OXIDATION PHENOMENA OF THE CORNISH LODES

by K. F. G. HOSKING, M.Sc.

INTRODUCTION

In this paper, the author has attempted to bring to the forefront those oxidation features of the Cornish lodes which are of unusual interest, rather than to describe yet again oxidation phenomena which are common to many other deposits of the world. In order, however, to put the reader "in the picture" he has given a brief outline of the mechanism of oxidation and allied sulphide enrichment, and has incorporated as an appendix a series of diagrams which indicate some of the mineralogical changes which take place. He has not included a list of the secondary lode minerals to be found in Cornwall as these appear in the Mineral Index published recently by this Society. (1)

He has generally avoided the use of chemical equations because the course of most of the reactions involved are as yet imperfectly understood.

Finally he has dealt with the oxidation of wolfram which has unavoidably led him away from the lodes and into the field of alluvial geology.

GENERAL PRINCIPLES

The process of oxidation takes place largely in that portion of a lode which is above the water-table, and results in the breakdown of the chemically reactive minerals there, followed by re-arrangement of the liberated ions and recombination amongst themselves, and also, in some cases, with ions introduced from extraneous sources.

Some or all of the following materials may occur in the oxidised portion of a lode :—

(a) Primary insoluble minerals (that is, insoluble as far as the available attacking solutions are concerned), such as quartz, cassiterite and gold.

(b) Insoluble oxides, oxy-salts and metals, produced as a result of chemical action, and which fall under the following major headings :—

(i) Oxides (notably limonite).
(ii) Carbonates, e.g. malachite and azurite.
(iii) Phosphates, e.g. vivianite.
(iv) Sulphates, e.g. anglesite.
(v) Arsenates, e.g. scorodite.
(vi) Chlorides, e.g. cerargyrite.
(vii) Silicates, e.g. chrysocolla.
(viii) Elements, e.g. native copper and silver.

Many of the so-called insolubles found in the oxidised zone are capable of solution under certain circumstances, and the top of a well-developed oxidised lode frequently carries only limonite and quartz.

(c) Kernels of primary, soluble ore which have escaped oxidation, sometimes because they have been surrounded by a protective coating of secondary insoluble material.
(d) Solutions of soluble salts, notably copper and ferric sulphates.
(e) Rarely, secondary sulphides derived from alteration of oxy-salts, e.g. pseudomorphs of galena after pyromorphite.

The process of oxidation is commenced by the oxidation of sulphides to sulphates by actively circulating oxygenated water, and in the process sulphuric acid and ferric sulphate are developed, which are important corrosive agents as far as sulphides generally are concerned. Of the two, the latter is usually the more powerful.

The rate at which a given mineral is dissolved depends also on the minerals with which it is associated, and when two different sulphides are in contact, the one goes into solution quicker, and the other slower, than if either of them were being attacked alone. This acceleration of reaction is connected with the generation of electric currents which appear when minerals of different potentials are brought into contact : the current flows from the mineral of the higher potential to the lower, and the latter is dissolved more rapidly than if it were being attacked alone.

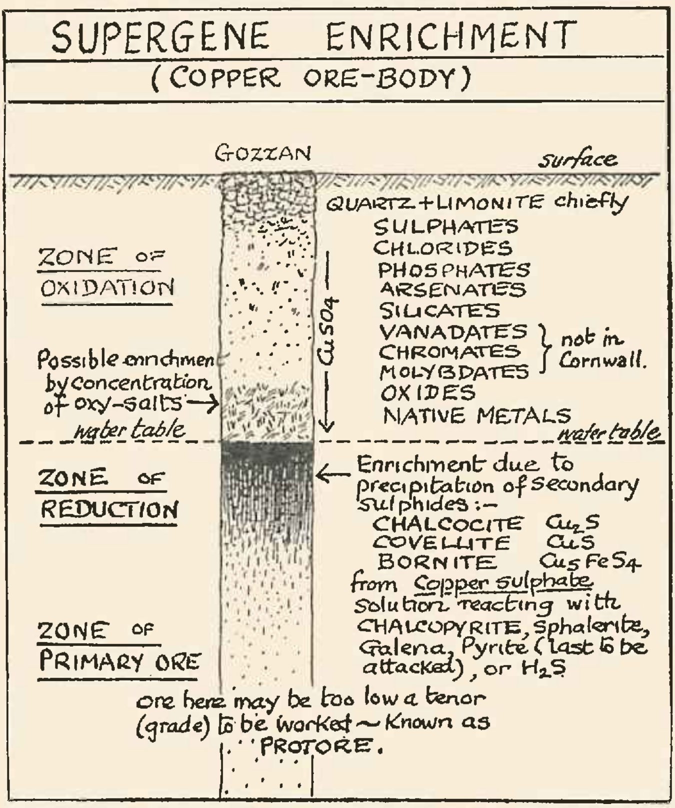
Having converted the sulphides to sulphates, which are generally soluble, a complete re-organisation of the primary lode pattern takes place. The sulphate solutions, by reacting between themselves and with reactive solids and with solutions from extraneous sources, produce the secondary insolubles mentioned above, and in so doing, frequently bring about, especially in the case of copper and silver lodes, locally-rich concentrations of ore.

Some of the solution produced in the oxidised zone migrates down below the water-table where reducing conditions are encountered. Here the water is almost stagnant, and, as a result of reaction with the wall-rock minerals, is alkaline. In this region, sulphate solutions migrating down from the zone of oxidation, replace primary sulphides by secondary sulphides, in accordance with the principles deduced by Schuermann.

Though it is known that secondary sulphides of silver, lead and zinc, can be produced in the zone of reduction, no enrichment of economic importance of these elements is known which has been brought about as a result of this. On the other hand, markedly rich bodies of secondary copper sulphides (usually chalcocite or bornite) are frequently produced in the zones of reduction of copper ore bodies.

