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THE NATURE OF ANAUXITE*

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Abstract—Anauxite crystals are reported to contain a higher $SiO_2:Al_2O_3$ ratio than the 2:1 ratio found in kaolinite. A structure proposed for anauxite places the excess silica in double silica sheets, but an exact structure for anauxite has never specifically been determined. Many workers believe that anauxite is kaolinite associated with some extremely fine-grained excess silica which is not a part of the structure. Eight specimens studied in this work included portions of type materials from Bilin, Czechoslovakia, and the Ione formation in California.

Amorphous silica and alumina are readily soluble in boiling (N/2)NaOH. Kaolinite is only slowly soluble in this reagent, but becomes readily soluble after dehydroxylation. Weight loss, differential solution rate, kinetic and X-ray diffraction studies were used to establish that the kaolinite clay fraction in the anauxite specimens had the composition of:

$$2{\cdot}01 \pm 0{\cdot}04\ SiO_2 : Al_2O_3 : 2{\cdot}09 \pm 0{\cdot}09\ H\ O$$

Some of the anauxite grains are single crystals, while others are aggregates. The latter appear to be bound together by an amorphous silica phase. Hot caustic leaching extracts the amorphous silica and breaks up the aggregates producing "fines." Improved characterizations of minor impurities were obtained when the residues from hot caustic treatments were studied with X-ray diffraction techniques.

INTRODUCTION

AT ONE time anauxite was thought to be a unique mineral. However, in the current literature there is considerable doubt that it is unique; the question thus has not been completely resolved. The objective of this paper is to clarify the nature of anauxite.

Samples obtained from kaolin deposits in the Ione formation in California and from near Bilin in Czechoslovakia have been used in most of the anauxite studies. Crystal specimens from both of these deposits occur in the form of books or aggregates that have a perfect basal cleavage parallel to the bedding of the rock. Cleaved surfaces tend to be hexagonal in shape, pearly white in color and have optical properties similar to those of kaolinite. They appear to be single crystals. Reviews covering the early anauxite literature can be found in articles by Dittler and Hibsch (1923); Ross and Kerr (1930); Grim (1953, 1962); Brindley (1961); and Langston (1967).

Ross and Kerr (1930) and Gruner (1932) present X-ray diffraction data showing that the patterns of anauxite and kaolinite specimens are essentially identical. Hendricks (1936) used rotating crystal techniques to conclude that the large anauxite crystals were, in fact, aggregates of smaller crystals that were nearly, but not quite, perfectly aligned.

The silica to alumina ratio found in the various anauxite specimens, as reported in the literature, is not constant. In all cases it is higher than the $2:1::SiO_2:Al_2O_3$ found in kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), and seems to have an upper limit near 3:1.

The optical properties of anauxite specimens have been determined by Dittler and Hibsch (1923); Allen (1928); Ross and Foshag (1928). They indicate that the optical property values are similar to those of kaolinite. Gruner (1937) found that the density of anauxite specimens ranged from 2·51 for samples having a $SiO_2:Al_2O_3$ ratio near 3:1, to 2·61 for samples having a $SiO_2:Al_2O_3$ ratio near the 2:1 ratio found in kaolinite. The accepted value for the density of kaolinite is approximately 2·61.

Workers using polarizing microscopes did not observe a separate silica phase in their anauxite specimens. To account for the "excess silica," Ross and Kerr (1930) suggested the existence of a kaolin-anauxite isomorphous series. Hendricks (1942) proposed that the "excess silica" in anauxite was present as a mixture of double silica layers interlayered with kaolinite type layers. Since the mixing of these kaolinite and silica types of layers was thought not to be regular, anauxite was not classified as a mixed layer type (such as chlorite). The dimensions and characteristics of a double silica layer would be about the same as those of a

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kaolinite layer; and, hence, such interlaminations would be crystallographically possible without materially changing the diffraction and other properties. Since the silica to alumina ratio in anauxite is known to vary, the relative abundance of the interlayered double silica layers would account for this variation in silica content.

The knowledge concerning the structure of anauxite has changed very little since 1942. Brindley (1961) came to this same conclusion. The silica, in excess of the 2 : 1 SiO_2 : Al_2O_3 ratio found in kaolinite, could be present in a double silica layer as part of the crystal structure or it could be present as amorphous silica. No direct proof has been presented in the literature. Grim (1962) believes anauxite is actually kaolinite with extremely fine-grained excess silica as an impurity and not as part of the anauxite structure, but he offers neither reference nor proof.

MATERIALS

The specimens described below were received with the understanding that they were anauxite or that they were weathered rocks that contained anauxite.

Anauxite-1. This material, from the Ione area in California, was received from the Owens-Illinois Co. and represents the clay fraction from their sand plant. It has the form of a reddish-brown to buff colored coarse powder. Aggregated silt to clay sized grains coat larger granules, the interior of which may be quartz crystals that have a maximum size of about 0·6 mm or anauxite crystals* that have a maximum size of 0·4 mm. In some cases the aggregates consist entirely of the iron-stained kaolinitic silt to clay sized particles.

The anauxite-2 series of samples, described below, were collected by Mr. C. W. Chesterman of the State of California Division of Mines who also contributed the comments concerning their location, bedding and weathering. These samples are from a prominent road cut on California State Highway 126, about 3·75 miles west of the junction with California State Highway 41 in Madera County. This is part of the Ione formation as shown on U.S.G.S. Raymond Topo Map, 1944 Edn, Section 35, T-10-S, R-20-E, MDBM. The samples were received in the form of large lumps.

