

SYNTHESIS OF IRON LAYER SILICATE MINERALS UNDER NATURAL CONDITIONS

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Abstract—The low temperature synthesis of iron silicate minerals with clay structures is possible at surface temperatures only under reducing conditions. Under oxidizing conditions clay minerals could not be synthesized. Instead quartz and quartzine were found in these X-ray amorphous Fe III hydroxide-silica precipitates after 14 days at low temperatures (20° and 3°C) as well as goethite or X-ray amorphous iron hydroxides. Only from solutions containing Fe-II could the different iron-containing clay minerals be built up within days at low temperatures. The presence of Fe-II enables an octahedral layer of the brucite-gibbsite type to be formed. This is necessary for the bidimensional orientation of SiO₄-tetrahedra leading to clay mineral formation. The presence of Fe²⁺- and/or Mg²⁺-ions is necessary for the formation of the Al³⁺- and Fe³⁺-containing octahedral layers. The reducing conditions were obtained in the experiments by addition of dithionite. With a high content of silica (ca. 20 ppm SiO₂, 7 ppm Fe) nontronite and lempbergite, the di-Fe-III and tri-Fe-II octahedral, three-layer silicates, were built up in several days at low temperatures. With a lower silica content, that is, a lower Si/Fe ratio (15 ppm SiO₂ and 20 ppm Fe), the two-layer silicate minerals greenalite and chamosite could be synthesized. A higher Mg content and more reducing conditions in the solutions favored the tri- as well as dioctahedral chamosite synthesis.

The conditions of formation of recent naturally formed nontronite fit well with the synthesis conditions. Chamosites in sedimentary iron ores are characterized by a low content of SiO₂, between 15–30% SiO₂. This low content of silica cannot be the result of primary precipitation from seawater. The iron and silica ratio in seawater or in river waters would lead to a precipitation of ~60% SiO₂ in the iron hydroxide precipitates. A probable origin for chamosite iron ores, which explains the low SiO₂ content, is diagenesis of the lateritic weathering crust. Indeed, investigations of recent tropical shoreline sediments and in particular their trace element content confirm that chamosite minerals have formed diagenetically from lateritic particles in reducing sediments.

Key Words—Chamosite, Greenalite, Iron, Lembergite, Nontronite, Synthesis.

INTRODUCTION

The silica content of sedimentary iron ores is found in quartz and different iron-containing clay minerals. Chamosite, greenalite, cronstedtite, nontronite, glauconite, and thuringite are common minerals in sedimentary iron ores. In general all these minerals are extremely fine grained so that X-ray powder data are necessary for their identification and elucidation of their structures. Greenalite, cronstedtite, and chamosite are structurally characterized by a serpentine (kaolinite)-like structure in which one silica tetrahedral layer is bound with one octahedral layer in a 1:1 mineral. Nontronite, ferrisaponite, and lempbergite are structurally characterized by a smectite or talclike structure in which two silica tetrahedral layers are bound with one octahedral layer in a 2:1 mineral. Glauconite is a complicated iron-rich mica-clay mineral. Thuringite has a clay mineral structure in which, between the smectite (talc) layer, is an independent Fe- "brucite" layer. Fe-II and Fe-III are found in different amounts in these Fe clay minerals. Di- and trioctahedral types can be distinguished in the different clay types. Since substitution of Al- and probably also of Fe-ions takes place, in both the smaller Si-tetrahedron position and the large octahedral position the chemical composition can be very variable. For these minerals oxidation and dehydration reactions are, to some extent, reversible by the conversion of some outer (OH)⁻-ions of the octahedral layer to (O)⁻².

The synthesis of some iron-containing clay minerals at elevated temperatures has been discussed previously. Ewell and Insley (1935), Hamilton and Furtwängler (1951) and others synthesized nontronite from mixtures of silica gel and ferric oxide at high temperatures and pressures. Iron-containing, chloritelike substances have been produced from montmorillonite (Orcel et al., 1949) by reaction with Fe(OH)₂ solutions. Swelling chlorites have been synthesized from Na-silicates and iron salts (Caillère et al., 1947). In the last few years many clay minerals have been synthesized at low temperatures. Harder (1972) showed that from magnesium-containing aluminum hydroxide-silica precipitates, tri- and dioctahedral montmorillonite could be synthesized at temperatures <3°C. With potassium in the solution illite also could be synthesized. The brucite-layer favors the formation of layer silicates of the smectite group. Since Fe(OH)₂ is isomorphous with brucite, it was reasonable to try a synthesis of hydrous iron silicate with iron-containing solutions under reducing conditions. It was possible to synthesize di- and trioctahedral 2:1 clay minerals (smectite) and di- and trioctahedral 1:1 minerals with a kaolinitelike structure (Harder, 1973). The question of iron clay mineral formation under surface conditions is in part a question of iron and silica precipitation from natural solutions.