These deposits of secondary copper sulphides are only of limited vertical extent and peter out gradually or sharply in depth, depending on the reactivity of the sulphides being replaced, their place being taken by primary sulphides which usually constitute a considerably lower grade of ore. In Cornwall, the extent of the secondary sulphide zone in copper lodes has been very variable and was most highly developed in the St. Just mines. On the other hand, at Tresavean (Lanner, Redruth), for example, very little secondary sulphide was encountered. These differences are, of course, largely due to the varying quantities of copper minerals which have undergone oxidation in the various areas, but other factors are also of importance. Thus, if the wall-rock in the zone of oxidation is chemically very reactive, most of the copper will be fixed in that zone ; also, the more chemically stable and insoluble the products of the oxidised zone, the less ready are they to liberate soluble copper. It is clear, then, that reactive wall-rock and stable, insoluble oxidation products, will result in the copper enrichment being found almost entirely in the oxidised zone.

Besides valuable deposits of secondary copper sulphides, valuable ore-bodies consisting of oxidation products of copper ore (i.e. oxides, oxy-salts and metal) have been encountered in Cornwall, and some of the best examples occurred in the Caradon Mines (Liskeard area). Collins has given the following description of the ore of South Caradon, which occurs in lodes in the granite :— "Near the surface the lodes contained much limonite, often in a cellular condition (gozzan), melaconite, cuprite, malachite, chessylite, native copper (a little), together with quartz and kaolin ; lower down, copper sulphides, such as chalcoite, bornite and chalcopyrite, with pyrite and mispickel, made their appearance, as also considerable quantities of chlorite and fluorspar." (2)



The foregoing constitutes a typical example of considerably oxidised copper lodes, and clearly indicates the presence of a zone of gozzan, a zone of copper oxy-salts, a zone of secondary sulphides and a zone of primary sulphides.

Valuable deposits of silver occurring both as the chloride and the native metal have also been formed by oxidation processes in some Cornish lodes. The majority of these secondary silver deposits have been derived from argentiferous galena, though some have doubtless been derived from argentite, pyrargyrite and proustite.

One of the most well-known examples of this type was found at the Perran Silver Mine where the gozzan was highly charged with crystals of cerargyrite (Ag Cl), and as some argentiferous galena was encountered, the cerargyrite was probably derived from it. (3)

It is probable that a fair amount of the native silver encountered in Cornwall is primary, and in several cases primary silver has been found in a late lode where it intersected an older copper lode, and in a manner suggesting that the copper minerals acted as precipitants of the silver. Deposits of this type were found at Wheal Herland (4), Wheal Brothers (5), and Newton and Queen Mine. (6)

OTHER CHARACTERISTICS OF OXIDATION ASSOCIATED WITH THE CORNISH LODES

When the oxidised portions of Cornish lodes are considered, the following three characteristics are noted :—

(1) The considerable depth of the oxidation zone.

(2) The great variety of minerals frequently encountered in the oxidation zone.

(3) The varying influence of different kinds of country rock on the degree of oxidation and the variety of "oxidation minerals" formed.

These three characteristics are dealt with below :—

1. Depth of Oxidation.

The greatest depth known to the author at which oxidation minerals have occurred in Cornwall was at Phoenix United Mine, where, in the Chanacombe portion "gozzan was found at a depth of 200 fathoms with some grey copper ore." (7)

Dewey remarks that "the lodes (of Cornwall) usually carried a good gozzan or 'iron-hat,' sometimes to a depth of 150 fathoms, below which came the black, or less commonly the red oxides (of copper) passing downwards into the sulphides." (8)

MacAlister states that "oxidising influences in the Camborne region have been at work from surface to a depth of at least a thousand feet, and in all probability below this." (9)

Although very deep oxidation has been noted in some of the Cornish lodes, this was by no means always the case. This variation is probably due to the width and texture of the lode, its position, the character of the country rock within which it was situated, and variations in the rate of erosion.

The following examples derived from Henwood's observations clearly indicate the variations in the depth of the oxidised zone in Cornwall :—

(a) East Wheal Damsel. (10)

In the Middle Lode, quartz, pink felspar, iron and copper pyrites and *melaconite* were encountered at the 180 fathom level. This is the lowest level recorded on the lode.

(b) Wheal Unity Wood (St. Day). (11)

No oxidation minerals were recorded in the lodes carrying iron and copper pyrites at or below 26 fathoms.

(c) Wheal Falmouth. (12)

Some *vivianite* was found in the lode striking 30° S. of W. at the 50 fathom level.

(d) Great St. George and Wheal Leisure (Perranporth) (13).

From the 26 to the 36 fathom levels, Kernick's Lode carried quartz, copper pyrites, *melaconite*, etc. From the 46 fathom level only quartz, iron and copper pyrites were recorded.

(e) Ting Tang Mine (St. Day). (14)

Basic copper carbonates were found in the lode at the 130 fathom level.

THE WATER TABLE : CORNWALL

	PERRAN CHURCHTOWN	PERRAN WHARF	MELLINGYE	TANNER'S DOWNS	FALMOUTH	TREGASWITH	Hr. POLLEAN	BODMIN	TREBARBER	DEVIS	TUBBAN	GOONHINGEY	CHYWOON
	Surface Rock SLATE								Surface Rock GRANITE				
Surface O.D. ft.	60	65	90	110	120	150	200	315	280	300	340	560	560
Depth of water table (max.) ft.	33.8	49.2	61.1	22.6	48.9	39.9	53	44.3	21.6	28.0	45.8	22.9	30.4
,, (min.) ft.	17.6	24.5	37.9	13.6	34.5	16.8	25.9	14.5	6.0	15.2	26.3	5.4	17.7
Difference ft.	16.2	24.7	23.2	9.0	14.4	23.1	27.1	29.8	15.6	12.8	19.5	17.5	12.7

Table based on information given by W. J. Henwood
("Metalliferous Deposits of Cornwall and Devon," p.440)

(f) United Mines (St. Day). (15)

Henwood's table indicates that here oxidation minerals did not occur below about 92 fathoms.

As very little oxidation normally takes place below the water-table, it is clear that the Cornish lodes must have developed their deep oxidation zones when the climate was very different from what it is to-day. At the present time the water-table is rarely at a depth greater than 40 feet, as the table, indicating depths to water in wells, will clearly show.