Anauxite-2a. This portion of the exposure is a deeply weathered granite type of bedrock which is part of the Sierra Nevada complex, and according to the U.S.G.S. is Cretaceous in age. The rock has a motley appearance, having a light reddish-brown matrix with islands of white to lightgray material. The latter contain well formed quartz crystals, which may be as large as 1 or 2 mm in diameter, embedded in hard chert-like material which in turn grades off into softer white material. The thin reddish-brown, iron-oxide-hydroxide, continuous matrix has a silt-like texture and, although running throughout the mass, also coats pockets of well formed anauxite crystals as large as 2 or 3 mm.

Anauxite-2a Crystal. Some of the anauxite crystals hand-separated from crushed anauxite-2a rock still had their outside edges coated with the reddish-brown iron-oxide-hydroxide impurity.

Anauxite-2b. This deeply weathered specimen, from a dike that cuts through the weathered bedrock, has a silty to sandy appearance. The matrix is light grey to reddish-brown in color. It contains anauxite crystals which are coated with reddish-brown matrix material up to about 0·2 mm size. Some creamy-white flakes and lenses also are present in the matrix.

Anauxite-2c. This sample is a portion of the overlying bedrock, is white to a light reddish-brown in color, and has a relatively coarse appearance. The anauxite crystals are suspended in a clay-like matrix which also contains some quartz crystals that have a maximum diameter of about 0·1 or 0·2 mm. The largest anauxite crystals have a diameter of about 0·6 mm. Of the Anauxite-2 series, this specimen most closely resembles the Allen (1928) material which is represented by specimen "Anauxite-3" in this paper.

Anauxite-3. This specimen obtained from Dr. C. S. Ross is a portion of the Ione anauxite collected by V. T. Allen and described by Allen (1928) and Ross and Foshag (1928). The rock contains anauxite crystals up to 1 mm in size that are closely packed in an iron stained clay to chalky matrix which cements them together.

Anauxite-4. This specimen is a portion of rock sample referred to in the paper by Ross and Foshag (1928) from which they obtained their Bilin anauxite. It was obtained from Mr. P. E. Desautels of the Smithsonian Institution of the United States Natural Museum. Their catalog number is 95535. The buff colored, clay-like matrix contains the anauxite crystals which have a maximum size of about 1 mm. These crystals are not as clean as those found in the Ione specimens and in some cases impurities are found between the laminations of the anauxite crystal. These crystals seem to be softer and to cleave more easily than the Ione anauxite crystals.

Anauxite-5. This specimen of beneficiated Ione

*The term "anauxite crystal" will be used in this paper to describe, as concluded by Hendricks (1929) (1936), a well oriented kaolinitic aggregate that has the physical appearance of a single crystal. Included in this term are the properties that the crystal cleaves easily, giving a flat surface that tends to be hexagonal in shape with a pearly white color.

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anauxite was obtained from Mr. Oliver Bowen of the State of California Division of Mines. The 2 g sample was concentrated, using water flotation techniques, from a 40 lb sample of crushed rock. His sample markings were: "E2, Cherokee Hydraulic Mine, Butte County, California, upper Sawmill Ravine NE 1/4, SE 1/4, Section 32, T21N, R4E, M.D.B. and in water floated concentrate from a 40 lb. sample of middle Eocene auriferous gravel. Contains sparse organic matter (root fibers) and probably a small amount of adhering grains of other mineral species." The sample was composed mostly of thin cleaved anauxite crystal platelets with maximum diameter of about 0·4 mm to which some very fine grains were adhering.

EXPERIMENTAL PROCEDURES

Chemical characterization

Hashimoto and Jackson (1960) have shown that amorphous silica and amorphous alumina can be extracted from a fine clay-like powder by boiling it for $2\frac{1}{2}$ min in (N/2) sodium hydroxide. Such extractable silica and alumina may occur naturally in the specimen or they may be the decomposition products that are formed by dehydroxylation of minerals such as kaolinite. By determining the amorphous or quickly soluble silica and alumina present in a kaolin specimen before and after dehydroxylation, one can determine the silica and alumina released due to dehydroxylation of the kaolin. In addition, if the loss in the weight of a specimen as the kaolin collapses is due to the loss of hydroxyl water from the kaolin, then one can calculate the $SiO_2 : Al_2O_3 : H_2O$ ration in the kaolin as well as the amount of kaolin present.

The relative dissolution rates of quickly soluble and relatively insoluble components must be considered when estimating the amount of silica and alumina released due to the collapse of the kaolin structures. Langston and Jenne (1964) studied the dissolution rate of a number of minerals of interest to this study. They found that the rate of solution of each type of mineral species, although being a heterogeneous reaction, followed a definite homogeneous reaction rate law, and that the rate constants of different specimens of any individual species varied. In the dissolution of kaolin minerals, the silica and alumina went into solution at a constant molar ratio of 2 : 1. These workers also considered the differences in dissolution rates of different species and used a combination of dissolution rate and chemical analysis data to estimate the amounts of various impurities, as well as the kaolinite, present in some of their specimens. Additional information concerning the use of such techniques has been presented by Langston (1967).

