

SYNTHESES OF GLAUCONITE AT SURFACE TEMPERATURES

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Abstract—Glaucanite has been synthesized at low temperature by precipitation of Fe-hydroxides from Si-, Fe-, Al-, and K-containing solutions under reducing conditions. The compositions favorable for the synthesis at 20°C and pH 8.5 are 1 ppm Fe, 0.15 ppm Al, 13 ppm SiO₂, 1000 ppm KCl, and 1000 ppm dithionite. The K-content of the solutions must be sufficiently high to fix K in the precipitate.

Under special early diagenetic conditions glauconite is formed in marine sediments, probably at the interface between reducing and oxidizing zones in the muddy sediments. The silica content of pore waters seems to control the formation of glauconite or chamosite rather than depth or temperatures of the bottom waters.

Key Words—Glaucanite, Diagenesis, Pore solutions, Synthesis.

INTRODUCTION

Although glauconite is quantitatively of minor mineralogical importance, the conditions and manner of its formation have been the subject of considerable investigation (Gümbel, 1886; Cayeux, 1897; Correns, 1939). Opinions on its mode of formation have been reviewed by Cloud (1955), McRae (1972), and Kohler (1977). Previously, all syntheses of glauconite have been carried out at elevated temperatures. Calderon *et al.* (1895) synthesized glauconite(?) from mixtures of oxides and hydroxide-SiO₂-gels. Noll (1932), Wise and Eugster (1964), and Velde (1965) synthesized different mica minerals including Fe-containing celadonite at high temperatures and pressures. Birdsall (1951) used colloidal solutions to synthesize a poorly crystalline glauconite. Glaucanite-smectite interlayered minerals have been synthesized at 2 kbar pressure at 200°–350°C by Velde and Odin (1975).

In the last few years many other clay minerals have been synthesized at low temperatures. Harder (1972) showed that tri- and dioctahedral smectites could be synthesized at temperatures <3°C from magnesium- or iron-containing aluminum hydroxide-silica precipitates. With potassium in the solution, illite also could be synthesized. Harder (1978a, 1978b) showed that hydroxide substrates enhance the formation of several different layer silicates. Since Fe(OH)₂ is isomorphous with brucite, it was reasonable to expect that hydrous iron silicate could be synthesized from such material in Fe-rich solutions under reducing conditions. Amorphous hydroxides of iron are capable of coprecipitating with SiO₂ by chemisorption from very dilute solutions. Also, K is enriched in the amorphous hydroxides relative to Na because of its lower hydration energy. The factors which control these chemisorption processes have been discussed in previous papers (Harder, 1965, 1978b; Flehmig, 1967; Kurze, 1971).

SYNTHESIS TECHNIQUE

Hydroxides were precipitated from solutions containing Fe, Si, K, and, in some cases, Al and Mg. Eh was measured by a platinum electrode with a calomel reference electrode. Tenth percent sodium or potassium dithionite solution produced an Eh of -0.6 V, and a pH of 8.0. A nitrogen atmosphere was used to stabilize these reducing conditions during handling. Silica (3–100 ppm SiO₂) was added as monomeric silicic acid. The Fe solution (0.3–10 ppm Fe) was always freshly prepared from FeSO₄. K and Na were introduced as KCl and NaCl in the range 0.1–1000 ppm K and 5–2000 ppm Na. Fe was precipitated from FeSO₄ solution by changing the pH. The precipitates were filtrated, washed with O₂-free water, and dried. The synthetic products are generally bright green, but, similar to natural glauconite, a variety of other colors from pale straw-yellow through various shades of green, blue, brown, or black were found also. The green-grey colors of some wet products were not stable, changing to black and grey and finally to brown upon exposure to air. The mica structure, however, did not change. These products could be dried under N₂ atmosphere without changes in color.

