

which corresponds to incidence angle 72.4° . The procedure used to average the spectra has been discussed by Jurgens (6) in an earlier study of the average scattering properties of Venus for incidence angles less than 45° . The averaged spectrum shown is in remarkably good agreement with the theoretical spectrum.

The results of this study and the previous study by Jurgens (6) clearly indicate that a homogeneous scattering model can represent the average scattering properties of Venus over a range of incidence at least as large as 75° , and that no latitude dependence is observable. Therefore, ice caps do not exist on Venus unless the very unlikely situation has occurred and their radar-scattering properties at large incidence angles are not significantly different from those of the equatorial region. Large fields of broken ice slabs could duplicate the radar-scattering behavior of the

equatorial region at large angles of incidence if the surface roughness were just slightly greater than the roughness of the equatorial material, but snow is excluded by these radar observations.

R. F. JURGENS

*Arecibo Ionospheric Observatory,
Cornell University,
Arecibo, Puerto Rico*

References and Notes

1. W. F. Libby, *Science* **159**, 1097 (1968).
2. J. Weertman, *ibid.* **160**, 1473 (1968).
3. W. F. Libby, *ibid.*, p. 1474.
4. D. O. Muhleman, *Space Sci. Rev.* **6**, 341 (1966).
5. I. I. Shapiro, *Astron. J.* **72**, 1309 (1967).
6. R. F. Jurgens *CRSR Report*, No. 297 (Center for Radiophysics and Space Research, Cornell University, 1968).
7. T. Hagfors, *J. Geophys. Res.* **69**, 3779 (1964).
8. I thank R. B. Dyce and F. D. Drake for helpful suggestions and R. B. Dyce, D. B. Campbell, and T. W. Thompson for assistance in observations.
9. The Arecibo Ionospheric Observatory is operated by Cornell University with the support of the Advanced Research Projects Agency under a research contract with the Air Force Office of Scientific Research.

31 July 1968

Kaolinite Layer Structure: Relaxation by Dehydroxylation

Abstract. *Single-crystal electron-diffraction data reveal features of metakaolin. The basal plane parameters increase 2.2 percent in formation of metakaolin produced by heating kaolinite in air at 700°C for 12 hours. This increase results from removal of the distortion of sheet structure (relaxation).*

Although the sequence of thermal reactions by which kaolinite (a triclinic, 1:1 layer silicate) passes through a poorly crystallized, and more or less anhydride phase (metakaolin), then through a spinel-type cubic phase to yield finally a chain silicate (mullite) plus excess silica (appearing finally as

cristobalite) was shown by Brindley and Nakahira (1) to be a structure-controlled process, the specific nature of metakaolin remains very difficult to evaluate. New single-crystal electron diffraction data, showing an expansion of the layer parameters, a and b , in the formation of metakaolin, provide

some valuable additional information.

The layer structure of kaolinite consists of a Si-O tetrahedral sheet linked with an Al-O,OH octahedral sheet; the OH ions are coordinated only with Al ions and not with Si ions. Dehydroxylation causes a major alteration of the Al-O,OH sheets, with the Al ions taking up fourfold, in place of their original sixfold, coordination as shown by x-ray fluorescence analysis (2), and also by infrared spectroscopic data (3, 4). The basal spacing of metakaolin is not directly observable by x-ray diffraction, and possibly is variable from crystal to crystal, and within crystals. An estimated average value based on density data (1) is about 6.3 \AA , while electron diffraction results (5) on single crystals turned edgewise to the electron beam have given values in the range 6.8 to 5.6 \AA , with an average of 6.2 \AA . From a detailed infrared analysis, Pampuch (4) recently has concluded that the Si-O sheets take up a higher symmetry after dehydroxylation, becoming hexagonal instead of ditrigonal, and that the Al-O,OH sheets break down into an arrangement of corner- and edge-shared AlO_4 tetrahedra forming chains.

Further structural information has now been obtained from electron diffraction measurements of single crystals with the use of an aluminum shadowing technique to provide accurate calibration rings on the diffraction spot patterns (6). Measurements have been made of the basal plane parameters of exceptionally well-crystallized kaolinite taken from geodes which occur near Keokuk, Iowa (7), and of the metakaolin produced by heating this kaolinite in air at 700°C for periods of 12 hours or longer to give 13.88 percent weight loss, that is, corresponding to essentially complete dehydroxylation. The b -parameter measurements, made on many crystals, have given the following results:

Initial kaolinite $b = 8.95 \pm 0.03 \text{ \AA}$
Metakaolin (700°C) $b = 9.145 \pm 0.035 \text{ \AA}$

