

## GEOCHEMISTRY OF GERMANIUM IN THE OXIDIZED ZONE OF THE TSUMEB MINE, SOUTH-WEST AFRICA\*

CLIFFORD FRONDEL AND JUN ITO, *Harvard University, Cambridge, Massachusetts.*

## ABSTRACT

The primary ores of the Cu-Pb-Zn deposit at Tsumeb contain germanium in solid solution in relatively large amounts in enargite, tennantite, renierite and germanite. Oxidation of the ores in a limestone environment has given rise to an extensive suite of secondary carbonates, sulfates, arsenates, phosphates, vanadates, and oxides. The chief cations are Cu, Pb, and Zn together with minor amounts of Ca, Mg, Fe, Ba, Cd, Mo, and Co. The germanium contained in the primary minerals is released during oxidation and is found in two valence states in the secondary minerals. It occurs very sparingly as divalent Ge in substitution for Pb in anglesite and cerussite (50–500 ppm) and in a new basic lead sulfate containing 8.18 weight per cent GeO. The bulk of the germanium in the oxidized zone is quadrivalent. It preferentially enters the early-formed arsenates, including mimitite, olivenite, and in particular bayldonite (with 500–5000 ppm Ge). The Ge<sup>4</sup> substitutes for As<sup>5</sup> in the (AsO<sub>4</sub>) tetrahedra, with Ge<sup>4</sup> 0.44 kX and As<sup>5</sup> 0.47 kX, analogous to the well-known substitution of Ge<sup>4</sup> for Si<sup>4</sup> in silicates. The later-formed minerals smithsonite, cerussite, azurite, and malachite, which comprise the bulk of the upper part of the oxidized zone, are low or lacking in Ge.

The Ge<sup>2</sup> ion is found at the immediate interface between the sulfide zone and the oxidized zone where, in line with the known chemical and Eh-pH relations of this ion, it appears to have formed under weakly acid and reducing conditions. With increasing Eh and pH of the environment the Ge<sup>2</sup> is converted to Ge<sup>4</sup> and is housed in early-formed arsenates stable under moderately acid and oxidizing conditions. In the upper part of the zone of oxidation, under alkaline and oxidizing conditions, the germanium apparently is leached as alkali germanates in the absence of hemimorphite and other secondary silicates stable under such conditions and suited to house Ge<sup>4</sup> in solid solution.

## INTRODUCTION

The primary sulfide ores of the Pb-Cu-Zn deposit at Tsumeb are notably enriched in germanium. We have investigated the distribution of the germanium among the various secondary minerals that have formed during the oxidation of the primary ores.

The Tsumeb mine is located in South-West Africa approximately 100 km. northwest of Grootfontein. The deposit has been described by Schneiderhöhn (1920) and Moritz (1933), and there is a large literature describing various of the primary and secondary minerals of the locality. The ore body consists of replacements along fracture zones in limestone and dolomite. The primary minerals are principally sphalerite, chalcopyrite, galena, pyrite, bornite, chalcocite, enargite, tennantite, renierite, germanite, and luzonite. The germanium is contained in solid solution

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largely in the enargite, tennantite, renierite, and germanite, the latter containing up to 10.2 weight per cent Ge. Single masses of germanite weighing up to 25 pounds have been found. The mine is commercially producing germanium from the primary ores at the present time. Details of the recovery of Ge from the ores are given by Ratledge, *et al.* (1955).

Surface oxidation at Tsumeb is extensive, with the formation of a remarkable variety of carbonates, sulfates, arsenates, phosphates, vanadates, and oxides (Table 1). The chief cations are Cu, Pb and Zn, together with minor amounts of Ca, Mg and Fe and trace amounts of Ba, Cd, Co, Mo and other elements. The most abundant secondary minerals are the carbonates cerussite, smithsonite, malachite, and azurite. Finely crystallized specimens are common. Secondary quartz is rare, and silicates such as hemimorphite and willemite apparently do not occur. There is also a zone of secondary enrichment containing chalcocite with covellite. The detailed paragenesis of the secondary minerals is discussed on a later page.