Amorphous hydroxides of iron are capable of coprecipitating SiO₂ by chemisorption from very dilute solutions (Harder, 1965; Flehmig, 1967). The precipita-

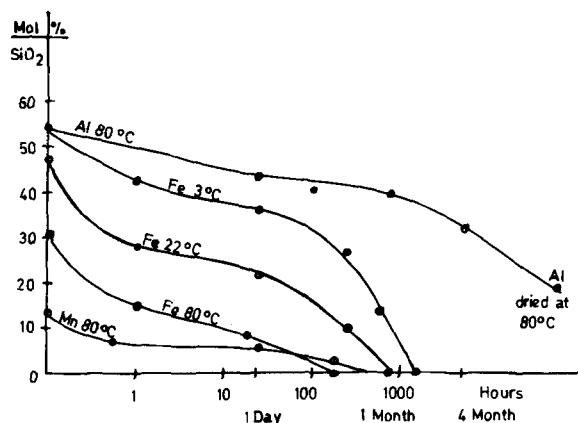


Fig. 1. Variation of the amount of silica taken up by aluminum, iron, and manganese hydroxides which have been aged for different times before the addition of silica to the solution.

Aging Conditions:

Al	80° C	pH 7	31 ppm Al ₂ O ₃	28 ppm SiO ₂	HARDER, 1965
Fe III	3° C	pH 7	29 ppm Fe ₂ O ₃	18 ppm SiO ₂	FLEHMIG, 1967
Fe III	22° C	pH 7	"	"	"
Fe III	80° C	pH 7	"	"	"
Mn III	80° C	pH 9	21 ppm MnO	28 ppm SiO ₂	MENSCHKE, 1970

tion of Fe-II and Fe-III hydroxides is a function of Eh and pH. Iron-III is insoluble at more common natural pH (>3); Fe-II, however, is much more soluble at all natural pH. The redox potential and the pH of the solution controls the amount of iron which is precipitated. For some experiments the SiO₂-content of the Fe-II and Fe-III, or more precisely, the mixtures of the Fe-II and Fe-III hydroxide precipitates are given in Table 1. The SiO₂-contents in the Fe-II and Fe-III hydroxide precipitates are more or less similar to the SiO₂-content in Al-Si precipitates. There are, however, some important differences in aging conditions of aluminum and iron hydroxides. Sorption is much less on crystallized substances (clay minerals, Fe-hydroxides, etc.) than on the X-ray amorphous hydroxides. If the hydroxides are aged before they are brought in contact with solutions containing silica they take up less silica. The precipitates of Fe(OH)₃ and Fe(OH)₂ are not stable and crystallize to goethite, FeOOH and magnetite, Fe₃O₄. Aged iron hydroxide precipitates for this reason adsorbed much less Si. The experiments of Flehmig (1967) have shown, (see Figure 1) that even at low surface temperatures, precipitated iron phases after several months lose adsorption capacity, if they are brought into contact with silica solutions. Under neutral pH conditions aluminum-hydroxides do not lose their adsorption capacity even after many years of aging. The presence of silica in solution during the precipitation of iron-hydroxides inhibits the crystallization to goethite or magnetite, slowing down the process. The difference in the aging conditions of iron, manganese, and aluminum-hydroxides is shown in Figure 1.

