

EFFECT OF SUBSTITUTIONS ON THE CELL DIMENSION OF TETRAHEDRITE

NEIL E. JOHNSON, JAMES R. CRAIG AND J. DONALD RIMSTIJD

Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

ABSTRACT

Linear regression analyses of published data for tetrahedrite define equations that predict the cell dimension of natural and synthetic tetrahedrite, in terms of compositions in atoms per formula unit, to within an average of ± 0.02 Å. The equations are: $a(\text{Å})_{\text{natural}} = 10.379 + 0.082(\text{Ag}) - 0.01(\text{Ag}^2) - 0.009(\text{Cu}^*) + 0.66(\text{Hg}) - 0.038(\text{As}) + 0.144(\text{Bi})$ and $a(\text{Å})_{\text{synthetic}} = 10.381 + 0.039(\text{Ag}) + 0.003(\text{Ag}^2) - 0.019(\text{Cu}^*) + 0.064(\text{Cd}) - 0.037(\text{As})$ for natural and synthetic tetrahedrites, respectively, where Ag, Hg, As, Bi and Cd are the number of atoms per formula unit, and Cu^* is equal to $2.0 - (\text{Fe} + \text{Zn} + \text{Hg} + \text{Cd})$. The equations have correlation coefficients R^2 of 0.9789 and 0.9893, respectively, and all of the regression coefficients β are significant at the 95% confidence level. Variation of the Fe/Zn ratio has no appreciable effect on a . Calculation of changes of molar volume with composition indicate that $\text{As} \leftrightarrow \text{Sb}$, $\text{Bi} \leftrightarrow \text{Sb}$, $\text{Cu} \leftrightarrow (\text{Fe}, \text{Zn})$, $\text{Hg} \leftrightarrow (\text{Fe}, \text{Zn})$ and $\text{Cd} \leftrightarrow (\text{Fe}, \text{Zn})$ substitutions may be ideal or nearly so, whereas the $\text{Ag} \leftrightarrow \text{Cu}$ substitution is not. Comparison of the equations for natural and synthetic tetrahedrite indicates that the intercepts are statistically equivalent and the coefficients for Cu^* are similar, but that the coefficients for As and Ag differ distinctly. The difference between natural and synthetic Ag-bearing tetrahedrite has been noted previously; the differing distributions of data for natural and synthetic samples of As-bearing tetrahedrite result in a falsely significant test that illustrates the need for caution in interpreting statistical results.

Keywords: tetrahedrite, linear regression, cell dimension, molar volume.

SOMMAIRE

On définit, par régression linéaire des données publiées pour la tétraédrite, la relation entre la maille élémentaire d'un échantillon naturel ou synthétique et sa composition (en atomes par unité formulaire), à ± 0.02 Å près. Pour un échantillon naturel, $a(\text{Å}) = 10.379 + 0.082(\text{Ag}) - 0.01(\text{Ag}^2) - 0.009(\text{Cu}^*) + 0.66(\text{Hg}) - 0.038(\text{As}) + 0.144(\text{Bi})$; pour un échantillon synthétique, $a(\text{Å}) = 10.381 + 0.039(\text{Ag}) + 0.003(\text{Ag}^2) - 0.019(\text{Cu}^*) + 0.064(\text{Cd}) - 0.037(\text{As})$. Ici, Ag, Hg, As, Bi et Cd représentent le nombre d'atomes par unité formulaire, et Cu^* est égal à $2.0 - (\text{Fe} + \text{Zn} + \text{Hg} + \text{Cd})$. Ces expressions montrent un coefficient de corrélation R^2 de 0.9789 et 0.9893, respectivement, et tous les coefficients de régression β sont significatifs à un niveau de confiance de 95%. Les variations dans le rapport Fe/Zn n'ont aucune influence sur a . Un calcul de la dépendance du volume molaire sur la composition indique que les substitutions $\text{As} \leftrightarrow \text{Sb}$, $\text{Bi} \leftrightarrow \text{Sb}$,

$\text{Cu} \leftrightarrow (\text{Fe}, \text{Zn})$, $\text{Hg} \leftrightarrow (\text{Fe}, \text{Zn})$ et $\text{Cd} \leftrightarrow (\text{Fe}, \text{Zn})$ pourraient être idéales (ou presque), tandis que la substitution $\text{Ag} \leftrightarrow \text{Cu}$ ne l'est pas. Une comparaison des équations pour les échantillons naturels et synthétiques indique que les interceptes sont statistiquement équivalents et les coefficients pour le Cu^* sont semblables, mais que les coefficients pour As et Ag sont définitivement différents. La distinction entre échantillons naturels et synthétiques de tétraédrite argentine a été signalée auparavant; les distributions différentes des données pour les échantillons naturels et synthétiques de tétraédrite arsenifère sont la cause des résultats erronés d'un test de signification, ce qui illustre bien la nécessité d'examiner les résultats d'analyses statistiques avec beaucoup de soin.