Solution rate before dehydroxylation. Alkali extractions on 100–110 mg portions of the specimens were made using the method described by Langston and Jenne (1964). An extraction series was run on each specimen with extraction periods that varied from 3 to as high as 60 min as indicated in Table 1. In this method, the weighed sample was introduced into 100 ml of stirred, boiling (N/2) NaOH and after the selected extraction period, the reaction was quenched with 100 ml of H_2O and then transferred to a 500 ml volumetric flask containing 100 ml of neutralizing (N/2) HCl. After adding water to make the correct volume in the volumetric flask, portions of centrifuged liquor were transferred to plastic containers for storage. Silica and alumina determinations were then made on aliquots of the clear liquor using the methods of Shapiro and Brennach (1956). The extraction data obtained on the unheated specimens are summarized in Table 1. Silica and alumina content of the liquors subjected to chemical analysis contained less than $\frac{1}{4}$ of the maximum amount that could have been dissolved.

Solution rate after dehydroxylation. These evaluations were made in the same manner as those described in the preceding section except that the specimens were fired for 1 hr at 600°C prior to being subjected to the extraction and only 50–70 mg of sample were used in each run. The weight factors used to calculate the equivalent weight of original material are based on data obtained from Table 4. The extraction data are summarized in Table 2, and the amounts of soluble silica and alumina are summarized in Table 3. These calculations are based on the unfired original weight of the material and are more fully explained in the section on calculations.

Total SiO_2 *and* Al_2O_3 *Content of specimens.* The total silica and alumina content of each specimen was evaluated by decomposing a sample, putting it into solution and then analyzing the liquor. Decomposition was accomplished by fusing 50–75 mg of -200 mesh material in 2·0 g of sodium carbonate for 15 min at a dull red heat in a platinum crucible. The resulting cakes were put into solution by allowing them to soak overnight in 300 ml of distilled water and then neutralizing the slush with 20 ml of 1 : 1 HCl. Each of the liquors was then washed into a 1 l. volumetric flask, and, after making the volume 1 l., aliquots were evaluated for their silica and alumina content using the methods of Shapiro and Brennach (1956). The data are tabulated in Table 3.

Weight loss

The recording balance used was similar to that developed by Mauer (1954). Approximately

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Table 1. Silica and alumina extracted from the specimens (before dehydroxylation) by the boiling N/2 NaOH method

Extraction		Weight extracted (%)		Moles extracted/100 g	
Specimen	Time (min)	SiO_2	Al_2O_3	SiO_2	Al_2O_3
Anauxite-1	3	0·64	0·51	0·0107	0·0050
-200 Mesh	6	1·25	0·78	0·0208	0·0077
	12	2·20	1·58	0·0366	0·0155
	24	3·54	2·67	0·0589	0·0262
	36	3·83	3·25	0·0638	0·0319
Anauxite-2a	3	5·93	Nil	0·0987	Nil
-65 Mesh	6	5·56	Nil	0·0926	Nil
	12	5·75	Nil	0·0957	Nil
	24	5·92	Nil	0·0986	Nil
Anauxite-2a-Cryst. -200 Mesh	30	6·90	1·92	0·1149	0·0188
Anauxite-2b	3	11·99	Nil	0·1996	Nil
-65 Mesh	6	12·54	Nil	0·2088	Nil
	12	12·86	Nil	0·2141	Nil
Anauxite-2c	3	9·55	0·06	0·1590	0·0006
-65 Mesh	6	10·61	0·23	0·1767	0·0023
	12	11·11	0·49	0·1850	0·0048
	24	11·31	1·18	0·1883	0·0116
Anauxite-3	12	18·74	1·76	0·3122	0·0173
-200 Mesh	24	20·02	3·12	0·3333	0·0306
	36	22·03	3·96	0·3668	0·0388
Anauxite-4	12	31·84	1·65	0·5301	0·0162
-200 Mesh	24	32·97	2·32	0·5489	0·0228
	36	34·95	3·16	0·5819	0·0310
	48	36·00	3·76	0·5994	0·0369
Anauxite-5	12	3·08	0·70	0·0513	0·0069
-200 Mesh	24	3·53	0·82	0·0588	0·0080
	60	6·54	3·60	0·1089	0·0353

250 mg of -200 mesh portions of each specimen was heated at a rate of 3°C per min. The data obtained are summarized in Table 4. Estimates of the loss in weight to 800°C, due to the kaolin dehydroxylation and other causes are presented in Table 5. This table also includes the results of calculations, which assume all of the loss in weight was due to water, and converts the weight per cent lost into equivalent moles of H_2O per 100 g of sample. Loss in weight due to the kaolin dehydroxylation was estimated by linear extrapolation of both the low and high temperature portions of the weight loss curve, and assuming the difference between them at 525°C to be the weight of water lost by the kaolinitic material. The balance of the loss in weight values reported on heating to 525°C, and also on heating from 525°C to 800°C, was due to impurities. This procedure provides an empirical correction for chert, opal, allophane, montmorillonite and other materials that lose weight on heating. Such losses may occur over a narrow temperature range for well crystallized material or over a wide range for an amorphous material such as opal. The 525°C value was selected because it represents the approximate mid-temperature over which the loss in weight due to the kaolinitic dehydroxylation occurred.

