THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 52 SEPTEMBER-OCTOBER, 1967 Nos. 9 and 10

IOWAITE, A NEW HYDROUS MAGNESIUM HYDROXIDE-FERRIC OXYCHLORIDE FROM THE PRECAMBRIAN OF IOWA

D. W. KOHLS AND J. L. RODDA, *Research Department, The New Jersey Zinc Company, Palmerton, Pennsylvania.*

ABSTRACT

Iowaite, a new hydrous magnesium-ferric oxychloride, was discovered in diamond drill core at a depth of 1000 to 1500 feet in Precambrian serpentinite from Sioux County, Iowa. It is associated with chrysotile, dolomite, brucite, calcite, magnesite, and pyrite, all of which post-date the serpentinization of the rock.

Iowaite occurs as bluish-green crystals up to 2–3 mm in length. On exposure to the atmosphere, it undergoes color changes from bluish-green to light green, to whitish-green, to whitish-green with a rusty red overtone, due to loss of zeolitic water. The mineral is insoluble in water and readily soluble in mineral acids. Its hardness is about 1.5; density (measured) 2.11 ± 0.02 g/cm^3; greasy luster; greasy or soapy feel; white streak; perfect basal (0001) cleavage. It is uniaxial negative, with $\omega = 1.543 \pm 0.005$ and $\epsilon = 1.533 \pm 0.005$; $B = 0.010$.

X-ray and electron diffraction indicates a hexagonal cell with $a = 3.119 \pm 0.005$, $c = 24.25 \pm 0.02$ Å, $C = 7.775 \pm 0.02$; $V = 204.3 \pm 1.5$ Å^3; $Z = 1$ [$4Mg(OH)_2 \cdot FeOCl \cdot xH_2O$] in the hexagonal unit. The amount of zeolitic water (x) may vary up to 4. The strongest X-ray lines are: 8.109 (100), 4.047 (40), 2.363 (27), 2.019 (23), 2.639 (17), 1.530 Å (13).

Iowaite contains zeolitic water which is continuously released on heating to 280°C, increasing the surface area from 2.15 to 12.7 m^2/g. The structure begins to collapse at 315°C. with the evolution of more water and the formation of periclase. At 400°C magnetite forms. Both phases become better developed on heating to 750°C.

Chemical analysis of the purified mineral gave: MgO 39.00 Fe_2O_3 21.16, Cl 8.50, NiO 0.10, SiO_2 2.00; ignition loss (due to water, hydroxyl, chlorine, iron, etc.) 39.82 percent.

Iowaite is named for its occurrence in the state of Iowa.

INTRODUCTION

During an examination of a diamond drill core from the Precambrian of Sioux County, Iowa, a material giving an unidentified X-ray diffraction pattern was persistently observed. Further investigation showed the pattern to be characteristic of a bluish-green, translucent, platy, soapy, mineral occurring in veinlets in a serpentinite. Physical and chemical tests indicated it to be previously undescribed hydrous magnesium hydroxide-ferric oxychloride which has been named iowaite.[1]

OCCURRENCE

Iowaite occurs in veinlets 1 to 20 mm wide in serpentinized ultrabasic rocks of Precambrian age. Associated with iowaite are chrysotile, dolomite, brucite, calcite, magnesite, and pyrite. The serpentinite in contact with these veins has been altered from a greenish-black, saccharoidal, serpentinite with a typical serpentine mesh structure to a light green, finely crystalline lizarditic serpentinite. The width of alteration varies from 0.5 to 10 cm and is directly proportional to the width of the veins. This alteration suggests that the introduction of the vein material postdates the serpentinization of the rock. On exposure to the atmosphere, iowaite undergoes color changes from bluish-green to light green, to whitish-green, to whitish-green with a rusty red overtone. On becoming whitish-green, the soapy, waxy mineral changes to a loose, friable powder.

MINERAL SEPARATION

Relatively pure pieces of blusih-green iowaite were hand-picked from the enclosing rock. This material was crushed and the -28 to $+270$ mesh fraction was separated on a Frantz isodynamic separator. The purity of the material was checked by X-ray and infrared analysis and a chemical analysis was made. The limited amount of mineral available, close association with the matrix and the tendency to alter by loss of water on exposure to air complicated the process of obtaining suitable material. It was necessary to consume all but a trace amount of the mineral in the various analyses which were undertaken.