From evidence derived from the minerals in the Budleigh Salterton Triassic beds in S. Devon, it is probable that the West of England granites were exposed in Triassic times.

In Triassic, Jurassic and Cretaceous times semi-desert conditions prevailed, and with such conditions would be associated a very deep water-table and consequently a deep oxidation-zone would develop.

In Eocene and Oligocene times the climate was humid, so that the water-table would not have been far below the surface. In Miocene times, all but the highest hills of Cornwall were submerged, and this submergence was followed by emergence which continued through Pleistocene times, and was accompanied then by a cold climate, so that, at that time, it is improbable that much oxidation took place. In Recent times the area was depressed about 60-100 feet and the climate was always much the same as it is now.

Thus, during Tertiary and Quaternary times, only in the Eocene, Oligocene and Recent stages was the greater part of the area above sea-level, and during these times the climatic conditions were such that the water-table was not far below the surface.

Therefore, since Cretaceous times, oxidation processes must have been largely concerned with the "re-working" of the upper horizons of the oxidised portions of lodes.

2. Minerals encountered in the oxidised zone.

The minerals developed in any given oxidised zone depend on the following :—

(i) The variety of minerals present which are capable of being broken-down by the solutions available in the zone.

(ii) The variety of "extraneous" ions available.

(iii) The nature of the wall-rock of the lode.

Oxidation and primary zoning.—In Cornwall, the most spectacular array of oxidation minerals occurs as a result of the oxidation of minerals of Davison's primary zones 4 and 5 which include the following elements, capable of producing a variety of reasonably stable oxy-salts and oxides :—Pb, Zn, Fe, U, Ni, Co and Cu. (16)

On the other hand, the oxidation of portions of lodes composed of minerals of zones 1 and 2, has produced little more than limonite and iron arsenates, as far as secondary minerals are concerned, but has, as a result of breakdown, and at least partial removal of components of the iron minerals, caused an increased concentration of cassiterite to appear in the gozzan.

Origin of Anions.— The wide variety of oxidation minerals encountered in some lodes is dependent not only on the metals present but also on the available anions. Sulphate ions are derived from the oxidation of sulphides ; arsenate ions from the oxidation of arsenides and sulpharsenides (notably arsenopyrite), and carbonate ions either from CO_2-rich descending ground-water, or from solutions charged with CO_2 as a result of acid attack on carbonate gangue minerals or of carbonates in the wall rock. Silicates such as *chrysocolla*, seem to be derived largely by the reaction between sulphate solutions of the heavy metals and silicate minerals such as felspar and mica : this will be mentioned again later. Whilst the source of the above-mentioned anions is clear, the source of the chloride and phosphate ions is less so, and in both cases several sources suggest themselves.

Origin of Chlorides.—The chloride ion seems to have been derived from one or more of the following sources :—

(i) Saline springs.

(ii) Sea water.

(iii) Spray from the sea.

(iv) The soil.

Saline springs certainly may have been the source of the chloride ions, as many have been encountered in mining operations in West Cornwall. In order to indicate the chemical composition of such saline springs the following analyses have been included :—

ANALYSIS OF WATER FROM WHEAL CLIFFORD SPRING

By Dr. W. A. Miller (Report of the Thirty-fourth Meeting of the British Association 1864, p.35)

	Grains per imperial gallon
Chloride of lithium	26.05
Chloride of potassium with a little chloride of caesium	14.84
Chloride of sodium	363.61
Chloride of magnesium	8.86
Chloride of calcium	216.17
Sulphate of calcium	12.27
Silica	3.65
Oxides of iron, aluminium and manganese	traces
	645.45

This water issued at a temperature of 125° F. and at the rate of 150 gallons per minute, in the 230- fathom level.

ANALYSIS OF WATER FROM HUEL SETON MINE

By J. A. Phillips: "On the Composition and Origin of the Waters of a Salt Spring in Huel Seton Mine," "Philosophical Magazine," Fourth Series, Vol. XLVI, 1873, p.26.

	Grams per gallon
Calcium carbonate	6.45
Iron carbonate	.31
Manganese carbonate	trace
Calcium sulphate	2.12
Cuprii chloride	trace
Calcium chloride	473.88
Magnesium chloride	11.98
Aluminium chloride	63.02
Potassium chloride	6.43
Caesium chloride	trace
Sodium chloride	409.09
Lithium chloride	34.22
Potassium bromide	trace
Potassium silicate (K_2SiO_3)	4.85
Ammonia	trace
Nitric acid	trace
Total found by addition	1012.35
Total found directly	1005.61
Free carbonic acid	2.61

This water issued at a temperature of 92° F. and at the rate of 50 gallons per minute, in the 160-fathom level.

These analyses clearly indicate the richness of these spring waters in chloride ion, and it is also notable that they sometimes carry silicate, sulphate and carbonate ions.

Clearly then, these waters may have contributed to the development of secondary minerals, and, if they did, then it is at least reasonable to suggest that some of the deeper-seated secondary oxy-minerals of Cornwall may have been due to these ascending solutions, and that these bear no relationship to the depth of the water-table, as suggested earlier. But, if this indeed were the case, then, on account of the great preponderance of chloride ions in such waters, one would expect to find considerable accumulations of chlorides in depth (such as atacamite, phosgenite, etc.) and this is not so.

It would appear probable, then, that saline reservoirs were effectively sealed in depth, and that they did not supply water unless the rock-seals were broken during mining operations, or by erosion. It is possible that saline springs may have supplied chloride and other ions, but that they did not come into operation until they were only covered by a fairly shallow burden of rock through which the water could emerge.

It is of interest to record in this connection that a note on a case in the museum of the Geological Survey in London relating to the formation of Cornish mimetite, suggests that this secondary mineral was formed by ascending solutions attacking galena, as mimetite is found at considerable depths. The author believes this theory to be erroneous because of the above statements and also because, as far as he is aware, no saline spring water of Cornwall has contained arsenic in any form.

It is also likely that many of the chloride minerals found in the Cornish deposits may have been formed by sea-water seeping into the lodes when the area was submerged in Tertiary times. The development of botallackite in the copper lodes beneath the sea in the St. Just area supports this.