TECHNIQUE OF SYNTHESIS

The low temperature synthesis of clay minerals is possible through the aging of freshly prepared hydroxide-silica precipitates under different conditions. The experiments were carried out in the following way. From solutions containing Fe, Si, and in some cases Al, and Mg, the hydroxides were precipitated in different amounts. The ratio of the two oxidation states of iron change with Eh-pH conditions. Oxidation-reduction conditions are very important for the formation of iron minerals. The reducing conditions in the experiments were produced by different chemicals, and the resulting Eh was measured by a platinum electrode with a calomel reference electrode. 0.1% sodium dithionite solution produced an Eh of -0.6 V, pH 8.0; 0.1% hydraziniumdichloride an Eh of -0.25 V, pH 8.0; a nitrogen atmosphere was used to stabilize these reducing conditions during the handling of the solution. Experiments with other reducing agents were not successful in producing clay minerals. Perhaps the crystallinity of the products was too pure. Silicon was added as monomeric silicic acid, and iron was added as a solution from freshly prepared FeSO₄. Iron was precipitated by change of hydrogen ion concentration (higher pH) or by change of the Eh. The pH was then kept constant by several additions of NaOH. The variation of pH and Eh is quite large in these experiments, but has a great influence on the reaction and the formation of the di- or trioctahedral iron-containing three- or two-layer minerals.

In the beginning all the hydroxide-silica-precipitates were X-ray amorphous, but after a short aging time, some of the precipitates showed X-ray reflections of clay minerals only. Others remained completely X-ray amorphous after the aging time. Many other precipitates showed sharper reflections from the hydroxides, oxides, quartz, feldspar, etc. with or without clay mineral reflections. The first X-ray reflections of clay minerals were detected after only 1 day of aging. The aging time with iron experiments was extremely short in relation to the Al-Mg-Si-experiments which needed several months for crystallization (Harder, 1972). The fast crystallization was very favorable as it was quite difficult to maintain the pH and Eh at the starting values for a long time. The wet, filtered precipitate was washed with O₂-free water and was dried after the aging time. The bluish-gray colors of some wet experimental products are not stable. A color change to black and gray and finally to brown takes place upon exposure to air. These products could be dried under a N₂ atmosphere without changes in color.

If the Fe-III-silica precipitates, which had been formed in an oxidizing solution, were aged under reducing conditions, iron clay minerals were formed. In this way chamosite was synthesized from an oxidizing solution after being aged for 1-30 days under reducing conditions. This mechanism for chamosite synthesis is

Table 1. Silica adsorption by iron hydroxides at different redox potential.

Na-Di- thionite %	pH	Temper- ature °C	Concentration in initial solution		C o m p o s i t i o n of precipitate			
			Fe ppm	SiO ₂ ppm	I r o n in solution ppm Fe	in precipitate ppm Fe	% SiO ₂ H ₂ O free calculated	
+)	-	7	3 ⁰	20	18.3	-	20	30
	0.3	8	3	20.6	20.25	16	4	32
	1	8	3	20.6	20.25	no precipitate		
+)	-	7	22	20	18.3	-	20	26
	0.1	8	20	20.6	20.25	6	15	24
	-	9	20	4	20	0.0	4	28
	0.03	8	20	4	20	0.4	2.8	32
	0.1	8	20	4	20	1.8	2.1	60
+)	-	7	22	0.20	18.25	0.04	0.16	56
	0.1	8.5	20	0.3	13	no precipitate		
	0.1	8.5	20	0.3 + 0.3 % Al ₂ O ₃	13	0.2	0.1 ca. 15 % Al ₂ O ₃	80

+) These values from W. Flöhmg (1967)

most important for diagenetic formation of chamosite in sedimentary iron minerals from detrital iron compounds under natural conditions.

X-ray analysis

Because the synthesis products were so poorly crystallized, only powder diagrams with the Debye-Scherrer camera were obtained, using CoK_α radiation. The diffraction patterns showed more or less diffuse (Table 2) broad peaks. Nevertheless, the X-ray powder diffraction data of the synthesis products agree with those of natural minerals.

The usual distinction between the clay minerals, based on the different basal reflections, was noted. The three-layer silicate minerals, nontronite, ferrisaponite, and lebergite are characterized by basal reflections between 14–16 Å. These basal reflections, like all smectite minerals, vary in their position, and are influenced by different factors, mostly the exchangeable cations. The two-layer silicates, greenalite, chamosite, etc. are characterized, like the kaolin-minerals, by a 7-Å basal reflection. The distinction between kaolin-type (7 Å) and chlorite-type structures is based on the absence of presence of a 14-Å reflection. The basal reflections of the synthetic products varied from 7–16 Å. After treat-

ment with ethylene glycol at higher temperatures nontronite shifted to about 17 Å. The reflections at 4.1 Å and 3.3 Å were weak and usually broad bands in the synthetic products. The (060)-reflections were relatively sharp and strong and lay between 1.49 and 1.54 Å (see Table 2). The differences have been used to differentiate between di- and trioctahedral iron-containing clay minerals in the synthetic products. It has been shown from the position of the (060)-reflections that incorporation of Fe-III and Al in the octahedral sheets leads to dioctahedral minerals. More Fe-II and Mg leads to trioctahedral compositions.