X-RAY POWDER DIFFRACTION ANALYSIS

Initially, all hydroxide-silica precipitates were X-ray amorphous, but after a short aging time in solution, some of the precipitates showed X-ray diffraction reflections of clay minerals. Others remained completely amorphous even after longer aging times. X-ray reflections of glauconite or other Fe clay minerals were detected after only 1 day of aging. The aging time in the Fe experiments was extremely short compared to those in the Al-Mg-Si-experiments where several months were needed for crystallization (Harder, 1972).

Because the synthetic glauconite products were

Table 1. X-ray powder diffraction data for natural and synthetic glauconites.

Indices hkl	Natural glauconite		Synthetic glauconite	
	d (Å)	Intensity	d (Å)	Intensity
001	9.9	medium	9–12	strong (broad band)
020	4.51	medium	4.5–3.3	medium (broad band)
	3.66	medium		
003	3.3	medium		
130	2.58	strong	2.55	strong
114	2.402	medium		
	2.14	weak		
	1.99	weak		
	1.65	medium	1.61	weak
060	1.515	strong	1.51 ¹	strong

¹ The (060) reflection varied in different experiments from 1.495 to 1.54 Å. Some reflections indicate dioctahedral and others trioctahedral synthetic products.

mostly poorly crystallized, only powder diffraction patterns with the Debye-Scherrer camera were obtained, using CoK α radiation. The diffraction patterns showed more or less diffuse, broad peaks (Table 1). Nevertheless, the X-ray powder diffraction (XRD) data of the products agree with those of young natural glauconites. The basal spacing of the Fe-containing clay mineral products varied in different experiments from 9 to 12 Å. The glauconite-rich synthetic products do not expand with ethylene glycol and show a prominent basal spacing of 10 Å regardless of the treatment. This indicates a nonexpandable, mica-type clay. But some of the synthesis products show a more diffuse basal spacing which changes on glycol treatment to 13–17 Å with a very diffuse peak and after heat treatment to a 10-Å spacing. The decrease in sharpness and the shift of the basal spacing indicate a material composed of smectites, mica, and/or chamosite layers and a variation in the extent of interlayer hydration of the synthetic products.

The reflections at 4.5 and 3.3 Å were weak and usually broad bands in the synthetic products. In young natural glauconites, fairly sharp (020) and (111) reflections can be observed, and in older natural glauconites additionally, the (021) reflection. In the synthetic products these reflections appeared as broad bands at 2.56 and 1.61 Å. (See also Figure 1.)

The (060) reflections of the synthetic products were relatively sharp and strong and were found between 1.495 and 1.54 Å (see Table 1). Both di- and trioctahedral products were apparently synthesized. Natural glauconites are dioctahedral mica-minerals. Burst (1958), Valeton (1958), and Thompson and Hower (1975) pointed out that material described as glauconite varies in composition from illite-smectite to glauconite mixed-layer minerals in different ratios. The synthetic products are closely analogous to natural glauconites, in that some appear to be micas and some appear to be mixed-layer phases.

CHEMICAL ANALYSIS

Some of the precipitates were analyzed for Fe, Al, Mg, Si, and K after drying and dissolving in HF and H₂SO₄. Fe was determined spectrophotometrically by the 0-phenanthroline method, Al after separation from Fe with 8-oxichinolin in CHCl₃, and Mg and K by atomic absorption spectrometry (AA).

It is not certain whether the material analyzed is monomineralic in composition or a mixture of clay minerals and X-ray-amorphous materials.

EXPERIMENTAL RESULTS FOR GLAUCONITE SYNTHESIS

The experimental conditions under which glauconites were formed are given in Table 2 along with the composition of the initial solutions and of the aged crys-

Table 2. Glauconite formation at pH = 8–9.

