tion H_2O 70.6%, Na_2O 15.4%, Al_2O_3 14%, under its own vapor pressure was gibbsite. The crystals in equilibrium with a solution of composition H_2O 56.7%, Na_2O 40.3%, Al_2O_3 3%, had the composition $Na_2O \cdot Al_2O_3 \cdot 3H_2O$ and were eight-sided tetragonal plates, uniaxial, negative, $\epsilon = 1.535$, $\omega = 1.535$. At 500° C. under a steam pressure of 100 atm crystals of anhydrous sodium aluminate, $Na_2O \cdot Al_2O_3$, were formed: optically $(-)$, small 2V, $\alpha = 1.560$, $\gamma = 1.580$.

At 130° C. the compound $K_2O \cdot Al_2O_3 \cdot 3H_2O$ was obtained by dissolving Al_2O_3 in KOH in the molecular proportion $K_2O : Al_2O_3$ in an autoclave, under the vapor pressure of the solution. The crystals were long lath-like monoclinic, biaxial, negative, large 2V, $\alpha = 1.485$, $\gamma = 1.512$. At a little higher temperature, 150° C., its crystals had the composition $K_2O \cdot Al_2O_3 \cdot 2H_2O$, probably uniaxial, $\alpha = 1.510$, $\gamma = 1.518$, and at 370° C. the crystals had the composition $K_2O \cdot Al_2O_3 \cdot H_2O$, uniaxial $(-)$, $\epsilon = 1.535$, $\omega = 1.550$. At 500° C. under a steam pressure of 100 atm, well-formed octahedral crystals of $K_2O \cdot Al_2O_3$ were formed, n $= 1.580$.

Under similar conditions at 500° C., using KOH and Fe_2O_3, ruby-red octahedral crystals of $K_2O \cdot Fe_2O_3$ were obtained, often in crystals several millimeters in diameter. They were rapidly attacked by atmospheric moisture and reacted with the index liquids.

STUDIES ON MANGANESE OXIDE MINERALS
VI. THALLIUM IN SOME MANGANESE OXIDES[1]

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Introduction

The occurrence of unusual amounts of thallium in manganese ores from the Apache mine, Gila County, Arizona, was reported to the U. S. Geological Survey in 1943 by John Herman, of Smith-Emery Company, commercial analysts serving the Federal stockpile in Phoenix, Arizona. In June 1944, specimens from the Apache mine were included in a group of samples submitted to the laboratory by one of us (M.D.C.) to verify the presence of thallium and to determine the chemical nature of its occurrence. Spectrographic analysis by K. J. Murata of three samples from this mine showed that thallium was indeed present, in amounts estimated to be a few tenths of one per cent. The samples were set aside

and no further work was done on them for many years. Recently we have resumed work on them and have found that thallium is present in many manganese oxide deposits in the western United States (unpublished data, Hewett, Conklin and Fleischer). The present note gives analyses for four samples from Arizona and two samples from New Mexico, with a discussion of data on thallium in manganese oxides from other localities.

GEOLOGIC CHARACTER

All the deposits from which the samples came are believed to be hypogene in origin. Five are of the hypogene oxide type, as defined by Hewett and Fleischer (1960); the other, Peach Springs, because it contains a small amount of gold and silver is presumed to be the oxidized outcrop of an ordinary base-metal vein.

Hypogene oxide deposits are shown by Hewett to be of ultrashallow low-temperature origin, possibly representing the eroded roots of manganese-bearing hot springs; although these deposits are generally closely associated with volcanic rocks or volcanism, they occur in a variety of host rocks. The veins and breccia zones at the Cochise group and at the Apache mine are in Gila(?) Conglomerate. Those at the Apache, which contain the largest amount of thallium, extend below the conglomerate into underlying Precambrian crystalline rocks. The Armer Wash (Sunset) deposit occurs in steeply dipping breccia zones in quartzite of the Apache Group of younger(?) Precambrian age (Farnham *et al.*, 1961).

The Niggerhead deposit in New Mexico is part of a geologically homogeneous province near Socorro that includes the Luis-Lopez district (Miesch, 1956; Jicha, 1956). This province is characterized by a series of extensive veins and breccia zones cutting massive rhyolite. From about 1952 to 1958, opencut mines in this province yielded about 1.5 million tons of mine-run ore ranging from 3 to 10 per cent manganese but probably averaging less than 5 per cent. From this material approximately 77,000 long tons of concentrates averaging 35.5 per cent manganese was produced by milling, and 18,000 long tons of crude ore averaging about 28 per cent manganese was produced by hand sorting or selective mining. Although the specimen analyzed here (Niggerhead) contained only 0.07 per cent thallium, specimens from the Red Hill mine nearby (the largest of the open-pit mines) appear from semiquantitative spectrographic determinations (unpublished data by Hewett, Conklin and Fleischer) to contain about as much thallium as the sample from the Apache mine.