#### EXPERIMENTAL OBSERVATIONS

The present investigation would be best based on samples collected in geological context at the mine, but the oxidized ores are now entirely mined out. We have utilized a collection of about 1500 specimens of Tsumeb minerals preserved in the Harvard Mineralogical Museum. The bulk of this collection had been made by a former manager of the Tsumeb mine, and notes were available in his catalogue as to the spatial relations and association of many of the specimens.

The germanium determinations were made spectrographically on a two-meter Baird Associates grating instrument. The methods employed were basically those of Kuroda (1939) and Harvey (1947), using cathode layer excitation at 220 volts DC, continuous arc. Direct Ge determinations by wet methods were made on a few samples that contained Ge in amounts over about 0.01 weight per cent. The experimental data are summarized in Table 1. These data, taken in hand with crystallochemical considerations and chemical tests to determine valence, indicate that germanium occurs in two valence states in the oxidized zone, as  $\text{Ge}^4$  and  $\text{Ge}^2$ , and that certain secondary minerals are separately enriched in these ions.

#### *Distribution of Quadrivalent Germanium*

The secondary heavy-metal arsenates, including olivenite, mimetite, duftite and, in particular, bayldonite are found to be notably enriched in germanium (Table 1). The six different specimens of bayldonite examined all contained Ge in the range 500 to 5000 ppm.

TABLE 1. GERMANIUM CONTENT OF SOME SECONDARY AND PRIMARY  
MINERALS AT TSUMEB  
(Numbers refer to the number of different specimens analyzed)

Name	Composition	5000-500 ppm.	500-50 ppm.	50-5 ppm.	5-0.5 ppm.	<0.5 ppm.
Bayldonite	$(\text{Cu}, \text{Pb})_2(\text{AsO}_4)(\text{OH})$	6				
Olivenite	$\text{Cu}_2(\text{AsO}_4)(\text{OH})$	1	2	1	3	
Duftite	$\text{PbCu}(\text{AsO}_4)(\text{OH})$	1				
Mimetite	$\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$		1	3	4	
Adamite	$\text{Zn}_2(\text{AsO}_4)(\text{OH})$			1	2	
Tsumebite	$\text{Pb}_2\text{Cu}(\text{PO}_4)(\text{OH})_3 \cdot 3\text{H}_2\text{O}$			1		
Pyromorphite	$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$		1			1
Mottramite	$\text{Pb}(\text{Cu}, \text{Zn})(\text{VO}_4)(\text{OH})$				1	
Vanadinite	$\text{Pb}_5(\text{VO}_4)_3\text{Cl}$				1	
Wulfenite	$\text{Pb}(\text{MoO}_4)$		(Ge present, not det.)			
Anglesite	$\text{Pb}(\text{SO}_4)$	1			3	
Barite	$\text{Ba}(\text{SO}_4)$				1	
Gypsum	$\text{Ca}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$				1	
Caledonite	$\text{Cu}_2\text{Pb}_5(\text{SO}_4)_3(\text{CO}_3)(\text{OH})_5$				1	
Linarite	$\text{PbCu}(\text{SO}_4)(\text{OH})_2$				1	
Un-named	$(\text{Pb}, \text{Ge})_2(\text{SO}_4)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$		(8.18 per cent GeO)			
Cerussite	$\text{Pb}(\text{CO}_3)$		2		1	7
Smithsonite	$\text{Zn}(\text{CO}_3)$				3	2
Otavite	$\text{Cd}(\text{CO}_3)$			1		
Calcite	$\text{Ca}(\text{CO}_3)$			1		3
Aragonite	$\text{Ca}(\text{CO}_3)$			1		4
Phosgenite	$\text{Pb}_2(\text{CO}_3)\text{Cl}$				1	
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$			1	3	
Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$				3	1
Rosasite	$(\text{Cu}, \text{Zn})_2(\text{CO}_3)(\text{OH})_2$			1		
Cuprite	$\text{Cu}_2\text{O}$				1	
Quartz	$\text{SiO}_2$					1
Chalcocite	$\text{Cu}_2\text{S}$					1
Enargite	$\text{Cu}_3\text{As}_4\text{S}_4$	1				
Galena	$\text{PbS}$					1
Pyrite	$\text{FeS}_2$					1
Tennantite	$\text{Cu}_{12}\text{As}_4\text{S}_{13}$	1				

Secondary minerals known from Tsumeb but not examined in the present study: schultenite, desclozite, dolomite, siderite, rhodochrosite, plumboan conicalchalcite ("parabayldonite," duftite  $\beta$ ), iron and manganese oxides.