X-ray diffraction

Powder patterns were made on -200 mesh portions of each of the anauxite specimens. Each powder was packed against a frosted glass plate

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Table 2. Alumina and silica extracted from dehydroxylated specimens by the boiling N/2 NaOH method

Extraction		Weight (%) extracted		Moles extracted/100 g	
Specimen	Time (min)	SiO_2	Al_2O_3	SiO_2	Al_2O_3
Anauxite-1-600°C	6	19·09	18·71	0·3178	0·1835
-200 Mesh	12	25·62	24·46	0·4266	0·2399
	24	27·95	25·69	0·4654	0·2520
	26	31·59	26·22	0·5260	0·2572
Anauxite-2a-600°C	6	24·76	16·07	0·4123	0·1576
-65 Mesh	12	29·59	20·37	0·4927	0·1998
	24	31·51	20·93	0·5246	0·2053
	36	31·56	21·40	0·5255	0·2099
Anauxite-2a-Cryst. -600°C -200 Mesh	30	41·98	30·72	0·6990	0·3014
Anauxite-2b-600°C	6	19·63	10·15	0·3268	0·0996
-65 Mesh	12	31·24	16·50	0·5201	0·1619
	24	34·97	19·12	0·5823	0·1876
	36	35·34	19·15	0·5884	0·1879
Anauxite-2c-600°C	6	20·92	13·36	0·3483	0·1311
-65 Mesh	12	26·45	15·51	0·4404	0·1521
	24	32·58	19·48	0·5425	0·1911
	36	32·88	18·91	0·5475	0·1855
Anauxite-3-600°C	6	24·05	9·50	0·4004	0·0932
-200 Mesh	12	27·72	10·30	0·4615	0·1010
	24	28·93	10·58	0·4817	0·1038
Anauxite-4-600°C	6	20·63	7·85	0·3435	0·0770
-200 Mesh	12	32·60	8·75	0·5428	0·0856
	24	41·69	10·46	0·6941	0·1026
	36	39·85	10·13	0·6635	0·0994
Anauxite-5-600°C	12	19·89	14·46	0·3312	0·1418
-200 Mesh	24	25·42	19·77	0·4232	0·1939

from the rear of the specimen holder and the NORELCO diffractometer was operated using copper radiation (35 kV, 20 mA, Ni filter) with a scan speed of $\frac{1}{8}°$ 2θ/min. Patterns were also obtained after the powders had been heated at 110°C, 400°C and 600°C. The lines lost due to the 600°C heat treatment were assumed to represent the collapse of the kaolinitic type (anauxite) structure. Similar kaolinitic patterns were obtained on all the specimens. The *d*-values and integrated intensities of these anauxite powder diagrams agree fully with the diagram for well-crystallized kaolinite as given by Brindley and Robinson (1946).

These powders and the residues from the caustic extractions were also studied with X-ray diffraction after they had been oriented onto a microscope slide. Diffraction patterns were obtained after the following processing steps: (1) drying at 1100°C, (2) glycolation and (3) firing at 600°C. Table 6 summarizes the crystalline varieties found in each of the specimens.

It was observed that the hot caustic treatment produced residues with more "fines." In addition, their lines in their X-ray diffraction patterns were sharper and their OOl reflections were more intense with respect to the quartz reflections which were used as an internal standard.

CALCULATIONS

Langston and Jenne (1964) presented data showing that the N/2 NaOH dissolution of amorphous silica or alumina is much faster than the dissolution of kaolinite, which in turn is much faster than the dissolution of quartz. Calculations were made with corrections for the slower dissolving components. The data for "Anauxite-2c" are used below to illustrate how the calculations were made which allows one to estimate the amount of amorphous silica, kaolinitic material,

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Table 3. Summary of chemical analyses data calculations

		SiO_2 in liquor			Al_2O_3 in liquor		
	Specimen	Amorphous*	Amorphous* plus dehyd. products	From Na_2Co_3 Fusion	Amorphous*	Amorphous* plus dehyd. products	From Na_2Ca_3 fusion
Calculated as weight percent of sample	Anauxite-1	0·22	31·59	55·96	Nil	26·22	28·37
	Anauxite-2a	5·79	31·53	60·27	Nil	21·16	22·38
	Anauxite-2a-Cryst.†	4·65	41·98	42·00	Nil	30·72	31·18
	Anauxite-2b	12·57	35·10	63·66	Nil	19·13	21·51
	Anauxite-2c	10·1	32·74	66·53	Nil	19·16	20·11
	Anaxuite-3	16·8	28·95	78·07	Nil	10·58	11·77
	Anauxite-4	38·6	40·79	59·34	Nil	10·30	16·37
	Anauxite-5†	2·35	25·42	47·02	Nil	19·77	28·91
Calculated as moles/100 g of sample	Anauxite-1	0·0037	0·5260	0·932	Nil	0·257	0·278
	Anauxite-2a	0·0964	0·5250	1·003	Nil	0·2076	0·220
	Anauxite-2a-Cryst.	0·0774	0·699	0·699	Nil	0·301	0·306
	Anauxite-2b	0·2075	0·5845	1·060	Nil	0·1877	0·211
	Anauxite-2c	0·171	0·546	1·108	Nil	0·1880	0·197
	Anauxite-3	0·2798	0·4820	1·300	Nil	0·1038	0·115
	Anauxite-4	0·4760	0·6790	0·988	Nil	0·1010	0·161
	Anauxite-5	0·0391	0·4223	0·783	Nil	0·1939	0·284

*Boiling N/2 NaOH extraction method as described in text.
†Fe_2O_3 analysis on these specimens: Anauxite-2a-Cryst. = 7·66%, Anauxite-5 = 1·46%.