CHEMICAL ANALYSIS

Some of the precipitates were analyzed chemically for Fe and Si and for Al and Mg when they were present. The determination of Fe and Si and, if necessary, of Al and Mg in the precipitates was done after drying and then dissolving in HF and H₂SO₄. Iron was determined spectrophotometrically by the O-Phenanthroline method, Al, after separating from Fe, with 8 oxichinolin in CHCl₃, and Mg by atomic absorption-spectrometry. The SiO₂ content of the chemical analyses given in the tables are calculated on a H₂O-free basis.

The chemical composition of the different clay min-

Table 2. X-ray powder data from synthetic three- and two-layer-iron clay minerals.

	Three Layer Fe-Clay Mineral	I n t e n s i t y		Two Layer Fe-Clay Mineral	
	d(Å)			d(Å)	
	11 - 16	v.str.	v.str.		7.6
	4.1	str.	w.		4.5
	3.3	w.	m.		3.8
	2.60	m.	m.		2.65
	2.49	m.	m.		2.49
Trioctahedral Lembergite or Diocahedral Nontronite	1.53-1.54	str.	str.	Trioctahedral Chamosite or Diocahedral Ferric-Cham- osite	1.53-1.55
	1.49-1.52	str.	str.		1.50-1.52

v. str. = very strong, str. = strong, m. = medium, w. = weak

eral-containing synthetic products is variable. It is not certain whether the material analyzed has a monomineralic composition or is a mixture of clay minerals and X-ray amorphous material. According to the X-ray results, uniform and sometimes different clay materials probably are present. The X-ray investigation agrees with the results relating to the chemical composition of the synthetic products. Synthetic products with 7-Å basal reflection have a low silica content, while the SiO₂-rich products have a basal reflection from 10 to 17 Å.

EXPERIMENTAL RESULTS FOR IRON LAYER SHEET SILICATE FORMATION

After aging, some precipitates showed reflections characteristic of hydroxides and quartz, some were still X-ray amorphous, and others showed X-ray reflections characteristic of iron-silicate minerals with a clay mineral structure. The experimental conditions for the formation of certain iron-containing clay minerals are given in Tables 3 and 4. The chemical composition of the X-ray amorphous precipitates are not given in the tables but the results of some of these investigations are discussed below.

The following conditions favor the formation of iron sheet silicate minerals:

(1) Only under *reducing conditions* could iron-containing clay minerals be synthesized in a short time at low temperatures. The silica-poor, two-layer Fe clay minerals of the greenalite and chamosite types, as well as the silica-rich three-layer Fe clay minerals of the nontronite type, need reducing conditions for their synthesis. Precipitates with only the dioctahedral Fe clay mineral reflections and a high content of iron-III have a dark green to black color. The trioctahedral Fe clay mineral precipitates are greener and the final Eh of the solutions giving these synthetic products are more negative than those of solutions producing dioctahedral minerals. The formation of the Fe-III layer silicate minerals is only possible if Fe-II is present in the solution during the formation of the three-layer silicate. If no dithionite or other reducing chemical was present during the experiments, or the Eh was not low enough, Fe-clay minerals were not built up. Iron-II or Mg in the solution stabilizes, as mixed layer, the formation of the octahedral layer built up mainly by Fe-III and fixes the silica on the octahedral layer.

(2) It seems that high pH favors a rapid Fe clay mineral formation. Di- and trioctahedral iron clay minerals

Table 3. Nontronite and chamosite formation at 20°C, pH 7-9.

Reducing condition % Na-Dithionite content	Concentration in initial solution				Composition of precipitate after 3 - 10 days aging time				X-ray reflection d(001) d(060) Å
	SiO ₂ ppm	Fe ppm	Al ppm	Mg ppm	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	MgO (%)	
-	20	4	-	-	28	72	-	-	no clay mineral formation
0.05	20	4	-	-	49	51	-	-	11 - 16 1.515
0.1	20	4	-	-	55	45	-	-	11 - 16 1.52
0.3	20	4	-	-	47	53	-	-	11 - 16 1.53
0.1	16	1	0.3	-	51	32	17	-	11 - 16 1.508
0.1	16	0.3	0.3	1290	60	5	22	13	11 - 16 1.53
0.1	20	20	-	1290	31	60	-	8	7.9 1.55
0.1	20	10	5	1290	34	23	13	30	9 (weak) 1.54

were formed from solutions with pHs over 7, mostly between 8 and 9. Higher pH and more negative Eh values are more favorable for and lead to a better crystallization of the synthesis products in shorter times. Natural Fe clay mineral formation may take place over a wider range of Eh and pH than reported here, as the Eh and pH conditions in nature are maintained for longer time periods and make possible good crystallization.