Reducing condition % dithionite	Concentration in initial solution						Composition of precipitate after 3–10 days aging time						X-ray diffraction reflection	
	SiO ₂ (ppm)	Fe (ppm)	Al (ppm)	Mg (ppm)	KCl (%)	NaCl (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	MgO (%)	K ₂ O (%)	Na ₂ O (%)	d(001) (Å)	d(060) (Å)
20°C														
0.1	13	1	0.15	300	0.1	0.1	55	16	10	11	6	1.9	11	1.50
0.03	13	0.6	0.15	300	0.1	0.1	57	15	13	7	6	2.1	9.6	1.51
0.1	13	0.6	0.15	300	0.1	0.1	48	22	14	9	5	2.2	9.8	1.52
0.1	11	1	0.15	100	0.1	0.1	40	31	18	4.6	5	2	10.8	1.53
0.1	11	1	0.15	100	0.1	0.001	36	11	38	2	9	0.4	11	1.52
0.1	11	1	0.15	—	0.1	0.1	35	42	18	—	3	2.4	9–12	1.53
0.1	11	1.5	0.15	—	0.1	0.001	36	43	17	—	2.9	0.4	12	1.51
3°C														
0.1	13	2	1	100	0.3	0.1	46	19	29	4.5	4.5	1.1	17–10	1.50
0.1	13	2	0.1	100	0.1	0.001	61	7	25	1.5	5	0.6	12–10	1.51
0.1	13	0.6	0.15	300	0.1	0.1	69	3.0	19	2.8	3.5	1.5	10	1.52
0.1	11	1.5	0.15	—	0.1	0.001	51	21	25	—	2.5	0.5	14–10	1.50

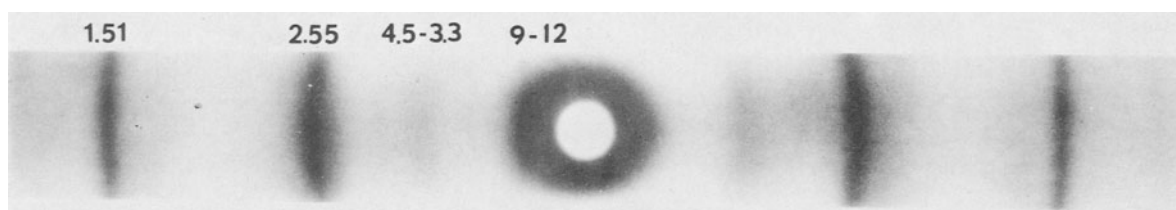


Figure 1. X-ray powder diffraction photograph taken with $\text{CoK}\alpha$ radiation of synthetic glauconite. Such products are poorly crystallized, showing only diffuse, broad peaks. d-spacings of the lines in Å.

talline precipitates. The chemical compositions of the X-ray-amorphous precipitates are not listed in the tables, but the results of some of these investigations are discussed below. From the data listed in Table 2, the following conditions favored the formation of glauconite:

