THE AMERICAN MINERALOGIST, VOL. 50, OCTOBER, 1965

SOLID SOLUTION IN THE SYSTEMS ZnS-ZnSe AND PbS-PbSe AT 300° C. AND ABOVE[1]

HAROLD D. WRIGHT, WALTHER M. BARNARD
AND JOSEPH B. HALBIG

Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pa.; Department of Geology, State University College, Fredonia, N. Y.; and Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pa.

ABSTRACT

The hydrothermal method has been used to study solid solution in the systems ZnS-ZnSe and PbS-PbSe at relatively low temperatures, preparatory to measurement of partition coefficients of selenium between sphalerite and galena. Continuous solid solution was found in both systems at 300° C., and extensive solid solution in the ZnS-ZnSe system extends at least down to 160° C.

Well formed crystals of Zn(S, Se) and Pb(S, Se) were grown, with a maximum size ranging from about .05 mm (for galena) and 0.5 mm (for sphalerite) at 300° C. to about 1 mm (for both minerals) at 400° C. and above. All runs produced only one crystalline phase. Crystals of both series grown in runs of less than five days at 300° C. had a higher Se/S than that of the starting materials, excess selenium being incorporated throughout the entire compositional range in both series. The initial selenium excess is believed to be metastable in the case of the Zn(S, Se) crystals, but this interpretation is considered less certain in the case of the Pb(S, Se) compositions. Less than six weeks is required for the Zn(S, Se) crystals to attain the Se/S of the starting materials at 300° C., and less than two days at 400° C. Pb(S, Se) crystals having the same Se/S as the starting materials were not obtained, even in runs of eight weeks at 550° C.

The apparent absence of natural examples of the Zn(S, Se) series probably reflects low selenium availability and the scarcity of analyses. Equilibration rates for trace level solid solutions in the sulfides apparently may vary greatly for different elements in the same sulfide. This factor, as well as crystalline solubility, requires laboratory evaluation in the selection of elements applicable to geological studies.

INTRODUCTION

An investigation into the solid solution of selenium in sphalerite and galena at relatively low temperatures was undertaken as part of a program to obtain experimental data on the distribution and solubilities of various trace elements commonly occurring in sulfide minerals. The studies to date have concentrated on solid solubility measurements, because these provide a logical basis for selection of elements and development of experimental procedures for study of the partitition of trace elements between two or more coexisting minerals. The use of trace element partition among coexisting minerals as a means of deducing the

---

[1] Contribution No. 64-66 from the College of Mineral Industries, The Pennsylvania State University, University Park, Pa.

compositions of ore-forming fluids and temperatures of deposition has been suggested by a number of authors. Holland (1956) and Barnes and Kullerud (1957) among others have discussed the theory of element partition with special reference to ore deposits and indicated some of the conditions which must be fulfilled. However, the necessary data on element partition between coexisting minerals, particularly at geologically significant temperatures, are extremely few, and McIntire (1963), in a comprehensive review of the theory and applications of trace element partitition coefficients in geology, has emphasized again the need for further experimental data.

SOME GENERAL CONSIDERATIONS IN EXPERIMENTAL STUDIES OF ELEMENT DISTRIBUTION IN SULFIDES

For partition studies applied to ore deposits, the common sulfides galena, sphalerite, pyrite, and chalcopyrite are of particular interest as host minerals because of their wide stability fields and widespread occurrence. Furthermore, their intricate textural relationships commonly supply evidence of contemporaneous deposition. This is a vital factor in the selection of sample material from the associated minerals representing a reasonable probability of coexistence—a necessary condition for valid application of the analyses to partition calculations.

Selection of elements well suited to study of partition between a given pair of sulfides involves a number of factors, some of which are not easily evaluated. The most important—and obvious—requirement is that of crystalline solubility in the minerals concerned, but such solubility data are rare, particularly for solid solutions limited to the trace level. The elements also should occur commonly in these minerals in concentrations well above the limit of sensitivity of the analytical method (and preferably, large enough to minimize the influence of minute amounts of contaminating phases), and yet well below the limit of solid solution, especially so in the case of non-ideal solid solutions. From the standpoint of equilibrium, those solid solutions which equilibrate most readily with the depositing solution, and hence are easily studied experimentally, are least apt to preserve their original composition through geological time, as has been pointed out by Barton *et al.* (1963). Experimental information on equilibration rates, in addition to solubility data and partition coefficients, therefore are important both as a guide in interpretation of data on natural samples, and for establishing that the experimental partition data represent equilibrium values throughout the range of temperature concerned.

