

ORIGIN OF BERTHIERINE IN IRONSTONES

DEBA P. BHATTACHARYYA

Earth and Planetary Sciences Department, Washington University
St. Louis, Missouri 63130

Abstract—To test the hypothesis that berthierine in oolitic ironstones formed by diagenetic transformation of detrital kaolinite, laboratory experiments simulating the early diagenetic conditions were conducted. Representative sets of the initial sediment were prepared in distilled water and artificial seawater suspensions by mixing 4–13 g/liter kaolinite with $\text{Fe}(\text{OH})_3$ precipitated from 0.1–0.3 M FeCl_3 solutions. $\text{Na}_2\text{S}_2\text{O}_4$ was added to the suspensions as a reducing agent, and inert N_2 atmospheres were used to maintain the required Eh between +100 and –400 mV. The pH of the suspensions was controlled between 8 and 5 with dilute HCl. Within 300 days, the iron content of the bulk kaolinite in the seawater suspensions progressively increased from 0.18 to 2.44% at pH = 7 and Eh between –250 and –350 mV. Energy dispersive X-ray analyses of individual clay platelets in the final products showed progressive, temporal increase in Fe, and concomitant decrease in Al and Si. X-ray powder diffractometry revealed small d(001)–d(002) shifts, marked intensity reversals of (001) and (002) reflections, and the development of additional characteristic berthierine reflections with time. These data suggest progressive transformation of kaolinite to berthierine. Microprobe analyses of natural berthierine in oolitic ironstones also showed parallel patterns, which substantiate such progressive transformation from the margin toward the core of the ooids. The transformation did not take place in distilled water. The addition of Mg^{2+} to the distilled water suspensions, however, promoted the transformation.

Key Words—Berthierine, Diagenesis, Ironstone, Kaolinite, Synthesis.

INTRODUCTION

Berthierine (formerly chamosite) is a trioctahedral ferri-ferrous clay mineral with the general composition $\text{Y}_6\text{Z}_4\text{O}_{10}(\text{OH})_8$, (Y = Fe^{2+} , Mg, Fe^{3+} , Al; Z = Si, Al, Fe^{3+}), similar to chlorite but structurally related to serpentine in having 7-Å basal spacing (Brindley, 1982). It is ubiquitous in Phanerozoic oolitic ironstones (James, 1966; Kimberley, 1979) including ferruginous fecal pellets and proto-ooids in Recent coastal sediments (Porrenga, 1967; Rohrlach *et al.*, 1969; Giresse and Odin, 1973; Allen *et al.*, 1979).

The dominant ferrous chemistry of berthierine (Table 1) and its restricted occurrence in Phanerozoic oolitic ironstones have been the focus of several investigations on the origin of these ironstones (Taylor, 1951; James, 1966; Schellmann, 1969; Karpov *et al.*, 1967; Bubenicek, 1971; Kimberley, 1980). Genetic discussions are generally divided between the possibility of primary chemical precipitation and of diagenetic replacement modes of formation. It has been demonstrated that primary precipitation of a ferrous mineral like berthierine from shallow, well-oxygenated surface waters is unlikely (Curtis and Spears, 1968; Crerar *et al.*, 1979), particularly in the light of fluctuating Eh, pH, and solution composition necessary for the precipitation of ferric oxide and ferrous silicate in alternate sheaths such as are commonly found in ferri-ferrous ooids. Moreover, concentrations of dissolved aluminum in fresh and seawaters at 0.001 ppm (Sacket and Arrhenius, 1962) and 0.3 ppm (Beck *et al.*, 1974), respectively, apparently are too low for the extensive berthierine precip-

itation needed to produce the oolitic iron formations (Kimberley, 1979). Most of the field and laboratory observations, on the other hand, suggest diagenetic origins, such as (1) dissolution of argillaceous sediments and reprecipitation (i.e., neoformation) as berthierine (Litvinenko, 1958 in Sokolova, 1964); (2) crystallization from noncrystalline $\text{SiO}_2\text{-Al}(\text{OH})_3\text{-Fe}(\text{OH})_3$ precipitates under reducing conditions (Caillère and Hénin, 1960; Bubenicek, 1971; Harder, 1978); (3) replacement of calcareous oolites (Kimberley, 1979, 1980), and (4) transformation of detrital kaolinite (Karpov *et al.*, 1967; Schellmann, 1969; Velde, 1977; Bhattacharyya, 1980; Iijima and Matsumoto, 1982).

Neoformation may contribute, in part, to the berthierine content of ironstones as pore-filling cement by processes (1) or (2), or a combination thereof. Berthierine in ooids could not have been formed by such a process, however, because neoformation would require the *in situ* formation of ooids. Geological evidence, such as cross bedding and sorting within the oolitic ironstones and ooid-filled burrows in the underlying sediments, indicate that the ooids had already formed prior to their deposition as oolitic ironstone (Bhattacharyya, 1980). Moreover, internal mineral fabric of the ferruginous ooids does not show the radial, spherulitic arrangement of the constituent minerals that is typical of crystallization fabric found in bauxite pisoids (Bhattacharyya and Kakimoto, 1982). Instead, the ironstone ooids show concentric tangential orientation of berthierine flakes and iron oxide minerals, similar to Bahaman calcareous ooids (Rohrlach, 1974). The latter have been interpreted

to possess a mechanical accretion fabric, in contrast to the radial crystallization fabric of the Salt Lake-type ooids (Sandberg, 1975). A dominant siliciclastic sedimentary association and facies sequences of the oolitic ironstones vitiate the calcareous oolite replacement hypothesis as the principal mode of formation of ferri-ferrous ooids (Bhattacharyya, 1980; Bradshaw *et al.*, 1980; Van Houten and Bhattacharyya, 1982). Moreover, radial fabric, common in carbonate oolites (Sandberg, 1975; Davies and Martin, 1976), has not been reported in the oolitic ironstones; neither have unequivocal carbonate ooids partially replaced by berthierine, even in thick and extensive ironstone deposits as young in age as Pliocene in the Kerch peninsula of the Soviet Union (Sokolova, 1964).

