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# ABHURITE, A NEW TIN HYDROXYCHLORIDE MINERAL, AND A COMPARATIVE STUDY WITH A SYNTHETIC BASIC TIN CHLORIDE*

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## ABSTRACT

Abhurite $Sn_3O(OH)_2Cl_2$ is a new mineral species found in blister-like protuberances on the surface of tin ingots submerged in a shipwreck about 100 years ago. The recovery site, at a depth of about 35 m, in an arm of the Red Sea known as Sharm Abhur, is located 30 km north of Jiddah, Saudi Arabia. Abhurite forms thin, platy, colorless, fragile, six-sided crystals averaging 1.5 mm in diameter. The plates show no birefringence, the uniaxial figure is positive, and $\omega$ is 2.06. No fluorescence for either shortwave or longwave ultraviolet light was detected. Density $D_x$ 4.34, $D_m$ 4.29 g/cm$^3$. The mineral dissolves rapidly in nitric acid and slowly in hydrochloric acid. Chemical analysis gives 73.4 wt.% Sn, 15.7 Cl, 11.0 O and 0.4 H, which corresponds to the formula $Sn_3O(OH)_2Cl_2$. Differential thermal analysis shows release of $H_2O$ at 235°C and of $SnCl_2$ at 525°C. X-ray-precession patterns show that the crystals are rhombohedral, space group $R\bar{3}m$, $R3m$ or $R32$, and commonly twinned on (0001). Guinier–Hägg powder data were refined to give hexagonal parameters $a$ 10.0175(3), $c$ 44.014(2) Å; $c/a$ 4.3937. The principal lines in the powder-diffraction pattern [$d$ in Å (I)($hkl$)] are: 4.139(50)(116), 3.634(35)(0.1.11), 3.404(50)(208), 3.271(35)(211), 3.244(35)(122), 3.142(35)(214), 2.9074(35)(217), 2.8915(70)(300), 2.8381(25)(303), 2.8175(50)(128), 2.5313(100)(1.1.15). Synthetic crystals prepared by Dr. R.A. Howie of the University of Aberdeen, Scotland are thin, colorless, hexagonal plates that show no birefringence, are uniaxial positive and produce an X-ray pattern nearly identical to that of abhurite. The two phases are dimorphous: abhurite is rhombohedral, the synthetic crystals are hexagonal.

*Keywords:* abhurite, tin chloride hydroxide, Saudi Arabia.

## SOMMAIRE

L'abhurite $Sn_3O(OH)_2Cl_2$ est une nouvelle espèce minérale qui se trouve dans des protubérances en forme d'ampoules à la surface de lingots d'étain submergés depuis environ cent ans à la suite d'un naufrage. Le site de la découverte est à environ 35 m de profondeur, dans un bras de la Mer Rouge appelé Sharm Abhur, à environ 30 km au nord de Jiddah, en Arabie Séoudite. L'abhurite forme des cristaux en plaquettes incolores à six côtés, minces et fragiles, d'un diamètre moyen d'environ 1.5 mm. Les plaquettes sont uniréfringentes; la figure uniaxe est positive, et $\omega$ égale 2.06. Nulle fluorescence ne fut détectée à aucune longueur d'onde de l'ultraviolet. Le minéral se dissout rapidement dans l'acide nitrique et lentement dans l'acide chlorhydrique. L'analyse chimique révèle 73.4% (en poids) Sn, 15.7% Cl, 11.0% O et 0.4% H, et correspond à la formule $Sn_3O(OH)_2Cl_2$. L'analyse thermique différentielle montre que l'eau se dégage à 235°C et $SnCl_2$, à 525°C. En diffraction X, les clichés de précession révèlent des cristaux rhomboédriques, de groupe spatial $R\bar{3}m$, $R3m$ ou $R32$, généralement maclés selon (0001). Les données de poudre Guinier–Hägg furent affinées pour arriver à une maille élémentaire hexagonale dont les paramètres sont $a$ 10.0175(3), $c$ 44.014(2) Å; $c/a$ 4.3937. Les raies principales du cliché de diffraction (méthode des poudres) [$d$ en Å(I)($hkl$)] sont: 4.139(50)(116), 3.634(35)(0.1.11), 3.404(50)(208), 3.271(35)(211), 3.244(35)(122), 3.142(35)(214), 2.9074(35)(217), 2.8915(70)(300), 2.8381(25)(303), 2.8175(50)(128), 2.5313(100)(1.1.15). Des cristaux synthétiques préparés par R.A. Howie de l'Université d'Aberdeen, en Écosse, se présentent en plaquettes hexagonales minces, incolores, uniréfringentes, uniaxes positives. Cette phase possède un cliché de diffraction presque identique à celui de l'abhurite. Les deux phases sont dimorphes, l'abhurite étant rhomboédrique et les cristaux synthétiques, hexagonaux.

(Traduit par la Rédaction)

*Mots-clés:* abhurite, hydroxychlorure d'étain, Arabie Séoudite.

## INTRODUCTION

Abhurite, a new mineral species of composition $Sn_3O(OH)_2Cl_2$, was found as a corrosion product on ingots of tin recovered from the cargo of a sunken ship, wrecked possibly 100 years ago, lying in a cove of the Red Sea known as Sharm Abhur. The site (Lat. 21°44′N, Long. 39°07′E) is about 30 km by air north of Jiddah, Saudi Arabia. The shoreline near the cove is bordered by coral reefs, and the area receives water runoff only intermittently. The tin ingot was located inside the cove on a sandy bottom at a depth of about 35 m in water of about 21°C.

An attempt to identify the geographic source of the ingot was made by comparing trace elements reported for cassiterite ores and the corresponding smelts (Rapp 1978). The data available are insufficient for positive identification but, on the basis of antimony content, tin ore from Bolivia seem to be a possible source for the tin ingot from Saudi Arabia.