PHYSICAL AND OPTICAL PROPERTIES

Iowaite occurs as bluish-green, translucent, platy crystals up to 2–3 mm in length. The mineral has a greasy luster, a greasy or soapy feel, white streak, and perfect basal (0001) cleavage. Its hardness is 1.5. The specific gravity, determined by the pycnometer method, using water as the immersion liquid, is 2.11 ± 0.02 g/cm^3. The calculated specific gravity varies with the amount of zeolitic water absorbed on the lattice.

Iowaite is colorless in transmitted light. The indices of refraction at room temperature, determined by the immersion method, were $\omega = 1.543 \pm 0.005$ and $\epsilon = 1.533 \pm 0.005$; $B = 0.010$. After removing the zeolitic

---

[1] Name approved by the Commission on New Minerals, International Mineralogical Association.

water from the structure by heating to 280°C the indices were $\omega = 1.57 \pm 0.005$ and $\epsilon = 1.56 \pm 0.005$; $B = 0.010$. It is uniaxial negative frequently appearing anomalously biaxial with a small (5°) axial angle. The crystals are length fast. The surfaces area measured by nitrogen adsorption increases due to loss of zeolitic water from 2.15 m^2/g at 110°C to 12.7 m^2/g at 280C.

INFRARED ADSORPTION ANALYSIS

An infrared spectrum of iowaite was obtained with a Perkin-Elmer spectrophotometer, using sodium chloride optics. KBr pellets were prepared using 0.25 and 0.50 mg, respectively, of fine powder in 500 mg of KBr.

The spectrum of iowaite consists of one major absorption band at 3.0 μ, representing the presence of H_2O and/or OH.

DIFFERENTIAL THERMAL ANALYSIS

A DTA device, using 22-gauge chromel-alumel thermocouples, was employed in the analysis. The thermal reactions were recorded on a standard electronic millivolt recorder. Iowaite was ground to −200 mesh to which 10 percent alundum was added. The heating rate varied from 6° to 15° per minute with alundum being used as a reference standard. The DTA curve of the decomposition of iowaite is shown in Figure 1. The loss

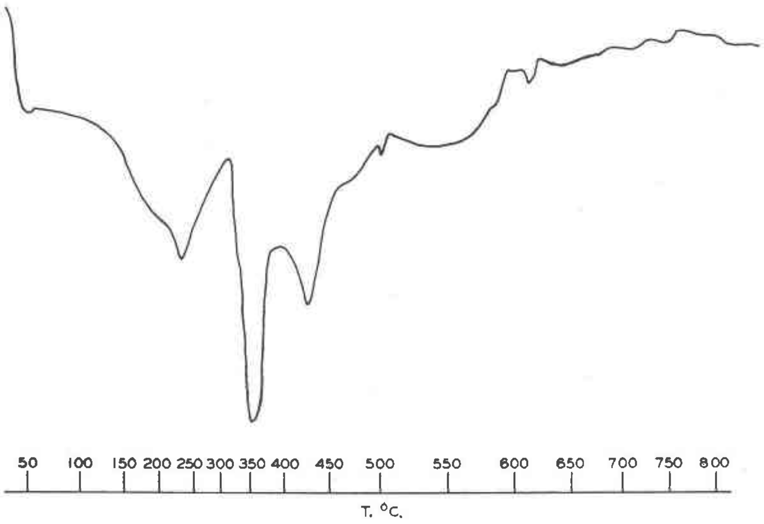

FIG. 1. Differential thermal analysis curve of iowaite.

TABLE 1. LOSS ON HEATING OF IOWAITE AT VARIOUS TEMPERATURES

Temperature °C.	% Weight Loss	Cumulative % Weight Loss
110	5.30	5.30
250	8.54	13.84
355	9.49	23.33
380	4.49	27.82
450	4.91	32.73
750	7.09	39.82

on heating determined at various temperatures is reported in Table 1. To explain the reactions involved in the decomposition, a small amount of the mineral was placed in a closed tube which was inserted into a copper block. Heat was supplied with a Bunsen burner, the temperature being measured with iron-constantan thermocouples enclosed in the block. The mineral was heated to the desired temperature, removed and X-rayed. The results of this analysis are given in Table 2.

