

ODINITE, A NEW DIOCTAHEDRAL-TRIOCTAHEDRAL Fe^{3+} -RICH 1:1 CLAY MINERAL

S. W. BAILEY

Department of Geology and Geophysics, University of Wisconsin-Madison, Madison, WI 53706, USA

(Received 11 March 1988; revised 27 June 1988)

ABSTRACT: Odinite is a Fe^{3+} -rich green clay that is widespread in the form of infillings or replacements of microtests, bioclasts, faecal pellets, or mineral debris on shallow marine shelves and reef lagoonal areas in tropical latitudes. The structure is based on a 1:1 serpentine-type layer that is intermediate between dioctahedral and trioctahedral. Octahedral cation totals range from 2.30 to 2.54 cations per 3.0 sites for 10 samples. The structural formula for the purest sample is $(Fe_{0.784}^{3+}Mg_{0.772}Al_{0.556}Fe_{0.279}^{2+}Ti_{0.016}Mn_{0.015})_{2.422}(Si_{1.788}Al_{0.212})O_5(OH)_4$. Both monoclinic and trigonal polytypes are present in most samples, with 1M more abundant than 1T. Unit-cell dimensions are 1M: $a = 5.373(3)$, $b = 9.326(7)$, $c = 7.363(6)$ Å, $\beta = 104.0(1)^\circ$; 1T: $a = 5.366(5)$, $b = 9.334(9)$, $c = 7.161(8)$, $\beta = 90^\circ$ (on orthohexagonal axes). The name is for Dr. Gilles Serge Odin, Département de Géologie Dynamique, Université Pierre et Marie Curie, Paris, who has done most of the pioneering work on this new mineral.

Résumé en Français page 247

Green clays identified originally as berthierine by Odin & Giresse (1972) and Odin & Matter (1981) (or "chamosite" of the older literature, e.g., Von Gaertner & Schellman, 1965; Porrenga, 1967) are present on many shallow marine shelves and reef lagoonal areas in tropical latitudes. The clays are closely associated with biogenic carbonate and continental fluvial detritus from river discharge systems. Odin (1985, 1988a), on the basis of more detailed study of a large number of samples, gave the green clay the temporary designation of phyllite V, and named the facies in which it occurs—the verdine facies. He pointed out that phyllite V differs compositionally from berthierine in containing less Al, less Fe^{2+} , more Mg, more Si, and considerably more Fe^{3+} . Phyllite V is a ferric dioctahedral-trioctahedral mineral whereas berthierine is a trioctahedral, dominantly ferrous mineral. Odin (1985) considered phyllite V most likely to belong to the chlorite group, but further work showed that the chlorite present is a secondary alteration product of a primary 1:1 layer-silicate (Odin *et al.*, 1988b). Thus, the original phyllite V is a mixture of two authigenic phases, 7 Å phyllite V and 14 Å phyllite V.

The present paper describes the primary 1:1 mineral on the basis of samples kindly provided by Dr. G. S. Odin to the writer in 1985. It illustrates Odin's belief that the chemistry of phyllite V is unique among known layer-silicate minerals, provides additional structural and crystallographic details, and proposes a new species name.

It is proposed that the temporary designation 7 Å phyllite V be replaced by the species name odinite. The name is in honour of Dr. Gilles Serge Odin, Département de Géologie Dynamique, Université Pierre et Marie Curie, Paris, who made the original identification and has done most of the pioneering work on this new mineral. The name has been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names. Type material from New Caledonia has been deposited in the Museum National d'Histoire Naturelle, Rue Buffon, Paris (MNHN 187.7), the Smithsonian National Museum of Natural History, Washington, D.C. (NMNH 165498), the British Museum of Natural History, London (BM 1987, 531), and the École des Mines Museum of Paris (under the letter O).

OCCURRENCE

Odinite is estimated to be a minor component (0.1–10%) of sediments that cover more than 100,000 km² of the present day sea bottom. Odin *et al.* (1988a) list eleven independent localities where it has been identified: (i) the Ogooue River prodelta (Congo); (ii) continental shelf between the Amazon and Orinoco Rivers; (iii) Niger River prodelta; (iv) Koukoure River prodelta and Los Islands (Guinea); (v) North Sarawak continental shelf; (vi) Congo River prodelta; (vii) continental shelf facing the Comoe River mouth (Ivory Coast); (viii) reef lagoon SW of New Caledonia; (ix) continental shelf of Cap Vert (Senegal); (x) east of Mayotte Island lagoon (Comoro); and (xi) within the estuary of the Casamance River (Senegal). Since that publication, odinite has also been identified off Martinique Island. The latitudes of these occurrences range from 23°S to 16°N.

The odinite is mixed in the sediments with quartz sand, often with a large component of carbonate bioclasts, plus smaller amounts of clay minerals and other detritus, and is most evident at shallow depths in areas where the detrital sedimentation rate is low. The authigenic odinite is then abundant enough to give the sediment a green colour, and it usually comprises < 1% of the total sediment. It can be separated from the associated minerals by electromagnetic separation, specific gravity, acid leaching (at the expense of some alteration), and careful ultrasonic cleaning.