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Few descriptions have been made of alteration products of tin ingots exposed to marine waters for long periods. Encrusted tin ingots recovered from a tidal river in the Kampar area, western Malaysia, have been described by Hosking (1970). In these crusts, investigators at the British Museum (Natural History) tentatively identified two phases of tin oxychloride. Hosking suggested that the tin oxychloride was formed by reaction with salt accidentally spilled on the ingot just after it had been poured. Another instance of saline corrosion was noted by Smythe (1946). He found that light greyish brown material occurring on a lead-containing tin ingot recovered from the sea at Falmouth Harbor, U.K., contains as much as 1.6 wt.% Cl. Five other samples from ingots that had been buried in soil have crusts that contain somewhat less Cl than the marine sample. Smythe considered that the chloride solutions were active in an initial electrochemical reaction in the corrosion process. Tin artifacts recovered from the Winnipeg River, Ontario carry incrustations of the new minerals romarchite SnO (Organ & Mandarino 1971) and hydroromarchite $3SnO \cdot H_2O$ (Howie & Moser 1973).

Fragile, colorless crystals of high index of refraction were found in blisters that formed on the ingot from Saudi Arabia. Semiquantitative spectrographic and energy-dispersion analysis (EDX) in the scanning-electron microscope (SEM) showed that tin is the only metallic component of the crystals. These crystals, named *abhurite* after the locality, and a closely similar synthetic polymorph, are described

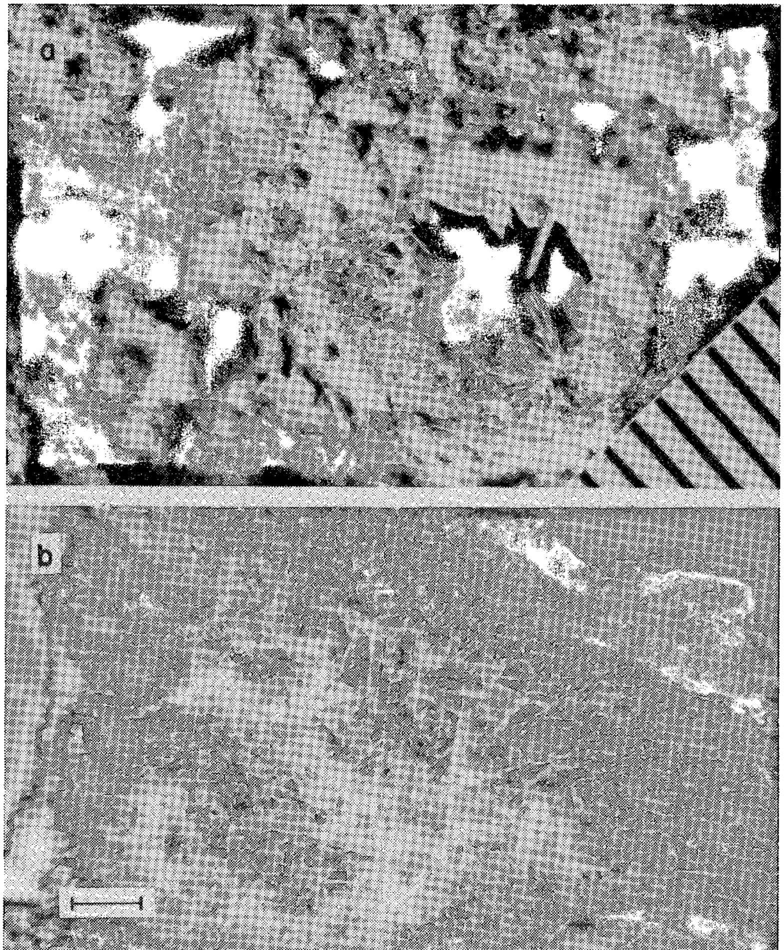

FIG. 1. (a) Abhurite crystals within a fractured pod (mm scale is shown); (b) abhurite crystals with massive cream-colored abhurite and black romarchite on outer rim (bar equals 1 mm).

in this paper. The name *abhurite* has been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. Ingots bearing abhurite crystals will be deposited at the Smithsonian Institution (Natural History Museum), Washington, D.C., and at the Royal Ontario Museum, Toronto, Ontario.

## OCCURRENCE AND MINERALOGY

The tin ingot on which the abhurite crystals are found is 18 cm long, 9 cm wide at one end and 8 cm at the other, and 3 cm thick. The ingot is principally tin, alloyed with minor amounts of Cu, Pb, Bi, Zn and Sb. The larger crystals of abhurite form within blisters or pods that contain a viscous mass of liquid and solids. Within a few months after removal from sea water, the blisters had dried out. The fluid has an acidity (pH) of 1, as determined by indicator paper. The pods, which cover all the surfaces of the ingot, rise as much as 7 mm above the ingot surface and penetrate as much as 5 mm below the surface. Their base dimensions range from about 1 to 10 mm. These podlike chambers permitted the formation of large, transparent crystals of abhurite (Fig. 1). Abhurite crystals that are unprotected by the blisters formed on the surface of the ingot to a depth of about 2 mm, and were interrupted in their development by a covering of romarchite and a subsequent precipitation (about 2 mm thick) of kutnohorite, aragonite and coral. This coating apparently protected the tin ingot from further reaction with the sea water, and also coated the pods.

Most of the abhurite contains fragments of the tin alloy and other crystallites. Apparently, not all of the tin is completely dissolved in the corrosion process, and the remaining fragments were incorporated into the abhurite crystals and masses. The white metallic-appearing spherical inclusions have been identified by X-ray diffraction as $\beta$-tin, similar to the ingot metal.