The evolution of water on heating to 280°C without changing the structure of the mineral, proves the zeolitic nature of this water. The loss of zeolitic water produces a very broad endothermic peak that begins below 110°C and reaches a peak at 216°C.

The collapse of the iowaite structure is represented by a sharp, large endothermic reaction beginning at 315°C and reaching a peak at 350°C. During this reaction, the material changes in color from light tan to dark brown; water is evolved; and periclase is formed.

TABLE 2. DECOMPOSITION OF IOWAITE—COLOR, PRODUCTS EVOLVED, AND PHASES PRESENT AT VARIOUS TEMPERATURES

Temperature °C.	X-ray Pattern Observed	Color of Material	Products Observed at End of Closed Tube
110	Iowaite	White	Colorless H_2O
230	Iowaite	White	Colorless H_2O
280	Iowaite	Light Tan	Colorless H_2O
320	Iowaite	Dark Brown	Colorless H_2O
330	Iowaite Periclase	Dark Brown	Colorless H_2O
388	Periclase Magnetite?	Dark Brown	Colorless H_2O
400	Periclase Magnetite	Dark Brown	
450	Periclase Magnetite	Dark Brown	Yellow-Colored Water
750	Periclase Magnetite	Dark Brown	

The third endothermic reaction begins at 405°C and peaks at 426°C. This reaction is accompanied by the evolution of yellow-colored water containing chloride and iron ions. Magnetite is formed or becomes well developed during this reaction. The identification of this material as magnetite by X-ray diffraction was confirmed by its magnetic properties.

The nature of the reaction represented by a small endothermic break starting at 607°C and peaking at 613°C is unknown.

At 750°C the material is dark brown in color, with a saccharoidal texture. X-ray analysis shows the material to contain well-cyrstallized periclase and magnetite.

EFFECT OF ZEOLITIC WATER ON DENSITY

The water expelled under 280°C is not given off at a definite temperature, as in the case of ordinary water of crystallization, but gradually as the temperature is raised. The proportion of water present therefore varies continuously with the temperature. The removal of this water occurs without destroying the crystalline structure of the mineral and results in an increase of the surface area from 2.15 to 12.7 m^2/g. The water is therefore zeolitic or absorbed water. The large increase in surface area suggests that surfaces formerly occupied by water are exposed when the water is removed.

The volume of the unit cell (204.3±1.5 Å3), calculated from the X-ray data, does not include the volume occupied by the absorbed water molecules. To get a realistic value for the calculated density, the effect of absorbed water must be considered:

Molecules of Water Absorbed on Surface	*Calculated Density* (*g/cm^3*)
0	2.77
1	2.54
2	2.37
3	2.23
4	2.11

The effect of absorbed water on the density of iowaite is readily apparent from these data. The measured density of iowaite is 2.11±0.02 g/cm^3 compared to be a calculated value of 2.11 g/cm^3 for four molecules of absorbed water.

X-RAY POWDER DATA

An X-ray powder diffraction pattern of iowaite was taken in a 114.59-mm diameter Debye-Scherrer camera with nickel-filtered copper radiation ($\lambda = 1.5418$ Å). In making spacing measurements, film shrinkage and camera radius errors were taken into account by using the Straumanis film mount and correction procedures. The interplanar spacings and intensities for the observed lines are given in Table 3, columns 3 and 4. The intensities were visually estimated by comparison with a calibrated intensity strip.

TABLE 3—X-RAY POWDER DATA FOR IOWAITE

Calculated		Measured	
hkl	d_{hkl}	d_{hkl}	*I*
00.3	0.083	8.109	100
00.6	4.042	4.047	40
00.9	2.694	2.697	<1
01.2	2.637	2.639	17
01.5	2.360	2.363	27
00.12	2.021	2.019	23
10.10	1.804	1.805	4
01.11	1.708	1.710	5
11.0	1.560	1.560	8
11.3	1.531	1.530	13
11.6	1.455	1.453	5
11.9	1.345	1.345	2
10.16	1.322	1.324	3
20.5	1.301	1.299	3
20.8	1.234	1.233	3
02.10	1.180	1.179	<1
10.19	1.154	1.154	2
12.2	1.017	1.016	<1
21.4	1.007	1.007	<1
12.5	0.999	0.998	1
12.8	0.968	0.967	1
21.10	0.941	0.940	<1
11.21	0.928	0.927	3
02.19	0.928		
03.0	0.900	0.901	<1
21.13	0.896	0.895	1
12.14	0.880	0.879	<1
11.24	0.848	0.848α1 0.848α2	1 1
22.0	0.780	0.780	1
22.3	0.776	0.776	1