1. Fe-containing mica minerals were synthesized only under reducing conditions in a short time at low temperatures. The formation of the Fe^{3+} layer silicate minerals was possible only when Fe^{2+} was present in the solution during the formation of glauconite-mica layer silicate. The dark green to black color of precipitates which gave only the XRD pattern of a dioctahedral Fe-clay mineral and which were rich in Fe^{3+} indicate that some Fe^{2+} was present. Mössbauer (Annersten, 1975) spectrographic investigation confirmed the presence of Fe^{2+} . Under reducing conditions, small amounts of Fe^{2+} in solution led to the formation of an Al-rich and Fe-poor three-layer mineral instead.
2. High pH favored rapid Fe-clay mineral formation. A glauconitic phase was formed from solutions with pH 7, mostly between 8 and 9. Natural glauconite formation may take place over a wider range of Eh than reported here due to longer reaction time.
3. Temperature had only minor influence on the synthesis of glauconites which formed at both 3° and 20°C. However, higher temperatures generally led to better and more rapid crystallization.
4. Silicate minerals formed at low temperatures (20° and 3°C) only in those precipitates that were in contact with monomeric silicic acid solutions (Harder and Flehmig, 1970). Polymerization of the silicic acid appears to have inhibited the formation of clay minerals. In polymeric solutions, the hydroxide-silica precipitates remained amorphous even when the composition of the precipitates was similar to those of the clay minerals. For glauconite formation, 13 ppm SiO_2 , together with 0.6 ppm Fe, was found to be the optimal condition. At silica contents between 10 and 15 ppm, glauconite formed. Crystal growth probably took place in the pores of the hydroxide-silica gels. Lower silica content, e.g., 7 ppm, led to the formation of chamosite. If the silica content in the solutions was <5 ppm SiO_2 or >100 ppm (at pH 8), clay minerals did not form.
5. The concentration of silica in such hydroxide-silica precipitates should be similar to the stoichiometric composition of glauconite, if mineral formation is to take place. Low concentrations of Fe (1 ppm) and Al (0.15 ppm) in the initial solution promoted glauconite crystallization. The SiO_2 content of precipitates was dependent on the composition and the ratio of hydroxide to Si of the initial solution and on the pH and Eh during the precipitation. The silica content in the precipitates controlled whether the silicate that formed was a three-layer or a two-layer clay mineral. If the silica content in the precipitates was between 35 and 60% SiO_2 (water omitted from the calculation) glauconite formed at low temperatures. Glauconite formed in solutions with Fe + Al to Si ratios between 1:10 and 1:6. When the ratio of Fe to Si in the solutions was between 1:1 and 1:2, the silica content in the precipitates was between 25 and 35% SiO_2 , and greenalite and chamosite formed. It seems that Mg was not absolutely necessary for the synthesis of glauconite. However, Mg aided in the crystallization of this phase, and it is universally present in seawater.
6. High K content in solution was necessary for glauconite formation. All products containing large amounts of glauconite or illite formed from solutions with high KCl content. For K to precipitate, the solution must have a KCl content ≥ 300 ppm. Lesser amounts of KCl in solution do not lead to K-rich precipitates.

These data indicate that the formation of synthetic glauconite from iron hydroxide precipitates requires slightly reducing conditions. The synthesis is possible over a fairly wide range of temperatures. Less than 1 ppm Fe, about 0.1 ppm Al, 10–15 ppm SiO_2 , and a high K content in solution are necessary for the synthesis of glauconite.

NATURAL GLAUCONITE FORMATION

The genesis of natural glauconite can be discussed in the light of recent investigations of clay mineral synthesis. The present experiments show that glauconite may form by the precipitation of Fe-hydroxides and adsorption of silica and K from dilute solutions at low temperatures at seawater pH and under slightly reducing conditions. Two mechanisms have been suggested for the formation of glauconite during diagenesis: (1) neof ormation and (2) transformation of detrital clay minerals into glauconite by a substitution of Fe for Al. The transformation mechanism was mentioned by Cayeux (1897), Gallihier (1936), Schumann (1940), Burst (1958), Morgarovski (1963), and others. Such a mechanism requires bond breakage and would be difficult under low surface temperatures. Kohler and Köster (1976) noted that the trace element contents of Ti, Cr, Mn, Ni, Co, Pb, Ba, and Li in magmatic micas are much higher than in glauconites, suggesting that glauconite could not have been formed by the direct transformation of primary micas. The present experimental data demonstrate that transformations of clay minerals are not necessary. Several of the neof ormation reactions suggested previously by Murray and Phillippi (1908), Andrée (1920), Berz (1921, 1926), Hummel (1922), Smulikowski (1954), and Borchert and Braun (1963) seem to be more suitable. Syngenetic glauconites in recent marine sediments have been known for a long time (Takahashi and Yagi, 1929; Porrenga, 1967; Gärtner and Schellmann, 1965).

Comparing the experimental results with natural conditions, it can be shown that the Fe and SiO₂ content of seawater are by far too low for the formation of glauconite. The concentration of these elements in river waters is of the right order of magnitude, but the lack of potassium prevents glauconite formation. Therefore, the elements necessary for the formation of glauconite (Fe, Al, SiO₂, K) must not originate from normal seawater or river water.