The liquid core containing the abhurite crystals is encased by a shell of milky white to tan cryptocrystalline material, which in turn is rimmed by a black to bluish black material containing romarchite (Fig. 1b), and may be followed again on the outer surface by more tan to white cryptocrystalline material. The abundant cryptocrystalline material has been identified by X-ray diffraction as abhurite. The blackish mineralized areas handpicked for X-ray tests show mainly abhurite, probably mixed with romarchite. An X-ray powder-diffraction pattern of single black grains shows the presence of romarchite, but another pattern of a similar sample shows only abhurite. Examination of these dark grains by SEM reveals a complex mixture of abhurite, tin oxides, and sulfates or sulfides of other metals such as lead and bismuth.

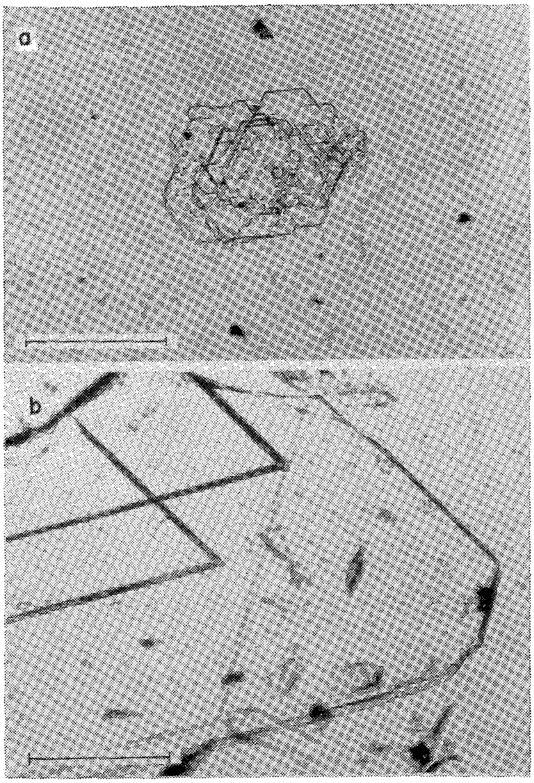

FIG. 2. (a) Abhurite crystals in multiple layers, with typical angles of 120°; (b) abhurite crystal with step angles of 60°. Bar equals 1 mm in both views.

Some crystal habits of abhurite are shown in Figures 2 and 3a. The hexagonal plates are bounded by rhombohedral faces that give poor optical goniometric signals at $\varrho \sim 43°$. For the negative rhombohedron $\{01\bar{1}5\}$, $\varrho$ is equal to 44.6°. Figures 2b and 3a show the common twin habit of abhurite, in which one individual twinned on (0001) coalesces on the basal face of the other, forming beveled triangular elevations. In crossed polarized light the crystals are bluish grey to colorless and show a positive uniaxial interference-figure. The physical and chemical properties of abhurite are summarized in Table 1.

As described in a later section, various attempts reported in the literature to synthesize a homogeneous basic stannous chloride have had diverse results. One conforming most closely with abhurite in composition and properties was very kindly prepared for us by R.A. Howie of the University of Aberdeen, Scotland. Using the method of Donaldson *et al.* (1963) (summarized below), Howie obtained hexagonal crystals that evidently are not the same as those of Donaldson *et al.*, but appear to be identical with abhurite in composition, X-ray crystallography and morphology. As shown in Figure 3b, Howie's hexagonal plates have very steep rounded edges that give no optical signal and show no rhombohedral aspect. The synthetic phase will be described in detail in the following sections.

## CHEMICAL ANALYSIS AND COMPOSITION

Crystals of abhurite, handpicked under the binocular microscope to be free of obvious inclusions, were analyzed by wet-chemical methods (Table 2). Semiquantitative spectrographic analyses were run on the separated crystals of abhurite and also the ingot to determine the composition of the alloy (Table 2).

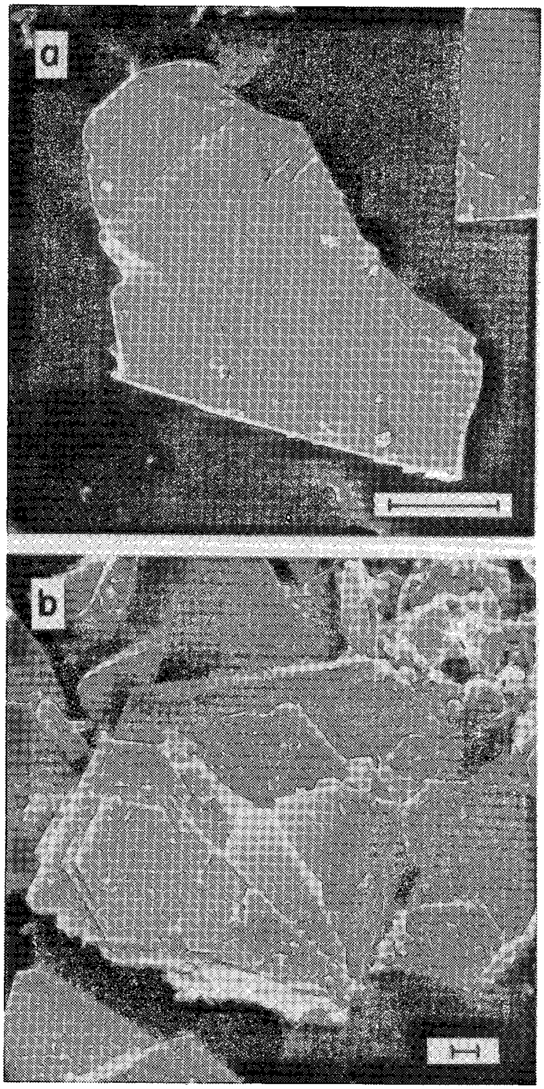

FIG. 3. Scanning-electron micrographs of crystals of (a) abhurite (natural), and (b) Howie's synthetic tin oxychloride. Photographs by E.J. Dwornik. Bar in lower right corner equals 0.1 mm in a), 0.01 mm in b).