Hexagonal cell constants, $a=3.119\pm0.005$ and $c=24.25\pm0.02$ Å, were determined from $\frac{1}{2}[(\cos^2\theta/\sin\theta)+(\cos^2\theta/\theta)]$ extrapolations using reflections in the range 40° to 83°. Interplanar spacings calculated from the X-ray cell constants on a digital computer are listed in Table 3, column. 2

ELECTRON MICROSCOPY

A good dispersion of mineral particles for electron microscopic examination was obtained using specimen preparation techniques described by Fuller *et al.* (1943, p. 201). An electron micrograph (Fig. 2) shows the good basal cleavage of this platy, flake-like mineral. A cylindrical-shaped contaminant, serpentine, is also apparent. A selected area electron diffraction pattern (Fig. 3) of these plate-like single crystals reveals the hexagonal nature of iowaite and indicates the *c* crystallographic axis to be perpendicular to the pronounced cleavage.

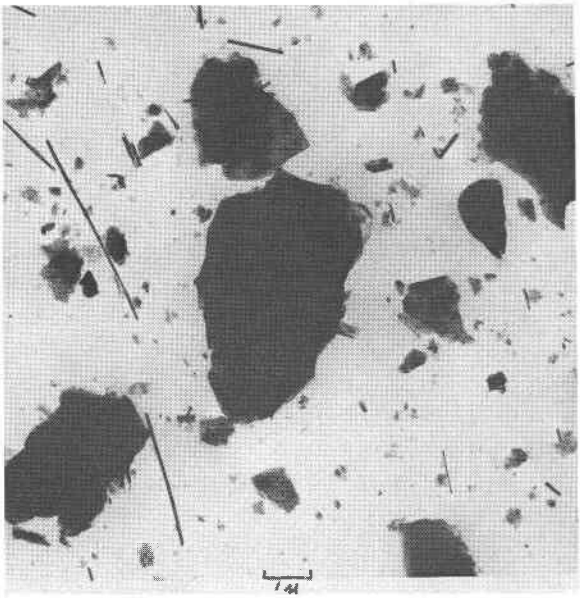

FIG. 2. Electron micrograph of iowaite.

This diffraction pattern exhibits reflections forbidden to a rhombohedral lattice. It is very similar if not identical to that of brucite, suggesting that the structures of these two minerals are related.

CHEMISTRY

The chemical analysis of hand-picked purified iowaite is as follows: MgO 39.0, Fe_2O_3 21.16, C1 8.5, NiO 0.10, SiO_2 2.0, F 0.05, and Ignition Loss 39.7 weight percent. The ignition loss includes some iron and chlorine as well as water. Additional elements detected spectrographically were: Mn 0.0X; Al, B, Mo 0.00X; and Cu 0.000X weight percent.