Table 4. Weight loss factors of anauxite samples obtained with a 3°C/min heating rate on a weight loss balance

Temp. °C	AN-1	AN-2a	AN-2a Cryst.	AN-2b	AN-2c	AN-3	AN-4	AN-5
R.T.	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
100	0·9992	0·9947	0·9923	0·9972	0·9963	0·9967	0·9685	—
200	0·9976	0·9931	0·9887	0·9939	0·9920	0·9937	0·9590	0·9874
250	0·9966	0·9918	0·9867		0·9907	0·9926	0·9556	0·9834
300	0·9956	0·9906	0·9824	0·9910	0·9888	0·9909	0·9524	0·9740
350	0·9952	0·9891	0·9791	0·9892	0·9860	0·9893	0·9484	0·9630
400	0·9936	0·9884	0·9770	0·9885	0·9840	0·9871	0·9456	0·9586
425	0·9928	0·9880	0·9754	0·9866	0·9830	0·9853	0·9441	0·9557
450	0·9912	0·9861	0·9746	0·9848	0·9799	0·9831	0·9430	0·9526
475	0·9888	0·9832	0·9721	0·9771	0·9704	0·9694	0·9341	0·9499
500	0·9840	0·9697	0·9685	0·9641	0·9511	0·9591	0·9259	0·9487
525	0·9591	0·9468	0·9603	0·9480	0·9386	0·9518	0·9109	0·9370
550	0·9215	0·9318	0·9521	0·9366	0·9240	0·9495	0·9082	0·9192
575	0·9031	0·9224	0·9000	0·9252	0·9182	0·9478	0·9051	0·8918
600	0·8984	0·9156	0·8822	0·9165	0·9155	0·9461	0·9032	0·8838
650	0·8921	0·9103	0·8688	0·9099	0·9116	0·9447	0·8999	0·8774
700	0·8902	0·9069	0·8637	0·9063	0·9085	0·9426	0·8973	0·8746
800	0·8873	0·9038	0·8596	0·9038	0·9064	0·9403	0·8943	(0·8718)
	900°			841°	850°	870°	928°	
	0·8867			0·9023	0·9053	0·9388	0·8923	

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Table 5. The results of weight loss calculations for anauxite specimens as (a) weight per cent and (b) M H_2O/100 g of sample

	Specimen	Loss prior to kaolinitic dehydroxylation	Loss due to kaolinitic dehydroxylation	Additional loss to 800°C	Total loss to 800°C
Loss as weight per cent of sample	Anauxite-1	0·94	10·08	0·25	11·27
	Anauxite-2a	1·55	7·51	0·56	9·62
	Anauxite-2a-Cryst.	2·63	10·83	0·58	14·04
	Anauxite-2b	1·87	7·21	0·54	9·62
	Anauxite-2c	1·93	7·04	0·39	9·36
	Anauxite-3	1·46	3·98	0·43	5·97
	Anauxite-4	5·83	4·13	0·61	10·57
	Anauxite-5	5·00	7·37	0·45	12·82
Loss in weight calculated as moles H_2O/100 g of sample	Anauxite-1	0·052	0·559	0·013	0·625
	Anauxite-2a	0·086	0·417	0·031	0·534
	Anauxite-2a-Cryst.	0·146	0·601	0·032	0·774
	Anauxite-2b	0·104	0·400	0·030	0·534
	Anauxite-2c	0·107	0·391	0·022	0·519
	Anauxite-3	0·081	0·221	0·024	0·331
	Anauxite-4	0·324	0·229	0·034	0·587
	Anauxite-5	0·277	0·409	0·025	0·711

Table 6. X-ray identification of crystalline species* found in anauxite powders and extraction residues

Specimen	Untreated oriented powder	Residue from "As Is" specimen extraction	Residue from dehydroxylated specimen extraction
Anauxite-1	*K*, *Q*	*K*, *Q*	*Q*, trace of *K*
Anauxite-2a	*K*, *Q*	*K*, *Q*	*Q*
Anauxite-2a-Cryst.	*K*	*K*	None
Anauxite-2b	*K*, *Q*	*K*, *Q*	*Q*
Anauxite-2c	*K*, *Q*, *M*	*K*, *Q*, *M*	*Q*, *M*
Anauxite-3	*K*, *Q*	*K*, *Q*	*Q*
Anauxite-4	*K*, Mont.	*K*, *Q*, Mont., *F*	*Q*, Mont., *F*
Anauxite-5	*K*, *Q*, *P*	*K*, *Q*, *M*, *P*	*Q*, *M*, *P*

*Species identifications are based upon the following *d*-spacings:
K = Kaolinitic material – 7·15 Å, 3·57 Å, 2·383 Å (the 00*l* reflections).
Q = Quartz – 4·26 Å, 3·343 Å, 2·458 Å and 2·282 Å.
F = Plagioclase feldspar – 6·5 Å and 3·24 Å on specimens heated to 600°C.
M = Mica – 10·0 Å that does not change with glycolation or heating to 600°C.
P = Pyrophyllite – 9·3 Å that does not change with glycolation or heating to 600°C.
Mont. = Montmorillonite – 14·7 Å that collapses to 10 Å when heated or increases to 17·8 Å when glycolated.

quartz and other components present in each of the various samples.

The data in Table 1 show the rate at which silica and alumina were taken into solution from material that had not been dehydroxylated. If it is assumed that the dissolved alumina originates from the dissolution of kaolinite, then one can apply a correction for the silica dissolved from the kaolinite and estimate the amount of silica that was quickly dissolved from the original material. The values below are in moles per 100 g for Anauxite-2c.

