

The chemical evolution of glauconite pellets as seen by microprobe determinations

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SUMMARY. Seven samples of pelletal glauconites with varying iron and potassium contents were investigated using the electron microprobe. In-sample variation of pelletal compositions is quite important, even for samples previously separated according to grain-size, density, and magnetic susceptibility. This observation should lead to a reconsideration of previous work based upon multi-grain samples.

During the evolution of pelletal material towards micaceous glauconite compositions it is apparent that iron can be added to as well as subtracted from the bulk pelletal composition. This transfer appears to be effected when the pellet contains a multiphase mineral assemblage as well as during the evolution of a single-phase mixed layered mineral.

A schematic phase diagram is presented which attempts to describe the phase changes as a function of K, Si, and Fe variables.

THE major aspects of the process of glauconitization of pelletal material are now more or less agreed upon by most workers. Argillaceous sedimentary material, concentrated by biologic action, is gradually transformed into a monophase, iron-rich, tetrasilicic, potassic micaceous mineral. The isolation of each grain in a sediment implies that the chemical system forming glauconite in each pellet is independent from those that operate in others. Certainly the chemical equilibria that form the glauconite in the grains do not apply to the encasing detrital silicates in the sediment since they appear to maintain their original mineral compositions even when glauconitization of the grains is advanced.

Pellets with a moderately 'mature' character, i.e. containing a significant proportion of the micaceous component with a K_2O content above 5%, are composed entirely of a mixed-layered mica-montmorillonite-type mineral. Normally no other silicates are present in these types of samples. This tendency towards a single-phase assemblage is typical of chemical systems where most components are intensive variables and their abundance within the solids is determined by their chemical potential in the liquid (Korzhinski, 1965). This liquid is usually sea water or, in some cases, pore fluid. In a poorly consolidated sediment, non-pelletal glauconite can be crystallized under other conditions.

Considering the above, one should assume that a geologic hand-sample containing glauconite grains will contain material in various stages of the process. Even after electromagnetic, density, and grain-size separations, which are normally used to purify and homogenize a sample, it would be necessary to assume that any multigrain sample is a collection of different systems. The following brief investigation is an

attempt to measure in an indicative way the extent of this inhomogeneity at various stages of the glauconitization process, for both iron-rich and iron-poor samples.

Experimental. Seven samples of pelletal marine glauconites have been used, which appear to represent the variations in Si, K, and Fe contents found in glauconite samples previously studied. Their ages vary from Cretaceous to Recent ocean sediments; their potassium content varies from 3.33 to 6.70 % for 300-mg grain aggregates (Table I) and from 1.10 to 8.20 % for 10- μ m diameter spots in individual

TABLE I. *Chemical and X-ray diffraction characteristics of samples (multigrain averages, \sim 300 mg)*

JH 63-3:	grains from a carbonate rock, Taft Hill formation, Cretaceous, Great Falls, Montana, U.S.A. 4.00 % K_2O , 0.26 % Na_2O ; 11.7 Å interstratified mica smectite determined for air-dried sample.
A 11:	thin section, shale, Cenomanian (Cretaceous), near Grasse, France. 6.54 % K_2O , 0.09 % Na_2O ; 10.2 Å plus other less precise reflections of expanding phases.
A 15:	thin section, carbonate, Albian (Cretaceous), near Grasse, France. 6.70 % K_2O , 0.16 % Na_2O ; 10.1 Å plus high background toward higher d spacings.
K 82:	grains separated to uniform size, density, and magnetic susceptibility. (Odin, 1972) Eocene sediments, Rodeberg, Belgium. 6.1 % K_2O , 0.25 % Na_2O ; 11 Å reflection.
K 92.8:	separated grains as above (K 82) core sample, sand, Eocene, Rodeberg, Belgium (Odin, 1972). 5.4 % K_2O , 0.15 % Na_2O ; 11 Å reflection.
PG 522:	separated grains, bottom sample, Gabon Coast (Giresse and Odin, 1973). 3.62 % K_2O , 0.27 % Na_2O ; 13.0 Å reflection plus small 7.2 Å Kaolinite reflection.
PG 517:	as above (Giresse and Odin, 1973). 3.33 % K_2O , 0.18 % Na_2O ; 13.0 Å reflection plus kaolinite plus iron oxides.

grains (Table II). An average of 10 grains were point-analysed for each sample, using a CAMECA microprobe; corrections were made using the EMPADR VII program (Rucklidge and Gasparrini, 1969).