A facies model and petrographic evidence derived from the studies of a number of Phanerozoic oolitic ironstones (Bhattacharyya, 1980; Van Houten and Bhattacharyya, 1982) suggest that early diagenetic transformation of detrital kaolinite, both in the matrix and the ooids of the ironstone precursor (i.e., oolitic, ferruginous sediment prior to diagenesis), is a probable mode of berthierine formation.

The model gains further support from the occurrence of kaolinite ooids in ironstones (Taylor, 1951; Adeleye, 1973), and also from the occurrence of 10–30% kaolinite mixed with berthierine in concentric sheaths in ooids (Bhattacharyya, 1980). But Taylor (1951) interpreted these occurrences as the product of leaching of berthierine by ground water, as opposed to kaolinite left over due to incompleteness of diagenetic transformation. Assuming that the diagenetic or leaching reactions progressed from margin to core of the ooids, a progressive iron enrichment and concomitant Si-Al depletion would be expected in the berthierine compositions from margin to core of the ooids in the event of progressive diagenesis. A reverse relationship would be observed in the leached products.

The purpose of the present study, therefore, was to investigate the possibility of transformation of kaolinite to berthierine in the laboratory simulating early diagenetic conditions (i.e., $T \sim 20^\circ\text{C}$, $P \sim 1 \text{ atm.}$, $\text{pH } 8\text{--}5$, $E_h = +100 \text{ to } -400 \text{ mV}$) and the Fe-Al-Si compositional gradients of berthierine within natural ooids using an electron microprobe to formulate an unambiguous genetic model for berthierine in ironstones.

MATERIALS AND METHOD

Iron-rich, kaolinitic sediments were simulated in the laboratory by mixing chemical grade kaolinite (N.F. 1591, supplied by the Georgia Kaolin Company) with an excess of $\text{Fe}(\text{OH})_3$ precipitates. Kaolinite suspensions containing 4–13 g/liter were prepared in distilled water, artificial seawater (prepared from the recipe of Lyman and Flemming, 1940, in Horne, 1964, p. 140), and distilled water spiked with 0.5% MgCl_2 . Washed and vacuum-filtered $\text{Fe}(\text{OH})_3$, freshly precipitated from

100 ml of 0.1–0.3 M FeCl_3 solutions, was added to each 100-ml aliquot of the kaolinite suspensions. The pH of the final suspensions was controlled between 8.5 and 5 by the addition of dilute HCl. Sodium dithionite (0.1–0.3 g) was added to the suspensions as a reducing agent. Several bottles in a set were sealed under specific pH, E_h , and inert nitrogen environments. The experiments with MgCl_2 -spiked distilled water suspensions were conducted to see if Mg also catalyzed the reaction, as observed by Harder (1978) during the clay mineral synthesis experiments with Fe-Mg-Al-Si hydroxygel precipitates. At periodic intervals between 30 and 300 days one bottle from each set was opened, the pH and E_h were determined, and the contents were filtered through 0.22- μm Millipore (R) filter paper. Dissolved Fe, Al, and Si in the filtrate were determined by atomic absorption spectroscopy, and the residue was analyzed by X-ray powder diffractometry and chemical analysis. Before chemical analysis, “free iron” was chelated out of the residue with NaHCO_3 -buffered sodium citrate solution following the method of Mehra and Jackson (1960). Small quantities of noncrystalline iron sulfide, produced by the reaction between $\text{Fe}(\text{OH})_3$ and $\text{Na}_2\text{S}_2\text{O}_4$, were removed by treatment with cold 0.1 M HCl for 8 hr under continuous agitation.

The iron content of the bulk clays thus prepared was determined by a Perkin-Elmer 603 Atomic Absorption Spectrometer. The standard HF + H_2SO_4 dissolution technique was used to make the spectrometric solutions. In addition, individual clay platelets of the starting kaolinite and the final products from two sets of experimental runs in artificial seawater under pH 8 and 7 were analyzed for Fe, Al, and Si by a scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) microanalyzer (PGT System III EDA). Spot analyses of berthierine in different concentric sheaths within the ooids were made by an ARL-EMX electron microprobe using a beam diameter of 1 μm . Twenty-one ooids showing well-developed alternate sheaths of clay and iron oxide minerals (Figure 1) were selected from 8 thin sections of the Aswan ironstones (Bhattacharyya, 1980) for the microprobe analyses.

RESULTS AND DISCUSSION

From the transformation data listed in Table 2 and the iron content-time relationship plotted in Figure 2, the kaolinite in the seawater and the MgCl_2 -spiked freshwater suspensions incorporated a significant amount of iron into its structure, probably converting it to proto-berthierine. The amount of incorporated iron increased with time. That the iron was not adsorbed on the surface but substituted within the clay structure is indicated by marked changes in the intensities of (001) and (002) basal reflections (see Brown, 1955), small but noticeable decreases in $d(001)$ and $d(002)$ (i.e., towards berthierine), and the appearance of characteristic berthierine reflections at 2.68, 2.51, 2.14, 1.77, and 1.55 Å (Table

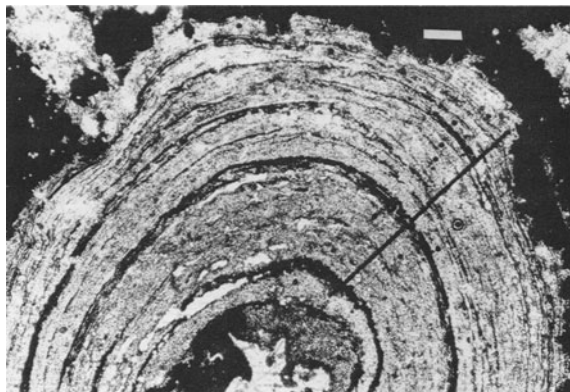


Figure 1. Typical ooid from the Aswan ironstone, Egypt, with alternate berthierine (light) and hematite (dark) sheaths. Used in core-to-margin spot analyses of berthierine in alternate sheaths under an electron microprobe. Dark spots (one circled) mark the location of berthierine analyzed. White bar = 0.1 mm.