The environment of formation is believed to be in marine waters at the sediment-water interface (Odin & Sen Gupta, 1988) where there is normal salinity, a basic pH (7.5–8.5), temperature near 25°C, an abundance of oxygen, and a positive Eh above the sediment. These are the conditions which exist today in the areas where odinite still seems to be forming (*e.g.*, New Caledonia, Los Islands, Mayotte). The observed mean water depths where odinite is forming are between 15 and 60 m within porous sediments having a particle size mostly > 500 µm. Circulating currents are required, and a continental ionic input with abundant Si, Mg, and Fe. These conditions allow a slow but constant water circulation through the sediments. Because odinite is found primarily as infillings due to impregnation or replacement of biogenic or detrital porous grains (in natural cavities, cavities of dissolution, fissures, cleavage planes, etc.), it is believed to have formed in a micro-environment within the pores and cavities. Some of these cavities (within bioclasts or faecal pellets) originally contained organic matter and thus were more reducing than the external environment. Some evidence of a localized reducing environment is indicated by the grey-black colour of many bioclasts which are shown by X-ray study to be due to a mixture of pyrite and goethite. Because of the circulating currents and the grain size of the sediments, cation exchange between the micro-environment and the external environment is possible by filtering through the external pores of the bioclasts. Because of the elevated temperature (~25°C), odinite tends to form rather quickly, 1,000 years as an order of magnitude compared to 10,000–100,000 years for Recent glauconitic materials forming at 10–15°C (Odin & Matter, 1981).

The verdine facies in which odinite forms is different in detail from that in which glauconite forms, specifically in the shallower depths and proximity to continental water input (Odin & Sen Gupta, 1988). In contrast to the oolitic habit of berthierine in ironstone deposits, odinite has never been observed as oolites, nor do the relatively compact sediments show any evidence of rolling or reworking. In contrast to berthierine it has never been observed crystallizing between bioclasts. In the deeper parts of the continental shelf (80–150 m), it is often found free of any substrate material and then is darker green in colour and more altered to chlorite (*e.g.*, in French Guiana). These dark green pellets are considered to

be older than the lighter green pellets found at shallower depths. The evolution sequence of light green odinite to dark green odinite to chlorite is a maturation process with increasing age and exposure to the marine environment. At depths shallower than ~ 20 m, odinite oxidizes rapidly to yellow and red brown colours.

The geologic evidence suggests that all the known odinite occurrences have formed within the last 12,000 years (Odin & Masse, 1988), *e.g.* sea water has only been present in the lagoon of New Caledonia for ~ 7 –8,000 years, following the Holocene transgression. Odinite is very susceptible to alteration and has not been recognized as yet in rocks older than the Recent Quaternary.

PHYSICAL PROPERTIES AND TESTS

Odinite is silky-green to dark-green in colour and quite similar to glauconite in appearance. Powdered material is grey-green and the lustre is silky to earthy opaque. The density of pure odinite could not be measured, but aggregates containing some quartz have a density less than that of bromoform and close to that of quartz (2.65). Although aggregates up to 0.4 mm in size were observed, optical properties could not be measured because of the small size of the clay-size crystallites within the aggregates. Odinite does not expand upon solvation with ethylene glycol. It becomes amorphous on heating at 490°C for 2 h.

The differential thermal analysis (DTA) curve of odinite from the Ivory Coast shows endothermic reactions at 125°, 410°, 550°, and 710°C (Fig. 1). Comparison with DTA curves from other samples from the Gulf of Guinea suggests that only the endotherms at $120 \pm 5^\circ$ and $550 \pm 5^\circ$ are unique to odinite. Because these samples are partly altered to chlorite, the endotherm at 120°C is interpreted as due to adsorbed water plus extraction of water from the

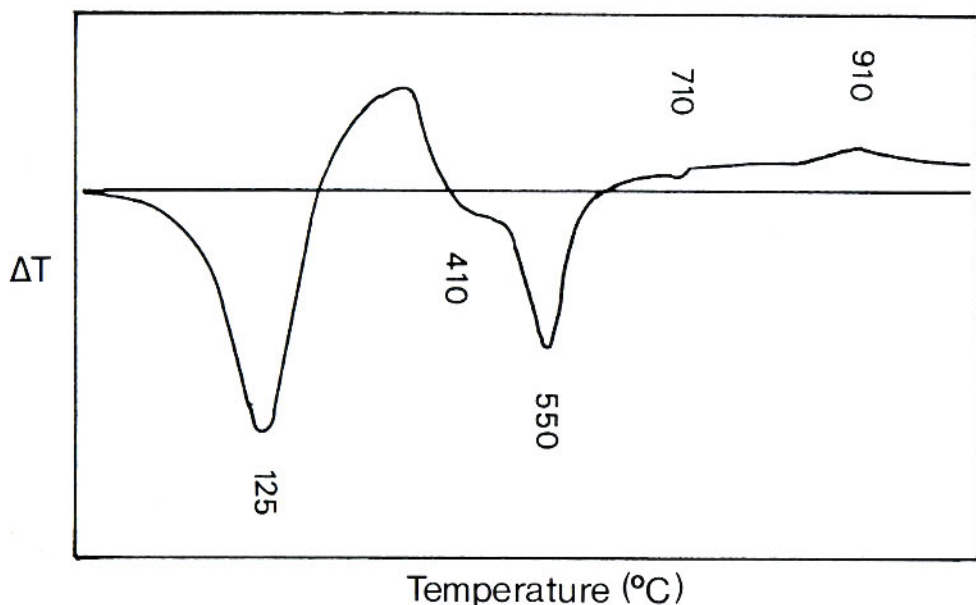


FIG. 1. DTA curve of odinite from Ivory Coast (from Odin *et al.*, 1988b). The temperatures for the reactions are shown in °C. Chlorite impurity present.