(3) It has been shown that magnesium in precipitates favors the synthesis of iron-containing, two-layer clay minerals. The pH affects the precipitation and coprecipitation of magnesium from solution (Harder, 1972). The synthesis results have shown that chamosite mineral formation is favored by seawater solutions with a relatively high pH and a high Mg content.

(4) Formation of silicate minerals takes place at low temperatures (20° and 3°C) only in those precipitates

that are in contact with monomeric silicic acid solutions. It seems that polymerization of the silicic acid inhibits the formation of clay minerals. If the SiO₂ solutions are polymeric, the hydroxide silica precipitates stay amorphous. This is also true even when the composition of the precipitates is similar to those of the clay minerals. Under neutral conditions at 20°C the solubility of silica is 120 ppm SiO₂. At higher pH (above 9) much more silica is soluble in monomeric form. However, it seems that much lower silica contents (10-20 ppm SiO₂) give a better and quicker clay mineral formation. This silica content may represent the *equilibrium* solubility of the three-layer minerals formed by the Fe hydroxide-silica adsorption.

(5) The concentration of silica in these hydroxide silica precipitates should be similar to the stoichiometric composition of the minerals if mineral formation is to

Table 4. Nontronite and chamosite formation at 3°C, pH 8-9.

Reducing condition % Na-Dithionite content	Concentration in initial solution				Composition of precipitate after 3 - 10 days aging time				X-ray reflection d(001) d(060) Å
	SiO ₂ ppm	Fe ppm	Al ppm	Mg ppm	SiO ₂ (%)	Fe ₂ O ₃ +FeO (%)	Al ₂ O ₃ (%)	MgO (%)	
-	20	7.5	-	-	35	65	-	-	no clay mineral formation
0.05	20	7.5	-	-	57	43	-	-	15 - 11 1.52
0.1	20	7.5	-	-	88	12	-	-	16 - 12 1.53
0.3	20	7.5	2	-	32	52	17	-	16 - 11 1.53
0.3	20	10	1	1290	39	36	22	2	7.8 1.55
0.3	20	7	2	1290	32	43	21	4	7.9 1.54

take place. The SiO_2 content in precipitates depends on the composition and the ratio of hydroxide to Si of the initial solution and on the pH and the Eh during the precipitation. It is quite difficult to change the experimental conditions in such a way that the precipitates have the right composition, particularly in solutions with low Fe and Al concentrations (<1 ppm). The silica content in the precipitates controlled the kind of clay mineral formed—a three-layer or a two-layer clay mineral. Too low SiO_2 concentrations in the precipitates inhibited clay mineral formation. During the aging period, goethite, hematite, and quartz can be formed in these hydroxide-silica gels with a positive Eh (Harder and Flehmig, 1970). If the silica content in the precipitate is between 35–80% SiO_2 (water omitted from the calculation) nontronite mineral formation is possible at low temperatures. Nontronite forms in solutions with Fe:Si ratios between 1:10 and 1:3. When the Fe:Si ratio in the solutions is between 1:1 and 1:2 this gives a silica content in the precipitate between 25–35% SiO_2 and greenalite and chamosite can be formed.

NATURAL IRON CLAY MINERAL FORMATION

The genesis of naturally occurring iron clay minerals can be discussed in the light of recent investigations of clay mineral synthesis. The formation of these iron clay minerals has been poorly understood because of the lack of sedimentary iron deposits and iron clay mineral formations in modern sediments. However, in the last few years both three-layer and two-layer Fe clay minerals have been found in recent sediments.

