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CHEMICAL VARIABILITY AND STRUCTURAL HETEROGENEITY OF GLAUCONITES

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ABSTRACT

The study of 20 samples of glauconites from the Bohemian Upper Cretaceous has confirmed the general (Burst /1958/ and Hower /1961/) thesis that the chemical variability of glauconites is due to their mineralogical heterogeneity. From this point of view the dependence between the percentage of expandable layers and the content of all main chemical components in the structure of the glauconites, has been examined. In glauconites with decreasing percentage of 14 Å layers, the content of K, Al^{IV} and Fe^{3+} rise linearly, while the Si, Al^{VI} and Mg content decrease linearly.

From the quantitative relations between the main chemical components and the proportion of expandable layers in natural (10 Å/14 Å) glauconites, the following crystalochemical formula has been derived by extrapolation for a homogeneous 10 Å glauconite:

$$K_{0.78}(NaCa)(\overset{3+}{Fe}_{1.03}Al_{0.45}Mg_{0.34}\overset{2+}{Fe}_{0.13})(Si_{3.69}Al_{0.31})O_{10}(OH)_2.$$

INTRODUCTION

The chemical composition of glauconites has been studied by many authors. In general, a considerable chemical variability has been established in glauconites; especially the contents of the oxides K_2O, Fe_2O_3 and Al_2O_3 are variable [compare the chemical analyses published by Hendricks, Ross (1941), Valeton (1958), Foster (1960), Borchert, Braun (1963) and others.]

The varying Fe:Al ratio is used by some authors as a basis of the chemical classification of glauconites; consider Smulikowski (1954), Lazarenko (1956), Gorbunova (1950), or Borchert and Braun (1963). These authors assumed that all the various combinations exist in glauconites from the ferric type (the so-called Fe-glauconites where $Fe > Al$) to the aluminium type (the so-called Al-glauconites where $Al > Fe$). Smulikowski has suggested giving the Al-glauconites a special name, "scolites."

Frequently an attempt is made to explain in some way this chemical variability of glauconites. Some authors see the decisive feature in the geological age of glauconites (Smulikowski, 1954; Urban, 1957); others point out the lithological character of the glauconite-bearing sediments (Hower, 1961; Bentor and Kastner, 1965) or the paleogeography of the sedimentation area (namely, the distance of the deposited material from the coast) (Gorbunova, 1950; Machinin 1951; Borchert and Braun, 1963).

Burst (1958) and Hower (1961) (also Manghnani and Hower, 1964) have recognized that the changes in the chemical composition of glauconites relate to the presence and amount of expandable layers in the structure of glauconites. On the basis of X-ray examination and chemical analyses, Burst has established a relation between the content of the 14 Å component of the glauconites and the K_2O and Fe_2O_3 contents. However, using the crystallochemical formulas of glauconites as a basis, expressed this dependence more accurately as a relation between the 14 Å (montmorillonite) component and the amount of the interlayer potassium and octahedral iron and aluminium. Therefore, the geological age, lithology and paleogeography can only be considered possible causes of a variable content of the 14 Å component in glauconites; they cannot be considered direct causes of the chemical variability of glauconites.

The aim of this paper is (a) to present a survey of the chemistry of glauconites from the Bohemian Upper Cretaceous, and (b) to derive the actual forms of dependencies between the content of all the main chemical components in the glauconites and the percentage of the 14 Å component in their structure.

EXPERIMENTAL METHODS

Chemical analyses. Chemical analyses of glauconites (Table 1) were made by Ing. F. Chaluš in the chemical laboratory of the Geological Institute of the Czechoslovak Academy of Sciences. Electromagnetically separated glauconites, which were handpicked under the binocular microsope, were used for analysis. The chemical analyses (after subtraction of apatite) were used to construct the crystallochemical formulas shown in Table 2. The formulas are based on an idealized unit cell of 12 oxygen atoms which can accommodate, after allowances for hydrogen, 22 cationic valences (for an example of the mode of calculation see Kelley, 1945). The subtraction of apatite has been carried out by subtracting all the P_2O_5 and an equivalent proportion of CaO.

X-ray diffraction. X-ray diffraction determinations were performed on oriented specimens of untreated, glycol-solvated, and potassium-treated (with a 1 N KCl solution) samples. The percentage of expandable layers was determined from the position of the combined $001_{10}/001_{15.5}$ $001_{10}/002_{17}$, and $001_{10}/001_{12.4}$ reflections. The percent of expandable layers was read from the curves of Brown and MacEwan (1951), which relate spacing to the amount and type of interlayering; it is reported in 5 percent intervals (see Table 2). It has been established that the proportion of the expandable (14 Å) layers ranges from <5 to 25 percent (Cimbálníková, 1970).

