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An Investigation of the Reported Occurrence of Tin at Juniper Ridge, Oregon

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With Geology By
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1942

AN INVESTIGATION OF THE

REPORTED OCCURRENCE OF TIN AT JUNIPER RIDGE, OREGON

by

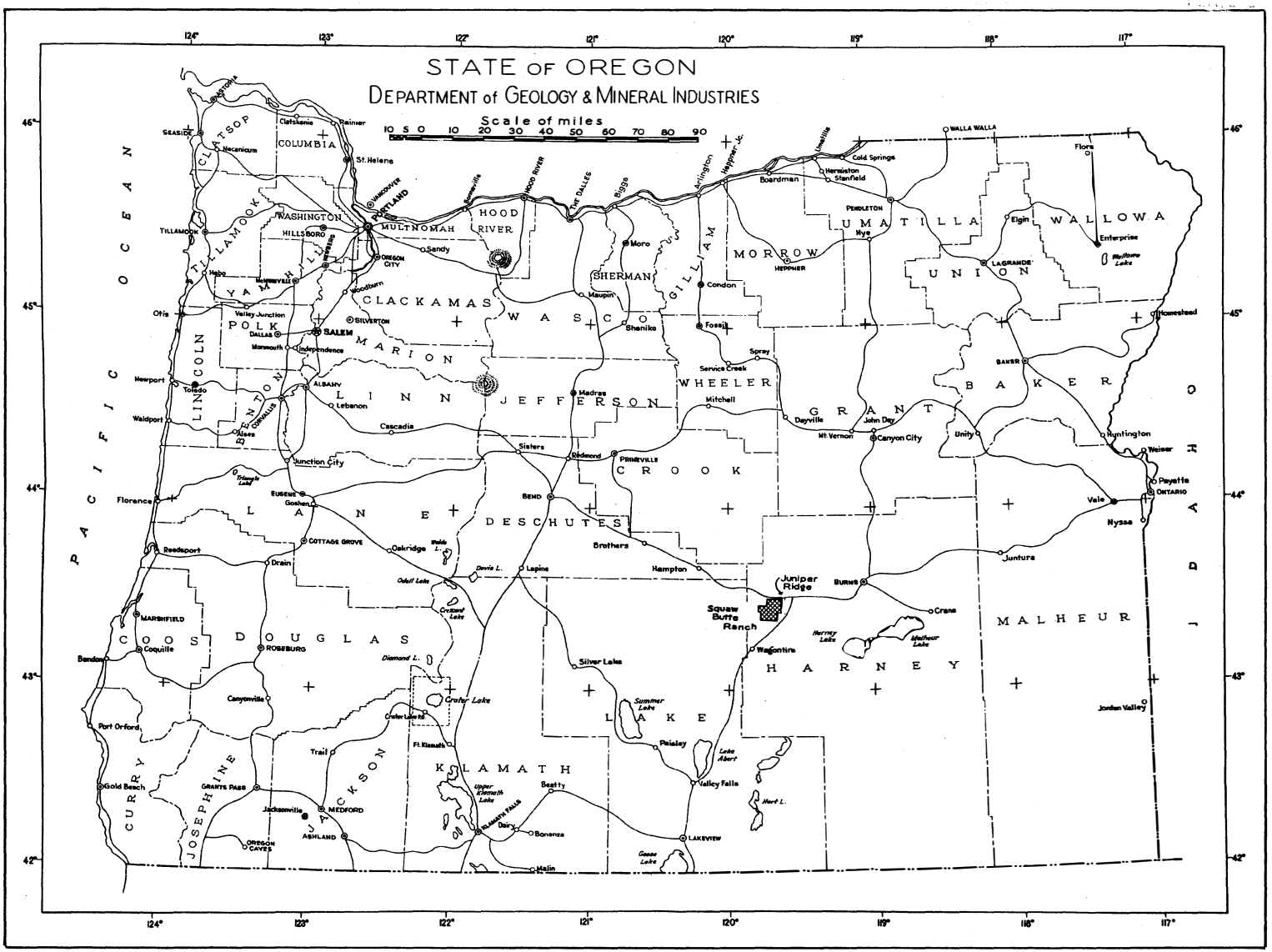
H. C. Harrison and John Eliot Allen

Table of Contents

Chapter		Paragraphs
	Foreword: Background and Results of Investigation for Non-Technical Readers. By Earl K. Nixon.	
	Abstract	
	Acknowledgements	
I	A short survey of tin, its history and occurrence	
	Introduction	(1)
	Early history	(2)
	Mineralogy	(3-6)
	Geologic occurrence	(7-10)
	References	(11)
II	Geologic investigation of a portion of Juniper Ridge	
	Introduction	(12-15)
	Literature	(16)
	Geology	(17)
	Distribution of rocks	(18)
	Petrography	(19-24)
	Mineralization	(25)
	Origin of the rocks	(26)
	Structures	(27-29)
	References	(30)
III	Samples from Juniper Ridge used in the investigation	
	Methods of sampling	(31)
	Description of samples taken	(32)
	Reduction of gross samples	(33)
	References	
IV	Chemical and spectrochemical analyses	
	Outline of chapter	
	Introduction	
	Methods of obtaining tin in a known form	(34)
	An investigation of reactions of test analytical reagents	(35-39)
	Experimental procedures using standard mixtures of tin in Juniper Ridge rock	(40-52)
	Experimental procedure using Juniper Ridge rock samples	(53-222)
	Conclusions	(223-225)
	References	
V	Summary and Conclusions	(226-231)

Illustrations

Plate			Opposite:
	Location of area		Foreword
I	Geology of a portion of Juniper Ridge	Paragraphs	(20-22)
II	Physiographic diagram of fault blocks at Juniper Ridge	"	(23-26)
III	Closed system and hydrogen reduction apparatuses	"	(142-153)
IV	"Jack Rabbit" furnace assembly	"	(154-162)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Scale of miles
10 5 0 10 20 30 40 50 60 70 80 90
PACIFIC OCEAN
COLUMBIA
CLATSOP
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GILLIAM
MORROW
UMATILLA
WALLOWA
UNION
BAKER
POLK
MARION
JEFFERSON
WHEELER
GRANT
LINCOLN
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DESCHUTES
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DOUGLAS
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CURRY
JOSEPHINE
JACKSON
KLAMATH
LAKE
HARNEY
MALHEUR
PORTLAND
SALEM
EUGENE
ALBANY
BEND
MEDFORD
ROSEBURG
KLAMATH FALLS
LAKEVIEW
PENDLETON
LA GRANDE
BAKER
ONTARIO
Juniper Ridge
Squaw Butte Ranch
Crater Lake
Wallowa Lake
Malheur Lake
Harney Lake
Lake Abert
Summer Lake
Silver Lake
Goose Lake
Upper Klamath Lake
Diamond L.
Odell Lake
Davis L.
Waldo L.
Hart L.
Triangle Lake
Crescent Lake
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FOREWORD

BACKGROUND AND RESULTS OF INVESTIGATION
FOR NONTECHNICAL READERS
by
Earl K. Nixon

The extensive experimental work presented in the accompanying report seemed justified for two principal reasons, namely, (1) since this country is dependent on restricted imports for our supplies of tin, discovery of a domestic source of supply would be of far reaching importance in war production; therefore, every possible means should be employed to find domestic deposits, and (2) statements were presented that standard methods of tin analysis were not satisfactory for determining the presence of tin in Juniper Ridge rock, so that it seemed imperative that such a possibility, however remote, should be investigated and if possible verified.

In 1939 this writer, accompanied by local interested people, visited the Juniper Ridge deposit, took some samples where tin was reported, and sent these to the U. S. Bureau of Mines for both spectrographic and chemical determinations. The Bureau reported that no tin was found in the samples by either of these methods, and the Bureau results were transmitted to the owners of the property.

The Bureau's analytical results, as well as some verifying results obtained in other laboratories, were questioned in various quarters, so that a thorough investigation seemed necessary in order to settle the matter.

In July, 1941, Dr. H. C. Harrison, chief chemist and spectroscopist of the Department, was given the duty of making the investigation. He was instructed to make the study of such scope and in such detail that there could be no question or doubt of the verity of the final result.

In order to obtain petrologic evidence, John Eliot Allen, staff geologist, studied and mapped the geology of the restricted area. His study included petrographic analyses of thin sections of the rock types. Results of the geologic investigation are included in one section of this report. Allen also supervised the taking of samples which were analyzed by Dr. Harrison.

Juniper Ridge rocks are all volcanic and a prominent type is obsidian or volcanic glass. The texture is perlitic, that is, the rock contains round grains. The rock was extruded from a volcanic vent and, as is characteristic of such rocks, cooled fairly quickly and before distinct crystallization could take place. Such unaltered rock is fairly common and is not known to contain tin in commercial amounts anywhere in the world.

Excepting the placers, commercial tin occurrences in various parts of the world in most cases are described as "deep seated". That is, the tin minerals are related to rocks that were deposited under high temperatures and at considerable depths below the earth's surface. Thus if Juniper Ridge rocks carried tin in commercial amounts the occurrence would be unique.

In his qualitative analytical work, Dr. Harrison selected from fifteen standard reagents four reagents which are specific for tin and whose reactions are not interfered with by constituents of Juniper Ridge rock. Each Juniper Ridge sample was tested with these four reagents. As companion tests, the same reagents were used on each sample to which tin was intentionally added. In this way proof of the reliability of the reagents for tin detection was obtained. In addition, some thirty-one different methods or techniques were employed in testing the samples. Some of these methods are standard; others were advocated by persons who had some special procedure which had been used by them.

In testing various reagents, methods, and techniques, a tremendous number of individual tests or trials were made. Many of them, of course, were very short and took very little time. As individual tests became routine in the investigation, the time consumed in making them was shortened.

Three standard quantitative chemical methods were studied. As a result of this study a combination method was used on each sample obtained in the field. For verification of the reliability of the method, as in the qualitative tests, duplicate tests were made on portions of samples to which a known amount of tin had been intentionally added.

Samples were also analyzed spectrographically. The spectrograph is an optical-electrical instrument used for determining both qualitatively and quantitatively the presence of a large number of chemical elements. Most chemical elements have extremely plain "finger prints" when tested in the spectrograph. Tin is one of those that can be readily detected by spectrographic means, no matter whether the tin occurs as metal or in some chemical combination in the sample.

In no case did samples, carefully taken for this investigation and guarded against contamination, contain more than normal traces of tin. Such traces were identified best by the spectrograph and showed percentages of tin in Juniper Ridge rock, not greater than five-thousandths of one percent. It is the conclusion, then, of this Department that the Juniper Ridge rocks do not contain commercial amounts of tin and that there is no reasonable justification for the expenditure of additional money or effort in trying to make tin deposits out of volcanic rocks that contain no more tin than dozens of other volcanic rocks occurring elsewhere. Traces of tin in igneous rocks are quite common.

The Department believes that the investigation was made with all possible thoroughness and with accurate attention to detail. The results as given in the report are, we believe, definite and final.

There is nothing that the Oregon Department of Geology and Mineral Industries would rather do than to demonstrate the presence of an important deposit of tin or any other strategic mineral in the State, but in the case of the Juniper Ridge deposit, this seems to be clearly impossible.

ABSTRACT

Tin is obtained principally from its oxide, cassiterite. Other minerals contain tin, but are of slight importance commercially. Traces of tin occur in many igneous rocks. Cassiterite is mined from placers, and from veins, pegmatites, and disseminations in granitoid rocks. Most of the world's production is derived from the Malay States and from Bolivia, although lesser deposits occur in many other parts of the world. In the United States, small sub-marginal deposits are known in South Dakota, North and South Carolina, Virginia, California, Idaho, New Mexico, and Nevada.

Preliminary to analytical testing of Juniper Ridge rock, a detailed geologic survey was made of about 1 square mile, covering a portion of Juniper Ridge in sec. 36, T. 23 S., and sec. 1, T. 24 S., R. 25 E. Mapping showed a volcanic complex composed of five closely related rock types, of which a black, sometimes red, perlitic obsidian is of particular interest from the standpoint of this investigation. Similar rocks have been described by a number of investigators as being characteristic of areas immediately to the east and west of Juniper Ridge, as well as other parts of eastern Oregon. Attitudes of flow banding and of lenses of the various types of rock often vary abruptly; in a few places they are highly contorted. Two centers of plug-dome intrusion, fan shaped in cross section, were indicated. Four northwest-southeast trending splinter faults are tributary to a main east-west fault which forms the north front of Juniper Ridge. All faults are down-dropped on their north side. No secondary alteration other than surficial weathering appears, even adjacent to the fault lines. All the rocks are remarkably fresh and unaltered, with no suggestion of mineralization or hydrothermal activity.

The rocks at Juniper Ridge were carefully sampled by standard methods, at points where "highest grade ore" was reported to occur. A total of fifteen samples were used in the chemical and spectrographic investigation.

Qualitative and quantitative chemical methods and spectrographic methods of analysis were used in analyzing samples of Juniper Ridge rock. Thirty-one different methods of converting tin or compounds of tin into a form suitable for identification or determination were investigated.

Four different analytical procedures were adapted for analyzing solutions containing, or suspected of containing tin. The reactions of fifteen different analytical reagents were studied, of which four were found to be most suitable for the detection of tin when in the presence of Juniper Ridge rock. Standard solutions of tin and mixtures of tin or tin compounds were intentionally added to portions of Juniper Ridge rock samples, which were then used as controls for studying the analytical reagents or tests.

A large number of methods were used to obtain tin in a solution which could then be tested qualitatively for the presence of tin, using the four analytical procedures.

Three different standard quantitative chemical procedures were studied, using pure compounds of tin, standard solutions of tin, mixtures of tin or compounds of tin intentionally added to Juniper Ridge rock samples. As a result of this study a combination method was used to make quantitative chemical determinations of the tin content of samples of Juniper Ridge rock.

A fire-assay method of tin recovery was tested, using samples containing known concentrations of tin. This method was then applied to samples of Juniper Ridge rock.

Qualitative and quantitative spectrographic determinations of the tin content of Juniper Ridge samples were made. Two different spectrographs, a large quartz prism spectrograph and a 3-meter grating spectrograph were used. A number of different methods of spectral excitation were used.

Chemical methods which detected the presence of tin in the control samples to which tin had been intentionally added, failed to show the presence of tin in Juniper Ridge rock samples in amounts greater than 0.005%. Spectrographic methods showed the presence of tin in Juniper Ridge rock samples in amounts varying from 0.001% to 0.005%.

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The hydrogen reduction experiments were performed in the laboratory of S. H. Williston of the Horse Heaven Mines, Inc., and assistance was given by Dr. L. W. Staples and Marion Morris of the same company.

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CHAPTER I

A SHORT SURVEY OF TIN, ITS HISTORY AND OCCURRENCE

INTRODUCTION

A background survey of all available literature concerning a metal is a prerequisite of a field and laboratory study made for the purpose of determining the presence and mode of occurrence of that metal. A very condensed summary of the historical and technological background of tin is presented herewith. (1)

Bibliographic references (given alphabetically at the end of this chapter) are condensed in the text so as to give only the name of the author, the last two digits of the date of publication, separated by a colon from the page reference. A reference to "Mineral Deposits" by Waldemar Lindgren, published by McGraw-Hill in 1928, page 277, is thus condensed to (Lindgren,28:277).

EARLY HISTORY

Tin is known to have been used since very early times. A metal referred to by Herodotus and Homer was undoubtedly tin. Some authors state that it was used in Egypt and China as early as 1600 B.C. At about 1000 B.C., the Phoenicians were carrying on an extensive tin trade between the "Cassiterides Islands", generally thought to be the British Isles, and Mediterranean ports (Mellor,27:276; Fawns,05). (2)

In the thirteenth century, much of the world's supply of tin came from Cornwall, but the metal was also discovered at about that time in Saxony and Bohemia; and a number of 16th century writers mention East Indian deposits that may have been a source of tin as early as the eighth century.