Time	SiO_2 dissolved	Al_2O_3 dissolved	SiO_2 amorphous
3 min	0·1590	0·0006	0·1578
6 min	0·1767	0·0023	0·1721
12 min	0·1850	0·0048	0·1754
24 min	0·1883	0·0116	0·1651

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The average of the last three values (0·171 M SiO_2/100 g) is equivalent to 10·3 weight per cent amorphous silica in Anauxite-2c. X-ray diffraction patterns indicate the presence of kaolin, mica and quartz in the residue. The amorphous silica is quite fine (colloidal) as it was completely dissolved within the initial 6 min of the caustic leach.

The dissolution data of the dehydroxylated material, from Table 2, indicate the kaolin particles were larger as it took approx 20 min to complete the dissolution. By subtracting 0·171 moles SiO_2 from the observed values, as indicated in the third column below, one then obtains an estimate of the silica and alumina that has been converted to the amorphous form due to the kaolin dehydroxylation. The data for specimen Anauxite-2c-600°C from Table 2 is tabulated:

Time	SiO_2	SiO_2 (corrected for amorphous)	Al_2O_3
6 min	0·3483	0·177	0·1311
12 min	0·4404	0·269	0·1521
24 min	0·5425	0·371	0·1911
36 min	0·5475	0·376	0·1855

Both the silica and alumina dissolution processes followed a first order rate law with the silica dissolution slightly slower than that of the alumina. The residue showed quartz and mica X-ray diffraction patterns. The average of the last two values indicate the kaolin dehydroxylation released 0·374 moles of SiO_2 and 0·188 moles of Al_2O_3 per 100 g of sample (or 48·7% kaolin). By making a chemical balance, it is estimated that the sample contains 32·5% quartz and 2·4% mica. The mica estimation is based on the alumina that was not assigned to the kaolinite.

Evaluation of the amount of water lost during dehydroxylation of the kaolin component was done using a plot of weight loss vs. temperature. First extrapolations were made of the low and high "flat" portions of the temperature curve. The low temperature extrapolation had weight factors of 0·9813 and 0·9800 respectively at 500°C and 550°C. The corresponding weight factors for the extrapolated portion of the high temperature section of the curve were 0·9106 and 0·9098. The difference at 525°C amounted to 0·391 moles H_2O/100 g (7·04 wt per cent) and was assumed to be due to kaolinitic dehydroxylation. From this same plot, calculations indicated 0·107 M H_2O/100 g lost before dehydroxylation occurred and 0·22 mole H_2O was also lost between 525° and 800°C.

The materials released during the dehydroxylation reaction for Anauxite-2c had the chemical composition of: $SiO_2 : Al_2O_3 : H_2O :: 1·99 : 1 : 2·08$.

Similar calculations for all of the specimens are summarized in Tables 3, 5, 7 and 8.

Table 7. Chemical composition of the kaolin dehydroxylation fraction in the anauxite specimens

Specimen	Mole ratios found SiO_2/Al_2O_3	Mole ratios found H_2O/Al_2O_3
Anauxite-1	2·03	2·01
Anauxite-2a	2·06	2·01
Anauxite-2a-Cryst.	2·07	2·00
Anauxite-2b	2·01	2·13
Anauxite-2c	1·99	2·08
Anauxite-3	1·95	2·12
Anauxite-4	2·01	2·27
Anauxite-5	1·98	2·11
Mean	2·01 ± 0·04	2·09 ± 0·09

The mean value for the chemical composition of the kaolinitic component (anauxite) of these samples had the formula of:

$$2·01 \pm 0·04\ SiO_2 \,.\, Al_2O_3 \,.\, 2·09 \pm 0·09\ H_2O$$

as shown in Table 7.

DISCUSSION

The results of the differential chemical extraction and the X-ray diffraction studies, summarized in Tables 7 and 8, show that the anauxite specimens contain a crystalline variety having the chemical formula of $2SiO_2 \,.\, Al_2O_3 \,.\, 2H_2O$. This crystalline variety is associated with some silica which is readily soluble in boiling $\frac{N}{2}$ NaOH as well as other phases such as quartz, feldspar and montmorillonite which are relatively insoluble.

Previous work had indicated the possible existence of (1) a double silica layer in a kaolinite-anauxite isomorphous series, or (2) a finely divided amorphous silica phase to account for the "excess silica".

The evidence in this work indicates the "excess silica" is amorphous. Previous workers probably failed to separate it completely from their "single crystals" prior to chemical analysis. The following evidence indicates the presence of amorphous silica:

(1) No X-ray diffraction reflections were lost by removal of the "soluble silica" by the hot caustic extractions (prior to dehydroxylation).

(2) The solution rate, as well as the kinetics (rate order), of the dissolution of the "excess silica" are similar to those found for allophane and other

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Table 8. Overall composition of the specimens

	Amorphous silica (wt. %)	Kaolin (wt. %)	Wt. loss to 800°C other than kaolinitic (wt. %)	Residue	Oxide difference (wt. %)
Anauxite-1	0·2	74·3	1·2	21·8% SiO_2 (Quartz)	2·5
Anauxite-2a	5·8	60·2	2·1	28·7% SiO_2 (Quartz)	3·2
Anauxite-2a-Cryst.	4·7	78·9	3·2	7·7% Fe_2O_3	5·5
Anauxite-2b	12·6	49·0	2·4	2·3% Al_2O_3, 28·5% SiO_2 (Quartz)	5·2
Anauxite-2c	10·3	48·7	2·3	2·4% as Mica 32·5% SiO_2 (Quartz)	3·8
Anauxite-3	16·8	29·6	1·9	47·4% SiO_2 (Quartz)	4·3
Anauxite-4	27·5	27·7	6·4	14% Montmorillonite 7% Feldspar, 4% Quartz	13·4
Anauxite-5	2·4	48·2	5·5	1·46% Fe_2O_3, 21·7% SiO_2 and 9·2% Al_2O_3 present in residue (Mica, Pyrophyllite, Quartz)	11·5

*Oxides not determined that might be present as exchange ions or in the residue include the R_2O and RO groups as well as TiO_2, Fe_2O_3 and additional water.

amorphous silica materials as reported by Langston and Jenne (1964).