2 and Figure 3). Structural substitution of the iron is further corroborated by the microchemical (SEM-EDX) analysis of the individual clay platelets of the original kaolinite and the experimental product clays in runs 18–27 (Table 2), the results of which are depicted in Figure 4. The analyses have not been corrected for oxygen stoichiometry; nevertheless, a progressive temporal Fe-enrichment and concomitant Al and Si depletion of the experimental clays are clearly demonstrated (Figure 4), and the bulk chemical analyses (Figure 2) compare well with SEM-EDX analyses of the individual clay platelets (Figure 4). In the experimental clays, however, only a few clay platelets show appreciable iron enrichment suggesting varying degrees of structural degradation in the experimental kaolinite, with the most degraded being the most susceptible to the intake of iron.

Electron microprobe analyses of berthierine in different concentric sheaths within ironstone ooids indicate that berthierine in ooids is progressively enriched in Fe and concomitantly depleted in Al and Si from the core towards the margin of the ooids. The pattern is similar to the variation depicted in Figure 4. This compositional variation of berthierine in natural ooids is interpreted as the result of progressive transformation of kaolinite to berthierine from the margin towards the center of the ooids. Post-diagenetic leaching (Taylor, 1951) could not have produced such a pattern. The 10–30% kaolinite in ironstone ooids and sporadic kaolinite ooids associated with ironstones (reported by Taylor, 1951; Adeleye, 1973) probably represent unreacted kaolinite in the parent rock.

Published analyses of berthierine show a wide variation in composition, and variable Al/Si and Al/(Al + Si) atomic ratios (Table 1) compared to the values 1.00 and 0.5, respectively, for kaolinite. A uniform Fe/(Fe + Al + Si) ratio of about 0.4 (Table 1), suggests mainly

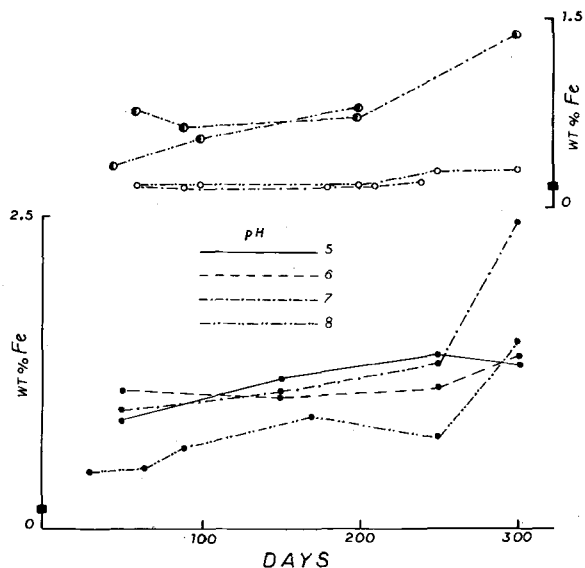


Figure 2. Plot of % Fe vs. time for product clays (AA-spectroscopic analyses, Table 2) showing progressive, temporal increase in the Fe content of the bulk clays. Solid squares = initial iron in the kaolinite (NF 1591); open circles = clays from freshwater suspensions; half solid circles = clays from MgCl₂-spiked freshwater; solid circles = clays from seawater.

substitution of Fe for Al and Si. The idealized kaolinite-berthierine transformation may be represented schematically by the following reactions:

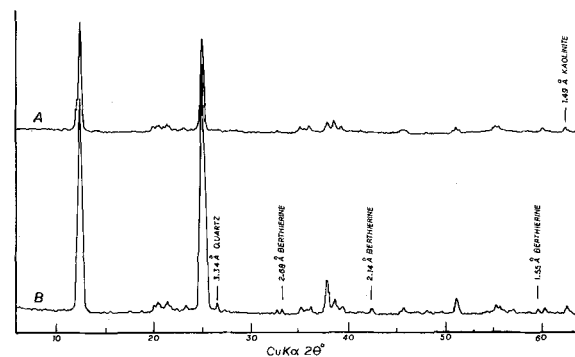
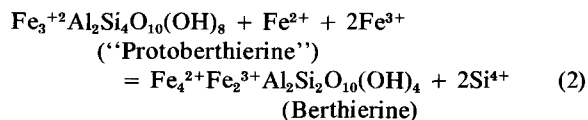
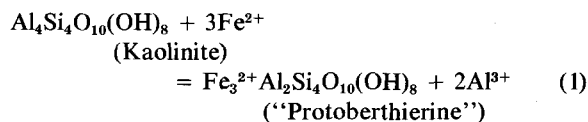


Figure 3. X-ray powder diffractograms of kaolinite (A, Georgia kaolinite NF-1591) and the product clay (B) in run 27 (Table 2). Note the reversal of the 001 and 002 peak intensities, and the appearance of new berthierine and quartz peaks in the product clays (B).

Table 1. Chemical compositions and structural distributions of cations¹ in berthierine.