The rare lead chloride minerals laurionite ($PbCl_2$ $Pb(OH)_2$), paralaurionite ($PbCl_2 . Pb(OH)_2$), and phosgenite ($PbCO_3 . PbCl_2$), noted by Sir Arthur Russell as occurring on the dumps of the cliff-edge mine Wheal Rose (17), may have been formed as a result of the attack of galena by spray blown in from the sea. The same minerals have been found in lead slags which have been exposed to the action of sea-water for about 2,000 years at Laurion in Greece.

Origin of phosphates.—Secondary phosphates are locally abundant in the oxidised portions of Cornish lodes.

The phosphate ion has been derived from one or more of the following sources :—

(i) Apatite in the granites and allied rocks, and in the dolerites.
(ii) Apatite in lodes themselves.
(iii) Phosphates dispersed in the sedimentary rocks.
(iv) Fish remains and other organic debris.

Practically every analysis of Cornish intrusives indicates that these rocks contain a certain amount of phosphorus.

The following figures indicate to what extent phosphorus (as P_2O_5) is present in such rocks :—

Granite and porphyry—average of 9 analyses ... 0.26%
Altered granite—average of 4 analyses 0.36%
Dolerites (including altered varieties)—
average of 13 analyses 0.45%

Sometimes also apatite can be identified in thin section as in slides prepared from the Watergate Bay porphyry dyke, and in the greisened granite of St. Michael's Mount, whilst in some pegmatites, such as those at Tremearne, apatite crystals can be seen in the hand-specimen.

It is likely then, that when secondary phosphates are found in lodes (and in joints) in the igneous rocks, that the phosphate ion was derived at least to some extent from the decomposition of the apatite of wall-rock.

Several of the early, high-temperature lodes carry a certain amount of apatite as a gangue mineral : it is found in some of the tin-tungsten, greisen-bordered lodes of St. Michael's Mount, and also in several of the tin lodes of the St. Agnes area, and this apatite has probably supplied a quota of phosphate ion for the development of secondary phosphates, though such lodes show little in the way of secondary phosphate development as they usually lack the necessary base metals for their formation (with the exception of iron).

Phosphates are widely dispersed in the sediments of Cornwall, and especially when they are somewhat calcareous. The average P_2O_5 in slates and hornfelses is 0.22% (8 analyses).

Associated with silicified, calcareous shale, and thin limestone seams in the Lusty Glaze and Criggans portion of the coast in the Newquay district, are bands of phosphatic nodules. (18)

This widespread occurrence of phosphate in sediments is due both to detrital apatite and to organic remains, and it is probably the source, or one of them, from which phosphate ion was derived during the formation of secondary phosphates in lodes in the sedimentaries.

However, on account of the occasional extensive deposits of secondary phosphates, such as the great masses of pyromorphite found in Wheal Alfred (Hayle), none of the above sources appear to be able to supply adequate amounts of phosphate. At Wheal Alfred there are sediments and a porphyry dyke which may have supplied some of the phosphate, but the author is inclined to the view that when the area was submerged in Tertiary times, the sea-bed in this area was covered with considerable organic remains, which, by breakdown during submergence and/or on emergence, supplied considerable quantities of phosphates to the underlying deposits.

3. The nature of the wall-rock of the lode.

The nature of the wall-rock has influenced the quantity and variety of oxidation minerals found in a given lode.

Granite, containing chemically reactive felspar, has contributed aluminium to the oxidation zone of lodes, largely as a result of breakdown of the mineral under acid attack, the acid being derived from the decomposing lode sulphides and also from overlying peaty and allied organic deposits. That acids derived from decomposing vegetation can liberate aluminium ions from felspar is clearly shown in certain granite caves in St. Levan parish, where encrustations of pigotite, an aluminium salt of mudescous acid ($4Al_2O_3$, $C_{12}H_{10}O_8$, $27H_2O$) are to be found. (19) This liberated aluminium has contributed to the development of such secondary minerals as liroconite (basic hydrated Cu, Al, arsenate); rashleighite and henwoodite (hydrated Cu, Al phosphates); wavellite (basic hydrated Al phosphate); tavistockite (basic Ca, Al phosphate); and chalcophyllite (hydrated sulphate and arsenate of Cu and Al).

Furthermore, it has been shown that copper solutions are capable of reacting with silicates such as felspar, muscovite, and kaolinite, by a process of "base exchange," which brings about the development of chrysocolla and basic sulphates such as brochanite. (20) In this connection, it is of interest to note that at Carn Brea, the felspars in the granite adjoining small veins of cuprite were converted into chrysocolla. (21)

Henwood noted that oxidation extends to greater depths in the granite than in the slate. This may be due to the ease with which the former can be broken down by descending solutions with the consequent development of channel ways, combined with the well-developed jointing to be found in granite.

There is also some evidence to show that where a portion of a lode is associated with a porphyry dyke, that there oxidation minerals are most concentrated, and in the greatest variety. This may be due to the chemical reactivity of the felspars of the porphyry, the possibility of base-exchange taking place due to the presence of suitable silicates, and above all to the ease with which solutions can move through a porphyry dyke as a result of its highly developed joint systems.

The following brief description of Davey's Lode at Wheal Buller and Beauchamp illustrates this :—"At 29 fathoms the west branch of the lode is in slate and consists of quartz and limonite, but where it meets a porphyry it is very rich in limonite. At 49 fathoms the lode is in slate but to the west porphyry falls in contact with the lode and the latter is then very rich, and consists of limonite, quartz, melaconite, chalcocite, chalcopyrite, cuprite, basic copper, carbonate, arseniate of copper, and semi-opal." (22)

(4) Other unusual oxidation phenomena seen in Cornwall.

1. THE OXIDATION OF WOLFRAM.

The breakdown and oxidation of tungsten minerals generally, and of wolfram specially, is a subject of considerable interest to mining geologists, and therefore the author thinks it worthwhile to record the following observations and conclusions, which he has made as a result of a study of the Cornish deposits.

