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TRACE-ELEMENT SUBSTITUTION IN GALENA

WILLIAM H. BLACKBURN
Department of Geology, University of Kentucky, Lexington, KY 40506 U.S.A.

JAMES F. SCHWENDEMAN
Phillips Petroleum Company, 3240 D. Juan Taba, N.E., Albuquerque, NM 97111 U.S.A.

ABSTRACT

Laser microprobe determinations of trace elements in galena show distinct chemical zoning of single crystals. In most cases, the trace-element content increases in the growth direction and both symmetric and asymmetric growth patterns are noted. Bismuth, silver and copper are always detected. Iron, zinc, nickel and tin are noted sporadically. Substitution is stoichiometric, with the capture of Bi^{3+} in the Pb^{2+} position counteracted by Ag^+ and Cu^+ substitution. No clear relationship is evident with regard to trace-element content and geological locale or history.

SOMMAIRE

Les éléments en traces dans la galène déterminés par une microsonde laser indiquent clairement une zonation chimique des monocristaux. Généralement, la teneur en éléments traces augmente au cours de la croissance et on note des modèles de croissance symétrique ou asymétrique. Le bismuth, l'argent et le cuivre sont toujours en concentration suffisante pour être décelés. On observe sporadiquement le fer, le zinc, le nickel et l'étain. La substitution est stoechiométrique, la substitution du Bi^{3+} au Pb^{2+} étant compensée par une substitution Ag^+ ou Cu^+. Il ne semble pas y avoir de rapport direct entre le contenu en éléments en traces et l'histoire géologique.

(Traduit par la Rédaction)

INTRODUCTION

Fleischer (1955) has summarized much of the trace-element data for galena. Antimony, arsenic, bismuth, and silver are the only elements that have been reported in amounts greater than 1 percent. Of these, Sb and As are thought to be the result of included tetrahedrite, tennantite or arsenopyrite. Craig (1967) reviewed experimental work on the solubilities of Bi and Ag in galena. The solubility of Ag_2S in galena is minimal and the solid solution of bismuthinite, Bi_2S_3, has a maxmum of 10 mole % (19 wt. %). However, the ternary minerals cosalite, $Pb_2Bi_2S_5$, and galenobismutite, $PbBi_2S_4$, albeit rare, are possible sources for high Bi values in PbS. Most likely, however, is the presence of matildite, $AgBiS_2$, in solid solution in galena (Ramdohr 1938; Wernick 1960; Van Hook 1960; Craig 1967). The common association of matildite and galena probably represents exsolution at a solvus with a crest at 215±15°C (Craig 1967). Above this temperature, the solid solution between these phases is complete. Both Tischendorf (1955) and Schroll (1955) considered that the Bi, Ag, and Sb contents of galena all vary directly with the temperature of formation.

Other trace elements commonly found in galena are Cd, Cu, Fe, Mn, Ni, Tl and Sn. Most of these are probably related to the presence of inclusions of other minerals in the galena. Brett & Kullerud (1967) found that the solubility of Fe in synthetic galena is too low to measure and is probably less than 0.1 wt. %. Further, Craig & Kullerud (1968) found little or no solubility of Cu in synthetic PbS. Galena forms solid solutions with clausthalite (PbSe) and altaite (PbTe). Data on Se and Te are, however, minimal.

Presumably, the entrance of a metal into solid solution in the close-packed galena structure would require substitution for lead. Most sulfides have mainly covalent bonding. Galena, however, may be described as having ionic-metallic bonding and thus the rules of ionic substitution are applicable. Table 1 lists the ionic radii, valences, and percent ionic bonding with sulfur for elements reported found in galena. Of the elements listed, silver most closely approximates the crystal-chemical parameters of lead. Silver is also known to be attracted to octahedral fields as present in galena. Three other elements (Cu^+, Bi^{3+}, Sn^{2+}) have parameters close enough to those of Pb for significant substitution. These have relatively large size differences but have reasonably similar bonding characteristics. The substitution of Bi^{3+} for Pb^{2+} necessitates a concomitant substitution of a monovalent ion to maintain neutrality. This is normally accomplished by the Bi^{3+}–Ag^+ couple but Cu^+ could replace Ag^+ in this role.