	1	2	3	4	5	6	7	8	9	10	11
SiO ₂	20.84	19.08	22.86	21.40	23.72	21.26	21.34	26.24	22.47	24.0	23.92
Al ₂ O ₃	28.02	26.88	26.66	25.40	24.33	23.61	22.66	22.17	21.82	21.4	20.55
Fe ₂ O ₃	5.38	4.29	3.85	0.25	3.75	5.08	0.46	6.62	0.22	4.3	5.50
FeO	32.29	34.52	32.20	37.40	29.64	34.62	35.79	32.54	37.24	36.4	35.00
MgO	2.02	1.55	0.97	2.04	7.13	2.92	1.91	1.58	2.57	3.2	2.54
MnO	—	—	—	0.05	—	—	0.04	0.035	—	—	—
H ₂ O	10.70	11.18	10.48	12.02	11.00	12.51	10.64	10.81	10.07	10.7	11.41
Σ	99.25	97.50	97.02	98.56	99.57	100.00	92.84	100.00	94.39	100.00	98.92
Si	1.146	1.097	1.274	1.224	1.276	1.207	1.287	1.427	1.325	1.335	1.357
Al (IV)	0.854	0.903	0.726	0.776	0.724	0.793	0.713	0.573	0.675	0.665	0.643
Al (VI)	0.961	0.919	1.025	0.936	0.818	0.787	0.897	0.848	0.841	0.737	0.730
Fe ³⁺	0.223	0.186	0.161	0.011	0.152	0.216	0.021	0.271	0.010	0.180	0.234
Fe ²⁺	1.485	1.661	1.501	1.790	1.334	1.644	1.805	1.480	1.836	1.693	1.660
Mg	0.165	0.133	0.081	0.174	0.572	0.247	0.172	0.128	0.226	0.265	0.215
Mn	—	—	—	0.002	—	—	0.002	0.002	—	—	—
□	0.166	0.101	0.232	0.087	0.124	0.106	0.103	0.271	0.087	0.125	0.161
Atomic ratios											
Al/Si	1.58	1.66	1.37	1.40	1.21	1.31	1.25	0.99	1.44	1.05	1.01
Al/(Al + Si)	0.61	0.62	0.58	0.58	0.55	0.57	0.56	0.50	0.53	0.51	0.50
Fe/(Fe + Al + Si)	0.37	0.39	0.35	0.38	0.35	0.40	0.39	0.38	0.39	0.41	0.41
	12	13	14	15	16	17	18	19	20	21	
SiO ₂	26.90	25.5	26.01	30.07	22.43	26.65	21.50	20.62	24.90	32.00	
Al ₂ O ₃	18.40	14.9	12.33	17.26	14.27	16.14	20.12	11.96	15.60	10.05	
Fe ₂ O ₃	—	—	5.32	3.66	11.98	6.69	14.89	5.11	7.20	38.10	
FeO	36.80	35.6	37.07	37.61	37.63	34.43	21.90	25.98	35.00	—	
MgO	8.15	5.6	6.13	1.69	3.42	4.47	1.92	3.07	4.60	4.70	
MnO	—	1.0	0.04	0.02	0.02	—	0.98	0.30	0.40	1.68	
H ₂ O	9.58	17.4	10.33	9.01	9.70	11.50	15.60	10.92	12.30	—	
Σ	99.83	100.0	97.23	99.32	99.45	99.88	96.91	79.96	100.00	86.53	
Si	1.457	1.535	1.517	1.637	1.308	1.496	1.284	1.525	1.431	1.683	
Al (IV)	0.543	0.465	0.483	0.363	0.692	0.504	0.716	0.475	0.569	0.317	
Al (VI)	0.631	0.592	0.365	0.741	0.287	0.561	0.698	0.566	0.846	0.305	
Fe ³⁺	—	—	0.233	0.150	0.524	0.282	0.666	0.284	0.310	1.503	
Fe ²⁺	1.667	1.792	1.808	1.706	1.829	1.610	1.089	1.602	1.675	—	
Mg	0.658	0.503	0.533	0.137	0.299	0.377	0.172	0.342	0.396	0.371	
Mn	—	0.051	0.002	0.001	0.001	—	0.05	0.018	0.019	0.038	
□	0.044	0.062	0.059	0.265	0.06	0.17	0.325	0.188	—	0.783	
Atomic ratios											Average
Al/Si	0.80	0.69	0.56	0.67	0.75	0.71	1.10	0.68	0.74	0.37	1.02 ± 0.36
Al/(Al + Si)	0.45	0.41	0.36	0.40	0.43	0.42	0.52	0.41	0.42	0.27	0.49 ± 0.09
Fe/(Fe + Al + Si)	0.39	0.41	0.46	0.40	0.51	0.42	0.39	0.42	0.44	0.39	0.40 ± 0.04

Sample locations: (Nos. 1–14, from Brindley, 1982, Table 1); 1, 2, 3—Belgorod district, Kursk, USSR; 4—Wabana, Newfoundland, Canada; 5, 6, 11—Voronezh anticline, Kursk, USSR; 7—Ayrshire, Scotland; 8—Sussex, England; 9—Corby, England; 10—Pegnitz, Germany; 12—Gunflint range, USA—Canada; 13—Sainte-Barbe, France; 14—Kuntzenberg, Czechoslovakia; (Nos. 15–19, from James, 1966, Table 3); 15—Chamozentze, Switzerland; 0.44% Na₂O, 0.16% K₂O, 0.02% TiO₂ not included; 16—Windgalle, Switzerland; 0.22% Na₂O, 0.04% K₂O, 0.19% TiO₂ not included; 17—Schmidefeld, Germany; 18—Gledic, Yugoslavia, contains 1.18% CaO; 19—Isle of Raasay, Scotland, 5.02% CaCO₃, 6.05% Ca₃(PO₄)₂ deducted to remove CO₂ and P₂O₅, also 0.09% Na₂O, 0.72% TiO₂ and excess 0.43% CaO not included; 20—Fordingham, England, (Hallimond *et al.*, 1939); 21—Loch Etive, Scotland (Rohrlich *et al.*, 1969); 0.72% CaO, 1.13% K₂O, 0.23% TiO₂, and 0.81% P₂O₅ not included.