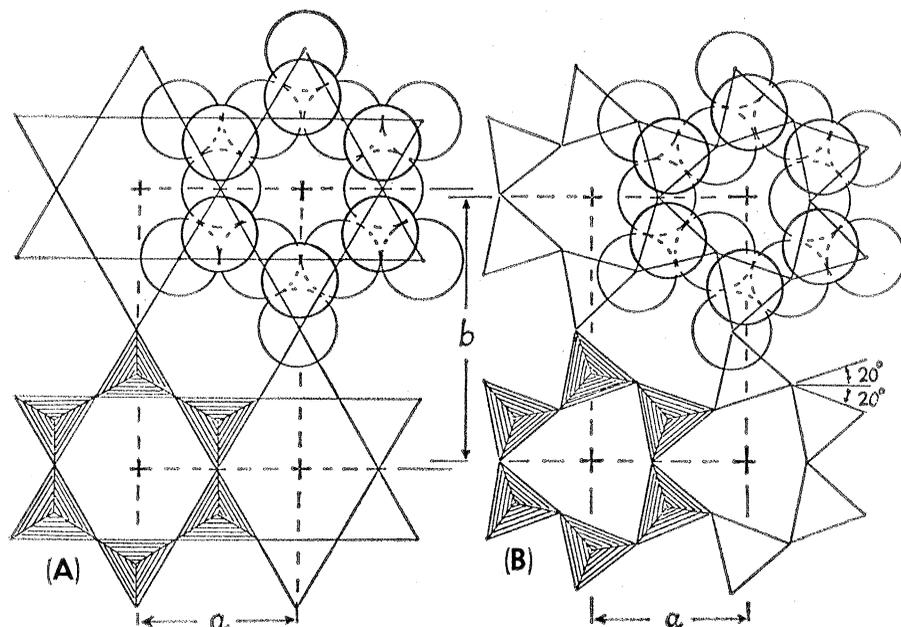


Fig. 1. Arrangement of silicon-oxygen, SiO_4 , tetrahedral groups in (A) ideal hexagonal sheet structure, (B) ditrigonal sheet structure, with tetrahedra rotated alternately $+20^\circ$ and -20° with respect to ideal positions. The b parameter arising from the rotations is reduced. The upper part of each diagram shows the oxygen atoms in tetrahedral groups; the silicon atoms at centers of tetrahedra are hidden. The lower part of each diagram indicates the tetrahedral faces connecting centers of oxygen atoms.

The significance of the 2.2 percent increase in b is interpreted as follows. The tetrahedral sheets of the kaolinite structure normally are constrained by their attachment to the Al-O,OH octahedral sheets by rotations of the tetrahedra through angles of about 11.3° (8) so that the sheet symmetry is not hexagonal but is more nearly ditrigonal. This is illustrated in Fig. 1, where larger rotations (20°) are shown in order to clarify the contraction of the sheet structure by these rotations. When the octahedral sheets are disrupted by dehydroxylation, the constraints on the tetrahedral sheets are removed, and the highly charged Si ions will repel each other to the maximum limit set by the Si-O bond length, 1.62 Å. The maximum relaxation of the tetrahedral sheet corresponds to the hexagonal arrangement shown in Fig. 1, and from the geometry of the tetrahedron it follows that $b = 4\sqrt{2}$ (Si-O) = $4\sqrt{2}$ (1.62) = 9.15 Å. This agrees exactly with the measured parameter for metakaolin.

The present results provide no direct confirmation for the Al-O chain arrangement in metakaolin proposed by Pampuch, but indirectly they indicate a similar conclusion. In attempting to fit an Al-O sheet structure with Al in fourfold coordination, to the original a and b parameters of the kaolinite

structure, Brindley and Nakahira (1) found that the Al-O tetrahedra must be very highly distorted. Indeed, if an Al-O sheet structure is maintained after dehydroxylation, some reduction in the a and b parameters is to be expected and certainly not an expansion. The considerable expansion now observed points strongly toward a disruption of the octahedral sheet structure, and to this extent the chain arrangement suggested by Pampuch is supported.

G. W. BRINDLEY

D. L. GIBBON

Department of Geochemistry and Mineralogy, Pennsylvania State University, University Park 16802

References and Notes

1. G. W. Brindley and M. Nakahira, *J. Amer. Ceramic Soc.* **42**, 311 (1959).
2. G. W. Brindley and H. A. McKinsty, *ibid.* **44**, 506 (1961).
3. V. Stubičan and R. Roy, *J. Phys. Chem.* **65**, 1348 (1961).
4. R. Pampuch, *Pol. Akad. Nauk Oddział Krakowie Kom. Nauk Mineral., Pr. Mineral.* **6**, 53 (1966).
5. O. E. Radczewski and J. Schädel, *Ber. Deut. Keram. Ges.* **39**, 48 (1962).
6. G. W. Brindley and C. DeKimpe, *Amer. Mineralogist* **46**, 1005 (1961).
7. J. B. Hayes, *Proc. Iowa Acad. Sci.* **70**, 261 (1963); W. D. Keller, E. E. Pickett, A. L. Reesman, *Proc. Int. Clay Conf. (Jerusalem)* **1**, 75 (1966).
8. S. W. Bailey, *Clays Clay Minerals, Proc. Nat. Conf. Clays Clay Minerals* **14**, 1 (1966).
9. Supported by the central fund for research of the Pennsylvania State University.