(Traduit par la Rédaction)

Mots-clés: tétraédrite, régression linéaire, maille élémentaire, volume molaire.

INTRODUCTION

Wide variations in cell dimensions and compositions of tetrahedrite-series minerals have been known for nearly 50 years (Machatschki 1928a,b). Bouska (1956), Bernard (1957, 1958), Bernard & Håk (1960) and Riley (1974) have documented changes in the cell dimension as a function of composition, but the only attempt to quantify the relationships has been that of Charlat & Lévy (1975), who fitted a linear equation to data gathered on a suite of 26 samples from widely scattered localities. They took into account the variations caused by Ag, Hg, Cu^{2+} (the latter designated as Cu^*) and As as these elements substitute in a standard tetrahedrite of composition $\text{Cu}_{10}(\text{Fe}, \text{Zn})_2\text{Sb}_4\text{S}_{13}$, with a unit-cell dimension of 10.386 Å. Subsequently, Mozgova *et al.* (1979) determined the effect of Bi on the cell dimension.

Tetrahedrite was one of the earliest mineral structures to be solved (Pauling & Neumann 1934), and subsequent refinements (Wuensch 1964, Wuensch *et al.* 1966, Johnson & Burnham 1985) have begun to define how the structure alters due to compositional differences. As noted by Johnson *et al.* (1986), a formula of the type ${}^{\text{IV}}\text{M1}_6{}^{\text{III}}\text{M2}_6[{}^{\text{III}}\text{X}^{\text{IV}}\text{Y}_3]_4{}^{\text{VI}}\text{Z}$ (where $\text{M1} = \text{Cu}, \text{Fe}, \text{Zn}, \text{Hg}$ and Cd , $\text{M2} = \text{Cu}$ and Ag , $\text{X} = \text{Sb}, \text{As}, \text{Bi}$ and Te , and Y and $\text{Z} = \text{S}$ and Se) describes the structure.

Implicit in the approach of Charlat & Lévy are two assumptions; (i) the effect on the cell dimension caused by varying the ratio of Fe to Zn is negligible,

a point made by Hall (1972), and (ii) there is no difference between natural and synthetic samples with regards to the effect of Cu^* . Their equation is valid only for samples containing less than 20 wt. % Ag. Neither Charlat & Lévy nor Mozgova *et al.* provided a statistical analysis of the fit of the equations other than a few examples of predictive ability. As part of a statistical analysis of tetrahedrite-series chemistry, Johnson *et al.* (1986) published revised estimates of the cell-dimension variations based on regression calculations. We have now completed a further analysis, using advanced regression-techniques that test the above assumptions, and report the results herein.

DATA ANALYSIS

Compositions of natural and synthetic tetrahedrite with corresponding values of the cell dimension (Johnson *et al.* 1986) were fitted to a multiple-term model that considers variation in the amount of Ag, Cu, *etc.* Because of the wide variation in the precision of the cell-dimension measurements (Δa varying from 0.01 to 0.0001 Å), a weighted least-squares scheme was chosen. The weights were set at $1/(\Delta a)^2$ for each measurement, as this ensures that the results are the best linear unbiased estimators (BLUE). Initial regression analyses were run using atomic % for the elements involved to avoid the bias inherent in the choice of a normalization scheme. Subsequent comparison with a statistical analysis using a normalization of 29 atoms per formula unit showed insignificant differences between the two. Hence, for ease of application of the regression equation and for consistency with previous work, a normalization scheme of 29 atoms per formula unit was used.

The first step in the regression analysis aimed to determine if any of the regressors included in the model at the outset do not contribute significantly to the equations because of insufficient data. In initial runs, the variables that represent the elements Cd, Pb, Te, Mn and Se for natural samples and Hg, Bi, Pb, Te, Mn and Se for synthetic samples were all found to have nonsignificant partial *F*-tests. Therefore, these variables were removed from the model, and compositions containing those elements were deleted from the data base.