The following tungsten minerals occur in Cornwall :—

(i) Wolfram, (Fe, Mn)WO_4.
(ii) Ferberite ; $FeWO_4$ (only at Penhale, and there not plentiful).
(iii) Scheelite ; $CaWO_4$.
(iv) Tungstic Ochre. WO_3 (essentially).
(v) Russellite. Bi_2O_3. WO_3.

Of these minerals, wolfram, ferberite and scheelite occur as primary minerals, and scheelite, tungstic ochre and russellite occur as secondary minerals.

At Penberthy Croft, and in Stamps and Jowl Zawn (St. Just), the scheelite occurs under conditions which clearly indicate that it is a primary mineral. In the latter area it occurs as yellowish crystals associated with quartz, chlorite and cassiterite, and small crystals of the latter "actually penetrate the scheelite crystals." (23)

On the other hand, at both New Dolcoath and E. Pool, scheelite replacing wolfram crystals has been recorded, and often associated with the scheelite is a rim of calcite. Since this alteration was found at considerable depths, and since the associated arsenopyrite is unattacked it is reasonable to believe that there the alteration was due to late, ascending solutions which were either charged with calcium bicarbonate derived from the depths, or by attacking the lime felspars of the associated dolerites. Considerable quantities of calcite were deposited in the late formed, mesothermal lodes.

It is of interest to note that where both primary and secondary scheelite occur in Cornwall, dolerites are to be found. That the lime derived from the felspars of the dolerites have been important in scheelite development is further suggested by the fact that in the St. Just area where tungsten is of rare occurrence, those mines in the slate and dolerites which had any tungsten minerals, had scheelite, whilst Balleswidden, in the granite, carried only wolfram.

The breakdown of Wolfram.

The author has examined specimens of wolfram from many Cornish deposits, including those which have been exposed to atmospheric agencies for considerable time, such as the veins in the cliffs of Cligga and St. Michael's Mount, but in only two cases was there any marked evidence of chemical breakdown, and these are described below.

(i) On the dump of Wheal Gorland (St. Day) wolfram specimens from greisen-bordered veins can be found. The wolfram here is very often cindery and covered with a veneer of oxide of manganese and also sometimes limonite. Occasionally negative, limonite-lined pseudomorphs after wolfram are to be found in quartz. No trace, however, of secondary tungsten minerals had ever been seen. The dump is a well-known hunting-ground for mineralogists as it contains excellent specimens of arsenates and phosphates of iron and copper. Of the primary minerals, considerable quantities of arsenopyrite, sphalerite, pyrite and chalcopyrite are to be found, and it seems probable that the wolfram breakdown in this case may be due to the attack of sulphuric acid and/or ferric sulphate, and/or possibly arsenic acid. Laboratory confirmation is not unfortunately at this period available.

(ii) A little to the west of the Caradon Mines, several prospect shafts and a small openwork have been developed on the granite-slate junction. In the openwork is a large quartz vein, and a pegmatite, and from this quartz vein some cassiterite and wolfram have been extracted.

The author found a small pile of wolfram (presumably taken from this working) on the surface, which showed most interesting oxidation phenomena. Much of the wolfram was coated by oxide of manganese and of limonite, and often both it and the surrounding quartz was coated with tungstic ochre. The wolfram was frequently pitted, and these pits were so aligned that it was clear that preferential decomposition was taking place along cleavage planes. Some of this pitted wolfram, which, when examined with a lens and the microscope, showed no tungstic ochre whatsoever, gave the typical blue colouration when powdered and warmed gently with hydrochloric acid and metallic zinc, which indicates that WO_3 or H_2WO_4 was enmeshed in the black oxide of manganese.

In this area no trace of sulphides were to be found, and it seems probable, therefore, that the breakdown of the wolfram was brought about, either by ground water charged with carbon dioxide and/or with humic and other organic acids derived from the decomposition of plants.

(iii) Russellite, $Bi_2O_3 . WO_3$.

This yellowish mineral was found in the form of pellets amongst the jig products of material from a stope between the Nos. 1 and 2 levels of Castle-an-Dinas Mine (St. Columb), but it was never located in situ.

It has been shown that it is an isomorphous mixture of Bi_2O_3 and WO_3 and not bismuth tungstate.

The Castle-an-Dinas lode is situated in Meadfoot slates and appears to "sit" on a tongue of granite, which, in fact, is later than the lode, as minor tongues of it penetrate the lode.

The lode consists essentially of wolfram and quartz, and locally considerable quantities of lollingite, but the following primary minerals have also been recorded : topaz, brown lithia-mica, tourmaline, cassiterite, bismuth, bismuthinite, together with the secondary minerals russellite, scorodite, wavellite, rashleighite, native copper and cuprite.

Sir Arthur Russell found the following minerals in the russellite pellets :—bismuth, wolfram, limonite, quartz, topaz, lithia-mica and black tourmaline, whilst Davison noted that bismuthinite also frequently occurred. (24)

The author believes this mineral may have originated as follows :—Bismuthinite in close proximity to wolfram was, as a result of attack by descending, oxygenated waters, converted via an unstable oxy-sulphate stage, to the oxide, and at the same time sulphuric acid was liberated. This sulphuric acid attacked the associated wolfram, converting some of it into WO_3, which united with the Bi_2O_3. The manganese liberated in the process was carried beyond the seat of reaction, whilst some, at least, of the iron liberated was rapidly oxidised from the ferrous to the ferric state and deposited as limonite.

The author believes that the reactions which produced Bi_2O_3 and WO_3 must have been connected, otherwise one would have expected to find an excess of one or the other oxides present in the pellets.

(iv) Wolfram and alluvial deposits.

Three important facts relating to the problem of alluvial wolfram are stated below, and certain conclusions have been drawn from them.

(a) Most of the rivers of Cornwall draining mineralised granite areas have carried considerable alluvial deposits of cassiterite, yet, despite the fact that at the time of the formation of these alluvials, considerable quantities of wolfram must have been liberated from the lodes with cassiterite none is found in the low-level alluvials.

(b) On the Marazion beach, pebbles and small boulders are frequently found which consist of fragments of greisen-bordered veins carrying cassiterite and wolfram, derived from St. Michael's Mount. The wolfram in these pebbles is often quite fresh, but sometimes coated with a film of oxide of manganese, and generally it has not been removed at a rate greater than the quartz in which it lies, so that the surface of the pebble is not depressed where wolfram crystals occur.