TABLE 1. CRYSTAL-CHEMICAL DATA FOR VARIOUS ELEMENTS REPORTED TO BE PRESENT IN GALENA

Element	Ion	Ionic Radius	% ionic bonding with sulfur
Antimony	Sb^{3+}	0.76	30.3
Bismuth	Bi^{3+}	0.96	30.2
Copper	Cu^{+} Cu^{2+}	0.96 0.72	34.7 21.2
Iron	Fe^{2+} Fe^{3+}	0.74 0.64	32.7 19.2
Lead	Pb^{2+}	1.20	36.4
Nickel	Ni^{2+}	0.69	24.5
Silver	Ag^{+}	1.26	35.2
Tin	Sn^{2+}	0.93	37.0
Zinc	Zn^{2+}	0.74	27.2

To evaluate the nature and extent of elemental substitution in galena, a general survey of a number of galena samples was conducted. The samples were obtained from various university and personal collections and represent a suite of samples from various geologic situations. In all, nearly 50 different galena crystals have been examined and the results of representative specimens are presented here.

CHEMICAL STUDIES

Most chemical data on galena previously described in the literature were of the bulk-sample type. Thus, no inference may be made as to the element distributions in or between galena crystals. Polished sections of the sample were examined microscopically in a search for exsolution and included microphases and, generally, these have been the only attempts at defining impurity distribution in single grains.

It was hoped that *in situ* chemical determinations in galena would give information as to element distribution in this mineral. Further, it was hoped that such information could be used to distinguish galena from a deposit associated directly with igneous activity from that of strataform deposits. It was thought that this could be done either through differences in zoning patterns or in absolute concentrations. Bethke & Barton (1971) showed galena to have a high rate of diffusivity compared with other sulfides and they believed that lead sulfides deposited at high temperatures would attain internal homogenization, thus losing any initial minor-element zoning. Galenas of this type would include those associated with igneous activity and any deposit heated after its formation (i.e., in orogenic areas). On the other hand, the lower temperature deposits of the Mississippi Valley type may retain more original characteristics.

Little information exists with regard to element distribution in single galena grains. Frondel *et al.* (1942) examined several crystals of galena by sectioning at various levels and staining with a solution containing HNO_3. They observed that the crystals were divided into regions of greater and lesser chemical reactivity. Analysis of these "light and dark" regions showed that the more reactive (dark) galena usually contained greater amounts of Ag (1-1000 ppm). The distribution of light and dark areas showed both sector and growth zoning. In some cases, the growth zoning showed asymmetric Ag values probably reflective of non-uniform growth rates.

Analytical technique

All *in situ* determinations were made using a Jarrell-Ash Mark II Laser Microprobe. This instrument has been described by several authors including Snetsinger & Keil (1967) and Blackburn *et al.* (1968). As in any microprobe technique, an initial problem exists in the selection of analytical standards. These must have a known composition but must also be homogeneous outside the resolution of the analysis spot. For this study, microprobe settings which produced a crater diameter of 0.2 mm were chosen so as to produce consistent results in the standards.

Estes (1972) has shown that laser microprobe standards may be produced by careful mixing of dry powders, followed by pelletizing. These findings have been corroborated by results in the laboratory of the senior author. This, however, was considered impractical and an alternate method was chosen. Standards were produced by melting together lead and the metals to be determined. Once the desired homogeneity was attained, an appropriate amount of sulfur was added and the metal mix plus sulfur reacted at a temperature sufficient for the production of PbS. All metals used were spectrographically pure. The sulfur was obtained from the Freeport Sulfur Company. Standards were made for the initial Pb-metal mixture by an addition technique and calibration and crystallinity were checked by emission spectrographic, X-ray diffraction and fluorescence techniques. Instrumental conditions are given in Table 2. Analytical precision

TABLE 2. INSTRUMENTAL CONDITIONS

Spectrograph	Jarrell-Ash, 1 m., Czerny-Turner mounted
Source	Jarrell-Ash Mark II Laser Microprobe
Photographic plates	Eastman Kodak 103-0 and S.A. No. 3
Analytical gap	2 mm
Position of electrodes	2 mm above sample
Laser output energy	0.5 joule
Cross-excitation voltage	2kV
Plate development	3 min. 50 sec. @ 19° C.
Analytical lines	Pb 2577.3Å; Cu 3273.9Å; Bi 2897.9Å; Ag 3280.7Å; Zn 3302.6Å; Ni 3414.8Å; Sn 2839.9Å; Fe 3020.6Å.

TABLE 3. STATISTICAL DATA FOR REPLICATE LASER MICROPROBE DETERMINATIONS ON SINGLE CRYSTALS

	n	$\bar{x}$	s	C(%)
Bi	3	123	12.4	10.1
Ag	4	29	5.6	19.5
Fe	4	28	5.4	19.3
Zn	3	125	12.6	10.1
Cu	4	24	2.7	11.4
Sn	4	58	6.8	11.8
Ni	4	42	4.7	11.2

n = number of determinations; $\bar{x}$ = average value; s = standard deviation; C(%) = coefficient of variation.

was checked many times by replicate determinations and typical data are given in Table 3. Precision is not high, but the variation in the elements within and between samples is substantially larger than the analytical error. The accuracy of the determinations was made by comparison with carefully prepared standards and, as is noted below, there is an internal consistency to the results.