Prediction of trace level substitutions in the sulfides from crystal chemical data (size, charge, electronegativity) is unsatisfactory because of inadequate knowledge of the complex metal-sulfur bond in each mineral and the uncertainty as to how best to use the available crystal chemical data. In the absence of a method—applicable to natural minerals—to detect solid solution at very low concentrations, experimental evidence of adequate solubility is necessary in most cases. Crystal chemical data, however, serve as a useful guide, together with analyses of trace elements in natural sulfides such as those summarized by Fleischer (1955), in the selection of promising elements for experimental solubility studies.

The great difference in the metal atom sites between the 4:4 coordinated, largely covalent bonded, B3 structure of sphalerite and the 6:6 coordinated, largely ionic bonded, B1 structure of galena would suggest that few, if any, metallic elements should be capable of extensive solid solution in both minerals at temperatures typical of ore deposition. No metallic element has been reported in both minerals in amounts greater than 1%, although Fleischer's (1955) summary, and crystal chemical considerations, suggest a number of potential substitutions of the same element in both minerals at the trace level. Among these are silver, arsenic, antimony, indium, mercury, and tin. Our studies, using radioactive tracers and the hydrothermal method of synthesis, have shown that the only elements among these which entered both galena and sphalerite in amounts greater than 1 ppm up to 600° C. were indium and mercury. Study of the partition of indium between coexisting sphalerite and galena is in progress. Thallium, manganese, copper and gallium are among the promising cation substitutions in galena and sphalerite yet to be studied.

With so few metallic elements apparently able to substitute appreciably in both galena and sphalerite, the obvious site to examine is their common anion, sulfur. This has an important advantage over the cation site in that a substitution possible in one sulfide probably will apply to all, enabling determination of more than one partition coefficient in cases where more than two sulfides coexist. On the other hand, few, if any, cations may be expected to substitute in more than two of the common sulfides, at least in amounts likely to be distinguishable from contaminating phases, considering the gross differences in size, coordination, and bonding involved. The experimental data obtained thus far, as noted above, support this statement. Expectable substitutions for sulfur include chlorine, selenium, tellurium, and oxygen. Selenium was considered to be particularly well suited for studies of partition between galena and sphalerite applicable to the relatively low temperatures of ore deposits: (1) it is chalcophile, (2) it may be expected to be present in many sulfide orebodies at the trace level, and (3) because its crystal chemical properties are closely similar to those of sulfur, as illustrated in Table 1, it may be expected to substitute readily in all of the sulfides down to very low temperatures. Bethke and Barton (1959) measured the distribution of selenium and cadmium between sphalerite and galena at temperatures of 599° to 890° C., and of selenium between chalcopyrite and galena in the range of 475° to 595° C.

Preliminary to an investigation of partition, recently begun, hydrothermal experiments in the systems ZnS-ZnSe and PbS-PbSe were carried out (1) to develop a suitable crystal growth procedure, (2) to evaluate the nature and extent of binary solid solutions in those systems, and (3) to obtain information on equilibration rates of the solid solutions. Continuous series at high temperatures between sphalerite and the isostructural zinc selenide, stilleite (Bethke and Barton, 1961; Klemm, 1961), and between galena and the isostructural lead selenide, clausthalite (Earley, 1950; Sindeyeva and Godovikov, 1959; Bethke and Barton, 1961), have been demonstrated using "dry" runs, and at temperatures as low as 400° C. for the galena-clausthalite series (Simpson, 1964). In nature, specimens covering the entire range of solid solution between galena and clausthalite have been described by Coleman (1959). In sharp contrast, no extensive sphalerite-stilleite solid solutions have been reported from natural deposits.

TABLE 1. CRYSTAL CHEMICAL PROPERTIES OF SULFUR AND SELENIUM

	Sulfur	Selenium
Tetrahedral covalent radius[1]	1.04 Å	1.14 Å
Ionic radius (divalent)[2]	1.84 Å	1.98 Å
Electronegativity[1]	2.5	2.4

[1] Pauling (1960).
[2] Ahrens (1952).