In most of the deposits of the hypogene oxide type, manganese oxides cement and encrust fractured, but almost unaltered wall rock; there is

generally no evidence of replacement. Gangue minerals are strikingly scarce; calcite, chalcedony, quartz, barite, and rarely a trace of fluorite or a zeolite are present in some deposits but not in all. The manganese oxide minerals in many of these deposits contain such large amounts of lead (up to 4.3 per cent) or zinc (up to 0.55 per cent) as to make them unusable commercially until blended with the other ores (Jicha, 1956, p. 248).

Although none of the deposits from which samples were obtained has been mined deeper than about 60 feet, one of the deposits near the Niggerhead, the Black Canyon mine (Farnham, 1961), was mined to a depth of 375 feet without significant change in character. This absence of primary carbonate or silicate minerals from which the oxides could be derived is the most direct evidence that the thallium-bearing manganese oxides are hypogene. At the same time, the absence of the typical suite of alteration and gangue minerals usually associated with hydrothermal deposits of mesothermal or epithermal type sets these deposits apart from their more deep-seated counterparts. The chemical and trace-element content of the hypogene oxide deposit as a group is dealt with more fully by Hewett and Fleischer (1960).

New Analyses and Analytical Methods

Analyses for thallium by colorimetric and x-ray fluorescence methods are given in Table 1, along with the x-ray identification of the minerals present.

The colorimetric determinations of thallium in the manganese ores were based on the thallium-dithizone mixed-color system (Clarke and Cuttitta, 1958). The dithizone data summarized by Sandell (1959) show that manganese and iron are major interferences. Manganese (II) forms a primary dithizonate complex in alkaline medium which is unstable (air oxidation) and forms brown flocs in chloroform. In addition, thallium dithizonate is also accompanied by the dithizonates of lead, bismuth (III), tin (II) and indium. The interference of iron, manganese, bismuth, lead, tin and indium in the spectrophotometric determination of thallium with dithizone was eliminated by the separation of thallium bromide by extraction to ethyl ether (or isopropyl ether) from 0.75 N HBr (Irving and Rossotti, 1952). At 0.5 to 1.0 N HBr hardly any ferric iron, gallium or indium are extracted. Very small amounts of tellurium, zinc, mercury, molybdenum, and antimony are extracted. These elements are removed from the ether layer by shaking the organic phase (back-stripping) with 1 N HBr. The extractibility of thallium (I and III) bromide into ethyl ether is greater than 99.9 per cent at room temperature using multiple extractions (3–10 ml portions of ethyl ether).

The ether extracts are evaporated to dryness on a stream bath using

TABLE 1. THALLIUM CONTENTS OF SOME MANGANESE OXIDES

Sample number	Tl (per cent)		BaO (per cent)	K₂O (per cent)	X-ray identification (by J. M. Axelrod and Mary E. Mrose)
	Colori- metric[1]	X-ray fluores- cence[2]			
A-15	0.007	<0.01	approx. 12[4]	none[4]	Psilomelane
A-2	0.017	0.02	approx. 12[4]	approx. 0.2[4]	Psilomelane
NG	0.07	0.07	9.75[3]	not detd.	Hollandite-cryptomelane
PS	0.23	0.23	5.5[3]	not detd.	Hollandite-cryptomelane
BF	0.28	0.29	8.0[3]	2.4[4]	Hollandite-cryptomelane
A-8	0.37	0.34	approx. 9[4]	approx. 2[4]	Hollandite-cryptomelane

[1] Frank Cuttitta, analyst, average of 3 determinations.

[2] H. J. Rose, Jr., analyst.

[3] M. Fleischer, analyst.

[4] Semiquantitative spectrographic analysis by Nancy Conklin.

Description of samples

A-15　Fine-grained mammillary, Cochise group, Pinal County, Ariz., collected by M. D. Crittenden.

A-2　Fine-grained mammillary, Armer Wash (Sunset) mine, Sierra Ancha district, Gila County, Ariz., collected by M. D. Crittenden.

NG　Botryoidal, with calcite, Niggerhead group, Socorro County, N. Mex.; collected by S. K. Neuschel

PS　Fine-grained, massive; from Peach Springs district, Coconino County, Ariz.; collected by C. F. Park, Jr.

BF　Fine-grained, botryoidal, from Black Feather claim, Socorro County, N. Mex.: collected by S. K. Neuschel

A-8　Botryoidal, from Apache mine, Sierra Ancha district, Gila County, Ariz.; collected by M. D. Crittenden

a petri dish as a platform. The organic residue is destroyed by wet-ashing with HNO_3. The thallium is then determined by the dithizone procedure using chloroform as the solvent. The samples, reagent blank and thallium standards used in the preparation of the standard spectrophotometric curve are carried through the procedure (ether extraction and the dithizone separation-determination steps) simultaneously. In the dithizone method, thallium is extracted with a chloroform solution of dithizone (40 mg per liter) from a citrate-sulfite-cyanide medium at a pH 10.6 and then stripped from this chloroform solution with dilute (0.08 N) HNO_3. The pH of the resulting acid solution is adjusted to 10.6 with an NH_4OH-KCN mixture. The pH variation for a given set of standards, reagent blank, and samples must be no more than 0.1 of a pH unit. A second extraction is made with dithizone (15 ml chloroform containing 0.4 mg dithizone) and the absorbance is determined at 505 mμ. The color system

conforms to Beer's Law for concentrations of thallium up to 100 micrograms/15 ml of solution when using a 1-cm light path.

