

FURTHER INFORMATION RELATED TO THE ORIGIN OF GLAUCONITE

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Abstract—Glaucouite–smectite and illite–smectite interlayered minerals are compared by various means in an attempt to establish the mineralogical relations between the two groups. Experiments at 2 Kb pressure and 200–350°C are reported as well as microprobe scans of pelletal glauconites. This new information is used along with published chemical data in order to establish that:

(1) Illite and glauconite mixed layered phases appear to be crystallographically similar. Both series show the same relations between potassium (mica) content and the amount of smectite layers apparent in the interlayered structure.

(2) Illite and glauconite mica or mica-like phases can be separated on the basis of Fe and K contents.

(3) Probable phase relations of the two mixed layered mineral series indicate that, when the starting materials contain mixed layered mica-smectites, increasing temperature produces an iron-rich mica in the case of glauconite and an aluminous mica in the case of illite. The mixed layered phases present at intermediate temperatures are not the same for illites and glauconites.

Apparently there is no mineralogical or chemical continuity between illite and glauconite when the potassium content is 6 wt % or greater. It might be possible that the potassic interlayered minerals near montmorillonite or nontronite could form a continuous solid solution.

INTRODUCTION

The literature pertaining to the origin and mineralogic nature of glauconite is voluminous. This information need not be reviewed here in detail. Even though much attention has been given to this mineral group, several questions remain largely unanswered. Does a continuous solid solution exist between illites and glauconites? Are the physical and chemical variables which form glauconite and illite the same? In sum, how are illite and glauconite related or unrelated as mineral groups?

We present here some aspects of the chemistry and phase relations of the two series of mica-smectite interlayered minerals. We would like to know whether or not glauconite is closely related to illite; whether phase equilibria concerning one will concern the other. Is glauconite a sub-species of the much more common illite?

CHEMICAL DATA

The smectite-illite mixed layered mineral series is known from a chemical standpoint (Hower and Mowatt, 1966; Schultz, 1969; Kossovskaya and Drits, 1970) as are its solid solution limits and general phase relations under various pressure and temperature

conditions (Velde, 1969; Velde and Bystrom-Brusewitz, 1972; Velde, 1972b). The solid solution or expandability of mixed layered minerals in nature has been observed by many authors to be depth and temperature sensitive (Velde, 1972b). We will use the data presented by the above authors to represent illite mixed layered as a basis for comparison between illite and glauconite mineralogy.

The examples of smectite-glaucouite minerals used here have been reported by Manghnani and Hower (1964); Macrae and Lambert (1968); Hower (1961), Cimbalkova (1971), Odin and Giresse (1972), Odin (1971). X-ray powder diffraction, chemical determinations and hydrothermal experiments were performed on material described by Giresse and Odin (1973) and Odin (1972).

The first point investigated is the possibility of mineralogical continuity between the mixed layered mineral series of illites and glauconites. Figure 1 shows the basal spacings of nine pelletal glauconites (Odin and Giresse, 1972 and Odin, 1971) as a function of their $K_2O + Na_2O$ content. Estimations of the per cent expandable layers present can be made using the infinite thickness curves for disordered mixed layered 10–14 Å phases (Brown, 1961). The split of a single reflection in the air-dried state into two reflections upon glycolation conforms with the model used to

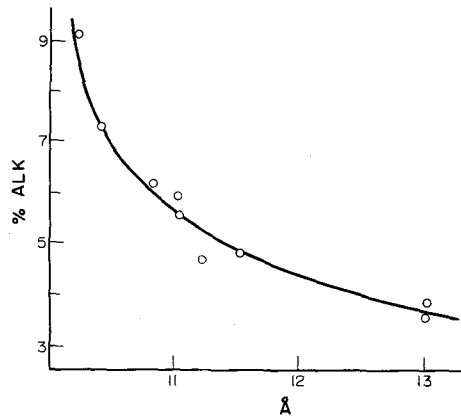


Fig. 1. Basal spacing (Å) of nine pelletal glauconites (air dried, oriented preparation) as a function of their $K_2O + Na_2O$ content (wt% alkali).

calculate the expandability curves. Similar expandability vs K_2O relations are reported by Manghnani and Hower (1964) and Macrae and Lambert (1968) for the expandability range of 50–10% smectite layers. If we compare these "glauconite" curves with that for illite-smectites (Hower and Mowatt, 1966) (Fig. 2), it is apparent that the two series, illite and glauconite, are crystallographically similar. For both of these mineral groups, alkali oxide contents of more than 7 wt% are necessary to obtain a 10% or less expandable phase. Thus, reported illites or glauconites with smaller amounts of alkalis present are either of greater expandability or contain other phases.