MINERALOGY

There are only two minerals, cassiterite and stannite, that have been mined for tin on a commercial scale. Of these, cassiterite, the oxide, is by far the more important. Theoretically pure cassiterite contains 78.6% tin by weight, but actually the percentage is usually slightly less, due to the presence of such impurities as iron, arsenic, zinc, etc. Cassiterite also frequently contains minor amounts of tantalum, silicon, and manganese (Dana,14:235). The color of cassiterite is usually brown or black, but sometimes it is red, gray, white or yellow. It belongs to the tetragonal system, frequently crystallizing in double pyramids. Hardness is 6 to 7, and specific gravity is 6.8 to 7.1. It is very resistant to weathering because it is practically insoluble. Due to its high specific gravity, it is concentrated by streams in placer deposits, from which over 80% of the world's supply of tin is derived (Hess & Graton, 05:161). Wood tin is cassiterite with a reniform shape and fibrous, divergent structure. (3)

Stannite, a complex sulphide of copper, iron, and tin, occurs as a steel-gray to iron black granular or massive substance, containing up to 27% pure tin. It is of minor importance as an ore. (4)

Native tin has been reported from several localities, only one of which, in New South Wales, has been verified.

According to Dana (22:676) other minerals containing tin as a part of their chemical makeup are: (5)

canfieldite	$4Ag_2S.SnS_2$	stokesite	$H_2CaSnSi_3O_{11}$
teallite	$PbSnS_2$	nielmite	Y,Fe,Mn,Ca,stanno-niobate

frankeite	$Pb_5Sn_3FeSb_2S_{14}$	nordenskioldine	$CaSn(BO_3)_2$
cylindrite	$Pb_3Sn_4FeSb_2S_{14}$	hulsite	$12(Fe,Mg)O.2Fe_2O_3.1SnO_2.3B_2O_3.2H_2O$

Mellor (27:283) reports the following:

cuprocassiterite	$4SnO_2Cu_2Sn(OH)_6$
plumbostannite	$Sn_2Sb_2Pb_2(Fe,Sn)_2S_{11}$

Mellor also lists as follows a number of other minerals which contain tin in small quantities as an accessory constituent: (6)

columbite	aeschinite	phonolite
plumbocolumbite	cyrtolite	microlite
tantalite	fredricite	olivine
yttrotantalite	polycrase	pyrophillite
ixiolite	eucrasite	kaolin
ilmenite	sipylite	cryolite
ferroilmenite	ferberite	mica
rutile	tapiolite	lepidolite
ilmenorutile	tritomite	manganoepidote
euclase	hjelmite	pyrolusite
fergusonite	tyrite	pyrite
samarskite	malacone	fahlerz
monazite	zircon	sperrylite
delorenzite	scheelite	zincblende
risorite	hatschettolite	thalenite
	tourmaline	

GEOLOGIC OCCURRENCE

Tin is not common enough to be listed among the 26 most abundant elements present in the igneous rocks of the earth's crust (Clarke,24:29) in which the amount has been estimated to be of the order of .00006% (Mellor,27:280); in acid igneous rocks the percentage is sometimes as high as .001% (Fries,42:283). (7)

The extensive literature regarding the occurrence of tin is summarized by Hess and Graton (05), Mellor (27:284), Johes (25) and Fawns (05), and a complete bibliography is given by Hess & Hess (12).

Tin occurrences are widely scattered on all the continents, but 85% of all the world's production comes from two areas, namely, the Malay States and Bolivia (Mellor, 27:280).

Approximately 70% of the world's production is obtained from alluvial deposits,or placers, mainly from the Malay Peninsula, the islands of Banca and Billiton near Sumatra, and from Nigeria and China (Lindgren,28:277). Minor amounts are mined in New South Wales, Victoria, and Tasmania. Small amounts of stream tin occur in Alaska (Knopf, 08; Johnson, 10; Harrington, 19; Chapin, 19; Fearing, 20; Steidtmann & Cathcart, 22; Waters, 34), in the Black Hills of South Dakota (Hess, 09; Darton & Paige, 25), in North and South Carolina (St. Clair, 35; Haney, 28) and in Mexico (Sampson, 27). (8)

The source rock of tin (cassiterite) is either granitoid rocks, pegmatites, or quartz veins. Tin-bearing veins are generally considered (Ferguson & Batemen, 12; Singewald, 12) to have a close genetic connection with the acidic granites, and to have been emplaced soon after the cooling of the major part of the granite, under "pneumatolytic" conditions (Lindgren,28:734-35). Cassiterite is found near the contacts of granites, sometimes in fissures, in Finland, Saxony, Tuscany, Devonshire (Lindgren, 28:817), and on the Seward Peninsula, Alaska (Knopf, 08; Harrington, 19; Steidtmann & (9)

Cathcart, 22). It is associated with a large number of contact metamorphic and lime-silicate minerals and sulphides; tourmaline is an especially common accessory mineral.

Tin-bearing pegmatite dikes have been mined in the United States in South Carolina near Gaffney (Haney,28), in the Black Hills (Smith & Page,41), and in Virginia (Ferguson,18).

The largest production of "hard rock" tin has been from high-temperature or hypothermal veins, that have a definite association with such ore minerals as molybdenite, arsenopyrite, wolframite, bismuth, and bismuthinite, with much less abundant pyrite, pyrrhotite, chalcopyrite, galena, and sphalerite. Quartz is the chief gangue mineral, accompanied by lepidolite, fluorite, topaz, tourmaline, axinite, and apatite (Lindgren, 28:725). Mines in this type of vein include those of Cornwall, Bolivia, Japan, New South Wales, Tasmania, Saxony, and in North America, Nova Scotia (Messervey,33; Davidson,33), Manitoba (DeLury,20; Wright,32), and British Columbia.

Some tin occurs in mesothermal replacement veins associated with silver. The Bolivian veins are the best examples of this type. Here cassiterite occurs in a gangue of quartz with pyrite, arsenopyrite, sphalerite, chalcopyrite, stannite, tetrahedrite, andorite, ruby silver, and jamesonite (Lindgren,28:657). Tin-silver veins also occur in British Columbia (Gunning,31).

The tin deposits of the western United States, although not of great economic importance, should come in for special notice. There are a number of occurrences in California (Pabst,38:123), some of which have been mined, as in Riverside County (Fairbanks, 97; Dudley, 35; Sampson, 35). Tin also is known to occur in Plumas and Trinity Counties (Hanks,84:410), in San Diego County (Penfield & Ford,16; Schaller,16), and in Siskiyou County (Pabst,38:123). Tin occurs in Idaho (Livingston,19), near Spokane, Washington (Anderson,28; Fernquist,35), and in Nevada and New Mexico. The Nevada and New Mexico cassiterite deposits are of especial interest, because the veins occur in Tertiary rhyolites. At Majuba Hill, Pershing County, Nevada (Smith & Gianella,42) they occur in an altered, tourmalinized, and sericitized plug of rhyolite porphyry breccia. In the Black Range of Catron and Sierra Counties, New Mexico, the tin-bearing ore stringers occur in fractured and altered zones of mid-Tertiary rhyolites, which have a fan-shaped cross-section of primary flow banding, suggesting extrusive vents (Hill,20; Naething,21; Fries,40). The cassiterite in northern Lander County, Nevada occurs in veinlets in Miocene rhyolites, as "incrustations deposited in fumarolic vents along fissures formed by differential contraction during the cooling of the lavas" (Fries,42:279; Knopf,16a,16b). It should be especially noted that in all these occurrences of tin in rhyolite, the cassiterite occurs in veins or veinlets in rock which has been hydrothermally altered, and that the fresh rock has only a normal, minute trace (.001%) of tin (Fries,42:283).

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CHAPTER II

GEOLOGIC INVESTIGATION OF A PORTION OF JUNIPER RIDGE

INTRODUCTION

In connection with the reported occurrence of tin in eastern Oregon obsidians, (12)
the author was instructed to make a detailed geological and petrographic survey of that portion of Juniper Ridge where the "best grade ore" was reportedly found. Since the chosen area lies largely just outside the U. S. Geological Survey Squaw Butte Ranch topographic sheet, overlapping the northeast corner of the map, it became necessary to extend the topography to cover the area.

On July 10th and 11th, 1941, a primary triangulation control network was established, and a major portion of one square mile was topographically mapped. A portion of the geology was plotted and samples were taken at that time. The area was revisited in October, additional samples were taken and the geologic field work was completed. Petrographic examination of these samples was made during the ensuing year in the laboratory at the Portland office of the State Department of Geology and Mineral Industries.

Bibliographic references (given alphabetically at the end of this chapter) are condensed in the text so as to give only the name of the author, the last two digits of the date of publication, separated by a colon from the page reference. A reference to "The Principles of Petrology" by G. W. Tyrrell, published by E. P. Dutton in 1929, page 98, would be thus condensed to (Tyrrell,29:98).

Location and General Features (13)

The Juniper Ridge area discussed in this report covers about one square mile, lying south of the east-west central Oregon highway (U. S. 20) approximately 96 miles east of Bend and 36 miles west of Burns. The area is crossed by the meridian of longitude, 119°, and the parallel of latitude, 43° 31' 15" N. It comprises the S.½ of sec. 36, T. 23 S., R. 25 E.; and the N.½ of sec. 1, T. 24 S., R. 25 E.W.M.

The area lies in part within the northeast corner of the U. S. Geological Survey Squaw Butte Ranch Sheet, near the east end of a prominence locally known as Juniper Ridge.

Relief and Drainage (14)

The area is traversed from southwest to northeast by an intermittent stream, which has cut a steep-walled and in places precipitous gully from 50 to 150 feet deep. The gully cuts across a series of benches which drop down by steps from an elevation of 5000 feet at the southwest corner of the area to 4500 feet at the highway. Another dry gulch runs northwesterly through the northeast quarter of the area, and nearly joins the main creek before turning north for 1500 feet where both creeks debouch (1500 feet apart) upon the north-sloping alluvial piedmont, along which runs the highway. Another east-trending gulch drains the southeastern quarter of the area.

Climate (15)

The climate of this part of Oregon is semi-arid, with an average annual precipitation of less than 10 inches. The summers are hot and dry; the winters are cold. The streams are intermittent, and springs are rare.

LITERATURE

The geologic literature related to the general area of east-central Oregon is not abundant. However most of these areas that have been mapped contain one or more rock formations similar to those at Juniper Ridge where banded rhyolitic lavas and perlitic obsidians predominate.

The Glass Buttes, only 15 miles west of Juniper Ridge (Waters,27), contain a rock sequence of perlite, obsidian, vitrophyre, dacite, andesite, and basalt whose characteristics are very close to those of Juniper Ridge, even to the pumice caps of the flows. The Glass Buttes rhyolite series, according to Waters, is probably correlative with the Steens Mountain lavas of Miocene age. Later workers (Lowry and Bowman, unpublished mss., 1943) believe them to be Pliocene.

Areal mapping of the Harney Basin to the east (Piper,39) extends to within twenty miles of Juniper Ridge. The Palomina Buttes, just south of the highway fifteen miles west of Burns, are composed of Miocene (?) extrusives that underly the Steens basalt, and are:

> "....inflated throughout and even pumiceous at some spots, and commonly disclose conspicuous flow banding. Their matrix is largely siliceous glass (index of refraction less than 1.54) in which perlitic cracks and shards are common. The common feldspar ranges from oligoclase to acidic andesine, but some orthoclase (?) is present. Hornblende has been abundant as a primary mineral but is largely altered to biotite. A few small crystals of apatite are present, but no other accessory minerals were recognized in the thin section. The rock of the Palomina Buttes has been ascribed provisionally to the older siliceous extrusives.
>
> "Where the older siliceous extrusives and the Steens basalt are in contact they are separated by an unconformity that has strong relief and involves considerable erosion and local angular discordance. The angular discordance is disclosed in the northern part of the Crowcamp Hills, in the eastern part of Riddle Mountain, and in the area east of Malheur Gap. In the last-named area the older siliceous extrusives are crumpled and fractured, whereas the Steens basalt lies nearly flat, is faulted in a rather simple pattern, and is not crumpled." (Piper,39:52)

Other rocks of later Pliocene age in the Harney Basin are similar to some of the spherulitic phases of the Juniper Ridge felsites. They are described in part as follows:

> "In the northern part of the area, the lower part of the Danforth formation comprises thick extrusive sheets and masses of reddish gray rhyolite. At some places its members are conspicuous owing to an abundance of evenly distributed spherulites and lithophysae ("stone bubbles") that are lined with opaline silica. These openings are usually discontinuous and do not impart perviousness to the rock.....
>
> "In the Sagehen Hills, west and southwest of Burns, the rhyolite that has been classified as the lower part of the Danforth formation includes considerable black glass, is massive, and is jointed so closely that its initial layers cannot be readily discriminated. Certain spherulitic facies in that locality may belong with the older siliceous extrusive rocks (p. 51), which they resemble closely in petrographic character." (Piper,39:46-47)

In the Baker Quadrangle farther to the northeast (Gilluly,37:50-53), there are, underlying Columbia River basalt, porphyritic flow-banded andesites and rhyolites which are associated with light gray pumiceous-appearing flow breccias. On the Owyhee river (Bryan,28:44) there is a red to black, flow-banded porphyritic rhyolite, without quartz

phenocrysts, which underlies the Miocene Owyhee basalt. Farther to the south in the Steens Mountain area (Fuller,31:60) there are spherulites and platy rhyolites underlying the Steens basalt which, since they show no quartz, are classified as rhyolite on the basis of their chemical composition. In the extreme southeastern corner of the state (Yates 42:324) Miocene lavas range from obsidians to porphyritic rhyolites, and in general exhibit well developed flow banding.

GEOLOGY (17)

Four distinct rock-types were distinguished at Juniper Ridge, three of them closely related in age. A tentative order of superposition was established (a larger area of mapping would be necessary to determine finally age relationships) as follows:

(D) Slightly vesicular, platy, gray, olivine basalt flow.

----------Unconformity----------

(C) Red, porphyritic, pumiceous obsidian, as dikes or lenses, and pale gray, porphyritic, pumiceous obsidian, mainly occurring as float.

(B) Black (and some red-banded), porphyritic, and perlitic obsidian, with lithophysae often abundant, occurring in lenses within the felsite (A).

(A) Finely-banded, platy or massive, red and gray, porphyritic felsite. The massive phase usually contains numerous lithophysae, with banded platy phase often contorted and folded. Surrounds and grades into (B).

Distribution of rocks (18)

Within the area studied, the most widely distributed rock type is the platy felsite (A) which, with the massive phase, forms all the "rim rock" with the exception of basalt (E) in the northeast corner of the area. Lenses of perlitic obsidian (B) occur below the massive felsite cliffs at several places east and southeast of the camp* (see plate I); in the creek bed just west of camp and also up the ridge for several hundred feet to the west; and in the creek bed and east of the creek 3500 feet to the southwest of the camp. Perlite also occurs on the flat-topped erosion surface of the main block 2500 feet south of the camp and at a point 2500 feet south-southwest of the camp. The length of the perlite lenses in this area is from a few tens of feet to nearly a thousand feet. Their thickness is from a few inches to several tens of feet. Red pumiceous obsidian (C) was observed in four localities on the level bench-surface of the main block, where it appears in narrow vertical (northwesterly-striking) dikes or lenses. The grey pumiceous obsidian occurs as float covering most of the flat-topped portions of the main block as well as portions of other blocks. It was found in place in only one cut north of the fence-line near the end of the upper road.

Petrography (19)

In hand specimen, the flow-banded phase of the porphyritic felsite (A) is made up of parallel layers of glassy black and less glassy pinkish material averaging less than 1 mm. in thickness, but varying from a maximum thickness of 3 mm. down to thicknesses measurable only under the microscope. The black bands weather on the surface to a darker red than that of the pink bands, which do not change color upon weathering.

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*The term "camp" as used in this report designates the location of the bunk houses, and little "pilot plant", on the south side of the creek, near the center of the south line of sec. 36, T. 23 S., R. 25 E.W.M.