CHEMISTRY OF GLAUCONITES AND ITS VARIABILITY

A survey of the chemical composition of the glauconites studied is presented in Table 1.

The relation between the percentage of expandable layers and the amount of the fundamental cations in the structure of glauconites (*i.e.* K, Si, Al^{IV}, Fe^{3+}, Fe^{2+}, Al^{VI} and Mg) is illustrated by fitted curves in Figures 1 and 2.

TABLE 1. CHEMICAL ANALYSES OF GLAUCONITES (IN WEIGHT PERCENT)

	70	9	49	71	41	73	22	43	74	80	79	14	37	77	15	76	10	8	38	62
SiO_2	49.58	50.36	51.19	49.57	50.07	49.49	48.47	50.03	50.99	51.55	52.85	49.56	50.33	52.36	50.59	51.31	50.25	50.56	53.09	50.80
TiO_2	0.12	0.28	0.13	0.17	0.093	0.03	trace	0.30	0.03	0.12	0.14	trace	0.29	0.17	0.14	0.23	0.25	0.38	0.17	0.18
Al_2O_3	6.80	9.23	9.33	8.11	7.07	9.86	10.34	8.91	10.54	7.05	9.60	9.29	10.50	7.95	8.37	9.04	8.51	8.88	8.90	6.26
Fe_2O_3	20.45	16.87	18.15	19.16	20.16	16.74	16.46	18.71	15.12	19.32	15.95	18.40	15.16	15.91	18.22	15.70	18.90	18.14	14.09	17.93
FeO	1.12	2.46	1.78	1.45	1.22	2.77	3.32	2.09	2.86	1.57	2.18	0.84	1.92	2.20	1.01	1.83	1.20	0.92	1.61	1.62
MnO	0.026	0.014	0.014	0.022	0.014	0.14	trace	0.016	0.11	0.02	0.01	trace	0.03	0.02	0.028	0.013	0.012	0.04	0.01	0.02
MgO	3.36	3.22	3.34	3.47	3.15	3.45	3.40	2.86	3.32	3.64	3.59	3.89	3.63	3.83	3.50	3.46	3.40	3.50	4.47	4.45
CaO	1.54	0.26	0.58	1.17	0.99	0.69	0.45	0.83	0.72	0.51	0.54	0.78	0.85	1.05	0.52	1.08	0.34	1.02	0.91	1.30
Na_2O	0.053	0.063	0.024	0.042	0.042	0.04	0.07	0.04	0.03	0.05	0.03	0.06	0.03	0.07	0.03	0.05	0.039	0.01	0.05	0.09
K_2O	8.11	8.12	7.98	7.77	7.63	7.65	7.54	7.32	7.45	7.15	7.34	7.17	7.05	6.96	6.59	6.58	6.30	6.33	6.26	5.96
P_2O_5	0.53	0.16	0.20	0.18	0.20	0.15	0.19	0.17	0.10	0.15	0.20	0.12	0.17	0.13	0.14	0.21	0.24	0.20	0.19	0.27
H_2O^+	6.07	6.59	5.21	6.20	6.44	6.98	6.91	6.31	6.71	6.50	6.09	5.75	7.15	6.52	8.12	6.56	8.77	6.41	7.04	6.84
H_2O^-	2.72	1.74	1.95	2.88	3.27	1.62	2.15	1.74	2.21	1.95	1.95	3.58	2.56	2.56	2.42	3.72	1.78	3.38	3.64	3.94
SrO	0.02	0.072	0.008	0.02	0.037	0.02	trace	0.032	0.03	trace	trace		0.02	trace	0.01	0.02	0.01	0.037	0.02	trace
Total	100.50	99.44	99.89	100.21	100.39	99.63	99.30	99.36	100.22	99.58	100.47	99.44	99.69	99.73	99.69	99.80	100.00	99.80	100.45	99.66