Let us now consider a second chemical variable; iron content. Glauconites are typified by a high amount of iron present essentially as Fe^{3+} ; illites and ferric illites contain significantly less iron (Gabis, 1963; Kossovskaya and Drits, 1970). If we suppose that $K_2O + Na_2O$ represent an acceptable measure of expandability, or smectite content, in the mixed

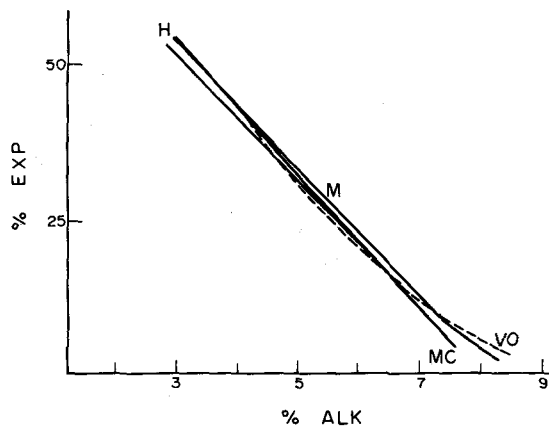


Fig. 2. Comparison between curves obtained for illite-smectite and glauconite-smectite series as a function of their alkali (% Alk.) and expandable layer content (% Exp.).

H = Hower and Mowatt (1966) illite minerals
 M = Manghnani and Hower (1969) on glauconites
 MC = MacRae and Lambert (1968) on glauconites
 VO = this paper on glauconites, dashed line

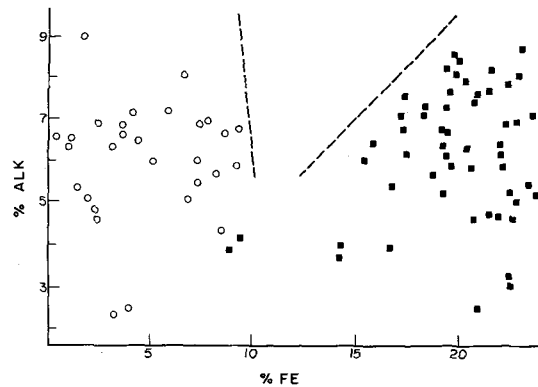


Fig. 3. Relation between interlayer cation content (weight % Alk.) and weight per cent $Fe_2O_3 + FeO$ content (% FE) in illite-smectite and glauconite-smectite series. Glauconites—■, illites—○.

Hower and Mowatt (1966): illitic minerals
 Kossovskaya and Drits (1970): ferric illites
 Cimbalnikova (1971),
 Parry and Reeves (1966),
 Hower (1961): glauconites
 New analyses of glauconites from Odin (1971, 1972) and
 Odin and Giresse (1972).

layered minerals (Fig. 2) it appears that illites and glauconites can be distinguished on the basis of their iron contents when alkali contents are high (approaching a mica-like phase) (Fig. 3). At lower alkali contents (higher smectite content) the two series appear to overlap though very few reported glauconites have less than 15% iron and no illite-smectite minerals have more than 10% iron (see Fig. 3). As already noted by Foster (1969) there is no linear relationship between iron and alkali content since the more highly expandable minerals show a great range of iron content. Thus there appear to be two distinct chemical types of mineral association in the sedimentary, potassic, smectite-mica interlayered mineral series.

