

DENSITIES AND STRUCTURAL RELATIONSHIPS OF KAOLINITES AND ANAUXITES

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INTRODUCTION

When the writer proposed the crystal structure of kaolinite in 1932¹ he also suggested the same structure for anauxite. Due to the higher $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of anauxite it would be necessary, however, for Si ions to occupy some of the Al positions. It was expected that this proposal would not go unchallenged. The first to question it was Machatschki² who in his review of the writer's paper suggested that there were vacancies with four coordinates in the structure where additional Si could be placed. He did not indicate these positions. Ksanda and Barth³ were able to secure some single crystals of dickite and obtained some x-ray reflections which had not been observed in powder photographs. Some doubt was therefore cast on the correctness of the structure of dickite as proposed by the writer.⁴ Since its structure is very similar to that of kaolinite it could not fail to raise doubts as to the acceptability of the structure of the latter. Quite lately, however, Hendricks has shown that the writer's structure of kaolinite is correct.⁵ He also came to the conclusion that anauxite has essentially the same structure as kaolinite. According to him the increase in the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio is brought about by a subtraction of Al ions from the structure instead of by substitution of Si for Al. This would leave "holes" in the structure, of course. In order to investigate this suggestion further the writer obtained as many purified and analyzed samples of anauxite and kaolinite as possible of the material described in detail by Ross and Kerr.⁶ He is greatly indebted to them and Dr. W. F. Foshag for these specimens, and to Messrs. Ernest Berg and Lynn Gardiner for assistance in the laboratory. Grants from the Graduate School of the University of Minnesota made this study possible.

¹ Gruner, J. W., *Zeits. Krist.*, vol. **83**, pp. 75-88, 1932.

² *Neues Jahrb., Referate I*, p. 439, 1933.

³ Ksanda, C. J., and Barth, T. F. W., *Am. Mineral.*, vol. **20**, pp. 631-637, 1935.

⁴ Gruner, J. W., The crystal structure of dickite: *Zeits. Krist.*, vol. **83**, pp. 394-404, 1932.

According to a written communication received from Dr. S. B. Hendricks, the space group of dickite is C_6^4 as proposed by me. The arrangement of the ions in individual layers may be somewhat different, however, from that proposed by the present writer.

⁵ Hendricks, Sterling B., Concerning the crystal structure of kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and the composition of anauxite: *Zeits. Krist.*, vol. **95**, pp. 247-252, 1936.

⁶ Ross, C. S., and Kerr, P. F., The kaolin minerals: *U. S. Geol. Survey, Prof. Paper 165-E*, pp. 161-165, 1931.

DENSITY MEASUREMENTS

The removal of Al^{3+} and of corresponding amounts of OH^- or O^{2-} from the structure should decrease the density of kaolinite. Reliable density measurements on analyzed samples of kaolinite and anauxite are scarce. The two factors which influence the trustworthiness of published observations most are, of course, the impurities and the grain sizes of the specimens. It was fortunate, therefore, that the writer had at his disposal seven actually analyzed and optically described samples. The following specimens were used:

- No. 2, Anauxite from Bilin, Czechoslovakia.
- No. 3, Anauxite from Mokelumne River, Lancha Plana, Calif.
- No. 4, Anauxite from Newman Pit, Ione, Calif.
- No. 7, Kaolinite from Roseland, Va.
- No. 8, 9, Kaolinite from 1 mile south of Ione, Calif.
- No. 10, Kaolinite from Abatik River, Northern Alaska.
- "Newton Creek" from Subway tunnel, Brooklyn, N. Y.

The first six numbered specimens are described in detail in Ross's and Kerr's paper.⁷ The "Newton Creek" kaolinite was described by Kerr in 1930⁸ and was the specimen used in the writer's structural analysis⁹ of kaolinite. Three of the specimens, namely Nos. 4, 8-9, and "Newton Creek" were available in sufficiently large quantities to make possible measurements with a silica glass pycnometer (10 cc.). Of the others the writer had only small amounts for determinations of the densities with heavy liquids. The pycnometer fluid used was tetrahydronaphthalene which is especially recommended for exceedingly fine-grained material since it wets the grains more thoroughly than does water. The density of the liquid was calculated from the known volume of the silica glass pycnometer and the weight of the liquid in it. Observations were also made with the Westphal balance. Great care was exercised in the removal of air bubbles. The mineral covered with fluid was shaken and stirred with a platinum wire occasionally during a period of four hours before the weighings were made.

Determinations were also made by centrifuging in heavy liquids. Bromoform diluted with alcohol was used at first. It was found, however, that alcohol was selectively adsorbed and all readings were much lower than when the bromoform was diluted with carbon tetrachloride. As a precaution against coagulation of the mineral powders the samples were shaken in the liquids of approximately the same density for an hour before they were centrifuged. It is obvious that there existed a slight

⁷ *Op. cit.*

⁸ Kerr, P. F., *Am. Mineral.*, vol. 15, pp. 153-154, 1930.