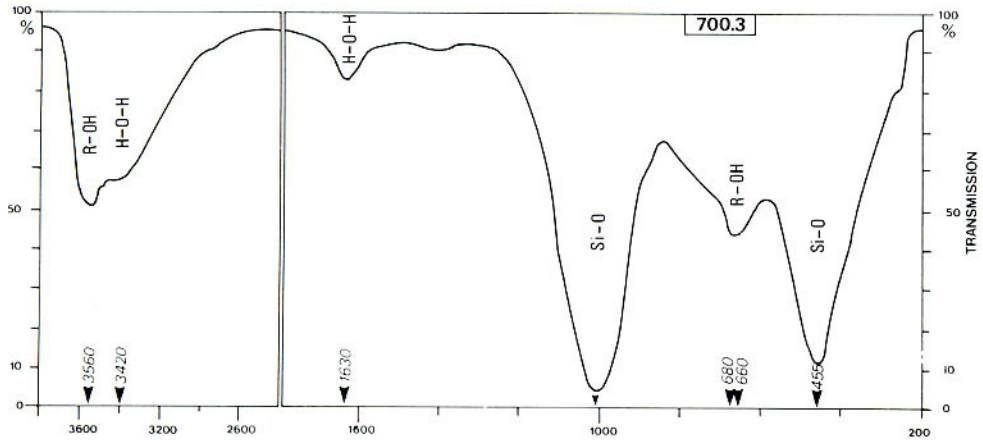


FIG. 2. IR spectrum of odinite from New Caledonia. The y axis shows the relative transmission in % on a linear scale that is linked to specific absorbance by $A = \log 1/T$. Spectrum run by F. Fröhlich.

unstable interlayer sheet of the chlorite. The 550°C endotherm represents water extracted from the octahedral sheets of odinite and chlorite. No major exotherm was observed, probably due to the low content of Fe^{2+} .

Infrared absorption spectra were kindly provided by F. Fröhlich (Muséum National d'Histoire Naturelle), and those obtained from purified samples from New Caledonia, Senegal, French Guiana, and Congo are comparable to one another. A double-beam spectrometer with optical compensation was used, including a reference beam with 300 mg KBr, and analyzer beam with 0.75 mg of clay heated at 105°C. Only six wide absorption bands are present (Fig. 2). Two medium intensity bands are attributed to adsorbed water, a stretching mode at 3420 cm^{-1} , and a bending mode at 1630 cm^{-1} . The OH-stretching mode band is at 3560 cm^{-1} , and a primary bending mode at 660 cm^{-1} with a barely resolved secondary band at 680 cm^{-1} . The largest bands are the Si-O stretching mode band at 1010 cm^{-1} with a complementary shoulder near 990 cm^{-1} and a bending mode band at 455 cm^{-1} (with a secondary band at 470 cm^{-1} for some samples). The low frequency of the OH-stretching mode band at 3560 cm^{-1} is attributed to the abundance of octahedral Fe^{3+} (Farmer, 1974). Its remarkable width suggests inhomogeneity of the octahedral site occupancy.

CHEMICAL COMPOSITION

Table 1 lists the chemical analyses of ten samples of odinite from four localities, obtained by a combination of wet chemical analysis and X-ray fluorescence. Because some of these samples were acid-treated prior to analysis and differ also in the amount of quartz and calcite impurities plus the degree of alteration to chlorite, the composition of odinite is obtained best from the purest individual sample #699 (light green material from the Los Islands in the Koukoure River mouth off Guinea). Considering the variabilities in the samples noted

TABLE 1. Chemical analyses and structural formulae of odinite (Odin *et al.*, 1988b)

a)	(3) 700.3AB	(3) 704.4	(3) 610.108	(2)* 601	(1) 508.103	(2)** 508.103	(1) 508.169	(1) 508.172	(1)+(2)** 508.175	*** Congo	(3) 699
SiO ₂	34.0	31.2	32.6	34.8	36.9	36.9	39.1	37.5	38.2	36	36.0
Al ₂ O ₃	6.13	5.2	5.9	9.3	11.0	12.0	11.8	10.8	10.8	12	12.2
Fe ₂ O ₃	22.0	23.1	25.1	21.7	17.9	18.3	19.5	19.5	18.8	20	19.5
FeO	6.95	9.4	6.9	6.6	6.5	5.0	5.7	6.1	5.4	5	6.21
TiO ₂	0.14	0.11	0.12	–	0.4	–	0.5	0.5	0.5	–	0.4
CaO	0.7	1.1	0.4	(0)	0.6	0.3	0.6	0.5	0.7	–	0.13
MgO	13.7	10.8	12.0	13.2	11.0	10.7	8.3	8.9	10.6	6.5	9.7
MnO	0.02	0.03	0.02	–	–	–	–	–	–	–	0.33
P ₂ O ₅	0.30	0.39	0.22	0.4	–	–	–	–	–	–	0.17
Na ₂ O	tr.	0.03	tr.	0.2	0.2	0.2	0.2	0.2	0.3	–	tr.
K ₂ O	0.16	0.18	0.17	0.5	1.4	1.1	1.3	1.3	1.2	–	0.35
H ₂ O ⁻	–	3.8	3.0	2.8	3.0	2.0	3.5	3.8	3.2	–	4.10
H ₂ O ⁺	15.2	–	–	–	–	–	–	–	–	–	–
(+CO ₂)	–	13.4	13.3	10.8	10.2	12.0	10.1	10.3	9.4	–	10.96
Total	99.30	98.7	98.73	99.9	99.1	98.5	99.4	99.4	100.1	–	100.05