ZONING AND GROWTH

In this study, 31 samples were investigated by microprobe techniques. A representative group of 14 was then chosen for detailed study which included sectioning and analytic traverses. An attempt was made, in all cases where traversing was attempted, to section the crystal parallel to a crystallographic face and through the geometric center. This was difficult to accomplish, especially with small crystals in matrix and such samples were given less weight in the data interpretation.

The samples investigated represent many types of galena deposits but can be divided simply into two groups on the basis of coexisting minerals and structures. *Replacement ores* are represented by samples from: (1) Northern Lights mine, Pine Lake District, Idaho; (2) Austinville, Virginia; (3) Bunker Hill mine, Coeur d'Alene District, Idaho; (4) Federal mine, St. Francis, Missouri. Ores which are best classified as *cavity fillings* are exemplified by: (1) Ottawa Co., Oklahoma; (2) Baxter Springs, Kansas; (3) Galena, Missouri; (4) Cumberland, England; (5) Felsobanya, Rumania; (6) Keystone mine, Crested Butte, Colorado; (7) Lafayette mine, Marion County, Kentucky. Generally, crystals of the replacement type were anhedral but cubic faces were evident in the sample from the Federal mine, Missouri, and cubic and cubo-octahedral faces were observed in the sample from Austinville, Virginia. Those crystals which grew by cavity or open-space fillings were nearly always euhedral and, of the samples studied, all had well-developed cubic (100) faces except that from Felsobanya, Rumania, which was dominantly {111} with minor {100}. The replacement types generally gave no clear indication of growth directions. The cavity-filling types, however, were easily distinguished as to growth directions. Even in small samples which were out of structural context and rather massive, decisions could be made as to growth directions by observing the euhedral faces.

The results of microprobe traverses across several galena crystals from cavity fillings are shown in Figures 1 and 2. The direction of growth is shown in each case and it becomes obvious that asymmetric growth leads to strong asymmetry in the chemical zoning pattern. In every case, the total contaminant level increases in the growth direction, albeit with minor fluctuations. This pattern is similar to that noted for contaminants in quartz growing into open space (Dennen & Puckett 1972). The zoning patterns observed for the samples from Baxter Springs, Kansas and Ottawa County, Oklahoma are symmetrical. As the diagrams also indicate, the growth of these specimens is generally symmetric as well, especially in the case of the Oklahoma specimen which exhibited six good cubic faces, all with lineage structure. The zoning patterns of galena crystals deemed as replacement types are shown in Figure 3. These are somewhat more complex but generally symmetric with total contaminant levels increasing with outward growth.

The patterns of chemical zoning in galena may represent growth of this mineral in a closed system in which the distribution coefficients of elements other than lead are less than unity. These elements would then build up in residual liquids, resulting in an increased concentration in later galena fractions. A closed system is, however, unlikely for the galenas of this study and the zoning patterns probably represent changing ore-fluid composition at approximately constant temperature. This mechanism allows distribution coefficients to remain constant and the activity of a specific element in the crystallizing galena would depend upon the activity of that element in the ore fluid and the solid phases present in the reacting system.

Furthermore, the inclusion of any foreign ion into the structure of a crystal increases the lattice energy in its vicinity. This increase in energy is the result of distortion caused by whatever differences exist in ionic radii and bond type between substituting and formulary ions. Even though entropic forces are conducive to complete homogenization of impurities, crystals will attempt to expel all foreign ions and other crystal defects, such as vacancies, in order to achieve the lowest possible energy configuration. If this