(c) On the high levels of Bodmin Moor several localities are known which contain deposits of fragmentary cassiterite and wolfram. The Buttern Hill Alluvial Works at Altarnun may be cited as a typical example. Here the alluvial deposits cover 200,000 square yards and rest largely on granite. Generally the deposit consists of three feet of peat resting on three or four feet of "pay-dirt," which in turn rests upon a "shelf" consisting of fragments of granite and vein quartz.

The "pay-dirt" is composed of fragments of granite and quartz, water-worn pebbles of cassiterite, water-worn fragments, fine-grains and occasional lumps of wolfram, and a large quantity of fine, granular ilmenite. (25)

From the various facts noted above the following conclusions can be made.

Wolfram can appear in alluvial deposits if largely protected by an inert mineral such as quartz. However, as soon as wolfram is liberated from gangue minerals it rapidly breaks down into exceedingly small fragments along its perfect cleavage. This latter fact is clearly recognised by mineral dressers, and fine grinding of wolfram ores is reduced to a minimum. The author's opinion is that wolfram does not appear in the low-level alluvials, because it was broken down into such exceedingly fine particles that it was transported almost entirely to the sea in an unchanged state. It is unlikely that much chemical breakdown of moving fragments takes place in fast currents of water. The ideal conditions for chemical breakdown, seem to be very slowly-moving, aerated water or dilute acid solutions slowly moving through fissures or across crystal faces. That little oxidation takes place in rapidly moving water is borne out by the fact that fresh arsenopyrite can always be found in the sands at the mouth of the Red River which carries away the tailings from South Crofty Mine, several miles up the valley.

The wolfram deposits of Bodmin Moor owe their existence to the fact that the wolfram present in them is largely eluvial, and that which is alluvial has travelled only a very short distance. Furthermore, it has probably been preserved from chemical breakdown because it accumulated in badly aerated basins in which reducing rather than oxidising conditions prevailed. Minerals which are extremely unstable under oxidising conditions can remain absolutely fresh under the reducing conditions to be found at the bottom of undrained pools. Thus, the author has seen absolutely fresh pyrite and arsenopyrite crystals derived from Malayan "alluvial" basins. Sir Cyril Fox declares that during the past war, when a peat bog was excavated in the course of building an aerodrome in Anglesea, iron swords of the Iron Age were found as fresh as the day they were placed there, except for an occasional small stain of vivianite.

2. WOOD TIN.

Wood tin has been considered by some to be secondary after stannite, and by others to be a primary mineral.

The circumstances under which wood tin was found in a lode at the 200 fathom level near the Metal Shaft in Wheal Vor, clearly indicates that it is, at least on some occasions, a primary mineral. At Wheal Vor the "wood tin appeared as a cementing material binding together fragments of killas, and some of it was sprinkled over with brilliant crystals of tin oxide . . ." (26)

However, stannite is of not infrequent occurrence in the Cornish lodes, and at Cligga and Stenna Gwyn it can often be found in a state of partial-oxidation (indicated by the development of malachite over its surface). Nevertheless, it has not been definitely proved that wood tin is one of the breakdown products of stannite, although it is almost certainly the case. Thus, although there is evidence which clearly shows some of the Cornish wood tin to be primary, there is at least an indication that some may be secondary after stannite.

3. THE IRON OXIDE DEPOSITS OF THE ST. AUSTELL AREA.

Iron in the form of haematite and limonite, and frequently closely associated with oxides of manganese, has been produced from a series of lodes in and near the St. Austell granite.

These lodes vary in strike from N.—S. to N. 50° W., and are of later origin that the tin lodes of the area, and probably also later than the uranium-nickel-cobalt lodes.

In the majority of cases it is only the oxidised portions of the lodes which have been worked and therefore one cannot always state the parent mineral from which the secondary minerals have been derived, with any degree of certainty. It is probable that some represent the oxidised portions of lodes which carry primary haematite in depth, whilst others represent oxidised siderite lodes, or siderite and haematite. However, evidence of the following kind helps towards the solution of the problem :

(i) If specular haematite occurred in the lode, as at Restormel, then it was the primary mineral, or one of them, from which the limonite was derived.

(ii) If oxides of manganese occur, then probably siderite was the primary mineral, or one of the primary minerals, as it almost always carries manganese, and neither rhodonite nor rhodochrosite have been found in Cornish lodes whose development was associated with the intrusion of the granitic.

(iii) Variation in mineral content as the lode is traced along its strike is sometimes suggestive of the origin of the iron oxides. Thus the Ruby Iron Lode (which reaches the coast between Appletree Beach and Crinnis Island) has yielded only a little sphalerite and siderite whilst in the slate, "but on entering the considerably kaolinised granite near Trethurgy it contains remarkably pure red haematite." (27) Here then, although oxides of manganese are not present to substantiate the argument, the red haematite was probably derived from oxidation of siderite. One wonders also, in connection with this example, whether or not, the potash liberated during the kaolinisation of the granite may have determined that haematite should be formed.

The following extract relating to an iron-copper system and not to an iron-zinc system is of interest as the two systems may be similar :—"Thus, whereas haematite does not precipitate during oxidation in an inert gangue (since it has no stability field in the quaternary system Fe_2O_3—CuO—SO_3—H_2O below at least 50°), it deposits readily instead of goethite (or along with it), if potash is present." (28)

4. THE DEVELOPMENT OF SECONDARY GALENA IN THE OXIDISED ZONE.

At Wheal Hope pseudomorphs of galena after pyromorphite were discovered, and one such specimen is in the British Museum, whilst others are in the possession of Sir Arthur Russell.

The author thinks that these pseudomorphs may have been formed as follows :—

In the proximity of the pyromorphite, residual sulphides became oxidised and as a result of this, sulphuric acid was liberated which attacked other residual sulphide so causing the formation of hydrogen sulphide. The hydrogen sulphide dissolved in the dilute acid solution and attacked the pyromorphite, converting it into galena, and at the same time liberating phosphate and chloride ions.