(3) Removal of the "excess soluble silica" produced fine-grained particles. Oriented specimens prepared with extracted material had stronger and sharper X-ray diffraction peaks when compared to material that had not been treated with hot caustic. These items indicate the extracted silica was acting as a binder forming aggregates of smaller crystals which were free to settle in an oriented position after the "excess silica" was removed.

(4) The calculated density of a double silica layer (8-SiO_2 units occupying the same volume as two $2SiO_2 . Al_2O_3 . 2H_2O$ units) is 2·52. The density of kaolinite is 2·61.

Gruner (1937) presents density and $SiO_2 : Al_2O_3$ composition values for three different anauxite specimens. If one assumes all of the alumina is in the form of kaolinite, and then calculates the density of the "excess silica" one obtains the values listed below:

	Ratio $SiO_2 : Al_2O_3$	Density g/cc	Density of "excess silica"
Ione anauxite	2·30	2·579–2·607	2·33
Bilin anauxite	2·74	2·524–2·530	2·13
Lancha plana anauxite	2·67	2·510	2·01
Kaolin	2·00	2·61	–

These values are erratic and lower than those expected from a uniform crystal structure as proposed by Hendricks (1942) and suggest that the "excess silica" phase is amorphous.

The powder patterns of the kaolinitic fraction in the anauxite specimens have the 7·16 Å basal spacing and other reflections associated with the polymorphic kaolinite group of minerals. However, it was not possible, from this data, to classify its structure. Samples of four of the anauxite materials were submitted to Dr. S. W. Bailey (1967) of the University of Wisconsin. He selected six single crystals from each of the four specimens for more detailed structure studies, and will report separately on their structure. However, he has given us permission to disclose some of his observations at this time:

(1) All the single crystal patterns (Laue, oscillation and Weissenberg) taken of the twenty four crystals were remarkably similar to one another, despite some differences in morphology, color, etc. In turn, they are practically identical with similar photographs that he has taken of "one hundred plus" single crystals of sedimentary kaolinites from New Jersey, Georgia, Texas and Colombia.

(2) The distinctive feature about these crystals is their twinning, which shows up on the films as multiplicity of spots. All twenty four of the anauxite crystals show two types of pseudo-twinning.

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First, there is rotation of ± 120° around the cleavage normal. Second, there is a change in the + and − directions of X and Y axes.

(3) He is still working on the exact symmetry operations of the twinning, but with respect to our study, he believes:

(a) The crystals are kaolinite, similar in all respects to other authigenic examples.

(b) The perfection of crystallinity is as good as the other examples. He did not discern any diffuse scattering between $k \neq 3n$ reflections that would indicate any appreciable disorder of stacking.

(c) From the observed perfection, he doubts that there could be any amorphous silica cementing plates together *within* the crystals examined.

(d) However, he did mention that one can find closely intergrown, semi-globular masses that were clearly aggregates of several crystals in the specimens. The different orientations could be seen under the microscope.

Hence, no evidence has been found to support Hendricks' (1942) proposal concerning the possible existence of double silica layers to account for the "excess silica." On the other hand, the hot caustic treatment dissolves some silica leaving a kaolinitic clay fraction with a 2:1 SiO_2:Al_2O_3 ratio. This hot caustic treatment, including the caustic extraction process after dehydroxylation, broke up aggregates and dissolved amorphous silica and alumina which effectively concentrated residual impurity phases. Improved X-ray diffraction identification results were obtained on these residues (using oriented specimens).

CONCLUSIONS

(1) "Anauxite" specimens have the characteristics of appearing to be large single crystals and containing an excess of silica as compared to that contained in kaolinite. They are pearly white in color and are easily cleaved along the basal plane and form platelets in the process. Their other properties are similar to kaolinite.

(2) The results of the present study indicate that excess amorphous silica is present over the normal content of kaolinite and that it is nonuniformly distributed between and among kaolinite platelets; thus the silica is acting as a bond and large, oriented or partially oriented aggregates form that appear to be single crystals. The X-ray powder diffraction patterns show that these samples contain a mineral whose structure belongs in the kaolin group of minerals. The excess amorphous silica can be chemically removed by means of differential solution rate techniques leaving a fine grained kaolinitic residue. The excess silica accounts for the observed difference between "anauxite" and kaolinite in properties such as density and index of refraction. It is necessary to use these associated chemical, kinetic and structural studies in order to establish the presence of the amorphous silica phase and to fix the composition of the different phases.

(3) No mineral species with a fixed chemical composition and crystal structure or an isomorphous series with a fixed structure that compares to "anauxite" has been identified. The kaolinitic clay fraction in the "anauxite" specimens has the chemical formula of $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$.

(4) It is possible that structure studies may disclose that these crystals have symmetry elements that will allow anauxite to be classified as a polymorph in the kaolin group of minerals. However, if the studies of S. W. Bailey show that the structure of the "anauxite" crystals are identical with kaolinite, the term "anauxite" should be abandoned.