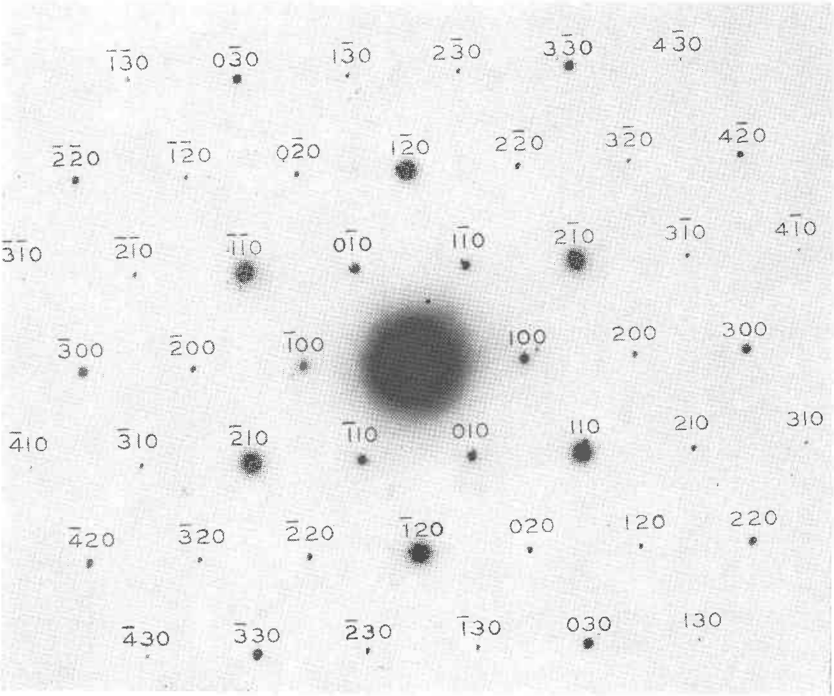

FIG. 3. Selected area diffraction patterns of a thin plate-like, single crystal of iowaite.

Qualitative tests of an HCl solution of the fresh, bluish-green mineral with ferrocyanide and with ferricyanide ions indicate that the iron is in the ferric state. The iron is therefore expressed in the analysis as Fe_2O_3, although it will be recognized that only two of its valences are satisfied by oxygen, the other being satisfied by chlorine.

It is known from the X-ray and infrared data that a small amount of serpentine is present. The silica has, therefore, been assigned to serpentine with its equivalent magnesia. The chlorine and equivalent iron were calculated as ferric oxychloride. The remaining magnesia and small amount of iron were calculated as hydroxide as shown in Table 4.

The formula of iowaite derived from the analysis is

$$4Mg(OH)_2 \cdot FeOCl \cdot xH_2O$$

with the molecules of zeolitic water (x) varying up to 4.

DISCUSSION

A magnesium hydroxide-ferric oxychloride has never, to the writers' knowledge, been described in the literature. However, a structurally

TABLE 4. COMPOSITION OF ANALYSED IOWAITE AND OF EQUIVALENT HYDROXIDES AND OXYCHLORIDES

Analyzed Sample		Equivalent Hydroxides and Oxychlorides				
				Mols Present		
	Wt. %	Component	Wt. %	With Zeolitic H_2O	Without Zeolitic H_2O	Molecular Ratio
		Serpentine ($H_4Mg_3Si_2O_9$)	4.61			
MgO	39.0	$Mg(OH)_2$	53.53	47.02	77.59	3.83
Fe_2OS	21.16	$Fe(OH)_2$	2.31	1.31	2.17	0.11
Cl	8.5	FeOCl	25.69	12.27	20.24	1.00
SiO_2	2.0	Zeolitic H_2O[2]	13.86	39.40	—	3.21
NiO	0.10		100.00	100.00	100.00	
F	0.05					
Ignition Loss[1]	39.7					

[1] Includes some iron and chlorine as well as water.

[2] Zeolitic water by difference.

similar compound, $4Fe(OH)_2 \cdot FeOCl \cdot xH_2O$, was originally synthesized and described by Feitknecht and Keller (1950). It has been subsequently investigated by Bernal *et al.*, (1959) who referred to it as "green rust." This ferrous hydroxide-ferric oxychloride can be prepared by the atmospheric oxidation of a ferrous chloride solution buffered with ammonium chloride to which excess ammonium hydroxide has been added or by the oxidation of a ferrous chloride solution partially precipitated with sodium hydroxide. In addition it has been prepared (Bernal *et al.*, 1959, p. 23) by the electrolytic solution of iron anodes in an N/20 solution of ammonium chloride.

According to Feitknecht and Keller (1950), the compound $4Fe(OH)_2 \cdot FeOCl \cdot xH_2O$ has a double-layer lattice in which layers of $Fe(OH)_2$ exist as in pure $Fe(OH)_2$ but with a 0.06 Å shortening of a; a ferric oxychloride (FeOCl) layer and possibly water lie between layers of $Fe(OH)_2$, increasing the c-dimension, 8 Å. They determined the hexagonal cell dimensions as $a = 3.22$ and $c = 24.0$ Å. Bernal *et al.*, (1959) considered the structure to be rhombohedral with hexagonal cell dimensions of $a = 3.198 \pm 0.01$ and $c = 24.21 \pm 0.1$ Å.

Subsequent work on these "green rusts" is contained in papers by Dasgupta and Mackay (1959) and Dasgupta (1961).