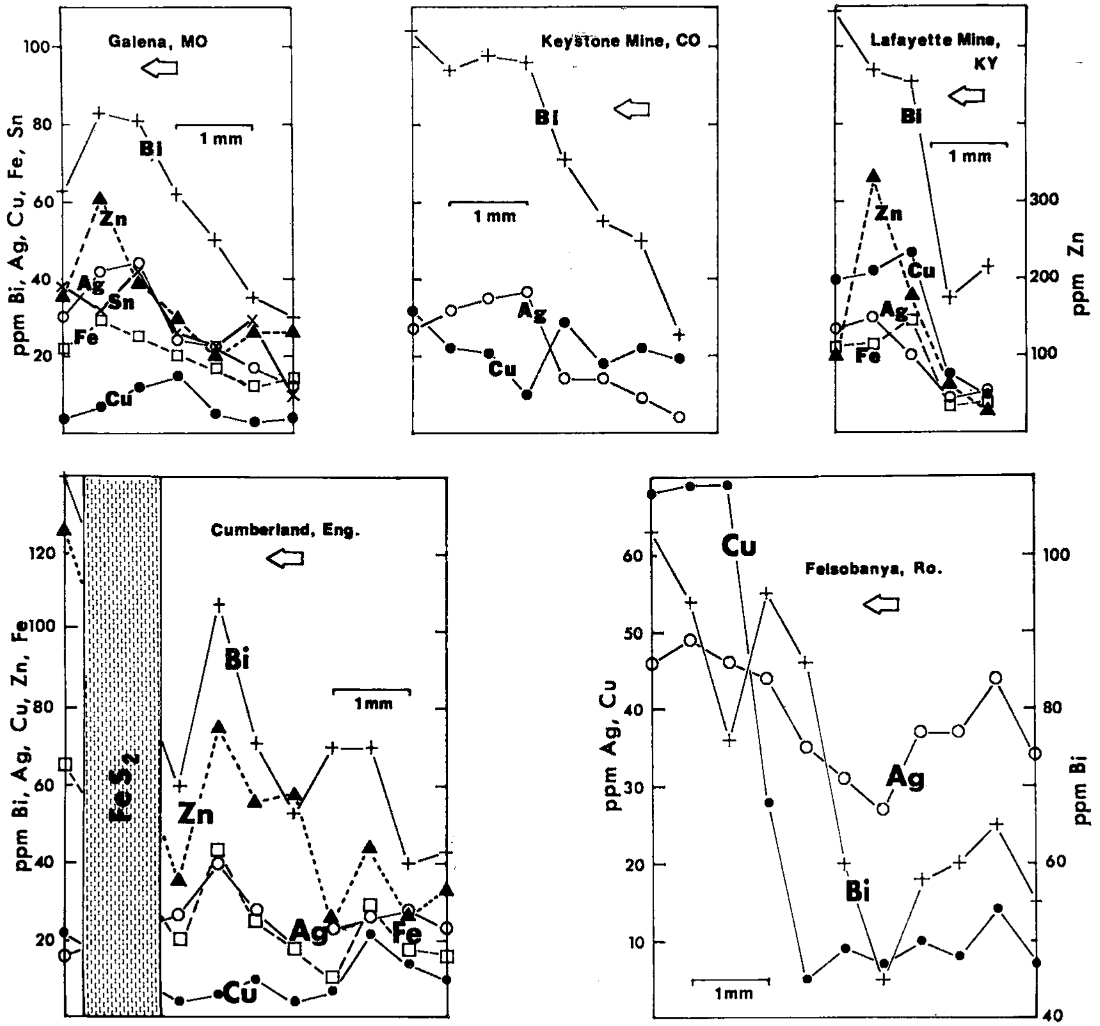

FIG. 1. Laser microprobe traverses across galena from cavity fillings. Growth directions as determined petrographically are shown by the arrows.

expulsion process is operative during and/or after crystallization, the observed increase of contaminants towards crystal edges would be expected. The asymmetric rise in contaminants in an asymmetrically grown crystal would, however, lead to a preference for a fractionation scheme rather than the last mentioned expulsion process.

As the diagrams indicate, Bi, Ag, and Cu are observed in all the galenas studied. Fe and Zn are noted in several, and Sn and Ni are only locally observed. Generally the levels are not high, with Zn and Bi the most abundant on a weight basis. Maximum Bi is close to 100 ppm, and Zn is noted at about 1000 ppm in the Coeur d'Alene sample (Fig. 3). The samples were carefully checked for inclusions prior to the microprobe determinations and the low levels of contaminant elements support the lack of observed inclusions.

In general there is a rather close correlation between Bi-Ag and Bi-Cu pairs. Correlation is also noted between Ni and Cu in the Baxter Springs sample (Fig. 2), the only sample in which Ni was ubiquitously found. Zn sometimes follows the patterns of Cu and Fe. Sn, when observed, generally correlates with Zn. The patterns for Fe are often erratic and bear little relation to other elements.