⁹ *Op. cit.*

range in the densities of different particles in the same sample. Therefore, no readings of the specific gravity were made at the very beginning of the sinking of the particles, neither after all the powdered material had settled. Readings with the Westphal balance were taken *before the bulk* of the sample had sunk and *after the bulk* of the sample had reached the bottom of the container. These two were averaged and constitute one determination in Table 1. All the observations are recalculated to 4°C. All samples (except No. 7 which was accidentally lost after centrifuging) were x-rayed. The dimensions of their unit cells (Table 1) are directly comparable with one another as they were run in the same camera. Unfiltered Fe radiation was used. Radius 57.3 mm. Diameter of specimens 0.6 to 0.7 mm.

TABLE 1. DENSITIES AND DIMENSIONS OF UNIT CELLS OF ANAUXITE AND KAOLINITE

No.	Ratio SiO ₂ : Al ₂ O ₃	Density			Theor.* Dens- ity	Unit Cell Dimensions ⁹			
		Cited in lit- erature	Calculated to 4°C.			<i>d</i> ₀₀₁	<i>b</i> ₀	<i>a</i> ₀	Vol. Å ³
			Pycnom- eter	Centri- fuge					
2	274:100	2.524 ¹ 2.525		2.530 ⁶	2.581	14.27	8.95	5.17	660
3	267:100			2.510 ⁷	2.589	14.28	8.93	5.16	658
4	230:100		2.607 ³	2.579 ⁸	2.601	14.26	8.92	5.15	655
"N.Cr."	201:100		2.581 ⁵	2.588	2.589	14.28	8.93	5.16	658
7	197:100			2.538					
8,9	195:100	2.585 ²	2.581 ⁴	2.572 ⁸	2.589	14.27	8.93	5.16	658
10	189:100			2.604	2.593	14.25	8.93	5.16	657

* Assuming theoretically pure kaolinite.

¹ Dittler and Hibsich, *Op. cit.*, p. 87. No method mentioned.

² Ross and Kerr, *Op. cit.*, p. 165. No method mentioned.

³ Contained some grains of quartz. Size of sample 3.2 g.

⁴ Hand picked but unground material. Size of sample 2.5 g.

⁵ Exceedingly fine-grained. Size of sample 1.5 g.

⁶ Average of 5 determinations.

⁷ Average of 4 determinations.

⁸ Average of 3 determinations.

⁹ ±0.01 Å for *b*₀ and *a*₀, ±0.02 Å for *d*₀₀₁.

DISCUSSION OF RESULTS

Hendricks,¹⁰ in discussing the writer's proposal, shows by plotting the results of actual analyses that the H₂O content does not decrease quite

¹⁰ *Op. cit.*

as rapidly in anauxite as would be expected. He does not include in his calculations any H_2O driven off below $110^\circ C$. Though this is a commonly accepted procedure to get rid of "adsorbed" water, it is questionable whether it leads to comparable results in kaolinities. One needs to inspect only the numerous analyses of anauxite from Bilin, Bohemia,¹¹ to conclude that the H_2O ratio can be used only in a very general way as an indicator of structural differences between anauxite and kaolinite. This is also brought out graphically in Fig. 1.

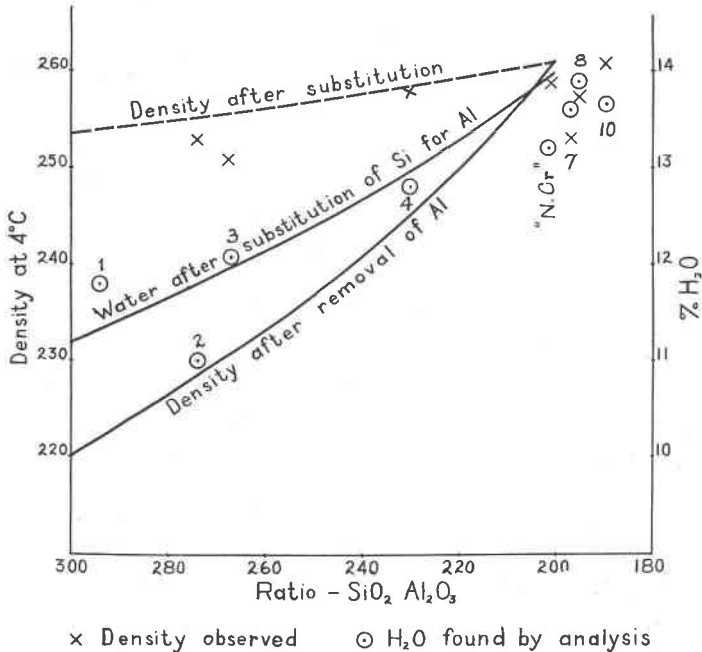


FIG. 1. Curves showing theoretical densities after removal of Al and on substitution of Si for Al respectively. Curve showing H_2O content on substitution of Si for Al and observed H_2O .