Crystallization of abhurite removed only tin from the ingot, although the ingot also contained minor but appreciable amount of Cu, Pb, Bi, Zn and Sb. SEM-EDX analyses of selected abhurite crystals confirm the presence of Sn and Cl only; Br was looked for but not detected. Differential-thermal analyses (DTA) and thermogravimetric analyses of the abhurite crystals in a helium atmosphere were done on a Mettler apparatus. Peaks were produced in the DTA at 235° and 525°C. At the latter temperature $SnCl_2$ is probably evolved, as the residue was shown by an X-ray powder pattern to be $SnO_2$ ($SnCl_2$ sublimes at 652°C). The residue produced at 235°C was not examined, but this point probably marks the evolution of rather tightly bound water.

Results of the chemical analysis (Table 2) conform well with the formula $SnCl_2{\bullet}2SnO{\bullet}H_2O$ or $Sn_3O(OH)_2Cl_2$. The DTA experiment indicates that the water is probably present as OH groups, as would be expected in a product of hydrolysis.

Laboratory experiments show that NaCl-saturated solutions attack tin shot over a period of about a year, to form very small crystals of abhurite and blackish rims of romarchite. A 10% solution of hydrochloric acid attacks the tin shot more rapidly, and in a year's exposure somewhat larger crystals of abhurite form. Globules of remobilized very fragile abhurite form on the crystals over a period of 4 years in the humid environment of the laboratory in Jiddah.

## X-RAY CRYSTALLOGRAPHY

Crystals of abhurite were studied by X-ray diffraction using Debye–Scherrer and Guinier–Hägg

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF ABHURITE

Physical properties

Optically uniaxial positive; strained plates show birefringence and small 2V with isogyres that remain separated on rotation.
Indices of refraction[1]: ω 2.06, ε >2.06, ~2.11 (Cargille liquid n 2.11 slowly attacks crystals).
Isotropic to nonextinguishing blue on centred uniaxial figure, to high birefringence on off-centre figures.
Colorless, transparent with opalescent lustre; white streak; no pleochroism.
No fluorescence or absorption with shortwave or longwave ultraviolet light.
Habit platy or tabular on hex. (0001); rhombohedral forms $\{01\bar{1}5\}$, $\{0001\}$.
Twinning common on (0001); step growths intersecting at 60° or 120°.
Fracture hackly; no cleavage observed.
Hardness 2; fusibility 1.
Density[2]: 4.29 g/cm$^3$.
Franz isodynamic concentration not clean, but best in 1.5 nonmagnetic.
Average crystal size: 1.5 mm.

Chemical properties

Insoluble in distilled water or Red Sea water; hydration to a crystalline mush within 60 days over water in a dessicator.
When heated on a hot plate turns brownish with metallic tin emanating from the abhurite at 230° to 260°C (as indicated by temperature pencils).
Ingot melts between 230° and 320°C (pure Sn melts at 232°C).
When heated in closed tube yields a white sublimate (probably $SnCl_2$).
Dissolves slowly in HCl (10% or conc.) without effervescence.
Does not dissolve in $H_2SO_4$ (10%), but surface etched to hexagonal outlines; crystallinity destroyed in conc. acid.
Dissolves in $HNO_3$ with effervescence, slight in 10% acid, strong in conc. acid.
No reaction in $NH_4OH$.

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[1] Interference microscopy determination by E. C. T. Chao and Jean Minkin (Chao 1976). [2] Density determined by John Marinenko using tetrachloroethylene in a micropycnometer. $D_m$ for Howie's synthetic crystals was determined as 4.25 g/cm$^3$ by the same method.

powder methods and Buerger-precession single-crystal methods. Abhurite is rhombohedral, with space group $R\bar{3}m$, $R3m$ or $R32$. Precession patterns of upper levels normal to $c^*$ in the hexagonal lattice, although not completely separated, clearly show the $3m$ symmetry. The $h0l$ net, shown in Figure 4a, is complicated by twinning on (0001), and shows strong deviations from expected $mm$ symmetry. A study of the intensity relationships shows that the paired arrangement of spots on rows parallel to $c^*$ with $h \neq 3n$ is consistent with two rhombohedral lattices superposed by twinning. This interpretation is confirmed by the upper-level images, one of which is shown in Figure 4b. A Guinier–Hägg focusing powder pattern made at 25°C with Cu$K\alpha_1$ radiation ($\lambda$ = 1.540562 Å) and $BaF_2$ as an internal standard ($a$ 6.1970 Å) gave 157 measured lines. These were indexed with the aid of intensities observed on the single-crystal patterns, and the $2\theta$ values were used in a least-squares refinement of the unit-cell dimensions (hexagonal cell) (Appleman & Evans 1973). The unit-cell dimensions and powder data are given in Table 3, along with corresponding data for Howie's synthetic polymorph of abhurite. If we assume that