The chief minerals of the main body of the oxidized zone at Tsumeb are smithsonite, cerussite, malachite, and azurite. These minerals all are very low in their content of Ge (Table 1). To be excepted here are certain rare specimens of cerussite and anglesite which, together with an associated new basic lead sulfate, are found on chemical tests to contain divalent Ge and which are discussed beyond. The secondary compounds of Ca, Cd, and Ba in the deposit that do not carry As or P also are very low or lacking in Ge. The correlation of the germanium thus appears to be with As<sup>5</sup> and not with the heavy metal cations or with the (CO<sub>3</sub>) or (SO<sub>4</sub>) anionic groups.

The bulk of the Ge contained in the outer crust of the Earth is dispersed in small amounts in solid solution in silicates. There is no direct evidence of the valence state of the Ge in natural silicates, but there is no doubt, from the isostructural relation of many silicates and germanates and of fluosilicates and fluogermanates, and from the existence of solid solution series between such compounds, that the Ge is present as Ge<sup>4</sup> in substitution for Si<sup>4</sup> in the tetrahedral framework. As<sup>5</sup> also goes in four-coordination with oxygen. Some arsenates are isostructural with silicates, such as berzelite and grossularite, and two of the arsenates at hand, olivenite and adamite, are isostructural with andalusite. A small extent of mutual substitution of As, P, and Si also has been observed in some silicates, phosphates, and arsenates. Direct evidence of the valence state of the Ge in the arsenates at Tsumeb is lacking. It is believed to be present as Ge<sup>4</sup> in substitution for As<sup>5</sup> in tetrahedral coordination. The ionic radius of Ge<sup>4</sup>, 0.44kX, is close to that of As<sup>5</sup>, 0.47kX, and in fact is closer to that of As<sup>5</sup> than it is to that of Si<sup>4</sup>, 0.39kX. Coupled valence compensation is required for the substitution of Ge<sup>4</sup> for As<sup>5</sup>. In the case of mimetite (and pyromorphite) this may involve omissions in the halogen positions, since the apatite-type compound Pb<sub>5</sub>(GeO<sub>4</sub>)(AsO<sub>4</sub>)<sub>2</sub> and solid solutions of the nature Pb<sub>5</sub>(Ge,SiO<sub>4</sub>)(P, As, VO<sub>4</sub>)<sub>2</sub> have been synthesized (Wondratschek and Merker (1956)). There is no evidence for the coupling mechanism in bayldonite and the other arsenates. The coupled substitution of (OH) for O in the coordination group of the (As,Ge) is a possibility, as is the coupled substitution of a trivalent cation such as Ga<sup>3</sup> for Cu<sup>2</sup> or Pb<sup>2</sup> in the cation position. Ga was in fact observed in all of our samples that contained Ge, but no quantitative measurements were made. One of the samples of pyromorphite examined contained 50–500 ppm. of Ge, indicating a substitution of Ge for P analogous to that for As. We wish to emphasize that we do not have experimental proof of the valence state of the Ge in these arsenates. It is possible, although unlikely in view of the Eh-pH relations obtaining in the arsenate stage of mineralization, discussed beyond, that the Ge is divalent and then presumably substitutes in the cation positions of these minerals.

*Distribution of Divalent Germanium*

Although the  $\text{Ge}^{2+}$  ion has not hitherto been identified in minerals, the evidence for its existence at Tsumeb is clear-cut. It is present in the amount of 8.18 weight per cent  $\text{GeO}$  in substitution for  $\text{Pb}$  in a new basic sulfate of lead\* and is present in the range 50–500 ppm. in the immediately associated, somewhat later-formed cerussite. Several other specimens of early-formed cerussite and a specimen of anglesite also were found to contain  $\text{Ge}$  in the range 50–500 ppm. Conclusive qualitative tests†\* for divalent  $\text{Ge}$  were obtained on the anglesite, cerussite, and the basic lead sulfate. A direct wet determination of  $\text{Ge}$  in one cerussite sample gave  $.015 \pm .005$  weight per cent  $\text{GeO}$ . The typical cerussite of the deposit is of a much later period of formation and is very low or lacking in  $\text{Ge}$ . Divalent germanium appears to be quite rare in the secondary minerals at Tsumeb, and will be shown to form under rather specialized conditions.

