having the highest octahedral occupancy, 2.22 and 2.24, were unusually high in  $\text{MgO}$ ,



8.54 and 9.32 percent, respectively, Hendricks and Ross concluded (p. 706) that these two analyses "must have been made on impure material, as a magnesium silicate (serpentine or saponite?) must have been present to account for the high percentages of MgO." They therefore omitted them in formulating their interpretation of the chemical composition of celadonite. In their later study of montmorillonite (Ross and Hendricks, 1945), they, as usual, allocated all the MgO to the octahedral layer, and obtained octahedral occupancies as high as 2.24 positions. From this, they concluded that octahedral occupancy in some dioctahedral minerals is not necessarily limited to just two-thirds of the available cationic octahedral positions, as had been presumed, but that as much as a fourth of the "vacant" third positions might actually be occupied. However, a subsequent study by Foster (1951) of the exchangeable cations in some of the same montmorillonite samples showed that all of those examined contained some exchangeable magnesium. In each sample the amount of exchangeable magnesium found was exactly sufficient, on recalculation of the formulas, to reduce octahedral occupancy to  $2.00 \pm 0.02$  ions per half cell. This study demonstrated that, in such minerals as montmorillonite, magnesium can occupy two different positions in the crystal structure, octahedral and interlayer, just as aluminum can occupy both tetrahedral and octahedral positions. This study also suggests that an octahedral occupancy in excess of 2.02 may be indicative of interlayer magnesium.

Kelley and Liebig (1934) found that cation-exchange clays that had been treated with sea water contained more replaceable magnesium than replaceable sodium, 48.35 and 39.13 milliequivalents, respectively. This relationship is due to the fact that, although the concentration of sodium in sea water is much greater than that of magnesium, its replacing power is much inferior. Because of the high replacing power of magnesium, exchangeable or interlayer magnesium is to be expected in any layer silicate mineral containing exchangeable cations if it comes from an environment that contains magnesium. Owens and Minard (1960) reported exchangeable magnesium in the two glauconites from coastal plain formations of New Jersey on which they had had cation-exchange determinations made. The presence of exchangeable magnesium in glauconites is not surprising as glauconites are commonly formed in a marine environment. The high octahedral occupancies calculated for many glauconites are probably due to allocation of all MgO present to the octahedral layer, whereas some of it is actually exchangeable and belongs in the interlayer. This is considered so probable that

in this study all octahedral cations in excess of 2.00 were considered to represent exchangeable magnesium and were transferred to the interlayer.

The two celadonite analyses that Hendricks and Poss (1941) considered to have been made on impure material, and that must have contained a magnesium silicate to account for their high percentages of MgO, yielded, on calculation, exceptionally high values for octahedral occupancy, 2.19 and 2.24 cations, respectively. Transference of the excess cations to the interlayer produced very high layer and interlayer charges,  $\pm 1.20$  and  $-1.14$  and  $+1.16$ , respectively. Thus, these analyses produce irrational formulas both when all the MgO is considered octahedral and when the excess above 2.00 is considered interlayer. Similar irrational formulas were produced by several other analyses of celadonite. Following Hendricks and Ross, such analyses were considered to have been made on impure material and were not included in this study. Analyses whose excess octahedral cations, transferred to the interlayer as magnesium, did not produce irrationally high-layer and interlayer charges, were considered acceptable and were included.

Customarily, bivalent interlayer cations like calcium and magnesium are reported in terms of charges, not in terms of cations. However, in this study interlayer calcium and magnesium are recorded as cations, in accordance with the usage followed for all the other cations in the formula. Thus, the notation  $(K_{.74}Na_{.02}Ca_{.02}Mg_{.04})^{+.88}_{.82}$  indicates a total of 0.82 interlayer cation that carries a combined positive charge of 0.88.

#### RELATION BETWEEN THE COMPOSITION OF CELADONITES AND GLAUCONITES

Analyses of celadonite and glauconite are given in tables 1-3. Analyses 1-9 in table 1 are of celadonites whose calculated atomic ratio for potassium is greater than 0.65 atom per half cell; analyses 10-13 of celadonites containing less than 0.66 atom of potassium. Table 2 presents analyses of glauconites whose calculated atomic ratio for potassium is greater than 0.65 atom per half cell, and table 3 presents analyses of glauconites having less than 0.66 atom of potassium per half cell. The limiting value of 0.65 potassium atom per half cell for differentiating high and low potassium celadonites and glauconites was chosen arbitrarily. Range and median values for the principal constituents in high potassium celadonites and glauconites, in terms of atomic ratios, for percent of octahedral positions occupied by bivalent cations, and for negative octahedral charge, are given in table 4. Similar data for low potassium celadonites and glauconites are given in table 5.

TABLE 1.—Chemical analyses, in percent, of celadonites, together with their calculated atomic ratios

Analysis.....	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
<b>CHEMICAL ANALYSES</b>													
	<b>Celadonites having more than 0.65 potassium atom per half cell</b> [n.d., not determined]							<b>Celadonites having less than 0.66</b> <b>potassium atom per half cell</b>					
SiO <sub>2</sub> .....	55.61	56.20	53.23	55.30	54.38	54.73	52.26	52.53	53.54	56.88	56.47	51.36	54.49
Al <sub>2</sub> O <sub>3</sub> .....	.79	2.05	2.13	10.90	5.41	7.56	1.62	4.97	12.02	11.06	9.09	1.69	12.60
Fe <sub>2</sub> O <sub>3</sub> .....	17.19	19.18	20.46	6.95	14.22	13.44	21.84	18.62	8.21	10.68	12.36	23.72	9.52
FeO.....	4.02	3.19	4.14	3.54	3.56	5.30	4.45	4.58	3.21	2.45	2.19	1.40	2.95
MgO.....	7.26	5.42	5.67	6.56	6.40	5.76	5.25	5.35	6.99	6.62	5.98	6.34	6.24
MnO.....	.09	Trace	.....	.....	.25	.....	None	.01	Trace	Trace	.12	.....	.05
CaO.....	.21	.27	.....	.47	.42	.00	Trace	.58	.49	.94	1.13	.54	.66
Na <sub>2</sub> O.....	.19	.64	.....	.00	.05	.....	None	None	.07	.19	.86	1.29	.48
K <sub>2</sub> O.....	10.03	8.26	7.95	9.38	9.23	7.40	10.04	7.99	8.43	3.54	6.49	6.62	7.41
TiO <sub>2</sub> .....	.....	.10	.....	n.d.	.14	.....	.....	.25	.09	.20	.13	Trace	Trace
H <sub>2</sub> O+.....	.....	4.86	6.18	5.21	4.80	.....	14.15	14.31	4.69	4.69	.....	5.87	3.59
H <sub>2</sub> O-.....	4.88	.25	.....	1.30	1.16	6.40	.10	1.15	2.35	2.29	5.32	1.11	1.60
Total.....	100.27	100.42	99.76	99.61	100.17	100.59	99.71	100.31	100.09	99.54	100.14	99.94	99.58
<b>CALCULATED ATOMIC RATIOS</b>													
Si.....	4.00	4.00	3.90	3.88	3.88	3.86	3.83	3.79	3.76	3.89	3.88	3.79	3.76
Al <sup>iv</sup> .....	.00	.00	.10	.12	.12	.14	.17	.21	.24	.11	.12	.21	.24
Al <sup>vi</sup> .....	.07	.16	.08	.78	.34	.49	.00	.21	.76	.79	.62	.00	.78
Fe <sup>+3</sup> .....	.93	1.03	1.13	.37	.76	.71	1.18	1.01	.43	.55	.64	1.25	.49
Fe <sup>+2</sup> .....	.24	.19	.25	.21	.21	.31	.27	.28	.18	.14	.13	.09	.17
Mg <sup>vi</sup> .....	.75	.68	.64	.63	.49	.57	.50	.65	.52	.61	.66	.56	.56
Mn.....	.01	.00	.....	.02	.00	.00	.00	.00	.00	.00	.01	.....	.00
Octahedral cations.....	2.00	1.96	2.00	2.00	2.00	2.00	2.02	2.00	2.02	2.00	2.01	2.00	2.00
Layer charge.....	-1.00	-.89	-.89	-.97	-1.06	-.94	-.95	-.99	-1.01	-.77	-.84	-.96	-.97
Mg <sup>+2</sup> .....	.03	.....	.08	.04	.05	.12	.00	.07	.08	.15	.....	.03	.08
Ca <sup>+2</sup> .....	.01	.02	.....	.04	.03	.....	.00	.05	.04	.07	.08	.04	.05
Na.....	.03	.09	.....	.00	.01	.....	.00	.00	.01	.02	.12	.19	.06
K.....	.92	.75	.74	.84	.84	.67	.94	.73	.76	.31	.57	.62	.65
Interlayer cations.....	.99	.86	.82	.92	.93	.79	.94	.85	.89	.55	.77	.88	.84
Interlayer charge.....	+1.03	+.88	+.90	+1.00	+1.01	+.91	+.94	+.97	+1.01	+.77	+.85	+.95	+.97

<sup>1</sup> Ignition loss.<sup>2</sup> Includes 0.15 percent Li<sub>2</sub>O, equivalent to 0.04 atomic ratio of Li.<sup>3</sup> Includes 0.03 percent Cr<sub>2</sub>O<sub>3</sub>.<sup>4</sup> Includes 0.03 atomic ratio of Fe<sup>+3</sup>.<sup>5</sup> Includes 0.06 atomic ratio of Fe<sup>+3</sup>.