Schwendeman & Blackburn (1974) reported that Mg may be present in the galenas studied. A re-examination of the data found no correla-

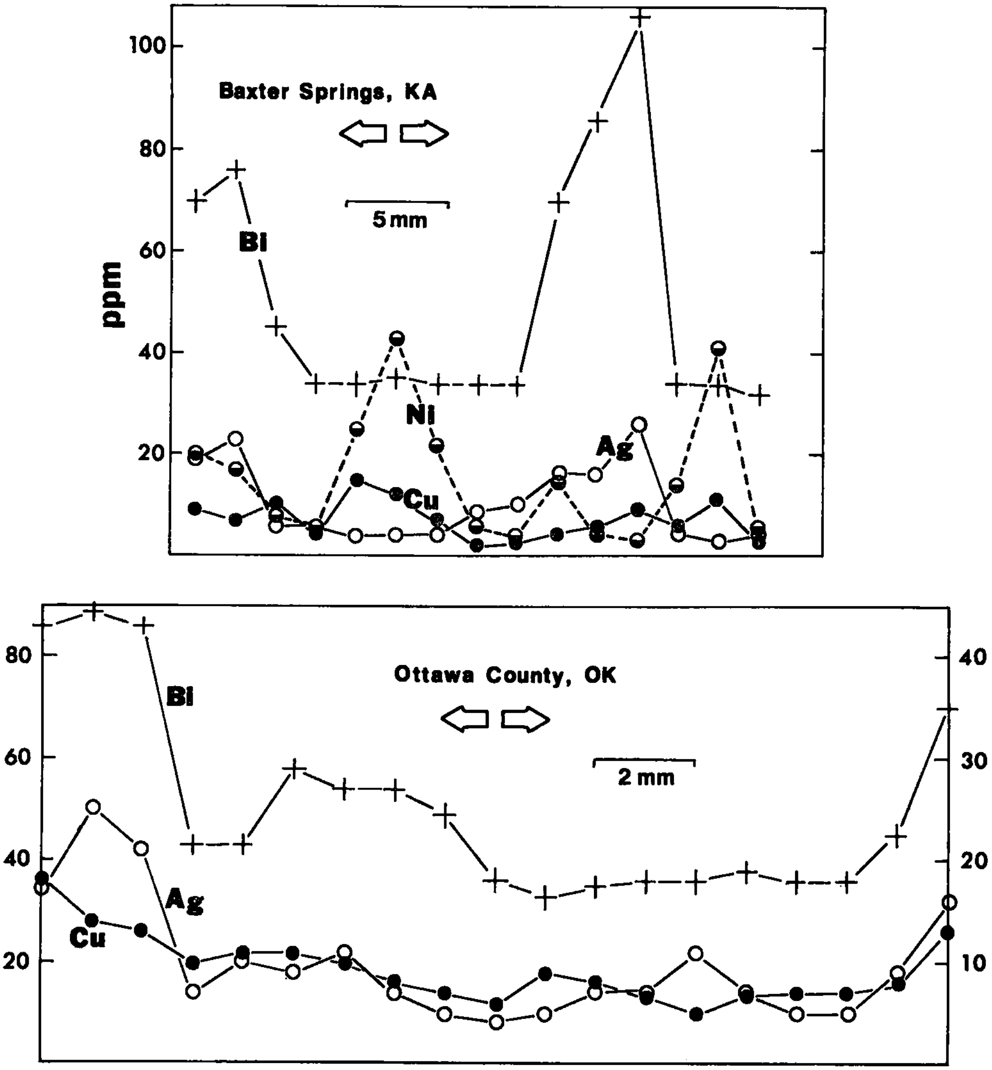

FIG. 2. Laser microprobe traverses across galena from cavity fillings. Both samples were euhedral with good {100} forms. The traverse on the Baxter Springs crystal is limited on the left side due to breakage.

tion with Ca. This relationship would be expected in these samples as they are generally carbonate-related. It is concluded that the abserved magnesium is due to contamination of the electrodes.

STOICHIOMETRY

Several elements may enter galena and the observation of zoning patterns for most has already been noted. This study could not evaluate the concentration of antimony or arsenic as both were always below detection limits of about 50 ppm. The possibility of anionic substitution of Se and Te was not considered. The presence or absence of defects in the galena structure were also immeasurable with present capabilities. Electrical neutrality must be maintained, however, and the evaluation of available data should reveal if charge balancing involves only cationic substitution. Obviously, substitution of divalent ions such as Fe^{2+}, Zn^{2+}, Sn^{2+}, Cu^{2+}, and Ni^{2+} for Pb^{2+} has no effect on electrical neutrality. Only substitutions such as Bi^{3+}, Ag^{+} or Cu^{+} need be considered. Their concentrations are recalculated on an atomic basis and plotted in terms of the number of atoms of the metal per 10^6 Pb atoms. These are plotted in diagrams