Diagenetic processes between detrital Fe-bearing minerals and pore waters seem to be more important than a primary formation. During diagenesis reducing conditions necessary for glauconite formation can be produced, e.g., in fossil-rich sediments or in fecal pellets. In such sediments the association of glauconite with organic residues is common (Ehrenberg, 1855; Takahashi and Yagi, 1929; Hadding, 1932; Wetzel, 1937). Reducing conditions develop in many sediments soon after deposition, mainly by bacterial decay of organic material which consumes oxygen of the pore waters. The Eh of the pore waters is dependent on oxygen diffusion from the sediment surface and the strength of reducing conditions in the sediments. Redox conditions change fast with depth. In a distinctly reducing hydrosulfuric medium produced by sulfate-re-

ducing bacteria, pyrite will form, and no glauconite formation is possible (Berz, 1921).

In a reducing zone, without O₂ and S²⁻, Fe is soluble, and dissolution of Fe from Fe-containing minerals, or more easily from colloidal iron hydroxide particles, is possible. Here, Fe becomes enriched in the pore solutions relative to Al. If this mobilized Fe migrates by diffusion towards zones with oxidizing conditions, most of it will precipitate in the form of Fe³⁺ hydroxides. Such precipitates will also sorb silica, Fe²⁺, Al, K, Mg, B, and other ions from the pore solutions. The silica in these pore solutions and in the deeper seawater was mainly derived by the dissolution of biogenic silica and by desorption processes. The Al content may also have been derived by the dissolution of detrital material, and the other ions could have originated from seawater included in the pore spaces during sedimentation. Since the K content must be high for glauconite formation, previous workers have discussed the influence of organic potassium (Correns, 1939; Conway, 1942). From the present experiments, it can be concluded that only under very high K concentrations (0.03–0.3% KCl) can crystalline glauconite be expected, and in solutions with lower K concentrations (<0.03% KCl) glauconite will not form. Here, smectite formation is the predominate reaction.

Dissolution processes under reducing conditions and precipitation processes under more oxidizing conditions lead to an enrichment of Fe relative to Al or Si in different phases of the mineral formation. Fe-rich glauconite may be followed by Al-rich glauconite mixed-layer minerals. Glauconite is present in natural sediments, not only in pellets, but also in fine clay fractions (Bentor *et al.*, 1965; Köster, 1965). If the silica content of precipitates is too high, quartz will form together with glauconite. This is in agreement with natural assemblages of glauconite and idiomorphic quartz (Bühmann, 1972) and with the synthetic formation of quartz in hydroxide-silica precipitates (Harder and Flehmig, 1970). If the SiO₂ content is too low, chamosite (7 Å) will form. Porrenga (1967) showed that authigenic chamosite forms in relatively warm (>20°C), shallow, marine environments, while glauconite develops in cooler (<13°C), deeper, marine environments. Thus, both temperature and depth of the water are important for the formation of these clay minerals. From the present synthesis experiments, however, the concentration of silica in such solutions appears to be of greater importance than either temperature or pressure (depth).

Through the activity of silica-consuming plants (diatoms) and animals (radiolarians), surface seawater becomes depleted in silica to only a few ppb SiO₂. If such water is trapped in shallow marine sediments, the silica concentration is too low for clay mineral formation. Only after slight enrichment of silica in the pore solu-

tions can chamosite form. Seawater at greater depth is richer in silica (~6 ppm SiO₂) because of the dissolution of dead siliceous organisms. If these waters are trapped in the sediments, the silica concentration will be favorable for the formation of glauconite. The chemical composition of pore waters therefore seems to be the controlling factor for the clay mineral formation rather than depth and temperature in these environments. Glauconite aggregates in coarse, relatively clean sand and silt and in impure clastic limestones and dolomites could only have formed from diagenetic solutions. It seems that these conditions of formation must be stabilized for a longer geological time to produce a significant amount of glauconite. Glauconite does not originate in areas with high sedimentation rates. Slow sedimentation and/or interruption of deposition are often connected with the natural formation of glauconite. Glauconites from coarse sediments show a greater XRD ordering than glauconites from finer sediments.