EXPERIMENTAL PROCEDURE

The hydrothermal method of crystal growth was employed in order to accelerate reaction rates, material transport, crystal growth, and equilibration. Well formed mixed crystals of Zn(S, Se) and Pb(S, Se) up to about one millimeter across were grown from high purity elemental zinc or lead, sulfur, and selenium, in 2 to 6 molal sodium hydroxide solutions using platinum-lined, 20-cc. Morey bombs. The charges, as shown in Table 2, were prepared at 10 mol.% compositional intervals for Zn(S, Se) runs at 300° C. and (at 70 mol.% ZnSe and above) at 400° C.

For the Pb(S, Se) runs, as shown in Table 3, the interval was decreased from 15 mol.% at 500° C. to 10 mol.% at 400° C. and 5 mol.% or less over most of the range at 300° C. A temperature gradient was maintained from the bottom (warmer) to the top (cooler) end of the liner to promote transport of dissolved nutrient across the thermal gradient. The run temperatures given in Table 2 apply to the region of crystal growth at the seal and have an estimated precision of ±5° C. Pressure was controlled by varying the per cent of fill, and measured for representative runs on 10,000 p.s.i. Heise gauges. It was found to be impractical to maintain constant pressure over the entire temperature range; for runs above 500° C., the percentage fill required to maintain pressure at a constant value of about 1500 p.s.i. (near the maximum feasible at 300° C.) was too small to provide sufficient transport for adequate crystal growth. The initial series of runs were held at temperature for periods of

TABLE 2. EXPERIMENTAL RUN DATA FOR HHYDROTHERMALLY SYNTHESIZED Zn(S, Se) CRYSTALS SYNTHESIZED NEAR 300° AND 400° C., AND SELECTED LOWER TEMPERATURES[1]

Run No.	Charge Composition (mol. % ZnSe)	Run Duration (hours)	Temperature (°C.)	Crystal Composition[2] (mol. % ZnSe)
450	90	113.7	295	95.3±0.8
514	80	118.8	297	92.7±0.3
452	70	114.1	299	74.7±0.5
453	60	90.0	300	81.8±0.8
515	60	66.6	298	80.8±0.1
454	50	90.0	300	62.4±1.4
455	40	90.4	301	55.3±0.8
457	30	88.3	297	44.0±0.2
458	20	88.7	298	29.9±0.2
459	10	88.3	297	14.8±0.2
—	50	42 days	303±6	50.8±0.4
447	90	40.9	400	90.5±0.5
448	80	40.9	400	78.5±0.5
449	70	41.1	399	71.5±0.7
—	50	28 days	401±4	49.8±0.2
463	50	195.3	250	61.6±0.1
462	50	219.7	200	69.0±0.0
509	60	166.3	159	84.0±2.8

[1] Approximate values for pressure (as determined from measurements on test runs) were 1400 p.s.i. at 300° C. and 4500 p.s.i. at 400° C.

[2] Determined by *x*-ray diffraction measurements using the (620) and (531) reflections. The plus-minus value indicates the range of composition about the mean, as calculated separately for the two peaks.

TABLE 3. EXPERIMENTAL RUN DATA FOR Pb(S, Se) CRYSTALS HYDROTHERMALLY SYNTHESIZED NEAR 300, 400, 500, AND 550° C.[1]