Densities should offer a much more reliable clue. For example, it would be possible though unlikely to place an SiO_4 group in the hexagonal ring shown in Fig. 2, a position to which Machatschki probably referred.¹² The density would be materially increased, however, and a very large part of the H_2O would be lost, obviously a condition not substantiated by the facts. Then there is Hendricks' proposal of taking

¹¹ Ross and Kerr, *Op. cit.*, p. 163, and Dittler, E., and Hibsich, J. E., *Tschermak's Min. Mitt.*, vol. 36, p. 87, 1925.

¹² *Op. cit.*

Al^{3+} ions out of the structure and for every Al^{3+} lost of removing two OH^- and changing one O^{2-} to OH^- . Under these conditions the theoretical densities would not agree with observations. In Fig. 1 the writer has plotted the curve on which the densities should lie and the actual points as measured with heavy liquids. While it is true that two of the three anauxites are somewhat lower than the kaolinites they are far from the curve on which they would be expected.

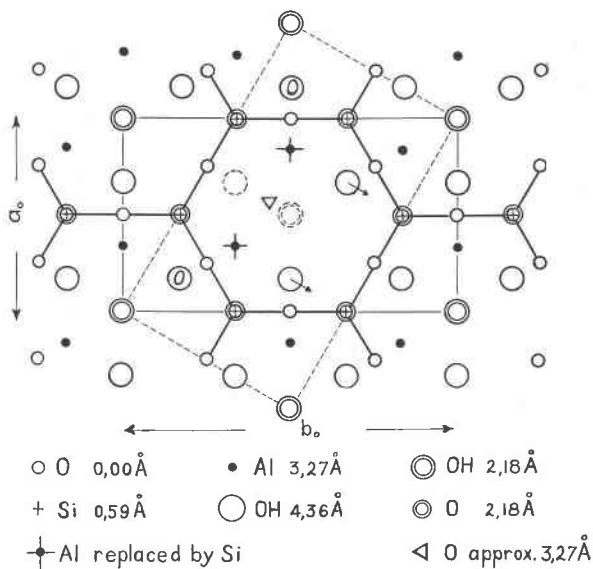


FIG. 2. Ionic positions in a single sheet of kaolinite and proposed changes in anauxite. The numbers indicate the heights of ions above the plane of projection.

The writer believes, therefore, that while his original proposal of placing Si ions in the positions of Al ions may have been too drastic, it is probable that whole units of tetrahedral SiO_4 occupy positions of octahedral units of $AlO_2(OH)_2$. The substitution may be explained with the aid of Fig. 2 which is a modification of one in the original paper¹³ on kaolinite. For every pair of Si^{4+} substituted for two Al^{3+} (large crosses) two OH^- are lost (dotted circles) and two OH^- are converted to O^{2-} (large circles containing the letter O). A new O^{2-} (small triangle) occupies a position between the new Si ions. The two OH^- groups designated by small arrows move slightly in the direction indicated. The structure is balanced, of course. But there must be some distortion of the octahedral

¹³ *Op. cit.*

groups and probably a slight one of the SiO_4 groups. The substitution will occur in pairs of SiO_4 groups which makes the retention of the original symmetry C_3^4 possible. If this were not the case it should be visible in a displacement of the lines in the powder photograph. Instead only a few slight differences in intensities are noticeable.

It may be thought that the H_2O content of anauxite should be much lower if the writer's proposal be correct. Inspection shows, however, that even with a ratio $\text{SiO}_2:\text{Al}_2\text{O}_3 = 300:200$ only 0.8 Al has been replaced by Si in each unit cell and the theoretical H_2O has decreased from 13.96 to only 11.17 per cent. The curve showing the theoretical percentages of H_2O remaining in the structures is plotted in Fig. 1. It is seen that the writer's proposed change agrees about as well with the analyses as that of Hendricks as far as loss of water is concerned. The theoretical densities decrease so gradually that their curve (dotted line Fig. 1) shows a gentle slope.

CONCLUSIONS

The problem of the differences in the structures of kaolinite and anauxite has been discussed lately by Hendricks who concludes that the higher $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio in anauxite is due to removal of Al^{3+} and OH^- leaving a defect structure with holes. Density observations on seven analyzed samples of anauxite and kaolinite do not seem to agree with this suggestion. While anauxite seems to be slightly lower in density in two out of three cases it is not very likely that the deficiency of Al can be explained satisfactorily in this manner. The writer proposes a substitution of tetrahedral SiO_4 groups for octahedral $\text{AlO}_2(\text{OH})_4$ groups. The loss of OH caused by this exchange is in as close agreement with analyses as can be expected. The method of density measurements by centrifuging in heavy liquids seems to give as accurate results as the use of the pycnometer if certain precautions are observed.