If we consider the examples of incipient glauconitization reported by Odin (1971, 1972) in the Ypresian series of the Belgian Tertiary Basin and that reported by Giresse and Giresse and Odin (1973) in recent kaolinite-rich sediments off the coast of Gabon, it appears that the change in iron content can be quite rapid, i.e. early in the process of glauconitization. These high iron contents (> 20 wt% total iron oxide) remain fairly constant for samples which contain larger amounts of K_2O or the mica component of the glauconite-smectite interlayer mineral. Ehlmann, Hulings and Glover (1963) in a study on recent sediments of the Southeast United States Coastal Province made similar observations. Figure 4 shows these iron-rich glauconite samples as they compare to illite-smectite minerals which contain relatively little iron. The glauconites which fall between these two series, at low potassium contents (Fig. 3) must reflect starting material which did not react in the same way as that which produced the high iron content glauconites.

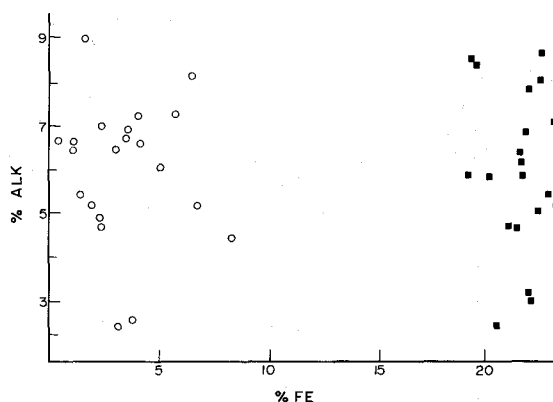


Fig. 4. Relation between interlayer cation content and $\text{Fe}_2\text{O}_3 + \text{FeO}$ content in two parallel mineralogical series.

○—data from Hower and Mowatt (1966)
 ■—data of pelletal glauconites from and Ypresian series where pellets are contained in aluminous smectite-bearing sediments and from Recent Atlantic Ocean sediments where the pellets are initially kaolinitic.

The trend during potassium enrichment of the aluminous glauconites is one of iron-enrichment (Hower, 1961).

Thus two mineral series can be separated by differences in their bulk compositions at the latter stages of evolution toward the micaceous end-members. These two series of interlayered minerals, although chemically different, appear to have the same crystallographic characteristics. We can answer the first question posed; there is no continuous solid solution between illite and glauconite. Glauconite cannot be a continuously altered or transformed illite or vice versa. The mineralogical continuity that appears to exist is between potassic smectites, aluminous or ferric.

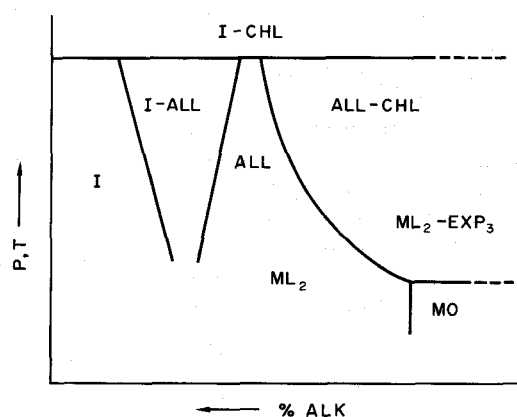


Fig. 5. General phase relations of illite-smectite minerals as a function of pressure and temperature (P, T) and alkali content. The percent of interlayer cations increases from right to left.

I—illite; Chl—chlorite; All—allevardite; ML_2 —dioctahedral mixed layered; Exp_2 —dioctahedral smectite; Exp_3 —trioctahedral smectite; MO—Montmorillonite, Di- and trioctahedral.

PHASE RELATIONS OF INTERLAYERED ILLITE AND INTERLAYERED GLAUCONITE MINERAL SERIES

The general phase relations of illite-smectite minerals as a function of pressure and temperature are known from observations of sequences of deeply buried sediments as well as from hydrothermal treatments of natural minerals in the laboratory, and from experiments in simplified chemical systems approaching the compositions of natural minerals (Velde, 1972b). Figure 5 attempts to summarize this information. Schematically, as temperature is raised the expandability of the mixed-layered phase decreases. This change in mineralogy is accompanied by the production of a Mg-Fe-rich phyllosilicate such as vermiculite, trioctahedral smectite or chlorite. In such a chemical system, the dioctahedral expandable phase can become ordered when 30–50% smectite layers are present. This phase will be called allevardite, although the type allevardite is 50% smectite. We see in the diagram that the initially continuous mixed layered series divides into two parts as temperature increases, one with an ordered, mixed layered phase and another with an illite-like phase which is alumina-rich.