The x-ray fluorescence method used in the analyses is being described elsewhere (Rose and Flanagan, 1962), $TlNO_3$, to which an appropriate amount of MnO was added, was used as standard and boric acid was used as diluent.

PREVIOUS DATA AND DISCUSSION

Thallium was first reported in manganese oxides by Murray and Renard (1891), who found 0.03 per cent Tl_2O in a nodule collected by the Challenger Expedition at Station 285 in the Pacific, which contained K_2O 0.25, BaO 0.12 per cent. Recently Riley and Sinhaseni (1958) reported 0.008–0.11 per cent Tl_2O in three nodules from the Pacific; they contained BaO 0.41–0.58, K_2O 1.33–1.45, and PbO 0.15–0.25 per cent.

Many analyses, mostly showing 0.01–0.03 per cent Tl but with two showing 0.08 and 0.11 per cent, have been published by Voskresenskaya and Usevich (1957), Maksimov (1960) and Voskresenskaya and Soboleva (1961), all from the Dzhezda manganese deposit in Central Kazakhstan. The ores are stated to contain psilomelane, braunite and hollandite; the thallium being concentrated preferentially in the psilomelane. The samples highest in thallium are generally high in lead (mostly 3–5 per cent Pb) and potassium (0.5–1.4 per cent K); it is implied that barium is present, but no analyses are given. The mineralogical determinations were apparently based on differential thermal analyses (letter of N. T. Voskresenskaya to Fleischer, May 1958); our experience has been that such determinations require confirmation by x-ray study. It seems likely that the "psilomelane" of the Dzhezda is a member of the hollandite-coronadite-cryptomelane group.

It will be noted from Table 1 that the highest thallium contents were found in minerals of the cryptomelane-hollandite group, as one would expect from consideration of the ionic radii: Tl^{+1} 1.47, K^+ 1.33, Ba^{2+} 1.34, Pb^{2+} 1.20 Å. One would expect that thallium will also be found in the lead member of the group, coronadite. Whether thallium enters the barium mineral psilomelane as readily as it does hollandite remains to be proved by more analyses.

Voskresenskaya and Usevich (1957) proved experimentally that large amounts of thallium can be adsorbed by synthetic preparations of manganese oxides and that this thallium can be removed by ion exchange. They therefore postulated that the thallium in naturally occurring manganese oxides of the Dzhezda district was adsorbed.

Such a mechanism is likely, especially for the oceanic manganese nodules, and perhaps even for samples like those we analyzed, which are botryoidal or mammillary and may have precipitated in collomorphic

forms. It should be pointed out, however, that this mechanism is not necessarily correct. Voskresenskaya and Usevich themselves report that only 1 per cent of the thallium in a psilomelane containing 0.016 per cent Tl could be exchanged. This agrees with unpublished results in our laboratory, which have shown that practically none of the potassium in natural cryptomelane or of barium in natural hollandite can be removed by ion exchange. Sreenivas and Roy (1961) reported that hollandite and psilomelane were unchanged when subjected to electrodialysis, but that cryptomelane lost potassium, natural material more slowly than synthetic. It seems probable, therefore, that thallium is firmly fixed in the lattice of naturally occurring manganese oxides, presumably replacing potassium, barium and lead.

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XENOTIME FROM RAYFIELD, NORTHERN NIGERIA[1]

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INTRODUCTION

In 1954, xenotime was identified by M. P. Jones[2] and the author in a jig concentrate submitted for examination to the Geological Survey by Amalgamated Tin Mines of Nigeria Ltd. The concentrate was obtained from the mineral dressing plant established at Rayfield ($9°50'N$; $8°55'E$) near Jos, Northern Nigeria to work the intensely decomposed biotite-granite for primary columbite.

The geology of the Jos-Bukuru Younger Granite Complex, which includes the Rayfield-Gona biotite-granite, has been described in detail by MacLeod (1956). A briefer account was given by Jacobson *et al.*, (1958), and the economic geology of the decomposed columbite-bearing granites has also been described (Williams *et al.*, 1956). The treatment of the decomposed granite for the recovery of the associated heavy minerals has been described in a series of papers by Williams (1956, 1957, 1959).

Subsequent to the identification of the xenotime, Amalgamated Tin Mines of Nigeria produced high grade concentrates of the mineral by a combination of gravity, magnetic and high tension separation. The work described in this note was carried out on a xenotime concentrate supplied by the company.

DESCRIPTION OF THE MINERAL CONCENTRATE

A screen analysis of the concentrate gave the following result:

British Standard Sieve No.	Size of sieve opening, mm.	Weight %
+36	+0.422	3
−36+52	−0.422+0.295	48
−52+100	−0.295+0.152	49
−100	−0.152	tr.

The concentrate consists of approximately 75% xenotime and 15%

[1] Published by permission of the Director, Geological Survey of Nigeria.

[2] Formerly on the staff of the Geological Survey of Nigeria.