## LOCATION OF SAMPLES AND REFERENCE

- C1. Reno, Nev., 23 miles east of (Hendricks and Ross, 1941, table 4, No. 1). In vesicular basalt. Analyst: R. C. Wells.
- C2. Krivoi Rog, U.S.S.R. (Serduchenko, 1965, p. 566). Replacing aegerine and riebeckite in fractures in iron-bearing quartzite. Analyst: M. M. Stukalova.
- C3. Brentonico, Monte Baldos, Italy (Hendricks and Ross, 1941, table 4, No. 2). Amygdulite masses in basalt. Analyst: G. Levi.
- C4. Vesuvius, Italy (Hendricks and Ross, 1941, table 4, No. 7). Occurrence and analyst not given.
- C5. Wind River quadrangle, sec. 3, T. 3 N., R. 73 W., Washington (Wise and Eugster, 1964, p. 1034, No. 15). Amygdulite filling in basalt. Analyst: O. von Knorring.
- C6. Vail, Arizona (Hendricks and Ross, 1941, table 4, No. 5). In basalt and basaltic tuffs. Analyst: G. A. Koenig.
- C7. Kursk Mountain, 80 miles northwest of, U.S.S.R. (Sudovikova, 1956, p. 544). In seams in iron-bearing quartzite of the Kursk magnetic anomaly. Analyst: B. S. Kopelovich.
- C8. Bug region, U.S.S.R. (Malkova, 1956, p. 308). Veins and vugs in metamorphic rocks. Analyst: K. M. Malkova.
- C9. Dolgoye Pole, West Volynya, U.S.S.R. (Shashkina, 1961, p. 400, No. 2). Weathered basalt crust. Analyst: Mineral Chemical Laboratory of A.N., U.S.S.R.
- C10. Berestovets, West Volynya, U.S.S.R. (Shashkina, 1961, p. 400, No. 4). Weathered basalt crust. Analyst: Mineral Chemical Laboratory of A.N., U.S.S.R.
- C11. Zonguldak, Turkey (Bayramgil and others, 1952, p. 245). Cavities in basaltic tuff. Analyst: Th. Hügl.
- C12. Contessa Entellina, Palermo, Sicily (Scherillo, 1935, p. 73). Cavities in basalt. Analyst: A. Scherillo.
- C13. Dolgoye Pole, West Volynya, U.S.S.R. (Shashkina, 1961, p. 400, No. 1). Weathered basalt crust. Analyst: Mineral Chemical Laboratory of A.N., U.S.S.R.

TABLE 2.—Chemical analyses, in percent, of glauconites having more than 0.65 potassium atom per half cell, together with their calculated atomic ratios

Analysis	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	G13	G14	G15	G16	G17	G18	G19
CHEMICAL ANALYSES																			
Glauconites having an interlayer charge higher than +0.88																			
SiO <sub>2</sub>	52.74	51.35	49.53	50.20	51.00	48.75	48.66	48.90	48.80	47.88	51.55	50.58	49.89	52.96	49.23	49.07	48.12	49.75	47.09
Al <sub>2</sub> O <sub>3</sub>	12.29	9.47	5.84	6.10	9.93	9.07	8.46	6.20	14.64	14.94	4.03	6.72	7.52	12.76	7.11	10.95	9.16	7.82	7.44
FeO	9.35	16.37	20.06	23.80	18.69	18.31	18.90	21.45	11.90	17.13	22.17	19.50	18.43	13.56	20.89	15.86	19.10	22.26	24.07
Fe <sub>2</sub> O <sub>3</sub>	6.80	4.75	5.95	2.35	1.98	3.27	3.98	3.16	2.80	2.68	3.54	2.96	3.00	3.34	3.06	1.36	3.47	2.86	1.84
MgO	4.05	3.17	2.92	2.70	3.35	3.63	3.66	4.20	3.62	2.45	3.86	4.10	3.75	4.11	3.44	4.49	2.36	3.25	2.85
MnO																			Trace
CaO	.55	.63	.56	.40	.87	.39	.62	.70	.70	.56	.69	.34	.25		Trace	.07	.76		.55
Na <sub>2</sub> O	.09	1.22	.46	.93	.35	.12	.00	.76	.60	.43	.55	.04	.11	.47	.11	.13	.22	.30	Trace
K <sub>2</sub> O	7.97	7.34	9.31	8.95	7.66	8.17	8.31	7.25	8.20	8.04	7.03	8.26	7.52	8.69	8.51	7.51	7.08	9.01	7.49
H <sub>2</sub> O <sup>+</sup>																			
H <sub>2</sub> O <sup>-</sup>																			
Total	199.40	199.50	199.54	199.18	199.16	199.54	199.08	199.27	199.39	199.02	199.04	199.83	199.69	199.80	199.06	199.20	199.33	199.91	199.84

Glauconites having an interlayer charge lower than +0.89

## CALCULATED ATOMIC RATIOS

Si	3.73	3.70	3.67	3.67	3.64	3.63	3.62	3.58	3.55	3.43	3.79	3.74	3.72	3.69	3.66	3.64	3.63	3.62	3.56
Al <sup>iv</sup>	.27	.30	.33	.33	.36	.37	.35	.42	.45	.57	.21	.26	.28	.31	.34	.36	.37	.38	.44
Al <sup>vi</sup>	.79	.60	.18	.20	.47	.43	.36	.14	.81	.69	.14	.32	.38	.74	.25	.60	.44	.29	.22
Fe <sup>2+</sup>	.80	.89	1.12	1.28	1.00	1.03	1.05	1.23	.65	.92	1.22	1.08	1.06	.71	1.17	.89	1.08	1.22	1.37
Fe <sup>3+</sup>	.37	.29	.37	.14	.12	.20	.25	.20	.17	.16	.22	.18	.19	.14	.19	.08	.22	.14	.11
Mg <sup>vi</sup>	.34	.34	.32	.29	.41	.34	.34	.43	.39	.23	.42	.42	.37	.43	.38	.43	.27	.35	.32
Mn																			
Octahedral cations	2.00	2.02	1.99	1.91	2.00	2.00	2.00	2.00	2.02	2.00	2.00	2.00	2.00	2.02	2.02	2.00	2.01	2.00	2.00
Layer charge	-.98	-.87	-1.04	-1.03	-.89	-.91	-.97	-1.05	-.95	-.96	-.85	-.86	-.84	-.82	-.85	-.87	-.83	-.87	-.81
Mg <sup>2+</sup>	.08					.06	.05	.05	.05	.03		.03	.05			.07			
Ca <sup>2+</sup>	.04	.02	.04	.03	.07	.00	.04	.00	.05	.04	.05		.00			.06	.08	.04	.04
Na <sup>+</sup>	.01	.17	.07	.13	.05	.02	.00	.11	.08	.06	.08	.01	.02	.06	.02	.02	.08	.04	.00
K <sup>+</sup>	.72	.68	.88	.83	.83	.77	.79	.71	.76	.73	.76	.78	.72	.77	.81	.71	.68	.84	.72
Interlayer cations																			
Interlayer charge	+.97	+.89	+1.03	+1.02	+.89	+.91	+.97	+1.04	+.94	+.93	+.84	+.86	+.84	+.83	+.83	+.87	+.83	+.88	+.80

<sup>1</sup> Includes 0.13 percent F.  
<sup>2</sup> Includes 0.35 percent P<sub>2</sub>O<sub>5</sub>. Equivalent CaO deducted in calculation of atomic ratios.  
<sup>3</sup> Includes 0.001 percent SrO, 0.053 V<sub>2</sub>O<sub>5</sub>, and 0.33 P<sub>2</sub>O<sub>5</sub>. CaO equivalent to P<sub>2</sub>O<sub>5</sub> deducted in calculating atomic ratios.  
<sup>4</sup> Includes 0.12 percent P<sub>2</sub>O<sub>5</sub>. Equivalent CaO deducted in calculation.  
<sup>5</sup> Includes 0.54 percent free SiO<sub>2</sub> and 6.32 ignition loss.  
<sup>6</sup> Includes 0.30 percent CO<sub>2</sub> and 0.27 P<sub>2</sub>O<sub>5</sub>. Equivalent CaO deducted in calculation.

## LOCATION OF SAMPLES AND REFERENCE

- G1. Tosterup, Scania, Sweden (Hendricks and Ross, 1941, p. 693, No. 30). Upper Cretaceous. Analyst: N. Sahlbom.  
 G2. Eriksberg, Öland, Sweden (Hendricks and Ross, 1941, p. 692, No. 23). Ordovician limestone. Analyst: N. Sahlbom.  
 G3. Ural, U.S.S.R. (Hendricks and Ross, 1941, p. 692, No. 5). Eocene sandstone. Analyst: Glinka.  
 G4. Ghent, Belgium (Hoebcke and Dekeyser, 1955, p. 114, No. 14). Eocene sand. Analyst: Not given.  
 G5. Trakymirov, Kiev province, U.S.S.R. (Smulikowski, 1954, table 3, No. 10). Tertiary sandstone. Analyst: Glinka.  
 G6. Walsrode, Germany (Valeton, 1958). Tertiary. Analyst: Harre.  
 G7. St. Joseph, Mo. (Hendricks and Ross, 1941, p. 692, No. 11). Cambrian dolomite. Analyst: G. V. Brown.  
 G8. Dnieper River region, U.S.S.R. (Dyadchenko and Khatunzeva, 1955, p. 152). Age: Not given. Analyst: Not given.  
 G9. Tjupholmen, Bulgaria (Atanasov, 1962, p. 145, No. 2). Jurassic. Analyst: L. Ivichova.  
 G10. Černoakoe, Niznij Novgorod, U.S.S.R. (Hendricks and Ross, 1941, p. 692, No. 1). Jurassic sandstone. Analyst: Glinka.  
 G11. Hokkaido, Japan (Hendricks and Ross, 1941, p. 692, No. 31). Upper Cretaceous. Analyst: Yagi.  
 G12. Sewell, N.J. (Hendricks and Ross, 1941, p. 692, No. 26). Upper Cretaceous sand. Analyst: R. K. Bailey.  
 G13. Tysmenica, Carpathian Mountains, U.S.S.R. (Smulikowski, 1954, table 3, No. 26). Lower Oligocene sandstone. Analyst: Szabartowski.  
 G14. Udrilas, E.S.S.R. (Hendricks and Ross, 1941, p. 692, No. 24). Ordovician limestone. Analyst: Glinka.  
 G15. Big Goose Canyon, 15 miles southwest of Sheridan, Wyo. (Hendricks and Ross, 1941, p. 692, No. 20). Age: Unknown. Analyst: G. Steiger.  
 G16. Milburn, Table Hill, Otago, New Zealand (Smulikowski, 1941, table 3, No. 10). Age: Not given. Analyst: Seelye.  
 G17. Lewes, Sussex, England (Hendricks and Ross, 1941, p. 692, No. 16). Age: Not given. Analyst: E. G. Radley.  
 G18. Nisanovo, near Smolensk, U.S.S.R. (Hendricks and Ross, 1941, p. 692, No. 10). Cretaceous cherty sandstone. Analyst: Glinka.  
 G19. Penisola Salentina, Puglia, Italy (Dell'anna, 1964, p. 534). Cretaceous limestone. Analyst: Not given.