Euhedral to subhedral feldspar phenocrysts up to 2 mm. in diameter make up about 5% of the rock. They appear almost exclusively within the black bands, which swell to lap around them. The massive phase of the felsite appears to have a composition similar to that of the reddish bands, but it is usually characterized by the presence of pink-colored lithophysae, frequently hollow, which grade in size up to 3 cm. in diameter, and sometimes make up as much as 30% of the rock.

Under the microscope the banded porphyritic felsite is seen to contain as phenocrysts about 5% subhedral andesine-oligoclase ($Ab_{65}An_{35}$) from 0.2 to 1.0 mm. long, and about 1% anhedral magnetite grains. The eutaxitic (Kemp & Grout,40:62) groundmass consists of 90% intergrown micro-spherulites probably composed of orthoclase (and possibly quartz), averaging .005 mm. diameter (Tyrrell,29:99). Elongated cavity fillings parallel to the banding are filled in by deuteric growth of the spherulites lining the cavities, and the centers of the cavities are filled with a nearly clear isotropic material, probably hyaline opal. Extremely minute longulites, probably of iron oxides (3 - 5%) are scattered throughout the groundmass parallel to the flow banding.

In hand specimen the black perlitic obsidian (B) appears to contain about 5% phenocrysts of white subhedral feldspar. The surfaces of the well-developed perlitic fractures have a brilliant black to pale gray gloss, depending upon the thickness of the individual shells of the "perls". Lithophysal phases contain up to 80% of globular and irregularly shaped pink material, which has a radiating fibrous texture and sometimes open cavities in their centers (Tyrrell,29:98). The boundaries of this material are usually sharp but sometimes grade into the glass. (20)

Under the microscope the phenocrysts make up about 8% of the rock. About 4% is resorbed andesine-oligoclase from .6 to 1 mm. in size. Darker cloudy areas of glass often occur around the resorbed feldspar phenocrysts. There is 2% subhedral augite 0.5 mm. or less in size, 1% hypersthene, and 1% iron oxides up to 0.1 mm. in size. The groundmass is perlitic glass, dusted with 5 - 10% of fine opaque needles, which are from 5 to 10 mumu (.005 - .01 mm.) long and from 0.1 to 0.5 mumu (.0001 - .0005 mm.) thick. These are probably magnetite, since grinding the rock yields 5 - 10% magnetic dust. The order of crystallization is magnetite - pyroxene - feldspar - magnetite longulites - glass.

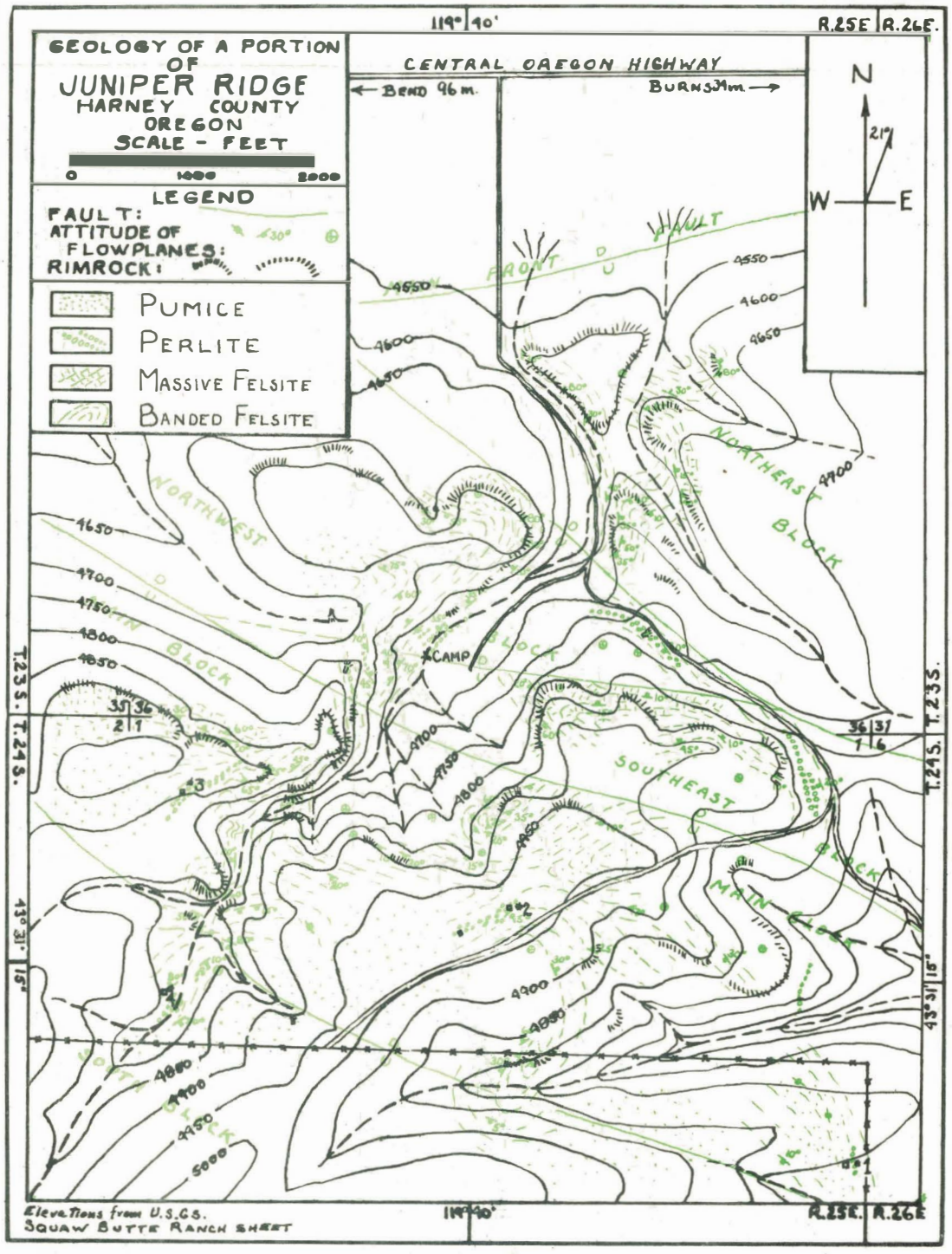
The pale gray pumiceous obsidian appears in hand specimen to have a porosity of only about 5%, but the tubules and directive texture in the glass is well defined in the hand specimen, and vitreous lustre is not universally apparent. There are a few xenoliths of basic rock up to 2 in. across, presumably torn from the walls of intruded rock. The specific gravity of a lump of pumiceous obsidian is only slightly less than that of adjoining rocks. White feldspar phenocrysts,averaging 1 - 2 mm. long, make up about 5% of the rock. A few minute black crystals of iron oxides are also apparent. (21)

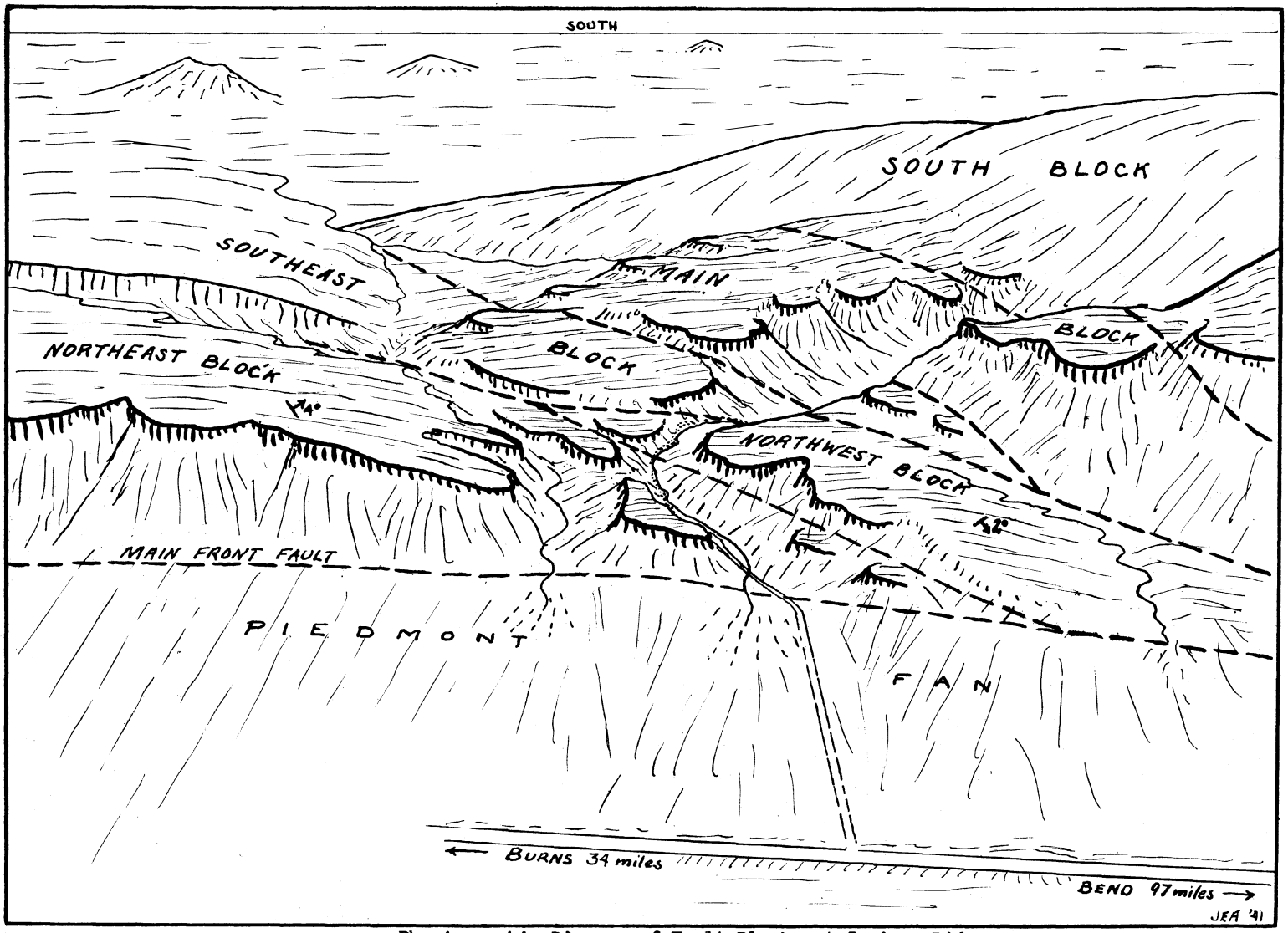
Under the microscope the gray pumiceous obsidian is seen to be composed of about 5% subhedral andesine-oligoclase ($Ab_{65}An_{35}$) phenocrysts (0.3 - 2 mm. in size) in a vitrophyric (Kemp & Grout,40:110) groundmass composed 75% of oriented tubules of clear glass with an index of 1.505 (71% SiO_2 according to George,24:353); 15% oligoclase-andesine microlites; and about 5% fine accessory iron oxide grains.

In hand specimen, the red porphyritic pumiceous obsidian contains large (up to 5 mm. long) oriented plates of white feldspar, which make up about 5% of the rock, in a groundmass composed of approximately equal parts of dark red unevenly fractured glass and paler, slightly pumiceous material. (22)

Under the microscope the phenocrysts of the red pumiceous obsidian are shown to be composed of 5% euhedral to subhedral and broken andesine-oligoclase (0.3 - 0.8 mm. diameter); and 1% euhedral, strongly pleochroic, iron-rich olivine averaging .3 mm. in diameter. The vitrophyric groundmass is composed of glass which retains a directive

PLATE I


GEOLOGY OF A PORTION OF
JUNIPER RIDGE
HARNEY COUNTY
OREGON
SCALE - FEET
0
1000
2000
LEGEND
FAULT:
ATTITUDE OF FLOWPLANES:
RIMROCK:
PUMICE
PERLITE
MASSIVE FELSITE
BANDED FELSITE
CENTRAL OREGON HIGHWAY
← BEND 96 m.
BURNS 39 m. →
119° 40'
R.25E.
R.26E.
T.23S.
T.24S.
43° 31' 15"
N
W
E
21°
FRONT FAULT
NORTHWEST BLOCK
NORTHEAST BLOCK
SOUTHEAST BLOCK
MAIN BLOCK
CAMP
4650
4700
4750
4800
4850
4900
4950
5000
4550
4600
35
36
2
1
31
6
Elevations from U.S.G.S.
SQUAW BUTTE RANCH SHEET



Physiographic Diagram of Fault Blocks at Juniper Ridge

Plate II

pumiceous texture, but the tubular openings are largely lacking. About half of the glass is clear and the other half is dark yellow, probably due to contained iron oxide, the latter distributed in irregular elongated blebs, strings, and patches.

The olivine basalt (E) is a dark gray, platy, and porphyritic lava with an aphanitic groundmass characterized in hand specimen by irregular patches of lighter material oriented parallel to the platy structure. Under the microscope the phenocrysts are seen to be composed of 10% subhedral to anhedral and corroded labradorite ($Ab_{30}An_{70}$) laths (0.2 to 1.5 mm. long), and about 2% anhedral resorbed augite from 0.2 to 1.0 mm. in diameter. There are a few large subhedral to anhedral olivine crystals (over 2 mm. in diameter), often more or less completely altered to iddingsite, and a few grains of subhedral prismatic hypersthene. The groundmass consists of about 60% andesine-oligoclase microlites with a felted or felsophyric texture; 15% interstitial anhedral clinopyroxene grains; and 10% iron oxides in subhedral crystals and in irregular blebs. (23)

The three rock-types A, B, and C have similar indices for their glass constituents (1.50 - 1.51) which indicate that they have a silica content between 68 and 72 per cent (George,24:353). The feldspars in A, B, and C are similar (averaging $Ab_{65}An_{35}$) and no quartz was identified. On a mineralogic basis the rocks would be called andesites, whereas on the basis of their chemical composition (judging from the glass index) they would be classified as rhyolites. The field term "felsite" (Kemp & Grout,40:62) is thus retained in referring to them in this paper. (24)

Mineralization (25)

None of the rock-types described showed secondary alteration other than slight weathering features, even adjacent to the faults. Limonite is developed very infrequently on the fractures of the black perlite and there has been deuteric alteration of the hypersthene and olivine of the basalts. Otherwise all the rocks are remarkably fresh, and there is no suggestion of hydrothermal mineralization.

Origin of the rocks (26)

The rhyolitic series of platy felsites and obsidians in the Juniper Ridge area were extruded as viscous, gas-charged lavas from a number of central or fissure vents, and spread out as thick, steep-sided flows or flattened domes (Williams,32:69,79; 35: 282; Tyrrell,31:31). This extremely viscous lava contained initial patches and layers differing in composition, gas content, viscosity, and degree of crystallization, so that movement of the mass drew the irregularities out into parallel bands and lines, which are characterized by varying portions of spherulites, glass microlites and stony material of slightly varying composition (Tyrrell,29:39). Similar banding in rhyolites at Mt. Katmai (Fenner,26:740) seems to be due to the streaking out of partly and completely fused inclusions of more basic lava (andesite), and is not banding of early crystallized magma or "schlieren". Certain lenticular areas within the glassy magma cooled so rapidly that not only did the chilled glass have no time to crystallize, but the contraction due to cooling caused fracturing of the glass around numerous closely spaced centers and produced the perlite lenses (Tyrrell,29:99).

The banding, the resorption of phenocrysts, and the apparent difference in composition between them and the glass suggest that possibly the original highly acid magma came up through a coarse grained andesite, picked up small portions of it which were largely dissolved, thus changing the composition of the lava.

Expansion of contained gases with possible explosive activity in slightly later extrusives of similar composition developed the gray pumiceous obsidians, of which the red phase resulting from oxidation of iron content (Fuller,27) seems, according to field relations, to represent an intrusive phase. This pumice cap is similar to that at Glass Buttes (Waters,27). Basaltic flows followed the felsites, and are later than the pumiceous obsidians.