The centres and edges of glauconite grains were analysed. Colour differences at grain edges (lighter or darker green colour, black rims of probable organic material) and local brown zones within the grains appeared to reflect only small compositional variations. It is most likely that colour variation in the green hues is due to crystal orientation more than mineral or compositional inhomogeneity. The main criterion for choosing a grain for analysis was therefore based upon grain size or shape in an effort to distinguish the widest variation between grains in the sample. However, ten analyses per sample can only be indicative of the total variation.

Sample K 92.8, which was separated both magnetically and by size, was treated differently in that 50 potassium analyses were made on different grain centres in an attempt to assess the variation in a well-defined case. X-ray diffraction using about a hundred sized and magnetically separated grains indicated an apparent single-phase sample. An analysis of 500 mg of glauconite grains gives 5.4 wt. % K_2O , while the microprobe values give an average of 5.56 % \pm 0.95 % standard deviation, with extreme values ranging from 7.73 to 3.39 wt. %, or \pm 39 % of the average.

The same procedure was used for sample K 82 giving a 6.14 \pm 0.70 % K_2O average

value and standard deviation. Extreme values indicated $\pm 31\%$ variation from the average. A 300-mg sample was analysed by flame photometry and determined to contain 6.1% K_2O .

The microprobe analyses of different grains (Na, Mg, Al, Si, Ca, K, Ti, and Fe) gave oxide totals that varied considerably in each sample, frequently $\pm 5\%$ of the oxide totals. This is probably due in part to different amounts of void space in the pellets (Odin, personal communication). Normally the microprobe gives $\pm 2\%$ variations for mineral analyses.

TABLE II

	Mg	Al	Si	K	Fe	Σ_{oct}	Mg	Al	Si	K	Fe	Σ_{oct}
	JH-63-3						A 11					
Ave	0.26	1.51	3.63	0.53	0.87	2.25	0.47	0.80	3.93	0.63	1.21	2.32
Max	0.38	1.74	3.92	0.67	1.21	2.57	0.69	1.01	4.03	0.75	1.31	2.56
Min	0.15	1.09	3.51	0.42	0.49	1.98	0.40	0.63	3.73	0.48	0.82	2.10
$\pm\%$	44	25	6	12	42	13	31	23	4	21	22	10
	A 15						K 82					
Ave	0.40	0.54	4.02	0.75	1.20	2.18	0.44	0.53	3.95	0.66	1.49	2.39
Max	0.45	0.78	4.11	0.83	1.46	2.31	0.53	0.67	4.09	0.80	1.73	2.67
Min	0.36	0.43	3.92	0.68	1.06	2.07	0.40	0.41	3.73	0.48	1.24	2.28
$\pm\%$	10	30	2	10	16	6	15	25	4	23	17	8
	K 92.8						PG 522					
Ave	0.34	0.58	3.91	0.54	1.62	2.43	0.38	1.25	3.57	0.40	1.77	2.67
Max	0.41	0.70	4.09	0.64	1.81	2.57	0.55	1.45	3.97	0.49	2.19	3.06
Min	0.30	0.52	3.71	0.40	1.38	2.22	0.31	0.58	3.13	0.35	1.15	2.30
$\pm\%$	17	15	5	22	13	7	32	35	12	17	29	14
	PG 517						number of analyses:					
Ave	0.46	1.01	3.10	0.27	2.56	3.15	JH-63-3 . . .	14	K 92.8 . . .	10		
Max	0.98	1.29	3.69	0.42	5.23	4.34	A 11 . . .	12	PG 522 . . .	13		
Min	0.30	0.69	1.98	0.09	1.88	2.62	A 15 . . .	7	PG 517 . . .	8		
$\pm\%$	73	30	12	66	75	27	K 82 . . .	9				

Ionic ratios calculated from microprobe analyses on the basis of $O_{10}(OH)_2$ per formula. All iron is assumed divalent, which tends to overestimate the ratios when Fe^{3+} is present (plus 5% for each Fe^{3+} atom present). $\pm\% = 100 \times (\max.-\min.)/2 \text{ ave.}$