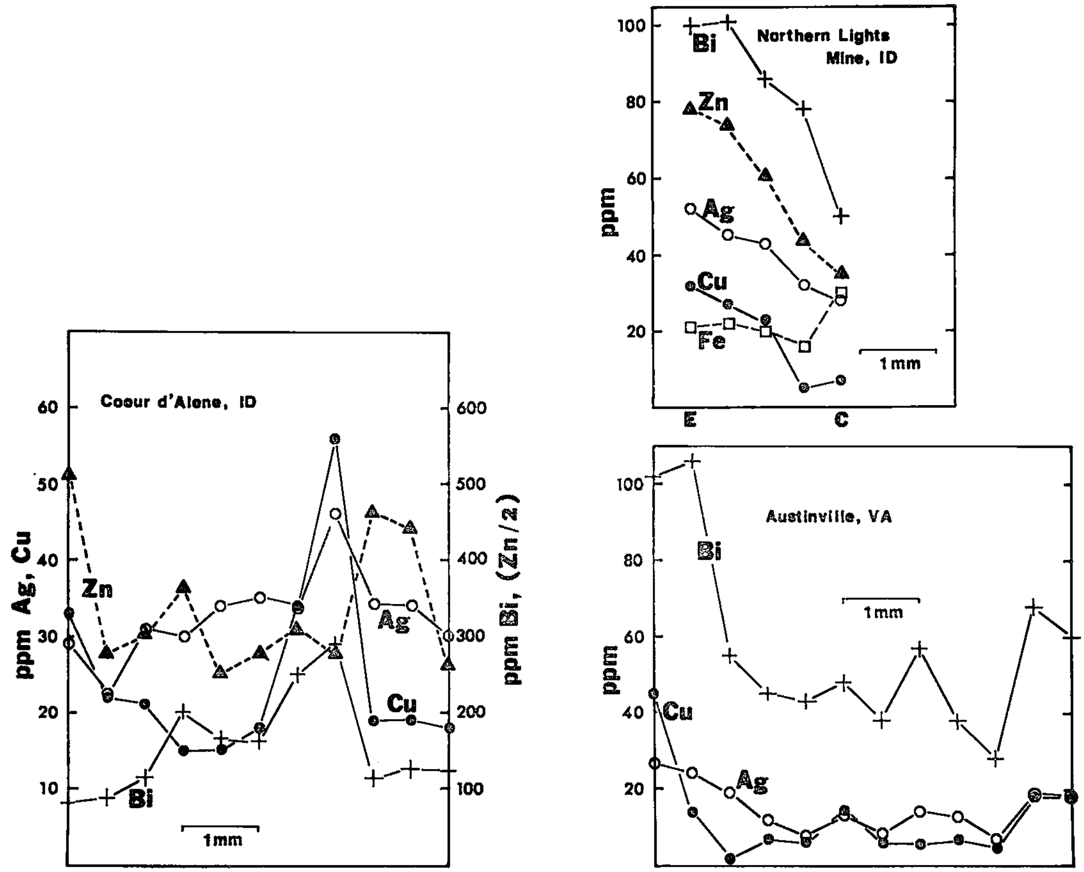

FIG. 3. Laser microprobe traverses across galena from replacement deposits. No clear growth directions for these crystals are indicated. The traverse on the Northern Lights crystal is from its center (C) to its edge (E).

where the ordinate represents the charge excess in the lead site and the abscissa represents the charge deficiency in the Pb site. A one to one ratio must be maintained between the two. Three distinct patterns emerge and these are discussed separately.

Bi^{2+}–Ag^{+} couple

Figure 4 represents stoichiometric substitution in natural galena where the charge balance is dependent only upon the coupled substitution of Bi^{3+} and Ag^{+}. Perfect charge balance and, thus, correlation of the atomic values of these elements would result in [Bi^{3+}]/[Ag^{+}]=1.00. The average value for all data points in the samples which fell in this group is 1.08. The samples in which stoichiometry may be satisfied by the coupled substitution of Bi^{3+} and Ag^{+} are: Galena, Missouri; Northern Lights mine, Idaho; Felsobanya, Rumania.

Bi^{3+}–(Ag^{+}+Cu^{+})

Figure 5 shows the stoichiometric substitution of Bi^{3+}, Ag^{+}, and Cu^{+} into samples from the Russell Cave mine, Kentucky; Henderson County, Kentucky; Columbia Shaft, Kentucky; Federal mine, Missouri; Baxter Springs, Kansas; Coeur d'Alene, Idaho; Cumberland, England; and Ottawa County, Oklahoma. In this group, the charge excess due to Bi^{3+} substitution for Pb^{2+} is balanced by atomic Ag^{+} plus atomic Cu^{+}. Again, for perfect charge balance, the ratio [Bi^{3+}]/[Ag^{+}+Cu^{+}] should equal 1.00 and the average value of this ratio for all data points from these samples is 1.06.