b)	Si	Al(IV)	Al(VI)	Fe ³⁺	Mg	Fe ²⁺	Σ3+	Σ2+	Σocta.
508.169	2.00	0.00	0.70	0.72	0.63	0.25	1.42	0.88	2.30
508.172	1.94	0.06	0.60	0.78	0.69	0.26	1.38	0.95	2.33
508.175	1.94	0.06	0.60	0.74	0.80	0.23	1.34	1.03	2.37
508.102	1.90	0.10	0.57	0.71	0.85	0.28	1.28	1.13	2.41
508.103	1.90	0.10	0.62	0.72	0.82	0.21	1.34	1.03	2.37
699	1.86	0.14	0.60	0.77	0.75	0.26	1.37	1.01	2.38
601	1.80	0.20	0.36	0.84	1.01	0.29	1.20	1.30	2.50
601.108	1.83	0.17	0.18	0.98	0.90	0.44	1.16	1.34	2.50
700.3	1.81	0.19	0.20	0.90	1.09	0.35	1.10	1.44	2.54
704.4	1.80	0.20	0.15	1.00	1.93	0.45	1.15	1.38	2.53

a) (1) wet chemistry by M. Lenoble, Département Pétrographie-Paris; (2) wet chemistry by E. Lebrun, École Normale Supérieure-Paris; (3) X-ray fluorescence by M. Lenoble; (*) Mean of 2 analyses after correction for CaCO₃ impurities; (**) Mean of 2 analyses for 2 sediments collected at the same site; (***) Mean of 2 analyses after correction assuming that Fe₂O₃ = 20%; Samples 700, 704 from New Caledonia, 601 from Senegal, 508 from French Guiana, 699 from Koukoure River mouth off Guinea. tr. - trace.

b) Allocation to structural formulae for a 1:1 type layer without correction for impurities.

above, the analyses are remarkably consistent and show less variation than found for pure samples of berthierine (Brindley, 1982) and chlorite (Foster, 1962) from different localities.

Table 1 shows odinite to be high in SiO₂ and Fe₂O₃, and low in Al₂O₃ and MgO relative to most other hydrous phyllosilicate minerals. After excluding the CaO, K₂O, and P₂O₅ contents as due to impurities, allowing for an estimated 3% quartz impurity based on the X-ray powder pattern, and recalculating to a 100% anhydrous basis, the structural formula for sample 699 on the basis of 14 positive charges in a 1:1 serpentine type layer is (Fe_{0.784}³⁺Mg_{0.772}Al_{0.556}Fe_{0.279}²⁺Ti_{0.016}Mn_{0.015})_{2.422}(Si_{1.788}Al_{0.212})O₅(OH)₄. No correction was made for the small amount of chlorite impurity known to be present. Relative to berthierine, odinite contains more Fe³⁺ and Mg, but less Fe²⁺. Odinite is thus shown to be a

Fe³⁺-rich clay with about 10% substitution in the tetrahedral sheet in this sample, this substitution appearing to be a maximum by comparison with other samples. The octahedral cation total of 2.42 atoms per formula unit is nearly intermediate between dioctahedral and trioctahedral, because the negative charge on the tetrahedral sheet is balanced by addition of divalent Fe + Mg in the third octahedral site of a normally dioctahedral structure. Octahedral R³⁺ cations are only slightly in excess of octahedral R²⁺ cations. Similar formulae are derived for the other samples in Table 1, producing a range of total octahedral cations from 2.30–2.54 without correction for quartz impurity. If converted to chlorite, these compositions might lead to a combination of dioctahedral and trioctahedral sheets. A simplified formula for odinite is $(R_{1.35}^{3+}R_{1.05}^{2+}\square_{0.60})(Si_{1.85}Al_{0.15})O_5(OH)_4$ with R³⁺ dominantly Fe, and R²⁺ dominantly Mg.

The accuracy of the Fe³⁺/Fe²⁺ ratios of Table 1 has been confirmed by Mössbauer analysis of sample 601 from Senegal. The Mössbauer spectrum (Fig. 3), kindly provided by Dr. G. A. Waychunas (Stanford University), assumes single doublets for octahedral Fe²⁺ and octahedral Fe³⁺. The relative areas of the doublets (73.6/26.4) give Fe₂O₃ = 21.4%, and FeO = 6.9%, in good agreement with Fe₂O₃ = 21.7% and FeO = 6.6% from Table 1. There is