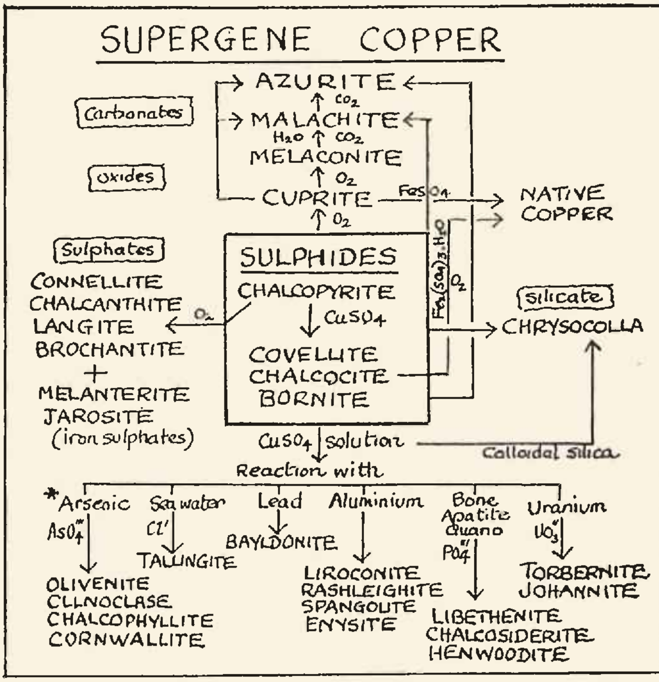
This example of the conversion of an oxy-salt into a sulphide in the oxidised zone is extremely interesting, but a note of it has never been seen by the author in any geological literature.

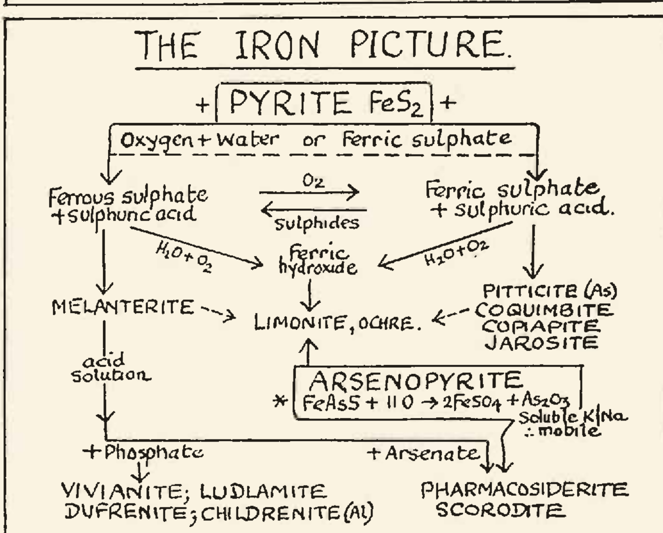
CONCLUSION

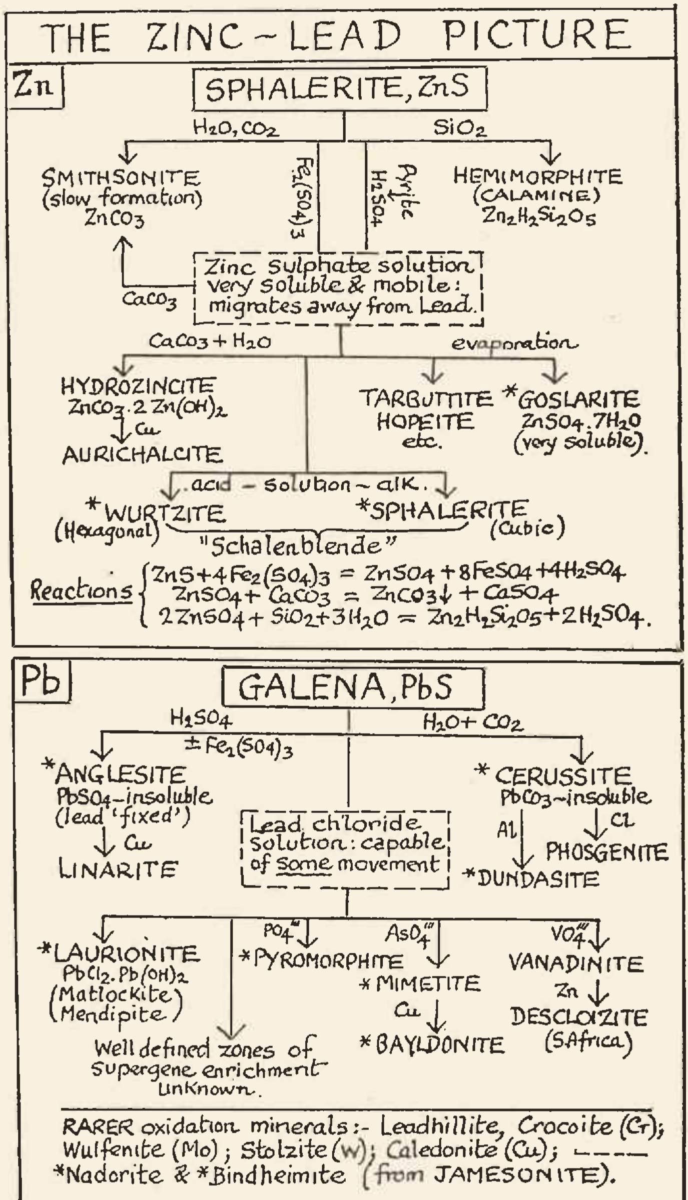
A great deal of the information in the above account has of necessity been derived from quite old reports which were written when many mines were in operation and before the oxidised portions of lodes had been completely removed All that one can do now in the nature of field-work in this sphere, is to examine the old mine dumps and specimens in museums. It is probable that many changes have taken place in some of the ores since they have been placed on the dumps, and therefore one cannot, by any means, always assume that all the dump products were formed in the vein before it was exploited.

The problem is also difficult because early workers often did not write really comprehensive accounts of what they saw, and because only comparatively recently has a fairly clear picture of oxidation and secondary sulphide enrichment been developed.