Experiments have been performed in conventional hydrothermal equipment (see Velde, 1969) over a one month period using natural iron-rich (20–25% $\text{Fe}_2\text{O}_3 + \text{FeO}$) glauconite pelletal material and distilled water sealed in gold capsules (samples 82-6b, 92-8b, 97-2b, Odin *et al.*, 1972 and the Franconia Fm. sample of Hower, 1961). Samples 82-6b, 92-8b and 97-2b are Tertiary pelletal glauconites. The Franconia glauconite is Cambrian. In Fig. 6 the average potassium content of the samples used is plotted against the temperature at which the experiments were run. The results (listed in Table 1) are used to construct

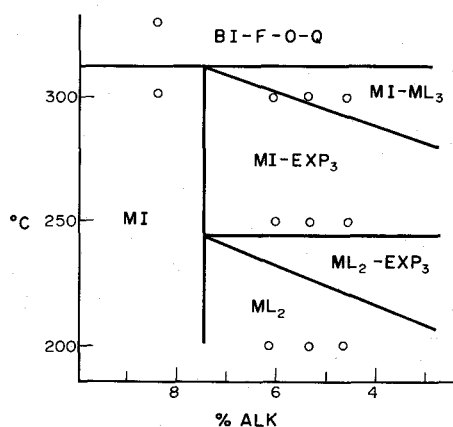


Fig. 6. Results of one month experimentation on four natural pelletal glauconites of different composition (% Alk.). Experiments were performed at various temperatures ($^{\circ}\text{C}$) under 2 KB pressure.

ML—glauconite mica-like mineral; ML_2 —dioctahedral mixed layered; ML_3 —trioctahedral mixed layered; Exp_3 —trioctahedral smectite; BI + F + O + Q: biotite + feldspar + oxides + quartz.

Table 1. Results of experiments using natural glauconites. The mean index of refraction was measured on the green fraction of the sample. The accompanying brown phase had a variable index, but it was in all cases superior to that of the green phase. (Index of refraction is a function of iron content)

Temperature °C	Mean Index	(060) Å	(001) air dry Å	(001) glycol Å
<i>Sample -97m</i> : % (K ₂ O + Na ₂ O) = 4.8				
25	1.590	1.514	11.5	10
200	1.598	1.513	10.6 + 14(?)	10 + 18?
250	1.604	1.517	10.6 + 14(?)	10
300	1.607	1.519	10.5	9.8 + 11.4
<i>Sample -92m</i> : % (K ₂ O + Na ₂ O) = 5.6				
25	1.600	1.515	11.0	10 + 18
200	1.602	1.514	10.6	10 + 18?
250	1.606	1.516	10.6	10 + slope
300	1.612	1.518	10.5	10 + 11.4
<i>Sample -82m</i> : % (K ₂ O + Na ₂ O) = 6.35				
25	1.602	1.519	11.0	10
200	1.604	1.519	10.8	10 + slope
250	1.606	1.515	10.8	10 + slope
300	1.611	1.521	10.4 + 14.9	10 + 16.7
<i>Sample Franconia</i> : % (K ₂ O + Na ₂ O) = 8.4				
25	1.624	1.517	10	10
250	1.624	1.517	10	10
300	1.626	1.519	10	10
350	no green mica	1.541	10	10

the phase diagram in multicomponent space. Several remarks must be made concerning these experimental results. First, no attempt has been made to verify the reaction rates of mineral transformation or to test whether the phases obtained at a given temperature at the end of one month at 2 Kb pressure are in fact those ultimately stable under these conditions. Experiments lasting six months do not guarantee the determination of phase boundaries in P-T space when natural phyllosilicate minerals are used as starting material (Velde and Bystrom-Brusewitz, 1972).