TABLE 3.—Chemical analyses, in percent, of glauconites having less than 0.66 potassium atom per half cell, together with their calculated atomic ratios

Analysis	G20	G21	G22	G23	G24	G25	G26	G27	G28	G29	G30	G31	G32
CHEMICAL ANALYSES													
Glauconites having an interlayer charge higher than +0.88							Glauconites having an interlayer charge lower than +0.89						
SiO <sub>2</sub>	50.36	49.4	49.0	48.5	47.6	49.29	50.20	48.54	49.00	49.53	48.10	48.19	49.09
Al <sub>2</sub> O <sub>3</sub>	7.04	10.2	9.2	9.0	9.9	3.17	7.80	7.82	8.35	13.32	11.07	10.83	15.21
Fe <sub>2</sub> O <sub>3</sub>	19.13	18.0	19.5	20.0	21.9	21.72	17.90	17.50	20.20	12.19	14.67	17.80	10.56
FeO	3.95	3.1	3.3	3.1	1.5	3.19	1.80	3.07	1.80	2.27	3.07	.97	3.06
MgO	4.08	3.5	3.6	3.7	3.7	3.85	3.23	3.26	3.31	3.89	3.78	3.19	2.65
MnO	.06					Trace				.06	Trace	Trace	
CaO	.91	.6	.5	.4	.8	.74	.81	.68	.77	1.53	1.92	1.06	.55
Na <sub>2</sub> O	1.58	1.4	.9	1.5	1.4	.12	Trace	.22	Trace	.89	.56	.48	1.21
K <sub>2</sub> O	6.62	5.1	6.3	6.1	5.3	6.02	6.42	5.87	6.80	6.02	5.49	6.37	6.05
TiO <sub>2</sub>	.02					.12				1.28	1.78	1.49	
H <sub>2</sub> O <sup>+</sup>	6.32	8.3	7.6	7.3	7.7	7.21	11.27	6.00	10.07	4.37	4.31	4.74	11.64
H <sub>2</sub> O						4.60	6.71			4.05	4.56	4.41	
Total	<sup>1</sup> 100.34	99.6	99.9	99.6	99.8	<sup>2</sup> 100.35	99.43	<sup>3</sup> 99.86	100.30	<sup>4</sup> 100.48	<sup>5</sup> 100.51	<sup>6</sup> 100.22	100.02
CALCULATED ATOMIC RATIOS													
Si	3.68	3.62	3.60	3.57	3.49	3.83	3.79	3.75	3.66	3.66	3.65	3.63	3.62
Aliv	.32	.38	.40	.43	.51	.17	.21	.25	.34	.34	.35	.37	.38
Alvi	.29	.50	.39	.35	.35	.12	.49	.46	.40	.82	.64	.60	.94
Fe <sup>3+</sup>	1.05	.99	1.08	1.11	1.21	1.27	1.02	1.01	1.14	.67	.84	1.01	.59
Fe <sup>2+</sup>	.24	.19	.20	.19	.09	.21	.11	.20	.11	.14	.19	.06	.19
Mgvi	.44	.32	.33	.35	.35	.40	.36	.33	.37	.37	.33	.33	.29
Mn	.00					.00				.00	.00	.00	
Octahedral cations	2.02	2.00	2.00	2.00	2.00	2.00	1.98	2.00	2.02	2.00	2.00	2.00	2.01
Layer charge	-.98	-.89	-.93	-.97	-.96	-.78	-.74	-.78	-.76	-.85	-.87	-.75	-.83
Mg <sup>2+</sup>	.00	.06	.06	.06	.06	.05	.00	.05	.00	.04	.10	.03	.00
Ca <sup>2+</sup>	.05	.05	.04	.03	.06	.03	.07	.04	.06	.01	.03	.02	.04
Na	.22	.20	.13	.21	.20	.02	.00	.03	.00	.13	.08	.07	.17
K	.62	.48	.59	.58	.50	.60	.62	.58	.65	.57	.53	.61	.57
Interlayer cations	.89	.79	.82	.88	.82	.70	.69	.70	.71	.75	.74	.73	.78
Interlayer charge	+.94	+.90	+.92	+.97	+.94	+.78	+.76	+.79	+.77	+.80	+.87	+.78	+.82

<sup>1</sup> Includes 0.01 percent Li<sub>2</sub>O and 0.26 P<sub>2</sub>O<sub>5</sub>. CaO equivalent to P<sub>2</sub>O<sub>5</sub> deducted before atomic ratio calculation.<sup>2</sup> Includes 0.32 percent P<sub>2</sub>O<sub>5</sub>. Equivalent CaO deducted before atomic ratio calculation.<sup>3</sup> Includes 0.05 percent S and 0.14 P<sub>2</sub>O<sub>5</sub>. CaO equivalent to P<sub>2</sub>O<sub>5</sub> deducted before atomic ratio calculation.<sup>4</sup> Includes 0.96 percent CO<sub>2</sub> and 0.12 P<sub>2</sub>O<sub>5</sub>. CaO equivalent to CO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> deducted before atomic ratio calculation.<sup>5</sup> Includes 0.67 percent CO<sub>2</sub> and 0.53 P<sub>2</sub>O<sub>5</sub>. CaO equivalent to CO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> deducted before atomic ratio calculation.<sup>6</sup> Includes 0.39 percent CO<sub>2</sub> and 0.30 P<sub>2</sub>O<sub>5</sub>. CaO equivalent to CO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> deducted before atomic ratio calculation.

## LOCATION OF SAMPLES AND REFERENCE

G20. Monte Brione, Garda Lake, Italy (Hendricks and Ross, 1941, p. 692, No. 21). Age: not given. Analyst: Schwager.  
 G21. Northwest of Norwalk, Wis. (Hendricks and Ross, 1941, p. 692, No. 14). Cambrian sandstone. Analyst: T. B. Brighton.  
 G22. Woodstown, N.J. (Hendricks and Ross, 1941, p. 692, No. 6). Cretaceous marl. Analyst: T. B. Brighton.  
 G23. Near Norwalk, Wis. (Hendricks and Ross, 1941, p. 692, No. 3). Cambrian dolomite. Analyst: T. B. Brighton.  
 G24. San Pedro, Calif. (Hendricks and Ross, 1941, p. 692, No. 2). Pleistocene marl. Analyst: T. B. Brighton.  
 G25. Whare Flat, East Taieri, Otago Land, New Zealand (Smulikowski, 1954, table 3, No. 21). Tertiary sandstone. Analyst: Seelye.  
 G26. Villers-sur-mer, France (Smulikowski, 1954, table 4, No. 39). Cretaceous sand. Analyst: Sabatier.

G27. Kahoko Creek, Otepopo, Otago Land, New Zealand (Smulikowski, 1954, table 3, No. 23). Tertiary sandstone. Analyst: Seelye.  
 G28. Cuise-la-Mothe, France (Smulikowski, 1954, table 3, No. 13). Tertiary sand. Analyst: Sabatier.  
 G29. Monte Bonifato di Alcamo, Italy (Pirani, 1963, p. 37, No. 3). Age: not given. Analyst: Pirani.  
 G30. Monte Barbaro di Sigesta, Italy (Pirani, 1963, p. 37, No. 2). Age: not given. Analyst: Pirani.  
 G31. Monte Bonifato di Alcamo, Italy (Pirani, 1963, p. 37, No. 1). Age: not given. Analyst: Pirani.  
 G32. Ashgrove, Elgin, Scotland (Hendricks and Ross, 1941, p. 692, No. 15). Cretaceous oolitic limestone. Analyst: not given.

TABLE 4.—Range and median values of principal constituents in high potassium (&gt;0.65 atom per half cell) celadonites and glauconites in atomic ratios

Principal constituents	Celadonites				Glauconites			
	Interlayer charge > +0.87 (9 analyses)		Interlayer charge > +0.88 (10 analyses)		Interlayer charge > +0.88 (10 analyses)		Interlayer charge < +0.89 (9 analyses)	
	Range	Median	Range	Median	Range	Median	Range	Median
Si	4.00–3.76	3.88±0.12	3.73–3.43	3.58±0.15	3.79–3.56	3.67±0.11		
Al(IV)	.00–.24	.12±.12	.27–.57	.42±.15	.21–.44	.33±.11		
Al(VI)	.00–.78	.39±.39	.14–.81	.48±.34	.14–.74	.44±.30		
Fe <sup>3+</sup>	.37–1.18	.77±.41	.50–1.21	.89±.39	.71–1.37	1.04±.33		
Fe <sup>2+</sup>	.18–.31	.25±.07	.12–.37	.25±.13	.11–.22	.16±.06		
Mg	.49–.78	.64±.15	.23–.43	.33±.10	.27–.43	.35±.08		
Percent R <sup>2+</sup> (VI)	38.9–50.8	44.9±6.0	19.5–35.5	27.5±8.0	21.3–32.0	26.6±5.3		
Percent R <sup>3+</sup> (VI)	49.2–61.1	55.2±6.0	64.5–80.5	72.5±8.0	68.0–78.7	73.4±5.3		
Octahedral charge	-.77–-.94	-.85±.09	-.39–-.71	-.55±.16	-.37–-.64	-.50±.14		

TABLE 5.—Range and median values of principal constituents in low potassium (&lt;0.66 atom per half cell) celadonites and glauconites in atomic ratios

Principal constituents	Celadonites				Glauconites					
	Interlayer charge <+0.89 (4 analyses)				Interlayer charge >+0.88 (5 analyses)		Interlayer charge <+0.89 (8 analyses)			
	Range		Median		Range		Median		Range	
Si	3.89–	3.76	3.82±	0.07	3.68–	3.49	3.59±	0.10	3.83–	3.62
Al (IV)	.11–	.24	.18±	.07	.32–	.51	.42±	.10	.17–	.38
Al (VI)	.00–	.79	.40±	.40	.29–	.50	.40±	.11	.12–	.82
Fe <sup>+3</sup>	.49–	1.25	.87±	.38	.99–	1.21	1.10±	.11	.59–	1.27
Fe <sup>+2</sup>	.09–	.17	.13±	.04	.09–	.24	.17±	.08	.06–	.21
Mg	.52–	.66	.59±	.07	.32–	.44	.38±	.06	.29–	.40
Percent R <sup>+2</sup> (VI)	33.0–	37.5	35.2 ±	2.2	22.0–	33.6	27.8 ±	5.8	17.0–	26.5
Percent R <sup>+3</sup> (VI)	62.5–	67.0	64.5 ±	2.5	66.4–	78.0	72.2 ±	5.8	73.5–	80.5
Octahedral charge	–.66–	–.75	–.71±	–.04	–.44–	–.62	–.53±	–.09	–.38–	–.61

#### HIGH POTASSIUM CELADONITES AND GLAUCONITES

The data given in table 4 show distinct differences between high potassium celadonites and glauconites, as well as certain differences between high potassium glauconites having an interlayer charge greater than +0.87 per half cell, and those having less. Silicon in the high potassium celadonites ranges from 4.00 to 3.76 cations per half cell, as compared with 3.73 to 3.43 cations in high potassium glauconites, both in glauconites with interlayer charges above and in those with interlayer charges below +0.88. Magnesium in the celadonites ranges from 0.49 to 0.78 cation per half cell (median value 0.64), as compared with 0.23 to 0.43 cation in the glauconites (median 0.33). The median value for bivalent iron, 0.25 cation, is the same in the celadonites and the high-charge glauconites, although the range is somewhat narrower in the celadonites. Thus, the difference in the percentage of octahedral positions occupied by bivalent cations, 44.9 percent in the celadonites and 27.5 in the high-charge glauconites, is due principally to the higher magnesium content of the celadonites, not to significant differences in bivalent iron content. Conversely, the median octahedral occupancy by trivalent cations is lower in the celadonites than in the high-charge glauconites, 55.2 percent as compared with 72.5 percent, but both range widely in relative content of octahedral aluminum and trivalent iron.