NONTRONITE GENESIS

The recent precipitation of nontronite in the hot (56°C) brines in the Red Sea (Bischoff, 1972, in Degens, 1972) and in Lake Malawi (Müller and Förstner, 1973) occurred when reducing conditions were present in the solutions. The measured pH in Lake Malawi was 8.5–7.7 and the pH of the hot brines was approximately 6 (or higher) and the Eh -0.100 V (Hartman, 1969). It seems that the low temperature experimental conditions reported in this paper and the recent natural precipitation of nontronite have similar pH and Eh conditions. These investigations further show that an iron clay mineral formation by precipitation of hydroxides and adsorption of silica is possible.

Iron is present in the water as ions in true solution, and probably as a component of organic complexes and as finely divided colloidal and suspended material. The iron content of river waters varies over a wide range. Livingstone (1963) gave mean values of dissolved constituents as 0.67 ppm Fe, 0.3 ppm Al and 13.1 ppm SiO_2 . Much higher iron content (several ppm) can be found in some rivers or in hot springs or in CO_2 -rich waters. Mixing of river or spring waters with ocean water removes iron as iron hydroxide flocs. These iron hydrox-

ides adsorb SiO_2 and some other elements from the seawater. The X-ray amorphous iron silica precipitates formed will be sedimented together with the colloidal and detrital iron component of the river load. These X-ray amorphous Fe-III-Al- SiO_2 precipitates, which mostly will have a high Si-content, are the parent material for clay mineral formation. The formation of iron-containing three-layer silicates is only possible under reducing conditions. In nature these reducing conditions will be present in the sediment or may be present in the bottom water layer. The reaction of these X-ray amorphous SiO_2 -rich precipitates in this reducing environment will produce three-layer silicates in this early stage of diagenesis. Nontronite and iron-containing three-layer mineral formation is possible under reducing conditions in freshwater sediments as well as in salt-water sediments. The implications of these experiments are not only important for the formation of nontronite, but for the formation of Al-rich three-layer silicates as well. Similarly to Mg, Fe under reducing conditions can help to build up an Al-montmorillonite at low temperatures.

CHAMOSITE, GREENALITE GENESIS

The formation of both chamosite, which is the major clay mineral in iron ores of minette type, and of greenalite, which is a clay mineral from some Precambrian iron ores, is poorly understood and has been much discussed. It has been suggested that reducing conditions are necessary for formation of these clay minerals. This point is in agreement with the experimental results reported here. Borchert (1952), and James (1954) considered that these facies reflect varying levels of oxygen availability in the seawater itself. On the other hand, Harder (1951, 1963), Strakhov (1959a) and others have maintained that diagenetic processes in pore water are the most important controls on the formation of iron clay minerals. An important argument for the diagenetic formation of chamosite from Fe-III hydroxides is that benthonic fauna is found in chamosite iron ores. Recently chamosite has been found in the marine environment (Gärtner and Schellmann, 1965) and in tropical shelves (Porrenga, 1965). Rohrlich et al. (1969) found chamosite fecal pellets in recent sediments of Loch Etive, Scotland.

Since recent chamosite has been found, early diagenetic processes in pore water seem to be more important than the facies conditions in the seawater itself. The chemical composition of the chamosite cannot result from the SiO_2 - and Fe-Al-content of a normal sea or river water. Nontronite could be formed from such SiO_2 -rich precipitates as mentioned before. The SiO_2 -poor two-layer minerals could be formed by diagenetic reaction in seawater sediments with iron-rich, but SiO_2 -poor, detrital particles from the lateritic weathering crust. In tropical deltas and shorelines these mixtures are quite common and recent diagenetic reactions

which formed chamosite have taken place (Gärtner and Schellmann, 1969). The trace element content (Harder, 1964) and low SiO₂-content between 15–30% SiO₂ confirm the hypothesis proposed by Harder (1951). Chamosite is also found in lateritic bauxites (Nikitina and Zvyagin, 1972). The chemical compositions of these two types of chamosite are very similar. A low content of SiO₂ and high content of Fe-II and Fe-III and also a relatively high content of Al and Mg typify the chemical composition. All these points agree with the conditions of synthesis. A high Mg-content, a high pH, and strongly reducing conditions in the solutions favor the tri- as well as the dioctahedral chamosite synthesis. The trace element content and investigation of recent tropical shoreline sediments confirm that chamosite minerals have been formed diagenetically from lateritic particles in the reducing sediments.