The close chemical and structural similarity between $4Fe(OH)_2 \cdot FeOCl$ and iowaite suggests that iowaite may be synthesized in a manner similar to that of the iron hydroxide-oxychloride.

The structure of iowaite also may be related to the carbonate-hydroxides described in papers by Frondel (1941), Glemser and Einerhand (1950a, 1950b), Jambor and Boyle (1964) and Lapham (1965). There have been two explanations of the structure of these carbonate-hydroxides. Frondel (1941) proposed a "double cell structure" (doubled *a* and *c*) for naturally occurring rhombohedral and hexagonal variants based on the whole number of atoms which are necessary to fulfill the lattice requirements for the particular symmetry involved.

Glemser and Einerhand (1950a, 1950b) proposed a nonstoichiometric stuffing of "layers" within a rhombohedral (or hexagonal) cell. Both these writers noted a structural relationship with brucite as a fundamental unit.

Lapham (1965) tentatively considered the structure of $Mg(OH_2) \cdot \frac{1}{4}(Ni,Fe)OOH$, a new mineral from Lancaster County, Pennsylvania, to be composed of $\frac{1}{4}(Ni,Fe)OOH$ embedded within the laminae of $Mg(OH)_2$ rhombohedral lattice, the consequence of which is a *c*-dimension five times that of brucite.

The *c*-dimension of iowaite is also approximately five times that of brucite.

Iowaite has been indexed on the basis of a hexagonal unit cell. All of the reflections obtained by X-ray diffraction satisfy the requirements of a rhombohedral lattice. The selected area electron diffraction pattern (Fig. 3), however, has reflections forbidden by the rhombohedral lattice. This diffraction pattern is very similar, if not identical, to that of brucite. The relationship $\rho = ZNM/V$ suggests that the unit cell contains 1 and not 3 or a multiple of 3 molecules as would be expected in a rhombohedral structure. For these reasons iowaite was indexed on a hexagonal unit cell rather than the more limiting rhombohedral form.

Note added in proof: On weathering iowaite alters to pyroaurite. This alteration has occurred to a depth of 250 feet below the Cretaceous-Precambrian contact, which is at an elevation of 750–800 feet in this area. Alteration decreases the chlorine content of the serpentinite from about 1 to 0.05 percent.

ACKNOWLEDGMENTS

The writers express appreciation to the other members of the Research and Exploration Departments of The New Jersey Zinc Company who gave assistance during the course of the investigation and in the preparation of the manuscript.

REFERENCES

BERNAL, J. D., D. R. DASGUPTA, AND A. L. MACKAY (1959) The oxides and hydroxides of iron and their structural interrelationships. *Clay Minerals Bull.* **4,** 15–30.

DASGUPTA, D. R. (1961) Topotactic transformation in iron oxides and oxyhydroxides. *Indian J. Phys.* **35,** 401–419.

——— AND A. L. MACKAY (1959) Beta-ferric oxyhydroxide and green rust. *J. Phys. Soc. Japan* **14,** 932–935.

FEITKNECHT, W. AND G. KELLER (1950) Über die dunkelgrünen hydroxyverbindungen des eisens: *Z. Anorg. Allg. Chem.* **262,** 61–68.

FRONDEL, C. (1941) Constitution and polymorphism of the pyroaurite and sjörgrenite groups. *Amer. Mineral.* **26,** 295–315.

FULLER, M. L., D. G. BRUBAKER, AND R. W. BERGER (1944) Mounting of pigments for electron microscopy. *J. Appl. Phys.* **15,** 201.

GLEMSER, O. AND J. EINERHAND (1950a) Über hohere Nickelhydroxide. *Z. Anorg. Allg. Chem.,* **261,** 26–42.

——— AND ——— (1950b) Die Struktur hohere Nickelhydroxide. *Z. Anorg. Allg. Chem.* **261,** 43–51.

JAMBOR, J. L. AND R. W. BOYLE (1964) A nickel hydroxide mineral from Rock Creek, British Columbia. *Can. Mineral.* **8,** 116–120.

LAPHAM, D. M. (1965) A new nickeliferous magnesium hydroxide from Lancaster County, Pennsylvania. *Amer. Mineral.* **50,** 1708–1716.

Manuscript received, November 8, 1966; accepted for publication, July 17, 1967.