Because of their greater content of bivalent octahedral cations and lesser content of trivalent octahedral cations, there is a greater deficiency of positive charges in the octahedral layer of high potassium-high charge celadonites than in that of high potassium-high charge glauconites. The positive charge deficiency ranges from  $0.85 \pm 0.09$  in the high potassium high-charge celadonites as compared with  $0.55 \pm 0.16$  in the high potassium-high charge glauconites. In a few celadonites, in which the tetrahedral layer is completely occupied by silicon, as for example, those from Reno, Nev., and

Krivoi Rog, U.S.S.R., Nos. C1 and C2, table 1, the entire negative layer charge is due to deficiency of positive charges in the octahedral layer. In this sense, therefore, the total negative layer charge in these celadonites may be thought of as originating in the octahedral layer.

High potassium glauconites with interlayer charges less than +0.88 are very similar in composition to those with interlayer charges greater than +0.87, except for their respective contents of bivalent and trivalent iron. In the high-charge glauconites the medians and ranges for bivalent and trivalent iron are  $0.25 \pm 0.13$  and  $0.89 \pm 0.39$ , respectively, whereas in the glauconites with lower charges they are  $0.16 \pm 0.06$  and  $1.04 \pm 0.33$ , respectively. With respect to content of other bivalent and trivalent cations, there is little difference, the high-charge glauconites having  $0.33 \pm 0.10$  cation of magnesium and  $0.48 \pm 0.34$  cation of octahedral aluminum, the lower charge glauconites having  $0.35 \pm 0.08$  cation of magnesium and  $0.44 \pm 0.30$  cation of octahedral aluminum. The lower interlayer charge in these glauconites is attributable, therefore, to their lesser content of bivalent iron and greater content of trivalent iron.

The differences in composition between high potassium celadonites and glauconites are shown graphically in figure 1. In these diagrams the left-hand column represents percent occupancy of the octahedral layer by Al<sup>+3</sup>, Fe<sup>+3</sup>, Fe<sup>+2</sup>, and Mg, the middle column represents percent occupancy of the tetrahedral layer by Si<sup>+4</sup> and Al<sup>+3</sup>, and the right-hand column indicates the number of potassium and exchangeable cations, Na, Ca, and Mg, present per half cell. The figures at the tops of the columns indicate the positive-charge deficiencies in the octahedral and tetrahedral layers (cols. 1 and 2, respectively) and the positive interlayer charge (col. 3). The sum of the octahedral and tetrahedral deficiencies should agree closely with the positive interlayer charge. These diagrams demonstrate graphically the higher magnesium content of the celadonites and their lower content of tetrahedral aluminum as compared

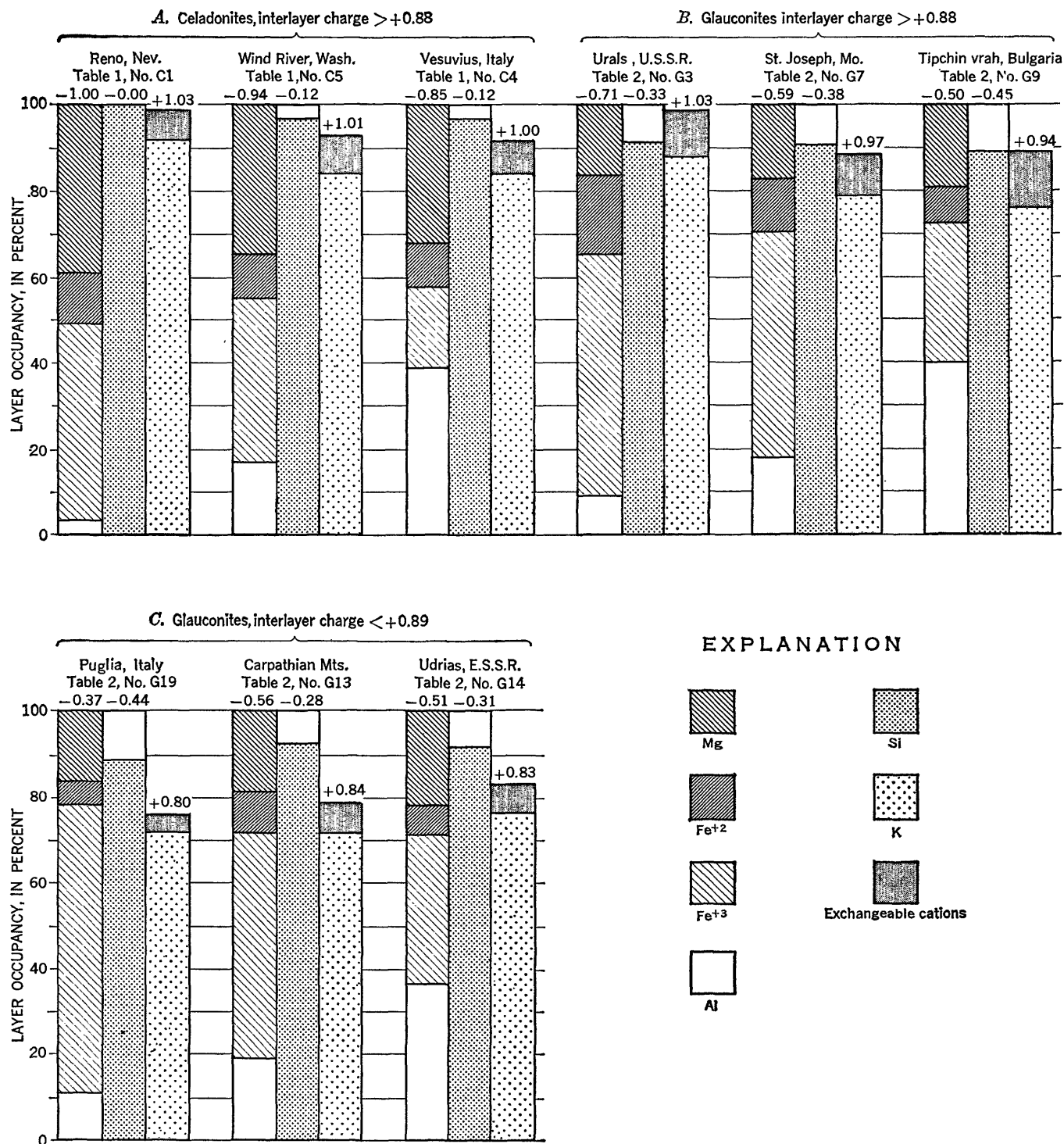


FIGURE 1.—Chemical composition of representative celadonites and glauconites having more than 0.65 potassium atom per half cell. Figures above the first and second columns of each diagram indicate the positive-charge deficiencies of the octahedral and tetrahedral layers; figures above the third column indicate the positive interlayer charge.

with glauconites. They also illustrate the greater occupancy of the octahedral layer by bivalent cations, Mg and  $\text{Fe}^{+2}$ , in celadonites. On the other hand, the diagrams show that the celadonites and glauconites are similar in that both range widely in content of octahedral aluminum and trivalent iron. In some celadonites and glauconites, iron is the greatly predominant trivalent octahedral cation; in others, aluminum is equal to, or even dominant, over iron. These two octahedral cations bear a general reciprocal relation to each other in that decrease in trivalent iron content is usually accompanied by increase in octahedral aluminum.

#### LOW POTASSIUM CELADONITES AND GLAUCONITES

Comparison of tables 4 and 5 shows that the range values for Si, Al (IV), Al (VI), and Mg in low potassium celadonites fall within or close to the range values for these constituents in high potassium celadonites, but that the range values for  $\text{Fe}^{+2}$  in the low potassium celadonites is lower than in the high potassium celadonites, 0.09–0.17 cation as compared with 0.18–0.31 cation, respectively. This decrease in  $\text{Fe}^{+2}$  content is reflected in the slightly higher range values for  $\text{Fe}^{+3}$  in the low potassium celadonites, in their lower occupancy by bivalent cations, and in their lower range of octahedral charge.

The low potassium glauconites, like the high potassium glauconites, are divided into two groups, depending on their interlayer charges. The first group, composed of five (table 3, G20–G24), have interlayer charges in excess of +0.88, because of their high contents of exchangeable cations, notably sodium, which contribute between 0.32 and 0.45 positive charge to the interlayer. These five glauconites are very similar to each other, as indicated by the small ranges in the values of their principal constituents. They are also similar, in composition, to diagram G7, figure 1, except for their low content of potassium and high content of exchangeable cations.

The second group of low potassium glauconites, consisting of eight (table 3, G25–G32), are characterized by interlayer charges of less than +0.89 per half cell. The ranges of values of the principal constituents in them are very similar to those of the low charge-high potassium glauconites. Like them, and also like the high charge-high potassium glauconites, they differ widely in content of trivalent iron and octahedral aluminum, but they are quite uniform in content of silica, tetrahedral aluminum, and magnesium. Compared with the high-charge glauconites, these glauconites are somewhat lower in bivalent iron content. Most of them are similar in exchangeable cation content, but others, nota-

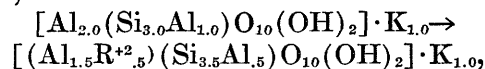
bly G29, G30, and G32, have high contents of exchangeable cations.

Thus, this study shows that celadonites, whether of high or low potassium content, are very similar in content of silicon, tetrahedral aluminum, bivalent iron, and magnesium content; but both groups range widely, and reciprocally, in content of trivalent iron and octahedral aluminum. Likewise, high and low potassium glauconites are relatively uniform in content of silicon, tetrahedral aluminum, and magnesium, and in percentage of octahedral positions occupied by bivalent cations; but they range widely, and reciprocally, in content of trivalent iron and octahedral aluminum. As a group, the celadonites are higher in silicon and magnesium and in bivalent-ion octahedral occupancy than the glauconites, and are lower in tetrahedral aluminum and trivalent-ion octahedral occupancy.