Structures

Attitudes of the flow-banded felsites vary from horizontal to vertical within tens of feet; in a few localities the contortion is so intense that attitudes could not be plotted on the map. On a large scale, however, plotted attitudes indicate a number of primary folded structures. These structures are seldom continuous beyond the fault blocks within which they lie, and there is little correspondence of axial trend between fault blocks. They undoubtedly represent primary intrusive features. In several localities there are areas of quaquaversal outward dips which are in turn surrounded by corresponding sequences of inward-dipping rock-types around the periphery of the structural domes. These are characteristic of viscous or plug dome type of intrusion (Williams,32). (27)

Jointing in the rocks of the area is most prominent parallel to the primary flow-banding, so that the rocks break up into thin platy polygons whose thickness depends primarily upon the degree of development of the flow-banding. Jointing has also been developed in other irregularly oriented directions but to a less degree. (28)

A well-defined system of northwest-southeast-trending normal faults divides the area into blocks having different elevations, all down-dropped on their northeast sides. Faults have been mapped on the basis of displaced erosion surfaces, offset or abruptly terminated perlite lenses, anomalously broken (rather than contorted) banding in the felsite, and physiographic ridge-saddles and adjacent ravines. (29)

The main front fault strikes N. 80° E., and is the only one which does not trend in the northwest quadrant. Displacement of 50 to 300 feet along this fault has resulted in the development of the north escarpment of Juniper Ridge, which more or less parallels the highway for several miles. Within the area mapped, the amount of displacement dies out rapidly on this fault from east to west, being taken up by other members of the system which join it. South of this fault, the warped surface of the northeast block slopes about 4° to the southwest.

The northwest block, whose surface slopes about 2° to the northwest, is separated from the northeast block by a fault striking N. 50° W. with a displacement of only a few tens of feet. The northwest and southeast blocks, lying between the northeast and the main blocks, are separated by a splinter-fault striking N. 80° W., with a displacement of over 100 feet.

The main block has a nearly horizontal surface, being bounded on the northeast by a fault which strikes N. 50°-60° W. and forms the main north escarpment of Juniper Ridge to the west of the area. The main block, which is from 2,000 to 2,500 feet wide, is separated from the warped east and southeast-sloping south block by a small displacement along a less well-defined fault which also strikes N. 50°-60° W.

The uniformly northeast trend of the main creek, structural anomalies and contorted, crumpled, and broken flow planes in the felsite at several localities along the creek, and the wind-gap between the two creeks northeast of the camp, all suggest a zone of movement trending N. 30° E. through the area. Since it does not displace the block-surfaces, it was probably of early development, antedating both the other fault movements and the erosion cycle which modified the surfaces of the fault blocks. It may even have been established contemporaneously with the outflow of the lavas.

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CHAPTER III

SAMPLES FROM JUNIPER RIDGE USED IN THE INVESTIGATION

Methods of Sampling (31)

On July 10 and 11, 1941, a survey party of the Oregon Department of Geology and Mineral Industries took samples of the rock at Juniper Ridge for analytic work. Only the three members of the survey party were present when the sampling was done, and at least two of them were present when each of Samples I to VI, inclusive, were taken. According to information volunteered to the party by those interested in the occurrence, the "highest grade ore" consisted of the perlitic obsidian and the banded felsite. Most of the location cuts dug in the area examined were in the perlite. Accordingly Samples I to VI, inclusive, were taken from cuts previously excavated. Later, in October, 1941, the property was revisited and Samples XII to XV, inclusive, were taken by members of the Department.

In taking the six bulk samples I to VI, inclusive, (which weighed from 40 to 60 pounds each), standard sampling procedure was followed. In every case where possible (all except sample III), channel samples were taken across the bedding planes of the perlite so as to give an average of the various portions of the perlite lenses exposed in the open cuts and pits. Before sampling, from 3 to 8 inches of the wall of the cut where the sample was to be taken was broken off by means of pick, moil, or in some cases, by use of light charges of dynamite, so that each sample was taken from a fresh rock surface. The sampling channels were then cut in the freshly exposed face, the vertical channels being from 4 to 6 inches wide and 1 to 2 inches deep, up and down the exposed face of rock. Moils and geologic picks were used to cut the rock as evenly as possible, and each channel was developed by going over its length at least twice.

All the samples (I to VII inclusive) were placed in new, unused canvas sacks labelled inside and outside. The sacks were tied, and were kept*[1] under lock and key until they were delivered and accepted*[2] July 12th at the Chemistry Department of Oregon State College.

Description of Samples taken (32)

Sample I: From Pit No. 2, located about 2000 ft. a little east of south of camp+ on flat-topped ridge 300 ft. north of road at elevation of 4975 ft. (see plate 1). Pit No. 2 is about 10 ft. deep and 4 ft. square, its west side is composed of perlitic obsidian, the flow planes of which strike N. 30° E. and dip 45° N. W. Sample I was taken[1,3,4] as a vertical channel 4 ft. long, from the center of the west side of the pit.

Sample II: From Pit No. 2 as described above. The upper 6 feet of the east side of the pit is in red banded perlite which overlies the black. Sample II was cut[3,4] from a vertical channel 8 ft. long near the center of the east side of the pit.

Sample III: From open cut 10 ft. long, 4 ft. deep, and 4 ft. wide, located 800 ft. due west of camp, on north side of ridge at an elevation of about 4775 ft. (see plate 1). This sample was a grab sample[3,4] from the boulders of perlitic obsidian poorly exposed through the slump of the partially caved open cut.

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* See references at end of this chapter.

+ The term "camp" as used in this report designates the location of the bunk houses, and little "pilot plant", on the south side of the creek, near the center of the south line of sec. 36, T. 23 S., R. 25 E.W.M.

Sample IV: From Pit No. 3, 6 ft. long, 4 ft. wide, and 4 ft. deep, located in perlitic obsidian, about 2500 ft. a little south of west of camp, near crest of ridge north of creek, at elevation 4900 ft. (see plate I). Sample IV was taken[3,4] as a composite of two 4 ft. vertical channels, one on the north and the other on the south side of the pit.

Sample V: From Pit No. 1, 10 ft. deep and 4 ft. square, located in perlitic obsidian 6000 ft. southeast of camp and 200 ft. west of the fence-line (see plate I). This was the only sample taken within the fence-line of the Squaw Butte Ranch Reservation. Pit No. 1 is on the north side of a shallow draw at elevation 4750 ft. Sample V was taken[1,3,4] from an 8 ft. vertical channel on the north side of the pit.

Sample VI: From pit No. 4, 12 ft. deep and 5 ft. square, located in banded perlitic and lithophysal obsidian, 3500 ft. southwest of camp just west of the creek bottom and 450 feet north of Squaw Butte Ranch fence-line (see plate I). Sample VI was taken[1,3,4] from a vertical channel 10 ft. long on the northwest side of the pit.

Sample VII: From outcrop of banded black and red felsite which has an attitude of N. 70° E., 60° S. Outcrop is 2900 ft. southwest of camp on the north side of the creek in the gorge just below the forks. Sample VII was composed of ½- to 1-pound fragments broken off[1] at intervals of from 1 to 2 ft. over a distance of 50 ft. along a line at right angles to the banding of the rock.

Sample VIII: Submitted[5] as being representative of the Juniper Ridge deposit. It consisted of one lump of perlite weighing from 1 to 2 pounds.

Sample IX: A part of a grab sample taken[6] from the ore-bin at the furnace plant at the Juniper Ridge camp.

Sample X: Submitted[7] as being representative of the Juniper Ridge deposit. The sample was reported to contain tin in commercial quantities. It consisted of powdered material in a 2 oz. bottle.

Sample XI: A composite of two samples submitted[8,9] as representative of rock from Claims no. 83 and no. 104.

Sample XII: A composite of two grab samples of rock totalling approximately 40 lbs. taken[2] from localities designated[8] as Claims no. 83 and no. 104.

Sample XIII: A grab sample of rock weighing approximately 40 lbs. taken[2] from locality designated[8] as Claim no. 29.

Sample XIV: A grab sample of perlite broken[1] from the large outcrop on the east side of the creek, 400 ft. northeast of Pit no. 4 and 3400 ft. southwest of camp.

Sample XV: A composite grab sample of perlite taken[1,2] from open cuts and outcrops in bed of creek just west of camp.

Reduction of Gross Samples

Samples I, II, III, IV, V, VI, and VII as received[2] from the field were composed of rock material in various sizes from 10 inches in diameter down to dust. The samples used for analysis were prepared according to standard sampling procedures.[10] Each sample was reduced to 4-mesh size by hand and by means of a small Braun Chipmunk Crusher,[11] and thoroughly mixed by rolling on a rubber sheet. The mixed sample was reduced in size by the cone and quarter method and the resulting 20 - 30 pound portion was crushed to 10 mesh size by means of a Roll Grinder[12] and thoroughly mixed again by rolling on a rubber sheet. This portion was further reduced in size by the cone and quarter method, and the resulting 10 - 15 pound portion was crushed to 20-mesh size by means of the roll grinder. After thorough mixing, a 5 - 8 pound sample was obtained by the cone and quarter method. One half of this portion was placed in a motor-driven agate mortar and pestle

grinding unit and reduced to 100 mesh or finer. These 100-mesh portions were used for analysis. In the case of each sample the discarded portions from each step in the reduction were recombined and resampled in the above manner whenever a new portion of that sample was needed for analysis.

Samples IX and X were submitted in the form of a fine powder of approximately 100-mesh size, therefore no further reduction in size was carried out but the samples were mixed by rolling on a rubber sheet.

Samples VII, XI, XII, XIV, and XV were reduced in size by grinding in an iron mortar by means of an iron pestle. These samples were reduced in size according to standard sampling procedures.

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CHAPTER IV

CHEMICAL AND SPECTROCHEMICAL ANALYSES

OUTLINE

Introduction

I Methods of obtaining tin in a known form (34)

II An investigation of reactions of test analytical reagents (35-39)

III Experimental procedures using standard mixtures of tin in Juniper Ridge rock (40-52)

IV Experimental procedures using Juniper Ridge rock samples (53-222)
- A. Qualitative experiments (53-198)
- B. Quantitative chemical analysis (199-207)
- C. Spectrochemical analysis (208-222)

V References

INTRODUCTION

In connection with the reported occurrence of tin in Oregon obsidians, the author was instructed to undertake a thorough analytical investigation to determine the presence or absence of tin in Juniper Ridge rocks.

There is no single universally accepted method of analysis for tin in any or all its compounds. The choice of method lies with the user. For this reason, it was found necessary to evaluate the different known methods during the course of this investigation, particularly as each applies to the present problem. A large number of entirely different methods of tin analysis was used. These include assaying by fire (smelting on a small scale), chemical analysis, and spectroscopic analysis. Some of the procedures used, and described herein, were tested at the suggestion of persons interested in the Juniper Ridge properties.

Qualitative Chemical Analysis

A survey of the analytical procedures used for the detection of tin disclosed a large number of possible procedures which were weighed one against the other to determine which was most likely to yield conclusive results.

In this investigation, Juniper Ridge rock samples were to be analyzed for the presence or absence of tin in any form or combination. The analytical procedure or procedures used must detect the presence of tin when associated with the other constituents of the sample. On the other hand each analytical procedure must not yield a positive test for tin as a result of interfering influences of other constituents in the sample, even though tin or its compounds are not present in the sample.

Fifteen different reagents or tests were selected for this investigation. These reagents were used to test samples of Juniper Ridge rock to which tin had been added in the form of metallic tin or as compounds of tin. Tin was added so the author could be certain that the metal existed in the sample portions used for testing the reagents. Four of these tests were chosen as being specific for tin when present in Juniper Ridge rock; that is, none of the constituents in Juniper Ridge rock interfered with the positive reaction for tin of any of these reagents. Further investigation showed that none of these reagents gave a positive reaction for tin when used with samples of Juniper Ridge rock to which tin or compounds of tin had not been added.

Quantitative Chemical Analysis

One fire assay method and two wet-chemical methods were investigated, using standard samples of Juniper Ridge rock to which metallic tin or compounds of tin had been added. The reason for this investigation was to determine the reliability of these methods in determining quantitatively the amount of tin added to the standard samples.

Spectrographic Analysis

A number of different methods of spectral excitation were used with standard samples of Juniper Ridge rock to which metallic tin or compounds of tin had been added, in order to determine the lowest concentration of tin which could be detected by all of the spectrographic methods investigated. Quantitative spectrographic analyses were made to determine the concentration of tin in the samples of Juniper Ridge rock as submitted for analysis.

I. METHODS OF OBTAINING TIN IN A KNOWN FORM

A. List of Methods (34)

The following procedures have been used for obtaining tin in a known form that is susceptible to further testing or identification:

1. Blow pipe fusion on charcoal, of a mixture composed of ore, potassium cyanide, and litharge.[49]
2. Fusion of the ore, potassium hydroxide, and sodium peroxide or carbon, depending upon the nature of the ore[79,80,81]
3. For ores of high copper content a nitric-hydrofluoric-sulphuric acid treatment followed by a hydrochloric-nitric acid extraction of residue and a subsequent potassium hydroxide fusion is sometimes employed.[82]
4. A nitric acid, aqua regia, potassium bisulfate, sodium carbonate, potassium nitrate treatment for qualitative analysis.[83]
5. Fusion of a mixture of ore, sodium carbonate, and potassium cyanide.[84]
6. Hydrochloric-sulphuric acid digestion of the sample.[84,85,86,95,96]
7. Alkali cyanide fusion using a fire-clay crucible.[87,10,88]
8. Sodium peroxide fusion.[89,16]
9. Low grade ores concentrated and reduced with charcoal before assaying.[90,54,52]
10. In presence of organic matter, a Kjeldahl digestion followed by hydrogen sulfide is frequently used.[91,92]
11. Fusion of a mixture of ore, sodium carbonate, and sulfur.[93,94,97]
12. Fusion of a mixture of ore, sodium carbonate, and charcoal.[93]
13. Reduction by means of hydrogen.[80,50]
14. Roasting ore in Jack Rabbit furnace.[34,60,61]
15. Roasting of a mixture of ore, coke, coal or charcoal in Jack Rabbit furnace.[17,60,61,34]
16. Roasting of ore, charcoal, and limestone mixture in Jack Rabbit furnace.[18]
17. Roasting a mixture of ore and borax in a Jack Rabbit furnace.[57]
18. Roasting a mixture of ore and sodium carbonate in a Jack Rabbit furnace.[57]
19. Roasting a mixture of ore and resin in a Jack Rabbit furnace.[60,61,34]
20. Roasting ore on a sage brush fire.[34,17]
21. Electro-thermal reduction of ore using carbon or graphite arc and a flux.[57]
22. Heating ore with hot fat for the purpose of coagulating small, metallic tin particles.[60,61]
23. Roasting mixture of ore, charcoal, and sugar solution.[17]
24. Digestion of ore with caustic soda solution, acidifying and evaporating to precipitate insoluble tin oxide.[67]
25. Roasting ore on wood fire followed by oil flotation and panning the oil float concentrate.[34]

26. Roasting sample on wood fire followed by oil flotation and subjecting float concentrate to electro-thermal reduction in carbon arc.[57]
27. Fusion of ore sample with potassium cyanide and cupric oxide mixture.
28. Fusion of ore, charcoal, borax glass, and sodium chloride.[98]
29. Fusion of sample and potassium bisulphate.[99,100]
30. Fusion of ore and various fluxes in a Whitton bomb.
31. Fusion of ore and various fluxes in a Parr bomb.

II. AN INVESTIGATION OF THE REACTION OF SOME ANALYTICAL REAGENTS (35)

The first step taken in the laboratory investigation was to determine what specific tests for the presence of tin are the most sensitive and reliable when used on standards prepared by adding tin to Juniper Ridge rock.

A survey of the literature[71,14,21,35,42] disclosed a large number of different reagents and chemical tests used for the detection of tin or its compounds. The majority of these depend upon the reaction of the reagent with stannous or stannic ions in an aqueous solution.