Glauconite forms at a very early stage of diagenesis. Newly formed glauconites in natural sediments show uniform optical orientation. Burrowing organisms, if they were present, may have destroyed this orientation in slightly older sediments, and later formed glauconite shows a turbulent orientation. This important observation was made by Valetton (1958) in Tertiary glauconites in northern Germany and suggests that glauconite formed soon after sedimentation.

It would seem that the interface between an oxidizing and a slightly reducing zone without S²⁻ ions in sediments is a suitable place for diagenetic glauconite formation. Slightly reducing zones produce Fe-containing pore waters; transition to a more oxidized pore-water zone, iron hydroxides will be precipitated, adsorbing silica and K⁺ from solutions and form the starting material for glauconite.

ACKNOWLEDGMENTS

For help in the laboratory I would like to thank Mrs. E. Cierny. The "Deutsche Forschungsgemeinschaft, Schwerpunkt Tonmineralogie," supported this study.

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(Received 26 December 1978; accepted 11 December 1979)

Резюме—Глауконит был синтезирован при низкой температуре и восстановительных условиях путем осаждения гидроокислов Fe из Si-, Fe-, Al-, и K-содержащих растворов. Составы, благоприятные для синтеза при 20°C и pH = 8,5 являются 1 ч/млн Fe, 0,15 ч/млн Al, 13 ч/млн SiO₂, 1000 ч/млн KCl, и 1000 ч/млн дитионита. Содержание K в растворах должно быть достаточно высоким чтобы фиксировать K в осадке.

При специальных ранних диагенетических условиях глауконит образуется в морских отложениях, вероятно на границе между восстановительными и окислительными зонами в грязевых отложениях. Содержание кремнезема поровых вод, по-видимому, контролирует образование глауконита или шамозита в большей степени, чем глубина или температура донных вод. [N. R.]

Resümee—Glaukonit konnte bei Oberflächentemperaturen nur unter reduzierenden Bedingungen aus Eisenhydroxid-Kieselsäureniederschlägen synthetisiert werden. Günstige Bedingungen für die Synthese bei 20°C und einem pH von 8,5 waren: 1 ppm Fe, ~ 0,15 ppm Al, 13 ppm SiO₂, 1000 ppm KCl, und 1000 ppm Dithionit. Ausreichend hohe Gehalte an Kalium-Ionen sind notwendig, um genügend hohe Gehalte an die Niederschläge zu binden.

Glaukonit wird erst frühdiagenetisch in marinen Sedimenten gebildet. Wahrscheinlich wird es zur Glaukonitbildung an der Diffusionsgrenze zwischen einer reduzierten und einer oxidierten Porenwasserlösung kommen. Ob sich Glaukonit oder Chamosit bildet, hängt vor allem von dem Gehalt an Kieselsäure in den Porenlösungen ab und weniger von der Tiefe und der Temperatur des Meerwassers, in dem die Sedimente abgelagert wurden.

Résumé—La glauconite a été synthétisée à température basse par la précipitation d'hydroxides Fe de solutions contenant Si, Fe, Al, et K sous des conditions de réduction. Les compositions favorables à la synthèse à 20°C et au pH 8,5 sont 1 ppm Fe, 0,15 ppm Al, 13 ppm SiO₂, 1000 ppm KCl, et 1000 ppm dithionite. Le contenu en K des solutions doit être suffisamment élevé que pour fixer K dans le précipité.

Sous des conditions diagénétiques spéciales, la glauconite est formée dans des sédiments marins, probablement à la surface de séparation des zones réduisantes et oxidantes des sédiments boueux. Le contenu en silice des eaux des pores, plutôt que la profondeur ou la température des eaux de fond semble contrôler la formation de glauconite ou de chamosite. [D.J.]