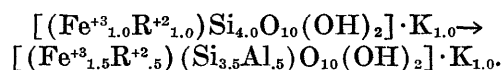
#### RELATION BETWEEN Si, $\text{R}^{+2}(\text{VI})$ , Al(IV), AND $\text{R}^{+3}(\text{VI})$

It has been shown (Foster, 1956) that progressive replacement in dioctahedral potassium micas of trivalent octahedral cations,  $\text{R}^{+3}(\text{VI})$ , by bivalent cations,  $\text{R}^{+2}(\text{VI})$ , is accompanied by equivalent increase in silicon and decrease in tetrahedral aluminum, Al(IV). Starting with muscovite,  $[\text{Al}_{2.0}(\text{Si}_{3.0}\text{Al}_{1.0})\text{O}_{10}(\text{OH})_2] \cdot \text{K}_{1.0}$ , the end result of such replacement is tetrasilicic dioctahedral potassium mica in which half of the octahedral cations are trivalent and half are bivalent, as  $[(\text{R}^{+3}_{1.0}\text{R}^{+2}_{1.0})\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2] \cdot \text{K}_{1.0}$ . Although analyses of natural micas representing all steps of this replacement may be found, Foster noted that, whereas the first part of this replacement series is represented by micas in which aluminum is the dominant octahedral cation, the latter part is represented by glauconites and celadonites, minerals in which iron is usually the dominant octahedral cation.

Thus, neither aluminum nor iron, as the dominant trivalent octahedral cation, appears to form a complete series from trisilicic to tetrasilicic or vice versa, but each a partial series, one starting at trisilicic (muscovite) end, the other at the tetrasilicic end, with neither extending, apparently, much beyond the middle of the range as,



and

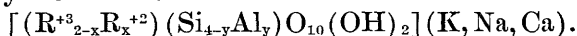


In these formulas bivalent-octahedral cations are represented by the general expression,  $\text{R}^{+2}$ , as the bivalent cations in both series are usually made up of both mag-

nesium and iron. The replacements taking place in both series can be represented by the expression



or by the formula



If the high potassium-high charge celadonites and glauconites belong to such a series, with a tetrasilic mica as the starting point, then in each sample the decrease in the atomic ratios of Si and of  $\text{R}^{+2}(\text{VI})$  and the increase in the atomic ratios of Al(IV) and of  $\text{R}^{+3}(\text{VI})$ , with respect to the theoretical tetrasilic end-member, should agree closely, and the sum of the decreases in Si and  $\text{R}^{+2}(\text{VI})$  should correspond with the sum of the increases in Al(IV) and  $\text{R}^{+3}(\text{VI})$ . Table 6 shows the atomic ratios for Si,  $\text{R}^{+2}(\text{VI})$ , Al(IV), and  $\text{R}^{+3}(\text{VI})$ , the amount of decrease or increase with respect to the end-member, the sums of the decreases in Si and  $\text{R}^{+2}(\text{VI})$ , and the increases in Al(IV) and  $\text{R}^{+3}(\text{VI})$ . Comparison of the amounts of  $\text{Si} + \text{R}^{+2}(\text{VI})$  decreases with  $\text{Al}(\text{IV}) + \text{R}^{+3}(\text{VI})$  increases for the samples studied shows that these sums correspond to each other within 0.02 atomic ratio, except for those for C2 and G4, which differ by 0.07 and 0.09 atomic ratio, respectively. The close agreement between the decreases in  $\text{Si} + \text{R}^{+2}(\text{VI})$  and the increases in  $\text{Al}(\text{IV}) + \text{R}^{+3}(\text{VI})$  is shown graphically in figure 2, in which these two sets of values are plotted against each other. All the points, except those for C2 and G4 fall on, or very close to, the 1:1 diagonal.

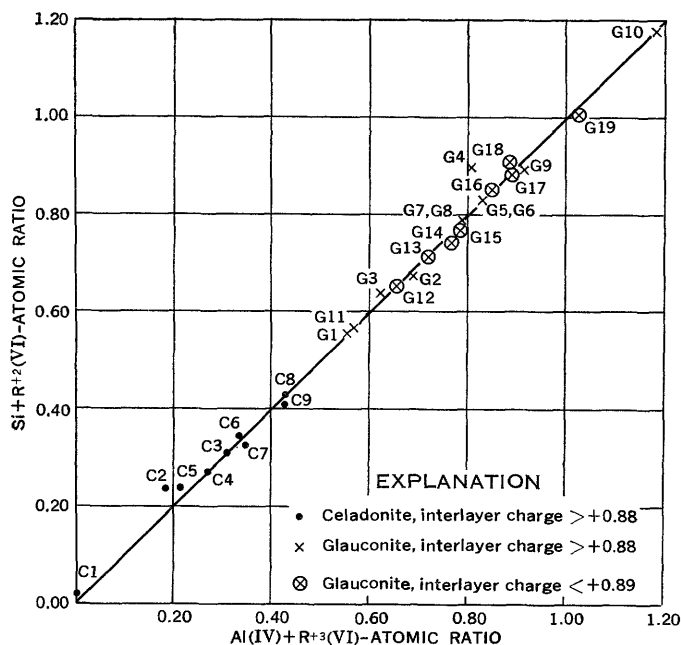


FIGURE 2.—Relation between  $\text{Si} + \text{R}^{+2}(\text{VI})$  decrease and  $\text{Al}(\text{IV}) + \text{R}^{+3}(\text{VI})$  increase in high potassium-high charge celadonites and glauconites.

However, the decrease in Si and the decrease in  $\text{R}^{+2}(\text{VI})$  are not the same in all the samples, nor is increase in Al(IV) always in agreement with increase in  $\text{R}^{+3}(\text{VI})$ . These relations are shown graphically in figures 3 and 4.

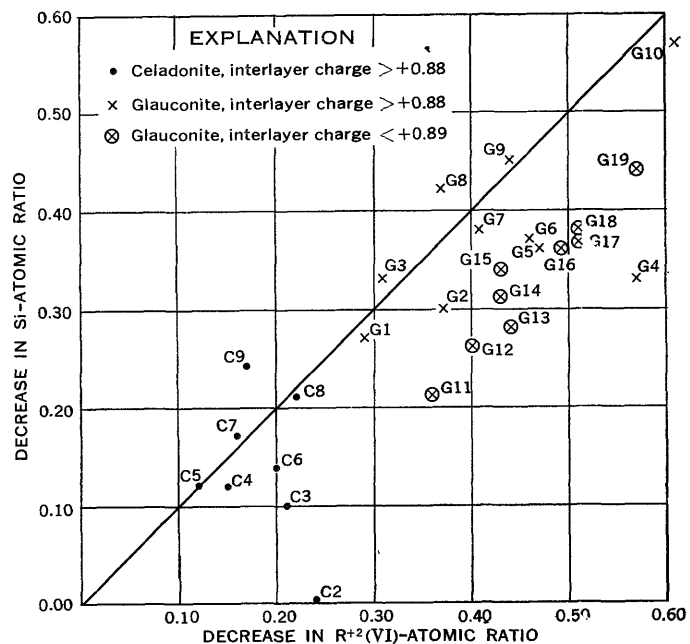


FIGURE 3.—Relation between decrease in Si and decrease in  $\text{R}^{+2}(\text{VI})$  in high potassium-high charge celadonites and glauconites.

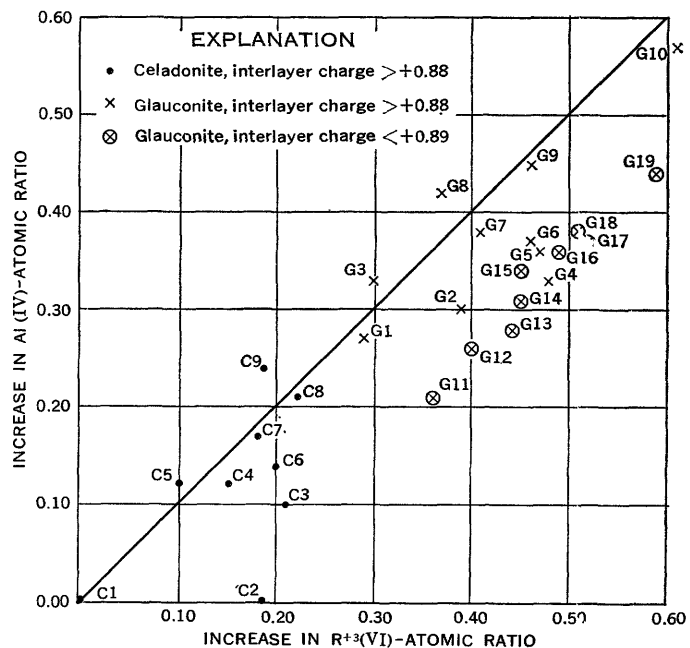


FIGURE 4.—Relation between increase in Al(IV) and increase in  $\text{R}^{+3}(\text{VI})$  in high potassium-high charge celadonites and glauconites.



respectively. The agreement between decrease in Si and decrease in  $R^{+2}(\text{VI})$  and between increase in  $\text{Al}(\text{IV})$  and increase in  $R^{+3}(\text{VI})$  is very good in about one-half of the samples, C1, C4, C5, C7, C8, G1, G3, G7, and G9. In two samples, C9 and G8, the decrease in Si is greater than the decrease in  $R^{+2}(\text{VI})$ , and the increase in  $\text{Al}(\text{IV})$  is greater than the increase in  $R^{+3}(\text{VI})$  by more

than 0.03 atomic ratio. In the other eight samples, decrease in  $R^{+2}(\text{VI})$  is greater than the decrease in Si, and the increase in  $R^{+3}(\text{VI})$  is greater than the increase in  $\text{Al}(\text{IV})$ . The fact that the excess of  $R^{+2}(\text{VI})$  decrease over Si decrease is almost identical with the excess of  $R^{+3}(\text{VI})$  increase over  $\text{Al}(\text{IV})$  increase strongly suggests oxidation in these samples.