Because Cu, and those elements substituting for Cu, are present in two crystallographically distinct sites in the tetrahedrite structure, it was deemed reasonable to include two different terms in the model. Using the tetrahedrite formula of $(\text{Cu}, \text{Ag})_{10}(\text{Cu}^*, \text{Fe}, \text{Zn}, \text{Hg})_2(\text{As}, \text{Sb})_4\text{S}_{13}$ that was suggested by Charlat & Lévy (1974), Cu^* was set equal to $\{2.0 - (\text{Fe} + \text{Zn} + \text{Hg} + \text{Cd})\}$ after all compositions were normalized to 29 atoms per formula unit. Cu was then calculated as total Cu minus Cu^* , and

regression analyses were run on this basis. Johnson *et al.* (1986) found, however, that Ag substituted only up to six atoms per formula unit, and Cu^* only up to two, leaving four Cu atoms for which silver does not substitute. Accordingly, a second format for analysis was investigated, with three types of Cu atoms included: (i) Cu_C , equivalent to Cu^* , expressed as $2 - (\text{Fe} + \text{Zn} + \text{Hg} + \text{Cd})$, (ii) Cu_B , expressed as $6 - \text{Ag}$, and (iii) Cu_A expressed as total Cu minus $[\text{Cu}_B + \text{Cu}_C]$. Of the two approaches investigated, the second, based upon the convention of Johnson *et al.* (1986), provides a better fit. Elimination of the Cu_A regressor improves the fit further, and is believed to be a valid step inasmuch as the Cu_A content corresponds to the four nonsubstituting Cu atoms in the tetrahedrite structure.

In the next step, natural tetrahedrite data that contain more than four atoms of Ag per formula unit were fitted to the equation. Here the usefulness of including a second-order polynomial term in both the models for the natural and synthetic data was examined. The second-order term for silver (Ag^2) improved the fit for both data-sets, but the second-order terms for all other regressor variables had nonsignificant partial *F*-tests and little overall effect; they were therefore discarded.

Throughout the preceding steps, the regression models that were produced completely specified a given composition in terms of Cu^* , Fe and Zn by including two of the three as regressors. In contrast, the model of Charlat & Lévy (1975) incompletely specifies these compositions by only including Cu^* . The completely specified model and the three possible incompletely specified models (each containing one of Cu^* , Fe or Zn) were compared for the two data-sets. The incompletely specified model containing Cu^* was found to be the best of those examined. Furthermore, the Zn- and Fe-containing models were effectively equivalent, indicating that the effects of Fe and Zn on the cell dimension are equivalent. Hence, all further models that were developed follow the convention of Charlat & Lévy (1975).

At this point the residuals were examined for normality by the use of Studentized residuals (Gunst & Mason 1980, Weisberg 1985). Those data whose Studentized residuals are sufficiently large ($> \pm 2.5$) that they represent outliers were eliminated from the data-sets. This resulted in improvement in the overall fit; owing to the size of the data-bases ($n_{\text{nat}} = 222$, $n_{\text{syn}} = 150$) and the small number of data removed (less than 10%), this appeared to be an acceptable step in view of the lack of control over the quality of the data that necessarily occurs when they are obtained from a variety of published sources.

When this stage was reached, the model was deemed complete, and validation procedures were initiated. In regression validation, the data are split

randomly into two groups, and the model to be validated is then run on one of the groups, after which the resultant regression equation is tested on the other group. Residuals between predicted and actual values for the second group indicate the validity of the equation for the population as a whole (Montgomery & Peck 1982). The mean values for the residuals calculated from this analysis were found to be at least an order of magnitude smaller than the published uncertainties for the actual cell-dimension, and plots of the residuals *versus* predicted values showed no systematic trends, with points clustered around zero. The model is therefore considered to be valid.

As a final step, the two regression equations for natural and synthetic samples of tetrahedrite were compared using an indicator variable. The indicator or "dummy" variable was added to both the synthetic and the natural data to distinguish between the two sets during calculation. The indicator and cross-products between the indicator and the other variables were then included in the list of regressors in the model. The resultant statistical tests of significance for the indicator variable and the cross-products give a quantitative measure of how similar the regressors are across the two groups (Montgomery & Peck 1982). Only those regressors common to both the natural and synthetic data can be so examined. The results of all final statistical analyses are contained in Tables 1-3 and lead to the equations $a(\text{\AA})_{\text{natural}} = 10.379 + 0.082(\text{Ag}) - 0.01(\text{Ag}^2) - 0.009(\text{Cu}^*) + 0.66(\text{Hg}) - 0.038(\text{As}) + 0.144(\text{Bi})$ and $a(\text{\AA})_{\text{synthetic}} = 10.381 + 0.039(\text{Ag}) + 0.003(\text{Ag}^2) - 0.019(\text{Cu}^*) + 0.064(\text{Cd}) - 0.037(\text{As})$.