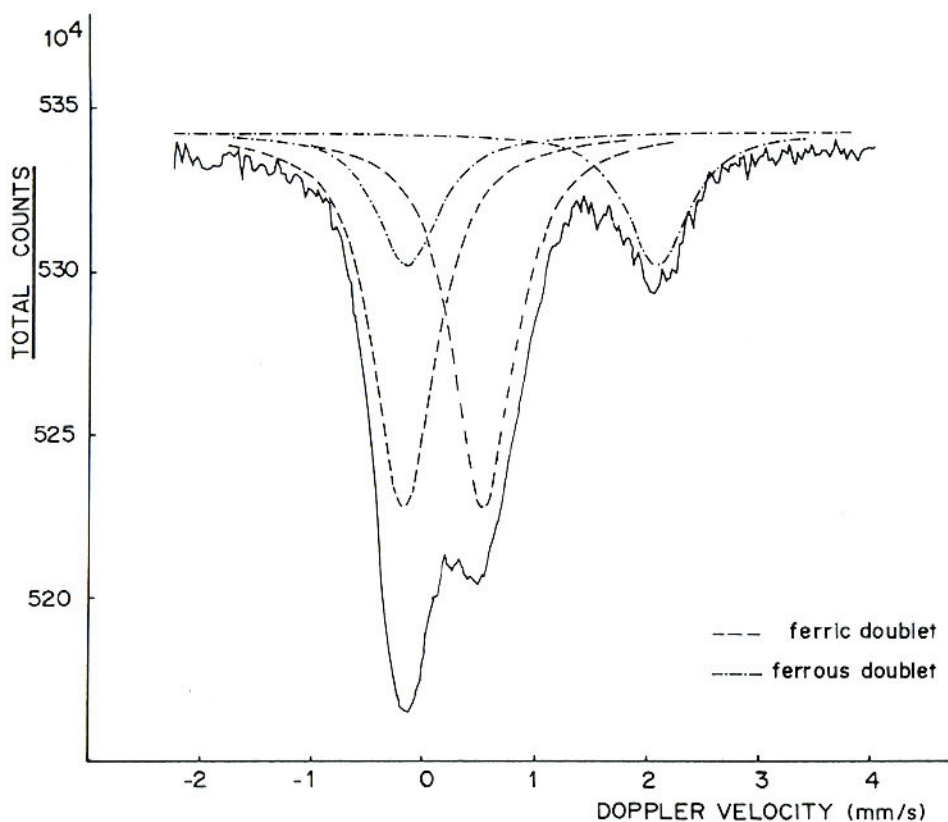


FIG. 3. Mössbauer spectrum for odinite sample 601-58 from Senegal. Chlorite impurity present. Spectrum run by G. A. Waychunas.

no tetrahedral Fe^{3+} . The breadth of the doublets and the considerable amount of chlorite known to be present in this sample preclude a more detailed interpretation, although the Fe^{3+} doublet is asymmetric and can be split into two doublets indicative of Fe^{3+} in two different locations.

Fig. 4 shows triangular diagrams illustrating the homogeneity of the composition of the odinite samples (squares) from Table 1 and its unique composition relative to that of berthierine (asterisks) as given by Brindley (1982), and chlorite (area within dashed lines) as given by Foster (1962). The only other Fe-rich hydrous 1:1 phyllosilicates to which odinite could be compared are greenalite, which is dominantly ferrous [$\sim(\text{Fe}_{2.4}^{2+}\text{Mg}_{0.3}\square_{0.3})\text{Si}_2\text{O}_5(\text{OH})_4$; Guggenheim *et al.*, 1982], and cronstedtite, which is characterized by substantial tetrahedral Fe^{3+} [$\sim(\text{Fe}_{1.6}^{2+}\text{Fe}_{0.5}^{3+}\text{Mg}_{0.7}\text{Mn}_{0.2}^{2+})(\text{Si}_{1.5}\text{Fe}_{0.5}^{3+})\text{O}_5(\text{OH})_4$; Geiger *et al.*, 1983]. The occurrences of greenalite and cronstedtite are also quite different from that of odinite, greenalite being a primary silicate phase in iron formations, and cronstedtite occurring in hydrothermal veins and in metamorphosed iron formations. Thus, the composition of odinite is unique among the hydrous phyllosilicates, and the sedimentary verdine facies in which it occurs is different in detail from the facies in which berthierine, glauconite and greenalite form.

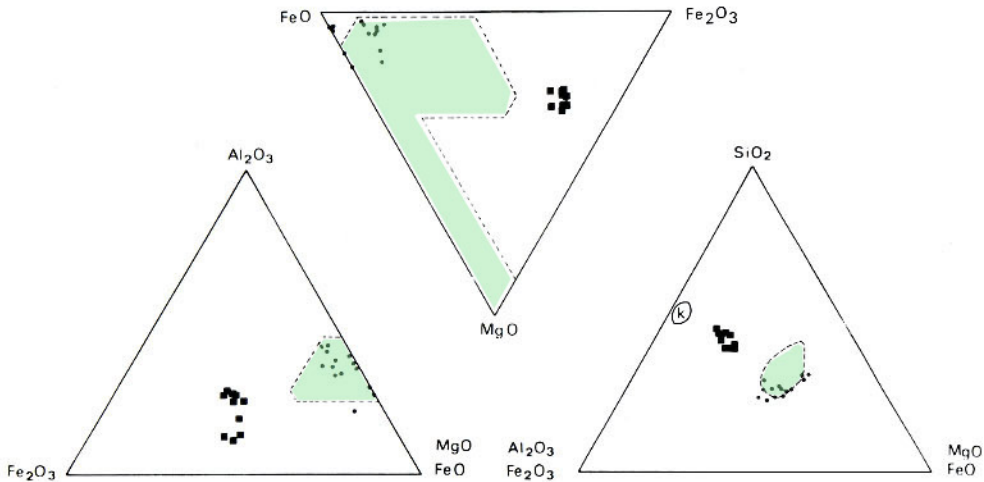


FIG. 4. Comparison of composition field of odinite (squares) with those of berthierine (asterisks, from Brindley, 1982) and chlorite (dashed line areas enclosing 154 samples from Foster, 1962). k = kaolinite. From Odin *et al.* (1988b).

CRYSTALLOGRAPHY

X-ray patterns of odinite were obtained in the form of diffractometer charts and Debye-Scherrer films, the latter obtained with graphite-monochromated $\text{Fe-K}\alpha_1$ radiation in cameras of 114.6 mm diameter. The purest and most informative patterns were the Debye-Scherrer patterns taken of individual microtest infillings and faecal pellets mounted (without grinding) on glass fibres.

Because odinite is very susceptible to alteration, the most mature and darkest green granules all yield an X-ray pattern with chlorite lines superimposed on those of odinite. The chlorite can be identified as the *Ib* ($\beta = 97^\circ$) structural form of Bailey & Brown

TABLE 2. Debye-Scherrer pattern of odinite sample 699-6 from the Islands of Los (off Guinea).