Run No.	Charge Composition (mol. % PbSe)	Run Duration (hours)	Temperature (°C.)	Crystal Composition[2] (mol % PbSe)
425	75	70.4	305	94.3±1.4
438	65	92.8	303	80.9±0.6
426	60	70.4	308	95.2±0.3
432	65	87.0	305	81.9±1.0
400	50	96.2	302	72.4±0.6
507	50	81.2 days	303	75.8±0.5
447	40	125.1	298	83.2±1.0
398	30	116.1	305	46.5±1.3
458	35	72.0	301	62.8±0.6
440	20	118.5	302	44.2±0.6
418	15	93.1	299	50.1±2.4
480	15	44.5 days	302	5.0±0.5
401	10	68.5	302	37.3±1.1
402	5	68.5	303	47.3±2.1
402	5	99.5	297	41.3±1.7
439	4	118.5	300	29.8±1.1
435	3	90.7	303	15.9±1.3
431	1	87.0	303	10.4±0.7
383	90	47.5	404	99.0±0.2
378	75	4..4	403	97.7±0.5
377	50	44.4	404	87.8±1.2
506	50	81.2	302	78.6±1.0
379	40	46.8	405	82.9±3.0
380	30	46.8	403	83.8±0.4
381	20	45.3	406	73.1±1.2
382	10	52.7	405	52.8±1.1
476	5	48.0 days	402	23.7±0.7
392	85	45.2	499	97.2±0.5
390	70	44.2	501	94.4±0.4
385	50	48.0	504	93.8±0.4
389	35	44.2	505	72.2±0.6
388	20	48.0	504	68.7±0.7
391	10	45.2	508	20.6±0.6
533	50	27.9 days	546	63.4±1.6
534	50	52.9 days	546	92.5±1.7
535	50	66.7	587	75.8±0.7

[1] Approximate values for pressure (as determined from measurements on test runs) were as follows: at 300° C., 1500 p.s.i.; at 400° C., 5800 p.s.i.; at 500° C., 10,000 p.s.i.; and at 550° C., 10,600 p.s.i.

[2] Determined by *x*-ray diffraction measurements using the (600), (620), (622), and (642) reflections. The plus-minus value refers to the compositional range about the mean as determined from the separate peak measurements.

about two days at 400° C. and above, to three to six days at 300° C. and below. Runs of longer duration were later made to evaluate the problem of equilibration.

The synthesized crystals were scraped from the platinum sealing disk, leached in 3 molal nitric acid for three minutes to remove surface contamination, washed in distilled water, elutriated in methyl alcohol and dried. The composition of the crystals from each run was determined by x-ray diffraction, using a Norelco or a Picker diffractometer with copper $K\alpha$ radiation, employing the linear relationship to cell edge for Zn(S, Se) crystals and to cell volume for Pb(S, Se) crystals determined by Bethke and Barton (1961). The values used for the lattice constants of pure ZnS, ZnSe, PbS and PbSe were those of Bethke and Barton. This procedure was independently checked for the Pb(S, Se) crystals by counting Se^{75}-tagged selenium introduced in the nutrient for one run; a value of 24.0 mol.% PbSe was found, compared with 23.3 mol.% as determined for the same crystals from the x-ray measurement. For Zn(S, Se) compositions the (620) and (531) reflections were used for the calculations, and for Pb(S, Se) compositions, the (600), (620), (622), and (642) reflections. Annealed silicon was used as an internal standard for the Zn(S, Se) measurements, and nickel was similarly employed for the Pb(S, Se) determinations. The compositions of the mixed crystals shown in Tables 2 and 3 are the mean of the calculations for separate reflections as shown in each table.

SOLID SOLUTION OF SELENIUM IN SPHALERITE AND GALENA AT MODERATE TO LOW TEMPERATURES

Selenium in Sphalerite. The data obtained for Zn(S, Se) solid solutions are shown in Table 2 and the relationship of their compositions to the original charge composition is illustrated in Fig. 1. Well formed crystals up to 0.5 mm in diameter and having various compositions across the entire range, ZnS-ZnSe, were grown at a temperature of 300° C., and at least extensive solid solution down to 160° C. is indicated by scattered exploratory runs. At temperatures near 400° C., runs with 90, 80, and 70 mol.% ZnSe produced crystals with essentially the same composition as the starting materials in only two days. A further run held 38 days at this temperature also produced crystals which matched the starting composition, corresponding to 50 mol.% ZnSe. (Because the main objective was to determine whether complete or at least extensive solid solution extends below 300° C., the series at 10 mol.% intervals was not completed, and all subsequent runs were made at lower temperatures.) At 300° C., however, all crystals from runs of less than five days are relatively enriched in selenium. Their compositions follow a fairly smooth curve (neglecting one point at 70 mol.% ZnSe) which reflects a maximum selenium excess of about 30 mol.% ZnSe and a minimum excess of less than 5% toward the compositional extremes. Three exploratory runs at lower temperatures—two at 250° and 200° C. containing 50 mol.% ZnSe, and one at 159° C. with 60 mol.% ZnSe—suggest that continuous solid solution may extend well below 300° C. Crystals from these lower temperature runs tend to contain greater excesses of selenium than those grown at 300° C.