A. Reagents chosen (36)

1. The following fifteen reagents or tests were selected as being the most promising.

1- cacotheline[8,49,47,23,33,55,1]
2- molybdic acid[101,78,111]
3- ferrous dimethylglyoxime[47,102]
4- ammonium phosphomolybdate[102]
5- diazene green[47,103,19]
6- flame test[104,105,106,51,64]
7- resorcinol[107,9]
8- mercuric chloride[108,109,110,111,27,66,112]
9- mercuric chloride and aniline[113,73]
10- sodium nitroprusside[22]
11- phosphomolybdic acid[24]
12- phenylarsonic acid[108,107,46,13,45,44]
13- uric acid[63]
14- nitrophenylarsonic acid[74]
15- hydrogen sulfide[114,20,115,116,27,117]

2. The selection of these reagents was based on reasons as follows: The acceptance of the reagent as shown by its use over a number of years by various scientists working on unrelated problems; the availability and stability of the reagent; the specific nature of the reagent in the presence of other ions; the sensitivity of the reagent for detecting either large or small concentrations of tin under ordinary laboratory conditions; and the ability of the reagent to indicate the presence of tin without the necessity of a number of separations of tin from the other elements in the sample with the subsequent danger of loss of tin during the separations.

B. Methods used in testing reagents

1. Standard solutions of tin in hydrochloric acid (37)

The fifteen selected reagents and tests were tested by using standard solutions prepared by dissolving c.p. shot-tin in hydrochloric acid. The standard solutions covered a range of concentrations from 5.0% tin to 0.05% tin in steps of 0.05%. Method 1. A unit volume (5 ml.*) of each different standard solution was tested at least twice by each different reagent in the method described under the directions for the use of that particular reagent. Method 2. The tin in a unit volume of each standard solution was precipitated by hydrogen sulfide and the resulting precipitate was concentrated by centrifuging and redissolving, and

* ml. - milliliter. One-thousandth liter, or practically equivalent to a cubic centimeter (.0338147 ounce liquid measure).

each reagent was used to test the resulting solution.

2. Standard mixtures of tin and Juniper Ridge rock (38)

a. Sample I and sample VII were selected as being representative of the two main types of Juniper Ridge rock. These two samples were prepared as described under sampling (33) and were of approximately 100 mesh particle size. Each of these samples was used as the matrix material in the preparation of samples containing known concentrations of tin added as metallic tin or known compounds of tin.

b. Four series of standard samples of tin in each of these base materials were prepared. Each series contained standards whose tin content were 5.0%, 3.0%, 1.0%, 0.5%, 0.3%, 0.1%, and 0.05%. The following forms of tin were used for the preparation of the standards: (1) shot-tin, (2) stannic oxide, (3) cassiterite, and (4) stannite. The standards containing cassiterite and the standards containing stannite were not as accurately prepared as the standards containing shot-tin and the standards containing stannic oxide, but it was thought that these naturally-occurring forms of tin should be used in the preparation of the standards. Spectrographic analyses later showed that these standards were of sufficient accuracy for the purpose for which they were used. The procedures used in testing these standard mixtures will be described under III, "Experimental Procedures Using Standard Mixtures of Tin and Juniper Ridge Rock."

C. Selection of reagents suitable for further experimental work. (39)

From information gained by a study of the reactions of the fifteen reagents and tests on the prepared standard mixtures of Juniper Ridge rock containing known concentrations of tin, four reagents were selected as being superior to the others for the purpose of this particular investigation. These reagents were selected because of their sensitivity, stability over a period of time, sharp color changes, and because they are specific in the detection of tin whenever this element or its compounds is present in Juniper Ridge rock. The reagents selected were: (1) cacotheline, (2) molybdic acid, (3) mercuric chloride and aniline, and (4) diazene green.

III. EXPERIMENTAL PROCEDURES USING STANDARD MIXTURES OF TIN IN JUNIPER RIDGE ROCK

A. Digestion of sample with hydrochloric-sulphuric acid mixture (40)

In the decomposition of materials containing tin it is necessary to take precautions to avoid the loss of tin due to volatilization of tin chloride when a hydrochloric acid solution of the metal is heated. H. B. Knowles found that no loss of tin occurs when dilute hydrochloric acid solutions containing tin are boiled if sulphuric acid is present in the solution, even if the solution is boiled to fumes.[118,86] For this reason sulphuric acid was added to all hydrochloric acid solutions in which tin was or might be present.

1. A 0.5 gram portion of each prepared standard containing shot-tin was treated with 5 ml. of hydrochloric-sulphuric acid mixture. (41)

2. The acid mixture containing the standard was brought to gentle boiling and held at that temperature for one minute, then kept in a hot water bath for five additional minutes. At the end of five minutes in the water bath the solution was separated from the residue by centrifuging, the filtrate was evaporated to a volume of 1 ml. which was then used for a tin test using one of the fifteen selected (42)

being the most promising. Each preparation of test-solution and each analytical reagent test was run in duplicate.

3. The above procedure was repeated to the point of bringing the acid mixture containing the standard to boiling and the solution was left for 24 hours at room temperature in a mechanical agitator. At the end of this period of leaching, the solution was centrifuged and concentrated, by boiling, to a volume of 1 ml. and the concentrated solution was tested with an analytical reagent. Each preparation of test solution and each of the fifteen analytical reagents were run in duplicate. (42-a)

4. a. The procedure described in (42) was repeated and after the digestion in the hot water bath the solution was centrifuged, concentrated to a volume of 1 ml. and cooled. The pH of the concentrated solution was adjusted and the tin was precipitated according to standard analytical procedures.[119,120,121] The precipitate was centrifuged, washed, dissolved and the tin was reprecipitated as tin sulphides. The sulphides were dissolved and the solution evaporated to a volume of 1 ml. and tested for the presence of tin using one of the selected analytical reagents. This procedure was repeated in duplicate with each of the different standards containing shot-tin and each of the remaining fourteen different analytical reagents. (43)

b. The same series of tests was repeated using the 1 ml. solution obtained by concentrating the room temperature leach as described in (42-a).

B. Blowpipe fusions* on carbon (charcoal) block (44)

1. Samples I, II, III, IV, V, VI, and VII were analyzed for the presence of sulphur and were found to be sulphur-free. Therefore, only those standards in which the tin had been added as shot-tin, stannic oxide, or cassiterite were used in the following series of tests. (45)

2. A 0.5 mg. sample of each individual member of each of the three series of standard samples mentioned above was subjected to the action of the reducing portion of a blowpipe flame. Every sample was fused on a carbon block with each of the following fluxes: (1) potassium cyanide, (2) a mixture of potassium cyanide and litharge, (3) a mixture of potassium cyanide and sodium carbonate, (4) a mixture of potassium cyanide and potassium carbonate, (5) a mixture of potassium cyanide, sodium carbonate, and potassium carbonate, (6) a mixture of potassium cyanide and borax, (7) a mixture of potassium cyanide and cupric oxide, (8) a mixture of potassium cyanide, cupric oxide, and borax, (9) sodium carbonate, (10) charcoal, (11) a mixture of potassium cyanide and charcoal, (12) borax. (46)

3. a. The fusion mixture resulting from each fusion was treated in the following manner; the fused mass was crushed in an agate mortar and the entire crushed sample was treated as described in (42). The resulting 1 ml. of solution was tested for the presence of tin using one of the fifteen analytical reagents. This procedure was repeated for each of the fifteen different analytical reagents and each fusion and test was run in duplicate. (47)

b. The above fusions were repeated and the fusion mixtures were treated as described in (43), and each resulting solution was treated with one of the fourteen different analytical reagents. This procedure was repeated for each of the fourteen different analytical reagents and each fusion and each test was run in duplicate.

* Throughout the report the term fusion is used to designate the result of subjection of a sample or mixture of sample and other substances to the influence of heat irrespective of the physical condition of the heated sample.

4. The selection of the four analytical reagents cacotheline, molybdic acid, mercuric chloride with aniline, and diazene green was based on the results of these series of tests. It was concluded that concentrations of tin in samples that are far below the grade of commercial ore can be detected with certainty, and that the concentration of the tin by the hydrogen sulphide precipitation procedure slightly increased the sensitivity of the tests. It was also found that more satisfactory results with regard to sensitivity and speed of analysis were obtained with the samples which had been boiled and then digested in a hot water bath than with those samples which had been subjected to a 24 hour leach at room temperature. (48)

5. Analytical procedures adopted

Throughout this investigation four different general analytical procedures were used. These procedures are as follows:

Analytical Procedure No. 1 (49)

The sample or mixture to be analyzed for tin is digested with a hydrochloric-sulphuric acid mixture by bringing to a gentle boil for one minute and then placing in a hot water bath for five minutes. At the end of five minutes in the water bath the solution is separated from the residue by centrifuging. The filtrate is evaporated to a volume of one ml. which is then tested for the presence of tin using each of the following test reagents: (1) cacotheline, (2) molybdic acid, (3) diazene green, and (4) mercuric chloride and aniline.

Analytical Procedure No. 2 (50)

The sample or mixture is panned down and the concentrate examined with the aid of a microscope to determine the presence or absence of metallic particles.

Analytical Procedure No. 3 (51)

This procedure is identical to Analytical Procedure No. 1 to the point where the filtrate is concentrated to a volume of 1 ml. At this point the pH of the concentrated solution is adjusted according to standard qualitative analysis procedures for the analysis of group II of the cations and the tin is precipitated by means of hydrogen sulfide. The precipitated sulphides are washed, dissolved, and the tin reprecipitated as tin sulphides. The sulphides are redissolved, the solution evaporated to a volume of 1 ml. and this solution is tested for the presence or absence of tin using each of the test reagents listed in Analytical Procedure No. 1.

Analytical Procedure No. 4 (52)

The sample or mixture to be analyzed for tin is digested with a hydrochloric-sulphuric acid mixture as described in Analytical Procedure No. 1 (49). At the end of the digestion period the contents of the digestion container are centrifuged, the residue labeled "R - 1" and the filtrate labeled "F - 1". The filtrate (F - 1) is concentrated by boiling to a volume of 25 ml. and after allowing to cool any precipitated material is centrifuged off and the filtrate is labeled "F - 2". Residue (R - 1) is digested with 25 ml. of hydrochloric-sulphuric acid mixture in the manner described in Analytical Procedure No. 1 and the resulting filtrate is added to filtrate (F - 2) and labeled "F - 3". Solution (F - 3) is concentrated to a volume of 5 ml. by boiling, centrifuged and the filtrate labeled "F - 4". A portion of filtrate (F - 4) is tested by means of the test reagents listed in Analytical Procedure No. 1 and another portion of (F - 4) is tested according to Analytical Procedure No. 3.

IV. EXPERIMENTAL PROCEDURE USING JUNIPER RIDGE ROCK SAMPLES

A. Qualitative analysis

1. Digestion of samples with hydrochloric-sulfuric acid mixture (53)

a. Juniper Ridge samples I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV were used and each experiment was carried out in duplicate. (54)

b. (1) Every sample (54) was treated according to the procedure described in Analytical Procedure No. 1 (49). (55)

(2) Every sample (54) was treated according to the procedure described in Analytical Procedure No. 3 (51) to the point where tin sulphides would precipitate if tin were present. Tin sulphides were not obtained in any of these tests.

c. Results: The presence of tin was not detected in any of these tests. (56)

2. Blowpipe fusions on carbon blocks (57)

a. Samples I, II, III, IV, V, VI, VII, VIII, IX, and X were used and each experiment was carried out in duplicate. (58)

b. Each sample was mixed with each of the fluxes listed in (46) and each fusion was carried out in duplicate. (59)

c. (1) One of each fusion mixture was treated in the manner described in Analytical Procedure No. 1 (49). (60)

(2) One of each fusion mixture was treated in the manner described in Analytical Procedure No. 3 (51) to the point where tin sulphides would precipitate if tin were present. Tin sulphides were not obtained in any of these tests.

d. Results: The presence of tin was not detected in any of these tests. (61)

3. Fusions in crucibles (62)

a. Open flame heat source (63)

(1) Samples I, II, III, IV, V, VI, VII, VIII, IX, and X were used in these series of tests and each sample was run in triplicate with each flux employed. (64)

(2) The following fluxes were used; (1) potassium cyanide, (2) a mixture of potassium cyanide and sodium carbonate, (3) a mixture of potassium cyanide and potassium carbonate, (4) potassium carbonate, (5) a mixture of sodium carbonate and sodium peroxide, (6) a mixture of sodium hydroxide and sodium peroxide, (7) charcoal, (8) charcoal mixed in a saturated solution of sugar, (9) potassium hydroxide and nitric acid, (10) potassium bisulphate, (11) charcoal, sodium bicarbonate flour and covered with a sodium chloride layer, (12) borax, (13) a mixture of borax and cupric oxide, (14) a mixture of potassium cyanide and litharge, (15) a mixture of sodium hydroxide and carbon, (16) a mixture of sodium carbonate and sulphur, (17) a mixture of sodium carbonate and carbon, and (18) metallic aluminum powder. (65)

(3) The heat for the fusions was obtained by means of a Meker blast lamp with laboratory gas and compressed air. No accurate temperature control was undertaken. Coors porcelain crucibles, nickel crucibles, fireclay crucibles, or iron crucibles were used depending upon the nature of the (66)

flux. All of these crucibles were covered with a top made of the same material as the crucible except in the case of the fireclay crucibles. Ten grams of sample were used for each fusion. Because of the corrosive action of some of the fluxes used, the nature and time of heating were not the same for all of the heat treatments. When the mixture to be heated did not attack a porcelain crucible this type of crucible and cover was used and the burner flame was adjusted to keep the outside of the crucible at a bright red color for a period of one hour. In those heat treatments where corrosive fluxes were used the selection of the type of crucible to hold the charge was based on the resistance of the crucible to that particular fusion mixture. The crucible and charge were heated until the outside of the crucible was a dull red color and the burner flame controlled to keep this temperature for as long a period as that particular crucible would withstand the action of the charge without breaking. None of these heating periods exceeded one hour.

(4) (a) One of each of the 18 fusion mixtures (65) was pannod down and the concentrates were examined with the aid of a binocular microscope. Particles of metal were detected in the fusions to which a metal oxide, serving as a tin collector, had been added. The concentrates were tested for the presence of tin by Analytical Procedure No. 1 (49). A slightly modified procedure was used in analyzing the concentrates containing metal derived from the metal oxides added to the fusion mixture. (67)

(b) Analytical Procedure No. 3 (51) was not employed because tin sulfides were not precipitated.

(c) Each of the two remaining fusions of each fusion mixture was treated in the following manner: The contents of the crucibles were removed by mechanical or chemical methods and placed in a beaker of water. After acidifying with a hydrochloric-sulphuric acid mixture, the beaker contents were treated according to Analytical Procedure No. 4 (52). Tin sulphides were not obtained by Analytical Procedure No. 3 (51).

(5) Results: The presence of tin was not detected in any of these tests. (68)

b. Fusions in electric muffle (69)

(1) Ordinary fusion method (70)

(a) The samples listed in (64) were used. (71)

(b) The fluxes listed in (65) were used. (72)

(c) In these series of tests the source of heat was a Hoskins electric muffle furnace. The temperature inside the muffle was controlled by a rheostat, a pyrometer and a chromel-alumel thermocouple encased in a protecting tube, the end of the metal junction being kept approximately one inch above the center of the muffle floor. The muffle floor was covered with a protecting layer of ground flint. The charged crucibles were placed in the muffle which was raised from room temperature to 1000° C. and held at that point for one hour in the cases of non-corrosive charges. In the cases of corrosive charges the temperature was maintained for as long a period as the crucible would withstand the action of the charge. None of the heating periods exceeded one hour. The types of crucibles described in (66) were used. (73)

Analytical Procedure No. 1 (49). The duplicate of each fusion mixture was treated in the manner described in Analytical Procedure No. 3 (51). Tin sulphides were not obtained in any of these tests.