The substitution of  $\text{Ge}^{2+}$  for  $\text{Pb}^{2+}$  raises the question of the radius of the  $\text{Ge}^{2+}$  ion. This is given as  $0.72 \text{ \AA}$  by Ahrens (1952) as calculated from ionization potentials. This value appears to be low. The only compounds of divalent germanium whose structures are known are  $\text{GeI}_2$  and  $\text{GeS}$ . In the deformed  $\text{NaCl}$ -type structure of  $\text{GeS}$ , described by Zachariasen (1932), the  $\text{Ge}$  is in distorted six-coordination with  $\text{S}$ . The two principal  $\text{Ge-S}$  distances are 2.58 and 2.97 kX. Using the measured  $\text{S-S}$  distance of 3.55 kX, the effective radii of the  $\text{Ge}^{+2}$  are 1.20 and 0.80 kX with the average 1.0 kX.  $\text{GeI}_2$  crystallizes in the  $\text{CdI}_2$  structure-type (Powell and Brewer, 1938). The asymmetrical coordination in this layer-structure results in strong polarization and this is reflected in a pronounced shortening of the  $\text{A-X}$  distance as compared to the value expected from the normal ionic radii in six-fold coordination. This amounts to 8.4 per cent in  $\text{CdI}_2$  and 13.1 per cent in  $\text{PbI}_2$ ; assuming a shortening of 10 per cent in the measured  $\text{Ge-I}$  distance, 2.927 kX, the normal ionic radius of  $\text{Ge}^{2+}$  is 1.0 kX. The  $\text{Pb}^{2+}$  ion in six-coordination has a radius of 1.32 kX. This differs considerably from 1.0, but extensive solid solution series have been

\* Formula  $(\text{Pb, Ge, Ga})_2(\text{SO}_4)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  from the analysis  $\text{PbO}$  63.34,  $\text{GeO}$  8.18,  $(\text{Ga}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3)$  0.86,  $\text{SO}_3$  15.06,  $\text{H}_2\text{O} + 11.35$ ,  $\text{H}_2\text{O} - 0.21$ , insol. 0.56, total 99.56. Dense white aggregates of hair-like fibers. Uniaxial (?) positive, with  $n\text{O}$  1.747,  $n\text{E} \sim 1.78$ . Unit cell uncertain, apparently hexagonal with  $a_0$  17.76  $\text{\AA}$ ,  $c_0$  10.89. DTA curve shows an endothermic break at  $263^\circ$  ( $\text{H}_2\text{O}$  lost) and an exothermic break at  $463^\circ$  ( $\text{Ge}^{2+}$  oxidized).

† For cerussite and the basic lead sulfate described the mineral is dissolved in  $\text{HCl}$  and lead removed as  $\text{PbSO}_4$  by addition of  $\text{H}_2\text{SO}_4$ . Addition of  $\text{H}_2\text{S}$  to the weakly acid solution precipitates yellow  $\text{GeS}$ . The  $\text{GeS}$  is soluble in warm  $\text{NH}_4\text{OH}$  solution, from which, after acidification by  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{S}$  precipitates white  $\text{GeS}_2$ . For the relatively insoluble anglesite, the very fine powder is treated with concentrated  $\text{HCl}$ .  $\text{PbSO}_4$  precipitates with  $\text{H}_2\text{SO}_4$  after dilution with  $\text{H}_2\text{O}$  and  $\text{GeS}$  is precipitated by  $\text{H}_2\text{S}$  from the moderately acid filtrate.

observed between other elements with as large a difference in size, as for example, the pair Ca-Pb in hedyphane-svabite, pyromorphite, aragonite, wulfenite and other minerals, and the pair Na-K.

#### DISCUSSION

Although germanium is markedly siderophile in its geochemical behavior, in the upper lithosphere it also shows both oxyphile and chalcophile tendencies and is found in some sulfidic ores. Here it occurs particularly in tetrahedrally coordinated sulfosalts that are structural derivatives of sphalerite, including tennantite and the related minerals renierite (with 6 to 7.7 weight per cent Ge), germanite and, in smaller amounts, in enargite, stannite, and sphalerite itself. Colusite, renierite, and germanite are essentially isostructural as shown by Murdoch (1954). We have found by qualitative chemical tests that the Ge in germanite and renierite is divalent. The formula for germanite probably is  $(\text{Cu}, \text{Ge})\text{S}$ . The Ge in argyrodite,  $\text{Ag}_8\text{GeS}_6$ , on the other hand, was found to be quadrivalent as expected.