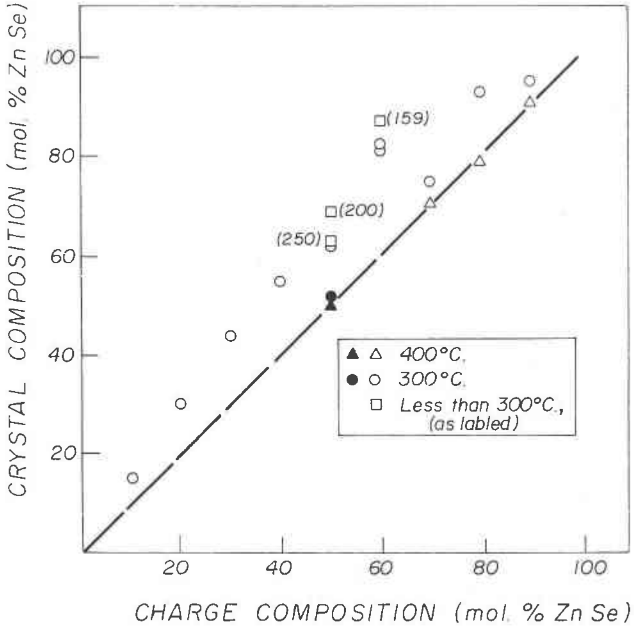

FIG. 1. Compositions of hydrothermally synthesized Zn(S, Se) crystals compared with original charge compositions. The solid symbols represent runs of greater than five days duration, except for the three low temperature runs (at 250°, 200°, and 159° C.). Compositions falling along the diagonal line represent 1:1 mol. ratios of ZnS:ZnSe.

In two relatively long runs, one at 401° C. for 28 days, the other at 303° C. for 42 days, no tendency toward exsolution was found. Crystals from both runs matched the starting compositions. This result for the 303° C. run indicates that the compositions of the Zn(S, Se) solid solutions grown at 300° C. in five days and less probably are metastable, and that a period of several weeks is required for equilibration.

Selenium in Galena. Figure 2 is a plot of the compositions of Pb(S, Se) crystals versus crystallization temperature. Figure 3 illustrates the relationship of the crystal compositions to the original charge composition. Data for the runs are shown in Table 3.

As in the case of the Zn(S, Se) compositions, continuous solid solution between PbS and PbSe was found to exist at least down to 300° C. Attempts to grow crystals at still lower temperatures failed, apparently due to inadequtae transport of material. The crystalline products of all runs synthesized at 300° C. consisted of a single phase. As a further check to establish the absence of a solvus above 300° C., the crystals from runs 398, 400, 401, 402, 418, and 420 were sealed in gold capsules and held at 300° C. for three months. A single phase of the same composition originally determined was found in each case.

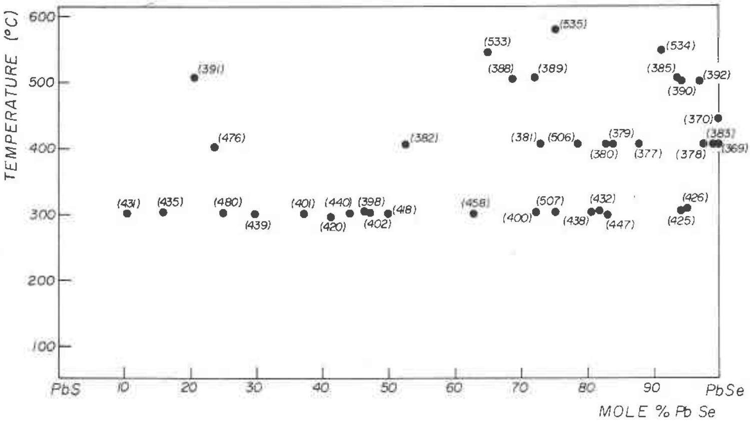

FIG. 2. Composition of hydrothermally synthesized Pb(S, Se) crystals versus crystallization temperature (run numbers are shown in parentheses).