RESULTS

For both the natural and the synthetic data, the R^2 and the adjusted R^2 (Montgomery & Peck 1982) are provided, and the partial F -tests and p -values are given for each of the individual regression-coefficients β (Table 2). All coefficients are significant at the 95% confidence level. An overall F -test is not given, as is often done, because it is not a valid measure of the overall goodness of fit. In simple linear regression, with only one regressor, the overall F -test is that of the single regressor. In multiple linear regression, the overall F -test is a weighted mean of the F -tests for each individual regressor. The adjusted R^2 gives a measure of the significance of all of the terms in the model; if nonsignificant regressors are added to the model, the adjusted R^2 decreases relative to the R^2 . The adjusted R^2 also indicates whether the standard R^2 is falsely high owing to clustering of the data. The p -values are the calculated probabilities that the null hypothesis ($\beta_n = 0$) will be rejected incorrectly; as shown in Table 2, these probabilities are less than 0.5%.

Table 3 provides the results of the comparison of

TABLE 1. PUBLISHED SOURCES OF DATA USED IN THIS PAPER INCLUDING NUMBER OF SAMPLES AND THEIR ORIGIN

Reference	Analyses	Reference	Analyses
Arana (1972)	1 N	Mozgova et al. (1979)	40 N
Atanasov(1975)	2 N	Mozgova et al. (1980)	1 N
Basu et al. (1981)	2 N	Oen et al. (1973)	1 N
Basu et al. (1984)	6 N	Patrick & Hall (1984)	25 S
Bernard (1957)	1 N	Riley (1974)	20 N
Bishop et al. (1977)	1 N	Rojkovic & Kristin (1978)	38 N
Brodin et al. (1979)	3 N	Shimada & Hirowatari (1972)	11 N
Charlat & Lévy (1974)	73 N	Sugaki et al. (1975)	38 S
Hall (1972)	10 S	Tatsuka & Morimoto (1973)	14 S
Indolev et al. (1971)	9 N	Tatsuka & Morimoto (1977)	10 S
Johan & Kvaček (1971)	1 N	Timofeyevskiy (1967)	2 N
Kvaček (1977)	1 N	Tsepin et al. (1977)	1 N
Lind & Makovický (1982)	4 S	Tsepin et al. (1979)	2 N
Luca et al. (1977)	35 S	Yui (1971)	3 N
Maske & Skinner (1971)	14 S	Yushkin (1978)	3 N

TABLE 2. RESULTS OF FINAL REGRESSION ANALYSES ON CELL DIMENSION FOR DATA ON NATURAL AND SYNTHETIC TETRAHEDRITE

Natural Samples:		R ²		
		0.9789		
		Adj-R ²		
		0.9782		
Variable	β	Std Error	F-value	p-value
Intercept	10.379	0.001	8627.548	0.0001
Ag	0.082	0.002	45.212	0.0001
Ag ²	-0.010	0.0004	-25.427	0.0001
Cu*	-0.009	0.003	-3.069	0.0025
Hg	0.066	0.002	39.573	0.0001
As	-0.038	0.001	-39.923	0.0001
Bi	0.144	0.034	4.215	0.0001
Synthetic Samples:		R ²		
		0.9893		
		Adj-R ²		
		0.9889		
Variable	β	Std Error	F-value	p-value
Intercept	10.381	0.003	3074.822	0.0001
Ag	0.039	0.003	13.728	0.0001
Ag ²	0.003	0.0004	6.375	0.0001
Cu*	-0.019	0.002	-7.472	0.0001
Cd	0.064	0.003	22.573	0.0001
As	-0.037	0.003	-21.260	0.0001

β is the regression coefficient; other values explained in text.

the two regression lines for natural and synthetic tetrahedrite. The low F -test and high p -value for the intercept term indicates that the two regression lines have a common intercept. The Ag, Ag², and As terms based on the significance of the tests differ between the natural and synthetic samples, but the Cu* term is very nearly a borderline case. On the basis of these data, it appears that the effects are the same regardless of the source of the data. However, a larger base of data for both may prove that Cu* differs between natural and synthetic data.