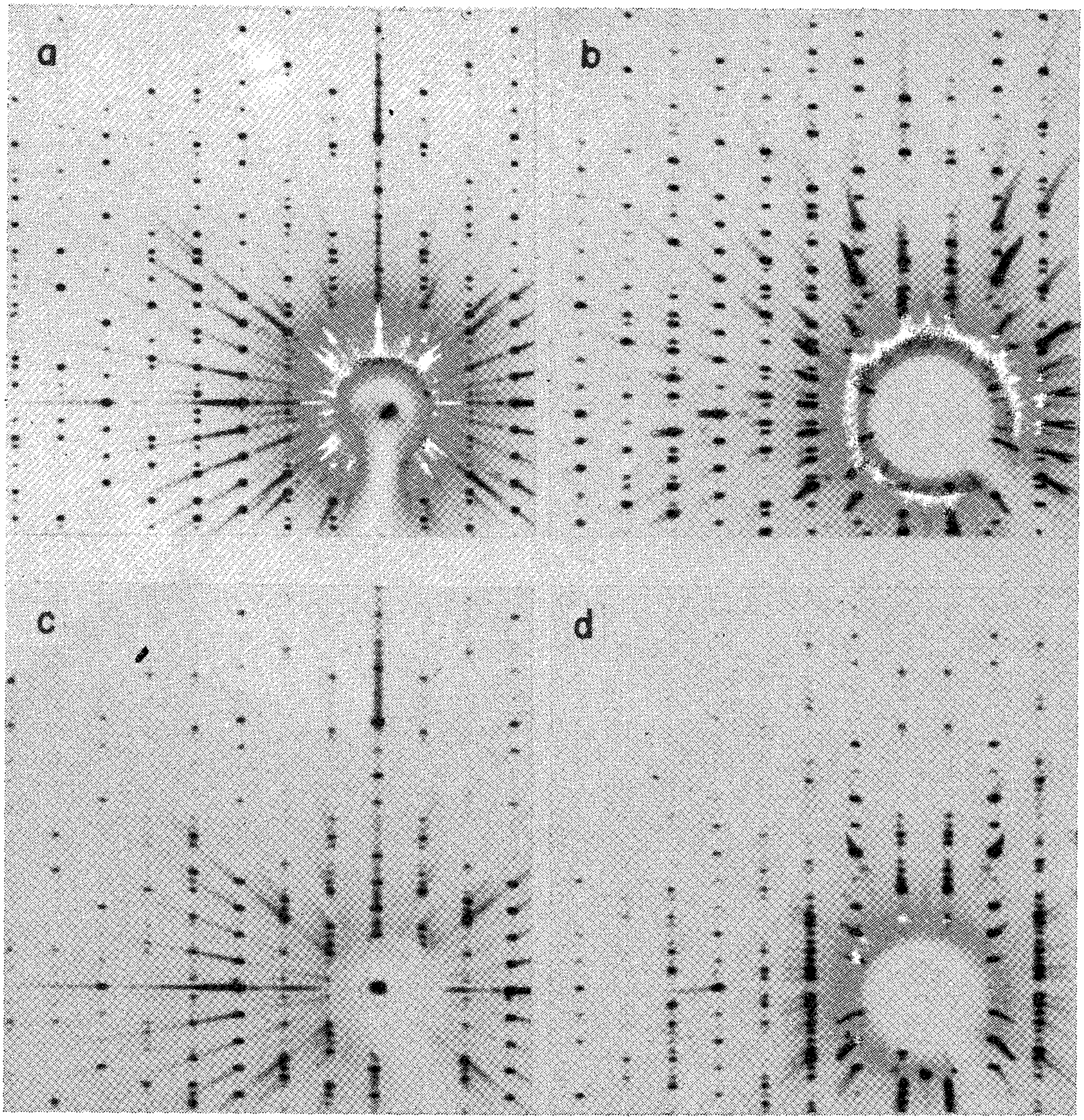

FIG. 4. X-ray-precession photograph of (a) the $h0l$ net of abhurite, and (b) the $h1l$ net; (c) the $h0l$ net of Howie's synthetic compound, and (d) the $h1l$ net. The $c^*$ axis is vertical in all figures.

TABLE 2. CHEMICAL COMPOSITION OF ABHURITE AND INGOT FROM SAUDI ARABIA

A. Major elements (wt.%)

| | Found | Theoretical |
|---|---|---|
| Sn(1) | 73.4 | 74.6 |
| Cl(2) | 15.7 | 14.9 |
| O(3) | 11.0 | 10.1 |
| H(4) | 0.4 | 0.4 |
| | 100.5 | 100.0 |

B. Minor elements (ppm)[5]

| | Abhurite | Ingot |
|---|---|---|
| Fe | 2000 | 3000 |
| Mg | 2000 | 500 |
| Be | 1 | 1 |
| Bi | nd | 300 |
| Co | nd | 50 |
| Cu | 1 | 1000 |
| Ni | 10 | 50 |
| Pb | nd | 1500 |
| Sb | nd | 200 |
| Zn | 200 | 300 |

[1] Average of determinations by P. Aruscavage, USGS.
[2] Average of two analysies by specific-ion electrode using permanganate and hydrofluoric acid 1:4, by E. Campbell, USGS. On the synthetic tin oxychloride 16.9% Cl was determined by the same method.
[3] Total oxygen determined on 3 samples. One of the samples dried at 105°C showed 2% less oxygen. Analyses by W. D. Ehmann, Univ. of Kentucky, by fast-neutron activation for total oxygen.
[4] H determined using CNH instrumentation by P. Aruscavage.
[5] Semiquantitative spectrographic analyses of samples by I. Moh'd Naqvi, USGS and Directorate General of Mineral Resources, Saudi Arabia. Symbol nd = not determined. Looked for but not found: As, B, Ba, Cd, La, Mn, Mo. Found in ingot but not in abhurite were 20 ppm Cr, Sc, Sr, and V.

the unit cell contains 21 formula units (a multiple of 3 as required by the rhombohedral symmetry), the calculated density $D_x$ is 4.35 g/cm$^3$.

## COMPARISON OF ABHURITE WITH PREVIOUSLY DESCRIBED BASIC STANNOUS CHLORIDES

Several stannous chloride–oxide–hydroxide phases have been previously described, none of which appear to be identical to abhurite. In terms of the general formula $x\mathrm{SnCl_2} \cdot y\mathrm{SnO} \cdot z\mathrm{H_2O}$, phases with various $(x,y,z)$ values have been reported as follows: (1,4,6), (1,1,4) and (2,3,6) by Ditte (1882); (1,1,0) by Keller (1917); (3,5,6) and (2,7,7) by Carson (1919); (1,1,2) by Randall & Murakami (1930); (1,1,1) by Hayek (1933); (1,3,3) by Donaldson *et al.* (1963); (1,2,1), abhurite and Howie's synthetic phase (this work).