An unexpected finding, considering the relative ease of equilibration found in studies of galena solid solutions cited by Barton *et al.* (1963), was that selenium excesses in the Pb(S, Se) crystals were greater than those in the Zn(S, Se) crystals for corresponding temperatures and compositions, and for crystals of similar size range. This is illustrated in Fig. 3, which indicates that in no case did the crystals match the Se/S of the starting materials, rather large selenium excesses remaining even in runs as long as 53 days at 550° C. This finding contrasts sharply with the results for Zn(S, Se) crystals described above, in which apparently equilibrium compositions resulted from two-day runs at 400° C. As with the Zn(S, Se) crystals, the selenium excesses in the Pb(S, Se) crystals decrease somewhat at the compositional extremes (it is apparent that at the high selenium end this is necessarily the case).

The great scatter of the Pb(S, Se) compositions plotted in Fig. 3 is interpreted as reflecting a variation in rate of approach to equilibrium as a function of (1) the considerable variation in maximum crystal size observed from run to run (the time required for the excess selenium to be relieved by diffusion out of the crystals varying with crystal size), and (2) the much larger compositional differences of the Pb(S,Se) crystals, compared with the starting materials, than those of the Zn(S,Se) crystals.

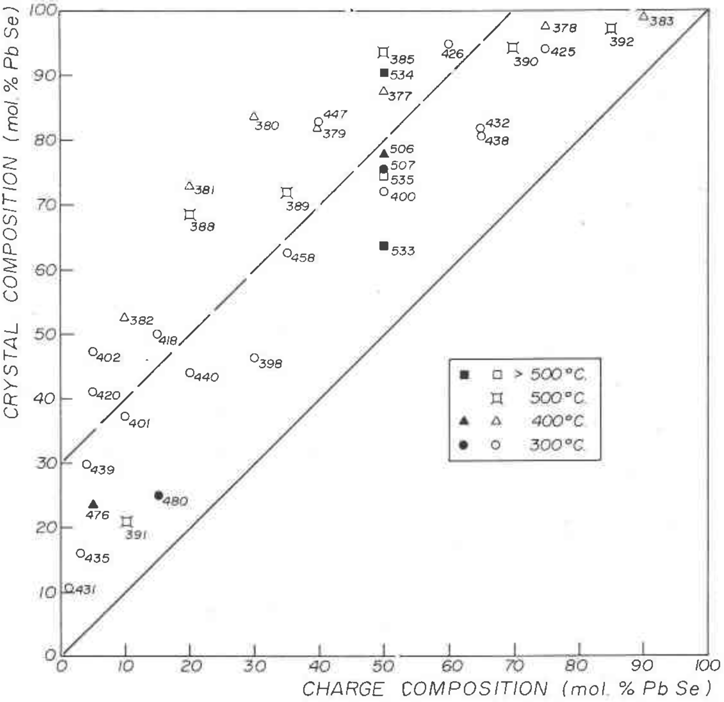

FIG. 3. Compositions of hydrothermally synthesized Pb(S, Se) crystals compared with original charge compositions. The solid symbols represent runs of greater than five days duration. Compositions falling along the solid diagonal line represent 1:1 mol. ratios of PbS:PbSe; the dashed line is arbitrarily drawn through points representing a compositional difference from the 1:1 values of 30 mol. % PbSe. Run numbers are given adjacent to each point.

The smaller selenium excesses in crystals grown at 300° than at 400° and 500° C. appear at first to be in conflict with the expected slower equilibration at the lower temperatures. The explanation is believed to be in the extremely fine size of the crystals grown at 300° C., a few hundreths of a millimeter in diameter compared with crystals over ten times this diameter in the 400° and 500° C. runs. This increase by an order of magnitude apparently more than offsets the presumably exponential increase in solid diffusion rate with increased temperature over the 200° C. range.