TABLE 2. CALCULATED FORMULAS FOR GLAUCONITES

		Samples no.	70	9	49	71	72	41	73	22	43	74	80	14	37	77	15	76	10	8	38	62
		Percent of expandable layers	<5	<5	<5	<5	<5	~5	5-10	5-10	~10	~10	10-15	10-15	10-15	10-15	10-15	15-20	~20	~20	20-25	~25
Cations in position	Tetrahedral	Si	3.72	3.72	3.72	3.69	3.75	3.75	3.67	3.63	3.70	3.73	3.80	3.65	3.72	3.84	3.78	3.80	3.75	3.74	3.87	3.83
		Al	0.28	0.28	0.28	0.31	0.25	0.25	0.33	0.37	0.30	0.27	0.20	0.35	0.28	0.16	0.22	0.20	0.25	0.26	0.13	0.17
		Total	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
	Octahedral	Fe^{3+}	1.15	0.94	0.99	1.07	1.07	1.13	0.93	0.93	1.04	0.83	1.07	1.02	0.84	0.88	1.02	0.88	1.06	1.01	0.77	1.02
		Fe^{2+}	0.07	0.15	0.11	0.09	0.08	0.08	0.17	0.21	0.13	0.18	0.10	0.05	0.12	0.13	0.06	0.11	0.07	0.06	0.10	0.10
		Al	0.32	0.52	0.51	0.40	0.40	0.37	0.53	0.55	0.48	0.63	0.41	0.52	0.63	0.53	0.51	0.59	0.50	0.51	0.64	0.38
		Mg	0.38	0.35	0.36	0.39	0.39	0.35	0.39	0.38	0.31	0.36	0.40	0.43	0.40	0.42	0.39	0.38	0.38	0.39	0.49	0.50
		Mn	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
		Ti	0.01	0.02	0.01	0.01	0.01	0.01	0.01	—	0.02	0.01	0.01	—	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.01
		Total	1.93	1.98	1.98	1.96	1.95	1.94	2.03	2.07	1.98	2.01	1.99	2.02	2.01	1.97	1.99	1.97	2.02	1.99	2.01	2.01
	Interlayer	K	0.77	0.76	0.74	0.74	0.74	0.73	0.72	0.72	0.69	0.69	0.67	0.67	0.66	0.65	0.63	0.62	0.60	0.60	0.58	0.57
		Na	0.01	0.01	—	0.01	0.01	0.01	0.01	0.01	0.01	—	0.01	0.01	—	0.01	—	0.01	0.01	—	0.01	0.01
		Ca	0.07	0.04	0.03	0.07	0.07	0.05	0.04	0.02	0.04	0.05	0.02	0.05	0.05	0.07	0.02	0.06	—	0.06	0.05	0.08
		Total	0.85	0.81	0.77	0.82	0.82	0.79	0.77	0.75	0.74	0.74	0.70	0.73	0.71	0.73	0.65	0.69	0.61	0.66	0.64	0.66
Charge		Tetrahedral	−0.28	−0.28	−0.28	−0.31	−0.25	−0.25	−0.33	−0.36	−0.30	−0.27	−0.20	−0.34	−0.28	−0.16	−0.22	−0.20	−0.25	−0.26	−0.13	−0.17
		Octahedral	−0.64	−0.56	−0.51	−0.58	−0.64	−0.60	−0.47	−0.40	−0.49	−0.52	−0.52	−0.44	−0.48	−0.64	−0.45	−0.56	−0.36	−0.46	−0.56	−0.57
		Total	−0.92	−0.84	−0.79	−0.89	−0.89	−0.85	−0.80	−0.76	−0.79	−0.79	−0.72	−0.78	−0.76	−0.80	−0.67	−0.76	−0.61	−0.72	−0.69	−0.74

70. Březová, n. Svit.
9. Kněživka, near Slaný.
49. Praha—Prosek.
71. Rozhraní, near Letovice.
72. Chrastová.
41. Slap, n. Bechlínem.
73. Nová Ves (37.5–39.0 m).
22. Smečno.
43. Chržín, near Kralupy.
74. Nová Ves (41.0 m).
80. Kojetice, near Neratovice.
14. Vísky, near Letovice.
37. Polanky, near N. Hrady.
77. Vrbice, near Poděbrady.
15. Písečná, near Letovice.
76. Kunratice, near Cvikov.
10. Dobrá, near Kladno.
8. Chlum, near Skalice n.Svit.
38. Písečná, near Žamberk.
62. Jíkev, near Nymburk.

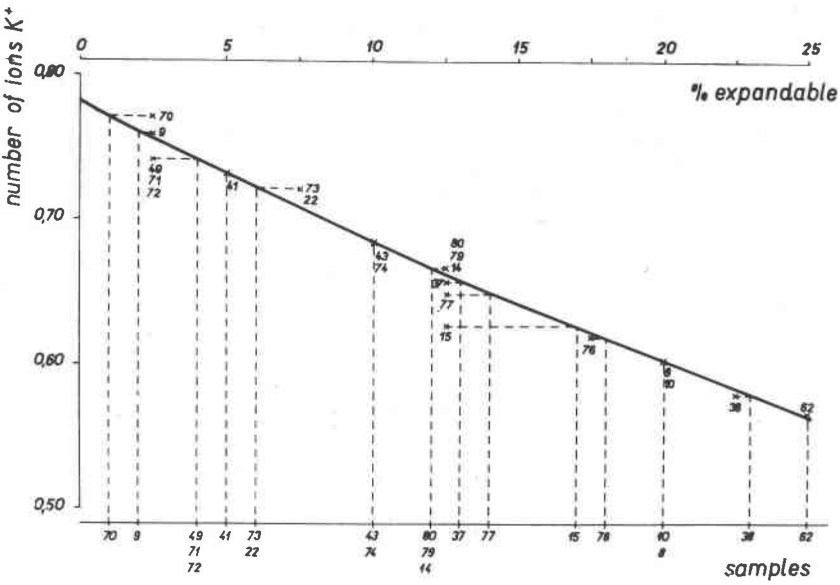

FIG. 1. Relation between the percentage of expandable layers and the number of potassium ions in glauconites.