(e) Results: The presence of tin was not detected in any of these tests. (75)

(2) Time-temperature draw trials - Series A (76)

(a) Samples I, II, III, IV, V, VI, VII were used in this series of tests. Each test was run in duplicate. (77)

(b) The charge consisted of a 5.0 gm. portion of sample mixed with 20 gms. of potassium cyanide. Two gms. of potassium cyanide were used as a cover for the charge. (78)

(c) -1- The electric muffle and temperature control unit described in (73) were used and the muffle rheostat was adjusted so that the inside temperature of the muffle rose from room temperature to 1150° C. in a period of about four hours. Large Coors porcelain crucibles were used to hold the charges. (79)

-2- The following procedure was used in making the draw trials: The muffle was filled with crucibles containing the charge of potassium cyanide and sample I. One crucible was removed at every 25° C. rise in temperature starting at 500° C. for the first crucible removed and ending at 1150° C. for the removal of the last crucible.* This procedure was repeated in duplicate using each of the samples listed in (77).

(d) The fusion mixtures obtained were each treated in the manner described in Analytical Procedures Nos. 2 and 4 (50) (52). One of each duplicate fusion mixture was analyzed by procedures described under Analytical Procedure No. 2 (50) and the concentrate analyzed according to Analytical Procedure No. 1 (49). The other duplicate was analyzed by the method described under Analytical Procedure No. 4 (52). Tin sulphides were not obtained. (80)

(e) Results: The presence of tin was not detected in any of these tests. (81)

(3) Time-temperature draw trials - Series B (82)

(a) (b) The same samples, charge compositions, and apparatus described in (77) (78) and (79) were used. (83) (84)

(c) The following procedure was used in making these draw trials: The muffle was filled with crucibles containing the charge of potassium cyanide and sample I. When the temperature of the muffle reached 500° C. one crucible was withdrawn from the muffle and the muffle rheostat was adjusted to hold the temperature of the inside of the muffle at 500° C. The remaining crucibles in the muffle were withdrawn at five-minute intervals over a period of one hour. This procedure was repeated at every 25° C. increase in temperature up to and including 1150° C. This procedure was repeated in duplicate for each sample from sample I through sample VII. (85)

(d) The fusion mixtures obtained were treated as described under draw trials Series A (80). (86)

(e) Results: The presence of tin was not detected in any of these tests. (87)

* The melting point of potassium cyanide is 634.5° C.; the melting point of metallic tin is 231.9° C. and its boiling point is 2260° C., below which temperature volatilization is negligible.

(4) Time-temperature draw trials - Series C (88)

(a) Duplicate portions of samples I, II, III, IV, V, VI, VII were used in these tests. (89)

(b) The charge consisted of a 5.0 gm. portion of sample mixed with 10 gms. of carbon and the mixture was placed in a Coors porcelain crucible and covered with 2 gms. of carbon. A porcelain crucible cover was placed on the crucible. (90)

(c) (d) The same apparatus, method of making the draw trials, and temperature conditions and treatment of the fusion mixtures were employed as described under (79) and (80). (91) (92)

(e) Results: The presence of tin was not detected in any of these tests. (93)

(5) Time-temperature draw trials - Series D (94)

(a) Duplicate portions of samples I, II, III, IV, V, VI, VII were used in these tests. (95)

(b) The same type of charge described in (90) was used. (96)

(c) The apparatus and experimental procedure were the same as described in (85). (97)

(d) The treatments of fusion mixtures were the same as described in (80). (98)

(e) Results: The presence of tin was not detected in any of these tests. (99)

c. Fusions in gas fired muffles (100)

(1) Sample, charcoal, sugar charges (101)

(a) Duplicate portions of samples I, II, III, IV, V, VI, VII were used. (102)

(b) The charge composition for this series of tests was 50 gms. of sample, 25 gms. of charcoal, and 25 gms. of a saturated solution of sugar in water.[17] The constituents of the charge were well mixed and the charge was placed in a fireclay crucible. A smaller crucible was inverted over the crucible containing the charge and the inverted crucible was forced down until it fitted as tightly as possible so as to form an air-tight cover. (103)

(c) The charged crucible was placed in the muffle of a gas fired assay furnace, the burners of which were adjusted to give maximum reducing conditions as evidenced by carbon deposition on the crucibles during the heat treatment. The charged crucibles were heated to a red heat and held at this temperature for twelve minutes. The fired crucibles were removed from the furnace and allowed to cool. (104)

(d) The charge was removed from the cooled crucible, ground in a mortar and panned.[4] One concentrate from each duplicate fusion was treated in the manner described in Analytical Procedure No. 1 (49). During the panning operation a considerable quantity of carbonaceous material floated to the top of the pan. This matter was filtered off during the panning process and combined with similar material obtained from the duplicate sample. The combined residues from these filtrations were dried and heated in hot mutton tallow for the purpose of coagulating small particles of tin if present. The tallow was decanted and the residue washed with an organic solvent and tested for the presence of (105)

tin by the procedure described in Analytical Procedure No. 1. The other concentrate from each duplicate fusion was tested according to Analytical Procedure No. 2 (50).

(e) Results: The presence of tin was not detected by any of these tests. (106)

(2) Potassium cyanide fusions (107)

(a) One or more portions of samples I, II, III, IV, V, VI, VII were used in this series of tests and a total of twenty-nine fusions was made. (108)

(b) The charge composition used in this series of tests was 2 gms. of potassium cyanide placed in the bottom of a fireclay crucible to which was then added a mixture composed of 20 gms. of potassium cyanide and 5 gms. of sample; 5 gms. of potassium cyanide were used as a cover. (109)

(c) Three different types of gas fired assay furnaces were used.[6] Atmospheric conditions within the furnaces, furnace temperatures, and periods of heating were varied. (110)

(d) After removal from the furnace and after being allowed to cool, each crucible was broken and the fusion mixture examined with the aid of a hand lens. The contents of each crucible including any adhering material was panned down and the concentrate was examined with the aid of a hand lens. The author did not participate in the manipulation of these tests except to weigh out the charge components and to check on the examination of the fusions after they were allowed to cool.[7] (111)

(e) Results: The presence of tin was not detected in any of these tests. (112)

4. Jack Rabbit furnace* fusion (113)

a. Description of furnaces (114)

Four different furnaces were used in these series of tests. Furnace No. 1 was constructed by the author as nearly as possible to agree with specifications given to him.[18] This furnace consisted essentially of a piece of 6-inch, iron pipe about 2 feet long into the top side of which, about midway of its length, a short piece of ½-inch pipe was introduced. One end of the 6-inch pipe was sealed with an iron cap; the other end left open.

(1) Furnace No. 1 was built to conform to the general specifications given above but with the following modifications: (1) the ½-inch pipe was placed at a point approximately 16 inches from the upper end of the body, (2) the upper end of the body was closed by a steel plate welded to the body, (3) the body of the furnace was mounted on legs so that it formed a vertical angle of about 45° and the bottom of the lower end of the body was approximately 6 inches from the base upon which the assembled unit was placed, (4) the body of the furnace was covered with a ½-inch layer of heat-insulating fiber which was held in place by a sheet metal cover and (5) several pieces of iron having different shapes and sizes were used to vary the character of the opening at the lower end of the body. (115)

(2) Furnace No. 2 was borrowed for the purpose of this investigation.[60] It was quite similar to No. 1, with the exception that it was slightly larger, had two feed pipes instead of one (one placed midway lengthwise of the furnace and the other half-way between the one so described and the upper end of the furnace), and the body of the furnace was set at an angle (116)

* Origin of terminology unknown.

of about 20°, instead of 45°, from the base.

(3) Furnace No. 3 was a smaller model of furnace no. 2. Its upper end cap was held on by clamps for easy removal. (117)

(4) Furnace No. 4 (Plate 4) was presented to the author.[60] This furnace was similar to furnace no. 3 and had the following specifications: The body of the furnace was a piece of iron tubing 6½ inches in length and 2 1/8 inches inside diameter. It was mounted on legs so that it was approximately horizontal. Two feed pipes were used; one was a standard 1 inch pipe coupling and was placed 1½ inches from the lower end of the body. The other was a standard half inch pipe coupling and was placed 5½ inches from the lower end of the body. Both feed pipes were displaced slightly from the normal; the smaller diameter pipe was displaced toward the lower end of the body and the larger diameter feed pipe was displaced toward the upper end of the body. (118)

b. Experimental procedure used with furnace no. 1 (119)

(1) Samples I, II, III, IV, V, VI, VII, IX were used. (120)

(2) Each sample was heated in duplicate runs without the use of flux and each sample was heated in duplicate with twice its weight of carbon. The charge consisted of one pound of rock or one pound of rock and carbon in equal proportions, both ground to 50-100 mesh particle size, in each case. (121)

(3) The furnace was heated by means of a large blast lamp placed in the opening at the lower end of the body of the furnace, fired with laboratory gas, and so adjusted as to use an excess of gas. The following different firing procedures were used: (1) charge placed in unheated furnace and the furnace brought to a barely visible red heat, (2) charge placed in unheated furnace, and furnace brought to a dull red heat, (3) charge placed in the unheated furnace and the furnace brought to a bright red heat, (4) charge placed in the furnace which had been preheated to a barely visible red heat and charge kept at that temperature for one hour, (5) conditions in "4" repeated and charge kept in furnace two hours, (6) charge placed in the furnace which had been brought to a dull red heat and "4" and "5" repeated. (122)

(4) Each heated charge was withdrawn from the furnace and panned down; the concentrates were examined with the aid of a binocular microscope and were then analyzed in the manner described in Analytical Procedure No. 1 (49). (123)

(5) Results: The presence of tin was not detected in any of these tests. (124)

c. Experimental procedures used with furnace no. 2 (125)

(1) The samples listed in (120) were used. (126)

(2) The following fluxes used were: carbon, sodium carbonate, calcium carbonate, calcium carbonate and charcoal, and sodium carbonate and charcoal; 200 gms. of sample used in each charge mixture. (127)

(3) The procedure described in (122) was used. (128)

(4) The fusion mixtures were treated by the procedures described in (123). (129)

(5) Results: The presence of tin was not detected in any of these tests. (130)

d. Experimental procedures used with furnace no. 3 (131)

(1) Duplicate portions of samples XI, XII, XIII were used. (132)

(2) The charge was 3 ounces of sample which had been crushed in a clean iron mortar to approximately 20-mesh size. (133)

(3) The closed end of the furnace was preheated in an open wood fire and then by blow torch.

(4) The sample charge was placed in the furnace through the feed pipe and the gasoline blast torch was placed at the open end of the body of the furnace. The flame was allowed to play on the inside of the body and on the charge. When the sample charge reached a red heat, approximately 20 grams of resin was added through the feed pipe and mixed with the sample by means of an iron spoon. The mixed charge was agitated at intervals so that all portions of charge reached a red heat. The flame was allowed partially to reflect from the wall of the furnace and partially to impinge directly onto the fusion mixture. (134)

At the end of the period of heating, the charge was scraped from the inside of the furnace and ground in the iron mortar until the entire charge passed through a screen of approximately 60-mesh. This ground charge was panned down, and the concentrates examined with the aid of a hand lens. The same procedure was repeated on several samples where resin was not employed. (135)

(5) Results: The presence of tin in any of the tests carried out by the author was not detected. (136)

e. Experimental procedures used with furnace no. 4 (137)

(1) Samples I, II, III, IV, V, VI, VII, IX, XI, XII, XIII, XIV, XV were used in these series of tests. (138)

(2) Each sample was heated in duplicate without the use of a flux, and each sample was heated in duplicate with each of the following fluxes; (a) charcoal, (b) borax, (c) calcium carbonate, (d) calcium carbonate plus charcoal, (e) borax plus charcoal, (f) sodium carbonate, (g) sodium carbonate plus charcoal, (h) resin. (139)

(3) The following different firing procedures were used: (a) charge placed in unheated furnace, then furnace temperature brought to a barely visible red heat and charge withdrawn from furnace, (b) condition "a" repeated and sample left in furnace at barely visible heat for periods of 10, 20, and 30 minutes before being withdrawn from furnace, (c) charge placed in unheated furnace and furnace brought to dull red heat, then charge withdrawn from furnace, (d) conditions in "c" repeated and charge left in furnace for periods of 10, 20, and 30 minutes before being withdrawn from furnace, (e) charge placed in unheated furnace, which was brought to bright red heat, and charge withdrawn from furnace, (f) conditions in "e" repeated and charge left in furnace for periods of 10, 20, and 30 minutes before being withdrawn from furnace. Furnace was heated by means of a gasoline blowtorch, the flame from which was allowed partially to reflect on the walls of the furnace and partially to impinge directly on the sample. Charges were stirred by means of an iron scraper during firings. Approximately 100 grams of sample ground to 50-100 mesh particle size were used per charge. (140)

(4) After being scraped from furnace and allowed to cool, each heated charge was panned down. The concentrates were examined with the aid of a binocular microscope and were then analyzed in the manner described in (141)

(5) Results: The presence of tin was not found in any of these tests. (142)

5. Fusions in closed systems (143)

Closed systems were employed to prevent the loss by diffusion or volatilization of any of the constituents of the sample or fusion mixture during the process of fusion. Two types of apparatus were employed--the so-called Whitton apparatus[122,123] and a Parr bomb.[124,68]

a. Whitton apparatus (144)

(1) The following samples were used in this series of tests: I, II, III, IV, V, VI, VII, VIII, IX. Duplicate charges were run. (145)

(2) The charges consisted of (1) sample without flux, (2) sample plus sodium carbonate, and (3) sample plus potassium carbonate plus sodium peroxide. Five grams of sample ground to 100-mesh particle size were used in each charge. (146)

(3) The Whitton apparatus used (Plate 3) was designed for the determination of mercury in ores by the distillation of the metal from the dry material by collecting the metal on a weighed metallic sheet. The apparatus consists of the following: (a) A stainless steel crucible, the approximate dimensions of which are 2" high and 1½" diameter and having a steel baffle at its top, holds the charge; (b) a 2½"-square sheet of pure silver is placed on the top of this crucible. The sheet is held in place by means of a (c) separate, flat-bottom, shallow, stainless steel crucible ---2" at base, 1" high and about 3" wide at the top. A short, quarter-inch rod, indented at the top, serving as a point of contact for the clamp screw, protrudes from the inside center base of the top crucible. The two crucibles and the silver plate are held in position by (d) a steel screw clamp, the arms of which fit under the baffle. The assembly is thus held together by tightening the screw of the clamp. (147)

(4) The following procedure was used: The charge was placed in the lower crucible, the units of the apparatus were assembled in their proper order and securely clamped in place. The lower crucible was inserted in a circular opening in an asbestos board just large enough for the crucible to fit tightly and protrude about half of its height below the board. The board plus assembly was placed on a ring stand. The upper crucible was kept filled with water throughout the heating period and during the period when the assembly was being cooled. A Meker burner was placed beneath the lower crucible which was heated with the full flame of the burner for thirty minutes. (148)

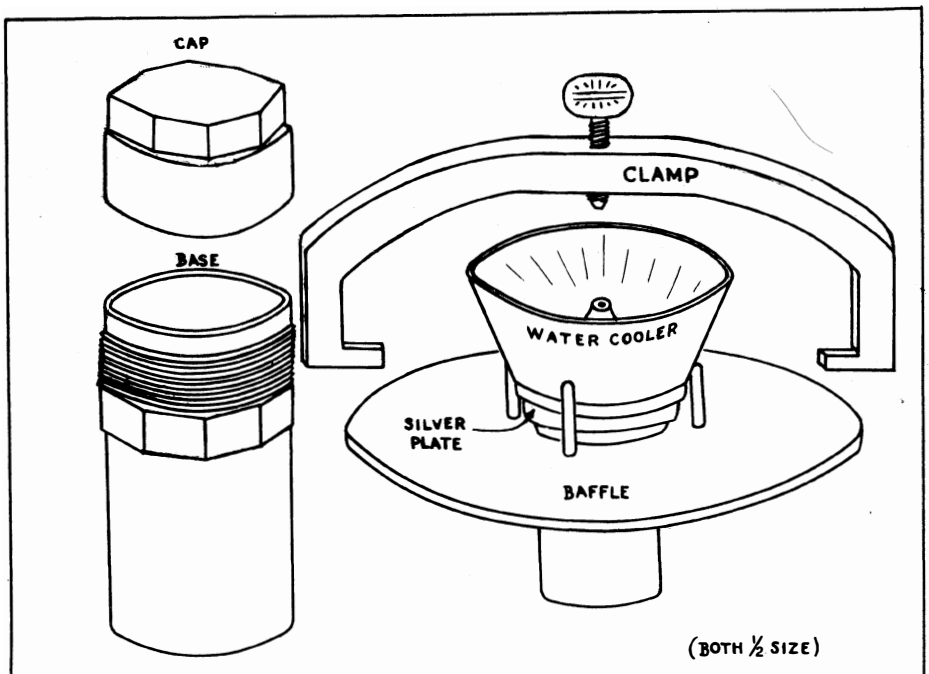
(5) After cooling the charge was placed in a beaker. The inside of the lower crucible and the silver foil were washed with hydrochloric acid-sulphuric acid mixture by means of carefully scrubbing with a rubber policeman, and these washings were added to the beaker. The contents of the beaker were then tested by the method described in Analytical Procedure No. 1 (49). Analytical Procedure No. 3 (51) was not used because tin sulphides were not obtained. (149)

