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KAOLINITE AND ANAUXITE IN THE IONE FORMATION, CALIFORNIA[1]

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ABSTRACT

Five new chemical analyses and X-ray studies of the kaolinite-like clays of the Ione Formation, near Ione, California give the correct kaolinite chemical formula with Si:(Al+Fe+Ti) ratios of 0.985, 1.012, and 0.995. X-ray powder patterns indicate partially disordered kaolinites.

A new chemical analysis of a sample from the sandstone of the Ione Formation of the Mokelumne River, California, confirms older analyses with high Si:(Al+Fe+Ti) ratios not compatible with the theoretical kaolinite formula. Treatment of this material with sodium hydroxide reduced the Si:(Al+Fe+Ti) ratio to 1.000. X-ray powder photographs before and after leaching with NaOH are identical and typical of disordered or partially disordered kaolinites. The excess silica is probably in the form of amorphous colloidal silica and may have been deposited within the kaolinite platelets after their deposition.

INTRODUCTION

Anauxite is the name given to specimens which resemble kaolinite structurally but which have a higher $SiO_2:Al_2O_3$ ratio. A controversy over the true nature of anauxite has lasted for more than forty years. It has been variously suggested that the excess silicon replaces some of the octahedral aluminum of the kaolinite structure, or that the excess SiO_2 is present either in an ordered form as irregularly occurring layers of SiO_2 or $4SiO_2 \cdot H_2O$ between the kaolinite layers (Hendricks, 1942), or as amorphous silica. Ross and Kerr (1931) summarized the chemical and optical data of anauxites examined before 1931.

In the present paper we report new chemical and X-ray analyses of kaolinites and anauxite from the important Ione locality (Allen, 1929), California, and suggest an origin for the excess silica found in this phase. A preliminary report of this work has been given (Allen, Fahey, and Ross, 1968).

OCCURRENCE

Kaolinite sample No. 1 was collected by Allen in 1964 at a strip mine operated by the American Lignite Products Company about five miles south of Ione, California. The clay underlying the lignite contains large six-sided crystal plates (as much as 2 mm across) of a pearly clay mineral stained amber or brown by solutions derived from the lignite. This strip mine has since been abandoned and the clay layers below were no longer accessible when the site was revisited in 1966.

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Kaolinite samples No. 2 and 3 were collected by Allen in 1927 from the face of the Newman pit, south of Ione. It seemed desirable to have additional chemical analyses of this material, for some samples from this pit were found to contain a high silica-alumina ratio and were called anauxite by Ross and Kerr (1931, p. 163, analysis 4).

Anauxite sample 4a was separated from slabs of the sandstone of the Ione Formation that was also collected in 1927 from a locality one mile west of Lancha Plana, California, on the banks of the Mokelumne River. Part of this sample was sent to Washington, D. C., and used in the investigation of Ross and Kerr (1931). In 1966, when this area was revisited the dam at Camanche across the Mokelumne River was completed and the locality from which this collection was made was no longer accessible.

Preparation of Samples

About 500 grams of sample No. 1 were treated with distilled water until complete disintegration of the lumps was attained. The material was allowed to settle and the water was slowly poured off. Repeated treatments with acetone removed the water and the acetone was removed by evaporation on a very slow steam bath over night. The sample was then sieved and the ($-20+60$) fraction was partly purified with the Franz Isodynamic Separator. The nonmagnetic fraction that contained the large crystals of kaolinite was separated from quartz and glassy grains of feldspar with a bromoform-acetone solution. After washing with acetone and drying a sample of kaolinite that weighed 9.5 grams was obtained.

Kaolinite samples 2 and 3, and anauxite sample 4a were purified by a similar treatment. No quartz was visible under the microscope or in the X-ray powder patterns of the purified samples.

Chemical Composition

The atomic ratios calculated from the chemical analyses given in Table 1 are listed in Table 2. Analyses 1, 2, and 3 give a chemical formula close to that of end-member kaolinite, $Al_2Si_2O_5(OH)_4$. These analyses are very similar to those given in the literature (*e.g.* Deer, Howie, and Zussman, 1962, p. 202–203; Ross and Kerr, 1931). Analyses of kaolinite, found in the literature, indicate that iron (usually reported as Fe_2O_3), titanium, and magnesium substitute in small amounts for octahedral aluminum. Reported alkalies and alkaline earths are assumed to be due to impurities. Some substitution of Ti^{4+} for Si^{4+} may also occur.

Anauxite (sample 4a, Tables 1, 2) from the Mokelumne River locality has an extremely high Si(Al+Fe+Ti) ratio of 1.502 and gives a chemical formula incompatible with that expected for kaolinite.