TABLE 3. COMPARISON OF THE DATA FOR NATURAL AND SYNTHETIC TETRAHEDRITE

Variable	F-test	p-value
Intercepts	-0.11	0.911
Ag	3.88	0.0001
Ag ²	7.14	0.0001
Cu*	1.56	0.1203
As	-3.55	0.0004

TABLE 4. COMPARISON OF PREDICTED AND ACTUAL VALUES FOR TETRAHEDRITE DATA NOT INCLUDED IN REGRESSION

Formula	Predicted	Actual	Residual	Reference
$Cu_{10.3}Zn_{1.4}Ag_{3.7}As_{3.5}Sb_{5.5}S_{13}$	10.264 Å	10.232 Å	0.032 Å	1
$Cu_{10.1}(Fe,Zn)_{.9}Hg_{1.3}As_{3.7}Sb_{.9}S_{13}$	10.323	10.300	0.023	2
$Cu_{12.1}Sb_{4.1}S_{13}$	10.343	10.327	0.016	3
$Cu_{13.7}Sb_{4.1}S_{13}$	10.343	10.448	-0.105	3
$Cu_{11.7}Zn_{1.3}Sb_{4.3}S_{13}$	10.362	10.351	0.011	4
$Cu_{10.7}Fe_{1.3}Sb_{4.3}S_{13}$	10.370	10.350	0.020	4
$Cu_{10.4}(Fe,Zn)_{1.6}Sb_{3.9}Bi_{.1}S_{13}$	10.390	10.391	-0.001	5
$Cu_{8.5}Fe_{1.4}Ag_{2.1}Sb_{2.7}As_{1.3}S_{13}$	10.417	10.530	-0.113	6
$Cu_{10.4}Hg_{1.8}Sb_{4.3}S_{13}$	10.481	10.453	0.028	7
$Cu_{5.7}(Fe,Zn)_{.2}Ag_{4.3}Sb_{3.2}As_{.9}S_{13}$	10.511	10.489	0.022	8
$Cu_{9.8}Ag_{2.2}Sb_{4.3}S_{13}$	10.493	10.503	-0.010	9
$Cu_{7.2}Zn_{2.1}Ag_{3.3}Sb_{4.4}S_{13}$	10.542	10.554	-0.012	10

References

- 1 Wüensch et al. (1966).
- 2 Vasil'yev & Lavrent'yev (1973), JCPDS card 29-569.
- 3 Tatsuka & Morimoto (1973), JCPDS cards 24-1317, 1318.
- 4 Ashworth & Hardy (1972), JCPDS cards 25-281, 25-324.*
- 5 Wüensch (1964).
- 6 Johnson & Burnham (1985).
- 7 Kapiunnik et al. (1980).
- 8 Thompson, R.M., JCPDS card 11-101.*
- 9 Kalbskopf (1972).
- 10 Hall & Pinsent (1975), JCPDS cards 27-190, 190A.*

*Data submitted directly to JCPDS with no other published reference.

Examples of the predictive capability of these two equations are found in Table 4. The values of the cell dimension given here have been collected from

published crystal-structure refinements or from the JCPDS data file. With the exception of the Cu-rich tetrahedrite of Tatsuka & Morimoto (1973) and the Ag, As-rich tetrahedrite of Johnson & Burnham (1985), predicted and actual dimensions differ by only an average of ± 0.02 Å, and are thus well within the prediction intervals of the regression equations. Makovicky & Skinner (1979) found that they could synthesize metastable Cu-rich tetrahedrite with a significant amount of "mobile" Cu in the structure, which undoubtedly increases the cell parameter, but is not modeled in our equation. Furthermore, analyses of Cu-rich tetrahedrite are uncertain owing to instability in the microprobe beam (Lind & Makovicky 1982). The Ag, As-rich tetrahedrite of Johnson & Burnham (1985) has an Ag:As ratio considerably different from most other reported samples of tetrahedrite (Fig. 1), *i.e.*, those that form the basis of these regression equations. Extrapolation of regression equations to regions of compositional space where little or no data exist results in a poor correspondence between predicted and actual values. Hence, although the equations in this paper model substitution of up to six atoms per formula unit of Ag and four atoms per formula unit of As, inclusion of greater than approximately one atom of each at the same time will provide unreliable estimates of the cell edge. Table 5 lists the approximate limits of composition over which these equations can be considered valid.