Ion totals for a structure (calculated assuming 11 oxygens per unit cell and $FeO =$ total iron) were variable, depending largely upon the iron content of the sample. The assumption that all iron is ferrous will increase the number of ions for a structure calculated on the basis of a fixed anionic charge if Fe_2O_3 is present in significant quantities. Fig. 1 indicates the possible consequence of total error, i.e. $Fe \text{ total} = Fe^{3+}$, as it affects the number of ions assigned to octahedrally coordinate sites. One Fe^{3+} ion gives a surplus of 1.25% atoms, 2.0 ions a surplus of 2.5% atoms, etc. We see that the excess octahedral ions (>2.00) in many of the grain analyses could be attributed to such a miscalculation. However, some samples fall outside this limit. A plausible explanation for these grains, generally of low potassium content, is that some free iron oxide is present in the pellet. This would tend to increase the octahedral occupancy, due to the arbitrary assignment of all iron to this structural position. A pure Fe_2O_3 specimen would give eleven octahedral ions. Thus the errors due to an arbitrary

assignment of the iron to the ferrous state can be considered to give possible maximum overestimation of between 3 and 7 % of the ionic totals for the entire structure. Thus Si^{4+} for instance, could be overestimated from 3.0 atoms to 3.21. Since the $\text{FeO}/\text{Fe}_2\text{O}_3$

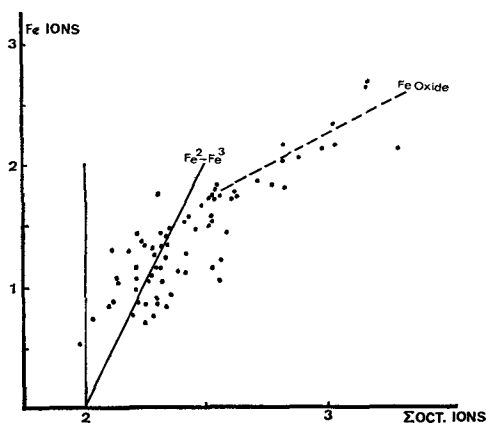


FIG. 1. Plot of the calculated iron ions, on the basis of $\text{Fe}_{\text{total}} = \text{FeO}$, versus the sum of the octahedrally coordinated ions calculated for the mineral analysis based upon $\text{O}_{10}(\text{OH})_2$ per unit cell. Strictly dioctahedral minerals should follow the line $2 = \Sigma_{\text{oct}}$ ions. The line $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ indicates the effect on the sum of calculated number of ions in the octahedral position when all of the iron is in fact Fe^{3+} . The dashed line indicates the effect on apparent octahedral occupancy of adding iron oxide to a mica sample.

(where $\text{K}_2\text{O} > 6\%$) one might use the data to indicate chemical variation in a single mineral structure. However, there is no certitude that only one phase is present in a given grain.

One must consider also the possibility of 'in-grain' inhomogeneity. Microprobe scans of the pellets with higher potassium contents, > 0.5 atoms per calculated formula, indicate only minor variations for most elements on the exposed pellet surface (Velde and Odin, in press). The most notable variation among the major elements is in iron content, which can increase by 10 % from edge to grain centre. There is, in some samples, a thin edge on the grains, about $10 \mu\text{m}$ wide, which is rich in aluminum and correspondingly poor in the other elements. The mineralogy of this zone, which must be different from the rest, has not been detected in X-ray diffraction diagrams. Undoubtedly, this is due to the small volume that this material represents, only a few per cent of each grain.

In the samples with low potassium content, especially < 0.3 atoms potassium, the composition within each grain is less homogeneous. This is probably due to the fact that the material contains other phases such as oxides and kaolinite, which are unevenly distributed in the grain. However, no systematic zoning was observed.

relation for published analyses of glauconites is usually less than one, we should consider all atomic values in Table II to be slightly overestimated. However, this is not important to the main observations that can be made upon these data.

In two samples, PG 522 and PG 517, iron oxide and kaolinite were detected by X-ray diffraction of multigrain preparations. There is no reason to assume that some individual grains analysed by the microprobe in other examples were not also multiminerall. What is important here is the relation between relative elemental abundances for grains at different stages of the process of pellet transformation from sediment to glauconitic mica. The calculated mica formulae here do not represent actual mineralogical solid solutions but do indicate relative elemental abundances in the pellets. When the grains appear to contain only one type of mineral

Irregularities in colour within a grain did not show systematic chemical variation. Since this material is less transformed, and therefore less homogenized by the process of glauconitization, one should expect greater variation from point to point in the sample.