Treatment of one gram of the anauxite sample 4a with 90 ml of 0.5N

TABLE 1.—CHEMICAL ANALYSES AND OPTICAL DATA FOR KAOLINITE AND ANAUXITE

Sample No.	1	2	3	4a	4b
SiO_2	45.45%	46.41%	45.88%	54.44%	45.15%
Al_2O_3	38.37	38.26	37.62	28.66	35.93
Fe_2O_3	0.32	0.67	1.00	2.06	2.51
TiO_2	0.89	0.35	1.16	1.24	1.22
CaO	0.00	0.00	0.04	0.00	0.00
MgO	0.00	0.00	0.11	0.00	0.00
H_2O (−110°C)	0.45	0.60	0.40	0.50	0.46
H_2O (+110°C)	14.64	13.81	13.60	12.94	14.54
	100.12	100.10	99.81	99.84	99.81
Specific Gravity	2.590	2.601	2.632	n.d.	n.d.
α	1.563	1.562	1.553	1.558	n.d.
β	1.569	1.566	1.558	1.562	n.d.
γ	1.569	1.567	1.558	1.563	n.d.
γ-α	.006	.005	.005	.005	n.d.
2V	18–35° neg.	36° neg.	—	38° neg.	—

1. Crystal plates of kaolinite (as much as 2 mm across) from an abandoned strip mine of the American Lignite Products Company, about 5 miles south of Ione, California.

2. Crystal plates of kaolinite from sandy clay at Newman pit, about 1 mile south of Ione, California.

3. Kaolinite prepared from the same hand specimen as 2.

4a. Crystal plates of anauxite containing colloidal silica; separated from the sandstone of the Ione Formation, 1 mile west of Lancha Plana, on the north bank of Mokelumne River.

4b. Crystal plates of anauxite treated with 0.5N NaOH by method of Foster (1953) on a part of sample 4a.

NaOH on a steam bath for 4 hours, by the method of Foster (1953) removed the excess SiO_2. After filtering, washing and drying the sample (4b) weighed 0.6241 g. Chemical analysis of the dried sample 4b (Table 1) gives an Si.(Al+Fe+Ti) ratio (Table 2) of 1.000 in exact agreement with the expected value for kaolinite.

The filtrate contained 0.1170 g of SiO_2 and 0.0299 g of Al_2O_3. This Al_2O_3 probably was the result of a partial breakdown of the kaolinite structure, and equivalent to about 0.0355 g of SiO_2 derived from the structure. The difference between the total amount of SiO_2 in the filtrate (0.1170 g) and 0.0355 g represents the extraneous SiO_2 in the anauxite.

The water determinations on these samples are somewhat variable, but due to the friable nature of the material and general difficulty of getting good H_2O measurements on many silicates, the variation is not considered significant.

TABLE 2. ATOMIC RATIOS FOR KAOLINITE AND ANAUXITE[a]

Sample No.	1	2	3[b]	4a	4b
Si	1.985	2.012	1.996	2.401	2.000
Al	1.976 }	1.955 }	1.929 }	1.490 }	1.876 }
Fe^{3+}	0.011 } 2.016	0.022 } 1.989	0.033 } 2.007	0.068 } 1.599	0.084 } 2.001
Ti	0.029 }	0.012 }	0.038 }	0.041 }	0.041 }
Mg	—	—	0.007 }	—	—
(OH)	4.265	3.993	3.946	3.807	4.296
Si (Al+Fe+Ti+Mg)	0.985	1.012	0.995	1.502	1.000

[a] Number of cations on the basis of Si+Al+Fe+Ti+Mg = 4.000. Sample designations are given in Table 1.
[b] CaO is assumed to be due to an impurity.

X-RAY DATA

The X-ray powder patterns of all five samples listed in Table 1 are identical and are typical of kaolinite or partially disordered kaolinite. No impurities including quartz were noted in the X-ray patterns. No differences could be seen in the powder patterns of the unleached and leached anauxite (sample 4a and 4b). X-ray powder data for sample 4a is given in Table 3 where it is compared to that given by Brindley and Robinson