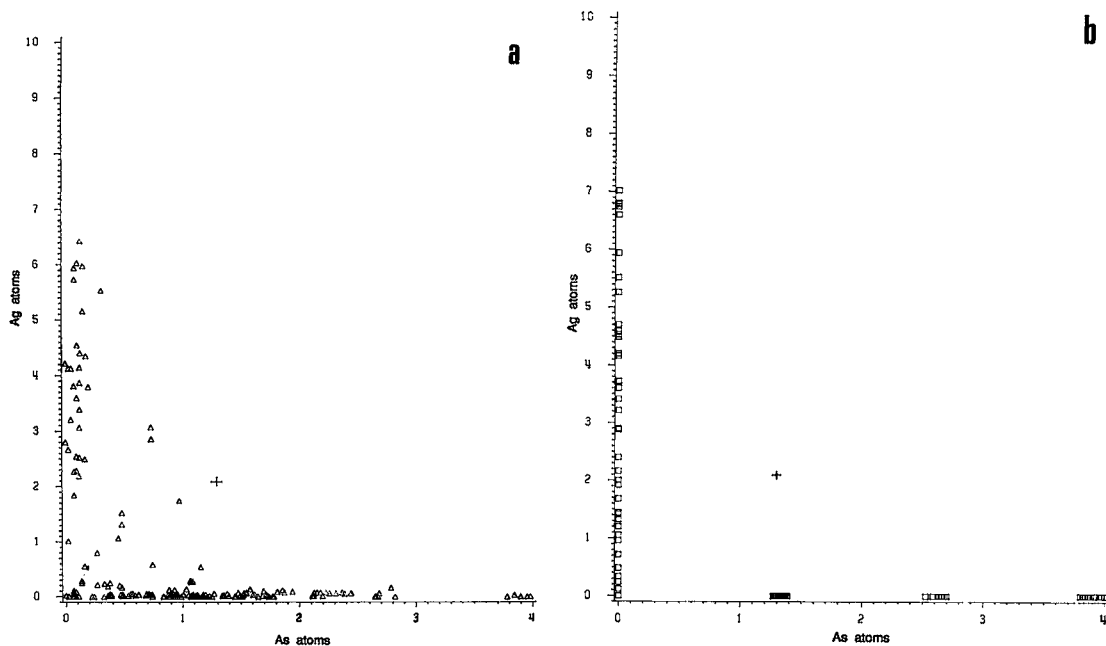


FIG. 1. Plots of As versus Ag for data used in this study: a) natural, b) synthetic samples. Point marked with (+) is synthetic tetrahedrite of Johnson & Burnham (1985).

TABLE 5. APPROXIMATE LIMITS OF APPLICABILITY FOR REGRESSION EQUATIONS IN ATOMS PER FORMULA UNIT

Element	Range	Restrictions
Hg	0-2	—
Cd	0-2	—
Bi	0-0.5	—
As	0-4	<1 atom Ag
Ag	0-6	<1 atom As
Cu*	0-1.5	—

DISCUSSION

The present analysis appears to substantiate the initial assumptions made by Charlat & Lévy (1975) for their data and provides refined regression-equations to define cell-dimension variations. Similarity of Cu between the natural and synthetic data-sets is to be reasonably expected, at least up to the limits of applicability, and the effects of Fe and Zn on the cell dimensions are sufficiently similar that they can be considered the same. This result does not provide any insight into the observed Zn-Ag antipathy (Patrick & Hall 1983, Raabe & Sack 1984, Johnson *et al.* 1986), other than to indicate that it is different from that which occurs between As and Ag (Johnson & Burnham 1985, Johnson *et al.*, in prep.). All other substituting elements, with the exception of Ag, affect the cell dimensions in a linear fashion.

The data for Bi are anomalous in that the coefficients for Bi differ from those of other regressors by approximately an order of magnitude, and the standard error for the β of Bi is also an order of magnitude larger. The probable cause for this is the paucity of data on the cell dimension of Bi-rich tetrahedrite and the limited range of Bi content found (0-0.5 atom per formula unit), which limits the usefulness of the Bi β term.