CONCLUSION

The synthesis of iron clay minerals is possible at low temperatures in a short time. Low silica concentration in solution is the most important condition for low temperature synthesis. High silica concentration in solution inhibits the formation of clay minerals. The synthesis—from natural waters with a low silica content—is possible through the chemisorption of silica by hydroxides. By aging of these X-ray amorphous hydroxide-silica precipitates, silicate minerals can be synthesized at low temperatures under certain conditions. For the synthesis of iron-containing clay minerals, reducing conditions are necessary. Only under *reducing* conditions could the tri- as well as the dioctahedral three- or two-layer Fe clay minerals be synthesized. Oxidized Fe³⁺-Si-precipitates do not crystallize to clay minerals. Fe²⁺ as well as Mg²⁺ are suitable for building up a brucitelike layer. The octahedral layers are necessary for bidimensional orientation of the SiO₄ tetrahedrons for clay mineral formation.

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REFERENCES

- Bischoff, J. L. (1972) A ferroan nontronite from the Red Sea geothermal system: *Clays & Clay Minerals* **20**, 217–223.
- Borchert, H. (1952) Die Bildungsbedingungen mariner Eisenerzlagertstätten. *Chem. Erde* **16**, 49–74.
- Brindley, G. W. (1951) The crystal structure of some chamosite minerals: *Mineral. Mag.* **29**, 502.
- Brindley, G. W. and Youell, R. F. (1953) Ferrous chamosite and ferric chamosite. *Mineral. Mag.* **30**, 57–70.
- Bubenicek, L. (1960) Recherches sur la Constitution et la Répartition des Minerais de fer dans L'Aalnier de Lorraine. Thèse Docteur, Nancy.
- Caillère, S., Hénin, S. and Méring, J. (1947) Passage expérimental de la montmorillonite à une phyllite à équidistance stable de 14 Å. *C. R. Acad. Sci. Fr.*, **224**, 842.
- Correns, C. W. (1952) Mineralogische Untersuchungen an sedimentären Eisenerzen. In *Symposium sur les gisements de fer du monde. Teil: Die Eisenerzlagertstätten Deutschlands*. (Edited by Bondel, F., et Marvier, L.) XIX^e Congrès Géol. Intern. Alger.
- Ewell, R. H. and Insley, H. (1935) Hydrothermal synthesis of kaolinite, dickite, beidellite, and nontronite. *J. Res. Natl. Bur. Stand.*, **15**, 173.
- Flehmig, W. (1967) Zur Erklärung des Kieselsäuregehalts in Nadel-eisenerzooiden. Dissertation, Münster/Westf.
- Gärtner von, H. R. and Schellmann, W. (1965) Rezent Sedimente im Küstenbereich der Halbinsel Kaloum, Guinea: *Mineral. Petrogr. Mitt.* **10**, 349–367.
- Hamilton, G. and Furtwängler, W. (1951) Synthese von Nontronit. *Tschermaks Mineral. Petrogr. Mitt.* **3**, F.
- Harder, H. (1951) Über den Mineralbestand und die Entstehung einiger sedimentärer Eisenerze des Lias. *Heidelb. Beitr. Mineral. Petrogr.* **2**, 455–476.
- Harder, H. (1963) Können Eisensäuerlinge die Genese der Lahn-Dill-Erze erklären? *Beitr. Mineral. Petrogr.* **9**, (5), 379–422.
- Harder, H. (1965) Experimente zur "Ausfällung" der Kieselsäure. *Geochim. Cosmochim. Acta* **29**, 429–442.
- Harder, H. (1972) The role of magnesium in the formation of smectite minerals. *Chem. Geol.* **10**, 31.
- Harder, H. (1973) Synthese von eisenhaltigen Tonmineralen bei niedrigen Temperaturen. *Naturwissenschaften* **60**, 517.
- Harder, H. and Flehmig, W. (1970) Quarzsynthese bei tiefen Temperaturen. *Geochim. Cosmochim. Acta* **34**, 295.
- Hartmann, M. (1969) Investigations of Atlantis II Deep Samples Taken by the FS METEOR. In *Hot Brines and Recent Heavy Metal Deposits in the Red Sea*. (Edited by Degens, E. T. and Ross, D. A.). Springer, Berlin, Heidelberg, New York.
- James, H. L. (1954) Sedimentary facies of iron formation. *Econ. Geol.* **49**, 235–293.
- Livingstone, D. (1963) Chemical composition of rivers and lakes. *U.S. Geol. Surv. Prof. Pap.* **440-G**.
- Menschel, G. (1970) Zum Vorkommen von Kieselsäure in sedimentären Manganerzen und zur Bildung von Mangansilikaten im Tief-temperaturbereich. Dissertation, Göttingen.
- Müller, G. and Förstner, U. (1973) Recent iron ore formation in Lake Malawi, Africa. *Mineral. Deposita* (Berl.) **8**, 278.
- Nikitina, A. P. and Zvyagin, B. B. (1972) Origin and crystal structure features of clay minerals from the lateritic bauxites in the European part of the U.S.S.R. *Proc. Int. Clay Conf.* Madrid.
- Orcel, J., Hénin, S. and Caillère, S. (1949) Sur les silicates phylliteux des minerais de fer oolithiques. *C. R. Acad. Sci. Fr.*, **229**, 134.
- Porrenga, D. H. (1965) Chamosite in recent sediments of the Niger and Orinoco deltas. *Geol. Mijnbouwkd.* **44**, 400–403.
- Porrenga, D. H. (1967) Glauconite and chamosite as depth indicators in the marine environment. *Mar. Geol.* **5**, 495–501.
- Rohrlich, V., Price, N. B. and Calvert, S. E. (1969) Chamosite in the recent sediments of Loch Etive, Scotland. *J. Sediment. Petrol.* **39**, 624–631.
- Schneiderhöhn, H. (1924) Untersuchungen über die Aufbereitungsmöglichkeiten der Eisenerze des Salzgitterhöhenzuges aufgrund ihrer mineralogisch-mikroskopischen Beschaffenheit. *Mitt. Kaiser Wilhelm Inst. Eisenforsch. Düsseldorf* **5**, 79–108.
- Strakhov, N. M. (1959a) Schema de la diagenèse des dépôts marins. *Ecologie Géol. Helv.* **51**, 761–767.
- Strakhov, N. M. (1959b) Sur les formes du fer dans les sédiments de la Mer Noire. *Ecologie Géol. Helv.* **51**, 753–761.