Keller (1917) described a new oxychloride of tin as brilliant crystals in a cavity within a lenticular mass of tin found in an aboriginal cemetery in Florida. Some of the crystals were readily separated from the tin, whereas others were found to be disseminated throughout the mass. The crystals occur as "thin plates"; a few are "distinctly acicular". A closed-tube test did not yield any water. Solubility in dilute acids without effervescence and other qualitative tests showed stannous tin and chlorine as principal constituents of the compound. Analyses showed 70.9 to 73.1 wt.% Sn and 21.7 to 22.0% Cl, from which Keller derived the formula $SnCl_2 \cdot SnO$. Keller suggested that the saline solution had access to the interior of the tin mass through openings at the surface.

TABLE 3. POWDER DATA FOR ABHURITE AND HOWIE'S SYNTHETIC POLYMORPH[1]

| | Abhurite[2] | | | Howie's synthetic crystals[3] | | | |
|---|---|---|---|---|---|---|---|
| h k ℓ | d(calc) | d(obs) | I(rel) | h k ℓ | d(calc) | d(obs) | I(rel) |
| 1 0 1 | 8.512 | 8.505 | 4 | 1 0 1 | 8.509 | 8.504 | 9 |
| 0 0 6 | 7.336 | 7.337 | 13 | 0 0 6 | 7.337 | 7.322 | 13 |
| 1 0 4 | 6.813 | 6.828 | 18 | 1 0 4 | 6.812 | 6.824 | 6 |
| 0 1 5 | 6.179 | 6.179 | 13 | 1 0 5 | 6.179 | 6.186 | 6 |
| 1 0 7 | 5.091 | 5.096 | 13 | 1 0 7 | 5.091 | 5.087 | 6 |
| 0 0 9 | 4.892 | 4.892 | 9 | 0 0 9 | 4.892 | 4.899 | 9 |
| 1 1 3 | 4.740 | 4.744 | 9 | 1 1 3 | 4.739 | 4.735 | 13 |
| 0 2 1 | 4.317 | 4.322 | 2 | 2 0 1 | 4.316 | | |
| | | | | 2 0 3 | 4.159 | 4.165 | 2 |
| 1 1 6 | 4.136 | 4.139 | 50 | 1 1 6 | 4.136 | 4.133 | 50 |
| 0 2 4 | 4.035 | 4.043 | 4 | 2 0 4 | 4.035 | 4.030 | 2 |
| 0 0 12 | 3.668 | | | 0 0 12 | 3.669 | 3.668 | 3 |
| 0 1 11 | 3.633 | 3.634 | 35 | 1 0 11 | 3.634 | 3.635 | 9 |
| 0 2 7 | 3.570 | 3.577 | 1 | 2 0 7 | 3.570 | | |
| 1 1 9 | 3.499 | 3.498 | 18 | 1 1 9 | 3.499 | 3.499 | 18 |
| 2 0 8 | 3.406 | 3.404 | 50 | 2 0 8 | 3.406 | 3.407 | 18 |
| 2 1 1 | 3.270 | 3.271 | 35 | 2 1 1 | 3.269 | 3.268 | 35 |
| 1 2 2 | 3.243 | 3.244 | 35 | 2 1 2 | 3.242 | 3.241 | 35 |
| | | | | 2 1 3 | 3.199 | 3.195 | 4 |
| 2 1 4 | 3.142 | 3.142 | 35 | 2 1 4 | 3.142 | 3.142 | 13 |
| 0 2 10 | 3.089 | 3.091 | 13 | 2 0 10 | 3.089 | 3.089 | 6 |
| 1 1 12 | 2.9592 | 2.9564 | 3 | 1 1 12 | 2.9594 | | |
| 0 1 14 | 2.9557 | | | 1 0 14 | 2.9562 | | |
| 2 0 11 | 2.9411 | 2.9411 | 2 | 2 0 11 | 2.9411 | | |
| 2 1 7 | 2.9074 | 2.9074 | 35 | 2 1 7 | 2.9069 | 2.9083 | 13 |
| 3 0 0 | 2.8918 | 2.8915 | 70 | 3 0 0 | 2.8910 | 2.8925 | 100 |
| 3 0 3 | 2.8372 | 2.8381 | 25 | 3 0 3 | 2.8365 | 2.8360 | 50 |
| 1 2 8 | 2.8167 | 2.8175 | 50 | 2 1 8 | 2.8163 | 2.8165 | 25 |
| | | | | 2 1 9 | 2.7231 | 2.7204 | 1 |
| 3 0 6 | 2.6903 | 2.6907 | 13 | 3 0 6 | 2.6897 | 2.6892 | 13 |
| 2 1 10 | 2.6295 | 2.6304 | 13 | 2 1 10 | 2.6292 | 2.6278 | 6 |
| 1 0 16 | 2.6222 | 2.6210 | 6 | 1 0 16 | 2.6227 | | |
| 2 0 14 | 2.5456 | 2.5457 | 1 | 2 0 14 | 2.5457 | | |
| 1 1 15 | 2.5318 | 2.5313 | 100 | 1 1 15 | 2.5321 | 2.5329 | 70 |
| 2 2 0 | 2.5044 | 2.5061 | 3 | 2 2 0 | 2.5037 | 2.5047 | 4 |
| 3 0 9 | 2.4892 | 2.4891 | 9 | 3 0 9 | 2.4888 | 2.4889 | 18 |
| 0 1 17 | 2.4809 | 2.4800 | 9 | 1 0 17 | 2.4814 | 2.4816 | 2 |
| 2 2 3 | 2.4687 | 2.4694 | 4 | 2 2 3 | 2.4680 | 2.4680 | 9 |