However in this last study where natural illite-smectite interlayered minerals were used as starting material, the mineralogy of the run products was found to correspond quite closely to those phases found in sequences of sediments and sedimentary rocks subjected to high grade diagenetic or epi-metamorphic conditions. There is also a close agreement with experiments in the synthetic system pyrophyllite-muscovite. It would appear that the experiments on natural minerals produce the same sequence of mineral facies which are found in nature. However, the temperatures at which the different assemblages are produced in the laboratory are undoubtedly too high. Thus the physical variables determined in the experiments do not represent thermodynamic equilibrium values establishing the limits between mineral assemblages. But, the sequences of "events" in a given system as a function of temperature can be used to compare two different mineral groups. Thus the tentative phase relations (in the form of a phase diagram) can be used as a method of determining differences or similarities between illite-smectites and glauconites.

It should be noted that the phase relations in Fig. 6 have been drawn only on the basis of the phases

observed in the experiments; variables such as the oxygen fugacity during the experiments and the variations in bulk composition of each sample have not been considered. Thus the experiments reported here must be taken only as an indication of the assemblages which will be produced in nature when a rock containing glauconite pellets experiences the initial phases of metamorphism.

If one compares the phase relations of the illite and glauconite mixed layered minerals series (Figs. 5 and 6), the major difference appears in the solid solutions of the mixed layered dioctahedral mineral. Illite-smectite forms an ordered mixed layered phase which is stable to relatively high temperatures, while glauconite solid solution diminishes rapidly as temperature rises. No evidence of ordering near 30% expandability was found for natural specimens. The phase relations of mixed layered glauconites and illites at elevated temperatures and pressures are thus distinctly different. However, they are similar in that higher temperature increases the exsolution of a trioctahedral phyllosilicate phase. In the case of the illite-mixed layered phase, the dioctahedral mineral is relatively enriched in alumina by this exsolution while glauconite is enriched in Fe³⁺ as evidenced by the increase in the (060) spacing and the index of refraction of the green mica produced in the experiments (Table 1). These two parameters increase as Fe³⁺ content increases in synthetic celadonite mica (Velde, 1972a). The mineralogical evolutions of mixed layered minerals toward a mica-bearing assemblage are parallel to the alkali vs iron plots for illites and glauconites (Fig. 3). One can assume that high grade diagenesis of low grade metamorphism will produce either illite-chlorite or glauconite(mica)-chlorite assemblages from originally mixed-layered minerals.

This is the stage preceding the destruction of glauconite during metamorphism as reported by Frey *et al.* (1973), where stilpnomelane is formed.

REMARKS ON THE MECHANISM OF PELLETAL GLAUCONITE FORMATION

Pelletal glauconite is found in localized zones in a sediment or rock which is usually rounded in shape. It is a generally accepted fact now that glauconite pellet formation is a small scale phenomenon which involves chemical transfer in a micro-environment (Odin and Giresse, 1972). In such processes a chemical gradient is established between the crystallizing mineral and the environment in which it forms. One can assume that chemical transfer is effected between aqueous solution and silicate. The sediments which will eventually surround the glauconite pellet upon burial will not show evidence of this transfer. When the process involves several elements which behave as perfectly mobile components, i.e. their chemical activity in solution determines their presence in solid phases, the glauconitized pellets should then be zoned in a simple manner with a small number of phases present in each zone (Korshinskii, 1965).

Electron microprobe scans of the pellets studied show a compositional zoning. Regardless of potassium content of the sample concerned (Fig. 1), the pellets are surrounded by a thin (roughly 10 μm) alumina-rich outer zone (about 15 wt % Al_2O_3 which is about twice that of the pellet centers). Due to the chemical variability from grain to grain, quantitative analyses were not made. In each case the determined composition was not that of a uniquely defined mineral. Further, the mineralogical character of the alumina-rich border could not be assessed. No evidence of a phase other than glauconite was found by X-ray diffraction in the global samples (50–100 grains). This not surprising since the 10 μm wide zone

often represents less than 1% of the volume of each glauconite pellet. Figure 7 shows this grain boundary as detected by microprobe scans giving a typical profile for Al, K and Fe content across a grain. There is a 10–15 % increase in the Fe content from edge to center of the pellet excluding the 10 μm fringe. Other elements, Si, Mg, Ca, did not show any consistent variations. These observations strongly suggest that there is a variation in the pellets of aluminum and iron and that it can be explained as a gradient in the chemical activity of these elements.