TABLE 6.— $\text{Al}(\text{IV})R^{+3}(\text{VI})$  replacement of  $\text{Si}R^{+2}(\text{VI})$  in high potassium-high charge celadonites and glauconites

	Si	Decrease in Si	$R^{+2}(\text{VI})$	Decrease in $R^{+2}(\text{VI})$	Decrease in $\text{Si}+R^{+2}(\text{VI})$	$\text{Al}(\text{IV})$	Increase in $\text{Al}(\text{IV})$	$R^{+3}(\text{VI})$	Increase in $R^{+3}(\text{VI})$	Increase in $\text{Al}(\text{IV})$ + $R^{+3}(\text{VI})$	Negative layer charge
Theoretical end-member.....	4.00		1.00		0.00	0.00		1.00		0.00	1.00
<b>Celadonites</b>											
Analysis:											
C1.....	4.00	0.00	1.02	0.02	(1)	0.00	0.00	1.00	0.00	0.00	0.96
2.....	4.00	.00	.76	.24	0.24	.00	.00	1.19	.19	.19	.91
3.....	3.90	.10	.79	.21	.31	.10	.10	1.21	.21	.31	.89
4.....	3.88	.12	.85	.15	.27	.12	.12	1.15	.15	.27	.97
5.....	3.88	.12	.88	.12	.24	.12	.12	1.10	.10	.22	1.06
6.....	3.86	.14	.80	.20	.34	.14	.14	1.20	.20	.34	.94
7.....	3.83	.17	.84	.16	.33	.17	.17	1.18	.18	.35	.95
8.....	3.79	.21	.78	.22	.43	.21	.21	1.22	.22	.43	.89
9.....	3.76	.24	.83	.17	.41	.24	.24	1.19	.19	.43	1.01
<b>Glauconites</b>											
Analysis:											
G1.....	3.73	0.27	0.71	0.29	0.56	0.27	0.27	1.29	0.29	0.56	0.98
2.....	3.70	.30	.63	.37	.67	.30	.30	1.39	.39	.69	.87
3.....	3.67	.33	.69	.31	.64	.33	.33	1.30	.30	.63	1.04
4.....	3.67	.33	.43	.57	.90	.33	.33	1.48	.48	.81	1.03
5.....	3.64	.36	.53	.47	.83	.36	.36	1.47	.47	.83	.89
6.....	3.63	.37	.54	.46	.83	.37	.37	1.46	.46	.83	.91
7.....	3.62	.38	.59	.41	.79	.38	.38	1.41	.41	.79	.97
8.....	3.58	.42	.63	.37	.79	.42	.42	1.37	.37	.79	1.05
9.....	3.55	.45	.56	.44	.89	.45	.45	1.46	.46	.91	.94
10.....	3.43	.57	.39	.61	1.18	.57	.57	1.61	.61	1.18	.96

<sup>1</sup> Increase 0.02.

<sup>2</sup> Includes 0.03 atomic ratio  $\text{Fe}^{+3}$ .

In the high potassium-high charge celadonites and glauconites, therefore, the relations between decrease in Si and  $R^{+2}(\text{VI})$  and increase in  $\text{Al}(\text{IV})$  and  $R^{+3}(\text{VI})$  indicate that these celadonites and glauconites belong to a  $\text{Al}(\text{IV})R^{+3}(\text{VI}) \rightarrow \text{Si}R^{+2}(\text{VI})$  replacement series, which starts with tetrasilicic mica, and which continues to about halfway between the tetrasilicic and trisilicic end-members, or to a replacement of about 0.5 Si and 0.5  $R^{+2}(\text{VI})$  by 0.5  $\text{Al}(\text{IV})$  and 0.5  $R^{+3}(\text{VI})$ . The discrepancies in some of the samples between  $R^{+2}(\text{VI})$  decrease and Si decrease, and between  $R^{+3}(\text{VI})$  increase and  $\text{Al}(\text{IV})$  increase indicate oxidation of  $R^{+2}(\text{VI})$  to  $R^{+3}(\text{VI})$ . In the most divergent samples, C2 and G4, octahedral occupancy is low, only 1.95 and 1.91 positions, respectively. This low octahedral occupancy may indicate faulty analysis or analysis of impure samples, which may account for the fact that the  $\text{Si}R^{+2}(\text{VI})$  and  $\text{Al}(\text{IV})R^{+3}(\text{VI})$  data for these analyses do not correlate with such data for the other high potassium-high charge celadonites and glauconites.

The data for  $\text{Si}R^{+2}(\text{VI})$  and  $\text{Al}(\text{IV})R^{+3}(\text{VI})$  relations in high potassium glauconites having interlayer charges less than +0.89 per half cell are given in table 7. In all these glauconites there is good agreement between  $\text{Si}+R^{+2}(\text{VI})$  and  $\text{Al}(\text{IV})+R^{+3}(\text{VI})$ . However, in these glauconites,  $R^{+2}(\text{VI})$  decrease is significantly greater than Si decrease, and  $R^{+3}(\text{VI})$  increase is greater than  $\text{Al}(\text{IV})$  increase. The amount that the decrease in  $R^{+2}(\text{VI})$  exceeds the decrease in Si agrees closely with the amount that the increase in  $R^{+3}(\text{VI})$  exceeds the increase in  $\text{Al}(\text{IV})$ . Thus, there is evidence of oxidation in all these glauconites, and this oxidation of bivalent to trivalent iron may account for the lower interlayer charge of these glauconites as compared with those having comparable contents of potassium but higher interlayer charges.

Data on  $\text{Al}(\text{IV})$  and  $R^{+3}(\text{VI})$  replacement of Si and  $R^{+2}(\text{VI})$  in celadonites and glauconites having less than 0.66 potassium ion per half cell, given in table 8, also show close agreement between  $\text{Si}+R^{+2}(\text{VI})$  decrease and  $\text{Al}(\text{IV})+R^{+3}(\text{VI})$  increase. In the low potassium

TABLE 7.—Al(IV)R<sup>+3</sup>(VI) replacement of SiR<sup>+2</sup>(VI) in high potassium (>0.65)-low charge (<+0.89) glauconites

	Si	Decrease in Si	R <sup>+3</sup> (VI)	Decrease in R <sup>+2</sup> (VI)	Decrease in Si+R <sup>+2</sup> (VI)	Al(IV)	Increase in Al(IV)	R <sup>+3</sup> (VI)	Increase in R <sup>+3</sup> (VI)	Increase in Al(IV) +R <sup>+3</sup> (VI)	Negative layer charge
Theoretical end-member.....	4.00		1.00		0.00	0.00		1.00		0.00	1.00
Analysis:											
G11.....	3.79	0.21	0.64	0.36	0.57	0.21	0.21	1.36	0.36	0.57	0.85
12.....	3.74	.26	.60	.40	.66	.26	.26	1.40	.40	.66	.86
13.....	3.72	.28	.56	.44	.72	.28	.28	1.44	.44	.72	.84
14.....	3.69	.31	.57	.43	.74	.31	.31	1.45	.45	.76	.82
15.....	3.66	.34	.57	.43	.77	.34	.34	1.45	.45	.79	.85
16.....	3.64	.36	.51	.49	.85	.36	.36	1.49	.49	.85	.87
17.....	3.63	.37	.49	.51	.88	.37	.37	1.52	.52	.89	.83
18.....	3.62	.38	.49	.51	.89	.38	.38	1.51	.51	.89	.87
19.....	3.56	.44	.43	.57	1.01	.44	.44	1.59	.59	1.03	.81

celadonites and glauconites that have interlayer charges greater than +0.85, the decrease in R<sup>+2</sup>(VI) agrees fairly well with the decrease in Si, and the increase in R<sup>+3</sup>(VI) with the increase in Al(IV), but in the low potassium-low charge glauconites the discrepancy between these values is considerably greater. Again, the close agreement between the amount that the decrease in R<sup>+2</sup>(VI) exceeds the decrease in Si and the amount that the increase in R<sup>+3</sup>(VI) exceeds the increase in Al(IV) suggests oxidation of bivalent to trivalent iron by the amount of the excess.

The data on decrease in Si and R<sup>+2</sup>(VI) and increase in Al(IV) and R<sup>+3</sup>(VI) indicate that the low potassium celadonites and glauconites belong to the same isomorphous replacement series as the high potassium celadonites and glauconites. However, the amount by which

the decrease in R<sup>+2</sup>(VI) exceeds the decrease in Si, and the amount by which the increase in R<sup>+3</sup>(VI) exceeds the increase in Al(IV) are greater in them, and therefore indicate greater degrees of oxidation.

As shown in figure 5, there is a close agreement between the excess of R<sup>+2</sup>(VI) decrease over Si decrease and layer charge excess or deficiency compared with -1.00, the layer charge of the theoretical end-member, regardless of the amount of excess or the charge excess or deficiency. As excess of R<sup>+2</sup>(VI) decrease over Si decrease suggests oxidation, and as oxidation reduces the layer charge by the number of ferrous ions oxidized, this close relationship implies that most of these celadonites and glauconites, whether high or low in potassium, originally had layer charges very close to the theoretical 1.00.

TABLE 8.—Al(IV)R<sup>+3</sup>(VI) replacement of SiR<sup>+2</sup>(VI) in low potassium (<0.66 per half cell) celadonites and glauconites

	Si	Decrease in Si	R <sup>+2</sup> (VI)	Decrease in R <sup>+2</sup> (VI)	Decrease in Si+R <sup>+2</sup> (VI)	Al(IV)	Increase in Al(IV)	R <sup>+3</sup> (VI)	Increase in R <sup>+3</sup> (VI)	Increase in Al(IV) +R <sup>+3</sup> (VI)	Negative layer charge
Theoretical end-member.....	4.00		1.00		0.00	0.00		1.00		0.00	1.00
<b>Celadonites</b>											
Analysis:											
C10.....	3.89	0.11	0.66	0.34	0.45	0.11	0.11	1.34	0.34	0.45	0.77
11.....	3.88	.12	.74	.26	.38	.12	.12	1.26	.26	.38	.84
12.....	3.79	.21	.75	.25	.46	.21	.21	1.25	.25	.46	.95
13.....	3.76	.24	.73	.27	.51	.24	.24	1.27	.27	.51	.97
<b>High charge glauconites (&gt;+0.88)</b>											
Analysis:											
G20.....	3.68	0.32	0.68	0.32	0.64	0.32	0.32	1.34	0.34	0.66	0.94
21.....	3.62	.38	.51	.49	.87	.38	.38	1.49	.49	.87	.89
22.....	3.60	.40	.53	.47	.87	.40	.40	1.47	.47	.87	.93
23.....	3.57	.43	.54	.46	.89	.43	.43	1.46	.46	.89	.97
24.....	3.49	.51	.44	.56	1.07	.51	.51	1.56	.56	1.07	.96
<b>Low charge glauconites (&lt;+0.89)</b>											
Analysis:											
G25.....	3.85	0.15	0.61	0.39	0.56	0.15	0.15	1.39	0.39	0.56	0.76
26.....	3.79	.21	.47	.53	.74	.21	.21	1.51	.51	.72	.74
27.....	3.75	.25	.53	.47	.72	.25	.25	1.47	.47	.72	.78
28.....	3.66	.34	.48	.52	.86	.34	.34	1.54	.54	.88	.76
29.....	3.66	.34	.57	.49	.83	.34	.34	1.49	.49	.83	.85
30.....	3.65	.35	.52	.48	.83	.35	.35	1.48	.48	.83	.87
31.....	3.63	.37	.39	.61	.98	.37	.37	1.61	.61	.98	.75
32.....	3.62	.38	.48	.52	.90	.38	.38	1.53	.53	.91	.83

<sup>1</sup> Includes 0.06 atomic ratio Fe<sup>+3</sup>.