(6) Results: The presence of tin was not detected in any of these tests. (150)

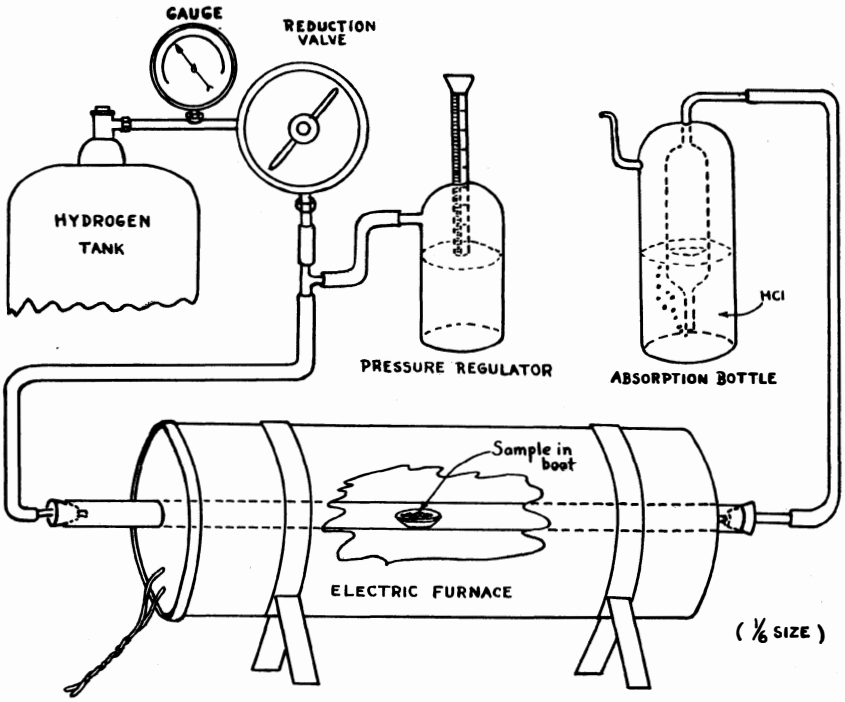
b. Parr bomb (151)

(1) The following samples were used in this series of tests: I, II, III, IV, V, VI, VII, IX. Duplicate charges were run. (152)

(2) The charges consisted of -a- sample without flux, -b- sample plus (153)



PARR BOMB WHITTON APPARATUS

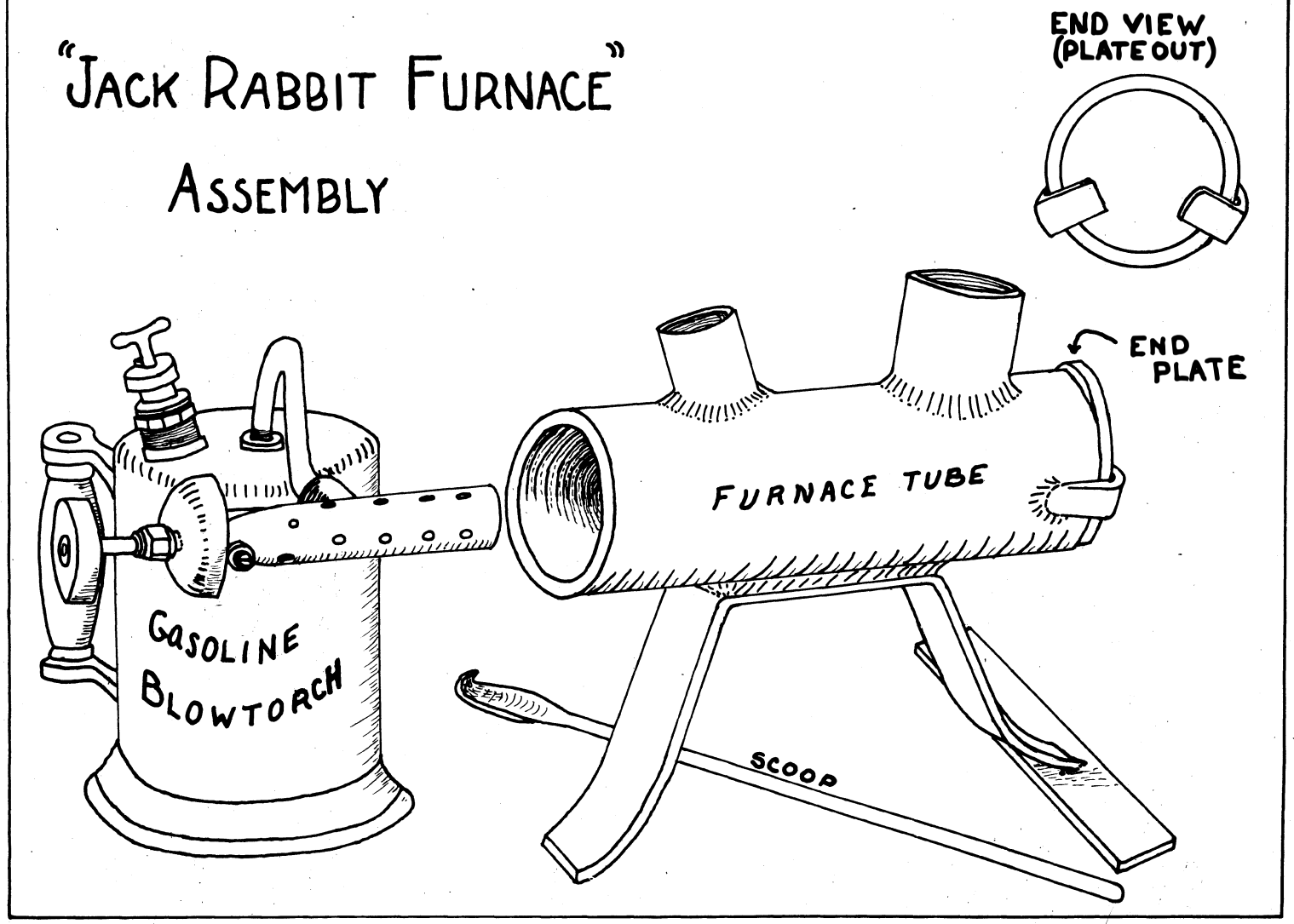


HYDROGEN REDUCTION APPARATUS

PLATE IV

"JACK RABBIT FURNACE"

ASSEMBLY



carbon, -c- sample, carbon, sodium peroxide, potassium perchlorate, -d- sample, sodium peroxide and -e- potassium perchlorate. A 5.0 gm. portion of each sample was used in each charge.

(3) The Parr bomb (Plate 3) used was designed for use in determination of the heating value of carbonaceous material. The bomb consists of a cylinder of heavy alloy-steel tubing, threaded on the outside of the open end and lined with a chemical-resisting metallic shell. The bomb was approximately 4" high and 2" in diameter. An octagon-shaped steel band was fastened on the outside of the cylinder just below the threads. A solid cap with octagon-shaped sides, slightly larger in diameter than the bomb and having threads to match the threading on the bomb, was screwed to the top of the bomb. Special wrenches which are constructed to fit the octagons on the top and on the bomb were used to fasten the top securely to the bomb. A rubber or asbestos gasket depending upon the condition of the experiment was used between the top and the bomb. (154)

(4) The following procedure was used: The charge was placed in the bomb and, after securely fastening the cover, the bomb was placed in a circular opening in an asbestos board just large enough to allow the lower half of the bomb to protrude below the bottom of the asbestos board. The assembly was placed on a ring stand. The lower end of the bomb was heated by means of the flame of a bunsen burner until (a) the ignition took place within the bomb as evidenced by a sudden rise in temperature of the bomb, or (b) in cases where no ignition took place within the bomb, the bomb was brought to a dull red heat and kept at that temperature for fifteen minutes. (155)

(5) After allowing to cool, the contents of the bomb were placed in a beaker. The inside of the bomb and the inside of the bomb cover were washed with a hydrochloric acid-sulphuric acid mixture by carefully scrubbing with a rubber policeman, and the washings were added to the beaker containing the charge. The contents of the beaker were tested by Analytical Procedures Nos. 1 (49) and 2 (50). Analytical Procedure No. 3 (51) was not used because tin sulphides were not obtained. (156)

(6) Results: The presence of tin was not detected in any of these tests. (157)

6. Wood fire roasting (158)

a. Samples number I, II, III, IV, V, VI, VII, IX, XI, XII, XIII, XIV, XV were used in these series of tests. (159)

b. Procedure was as follows for each sample: A sheet of iron 4 feet square was placed on the ground and a brush fire ignited on top. Brush was added until a bed of coals approximately 10" thick was obtained. Then pieces of sample ranging in size from 1/8" in diameter to 6" in diameter were placed on top of the coals. More brush was added, and after a layer of coals was formed on top of the rock, another layer of rock was added and more brush placed on top. This procedure was repeated until the mass was four layers high. The fire then was heaped with brush and allowed to burn. After cooling, pieces of rock were removed from the fire after which the ashes were cooled and saved for testing. (160)

c. Treatment of roasted rock and ashes (161)

(1) (a) Much of the roasted rock had a brownish, sub-metallic luster. Samples were crushed to approximately 10-mesh size, a representative portion was placed in an iron mortar and ground to approximately 80 to 100 mesh. This was examined with the aid of a binocular microscope (162)

and then panned down. The concentrate was examined with the aid of a binocular microscope and was then tested by Analytical Procedure No. 1 (49). Analytical Procedure No. 3 (51) was not used because tin sulphides were not obtained.

(b) Representative 10 gm. portions of each roasted sample were heated in an iron crucible with mutton tallow to coagulate any small particles of metallic tin. The hot tallow was decanted and the residue washed with organic solvents. The washed residue was examined with the aid of a binocular microscope; and the concentrates, after visual examination, were treated in the manner described in Analytical Procedure No. 1 (49). Analytical Procedure No. 3 (51) was not used because tin sulphides were not obtained.

(c) Representative 10 gm. portions of each roasted sample were subjected to the electro-thermal action of a carbon arc. In the arc procedure each sample was used (1) alone, (2) with potassium hydroxide, (3) with sodium carbonate, and (4) with borax.

(2) Testing of ashes obtained from wood fire roasting: Portions of each sample of ashes were treated by the procedures described under treatment of roasted rock (162). (163)

d. Results: The presence of tin was not detected in any of these tests. (164)

7. Flotation experiments (165)

a. Portions of samples I, II, III, IV, V, VI, VII, XI, XII, XIII, XIV, and XV which had been roasted in the manner described under (160), samples of the ashes from the wood fires used in the roasting procedures (160), and samples of the unroasted rock were used for the oil flotation tests. (166)

b. Standard oil flotation procedures used in the flotation of cassiterite from the silicate gangue by the use of fatty acids, soaps and sodium silicate were employed.[11] (167)

c. (1) Portions of each float concentrate and each float residue was examined by the methods described under Analytical Procedures Nos. 1 (49) and 2 (50). Analytical Procedure No. 3 (51) was not used because sulphides were not obtained. (168)

(2) Portions of each float concentrate and each float residue were subjected to the electro-thermal action of the carbon arc. Each was placed in the arc alone and with the following fluxes (a) potassium hydroxide, (b) sodium carbonate, (c) borax, and (d) powdered graphite. The resulting fusion mixtures were examined in the manner described in (168). (168-a)

d. Results: The presence of tin was not detected in any of these tests. (169)

8. Table concentration experiments[31] (170)

a. Samples I, V, and VII were used. (171)

b. Separate portions of each of these samples were treated on a laboratory model concentrating table[65] and the concentrates, middlings, and tailings were examined for the presence or absence of tin or tin compounds. (172)

c. The concentrates, middlings and tailings were each tested by Analytical Procedures Nos. 1 (49) and 2 (50). Analytical Procedure No. 3 (51) was not used because tin sulphides were not obtained. (173)

No visible gravity separations could be detected as a result of the tabling.

d. Results: The presence of tin was not detected in any of these tests. (174)

9. Electromagnetic separation experiments (175)

a. Portions of samples I, II, III, IV, V, VI, and VII were used. (176)

b. The samples were passed through a standard, laboratory size electromagnetic separator[31] and the resulting fractions were examined for the presence or absence of tin or tin compounds. (177)

c. A portion of each fraction obtained was crushed to 100 mesh and examined according to Analytical Procedures Nos. 1 (49) and 2 (50). Analytical Procedure No. 3 was not used because tin sulphides were not obtained. (178)

d. Results: The presence of tin was not detected in any of these tests. (179)

10. Electrostatic separation experiments (180)

a. Portions of samples I, II, III, IV, V, and VII were used. (181)

b. The samples were passed through a standard, laboratory size electrostatic separator[31] and the resulting fractions were examined for the presence or absence of tin or tin compounds. (182)

c. A portion of each fraction obtained was crushed to 100 mesh and examined by Analytical Procedures Nos. 1 (49) and 2 (50). Analytical Procedure No. 3 (51) was not used because tin sulphides were not obtained. (183)

d. Results: The presence of tin was not detected in any of these tests. (184)

11. Digestion of samples with caustic soda solution (185)

a. Samples I, II, III, IV, V, VI, VII, XI, XII, XIII, XIV and XV were run in duplicate. (186)

b. A twenty gram portion of each sample was treated in the following manner: "Cook three hours in a strong solution of caustic soda. Filter, wash, dilute, make slightly acidic with nitric acid and evaporate to dryness--take up in boiling water several times to get rid of all sodium nitrate. Test remaining white precipitate for tin oxide."[67] (187)

c. The residue remaining after the above treatment were tested by blow-pipe fusions using potassium cyanide-litharge flux and cacotheline as the test reagent.[49] (188)

d. Results: The presence of tin was not detected in any of these tests. (189)

12. Hydrogen reduction (190)

a. Samples I, II, III, IV, V, VI, VII, and X were run in duplicate. A portion of sample I to which stannic oxide had been intentionally added was run as a control. (191)

b. The apparatus used for the hydrogen reduction was similar to that used for the reduction of organic compounds. A typical set-up of this type of apparatus is shown in plate 3. The assembled apparatus consisted of a tank of compressed hydrogen fitted with a regulating valve. The rate of flow of the gas stream was controlled by means of a pressure regulator. The samples were placed in porcelain boats which were set inside of a mullite combustion tube. The latter was placed inside of an electric combustion furnace whose temperature was regulated by means of a rheostat. A stopper in the inlet end of the combustion tube contained a glass tube through which the hydrogen and the thermocouple entered. The inside temperature of the combustion tube was measured by means of a chromel-alumel thermocouple and a pyrometer. A gas washing (192)

bottle containing hydrochloric acid was placed on the exit end of the combustion tube.

c. After placing the boat containing the sample inside of the cold combustion tube the individual units of the assembly were connected and hydrogen gas was allowed to flow through the assembly. When the air had been displaced from the assembly the temperature of the combustion tube was brought to 960°C. and kept at this temperature for one hour. Then the furnace was cooled without interrupting the flow of hydrogen gas. (193)

d. The cooled samples were analyzed for the presence of tin according to Analytical Procedure No. 1 (49). The contents of the gas washing bottle was analyzed by reduction with metallic magnesium and the reduced solution tested by means of cacotheline. (193-a)

e. Results: Only that sample to which tin had been intentionally added as a control showed the presence of tin. (194)

13. Thermit reactions (195)

a. Theory (195-a)

Goldschmidt's "thermit" process for the reduction of a metallic oxide to the metal depends upon the great evolution of heat resulting from the combination of aluminum with oxygen. This process was developed specifically for the reduction of iron oxides but has also been used for the reduction of difficultly reducible oxides. Fink and Mantell have studied the application of the "thermit" reaction to tin concentrates.