A great deal of laboratory work remains to be done, especially in order to work out the factors determining the formation of such minerals as malachite and azurite, and the arsenates and phosphates of iron and copper.


SUPERGENE COPPER
AZURITE
Carbonates
MALACHITE
MELACONITE
oxides
CUPRITE
NATIVE COPPER
Sulphates
CONNELLITE
CHALCANTHITE
LANGITE
BROCHANTITE
+
MELANTERITE
JAROSITE
(iron sulphates)
SULPHIDES
CHALCOPYRITE
COVELLITE
CHALCOCITE
BORNITE
Silicate
CHRYSOCOLLA
CuSO4 solution
Colloidal silica
Reaction with
*Arsenic
Sea water
Lead
Aluminium
Bone Apatite Guano
Uranium
OLIVENITE
CLINOCLASE
CHALCOPHYLLITE
CORNWALLITE
TALLINGITE
BAYLDONITE
LIROCONITE
RASHLEIGHITE
SPANGOLITE
ENYSITE
LIBETHENITE
CHALCOSIDERITE
HENWOODITE
TORBERNITE
JOHANNITE


THE IRON PICTURE.
PYRITE FeS2
Oxygen + Water or Ferric sulphate
Ferrous sulphate
+ sulphuric acid
sulphides
Ferric sulphate
+ sulphuric acid.
Ferric hydroxide
MELANTERITE
LIMONITE, OCHRE.
PITTICITE (As)
COQUIMBITE
COPIAPITE
JAROSITE
acid solution
ARSENOPYRITE
* FeAsS + 11O → 2FeSO4 + As2O3
Soluble K/Na
∴ mobile
+ Phosphate
+ Arsenate
VIVIANITE; LUDLAMITE
DUFRENITE; CHILDRENITE (Al)
PHARMACOSIDERITE
SCORODITE



*OCCUR IN W. ENGLAND.

APPENDIX

SILVER ores, principally Argentite, Ag_2S, Argentiferous galena ; sulphantimonites and sulpharsenites (of late hypergene or supergene origin), are attacked by oxygen or acid ferric sulphate to form silver sulphate, which is fairly soluble in water. Native silver is similarly attacked. The silver sulphate may react :

(a) Near the surface, and especially in arid climates, with soluble chlorides to form Cerargyrite (transported as a colloid protected by silica); with bromide (Bromyrite) or iodide (Iodyrite). The first only occurred in Cornwall (e.g. Perranuthnoe).

(b) Native silver forms by reduction of the sulphate by organic matter ; copper, chalcocite, covellite, enargite, simple arsenides.

(Note : Pyrite, chalcopyrite, galena and sphalerite are inactive as silver precipitators).

(c) Argentite enrichment may occur by reaction with H_2S (formed by sulphuric acid attack on sphalerite, galena or pyrrhotine); also by precipitation by sulphides of lead, copper, zinc or iron ; and by kaolin, clay and orthoclase.

(d) By complex reactions, the occasional formation of sulphosalts (Pyrargyrite, Proustite) takes place.

The average zoning sequence is as follows :—

Oxidation Zone.....	Gozzan, Kaolin, etc.
	Cerargyrite.
	Bromyrite.
	Iodyrite.
	Native Silver.
Enrichment...........	Argentite.
Primary Ore..........	Argentite, Galena, etc.
	Pyrargyrite.
	Proustite.
	Stephanite, Polybasite, etc.
	Native Silver.

REFERENCES

1. Robson, J. (1948): Cornish Mineral Index: Tr. R.G.S.C., Vol. 17, p.455.
2. Collins, J. H. (1912): "Obs. of W. England Mining Region": Tr. R.G.S.C., Vol. 14, p.253.
3. ,, ,, : op. cit., p.345.
4. Carne, J. (1818): Tr. R.G.S.C., Vol. 1, p.118.
5. "Geology of Tavistock and Launceston": Mem. Geol. Sur. (1911), p.92.
6 ,, ,, ,, ,, : p.p.101-2.
7. Webb & Geach: "Mining in Caradon" (1863), p.30.
8. Dewey, H. (1923): "Copper Ores of Cornwall and Devon": Mem. Geol. Sur., p.3.
9. MacAlister, D. A. (1906): "Geology of Falmouth and Camborne": Mem. Geol. Sur., p.194.
10. Henwood, W. J. (1843): Tr. R.G.S.C., Vol. 5, Table LXIV.
11. ,, ,, ,, : op. cit., Table LXVI.
12. ,, ,, ,, : op. cit., Table LXVII.
13. Dewey, H.: op. cit., p.18.
14. Henwood, W. J.: op. cit., Table LX.
15. ,, : op. cit., Table LXI.
16. Davison, E. H. (1930): "Handbook of Cornish Geology" (Blackford), p.70.
17. Russell, Sir A. (1927): "On Laurionite and Associated Minerals from Cornwall": Min. Mag., Vol. 21, p.221.
18. "Geology of Country near Newquay": Mem. Geol. Sur. (1906) p.15.
19. Lawrence, J. (1948): "Some Caves in St. Selevan Parish": Tr. R.G.S.C., Vol. 17, p.493.
20. Sullivan, E. C. (1907): "Interaction between minerals and Water Solutions": U.S. Geol. Sur. Bull. 312, pp. 37-64.
21. Semmons, W. (1878): Min. Mag., Vol. 2, p.200.
22. Henwood, W. J.: op. cit., Table LVIII.
23. Russell, Sir. A. (1920): "On occurrence of Phenacite and Scheelite at Wheal Cock, St. Just, Cornwall": Min. Mag.; Vol. 19, p.22.
24. Hey, Bannister & Russell (1936): "Russellite": Min. Mag., Vol. 25, p.41.
25 Dewey, H. and Dines, H. G. (1923): "Tungsten and Manganese Ores": Mem. Geol. Sur., p.29.
26. Collins, J. H.: op. cit., p.117.
27. ,, : op. cit., p.224.
28. McKinstry (1948): "Mining Geology" (Prentice-Hall, N.Y.), p.255.