| 1 3 1 | 2.4025 | 2.4039 | 6 | 3 1 1 | 2.4019 | 2.4011 | 6 |
| 3 1 2 | 2.3919 | 2.3918 | 9 | 3 1 2 | 2.3912 | 2.3909 | 9 |
| 2 2 6 | 2.3701 | 2.3709 | 4 | 2 2 6 | 2.3695 | 2.3696 | 9 |
| 2 1 13 | 2.3554 | 2.3568 | 6 | 2 1 13 | 2.3553 | 2.3556 | 2 |
| 1 3 4 | 2.3506 | 2.3507 | 4 | 3 1 4 | 2.3500 | 2.3494 | 3 |
| 3 1 5 | 2.3210 | 2.3206 | 2 | 3 1 5 | 2.3204 | | |
| 3 0 12 | 2.2709 | 2.2696 | 25 | 3 0 12 | 2.2707 | 2.2703 | 25 |
| 1 0 19 | 2.2381 | 2.2379 | 6 | 1 0 19 | 2.2385 | | |
| 2 2 9 | 2.2291 | 2.2291 | 13 | 2 2 9 | 2.2287 | 2.2286 | 25 |
| 1 1 18 | 2.1973 | 2.1968 | 6 | 1 1 18 | 2.1976 | 2.1990 | 4 |
| 4 0 1 | 2.1662 | 2.1665 | 2 | 4 0 1 | 2.1656 | 2.1649 | 4 |
| 0 4 2 | 2.1584 | 2.1596 | 1 | 4 0 2 | 2.1578 | 2.1578 | 1 |
| 4 0 4 | 2.1279 | 2.1281 | 6 | 4 0 4 | 2.1274 | 2.1269 | 4 |
| 1 3 10 | 2.1112 | 2.1093 | 4 | 3 1 10 | 2.1109 | 2.1092 | 3 |
| 2 1 16 | 2.1074 | 2.1075 | 9 | 2 1 16 | 2.1075 | | |
| 0 4 5 | 2.1059 | | | 4 0 5 | 2.1059 | | |
| 2 2 12 | 2.0682 | 2.0674 | 4 | 2 2 12 | 2.0680 | 2.0681 | 6 |
| 3 1 11 | 2.0620 | 2.0615 | 9 | 3 1 11 | 2.0617 | 2.0622 | 4 |
| 1 2 17 | 2.0320 | 2.0317 | 3 | 2 1 17 | 2.0321 | | |
| 0 4 8 | 2.0177 | 2.0165 | 6 | 4 0 8 | 2.0173 | 2.0174 | 4 |
| 3 2 1 | 1.9882 | 1.9891 | 9 | 3 2 1 | 1.9877 | 1.9885 | 9 |
| 2 3 2 | 1.9822 | | | 3 2 2 | 1.9816 | 1.9819 | 9 |
| | | | | 3 2 3 | 1.9717 | 1.9730 | 2 |
| 2 0 20 | 1.9626 | 1.9617 | 9 | 2 0 20 | 1.9628 | 1.9630 | 3 |
| 1 3 13 | 1.9613 | | | 3 1 13 | 1.9611 | 1.9630 | 3 |
| 3 2 4 | 1.9585 | 1.9585 | 9 | 3 2 4 | 1.9580 | 1.9598 | 4 |
| 2 3 5 | 1.9413 | 1.9419 | 1 | 3 2 5 | 1.9408 | | |
| 0 4 11 | 1.9068 | 1.9064 | 4 | 4 0 11 | 1.9064 | 1.9055 | 3 |
| 3 2 7 | 1.8975 | 1.8992 | 2 | 3 2 7 | 1.8970 | | |
| 4 1 0 | 1.8931 | 1.8928 | 35 | 4 1 0 | 1.8926 | 1.8924 | 50 |
| 1 4 3 | 1.8776 | 1.8781 | 2 | 4 1 3 | 1.8771 | 1.8774 | 6 |
| 2 3 8 | 1.8716 | 1.8718 | 13 | 3 2 8 | 1.8712 | 1.8714 | 6 |
| 0 0 24 | 1.8339 | 1.8332 | 9 | 0 0 24 | 1.8343 | 1.8327 | 6 |
| 1 4 6 | 1.8331 | | | 4 1 6 | 1.8326 | 1.8327 | 6 |
| 4 0 13 | 1.8263 | 1.8261 | 13 | 4 0 13 | 1.8260 | 1.9267 | 6 |
| 3 2 10 | 1.8135 | 1.8136 | 13 | 3 2 10 | 1.8131 | 1.8131 | 9 |
| 2 3 11 | 1.7820 | 1.7817 | 9 | 3 2 11 | 1.7817 | 1.7823 | 4 |
| 1 4 9 | 1.7655 | 1.7655 | 3 | 4 1 9 | 1.7651 | 1.7644 | 3 |
| 3 1 17 | 1.7625 | 1.7622 | 9 | 3 1 17 | 1.7624 | 1.7615 | 3 |
| 2 2 18 | 1.7496 | 1.7501 | 6 | 2 2 18 | 1.7495 | 1.7498 | 6 |
| 1 1 24 | 1.7221 | 1.7220 | 1 | 1 1 24 | 1.7224 | 1.7233 | 1 |
| 3 2 13 | 1.7158 | 1.7157 | 2 | 3 2 13 | 1.7155 | | |
| 2 1 22 | 1.7078 | 1.7073 | 3 | 2 1 22 | 1.7080 | | |
| 4 0 16 | 1.7032 | 1.7029 | 6 | 4 0 16 | 1.7030 | 1.7025 | 1 |
| 0 3 21 | 1.6970 | 1.6971 | 4 | 3 0 21 | 1.6971 | 1.6978 | 1 |
| 1 4 12 | 1.6816 | 1.6817 | 9 | 4 1 12 | 1.6820 | 1.6816 | 9 |
| 3 3 0 | 1.6696 | 1.6695 | 4 | 3 3 0 | 1.6691 | 1.6686 | 13 |

[1] Guinier-Hägg method using $CuK\alpha_1$ radiation (λ=1.540562Å). Intensities estimated by comparison with a calibrated film. Complete data for abhurite (to d 1.11 Å) deposited with the Joint Committee for the Powder Diffraction File.
[2] Rhombohedral, space group $R\bar{3}m$, $R3m$, or $R3$; a 10.0175(3), c 44.014(2) Å.
[3] Hexagonal, space group $P6/mmm$, $P\bar{6}m2$, $P6mm$, or $P622$; a 10.0147(4), c 44.024(4) A.