Essentially the reaction is:

$$3\ SnO_2 + 4\ Al = 3\ Sn + 2\ Al_2O_3 + \text{heat}.$$

When the reduction is performed using metallic aluminum the oxide is aluminothermically reduced and when the reduction is performed with metallic magnesium the oxide is magnesiothermically reduced.

A comparison of the thermodynamics of the iron oxide and the stannic oxide reductions shows that the two reactions have nearly the same order of magnitude.

$$Sn + O_2 = SnO_2 + 141{,}300 \text{ calories.}$$
$$2\ Fe + 3/2\ O_2 = Fe_2O_3 + 195{,}000 \text{ calories.}$$
$$3\ SnO_2 + 4\ Al = 3\ Sn + 2\ Al_2O_3 + 361{,}000 \text{ calories.}$$
$$2\ Fe_2O_3 + 4\ Al = 4\ Fe + 2\ Al_2O_3 + 394{,}000 \text{ calories.}$$

b. Samples I, III and VII were run in duplicate. (196)

c. Portions of each sample were subjected to aluminothermal reduction and also to magnesiothermal reduction. (197)

(1) The aluminothermal reduction experiments were performed by preparing a mixture composed of equal weights of sample and powdered aluminum. Each mixture was placed in a crucible and a cartridge of magnesium powder was placed in a depression in the mixture. The cartridge was kindled by a small piece of magnesium ribbon.

(2) The magnesiothermal reactions were performed in the same manner as the aluminothermal reactions except that the aluminum powder was replaced by magnesium powder.

Each fusion mixture was treated in the manner described in Analytical Procedure No. 1 (49).

d. Results: The presence of tin was not detected in any of these tests. (198)

B. Quantitative chemical analyses (199)

1. Standard analytical procedures (200)

The following procedures were investigated to determine the best analytical procedure to use in the quantitative chemical determination of tin.

a. Pierce-Low method[125] (201)

This method has been applied to nearly all grades and types of tin ores and gives excellent results when the procedures are closely followed. Appreciable amounts of copper, molybdenum, vanadium, and oxidizing agents may cause erroneous results. Spectrographic analysis of Juniper Ridge samples showed that these interfering elements, when present, were in negligible quantities. Solution of the tin is obtained by an alkaline-sodium peroxide fusion. In some instances the peroxide is replaced by carbon. After allowing to cool the fused sample is put into solution by means of hydrochloric acid, care being taken to include all of the fused material left in the fusion crucible. The solution and any undissolved material is placed in an Erlenmeyer flask, the acidity is adjusted, volume of solution is adjusted, a reducing agent is added, and digestion carried on for a stated length of time. The reduced solution is titrated with a standard solution of iodine using starch indicator. The titration is carried on in a non-reducing atmosphere of carbon dioxide, and an indicator blank is run.

b. Hillebrand and Lundell method[126] (202)

This method is very similar to the Pierce-Low method except that a stream of carbon dioxide is bubbled through the solution during the reduction and the titration, and the reduction is carried out by means of test lead.

c. The cyanide method[87,88] (203)

This method depends upon the reduction of tin oxide to the metal by the action of potassium cyanide. The tin is obtained in the fusion product in the form of a metallic button which is then analyzed for content of tin using one of the volumetric procedures.

2. Analytical procedure used (204)

An iodine solution was prepared and standardized using arsenious oxide as the primary standard and starch as the indicator. The tin titre of the iodine solution was checked with standard solutions of tin prepared by dissolving a weighed quantity of tin in hydrochloric acid and diluting to a definite volume in a volumetric flask. Aliquot portions of this solution were used to check the standardization of the iodine solution. The Hillebrand and Lundell modification of the Pierce-Low volumetric method was used to analyze the standard solutions of tin.

a. (1) Two different samples of cassiterite were analyzed by this procedure. (205)
Results of analysis: 78.0% tin and 76.1% tin.

(2) Duplicate samples of a mixture of sample I and SnO_2 added in such proportions that the mixture contained 1.00% SnO_2 were analyzed by the above procedure. Results of analysis 1.02% tin and 0.96% tin.

(3) Duplicate samples of Juniper Ridge rock samples I, II, III, IV, V, VI, VII, VIII, and IX were analyzed by the above procedure.

c. Results of analysis: (206)

Sample	1	2
I	0.000% Sn	0.000% Sn
II	0.000% Sn	0.001% Sn
III	0.001% Sn	0.003% Sn
IV	0.001% Sn	0.001% Sn
V	0.005% Sn	0.002% Sn
VI	0.000% Sn	0.000% Sn
VII	0.001% Sn	0.003% Sn
VIII	0.003% Sn	0.003% Sn
IX	0.003% Sn	0.002% Sn

3. Check on cyanide procedure (207)

Shot-tin was thoroughly mixed with portions of Juniper Ridge rock which had been ground to 100 mesh. Samples I, II, and III were used. The tin concentration of each mixture was 20.00% added tin and these mixtures were analyzed by the cyanide fusion method in the following manner. Ten grams of each mixture were mixed with 20 grams of potassium cyanide. A small fireclay crucible was used for the fusion and its bottom was covered with 2 grams of potassium cyanide. The mixture of potassium cyanide and sample was placed on top of the potassium cyanide layer; the charge was covered with 3 grams of potassium cyanide capping and the crucible was covered. The crucible containing the charge was heated in an electric muffle to 900° C. and kept at that temperature for thirty minutes. Each button was removed from the cooled charge and analyzed by the volumetric procedure as previously described (204). Results of analysis: Sample I, 18.26% tin, sample II, 18.2% tin, and sample III, 17.88% tin. These represent tin recoveries by this method of 91.3%, 91.0%, and 89.4% respectively. These are not unsatisfactory recoveries for high concentrations of this metal when assayed by fire methods. Such recovery applied to a 2.00% tin ore would give a range of 1.82% to 1.78%. Therefore, a commercial tin ore even of marginal grade would be determined with satisfactory accuracy by this method.

The cyanide fusion method of tin analysis applied to the samples of Juniper Ridge rock failed to recover a metallic button from any of the fusion melts.

C. Spectrochemical analysis (208)

1. Experiments performed at the New York State College of Ceramics, Alfred, New York (209)

a. Two samples of Juniper Ridge rock were sent to the author at the New York State College of Ceramics.[56] One sample was unnumbered and consisted of pieces of rock approximately 1/16" in size, the sample weighing approximately six pounds. A representative portion of this sample was ground to 100 mesh size and used for analysis. The other sample was numbered K-29 (X) and consisted of about two ounces of powder of 100 mesh size. The K-29 sample (X) was thoroughly mixed and divided into three equal parts. One part was held for analysis and the two remaining parts were sent to two different spectrographic laboratories for check analysis. (210)

b. The spectrographic laboratory at the New York State College of Ceramics is equipped with a large Littrow-model quartz spectrograph manufactured by the Bausch and Lomb Optical Company.[5] A projection enlarger, a spectrum measuring magnifier,[127] and a microscope with an eyepiece with a fixed scale were used to study the spectrograms. A photoelectric density-comparator was used to measure spectrum line densities. A motor-generator set was used to furnish d.c. voltage for the arc. "Spec-Pure" Acheson graphite electrodes and Hilger copper electrodes, laboratory no. 10,300 were used as electrodes for the d.c. (211)

arc. C.p. stannic oxide and c.p. shot-tin were used to produce reference spectrograms of tin. Every spectrum was photographed in juxtaposition with the spectrum of pure iron. Hilger iron rods, laboratory no. 8038, were used to furnish the iron spectrum.

c. D.c. arc excitation was used and every sample was burned to completion. (212)
Graphite electrodes of the following sizes were used: 5/16", 4/16", 3/16", and 2/16". Three-sixteenth in. in diameter copper rods were also used as electrodes. The spectrum range from 2300A to 5000A was studied. Eastman 33, Eastman Process and Eastman PanProcess plates were used depending upon the spectrum region under investigation. The wavelengths of the lines in the spectrograms were measured with reference to known iron lines in the spectrum of pure iron and also with reference to known iron lines in the spectrograms under investigation thus taking advantage of an internal standard. Line measurements were made on the projected image of the spectrograms and also by means of a microscope with a calibrated eyepiece. Wavelength measurements were accurate to 0.05A. Each of the above listed graphite electrodes were used to hold the sample for each of the analytical methods used. Samples varied in size from 10 mg. to 100 mg. depending upon the size of the electrodes used. The sample was held in the cup made in the end of an electrode. A special cutting tool enables cups of known depth, uniform wall thickness and flat-topped end to be obtained. The upper electrode was pointed.

(1) Qualitative spectrochemical analysis (213)

Methods used to produce spectra.

1. D.c. arc using sample alone in lower carbon which was made positive. (213-a)
Repeated with (a) mixture of sample and graphite dust,[48,43] (b) mixture of sample and sodium carbonate,[58] and (c) mixture of sample and ammonium nitrate.[43]

2. D.c. arc sample in lower carbon which was made negative. Repeated using mixtures listed in (213-a).

3. Cathode layer method[72] using sample alone. Repeated using mixtures listed in (213-a).

4. Fractionating electrodes[38] using sample alone. Repeated using mixtures listed in (213-a). The electrode holding the sample was made positive in one series of tests and was made negative in another series of tests.

5. High streaming velocity arc[39] using the sample alone. Repeated using mixtures listed in (213-a). The electrode holding the sample was made positive in one series of tests and was made negative in another series of tests.

6. Duplicate portions of unnumbered sample and sample K-29 (X) were analyzed using Hilger copper electrodes, laboratory no. 10,300. Arc conditions were 110 volts - 5 amps., 3 mm. electrode gap, and sample was burned to completion.

Each procedure, where graphite electrodes were used, was carried out under the following different arc conditions: (a) 110 volts - 3 amps., (b) 110 volts - 6 amps., (c) 150 volts - 12 amps., (d) 3 mm. electrode gap, a rotating sector was used between the arc and the slit of the spectrograph to avoid excess background on the photographic plate.

The following spectrum lines were used for the identification and estimation of tin: (214)

2345.84[75,41]

2429.50[75,129,41,12]

2546.55[75,41,12]

2661.25[75,41,12]

2706.50[75,130,129,41,69,12]

2839.989[36,72,75,130,129,41,30,131,53,132,12,133]

2863.327[36,15,25,75,130,129,41,30,29,131,53,132,12,133]

3009.147[36,75,129,41,30,131,69,53,132,12]

3032.8[15,41,12]

3034.121[36,72,75,129,41,30,131,69,53,132,12]

3175.019[36,72,15,75,130,129,41,30,131,69,53,132,12,133]

3262.328[36,15,25,75,130,129,41,30,131,53,132,12,133,29]

3330.6[15,75,130,129,41,69,53,12]

3801.0[130,129,41,53,76,12]

4524.741[36,130,129,41,53,132,76,12]

Tests were run independently by two different operators.

(a) Results of analysis (215)

The unnumbered sample and K-29 sample (X) were found to contain approximately 0.001% of tin.

(2) Quantitative spectrochemical analysis (216)

A series of standard samples were made using a basic compound composed of 100 parts alumina and 25 parts anhydrous silicic acid[128] as the matrix and stannic oxide as the source of tin. The standards contained the following concentrations of tin: 5.0%, 3.0%, 1.0%, 0.5%, 0.1%, 0.05%, 0.01%, 0.005%, 0.001%, and 0.0005%. The procedure used for the spectrographic analysis of enamel frits was used.[127] One-one thousandth percent of tin could be detected using the standards.

(a) Results of analysis (217)

The unnumbered sample and sample K-29 (X) contained approximately 0.005% to 0.001% tin.

2. Experiments performed at the Portland office of the Oregon State Department of Geology and Mineral Industries (218)

a. Duplicate portions of samples I, II, III, IV, V, VI, VII, VIII, and IX were used. (219)

b. The spectrographic laboratory of the Oregon State Department of Geology and Mineral Industries is equipped with a 3-meter grating spectrograph manufactured by Baird Associates. A projection enlarger, a spectrum measuring magnifier,[127] and a binocular microscope equipped with eyepiece scales were used to study the spectrograms. A Gaertner microdensitometer[134] was used to measure spectrum line densities. A motor-generator set was used to furnish d.c. voltage. "Spec-Pure" Acheson Graphite electrodes were used for analysis, (220)

and Hilger iron rods, laboratory no. 6038, were used to furnish iron spectra.

c. D.c. excitation was used and all samples were burned to completion. The spectrum range 2150A to 5500A was investigated. Eastman 33, Eastman Process, and Eastman PanProcess plates were used depending upon the portion of the spectrum under investigation. The same type of graphite electrodes and the analytical procedures described under (212) (213-a) (216). (221)

d. Results of analysis: All of the Juniper Ridge rock samples analyzed showed the presence of slight traces of tin, ranging in concentrations of between 0.005% and 0.001%. (222)

CONCLUSIONS

1. Qualitative chemical procedures, which were found to give positive tests with standard samples of Juniper Ridge rock to which metallic tin or compounds of tin had been intentionally added, failed to detect the presence of tin or its compounds in the Juniper Ridge rock samples submitted for analysis. These tests show that Juniper Ridge rock samples analyzed do not contain tin or tin compounds in concentrations as high as 0.1% tin. (223)

2. Quantitative chemical procedures, which had given satisfactory results when used to analyze standard samples of Juniper Ridge rock to which metallic tin or compounds of tin had been intentionally added, failed to show the presence of tin or tin compounds in the Juniper Ridge rock samples submitted for analysis to be present in concentrations greater than 0.005%. (224)

3. Spectrochemical analysis showed the concentration of tin or tin compounds in Juniper Ridge rock samples submitted for analysis to be from 0.005% to 0.001% tin. (225)

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CHAPTER V

SUMMARY AND CONCLUSIONS

A. Cassiterite and, to a very minor extent, stannite are the tin-bearing minerals in all the 340-odd properties which have in the past or are still producing commercial tin throughout the world. These minerals were neither seen nor found in Juniper Ridge samples. (226)

B. None of the other fifty-six minerals listed by various authorities, as containing tin as an essential or accessory constituent, was identified in Juniper Ridge rock. (227)

C. Recorded occurrences of tin throughout the world show them to occur as deposits either in or associated with well-defined pegmatites, high-temperature or replacement veins and contact metamorphic deposits, usually within or adjacent to granitoid rocks. They also occur in placers derived from such deposits. This association with granitic rocks or vein systems appears to be universal. At Juniper Ridge, there is no granite rock nor is there any sign of hydrothermal or metasomatic activity, always associated with the above types of mineralization. (228)

D. Qualitative chemical procedures which were found to give positive tests with standard samples of Juniper Ridge rock to which metallic tin or compounds of tin had been added failed to detect the presence of tin or its compounds in the Juniper Ridge rock samples analyzed. These tests show that Juniper Ridge rock does not contain tin or tin compounds in concentrations as high as 0.1% tin. (229)

E. Quantitative chemical procedures which had given satisfactory results when used to analyze standard samples of Juniper Ridge rock to which metallic tin or compounds of tin had been added failed to show the presence of tin or tin compounds in Juniper Ridge rock samples analyzed in concentrations greater than .005% tin. (230)

F. Spectrographic analysis showed the concentration of tin in Juniper Ridge rock samples analyzed to be from one thousandth to five thousandth of one percent (0.001% to 0.005%) tin; which generally conforms to percentages of tin occurring in many similar acid igneous rocks throughout the world. Commercial lode tin ore, as in the Bolivian tin deposits, averages from one to three percent tin; in Cornwall, one to three percent; and in Tasmania, two to three percent (Lindgren,28:657, 737, 741). (231)

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