Observations. The first and most evident observation is that each glauconite sample contains grains that differ significantly in composition. If we consider the most characteristic elements K, Fe, and Si we see that in-sample extremes, i.e. the highest minus lowest values in a sample show variations from 0.16 to 0.34 atoms K, 0.35 to 1.00 atoms Fe, and 0.16 to 0.70 atoms Si. The highest permissible values for a mica are 1.00 atoms K, 1.80 atoms Fe, and 4.00 atoms Si for the most iron-rich celadonite mica synthesized, $K Fe_{1.0}^{3+} Fe_{0.8}^{2+} Mg_{0.2} Si_{4.0} O_{10} (OH)_2$ (Velde, 1972).

It is known that the potassium contents of single phase 2 : 1 structures can vary between 0.8 and 0.3 atoms going from glauconite micaceous minerals (non-expanding structures) to potassic montmorillonites. The in-sample variation for glauconite grains found here is between 32 and 68 % of this variation. This means that each group of ten glauconite grains analysed from a single geological sample is composed of mineral pellets that cover much of the possible compositional variation even when these pellets were separated by density, size, and magnetic susceptibility.

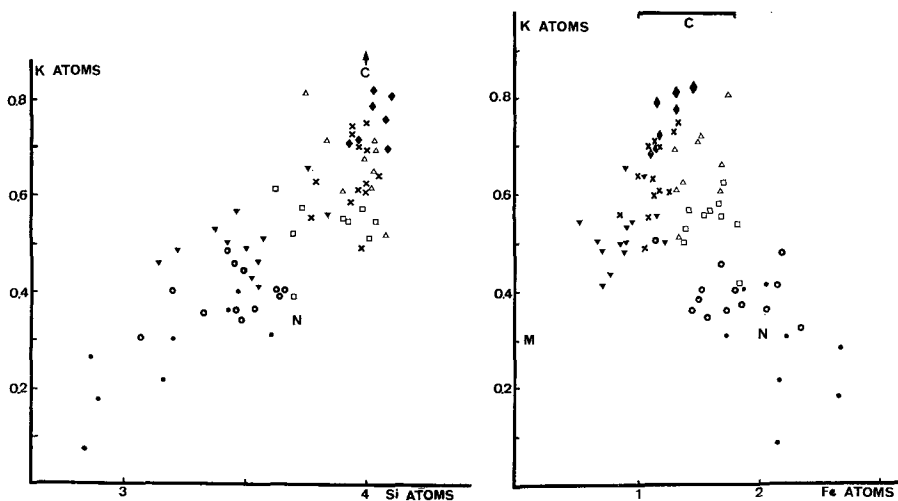
If we consider that the major compositional variations can be described using the three elements Fe-Si-K, two figures can be used to illustrate the most important relations. The K-Si and K-Fe atomic proportion plots of figs. 2 and 3 present these data.

Fig. 2 shows that an increase in potassium content is accompanied by silica increase until the tetrahedral sites are filled and the mineral becomes tetrasilicic. No grains were found to correspond to a nontronite or a montmorillonite (tetrahedrally or octahedrally charged expanding minerals), as these minerals would project on this plot. Nor is there an apparent tendency for an initial kaolinite bulk composition since potassium-poor samples are quite silica-poor. Thus one can deduce that the original sedimentary material of these samples was quite silica-poor, a mixture of oxide and silicate materials with low alkali contents. It is interesting to note that no simple single sequence is followed in the process of glauconitization. This would suggest that there is no stepwise mineral transformation, i.e. formation of a potassic nontronite mixed layered phase and then a potassic mica, etc. . . . Both types of sample, iron-poor and iron-rich, follow the same general trend on the K-Si plot, which does not pass through the compositions of expanding dioctahedral mineral (smectite) end members.

Fig. 3 relates potassium abundance and iron content. Here we see a more complex distribution where decreasing potassium content is accompanied by a wider variation in iron content. It appears that when potassium content is highest, the variation in iron content falls roughly in the range found for synthetic celadonites; between 1.0 and 1.8 atoms per formula (Velde, 1972).

The data in the figures and table indicate that as potassium content increases there is a general tendency toward chemical homogeneity between different grains in the same sample. None the less, the scatter of the analyses from grain to grain in each sample shows that there is no single path in the glauconitization process for material

with the same or similar starting composition, since each sample would have contained roughly the same initial sedimentary material. This emphasizes the deduction that each grain is a separate chemical system in the sediment, subject to local chemical conditions.