We have looked for this zonation in other glauconite samples, coming from Cretaceous and older rocks. No zoning was found. It is possible that the thin edge of the grain was eroded during the sedimentation processes or perhaps epi-metamorphic or diagenetic conditions (temperature > 50°C for example) have homogenized these materials.

CONCLUSION

The experimental evidence reported here tends to confirm certain hypotheses proposed concerning glauconite genesis. We might summarize our view by responding to the questions posed in the introduction of this paper as follows:

(1) Glauconites are chemically distinct from illite-smectite mixed layered minerals as evidenced by the alkali and iron content of the two types of minerals.

(2) The phases produced at elevated pressures and temperatures are different in the two series, the illites become alumina-rich and glauconites become more ferric.

(3) Illite and glauconite, if formed in the sedimentary environment, are produced by different chemical processes. Pelletal glauconites are the result of the imposition of a chemical gradient upon sediments in a distinct spatial localization. Illites are probably formed in most cases through variations in the bulk composition of the sediments. Single-phase illite is rare in sediments. In any event, the production of illite necessitates a high alumina content with an increase in K_2O content, while the evolution of sediments toward glauconite compositions necessitates high iron content and an increasing potassium content as a more mica-rich phase is produced.

These points emphasize the conclusion that glauconite is not a subspecies of illite, thus ferric illites are not intermediate forms of a continuous illite-glauconite compositional series. Any graphical representation of illite and glauconite, then, must separate the two types by variations along a $\text{Al} - \text{Fe}^{3+}$ compositional line. Projections into a simplified R^{3+} coordinate will superpose the two chemically distinct mineral groups.

Concerning the process of glauconitization, it seems that the initial starting material is not of great importance to the process, either iron-poor or iron rich. Physiochemical properties of the pelletal aggregate such as the organic content (Eh) or porosity of the

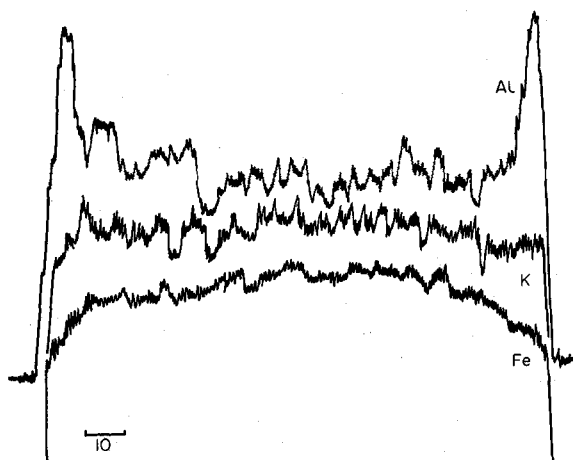


Fig. 7. Representative microprobe scans for K, Fe, Al in pelletal glauconites. The figure indicates the existence of an aluminum-rich, iron-poor external zone. Potassium is regularly distributed as are silica, magnesium and calcium.

material will play an important role, (Aubry and Odin, in press). It is possible that similar processes produce illites or mixed layered minerals such as those found in so called meta-bentonites.