Bi^{3+}–(Ag^{+}+Cu^{+})+Cu^{2+}

In samples from the Keystone mine, Colorado; Austinville, Virginia; and the Lafayette mine, Kentucky, the amount of Ag^{+} was insufficient to make up the charge excess imposed by Bi^{3+} substitution. On the other hand, the simple addition of Ag^{+} and Cu^{+}, as previously described, resulted in a charge deficiency in the Pb site. It is possible, however, that both Cu^+ and Cu^{2+} are present. A data point on each sample was picked at random and the $Cu^+/(Cu^+ + Cu^{2+})$ ratio calculated which would give just enough Cu^+ for all other data points on this sample. This method assumes that Cu^+/Cu^{2+} is the same throughout the crystallization history of that crystal. The results are given in Figure 6 where the Cu^+/Cu^{2+} ratio for each sample is given along with the charge-balance ratio resultant from the Cu^+ calculation. The overall average value of the ratio $[Bi^{3+}]/[Ag^+ + Cu^+] = 1.08$.

The role of iron

Some of the iron may be present as Fe^{3+} although the crystal chemistry of this ion would preclude its wholesale substitution into the galena structure. However, if some Fe^{3+} is present, it must be considered along with Bi^{3+} as causing a charge excess in the Pb^{2+} position. Data points which still have an excess of Cu^+ following the correlation procedure described above may be balanced by the conversion of a rather small amount of Fe^{2+} to Fe^{3+}. Indeed, those data points in Figure 6 which have a charge deficiency even after conversion of Cu^+ and Cu^{2+}

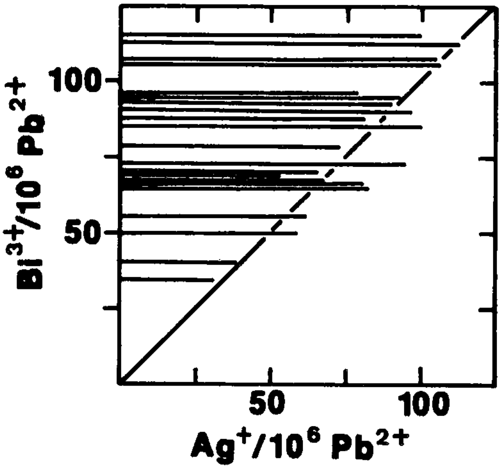

FIG. 4. Stoichiometric substitution in galena from Galena, MO., Northern Lights mine, Idaho, and Felsobanya. The ordinate gives the charge excess in the lead site and the abscissa gives charge deficiency in this same site.

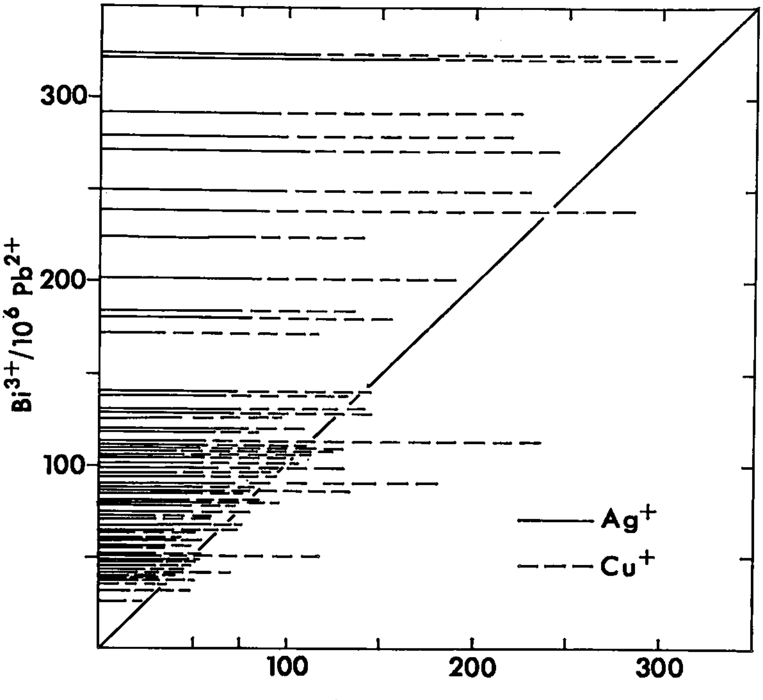

FIG. 5. Stoichiometric substitution in galena from Russell Cave mine, KY., Henderson County, KY., Columbia Shaft, KY., Federal mine, MO., Baxter Springs, KA., Coeur d'Alene, ID., Ottawa County, OK., and Cumberland, Eng. The ordinate and abscissa represent charge excess and deficiency, respectively, in the Pb site.