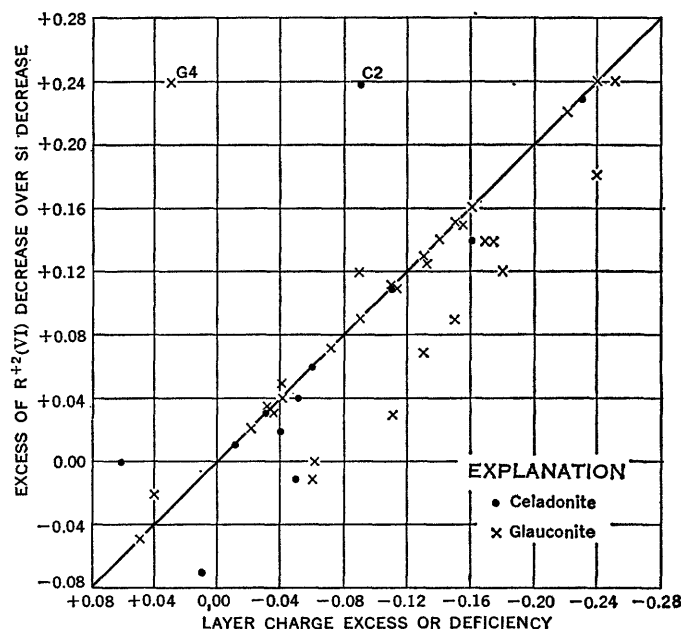


FIGURE 5.—Relation between excess of  $R^{+2}(VI)$  decrease over Si decrease and layer charge excess or deficiency.

## INTERPRETATION OF GLAUCONITE COMPOSITION

### RELATION BETWEEN TRIVALENT IRON AND OCTAHEDRAL ALUMINUM

In the first part of this study it was shown that except for deficiency in potassium content, potassium-deficient glauconites are very similar in composition to the high potassium glauconites. Aside from potassium content, the most variable constituents in these glauconites are the trivalent octahedral cations, iron and aluminum, which bear a reciprocal relation to each other (fig. 6). These relations, especially when found in high potassium-high charge glauconites, suggest that a high content of octahedral aluminum in a glauconite may not necessarily indicate degradation or admixture, but might be indicative of the environment in which the glauconite developed specifically with reference to the concentration of iron.

Because many glauconites are high in iron, it has been generally postulated that glauconite is developed in environments rich in iron. Even in such environments, however, iron concentration differs greatly, and these differences are reflected in the iron content of the glauconite.

### THE $Fe^{+3}:Fe^{+2}$ RATIO

Theoretically, the relation between bivalent and trivalent iron in a glauconite is determined by the oxidation potential in the environment of its development. With change of environment, however, a glauconite may un-

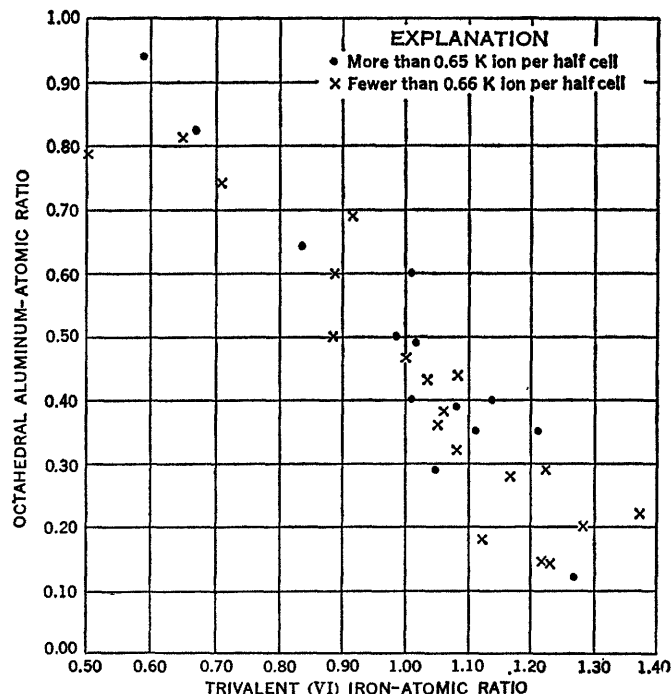


FIGURE 6.—Relation between  $Fe^{+3}$  and  $Al(VI)$  in glauconites.

dergo oxidation; this appears to have happened to many of the glauconites under review. As has been pointed out, oxidation is strongly suggested when the decrease in  $R^{+2}(VI)$  is greater than the decrease in Si, and the increase in  $R^{+3}(VI)$  is greater than the increase in  $Al(IV)$  compared with the theoretical tetrasilicic end-member, and when the amount by which the decrease in  $R^{+2}(VI)$  exceeds the decrease in Si agrees closely with the amount by which the increase in  $R^{+3}(VI)$  exceeds the increase in  $Al(IV)$ .

The only glauconites included in this study in which  $R^{+2}(VI)$  decrease agreed closely with Si decrease, and  $R^{+3}(VI)$  increase agreed closely with  $Al(IV)$  increase, indicating little or no oxidation, are those high potassium glauconites that also have layer charges close to  $-1.00 \pm 0.05$ , G1, G3, G4, G7, and G9. In all the others, the relations between  $R^{+2}(VI)$  and Si and between  $R^{+3}(VI)$  and  $Al(IV)$  indicate that some oxidation has taken place, and that  $Fe^{+3}:Fe^{+2}$  ratios calculated from the analytical results do not reflect the true oxidation-potential of the respective environments of development. For glauconites that have undergone only a minor degree of oxidation, the calculated  $Fe^{+3}:Fe^{+2}$  approximates the  $Fe^{+3}:Fe^{+2}$  relation in the original glauconite. If, however, two-thirds or more of the original bivalent iron has been oxidized, as in G26, G28, and G31, such calculated ratios would be very misleading, unless the amount of oxidation, as indicated by the amount by which the decrease in  $R^{+2}(VI)$  exceeds the decrease

in Si and the amount by which the increase in  $R^{+3}(VI)$  exceeds the increase in  $Al(IV)$ , is taken into consideration.

#### RELATION BETWEEN IRON AND POTASSIUM

As is obvious from figure 7, there is no correlation between potassium and iron in glauconites. Glauconites high in potassium may be high, medium, or low in iron, and others low in potassium may be high, medium, or low in potassium. This is contrary to Hower's (1961) conclusion that in glauconites, potassium and iron should be directly proportional to each other. However, these constituents are incorporated into the structure by different processes, and any proportionality between them is coincidental.

After a study of glauconite formation in modern foraminiferal sediments of the southeastern coast of the United States, Ehlmann, Hulings, and Glover, (1963, p. 95) concluded that "the earliest stage material having an  $Fe_2O_3$  content of 20 percent may be regarded as a potassium-deficient prototype of glauconite with iron already incorporated into the structure." This conclusion supports the present hypothesis that glauconitization consists of two separate, unrelated processes, incorporation of iron into the crystal structure and fixation of potassium in interlayer positions, with incorporation of iron and development of negative layer charge

preceding complete fixation of potassium. Thus, there is not necessarily a relation between iron and potassium in a glauconite, as has been postulated by some investigators.

#### FIXATION OF POTASSIUM

Fixation of potassium may begin to take place relatively early in the development of a glauconite, especially if the parent material is a stripped and degraded layer silicate, with potassium first being taken into exchange positions before becoming fixed. As the potassium gradually settles into fixed positions and thus changes the relative proportions of the exchangeable cations present, continual readjustment is required between the exchangeable cations present and the cations of the surrounding water, usually sea water. Eventually, if the process is not interrupted, most of the negative layer charge is neutralized by potassium. As more and more potassium becomes fixed, the sheets become more and more tightly bound together, and further entry of potassium becomes increasingly difficult. Thus, it may be that fixation never proceeds to completion in a glauconite, and that most glauconites contain some exchangeable cations. An occupancy of about 85 percent of the possible interlayer positions, as in G3, G4, G15 and G18, may be the maximum to be expected in glauconites, even though their negative layer charges are equivalent, as in G3 and G4, to those of true micas.

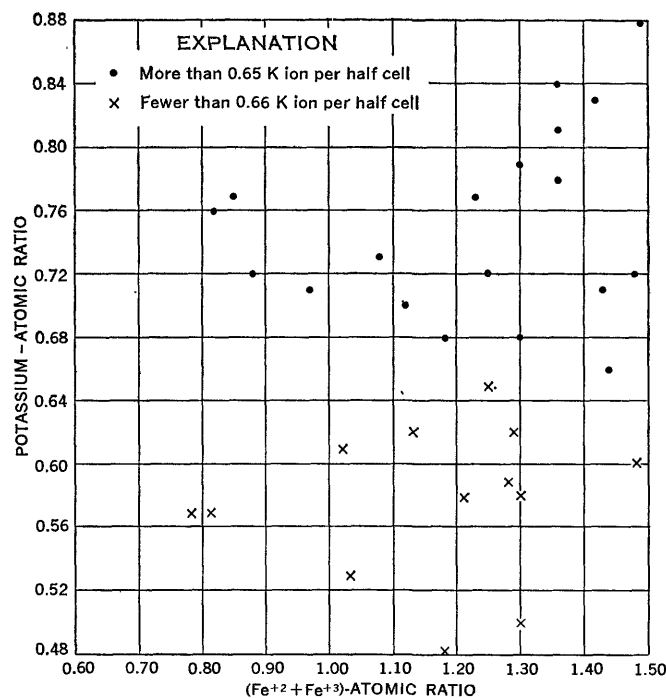


FIGURE 7.—Relation between total iron and potassium in glauconites.