Seven runs of longer duration, 28 to 81 days, were made in an attempt to determine whether the compositions of the Pb(S,Se) crystals, like those of the Zn(S, Se) crystals grown at 300° C., represent metastability and, if so, to obtain information on rates of equilibration. The problem was explored in two portions of the compositional range: at the midpoint (runs no. 506, 507, 533, 534 and 535), where PbSe excesses of more than 40 mol.% were observed, and in the range of 8–13 mol.% PbSe (runs no. 476 and 480) where the maximum relative selenium excesses were found. None of these runs (nos. 476, 480, 506, 507, 533, 534, and 535, represented by the solid symbols in Fig. 3) produced crystals having the Se/S of the starting materials. Taken together, the crystal compositions from these longer runs represent a closer approach to the starting compositions than that shown by the shorter runs (five days or less), and this is evidence that all compositions are metastable. The great variability of individual runs representing similar starting composition and duration (particularly nos. 391 and 534) indicates that other factors —probably crystal growth rate and size distribution in particular—are not constant from run to run and interfere with comparison of crystal compositions in terms of equilibration. These factors are difficult if not impossible to control under our experimental conditions. Additional runs are being made at higher temperatures (using bombs machined from high-strength alloys) and for longer periods of time to evaluate further the equilibrium problem in the case of the Pb(S,Se) crystals and to establish equilibration rates.

Discussion

The explanation for the excess selenium incorporation in both galena and sphalerite could lie in (1) a possible difference in availability of selenium and sulfur (reflecting differences in solubility, degree of polymerization, or formation of complex ions and their equilibria, between sulfur and selenium) or (2) metastability, with crystal growth too rapid to permit an equilibrium redistribution of the selenium and sulfur atoms in the growing crystal faces before addition of succeeding layers, coupled with low solid diffusion rates. In the absence of data—applicable to the temperature range concerned here—on aqueous solubility, ionic species and their stabilities and equilibria, polymerization, and diffusion rates for sulfur and selenium in galena and sphalerite, the correct explanation probably cannot be established with certainty. Data at low temperatures indicate little difference in polymerization of sulfur and selenium. The Eh-pH diagrams for sulfur and selenium (Pourbaix, 1963) indicate that—at low temperatures—sulfur would be more extensively oxidized than selenium, resulting in a greater availability of selenium ions than of sulfur relative to the Se/S of the starting materials. However, it is considered unsafe to use data at 25° C. to predict the kinetics of reactions in these systems in the range of temperature concerned. A number of hydrated sulfides, sulfates, selenides, and selenates of sodium are known and their large solubilities, together with the rapid material transport and growth of crystals observed in short term runs indicate that extensive solubilities of both sulfur and selenium would be expected under our conditions. This is supported by the absence of any precipitate in the cooled solutions at the conclusion of the runs, even in the case of the Pb(S,Se) runs having compositional differences of 40 mol.% PbSe between crystals and starting materials.

The facts that Zn(S,Se) crystals having the same sulfur/selenium ratio as the starting materials were grown in only two days at 400° C., and that equilibration of the solid solutions formed at 300° C. required only a few weeks, together with the observation of relatively slow equilibration of sphalerites containing iron and other substitutions below 500° C. (Barton *et al.*, 1963) indicate that metastability rather than availability is the explanation for the Zn(S,Se) compositions, at least. The observed tendency for the Pb(S,Se) crystals to approach—if slowly—the starting compositions is evidence (albeit inconclusive) that metastability is involved here too, because large changes in availability over weeks or months due either to changes in polymerization or composition of ions in solution seem improbable.

Because it appears probable that metastability is involved in both cases, it is tempting to assume that it is the complete explanation and that availability is not a factor. However, the slow equilibration of the Pb(S, Se) crystals as high as 550° C. was not expected in view of the findings of Simpson (1964), who obtained equilibrium Pb(S, Se) compositions at 400° C. in dry runs of somewhat more than six months' duration. Further runs of greater duration and at higher temperatures are necessary to settle the problem of the Pb(S, Se) compositions.

It is interesting to note that the problem of equilibration rates of trace level crystalline solutions of indium in sphalerite and galena appears to be just the opposite of the results obtained with selenium (Barnard, 1965; Halbig, 1965). The indium-bearing galenas grown at 400° C. (where the solubility is about 20 ppm) appear to reach equilibrium compositions within a few days. The indium-bearing sphalerites, on the other hand, require more than two months for equilibration at 600° C. (where the solubility is about 170 ppm).