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Résumé—Les crystaux d'anauxite ont un rapport $SiO_2 : Al_2O_3$ plus élevé que le rapport de 2 : 1 trouvé dans le cas de kaolinite. Une structure proposée pour l'anauxite suggère l'excédent de silicium sous forme de double feuilles de silicium, mais on n'a jamais déterminé une structure précise de l'anauxite. Beaucoup de rechercheurs supposent que l'anauxite est du kaolinite associé avec une certaine quantité de silicium excédentaire à grains très fins qui ne fait pas partie de la structure. Huit spécimens étudiés ici comprenaient des matériaux en provenance de Bilin, Tchéchoslovaquie et de la formation Ione en Californie.

Le silicium et l'alumine amorphes sont facilement solubles dans du N/2 NaOH bouillant. Le kaolinite est lentement soluble dans ce réagent, mais devient facilement soluble après la déhydroxylation. On a fait emploi de la perte de poids, du taux de solution différentiel d'études kinétiques et de diffraction aux rayons X afin d'établir que la fraction d'argile kaolinitique dans les spécimens d'anauxite avait la composition suivante:

$$2{,}01 \pm 0{,}04\ SiO_2 : Al_2O_3 : 2{,}09 \pm 0{,}09\ H_2O.$$

Dans le cas de certains grains d'anauxite il s'agit de crystaux uniques, tandis que d'autres sont des agrégats. Ceux-ci semblent être liés ensemble par une phase de silicium amorphe. La lixiviation chaude et caustique extrait le silicium amorphe et brise les agrégats pour donner des fines. On a obtenu une meilleure caractérisation des impuretés mineures en étudiant le résidu du traitement caustique chaud au moyen de techniques de diffraction aux rayons X.

Kurzreferat—Anauxitkristalle sollen ein höheres $SiO_2 : Al_2O_3$ Verhältnis enthalten, als das im Kaolinit festgestellte Verhältnis von 2 : 1. Gemäss einem Vorschlag für die Struktur des Anauxits befindet sich die überschüssige Kieselerde in doppelten Kieselerdeblättern, doch ist die Struktur des Anauxits nie eigentlich bestimmt worden. Viele Forscher sind der Ansicht, dass Anauxit ein Kaolinit ist, dem äusserst fein verteilte überschüssige Kieselerde beigemengt ist, die jedoch nicht einen Teil der Struktur darstellt. Die acht in dieser Arbeit untersuchten Proben umfassten Anteile an typischem Material von Bilin in der Tschechoslowakei und aus der Ione Formation in Kalifornien.

Amorphe Kieselerde und Tonerde sind in kochender N/2 NaOH ohne weiteres löslich. Kaolinit löst sich in diesem Reagenz nur langsam, wird jedoch leicht löslich nach Dehydroxylierung. Aufgrund des Gewichtsverlustes, der unterschiedlichen Lösungsgeschwindigkeit, sowie kinetischer und Röntgenbeugungsuntersuchungen wurde festgestellt, dass der kaolinitischen Tonfraktion in den Anauxitproben die folgende Zusammensetzung zuzuschreiben ist:

$$2{,}01 \pm 0{,}04\ SiO_2 : Al_2O_3 : 2{,}09 \pm 0{,}09\ H_2O.$$

Manche der Anauxitkörner sind Einzelkristalle, während andere in Aggregaten auftreten. Die letzteren scheinen durch eine amorphe Kieselerdephase verbunden zu sein. Durch Behandlung mit heisser Lauge wird die amorphe Kieselerde extrahiert, und die Aggregate werden zu feinem Material abgebaut. Bei der Untersuchung der Rückstände nach Behandlung mit heisser Lauge mittels Röntgenbeugungsmethoden konnten Verbesserungen in der Charakterisierung geringerer Verunreinigungen erzielt werden.

Резюме—Как сообщают, анокситовые кристаллы имеют большее соотношение $Si0_2 : Al_20_3$, чем 2:1, которое встречается в случае каолинита. Предлагаемая для аноксита структура помещает излишек кремнезема в двойных силикатных слоях, но точная структура никогда не была полностью определена для аноксита. Многие научные работники считают, что аноксит это каолинит, связанный с некоторыми исключительно мелкозернистыми излишками кремнезема, не являющимися частью структуры. Восемь образцов, исследованных в настоящей статье, включают части типовых материалов из Билин (Чехословакия) и из формации Ион в Калифорнии.

Аморфный кремнезем и глинозем легко растворимы в кипящем N/2 NaOH. Каолинит лишь медленно растворяется в этом реактиве, но становится легко растворимым после

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дегидрогенизации. Потери в весе, дифференциальная скорость растворения, а также кинетические исследования и изучение диффракцией рентгеновских лучей применялись для того, чтобы установить, что фракция каолиновой глины в образцах аноксита имеет нижеследующее содержание:

$$2{,}1 \pm 0{,}04\ SiO_2 : Al_2O_3 - 2{,}09 \pm 0{,}09\ H_2O.$$

Некоторые зерна аноксита это единичные кристаллы, в то время как другие являются агрегатами. Повидимому, агрегаты эти связаны вместе аморфной кварцевой фазой. Выщелачивание горячим каустиком извлекает аморфный кремнезем и фракционирует агрегаты, что дает «мелкие фракции». Достигнута была улучшенная характеризация мелких загрязнений, когда остатки обработки горячии каустиком исследовались методами диффракции рентгеновских лучей.

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