¹ Nos. 15–21 calculated following the method of Brindley (1982). □ = Vacant octahedral sites.

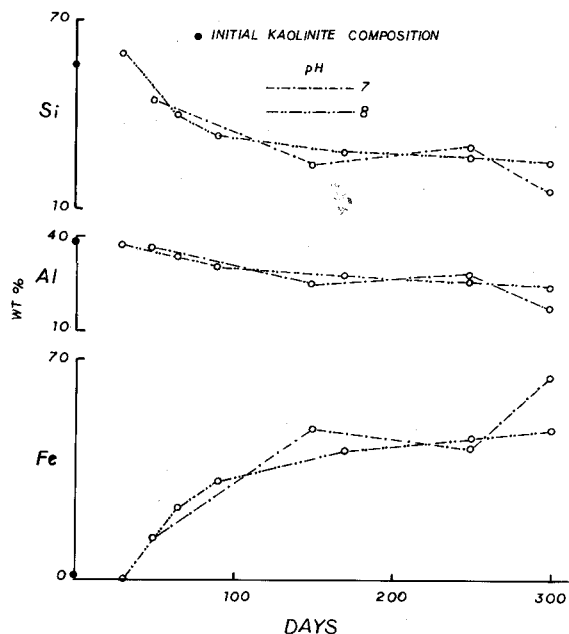


Figure 4. Plot of % Fe, Al, Si (SEM-EDX analyses) vs. time for the individual clay platelets in runs 18–27, Table 2, illustrating progressive Fe substitution in kaolinite to produce berthierine.

The natural reactions, understandably, are more complex and variable. However, under the ambient pH and Eh required for the mobilization of Fe^{2+} and Fe^{3+} , similar reactions are promoted in an iron-rich environment. These reactions would especially be favored in moderately reducing diagenetic environments. Early diagenetic lowering of pH and Eh in Recent sediments from a variety of marginal marine environments has been documented (Friedman and Gavish, 1970), and the fact that berthierine is restricted essentially to ironstones points to its close relationship with initially iron-rich environments.

Eqs. (1) and (2) suggest that substantial amounts of Al and Si are released during these reactions. In the experiments, however, as much as 5 ppm Al, but no Si at the ppm level, was detected in the filtrate. Nevertheless, a number of XRD patterns of the product clays showed the 3.34-Å reflection of quartz that was not present in the initial material (Figure 3). Rarely, scanning electron micrographs of the product clays also showed small, euhedral crystals of quartz (Figure 5). The low concentrations of dissolved Al and Si in the filtrate are probably caused by chemisorption of these ions by excess of $\text{Fe}(\text{OH})_3$ present in the suspension (Harder, 1978). Si is further depleted in the solution because of its rapid polymerization into crystalline quartz in the presence of $\text{Fe}(\text{OH})_3$ precipitates (Harder, 1978). SiO_2 polymerization is also presumed to be enhanced by Mg^{2+} in the solution (see below). The occurrence of silica spherules within the ironstone ooids (Rohrlich,

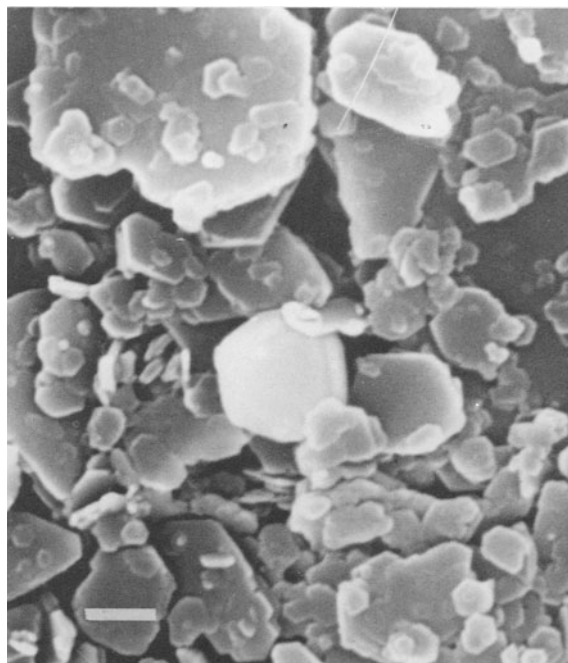


Figure 5. Scanning electron micrograph of neoformed, euhedral crystal of quartz (bright crystal in the center) in the product clay. White bar = 1 μm .

1974; Bhattacharyya and Kakimoto, 1982) is possibly due to such polymerization. Parts of the released Al and Si probably contributed to the neoformation of berthierine cement in the ironstones (Bhattacharyya and Kakimoto, 1982). In the experimental products, however, the relatively large size of the berthierine flakes ($\geq 1 \mu\text{m}$), even in runs as short as 30 days, and the temporal compositional variation of berthierine (Figure 4) suggest progressive substitution rather than neoformation.

In the artificial seawater suspensions, the most favorable chemical environment for the transformation of kaolinite to berthierine was found to be at or near pH 7 and Eh between -200 and -300 mV (Table 2). But the reactions seemed to take place at a variable rate over the pH and Eh range of natural, early diagenetic environments ($5 < \text{pH} < 8$; $-300 < \text{Eh} < 100$ mV). Theoretical considerations of the stability relations of sedimentary iron minerals (Garrels and Christ, 1965; Figures 7.21, 7.23) support this mechanism if the variability of dissolved S and CO_2 and the degree of saturation with noncrystalline SiO_2 are taken into account. However, the stability field of iron aluminosilicate (berthierine) would probably be larger and somewhat modified relative to the FeSiO_3 analogue chosen for theoretical calculations (Garrels and Christ, 1965, p. 226), because such materials in nature (i.e., ortho- or clinoferrrosilite) are high-temperature phases and their thermodynamic properties are not representative of those

Table 2. Results of kaolinite to berthierine transformation experiments at room temperature.