In summary, continuous solid solution exists between PbS and PbSe and between ZnS and ZnSe at temperatures as low as 300° C., and widespread solid solution in the latter system extends at least down to 160° C. Although natural examples of the Zn(S, Se) series have not been reported (Klemm, 1961), it appears probable that this reflects simply the scarcity of analyses and the low availability of selenium in many natural sulfide deposits.

Pb(S, Se) crystals up to 0.05 mm in diameter and Zn(S, Se) crystals up to 0.5 mm in diameter, grown in five days or less at 300° C., have apparently metastable compositions, an excess of selenium being incorporated throughout the compositional range in both cases. Zn(S, Se) crystals grown in two days at 400° C. and ranging up to 1.0 mm in size have compositions matching the starting materials, indicating that these crystals had equilibrated. On the other hand, equilibration of Pb(S, Se) crystals has not been achieved in runs of two months at 550° C. It appears that rates of compositional equilibration in sulfide minerals may vary greatly with the elements involved, and may serve as a further limitation—in addition to crystalline solubility and adequate availability—in the selection of elements for laboratory measurements of partition coefficients applicable to geological studies.

ACKNOWLEDGMENTS

This study was supported by grants no. G-24281 and GP-2813 from the National Science Foundation. Dr. H. L. Barnes of The Pennsylvania State University contributed valuable discussion of the problem of metastability.

REFERENCES

AHRENS, L. H. (1952) The use of ionization potentials. Part 1. Ionic radii of the elements. *Geochim. Cosmochim. Acta* **2,** 155–169.

BARNARD, W. M. (1965) Solubilities of selected chalcophile elements in hydrothermally synthesized β-ZnS (sphalerite). Ph.D. thesis, Pennsylvania State University.

BARNES, H. L. AND G. KULLERUD (1957) Relations between composition of ore minerals and ore solutions. *Econ. Geol.* **52,** 825–830.

BARTON, P. B., JR., P. M. BETHKE AND P. TOULMIN (1963). Equilibrium in ore deposits. *Mineral Soc. Am. Spec. Paper* **1,** 171–185.

BETHKE, P. M. AND P. B. BARTON, JR. (1959) Trace-element distribution as an indication of pressure and temperature of ore deposition (Abstract). *Geol. Soc. Am. Bull.* **70,** 1569–1570.

——— (1961) Unit-cell dimension versus composition in the systems PbS-CdS, PbS-PbSe, ZnS-ZnSe, and $CuFeS_{1.90}$-$CuFeSe_{1.90}$. *U. S. Geol. Surv. Prof. Paper* **424-B,** 226–270.

COLEMAN, R. G. (1959) The natural occurrence of galena-clausthalite solid solution series. *Am. Mineral.* **44,** 166–175.

EARLEY, J. W. (1950) Description and synthesis of the selenide minerals. *Am. Mineral.* **35,** 337–364.

FLEISCHER, M. (1955). Minor elements in some sulfide minerals. *Econ. Geol. Fiftieth Ann.* Vol., Pt. **2,** 970–1024.

HALBIG, J. B. (1965) Solubility studies of selected chalcophile elements in hydrothermally synthesized galena. M.S. thesis, Pennsylvania State University.

HOLLAND, H. D. (1956) The chemical composition of vein minerals and the nature of ore-forming fluids. *Econ. Geol.* **51,** 781–797.

KLEMM, D. D. (1961) Über die Mischkristallreihe Zincblende-Stilleit. *Neues Jahrb. Mineral. Monatshefte,* 1961, 253–257.

McINTIRE, W. L. (1963) Trace element partition coefficients—a review of theory and applications to geology. *Geochim. Cosmochim. Acta* **27,** 1209–1264.

PAULING, L. (1960). *The Nature of the Chemical Bond and the Structure of Molecules and Crystals,* 3rd ed. Cornell Univ. Press, Ithaca, N. Y., 664 p.

POURBAIX, M. (1963) *Atlas D'Équilibre Électrochimiques.* Gauthiers-Villars. Paris.

SINDEYEVA, N. D. AND A. A. GODOVIKOV (1959) Isomophism between sulfur and tellurium in galena. *Akad. Nauk. S.S.S.R. Dokl. Earth Sci. Sect.* **127,** 620–623.