#### DEFICIENCY IN POTASSIUM CONTENT

Deficiency in potassium content may be due to failure to attain maximum fixation because of change of environment, burial, uplift, or dilution, or to oxidation, with accompanying decrease in layer charge and loss of some potassium that had been fixed. Failure to attain maximum fixation of potassium is exemplified by glauconites G20-G24. These five glauconites all have high layer charges, ranging from  $-0.89$  to  $-0.97$ , per half cell, but they contain only from 0.48 to 0.62 ions of potassium, with exchangeable cations neutralizing the remainder of the layer charge. Although a slight excess of  $R^{+2}(VI)$  decrease over Si decrease and excess of  $R^{+3}(VI)$  increase over  $Al(IV)$  increase indicate some oxidation in those with layer charges less than  $-0.95$ , their very high content of exchangeable cations, averaging 0.39 positive charge per half cell, and particularly their content of exchangeable sodium, averaging 0.19 ion per half cell, is very suggestive of immaturity. The fact that the  $R^{+2}(VI)$  and Si and the  $R^{+3}(VI)$  and  $Al(IV)$  relations in these glauconites indicate that they have undergone little oxidation also suggests immaturity as the cause of the low content of potassium.

Many of the glauconites that have undergone oxidation are characterized by relatively lower contents of bivalent iron, lower layer and interlayer charges, lower exchangeable cation content, and a somewhat lower potassium content. For example, the relations between decrease in  $R^{+2}$  (VI) and in Si, and between increase in  $R^{+3}$  (VI) and in Al(IV) in seven high potassium glauconites having layer charges of  $-0.95$  or more, G1, G3, G4, and G7-G10, indicate that these glauconites have undergone no oxidation; whereas in six other high potassium glauconites, G11, G13-G15, G17, and G19, the relations between decrease in  $R^{+2}$  (VI) and in Si and between increase in  $R^{+3}$  (VI) and in Al(IV) indicate that from  $0.10$ - $0.16$  ion of bivalent iron has been oxidized to trivalent iron. As a result of this oxidation these glauconites have not only lower layer charges, averaging  $-0.83$  compared with an average of  $-1.00$  in the seven unoxidized glauconites, but an average of  $0.13$  fewer bivalent iron cations, and only about half as many exchangeable cation charges, averaging  $+0.10$  as compared with  $0.21$ . Although there is also a slight decrease in average potassium content, from  $0.77$ - $0.73$ , most of the loss in negative layer charge has been offset by the release of exchangeable cations, not of fixed potassium.

In some of the low potassium glauconites it is difficult to determine whether potassium deficiency is due to oxidation or immaturity. The relations between decrease in  $R^{+2}$  (VI) and in Si and between  $R^{+3}$  (VI) and Al(IV) in these glauconites indicate that they have lost an average of  $0.24$  cation of bivalent iron by oxidation. In terms of the individual glauconites this means that one-half (for G25 and G27), two-thirds (for G26 and G28), and three-fourths (for G31) of the bivalent iron originally present has been converted to trivalent iron. It also means that there has been a loss in negative layer charge corresponding to the loss in bivalent iron content, as these glauconites have an average layer charge of  $-0.76$ . With an average exchangeable cation charge only  $+0.05$  less than that in the unoxidized high charge-high potassium glauconites, G1, G3, G4, and G7-G10, it is difficult at this stage to resolve the reason for the deficiency in potassium in these glauconites, which averages only  $0.61$  ion per half cell—whether it is due to release because of oxidation, or to immaturity, failure to attain maximum fixation, as in G20-G24, or to a combination of the two.

#### RELATION BETWEEN GLAUCONITE COMPOSITION AND GEOLOGIC AGE

Attempts to correlate glauconite composition with geologic age have not been altogether successful; too few analyses of glauconites can be reliably referred to

definite geologic periods to furnish adequate information as to trends in composition over the eons of geologic time. Smulikowski (1954) based a correlation on average values of the principal constituents of the glauconites assigned to various geologic periods. He concluded (p. 77) that "the older the geological formation, the smaller in its glauconite the prevalence of ferric iron over aluminum in the octahedral layer and the greater in its glauconite the total amount of interlayer cations." He based these broad conclusions on six analyses for the Quaternary Period, 18 for the Tertiary, 13 for the Cretaceous, none for the Triassic, Permian, Carboniferous, and Devonian, two for the Silurian, five for the Ordovician, and three for the Cambrian. Smulikowski excluded from consideration five analyses of Jurassic glauconites because all were by the same analyst, and represented glauconites from only two localities, both in Russia. However, four of his five Ordovician analyses were from limestone in Sweden, and these he did include. All in all, he had no data for the long period of time between the end of the Silurian and the beginning of the Cretaceous, and only scanty data (10 analyses) for the Silurian, Ordovician, and Cambrian, which he grouped together as early Paleozoic, a period of almost 200 million years.

Smulikowski's average values for octahedral aluminum in Tertiary, Cretaceous, and early Paleozoic glauconites,  $0.399$ ,  $0.426$ , and  $0.501$  ion per half cell, respectively, differ by only  $0.102$  ion for a length of time of more than 500 millions of years. This is a very small difference in amount of octahedral aluminum and very scant data upon which to base the broad conclusions he came to, particularly in view of the great variations in the compositions of the Tertiary and Cretaceous glauconites upon which his averages for these periods are based. Thus, his average value of octahedral aluminum in Tertiary glauconites is based on values that range from  $0.121$  to  $0.686$  ion per half cell, and in Cretaceous glauconites from  $0.135$  to  $0.942$  ion. The variation in content of octahedral aluminum in glauconites referred to each of these periods is more than six and nine times greater than the average difference between octahedral aluminum in the Tertiary and early Paleozoic glauconites.

The great variety of composition to be found in glauconites from the Cretaceous and Tertiary, the periods best represented in the glauconites included in this study, is indicated in figure 8. The range in content of octahedral aluminum, bivalent and trivalent iron, potassium and interlayer charge among the eight Cretaceous glauconites is almost as great as among the entire suite of analyses studied. They range from the highly ferruginous, as illustrated by G11, in figure 8, to the

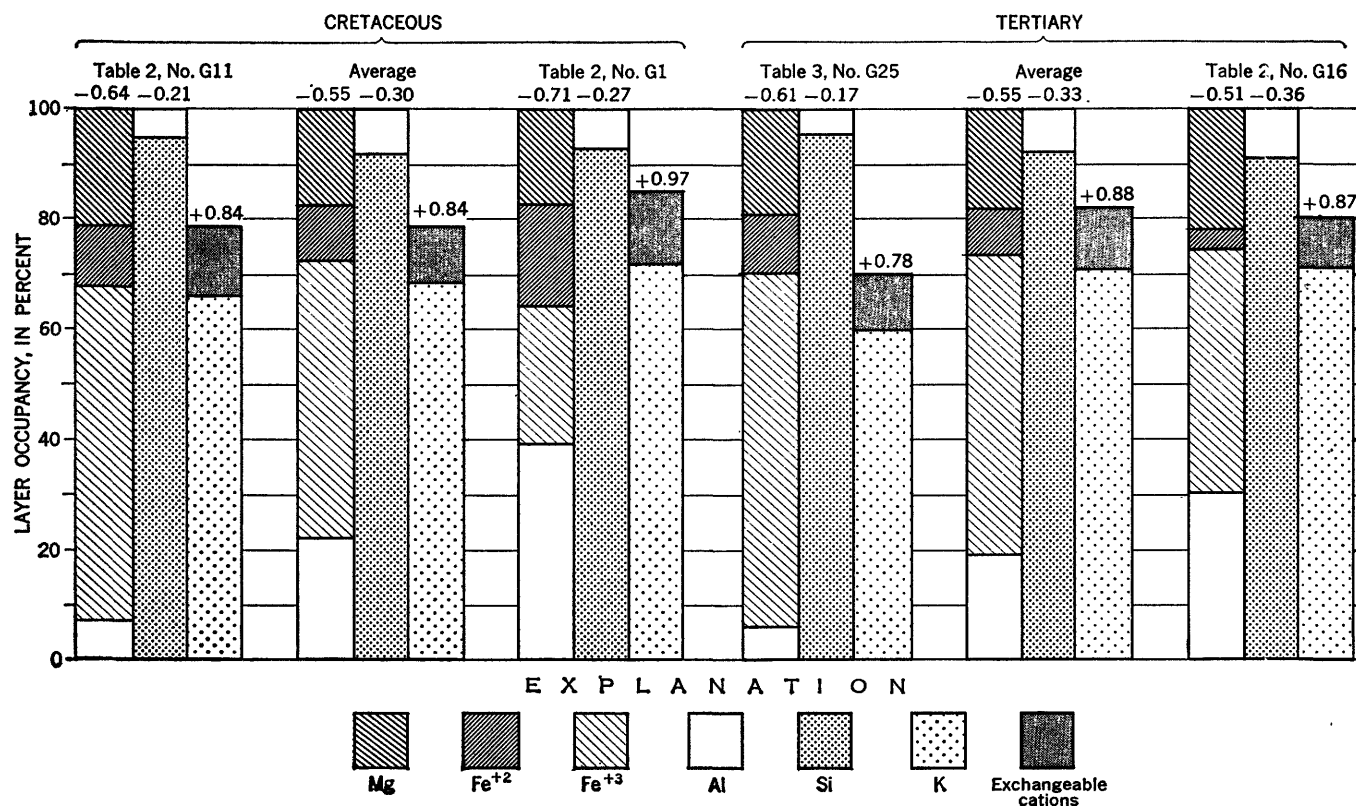


FIGURE 8.—Extreme and average compositions of Cretaceous and Tertiary glauconites. Figures above the first and second Columns of each diagram indicate the positive-charge deficiencies of the octahedral and tetrahedral layers; figures above the third column indicate the positive interlayer charge.

highly aluminous, as illustrated by G1, in figure 8. They are equally variable in potassium content and in interlayer charge, ranging from 0.84 to 0.57 ion of potassium per half cell, and +0.97 to +0.76 interlayer charge per half cell. Some of the Tertiary glauconites studied are as ferruginous as any of the Cretaceous glauconites, but none of the Tertiary glauconites were as high in octahedral aluminum as G1, the highest octahedral aluminum content occupying only 30.0 percent of the octahedral layer. The range in potassium content in the Tertiary glauconites, from 0.88 to 0.58 ion per half cell, is very similar to that in Cretaceous glauconites,

as is also the range in interlayer charge, from +1.03 to 0.77.

The variety of compositions found among both the Cretaceous and Tertiary glauconites suggests that geologic age has little to do with the composition of glauconites. Other factors, such as the specific environment in which the glauconite is formed—particularly its degree of iron concentration and its oxidation-reduction—and opportunities for potassium fixation and for oxidation, are of far greater importance in determining the composition of a glauconite than the geologic age in which it was formed.

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