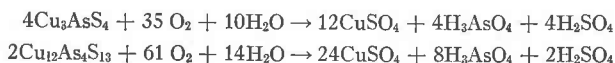
When deposits containing primary sulfarsenides are exposed by erosion to chemical attack by surface waters, the S and As are oxidized to sulfate and arsenate, and the metal cations, including trace elements such as Ge, are freed to combine with oxygen or oxygenated anions available in the attacking solution. Certain elements, notably copper, may also be in part carried downward to the water table where they may be reprecipitated as sulfide. The details of the oxidation process vary widely with the mineralogy of the primary ores, climatic and other factors, and particularly with the nature of the country rock. In a limestone environment such as at Tsumeb the free acid formed during oxidation at the interface with the primary sulfosalts and sulfides is neutralized by reaction with  $\text{CaCO}_3$  to produce solutions saturated with  $\text{CO}_2$ . The upper part of the zone of oxidation may then be characterized by a carbonate mineralogy.

#### *Paragenesis of the Secondary Minerals at Tsumeb*

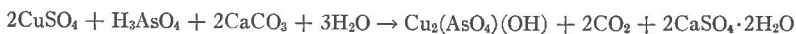
The observed mineral association and sequence of mineralization in the oxidized zone at Tsumeb may be outlined to provide a background against which the Eh and pH relations and their control over the distribution of the Ge may be discussed.

The heavy-metal arsenates are in general the earliest formed of the secondary minerals at Tsumeb, and are developed chiefly toward the bottom of the zone of oxidation at or near the boundary with the sulfide zone. Of the several arsenates, mimetite and bayldonite appear to be first formed and often are found directly altering from sulfosalts. Oliv-

enite occasionally is found directly deposited upon sulfosalts and chalcocite, but usually is later than bayldonite and sometimes forms pseudomorphs after that species. Adamite, like zinc compounds in general in the zone of oxidation, appears to have been relatively mobile and is found locally in the upper carbonate-rich portion of the oxidized zone. The chemistry of the oxidation of the original sulfarsenides and the reported syntheses of these arsenates, recently summarized by Guillemin (1956), indicates that the secondary arsenates at Tsumeb formed in an acid environment. Thus, duftite has been synthesized over the range pH 2.5-4, and bayldonite has been obtained from pH 5-8. Olivenite, adamite and mimetite also are obtained from acid solutions. Schultenite, which can be crystallized from boiling  $\text{HNO}_3$ , is earlier than anglesite at Tsumeb, and is associated with bayldonite. The following expressions for the oxidation of enargite and tennantite have been written by Guillemin (1956):



The dissociation constant of  $\text{H}_3\text{AsO}_4$  is about 1/25 that of  $\text{H}_2\text{SO}_4$ . The formation of secondary copper arsenates such as olivenite by reduction of the acidity of the solution, such as by reaction with waters carrying  $\text{CaCO}_3$ , can be suggested by the following expression:



At Tintic, Utah, where there has been extensive oxidation in a carbonate environment of primary ores rich in enargite, olivenite is one of the earliest of the secondary minerals. In part it is contemporaneous with chalcocite. The alteration of the enargite to olivenite and chalcocite has been represented by Lindgren and Loughlin (1919) by the following expression:



Anglesite, at Tsumeb as elsewhere, is a relatively early mineral. It forms in an acid environment. Anglesite is developed only locally at Tsumeb, in parts of the ore body relatively rich in galena, and sometimes is found deposited upon altering galena and other sulfides. In the few specimens available where the sequence could be determined, anglesite is later than bayldonite. It is not, however, a typical mineral of the overlying carbonate stage and falls in its general position in the lower, arsenate-rich, acid portion of the oxidized zone. The one specimen of anglesite found to be rich in Ge<sup>2</sup> was associated with covellite and altering galena and tennantite. The anglesite was pale yellow brown in color, and was in

part coated by or included black grains of an unidentified black, sulfide mineral.