FIGS. 2 and 3: FIG. 2 (left). Plot of K and Si calculated atomic abundances. JH63-3 solid triangles; A11 crosses, A15 diamonds; K82 open triangles; K92, 8 squares; PG522 open circles; PG517 dots. N = ideal nontronite composition; C = celadonite mica. FIG. 3 (right). K and Fe atomic abundances. Symbols as in Fig. 2. M = ideal montmorillonite, N = nontronite and C indicates the range of iron content for synthetic celadonite micas.

If we consider the process of glauconitization of sedimentary oxide and silicate minerals to be mainly a variation of K, Al, and Fe variables, a description of this process could be shown by a diagram such as that in Fig. 4. Here we assume that potassium content increases toward maximum values that produce a mica-like phase, either illite for Fe-poor compositions and glauconite for more iron-rich compositions. The two inter-layered series smectite-illite and nontronite-glauconite are assumed to be distinct for all compositions. This is assumed arbitrarily. It is most likely impossible to tell when montmorillonite and nontronite are present in a mechanical mixture or when they form a true mineral solid solution.

Three different possible series of mineral transformations are traced:

Montmorillonite + kaolinite + nontronite-smectite → ferro-ferric mixed layered glauconite-nontronite + aluminous mixed layered illite-smectite → mixed layered glauconite-nontronite → glauconite mica.

Nontronitic smectite + kaolinite + iron oxide → nontronite + kaolinite → mixed layered glauconite-nontronite → glauconitic mica.

Nontronitic smectite + kaolinite + iron oxide → nontronite + iron oxide → mixed layered glauconite-nontronite + iron oxide → mixed layered glauconite-smectite → glauconitic mica.

Minerals of the first sequence I were reported by Hower (1961), those of the second and third by Giresse and Odin (1973). Other samples reported in the literature appear to fall between these extremes.

It is possible that the same mechanism, in an environment of low iron activity, could produce 'metabentonite' layers frequently reported in the literature. Such a sequence would move parallel to the K axis or possibly show a decrease in iron content, remaining on the alumina-rich side of the diagram within the illite-smectite compositional series.

Based upon the data presented here one can surmise that two extreme trends of glauconitization can occur: one by iron enrichment, and one by iron impoverishment.

Conclusions. The transition from a multiphase silicate sediment to a monophase, mica-like mineral in a pellet involves a complex chemical and mineralogical change, which does not seem to follow any simple mineralogical sequence. Even for pelletal samples where there was apparently only a mixed-layered mineral present, one cannot draw a line from any simple end-member mineral to celadonite mica that would include the natural pelletal glauconite compositions reported here.

Detrital mineral assemblages that contain kaolinite, aluminous smectite, and iron oxide evolve into a monomineralic glauconite through the destabilization of some phases and the crystallization of others. The evolution of a single glauconite pellet during the process can be considered as a distinct chemical system that is independent from the other pelletal glauconite systems present. Compositional homogeneity is attained when the pellet becomes monophase.

The grain to grain variations even in 'homogenized' material are great enough so that any multigrain determinations must be assumed to represent more than one mineralogical sample. For example, infra-red studies should be performed on one grain only and not on several at a time. Most cation exchange as well as X-ray diffraction studies that have been reported are representative of multiphase or heterogeneous materials and show only average values for a given sample.

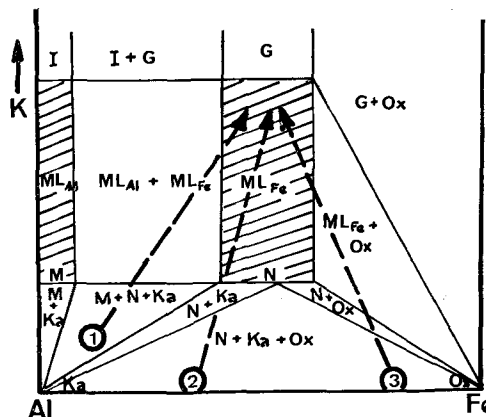


FIG. 4. Proposed relations at about 20 °C and several atmospheres water pressure for aluminous and ferric-ferrous micaceous minerals. Symbols are as follows: I = illite, G = glauconite mica, Ox = iron oxide, Ka = kaolinite, M = montmorillonitic smectite, N = nonttronitic smectite, ML_{Al} = aluminous illite-smectite interlayered minerals, ML_{Fe} = iron-rich glauconite mica-smectite interlayered minerals. Dotted lines 1, 2, and 3 indicate the path three different starting materials might take during the process of glauconitization. The process involves increase of potassium content and the attainment of an iron-rich octahedral layer in a mica structure.

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