Резюме- Низкотемпературный синтез железистых силикатных минералов с глинистыми структурами возможен при наземной температуре только в восстановительной среде. В окислительной среде глинистые минералы не синтезируются. Вместо этого в аморфных к рентгеновским лучам кремнеземных осадках, содержащих гидроксид Fe-III, после 14 дней содержания при низкой температуре /20° и 3°С/ были обнаружены кварц и кварцин, а также гетит или аморфные к рентгеновским лучам железистые гидроксиды. Только из растворов, содержащих Fe-II, могут образоваться различные железо-содержащие глинистые минералы в течение нескольких дней при низкой температуре. Присутствие Fe-II способствует образованию октаэдрического слоя брусито-гипсита типа. Это необходимо для двумерной ориентации тетраэдров SiO₄, ведущей к формированию глинистых минералов. Присутствие ионов Fe²⁺ и /или/ Mg²⁺ необходимо для формирования содержащих Al³⁺ и Fe³⁺ октаэдрических слоев. При экспериментах восстановительная среда достигалась добавлением дитионита. При высоком содержании кремнезема /около 20 ч/млн SiO₂ и 7 ч/млн Fe/ были получены нонtronит и лембергит, двухоктаэдральный с Fe-III и трехоктаэдральный с Fe-II трехслойные силикаты, в несколько дней при низкой температуре. При низком содержании кремнезема, т.е. при низком отношении Si/Fe /15 ч/млн SiO₂ и 20 ч/млн Fe/ были синтезированы двухслойные силикатные минералы гриналит и шамозит. Более высокое содержание Mg и усиление восстановительных свойств раствора способствует синтезу трех- и двухоктаэдрического шамозита.

Условия современного формирования природного нонtronита хорошо соответствуют условиям синтеза. Шамозит в осадочных железных рудах характеризуется низким содержанием SiO₂, от 15 до 30% SiO₂. Низкое содержание кремнезема не может быть результатом первичного осаждения его из морской воды. Соотношение железа и кремнезема в морской или речной воде должно привести к осаждению примерно 60% SiO₂ в гидроксидных железистых отложениях. Возможное происхождение шамозитовых железных руд, которое объясняет низкое содержание SiO₂, связано с диагенезом продуктов латеритового выветривания поверхностных отложений. Действительно, исследования современных тропических прибрежных осадков и в особенности содержащихся в них рассеянных элементов убеждают, что шамозитовые минералы образовались диагенетически из латеритовых частиц в восстановительной среде.