TABLE 3. X-RAY POWDER DATA FOR KAOLINITE AND ANAUXITE

anauxite (sample 4a)[a]		kaolinite[b]		
I	*d* (obs.) Å	*hkl*	*d* (obs.) Å	*I*
vs	7.22	001	7.16	10+
vw	4.47	020	4.46	4
w	4.36	$1\bar{1}0$	4.36	5
w	4.18	$1\bar{1}1$	4.18	5
—	—	$1\bar{1}\bar{1}$	4.13	3
vw	3.85	$02\bar{1}$	3.845	4
—	—	021	3.741	2
vs	3.590	002	3.573	10+
w	3.35	111	3.372	4
	—	$11\bar{2}$	3.144	3
	—	$1\bar{1}\bar{2}$	3.097	3
	—	022	2.753	3
w	2.571	{$1\bar{3}0$, $20\bar{1}$, 130}	2.558	6
vw	2.536	{$1\bar{3}1$, $1\bar{1}2$}	2.526	4
w	2.501	{$1\bar{3}1$, 200, 112}	2.491	8
w	2.390	003	2.379	6
w	2.344	{$20\bar{2}$, $1\bar{3}1$, 113}	2.338	9
vw	2.298	{$1\bar{3}\bar{1}$, 131}	2.288	8

[a] Anauxite from Ione Formation, Calif. CuKα radiation (λ = 1.5418 Å), Ni filter. X-ray powder diffractometer technique. vs = very strong w = weak, vw = very weak.
[b] Brindley and Robinson (1946).

(1946) for kaolinite. A number of reflections where $k \neq 3n$ (*e.g.* $1\bar{1}\bar{1}$, 021, $11\bar{2}$, $1\bar{1}\bar{2}$, 022) do not appear in the powder pattern of anauxite which indicates that this material is partially disordered kaolinite. Single-crystal X-ray Buerger precession photographs of hexagonal platelets from sample 4a confirm this. The *h0l* pattern shows no evidence of layer disorder although the spots are streaked into arcs because of mechanical distortion. There is no diffuse scattering discernible parallel to c^* which would be expected in the *h0l* patterns if there was rotational layer disorder involving random 60°, 180°, or 300° layer rotations (Ross, Takeda, and Wones, 1966) or if there were random shifts of the layers along the *a*-axis. The *0kl* precession photographs, on the other hand, show considerable diffuse scattering parallel to c^* for row lines where $k \neq 3n$.

The origin of diffuse X-ray scattering in X-ray photographs of kaolinite has been generally attributed to random layer displacements parallel to the *b*-axis of $nb/3$ (Brindley *in* Brown, 1961, p. 64). Such displacements will cause diffuse streaking of the type seen in the *0kl* photographs of anauxite. This streaking could also be caused by random layer rotations about c^* of 120° and 240°. Rotational layer disorder of this type occurs commonly in biotites (Ross, Takeda, and Wones, 1966). The diffuse scattering in the anauxite photographs is not continuous and some fairly sharp reflections appear which indicates that the structure is only partially disordered. The occurrence of polytypes with large *c*-axis repeats in this material cannot be ruled out. X-ray patterns from such polytypes may show "apparent" diffusing streaking due to the limited resolving powder of short wavelength X-rays.

There is no X-ray evidence that the excess silica occurs as extra layers of SiO_4 tetrahedra between the kaolinite sheets as suggested by Hendricks (1942).

Discussion

The X-ray and chemical data of anauxite from the Mokelumne River locality show that it is partially disordered kaolinite. Four other analyses, previously reported for anauxite from this same locality (Allen, 1928, p. 147) also show a large excess of SiO_2 and were the basis for assigning it the name anauxite. The excess silica may be in the form of amorphous colloidal silica, and may have been deposited irregularly within the kaolinite platelets after their deposition. A possible source of the amorphous silica was the clay-rock which overlies the sandstone of the Ione Formation unconformably and is the lowest member of the rhyolitic series. The alteration of volcanic glass to clay minerals is recognized in other regions as furnishing silica that is deposited lower stratigraphically. Addition of silica is indicated at the Mokelumne River sandstone locality and in local layers in the sand at the Newman pit to produce at the former a well-cemented sandstone and at the latter a few loosely cemented lenses.

The Si:(Al+Fe+Ti) ratio of the anauxite from the Mokelumne River sandstone (sample 4a) of 1.502 appears to be the highest yet reported. Ross and Kerr (1931, p. 163) report Si:(Al+Fe+Ti) ratios of 1.475, 1.375, 1.323, and 1.139 for anauxites from respectively (1), (2) Bilin Czechoslovakia, (3) Mokelumne River, California, and (4) Newman pit, California. The last two samples were collected from the same localities as were samples 2, 3, and 4a reported here suggesting a large chemical variability within a given locality.

It is concluded that anauxites have a kaolinite composition with the excess silica, in the form of amphorous SiO_2, dispersed within the kaolinite platelets in an irregular way. The anauxite crystal structure is partially disordered through random layer rotations and/or random *b*-axis translations. Some anauxites may be multilayer polytypes with large *c*-axis repeats.

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