The main body of the oxidized zone at Tsumeb extends upward from the arsenate stage to the surface. It is characterized by the development of carbonates, chiefly cerussite, smithsonite, azurite, and malachite. The carbonates calcite, aragonite (in large part plumboan), dolomite, otavite and phosgenite also are minerals of this stage. In detail most of these minerals show quite varied associations and sequences of formation on a hand specimen scale, at least, and in small amounts cerussite, smithsonite, and azurite are found locally throughout the zone of oxidation. In a broad way, azurite and malachite, the latter generally following azurite and often pseudomorphous after it, are uppermost and last formed.

The observed host minerals for  $\text{Ge}^2$  apparently have formed locally in a thin zone transitional between the sulfides and the overlying arsenate zone. These minerals occur directly deposited upon altering sulfarsenide and are associated with a sooty black unidentified secondary sulfide containing much Cu and a small amount of Ge. The secondary sulfide locally coats mimetite in part, indicating some fluctuation in environmental conditions. Other specimens from the same general level in the deposit showed chalcocite associated with native copper, native silver or, more abundantly, cuprite. Chalcocite itself forms under reducing conditions, and the upper boundary of the chalcocite Eh-pH stability field (Garrels, 1954) is virtually coincident with the calculated  $\text{GeO-GeO}_2$  boundary. The occurrence of cerussite at this level of the deposit seems anomalous, but it may be noted that the stability fields in the galena-anglesite-cerussite Eh-pH diagram (Garrels, 1954) indicate that cerussite can form in an acid environment, with the anglesite-cerussite boundary located roughly in the region from pH 5.5 to 6, with anglesite forming at lower pH. The formation of cerussite at this level would be dependent on a supply of  $\text{CO}_2$ , presumably from gangue minerals in the primary ore if the overlying arsenate zone of high acidity blocks a downward transport of carbonate ion, and on a sufficiently low concentration of sulfide ion.

The idealized Eh-pH relations in the oxidized zone at Tsumeb, based on the foregoing discussion and on the general summary by Garrels (1954), are indicated in Fig. 1. These relations are primarily dependent on the access of oxygen. Assuming access of oxygen from the surface, the minimal concentration of oxygen is reached at the interface with the sulfide zone. Below this level, which ideally is coincident with the water table, the environment is alkaline and reducing. At or slightly above the interface the supply of oxygen is adequate to completely oxidize S and As to  $(\text{SO}_4)^{-2}$  and  $(\text{AsO}_4)^{-3}$ . The acid environment here generated passes



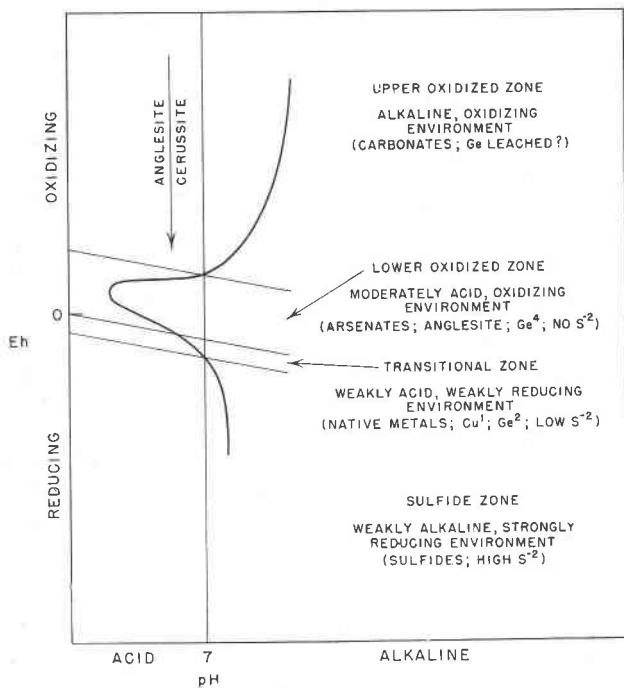


FIG. 1. Idealized Eh-pH relations in the oxidized zone at Tsumeb.

upward, through reaction with the carbonate country rock to produce solutions saturated with CO<sub>2</sub>, into the alkaline and oxidizing environment of the upper, carbonate zone. The actual mechanism is perhaps best envisaged as a set of essentially static Eh-pH environments, moving downward as erosion progresses, each mineralogical zone being continually reworked, rather than as one based on active circulation.