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REFERENCES

- Aubry, M. P. et Odin, G. S. (1975) Sur la nature minéralogique du verdissement des craies: *Bull. Soc. Géol. Normandie*. In press.
- Brown, G., Editor (1961) *The X-ray Identification and Crystal Structure of Clay Minerals*: Mineral Soc. London, 544.
- Cimbalnikova, A. (1971) Chemical variability and structural heterogeneity of glauconites : *Am. Miner.* **56**, 1385–1398.
- Ehlmann, A. J., Hulings, N. C. and Glover, E. D. (1963) Stages of glauconite formation in modern foraminiferal sediments : *J. Sedim. Petrol.* **33**, 87–96.
- Foster, M. D. (1969) Studies of celadonites and glauconites : *Geol. Survey prof. Paper*, U.S.A. **614F**, p. 17.
- Frey, M., Hunziker, J. C., Roggwiler, P., and Schindler, C. (1973) Progressiv niedriggradige Metamorphose glaukonitführender Horizonte in den Helvetischen Alpen : *Contr. Mus. Pet.* **39**, 185–218.
- Gabis, V. (1963) Etude minéralogique et géochimique de la série sédimentaire oligocène du Velay : *Bull. Soc. franç. Minér. Crist.* **86**, 315–314.
- Giresse, P. et Odin, G. S. (1973) Nature minéralogique et origine des glauconies du plateau continental du Gabon et du Congo : *Sedimentol.* **20**, 457–483.
- Hower, J. (1961) Some factors concerning the nature and origin of glauconite : *Am. Miner.* **46**, 313–334.
- Hower, J. and Mowatt, T. C. (1966) The mineralogy of illite and mixed-layer illite–montmorillonite : *Am. Miner.* **51**, 825–854.
- Korzhinskii, D. S. (1965) The theory of systems with perfectly mobile components and processes of mineral formation : *Am. J. Sci.* **263**, 193–205.
- Kossovskaya, Q. G. and Drits, V. A. (1970) The variability of micaceous minerals in sedimentary rocks : *Sedimentol.* **15**, 83–101.
- Lamboy, M. (1967) Répartition de la “glauconie” sur le plateau continental de la Galice et des Asturies (Espagne): *C.r. Acad. Sci.*, Paris **265**, 855–857.
- Macrae, S. G. and Lambert, J. L. M. (1968) A study of some glauconites from cretaceous and tertiary formations in southern England : *Clay Minerals* **7**, 431–440.
- Manghnani, M. and Hower, J. (1964) Glauconites : cations exchange capacities and i.r. spectra : *Am. Miner.* **49**, 586–598.
- Odin, G. S. (1971) Sur la genèse des glauconies et leur signification sédimentologique : *C.r. Acad. Sci. Paris* **272**, 697–699.
- Odin, G. S. (1972) Modalités du passage continu du sédiment argileux au minéral glauconite dans les formations éocènes du Rodeberg : *C.r. Acad. Sci. Paris* **274**, 660–663.
- Odin, G. S., Blondeau, A., Damotte, R., Durand, S., Ollivier, M. F., Le Calvez, Y., Lezaud, L., Perreau, M. et Pomerol, C. (1972) Le sondage de Cassel : *Bull. Inf. Bass. Paris* **32**, 21–52.
- Odin, G. S. et Giresse, P. (1972) Genèse de sédiments phylliteux (berthiérine, smectite ferrique, glauconite ouverte) dans les sédiments du golfe du Guinée: *C.r. Acad. Sci. Paris* **275**, 177–180.
- Parry, W. T. and Reeves, C. C. (1966) Lacustrine glauconitic mica from plural Lake Mound, Lynn and Terry Counties, Texas : *Am. Miner.* **51**, 229–235.
- Schultz, L. G. (1969) Lithium and potassium adsorption; dehydroxylation temperature and structural water content of aluminous smectites : *Clays and Clay Minerals* **17**, 115–149.
- Velde, B. (1969) The compositional join muscovite–pyrophyllite at moderate temperatures and pressures : *Bull. Soc. franç. Min. Cristallogr.* **92**, 360–368.
- Velde, B. (1972a) Celadonite mica : solid solution and stability : *Contrib. Min. Petr.* **37**, 235–247.
- Velde, B. (1972b) Phase equilibria for dioctahedral expandable phases in sediments and sedimentary rocks : *Proc. Int. Clay Conf. Madrid* 285–300.
- Velde, B. and Bystrom-Brusewitz, A. M. (1972) The transformation of natural clay minerals at elevated temperature and pressure : *Geol. For. Foch.* **94**, 449–458.
- Zumpe, H. H. (1971) Microstructure in cenomanian glauconite from the Isle of Wight, England : *Min. Mag.* **38**, 215–224.