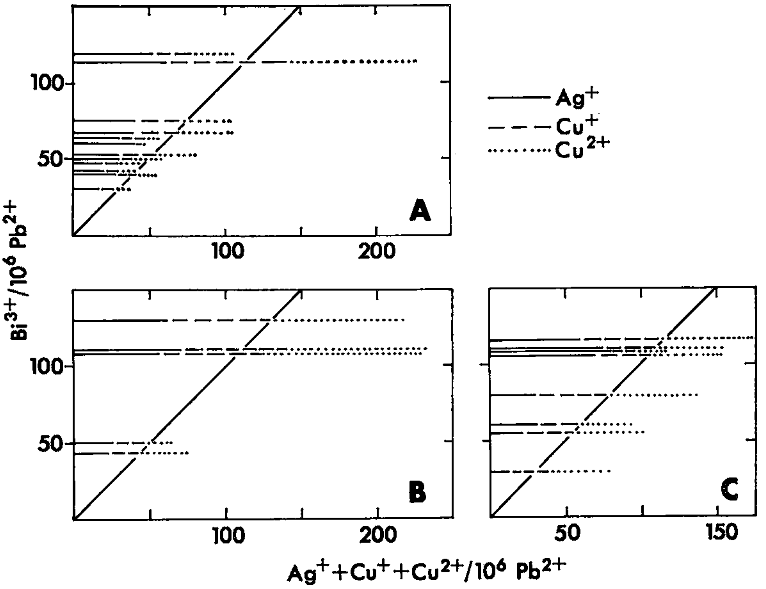

FIG. 6. Stoichiometric substitution in galena. (A) Austinville, VA., $[Bi^{3+}]/[Ag^{+}+Cu^{+}]=1.15$; $[Cu^{+}]/[Cu^{2+}]+0.93$. (B) Lafayette mine, KY.; $[Bi^{3+}]/[Ag^{+}+Cu^{+}]=1.02$; $[Cu^{+}]/[Cu^{2+}]=0.77$. (C) Keystone mine, CO.; $[Bi^{3+}]/[Ag^{+}+Cu^{+}]=0.99$; $[Cu^{+}]/[Cu^{2+}]=0.78$.

are also high in iron. This is especially evident in Figure 1 where Fe and Cu correlate closely.

CONCLUSIONS

Galena crystals of both replacement and cavity-filling types were examined. The galenas were from several types of deposits, including the Mississippi Valley type and the igneous-related deposit at Coeur d'Alene, Idaho. Bismuth, silver, and copper are ubiquitous in these samples, zinc and iron are commonly found, and Sn and Ni were rarely noted.

Individual crystals were sectioned and the chemical zoning evaluated. Generally, it was found that the total contaminated level increased with growth. This observation is most evident in samples which grew into open space as their zoning patterns are clearly asymmetric. Symmetric zoning patterns were found in generally anhedral crystals from replacement deposits and from cavity-filling crystals which are euhedral and symmetric (equidimensional).

Stoichiometry can be assumed in natural galenas and the charge balance configuration may be one of three types. The excess charge in the octahedral Pb^{2+} position caused by substitution of Bi^{3+} may be balanced by concomitant substitution of Ag^{+} for Pb^{2+} or by Ag^{+} plus Cu^{+}. In certain galenas copper exceeds the Cu^{+} needed for stoichiometry. A Cu^{+}/Cu^{2+} ratio may be calculated which corrects for this and which remains constant throughout the galena crystal. This feature might indicate that the factors controlling the oxidation potential in the ore solution remain relatively constant over at least that period of time necessary for crystallization of a single galena crystal. A complete electronic analysis is required, however, to support or refute this speculation. Ferric iron may add to the charge excess but this effect is probably minimal considering the oxidation potentials involved and the crystal chemistry of the Fe^{3+} ion.

Lead deposits which are igneous-related and those which are stratabound with no probable kinship to igneous processes may be distinguished (Sangster 1970) on the basis of their structure and bulk chemistry. It was originally considered that *in situ* determinations of the chemical impurities in the galena would provide information regarding contaminant solubilities in this mineral under varying conditions of deposition. The results of the present study, however, allow no decision with regard to trace-element chemistry and the type of deposit or its temperature of deposition. Deposits in orogenic areas and possibly associated with igneous activity such as the sample from the Coeur d'Alene District and the Pine Lake District of Idaho, the Keystone mine in Colorado, and the Austinville mine in Virginia show no abnormal zoning patterns. The Coeur d'Alene sample is higher in total contaminant, especially Bi and Zn, than most but the others are not significantly different.

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