Run	Days	pH		Eh (mV)		Fe		Iron minerals present	X-ray powder diffractometry				3.34 Å quartz reflection
		Initial	Final	Initial	Final	In clay (%)	In the filtrate (ppm)		Basal reflections		Berthierine reflections (Å)		
									(001) (Å)	(002) (Å)		$h^*(001)$	
Georgia kaolinite N.F. 1591													
Runs in distilled water suspension with 0.3 M Fe, 3.87 g/liter kaolinite, and 0.3% Na ₂ S ₂ O ₄ .													
1	60	8.60	8.52	-440	-450	0.18	n.d.	Go, Py	7.13	3.56	1.1		
2	100	8.53	8.49	-460	-370	0.19	n.d.	Go, Py	7.13	3.56	1.1		
3	200	8.58	8.68	-450	-370	0.19	0	Go, Py	7.13	3.56	1.12		
4	250	8.58	7.71	-440	-320	0.29	33	Go, Py	7.13	3.56	1.1		
5	300	8.54	7.43	-430	-320	0.27	60	Go, Py	7.13	3.56	1.1		
6	60	7.00	6.49	-465	-435	0.18	n.d.	Go, Py	7.13	3.56	1.13		
7	90	7.00	6.37	-480	-440	0.18	n.d.	Go, Py	7.13	3.56	1.14		
8	180	7.00	6.20	-470	-400	0.185	n.d.	Go, Py	7.13	3.56	1.12		
9	210	7.00	6.10	-460	-440	0.19	60	Go, Py	7.13	3.56	1.1		
10	240	7.00	6.10	-460	-345	0.21	100	Go, Py	7.13	3.56	1.1		
Runs in distilled water suspension with 0.1 M Fe, 5.16 g/liter kaolinite, 0.3% Na ₂ S ₂ O ₄ , and 0.5% MgCl ₂ .													
11	45	8.61	6.89	-550	+220	0.33	n.d.	Go, He	7.10	3.56	1.00		
12	100	8.68	7.58	-560	-195	0.547	0	Go, He, Le, Py	7.08	3.55	0.85		2.68, 2.14, 1.55
13	200	8.59	7.53	-550	-290	0.8	10	Go, He, Le, Py	7.08	3.55	0.86		2.68, 1.55
14	60	7.01	5.16	-335	+50	0.78	n.d.	Go, He, Le	7.08	3.55	0.9		2.14, 1.55
15	90	7.01	7.00	-365	-355	0.64	n.d.	Go, He	7.10	3.56	1.00		1.55
16	200	7.00	7.04	-365	-290	0.73	70	Go, He	7.10	3.55	1.00		1.55
17	300	7.02	7.03	-365	-300	1.39	80	Go, He	7.08	3.55	0.86		2.14, 1.55
Runs in seawater suspensions with 0.1 M Fe, 12.9 g/liter kaolinite, and 0.1% Na ₂ S ₂ O ₄ .													
18	30	8.25	8.09	-100	+80	0.46	n.d.	Go	7.13	3.56	1.1		
19	65	8.28	7.7	-100	-220	0.48	n.d.	Go	7.13	3.56	1.00		
20	90	8.24	7.68	-100	-190	0.64	50	Go	7.08	3.55	1.00		
21	170	8.39	7.84	-220	-200	0.89	60	Go, He	7.08	3.55	1.00		2.68, 1.55
22	250	8.26	7.73	-100	-90	0.72	50	Go, He	7.08	3.55	0.84		2.68, 2.14, 1.55
23	300	8.24	7.12	-110	-80	1.49	55	Go, He, Fh	7.03	3.55	0.86		2.68, 2.51, 2.14, 1.55
Runs in seawater suspensions with 0.1 M Fe, 12.9 g/liter kaolinite, and 0.3% Na ₂ S ₂ O ₄ .													
24	50	7.00	6.76	-260	-320	0.94	210	Go	7.10	3.55	1.02		
25	150	7.00	6.96	-260	-285	1.07	220	Go	7.08	3.56	1.06		2.68, 1.55
26	250	7.00	6.67	-260	-135	1.33	240	Go	7.04	3.55	1.00		2.68, 1.55
27	300	7.00	6.71	-270	-250	2.44	292	Go, Fh	7.03	3.53	0.85		2.68, 2.14, 1.55
28	50	6.00	5.60	-100	-90	1.10	490	Go	7.10	3.56	1.09		2.68, 2.14
29	150	6.00	5.40	-80	-10	1.02	450	Go	7.10	3.55	1.00		2.68, 2.14, 1.55
30	250	6.00	5.74	-95	+35	1.12	485	Go, He	7.04	3.53	1.02		2.68, 2.51, 2.14, 1.55
31	300	6.00	5.72	-110	-100	1.37	573	Go, Fh	7.04	3.53	0.85		2.68, 2.14, 1.55

Table 2. Continued.

Run	Days	pH		Eh (mV)		Fe		Iron minerals present	Basal reflections			Berthierine reflections (Å)	3.34 Å quartz reflection
		Initial	Final	Initial	Final	In clay (%)	In the filtrate (ppm)		(001) (Å)	(002) (Å)	$\frac{h^*(001)}{h^*(002)}$		
32	50	5.00	4.60	+80	+70	0.86	470	Go, Fh, He	7.10	3.56	1.10		
33	150	5.00	4.86	+30	+55	1.19	590	Go, Fh, He	7.08	3.56	1.00	2.68, 1.55	
34	250	5.00	4.64	+40	+180	1.39	600	Go, Fh, He	7.04	3.55	0.96	2.68, 1.55	X
35	300	5.00	4.89	+30	+5	1.29	675	Go, Fh, He	7.04	3.53	0.93	2.68, 1.55	X

Go = Goethite; Py = Pyrite; He = Hematite; Le = Lepidocrocite; Fh = Ferrhydrite; n.d. = not determined.