9 September 1968; revised 23 October 1968 ■

Genetics of Diego Blood Groups in Guatemalan Indians: Use of Antiserums to Diego a and Diego b Antigens

Abstract. Red blood cells of 255 inhabitants of San Antonio Palopó, an Indian community on the eastern shore of Lake Atitlán, Guatemala, have been typed with antiserum to Diego a (Di^a) and the newly discovered antiserum to Di^b . Individuals with erythrocyte antigenic types $Di(a+b-)$, $Di(a+b+)$, and $Di(a-b+)$ have been found, but the type $Di(a-b-)$ has not been encountered. Population frequencies of antigenic types and family studies support the hypothesis that the erythrocyte antigens, Di^a and Di^b , are controlled by two codominant alleles at a single autosomal locus.

The discovery of the antiserum to Diego b (Di^b) antigen (1) provides additional information on the genetics of the Diego blood group system, a polymorphism in American Indians and some Asian populations, and a monomorphism in Caucasians and Negroes (2). Initially, a single erythrocyte antigen, Diego a (Di^a), was detected by antiserum to Di^a (3), and subsequently it was found that the frequency of the phenotype $Di(a+)$ varied from 0 to 0.5 in American Indians (4). Genetic analysis of data from families studied with the antiserum to Di^a has shown that the polymorphism consists of two (or more)

alleles at a single autosomal locus, one of which, Di^a , is dominant and controls the antigen, Di^a (3, 5). We have been studying the distribution and the inheritance of the erythrocyte antigens Di^a and Di^b in Mayan Indian descendants in Guatemala, and we present here the results of our initial genetic analysis. To our knowledge, these are the first genetic studies with both antiserum to Di^a and antiserum to Di^b .

The antiserum to Di^b was discovered in two $Di(a+)$ Mexican Indian women with blood transfusion compatibility problems (1). Their serums, which did not react with their own red blood cells,

Table 1. Frequency distributions of Diego erythrocyte antigenic types determined from reactions with antisera to Di^a and Di^b antigens.

Antigens	Distribution		
	Males	Females	Total
$Di(a+b-)$	1	2	3
$Di(a+b+)$	15	39	54
$Di(a-b+)$	70	128	198
$Di(a-b-)$	0	0	0
	86	169	255

Test for association of antigen types with sex: $\chi^2_{(1)} = 1.050^*$; $P > .30$

* Types $Di(a+b-)$ and $Di(a+b+)$ were pooled because of the small numbers of individuals of the former type.

reacted consistently with $Di(a-)$ and $Di(a+)$ erythrocytes selected at random with respect to other antigenic types. Red blood cells from the parents and siblings of one of the women were $Di(a+)$ in each case, and, except for cells from one sibling, they reacted with the newly discovered serums.

The antiserum to Di^a was provided by Dr. M. Layrisse, and the antiserum to Di^b was made available to us by Hyland Laboratories. Both antisera require antiserum to human globulin for the detection of the respective antigens (6). Blood was collected in ACD (citric acid, trisodium citrate, dextrose) solution and immediately refrigerated until processed. A volume of packed red blood cells was suspended in two volumes of 40-percent buffered glycerol (7) and then stored at -20°C . No more than 1 week (and usually less time) elapsed between obtaining a blood specimen and suspending the erythrocytes in glycerol. All samples were typed for erythrocyte antigens within 4 months from initial collection. In this laboratory, frozen stored erythrocytes show agglutination reactions with antisera to Di^a or to Di^b identical to those of fresh red blood cells. The individuals studied in this investigation are Cakchiquel-speaking, Mayan Indian inhabitants of San Antonio Palopó, an Indian community on the eastern shore of Lake Atitlán, Guatemala. This population shows high frequencies of blood types O, M, and MN, and a very low frequency of type rh (cde). Previous studies in two other lakeshore communities (8) revealed frequencies of 0.116 and 0.200 of the $Di(a+)$ phenotype.

The sample studied was made up of 255 Indian inhabitants of San Antonio Palopó. The sample contained complete "nuclear" families (father, mother, and one or more offspring), fragments of nuclear families, and individuals of