Int.	$d(\text{meas.})$	$d(\text{calc.})$	hkl : Joint	$1M$	$1T$
100	7.15 Å	7.14-7.16 Å	001		
40	4.65	4.66-4.67	020		
20	4.53	4.55		110	
85	3.58	3.57-3.58	002		
1	2.84	2.84	022		
40	2.67	2.66-2.69		20 $\bar{1}$, 130	200, 130
7	2.56	2.56		112	
3	2.51	2.51-2.52			201, 131
30 B	2.41	2.40-2.41		20 $\bar{2}$, 131	
5	2.34	2.33	040		
1	2.15	2.15			202, 132
10 B	2.02	2.02		20 $\bar{3}$, 132	
1	1.90	1.90		202, 13 $\bar{3}$	
7 B	1.74	1.74-1.76	150, 240		
7 B	1.67	1.67-1.68		20 $\bar{4}$, 133	
2	1.62	1.63		15 $\bar{2}$, 241	
65	1.552	1.551-1.556	060	33 $\bar{1}$	330
10	1.517	1.517	061	330	331
3	1.49	1.49			204, 134
5 B	1.43	1.42-1.43	062	331	
15 B	1.33	1.32-1.33		{ 204, 13 $\bar{5}$ 400, 40 $\bar{2}$	

Pattern taken in camera of diameter 114.6 mm with graphite-monochromated Fe- $K\alpha_1$ radiation. Intensities estimated visually. Two weak, spotty lines of quartz at $d = 4.26$ and 3.34 Å deleted from pattern.

(1962), or *Iba* in the revised terminology of Bailey (1988), from the presence of a broad intense line at 2.46 Å. This is the chlorite believed by Bailey & Brown to be the least stable, and to form at the lowest temperature with the smallest amount of tetrahedral Al. The observed (001) chlorite line at 14.45 Å corresponds to an Al^{IV} content of 0.5 atoms per 4.0 sites according to the spacing graph of Shirozu (1958). The (060) spacing of 1.55 Å coincides with that of odinite, so both phases are very Fe-rich. The chlorite is not well crystallized, but the structure is well enough organized that most of the interlayer sheets have a fixed *ba* relationship relative to the 2:1 layers below and above, respectively. Imperfections in the form of $\pm b/3$ layer shifts are indicated by the presence of 2-dimensional bands for reflections of index $k \neq 3n$. Shifts of some layers from *b*-type superpositions to *a*-type relative to the interlayer (disrupting the ideal *baba* sequence along *Z*) are indicated by the breadth of some of the (20 l) reflections.

The younger, lighter-green odinite granules are less altered to chlorite and a few are unaltered. A pattern of such an unaltered sample is listed in Table 2 and can be interpreted as a mixture of two 1:1 layer-silicate phases plus a small amount of quartz impurity. The most abundant 1:1 phase is monoclinic, corresponding to a group A structure of Bailey (1969), and the polytype can be identified as *1M* (space group *Cm*) due to the presence of two non-overlapped lines with $k \neq 3n$. A few granules were found to consist entirely of the monoclinic phase. The minor 1:1 phase is trigonal or hexagonal and corresponds to a group C structure.

As no non-overlapped lines with $k \neq 3n$ of the group C phase are present, the precise polytype cannot be specified but it is indexed in Table 2 for convenience as $1T$ (space group $P31m$). Unit-cell dimensions derived for each phase by least squares fit are: $1M$: $a = 5.373(3)$, $b = 9.326(7)$, $c = 7.363(6)$ Å, $\beta = 104.0(1)^\circ$; $1T$: $a = 5.366(6)$, $b = 9.334(9)$, $c = 7.161(8)$ Å, $\beta = 90^\circ$ if indexed on orthogonal axes, or $a = 5.366(6)$, $c = 7.161(8)$ Å, $\gamma = 120^\circ$ on hexagonal axes. All the odinite lines are broad, indicative of a fine grain size and poor crystallinity similar to that of the *Iba* chlorite. This is a common phenomenon for clays crystallized at low temperature.

A mixture of group A and group C phases is also found in berthierine and its Ni-rich analogue brindleyite, and in greenalite and its Mn-rich analogue caryopilite. However, as pointed out in the previous section, the composition of odinite is quite different in detail from these minerals.

ALTERATION

Odinite changes to a darker green colour as it matures and becomes harder. The darker green granules are judged to be older than the lighter green pellets because they are found nearly exclusively in the deepest deposits, and often are free of substrate material (perhaps dissolved during maturation on the sea floor). The lighter green material is found in the shallower sediments and is always surrounded, at least partly, by carbonate microclasts. All of the individual darker green pellets examined by X-ray methods have a medium to strong intensity line at 14 Å as a result of partial alteration to *Iba* chlorite. The lighter green pellets show a much weaker 14 Å line, and a few are pure 7 Å phases. The patterns of the darker green pellets with the most alteration cannot be interpreted as those of pure chlorite, however, because the intensities of the (00 l) reflections cannot be simulated by any possible distribution of the bulk octahedral composition between the 2:1 octahedral sheet and the interlayer sheet. The intensities of the even (00 l) orders are too large relative to those of the odd orders, and this intensity distribution requires either a physical mixture of 7 Å and 14 Å phases, or a random interstratification of the two types of layers.