$\frac{h^*(001)}{h^*(002)}$ = ratio of (001) and (002) peak heights on the diffractograms.

of a low-temperature, (OH)-bearing phase like berthierine. In the ironstones, the paragenetic sequence of the three common iron-bearing minerals is goethite, berthierine, and siderite, in that order, and siderite commonly replaces berthierine (Schellmann, 1969; Bubenicek, 1971; Bradshaw *et al.*, 1980; Bhattacharyya, 1980). These relationships also suggest that berthierine is stable under conditions intermediate between those required for the formation of $\text{Fe}(\text{OH})_3$ and FeCO_3 .

In the freshwater suspensions, the transformation of kaolinite to berthierine was negligible. The presence of Mg^{2+} in the solution apparently promoted the conversion (Table 2, Figure 2), as noted by Harder (1978). A similar, apparently catalytic effect of Mg^{2+} on the diagenetic transformation of noncrystalline SiO_2 into opal-CT has also been noted (Kastner *et al.*, 1977).

Commonly, berthierine and glauconite are mutually exclusive in any specific ironstone bed, but are related to each other by lateral and vertical lithofacies variation within the iron formations. Berthierine occurs in presumably near-shore and glauconite in off-shore facies, as in the Silurian Clinton Group of the eastern United States (Hunter, 1970), the Devonian iron formations in the southwestern part of the Soviet Union (Karpov *et al.*, 1967), the Jurassic carbonate and argillaceous deposits in Europe (Gygi, 1981), and the Cenozoic arenaceous deposits in the southern United States (Jones, 1969). In Recent sediments, berthierine and glauconite occur in zones along coasts at water depths of 50 and 150 m, respectively (Porrenga, 1967; Giresse and Odin, 1973; Odin and Matter, 1981). In ancient sediments such a differential distribution has been attributed to differential salinities of the seawater (Hunter, 1970). In Recent sediments, differences in sedimentary environment (Giresse and Odin, 1973; Odin and Matter, 1981) or differences in temperature due to variation in water depth (Porrenga, 1967; Odin and Matter, 1981) have been suggested as possible causes. However, the distribution of glauconite and berthierine in Recent sediments (Rohrlich, 1969; Odin and Matter, 1981) does not substantiate the control of seawater salinity and temperature on the formation of these minerals.

An important aspect indicated by the studies of present-day coastal sedimentation is the coincidence of berthierine- and glauconite-forming zones with the coast-parallel zones of kaolinite and smectite sedimentation, respectively (Pinsak and Murray, 1960; Porrenga, 1967; Doyle and Sparks, 1980). Differential flocculation and settling properties of the detrital clays (Whitehouse *et al.*, 1960) are probably responsible for this zonal distribution of kaolinite and smectites. But all kaolinite and smectite sedimentation zones are not berthierine or glauconite producing, probably because in areas of high sedimentation rate the sediments are not enriched in iron. Only in sediment-starved environments would these two clay sedimentation zones be relatively enriched in iron supplied by rivers and other sources.

Commonly, the near-shore kaolinite zone is associated with dominant detrital lithofacies, whereas the off-shore smectite zone is associated with carbonates. The occurrence of berthierine and glauconite in sediment-starved condensed sequences (Bhattacharyya, 1980; Gygi, 1981; Odin and Matter, 1981), their common association with detrital and carbonate rocks, and their coincidence with coast-parallel zones of kaolinite and smectite sedimentation, respectively, all point to a common genetic process acting on different detrital precursors to produce berthierine and glauconite (Bhattacharyya, 1980; Van Houten and Bhattacharyya, 1982).

Normally, glauconite occurs as peloids, and berthierine forms both ooids and peloids; but most ooids have a peloidal nucleus (Bhattacharyya, 1980). The distinction probably reflects a basic difference in bond strength between precursor clay particles. Unlike smectite, kaolinite with a higher bond strength between platelets (Whitehouse *et al.*, 1960; van Olphen, 1977) is susceptible to mechanical accretion into ooids around peloidal or other granular mineral nuclei in near-shore, relatively high-energy and sediment-starved environments (Bhattacharyya and Kakimoto, 1982). Most of the peloids are probably fecal, in which the particles are held together by fecal mucus.

CONCLUSION

Berthierine is essentially diagenetic in origin and is genetically related to a detrital precursor, kaolinite. After deposition, early diagenetic remobilization of iron initiates substitutive transformation of kaolinite to berthierine, forming the bulk of the mineral in ironstones. Al and Si, released during such reactions, contribute to the neoformation of berthierine cement as well as opaline SiO₂ in ironstones. Geologic, chemical, and petromineralogic constraints on the genetic model for berthierine in ironstones are:

1. Restricted occurrence in marginal marine, shoaling upward, detrital sediments marked by sediment-starved conditions;
2. Dominant ferrous chemistry of berthierine in an otherwise well-oxygenated sediment-water interface, indicated by a profusion of feeding benthos (burrowers);
3. Concentric-tangential accretion fabric of ironstone ooids;
4. Alternate ferric and ferrous mineralogy in the concentric sheaths within ooids;
5. Association with kaolinite and kaolinitic claystones in space and time.

Most of these constraints vitiate primary precipitation, diagenetic carbonate oolite replacement, and diagenetic neoformation for the bulk of the berthierine in ironstones. Among other necessary conditions, the most important is an initial enrichment of the sediments in

iron to promote mass action. The presence of ions such as Mg²⁺ may catalyze the transformation.