The first detailed description of the hydrous reactions of $SnCl_2$ with water was given by Carson (1919). His procedure consisted of refluxing solutions of $SnCl_2$ in water and also in KOH solutions in various ratios under nitrogen for 6 to 8 hours, followed by analysis of the precipitates and the mother liquors. Consistent results were obtained for the crystalline products formed on cooling the filtered boiling solutions. Carson observed the formation of "hexagonal rosets made up of thin, transparent, colorless plates." These crystalline products were found to contain 73.5 ± 0.5 wt.% Sn and 16.3 ± 0.6% Cl; the formula $3SnCl_2{\cdot}5SnO{\cdot}3H_2O$ offered by Carson requires 73.3% Sn and 16.4% Cl. The product synthesized by Carson is interesting in its chemical and morphological similarity to Howie's synthetic tin oxychloride.

Donaldson *et al.* (1963) have also carefully studied the products of hydrolysis of $SnCl_2$ solutions. They prepared an acid solution with concentrated HCl under nitrogen and adjusted acidity with 2N ammonium hydroxide so that the hot solution just began to precipitate, and allowed the filtered solution to cool. The crystallized product gave consistent values that averaged 73.2% Sn, 10.8% Cl and 8.4% $H_2O$; their formula, $SnCl_2{\cdot}3SnO{\cdot}3H_2O$ [or $Sn_4(OH)_6Cl_2$], requires 73.3% Sn, 11.0% Cl and 8.3% $H_2O$. This compound is obviously different from Carson's and also from abhurite. Donaldson *et al.* obtained powder and single-crystal X-ray data for their compound, which permit closer characterization and differentiation from abhurite. The compound consists of "six-sided crystals, which show parallel extinction" and "high birefringence." Rotation and Weissenberg photographs showed an orthorhombic unit-cell in space group *Pbcn*, with *a* 10.18(2), *b* 17.06(3), *c* 14.66(2) Å, and $Z = 8$. This pseudohexagonal cell has dimensions that show an approximate relationship to those of abhurite ($a \sim a_{ab}$, $b \sim \sqrt{3}a_{ab}$, $c \sim c_{ab}/3$), but the disparity of the optical and X-ray powder data shows that the two phases are quite distinct.

An associate of Donaldson, Dr. R.A. Howie of the University of Aberdeen, has attempted to repeat the preparation of Donaldson *et al.* in order to provide us with material to compare with abhurite. Dr. Howie's synthetic crystals are thin, colorless, hexagonal plates that show no optical extinction (uniaxial positive) and produce an X-ray powder pattern that is nearly identical with that of abhurite (Table 3). Close examination of the single-crystal patterns (Figs. 4c, d) and Guinier–Hägg powder patterns (Table 3) shows that in fact the two phases are different, but dimorphous. Both have practically identical unit-cell dimensions, but whereas abhurite is rhombohedral, the synthetic crystals are hexagonal with space group *P6/mmm* or subgroup thereof. The spacings of the powder pattern of Howie's crystals listed in Table 3 are practically indistinguishable from those of abhurite (only 4 lines are present that are not consistent with the *R* lattice of abhurite), but there are distinct differences in the details of intensity distribution. The intensity differences are most clearly seen on precession photographs of the *h*0*l* and *h*1*l* nets, shown in Figure 5. In abhurite, when $h+2k \neq 3n$, only reflections with $l \neq 3n$ are observed, corresponding to the *R* centring with the twin lattice superposed. In the synthetic crystals, reflections appear in these groups for all *l* (except 0). The latter patterns always show true *mm* symmetry, unlike the abhurite patterns. Laue patterns show that the synthetic crystals are not of as good quality as the abhurite crystals and possibly show some disorder along the *c* axis. The precession patterns could possibly result from finely twinned rhombohedral lattices of abhurite plus a superposed hexagonal lattice with *c* axis either equal to or ⅓ that of abhurite. On the other hand, there is no real evidence to indicate that the synthetic crystals are not a single homogeneous phase.

Evidently, there are many compounds, each with a different proportion of *x*, *y*, and *z*, but the particular phase that forms is very sensitive to the method of preparation (heating regime, method of pH adjustment, acids and alkalis used, *etc.*). Presumably, the overall reaction of Sn metal with acid brine containing dissolved oxygen can be generally represented as follows:

$$(x+y)\mathrm{Sn} + (x/2+y/2)\mathrm{O_2} + 2x\mathrm{HCl} + (z-x)\mathrm{H_2O} \rightarrow x\mathrm{SnCl_2}{\cdot}y\mathrm{SnO}{\cdot}z\mathrm{H_2O}$$

The product of natural alteration may vary with particular conditions of formation but cannot be predicted. The source of the acid is not clear. The availability of oxygen must be restricted to avoid oxidation of $Sn^{2+}$ to $SnO_2$ (cassiterite).

The development of abhurite in sea water may take place in two stages: (1) oxidation of Sn metal by $O_2$ or $H_2O$ while $OH^-$ is dissipated and $SnCl_2$ is concentrated; (2) hydrolysis of $SnCl_2$ with the formation of abhurite, romarchite, and free acid.

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