In Figure 1 the 5 percent intervals of the expandable component determined by Xrays (Table 2) are refined by their known relation to the content of K^+ ions (Manghnani and Hower, 1964). Samples were plotted approximately along the x axis according to the X-ray estimates of expandable layers, and along the y axis according to the chemically determined potassium content. A curve (quadratic parabola, comp. Manghnani and Hower, 1964) was fitted by the least-squares method. The potassium content is known with an accuracy of $\pm 2\%$, and the fitted curve gives more accurate values for the percent expandable layers. These values are then used as a basis for the plots of other elements in Figure 2.

From Figures 1 and 2 the following general conclusions may be drawn and dependencies inferred:

1. The chemical variability of natural (10 Å/14 Å) glauconites depends on the percentage of expandable layers in their structure (as has been concluded by Burst, 1958 and Hower, 1961). The proportion of the expandable layers affects the contents of K, Si, Al^{IV}, Fe^{3+}, Al^{VI}, Mg and Fe^{2+}.[1]

2. With the increasing proportion of the 14 Å component in glauconites:

(a) The content of potassium decreases in the interlayer spaces;

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[1] Fe^{2+} decrease is not significant; statistical analysis of a greater number of samples to examine this relation should be used in general.

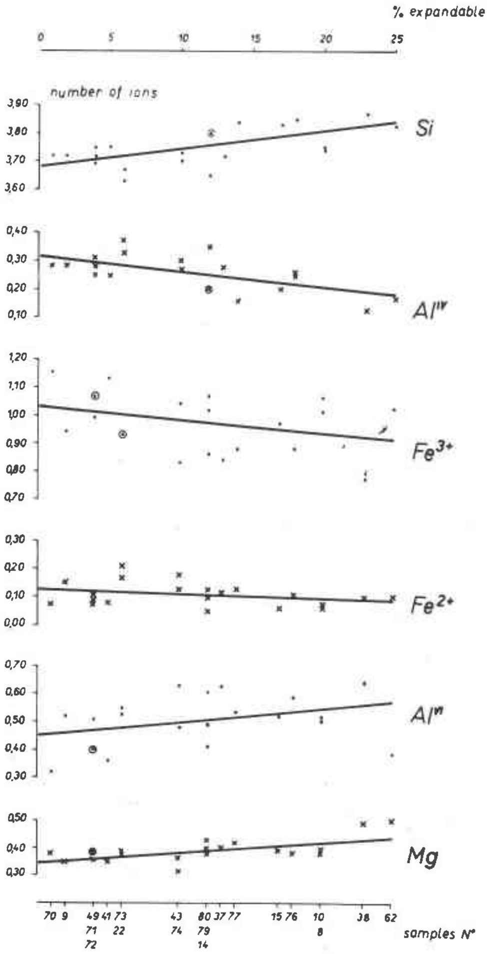

FIG. 2. Relation between the percentage of the expandable layers and the number of Si, Al^{IV}, Fe_3^+, Fe^{2+}, Al^{VI} and Mg ions in glauconites.

(b) The content of Fe^{3+} decreases, and the Al^{VI} and Mg content increases in the octahedral sheets;

(c) The Si content increases and the amount of Al^{IV} decreases in the tetrahedral sheets.

3. The chemical composition of homogeneous (10 Å) glauconites is, therefore, not as variable as is usually assumed. The amounts of the chemical components (in atomic proportions) can be extrapolated from

Figure 1 and 2. Hence, the approximate structural-chemical formula of a 10 Å glauconite is as follows:

$$K_{0.78}(NaCa)(Fe^{3+}_{1.03}Al_{0.45}Mg_{0.34}Fe^{2+}_{0.13})(Si_{3.69}Al_{0.31})O_{10}(OH)_2.$$

Therefore, it follows that glauconites can be classified, in the first place, according to the mineralogical-structural criteria, *i.e.* according to the percentage of expandable layers in their structure. In classifying them from the chemical point of view, only such criteria can be accepted which reflect this structural aspect without distorting it. From Figure 2, it is evident that the ratio of octahedral Fe and octahedral Al can represent such a criterion. The ratio of total Fe and total Al, however, cannot serve this purpose, as both coordination forms of Al behave quite contrary to the proportion of the expandable component. The Al^{VI} content increases with a rising expandable percentage, whereas under the same condition, the Al^{IV} content decreases.

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