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Резюме—Проводились лабораторные эксперименты, симулирующие условия ранней диагенезы для проверки гипотезы, что бертьерин в оолитовых железных рудах формировался путем диагенетической трансформации детритового каолинита. Характерные образцы первоначального осадка были приготовлены как суспензии в дистиллированной воде и искусственной морской воде путем смешивания 4–13 г/литр каолинита с $\text{Fe}(\text{OH})_3$, осажденным из 0,1–0,3 М раствора FeCl_3 . Вещество $\text{Na}_2\text{S}_2\text{O}_4$ было добавлено до суспензии в качестве редуцирующего агента и инертная N_2 атмосфера использовалась для поддержания уровня величины Eh между +100 и –400 мВ. Величины pH суспензии были контролированы между 8 и 5, используя растворенную HCl. В течение 300 дней содержание железа в каолините и суспензиях морской воды постепенно увеличивалось от 0,18 до 2,44% при pH = 7 и Eh между –250 и –350 мВ. Энерго-дисперсионный рентгеновский анализ индивидуальных пластинок глины в конечном продукте показал постепенное временное увеличение содержания Fe и сопутствующее уменьшение содержания Al и Si. Рентгеновская порошковая дифрактометрия показало небольшие сдвиги d(001)–d(002), значительный риверс интенсивностей отражений (001) и (002) и развитие добавочных характеристических отражений бертьерина по времени. Эти данные указывают на прогрессивную трансформацию каолинита в бертьерин. Анализ натурального бертьерина из оолитовых железных руд при помощи рентгеновского микроскопа тоже показал параллельные структуры, что подтверждает эту прогрессивную трансформацию от края до центра ооидов. Эта трансформация не происходила в дистиллированной воде. Однако, добавление ионов Mg^{2+} к суспензии с дистиллированной водой способствовало этой трансформации. [E.G.]

Resümee—Um die Annahme zu prüfen, daß Berthierin in oolithischen Eisensteinen durch diagenetische Umwandlung von detritischem Kaolinit entsteht, wurden Laborexperimente durchgeführt, die frühdiagenetische Bedingungen simulierten. Repräsentative Reihen des ursprünglichen Sedimentes wurden in Suspensionen mit destilliertem Wasser und Künstlichem Meerwasser hergestellt, indem 4 bis 13 g/l Kaolinit mit $\text{Fe}(\text{OH})_3$ gemischt wurde, das aus 0,1–0,3 M FeCl_3 -Lösungen ausgefällt wurde. $\text{Na}_2\text{S}_2\text{O}_4$ wurde zu den Suspensionen als Reduktionsmittel hinzugefügt. Außerdem wurden die Experimente in inerter N_2 -Atmosphäre durchgeführt, um den erforderlichen Eh-Wert zwischen +100 und –400 mV konstant zu halten. Der pH-Wert der Suspensionen wurde zwischen 8 und 5 mittels verdünnter HCl kontrolliert. Innerhalb von 300 Tagen nahm der Eisengehalt des gesamten Kaolinit in den Meerwassersuspensionen ständig von 0,18 auf 2,44% zu, bei einem pH = 7 und Eh zwischen –250 und –350 mV. Energiedispersive Röntgenanalysen von einzelnen Tonblättchen in den Endprodukten zeigten eine fortschreitende, zeitabhängige Zunahme an Eisen und eine entsprechende Abnahme an Aluminium und Silizium. Röntgenpulverdiffraktometeraufnahmen ergaben geringe Verschiebungen von d(001)–d(002), beachtliche Intensitätsumkehrungen der (001) und (002) Reflexe und die Ausbildung von zusätzlichen charakteristischen Berthierin-Reflexen mit zunehmender Zeit. Diese Ergebnisse deuten auf eine zunehmende Umwandlung von Kaolinit in Berthierin hin. Mikrosondenanalysen von natürlichem Berthierin in oolithischen Eisensteinen zeigten ebenfalls Doppelreflexe, die diese zunehmende Umwandlung vom Rand gegen den Kern des Ooides verdeutlichen. Diese Umwandlung fand in destilliertem Wasser nicht statt. Die Zugabe von Mg^{2+} zu den Suspensionen mit destilliertem Wasser förderte jedoch die Umwandlung. [U.W.]

Résumé—Pour vérifier l'hypothèse que la berthiérine dans des roches oolithiques de fer a été formée par la transformation diagénétique de kaolinite détritique, on a fait des expériences au laboratoire simulant les conditions du début de la diagénèse. Des groupes représentatifs du sédiment initial ont été préparés dans l'eau distillée et des suspensions d'eau de mer artificielles en mélangeant 4–13 g/litre de kaolinite avec $\text{Fe}(\text{OH})_3$ précipité à partir de solutions de 0,1–0,3 M FeCl_3 . $\text{Na}_2\text{S}_2\text{O}_4$ a été ajouté aux suspensions comme agent réductif, et des atmosphères inertes de N_2 ont été utilisées pour maintenir l'Eh requis entre +100 et –400 mV. Le pH des suspensions a été contrôlé entre 8 et 5 avec de l'HCl dilué. En 300 jours, le contenu en fer de la kaolinite en masse dans les suspensions d'eau de mer a progressivement augmenté de 0,18 à 2,44% au pH = 7, et Eh entre –250 et –350 mV. Des analyses aux rayons-X dispersant l'énergie des paillettes d'argile individuelles des produits finaux ont montré une augmentation progressive, temporelle de Fe, et une diminution concordante d'Al et de Si. La diffraction poudrée de rayons-X a révélé des petits déplacements de d(001)–d(002), des renversements marqués de l'intensité des réflexions (001) et (002) et le développement de réflexions de berthiérine typiques avec le temps. Ces données suggèrent une transformation progressive de kaolinite en berthiérine. Des analyses microprobes de berthiérine naturelle dans des roches oolithiques de fer ont aussi montré des diagrammes parallèles, ce qui justifie qu'une telle transformation progressive se produit de l'extérieurs vers le centre des ooides. La transformation ne s'est pas produite dans l'eau distillée. L'addition de Mg^{2+} aux suspensions d'eau distillée a cependant provoqué la transformation. [D.J.]