#### *Chemistry and Geochemistry of Ge<sup>2</sup> and Ge<sup>4</sup>*

The Group IVb elements Ge, Sn, and Pb all form compounds in both the +2 and +4 oxidation states. With Ge, opposite to Pb, the +2 state is less important than the +4 state. In acid solutions germanous salts and the halide complex ions of Ge<sup>2</sup> are fairly stable in the absence of oxidizing agents. In alkaline solutions the complex ions evolve hydrogen with oxidation of the Ge<sup>2</sup> to Ge<sup>4</sup>. Germanites such as Na<sub>2</sub>GeO<sub>2</sub> also are known. GeO is stable in dry or moist air at ordinary temperatures, and in dry air oxidizes to GeO<sub>2</sub> only at elevated temperatures. Both GeS and GeS<sub>2</sub> are stable phases. GeS sublimes at 430° and is soluble in hot alkaline solutions. GeS<sub>2</sub> is soluble in excess of sulfide ion with the formation of thiogermanates. The Ge<sup>4</sup> ion is stable under oxidizing conditions in both

acid and alkaline solutions.  $\text{Ge}^4$  has a more acidic character than do  $\text{Ge}^2$ , Sn and Pb.

Among systems containing Ge, the Eh-pH relations have been calculated only for the system Ge- $\text{H}_2\text{O}$  (Zoubov, Deltombe and Pourbaix (1955)). In this system at  $25^\circ$ , the diagram shows fields for  $\text{GeO}_2$  (hexagonal polymorph), GeO, and Ge, with the GeO- $\text{GeO}_2$  boundary extending from Eh 0 at pH -2 to Eh -0.7 at pH 10. The chemistry of germanous salts in general suggests that in other systems the boundary between  $\text{Ge}^2$  and  $\text{Ge}^4$  would be near or below the approximate, generalized Eh-pH boundary which Garrels (1954) has indicated as separating the zone of oxidation from the zone of stable sulfides in the weathering of sulfidic ore deposits. This boundary extends from Eh 0.2 at pH 2 to Eh 0.2 at pH 10. In the case of  $\text{Ge}^2$ , in view of the very low solubility of GeS, the existence of germanous ion in this general Eh-pH region, leading to the formation of germanous oxysalts or to the entrance of  $\text{Ge}^2$  into solid solution in oxysalts, would be dependent on a low concentration of sulfide ions.

The Ge derived from the primary ores at Tsumeb in a sense follows the Eh-pH path in the oxidized zone indicated in Fig. 1. The Ge is initially released in a more or less acid and weakly reducing environment, favoring the formation of the  $\text{Ge}^2$  ion. The  $\text{Ge}^2$  ion may then enter into solid solution in substitution for  $\text{Pb}^2$  in secondary lead minerals stable under such conditions. It possibly also could concentrate sufficiently to crystallize as a germanous compound such as GeO. The downward transportation of  $\text{Ge}^2$  and its reprecipitation in the zone of secondary enrichment as GeS is a further possibility. With increasing Eh, the  $\text{Ge}^2$  is oxidized to  $\text{Ge}^4$ . The  $\text{Ge}^4$  may then enter solid solution in substitution for  $\text{As}^5$  in the secondary arsenates characteristic of the lower, acidic and oxidizing part of the zone of oxidation. When these arsenates are reworked in the passage to the alkaline and oxidizing environment of the overlying carbonate zone, the  $\text{Ge}^4$  then released may be leached as soluble alkali germanates, in the absence of host minerals in this zone crystallographically suited to house  $\text{Ge}^4$ . Such minerals would be secondary silicates such as hemimorphite and willemite. The studies of Schroll (1953) and others show that  $\text{Ge}^4$  can in fact preferentially enter hemimorphite, but as noted, secondary silicates are not present at Tsumeb. Our data indicate that the carbonates of the upper part of the oxidized zone at Tsumeb are low or lacking in Ge, in line with the studies by Lopez de Azcona (1942) and others on cerussite in general, and it is presumed that Ge has been lost from this part of the deposit.

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