High resolution transmission electron micrographs of microtomed sections of odinite pellets were kindly provided by M. Amouric (Centre de Recherche sur les mécanismes de la croissance cristalline). Pellets from New Caledonia produce predominant lattice fringes near 7 Å, usually 15–20 layers thick and >0.1 µm long. Some layers are irregular in thickness from 6–10 Å. Light green pellets from Guinea have $>90\%$ spacings near 7 Å with a mean of 7.3 Å, whereas darker green pellets from Senegal are more varied. Four types of particles were identified in the latter with spacings at ~ 7 , 10, 14, and mixed-layer 7/14 Å. The 7 Å phase is frequently dominant with sometimes a 14 Å phase dominant in older samples. It is tempting to interpret the 7/14 Å mixed-layer clay as intermediate in evolution from the 7 Å to the 14 Å *Iba* chlorite.

Odinite has not been recognized as yet in rocks older than the Recent Quaternary. Based on the ease of alteration of odinite to chlorite during the maturation process observed in the study of Odin (1988a), the 7 Å odinite structure must be very unstable relative to the 14 Å chlorite when it is no longer sheltered within the micro-environment in which it formed. It did not prove possible to obtain the composition of the chlorite directly. However, it is unlikely to have exactly the same composition as odinite which is required to have neutral layers. Although a chlorite with neutral 2:1 layers and interlayers is theoretically possible, provision of a layer charge greatly increases its stability (Bish & Giese, 1981). The lowest

known layer charge from a *Iba* chlorite is 0.4–0.5 per formula unit, and this is the Al^{IV} content suggested by the observed *d*(001) value of 14.45 Å. A structural change also is required to introduce interlayer sheets and to convert the dioctahedral-trioctahedral odinite to a trioctahedral or di, trioctahedral chlorite. It is not known how far this transformation has gone in the incomplete maturation process represented by the samples studied because no pure authigenic chlorite could be obtained. There are no known chlorites with the high Fe₂O₃/FeO ratios of odinite (Fig. 4).

ASSOCIATED CLAY MINERALS

Detrital clay minerals associated with minerals of the verdine facies at several localities include kaolinite, smectite, illite, illite/smectite, and chlorite. No study was made of the associated clay minerals, except for a second authigenic green clay.

The light green odinite pellets do not expand upon solvation with ethylene glycol, and they become amorphous on heating at 490°C for 2 h. A second authigenic green clay with different properties co-exists with odinite at several localities and was given the provisional designation phyllite C by Odin & Masse (1988). It is mainly in the form of replaced faecal pellets, and is olive green in colour rather than the clear to dark green colour of odinite. Compositionally it is somewhat similar to odinite but contains more Si and less Fe and thus can be separated magnetically from odinite. Its X-ray pattern is characterized by a very strong peak between 14 and 15 Å and a (060) peak near 1.52 Å. This material expands to 16 Å upon solvation with ethylene glycol and contracts to a broad band between 10 and 14 Å on heating at 490°C. It must have an appreciable smectite component, therefore, but neither the expansion nor the contraction are complete, indicating that some of the layers are held together by chloritic interlayers and that the entire assemblage is an interstratified chlorite/smectite. It is a swelling chlorite in a sense, but the number of expanding layers is much greater than in those clays to which this name usually is given.

ACKNOWLEDGMENTS

This research was supported in part by NSF grant EAR-8614868, and in part by PRF grant 17966-AC2-C, administered by the American Chemical Society. I am indebted to Dr. G. S. Odin for providing the opportunity to study his samples, and to Dr. G. A. Waychunas, Dr. F. Fröhlich, and Dr. M. Amouric for providing Mössbauer, infrared, and HRTEM data, respectively.

REFERENCES

- BAILEY S.W. (1969) Polytypism of trioctahedral 1:1 layer silicates. *Clays Clay Miner.* **17**, 355–371.
- BAILEY S.W. (1988) X-ray identification of the polytypes of mica, serpentine, and chlorite. *Clays Clay Miner.* **36**, 193–213.
- BAILEY S.W. & BROWN B.E. (1962) Chlorite polytypism. I. Regular and semi-random one-layer structures. *Am. Miner.* **47**, 819–850.
- BISH D.L. & GIESE R.F., Jr. (1981) Interlayer bonding in *Iib* chlorite. *Am. Miner.* **66**, 1216–1220.
- BRINDLEY G.W. (1982) Chemical compositions of berthierines—a review. *Clays Clay Miner.* **30**, 153–155.
- FARMER V.C. (1974) *The Infrared Spectra of Minerals*. Mineralogical Society, London.
- FOSTER M.D. (1962) Interpretation of the composition and a classification of the chlorites. *U.S. Geol. Surv. Prof. Pap.* **414-A**, 33 pp.
- GEIGER C.A., HENRY D.L., BAILEY S.W. & MAJ J.J. (1983) Crystal structure of cronstedtite-2H₂. *Clays Clay Miner.* **31**, 97–108.