Sack & Loucks (1985) have suggested that an excellent first approximation, the As \leftrightarrow Sb, Cu \leftrightarrow (Fe,Zn) and Ag \leftrightarrow Cu exchanges in tetrahedrite-series minerals can be considered ideal. Linear changes in molar volume are a necessary, but not sufficient, condition for ideal mixing of components in a solid solution; however, linear changes in the cell dimension, as we have postulated, preclude the possibility of linear changes in molar volume. Multiple linear regression analyses were therefore run with molar volume instead of cell dimension as the dependent variable. The results of these analyses (Table 6) are that the second-order polynomial terms for Cu*, Hg, Cd, As and Bi are of low significance, indicating that any deviation from linearity is not large enough to be clearly distinguished from the existing scatter in the data. Second-order terms for Ag are sufficiently significant to indicate a large deviation from linearity. These results therefore support

TABLE 6. RESULTS OF FINAL REGRESSION ANALYSES ON MOLAR VOLUME FOR DATA ON NATURAL AND SYNTHETIC TETRAHEDRITE

Natural Samples:		R ²	0.9785		
		Adj-R ²	0.9778		
Variable	β	Std Error	F-value	p-value	
Intercept	559.005	0.195	2864.926	0.0001	
Ag	13.440	0.301	44.693	0.0001	
Ag ²	-1.664	0.066	-25.113	0.0001	
Cu*	-1.505	0.493	-3.055	0.0026	
Hg	10.625	0.270	39.314	0.0001	
As	-6.150	0.154	-39.876	0.0001	
Bi	23.373	5.605	4.170	0.0001	

Synthetic Samples:		R ²	0.9888		
		Adj-R ²	0.9885		
Variable	β	Std Error	F-value	p-value	
Intercept	559.386	0.549	1019.310	0.0001	
Ag	6.155	0.474	12.965	0.0001	
Ag ²	0.548	0.075	7.265	0.0001	
Cu*	-3.086	0.414	-7.446	0.0001	
Cd	10.839	0.484	22.406	0.0001	
As	-5.849	0.274	-21.376	0.0001	

Values are as in Table 1.

the conclusion of Sack & Loucks (1985) that As \leftrightarrow Sb and Cu \leftrightarrow (Fe,Zn) are "ideal", but differ in that Ag \leftrightarrow Cu is distinctly nonideal. Furthermore, the results of these regressions indicate that Cd, Hg and Bi substitutions also may be ideal or nearly ideal.

The difference in behavior of Ag between natural and synthetic tetrahedrite is not readily explained. Patrick & Hall (1983) attributed it to ordering of Ag in natural Ag-rich tetrahedrite whereas, as Johnson *et al.* (1986) pointed out, it may be due to metastability in synthetic Ag-rich tetrahedrite. It has been noted (R.C. Peterson, pers. comm.) that in Ag-rich tetrahedrite, the S atom co-ordinated to the six Cu sites, in which Ag substitutes, has a considerably larger isotropic temperature-factor than does non-Ag-bearing tetrahedrite. This can be interpreted as a "smearing-out" of displacements of the S atom over the entire crystal; how this may affect the unit cell is unknown. In any event, the nonlinearity of Δa as Ag increases from four to six atoms per formula unit indicates that Ag does not substitute ideally for Cu over the entire compositional range, and that the Ag \leftrightarrow Cu substitution is less simple than previously believed.

An important fact to note is that despite the close correspondence of the β terms for As for the two data-sets, the quantitative statistical tests indicate that the two populations (natural and synthetic) are statistically distinct. There is no *a priori* reason for As to differ between natural and synthetic tetrahedrite, and in fact, there may be no difference. Whereas the data for natural As-bearing tetrahedrite are scattered randomly between zero and four atoms of As, the As-tetrahedrite synthesized is found in