- GUGGENHEIM S., BAILEY S.W., EGGLETON R.A. & WILKES P. (1982) Structural aspects of greenalite and related minerals. *Can. Miner.* **20**, 1–18.
- ODIN G.S. (1985) La "verdine", facies granulaire vert marin et cotier, distinct de la glauconie: distribution actuelle et composition. *C.R. Acad. Sci. Paris* **301**, 105–108.
- ODIN G.S. (1988a) *Green Marine Clays*. (Developments in Sedimentology **45**). Elsevier, Amsterdam. 439 pp., (in press).
- ODIN G.S. (1988b) The verdine facies from the lagoon off New Caledonia. Pp. 57–81 in: *Green Marine Clays* (G.S. Odin, editor), (Developments in Sedimentology **45**). Elsevier, Amsterdam (in press).
- ODIN G.S., BAILEY S.W., AMOURIC M., FRÖHLICH F. & WAYCHUNAS G.A. (1988b) Mineralogy of the verdine facies. Pp. 159–206 in: *Green Marine Clays* (G.S. Odin, editor), (Developments in Sedimentology **45**). Elsevier, Amsterdam (in press).
- ODIN G.S., DEBENAY J.P. & MASSE J.P. (1988a) The verdine facies deposits identified in 1987. Pp. 131–158 in: *Green Marine Clays* (G.S. Odin, editor), (Developments in Sedimentology **45**). Elsevier, Amsterdam (in press).
- ODIN G.S. & GRESSE P. (1972) Formation de minéraux phylliteux (berthiérine, smectites ferrifères, glauconite ouvertes) dans les sédiments du Golfe de Guinée. *C.R. Acad. Sci., Paris* **275**, 177–189.
- ODIN G.S. & MASSE J.P. (1988) The verdine facies from the Senegalese continental shelf. Pp. 83–103 in: *Green Marine Clays* (G.S. Odin, editor), (Developments in Sedimentology **45**). Elsevier, Amsterdam (in press).
- ODIN G.S. & MATTER A. (1981) De glauconiarum origine. *Sedimentology* **28**, 611–641.
- ODIN G.S. & SEN GUPTA B.K. (1988) Geological significance of the verdine facies. Pp. 205–219 in: *Green Marine Clays* (G.S. Odin, editor), (Developments in Sedimentology **45**). Elsevier, Amsterdam (in press).
- PORRENGA D.H. (1967) Clay mineralogy and geochemistry of recent marine sediments in tropical areas. *Publ. Fysisch-Geographisches Lab. Univ., Dort-Stolk, Amsterdam*, **9**, 145 pp.
- SHIROZU H. (1958) X-ray powder patterns and cell dimensions of some chlorites in Japan, with a note on their interference colours. *Miner. J.* **2**, 209–223.
- VON GAERTNER H.R. & SCHELLMAN W. (1965) Rezent sedimenten in Küstenbereich der Halbinsel Kaloun, Guinea. *Tscher. Miner. Pet. Mitt.* **10**, 349–367.

RESUME: Le minéral odinite est une argile verte très riche en Fe³⁺ répandue sur les plateformes peu profondes et en particulier dans les lagons récifaux, sous les latitudes tropicales des mers actuelles. Il se rencontre sous la forme de remplissages ou de remplacements de microtests, de bioclasts, de coprolites ou de débris minéraux. Sa formation à des profondeurs moyennes de 15–60 m se déroule vers 25°C à l'intérieur de sédiments globalement poreux ordinairement sableux. Cette argile verte prend naissance dans les microcavités de supports granulaires de nature quelconque; ces microcavités déterminent un micro-environnement plus réducteur que l'environnement marin externe franchement oxydant; le minéral évolue rapidement après sa formation vers un chlorite *Iba* ($\beta = 97^\circ$) ferrique au contact eau de mer/sédiment.

La structure de l'odinite est basée sur un feuillet de type serpentine (1:1) et est mi-diocta mi-trioctaédrique. La somme des cations octaédriques va de 2.30–2.54 pour 3 sites d'après l'analyse de 10 échantillons. La formule structurale calculée pour l'échantillon le plus pur est la suivante: $(\text{Fe}_{0.784}^{3+}\text{Mg}_{0.772}\text{Al}_{0.556}\text{Fe}_{0.279}^{2+}\text{Ti}_{0.016}\text{Mn}_{0.015})_{2.422}(\text{Si}_{1.788}\text{Al}_{0.212})\text{O}_5(\text{OH})_4$. Les deux polytypes monoclinique et rhomboédrique sont présents dans la plupart des échantillons avec la forme 1M plus abondante que la forme 1T. Toutes les raies de diffraction X sur poudre sont larges. Parmi les 20 raies reconnues les plus intenses sont les suivantes avec dans l'ordre (distance observée en Å, intensité observée en %) (indexation *hkl*): 1M et 1T—7.15(100)(001); 4.62(40)(020); 3.58(85)(002); 1.550(65)(060); 1M—2.67(40)(20 $\bar{1}$,130); 2.42(30)(20 $\bar{2}$,131); 2.02(10)(20 $\bar{3}$,132); 1.67(7)(20 $\bar{4}$,133); 1.32(15)(204,13 $\bar{5}$, 400, 40 $\bar{2}$); 1T—2.67(40)(200); 2.51(3)(201); 2.14(1)(202); 1.492(10)(204). Les caractéristiques de la cellule unité sont pour la forme 1M: $a = 5.371(5)$, $b = 9.316(9)$, $c = 7.361(8)$ Å, $\beta = 103.9(6)^\circ$; et pour la forme 1T: $a = 5.369(5)$, $b = 9.307(9)$, $c = 7.17(1)$ Å, $\beta = 90^\circ$ (sur axes orthohexagonaux). Les courbes d'analyse thermodynamiques montrent deux pics endothermiques à $120 \pm 5^\circ\text{C}$ et 550°C et pas de pic exothermique majeur. Les spectres infra-rouges montrent six larges bandes d'absorption. La microscopie électronique haute résolution des échantillons les plus purs indique des espacements moyens vers 7.3 Å. Le nom du minéral est d'après Gilles Serge Odin, Université Pierre et Marie Curie, Paris VI, qui a accompli l'essentiel du travail de découverte de ce nouveau minéral.