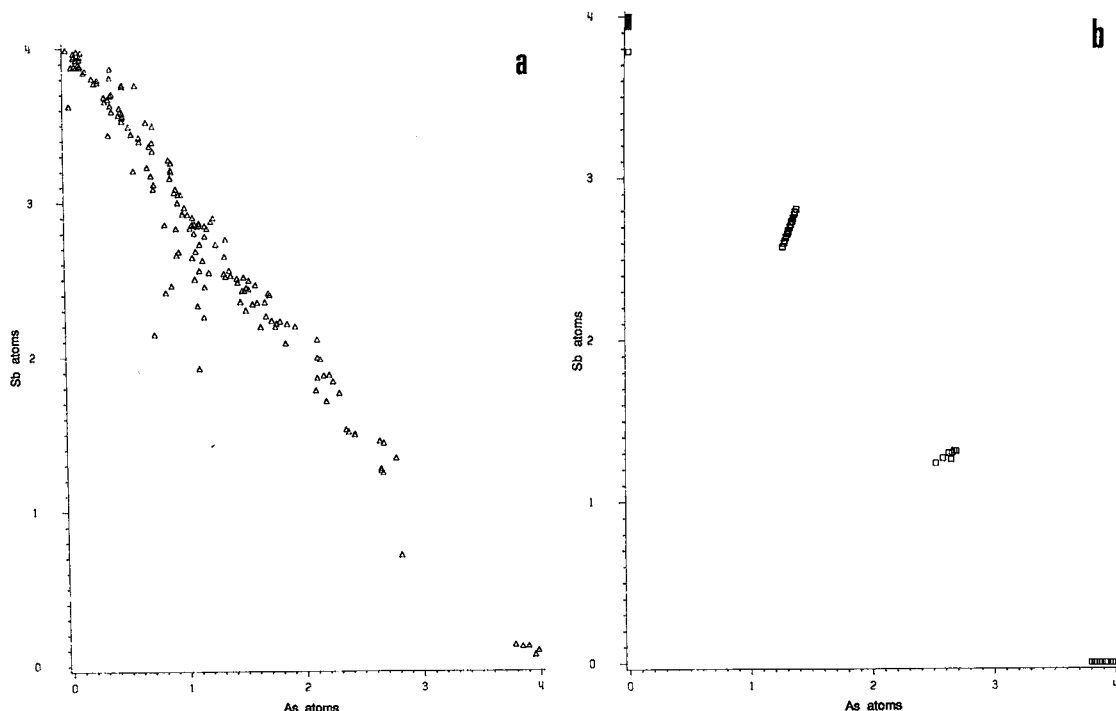


FIG. 2. Plots of As versus Sb for data used in this study: a) natural; b) synthetic samples.

groups along the As-Sb composition line (Fig. 2). The difference in the distribution of data, randomly dispersed versus tightly clustered, is probably what is reflected in the statistical test, which would then mask any other possible differences. This illustrates the principle of *caveat lector*, the need to carefully examine data prior to accepting a numerical result from a "canned" statistical computer-package.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. R.C. Peterson for his helpful discussion, and Robert R. Seal II and an anonymous reviewer for their careful reviews of the manuscript. This work was supported in part by a U.S. Bureau of Mines (MMRRI) allotment grant.

REFERENCES

- ARANA, R. (1977): Nota sobre de la tenantita de Molvizar (Granada). *Estud. Geol.* **33**, 219-222.
- ATANASOV, V.A. (1975): Argentinian mercurian tetrahedrite, a new variety, from the Chiprovtsi ore deposit, western Stara-Planina Mountains, Bulgaria. *Mineral. Mag.* **40**, 233-237.
- BASU, K., BORTNIKOV, N.S., MOOKHERJEE, A., MOZGOVA, N.N., SVITSOV, A.V., TSEPIN, A.I. & VRUBLEVSKAJA, Z.V. (1984): Rare minerals from Rajpura-Dariba, Rajasthan, India. V. The first recorded occurrence of a manganoan fahlore. *Neues Jahrb. Mineral. Abh.* **149**, 105-112.
- _____ & TSEPIN, A.I. (1981): Rare minerals from Rajpura-Dariba, Rajasthan, India. III. Plumbian tetrahedrite. *Neues Jahrb. Mineral. Abh.* **141**, 280-289.
- BERNARD, J.H. (1957): On the isomorphism of the elements in the group of tetrahedrites. *Rozpr. Cesk. Acad. Ved. Rada Mat. Prirad Ved. Roc. Uik.* **67**(3), 1-20 (in Czech).
- _____ (1958): Chemistry and unit cell dimensions of the tetrahedrites of the Spissko-gemerske Rudohori (Slovakia). *Rozpr. Cesk. Ved. Rada Mat. Prirad Ved. Roc. Uik.* **68**(14), 1-74 (in Czech).
- _____ & HAK, J. (1960): Argentiferous tetrahedrite from Kutna Hora, Stara Vozice and Pribam (central Bohemia). Investigation of minerals of the tetrahedrite group. *Cas. Mineral. Geol.* **5**(1), 1-9.
- BISHOP, A.C., CRIDDLE, A.J. & CLARK, A.M. (1977): Plumbian tennantite from Sark, Channel Islands. *Mineral. Mag.* **41**, 59-63.
- BOUSKA, V. (1956): The change of the lattice constant of mercurian tetrahedrites as a result of different chemical composition. *Rozpr. Cesk. Acad. Rada Mat. Prirad Ved. Roc. Uik.* **66**(13), 1-24 (in Czech).

- BRODIN, B.V., OSIPOV, B.S. & KACHALOVSKAYA, V.M. (1979): Silver bearing hakite. *Zap. Vses. Mineral. Obshchest.* **108**, 587-590 (in Russ.).
- CHARLAT, M. & LÉVY, C. (1974): Substitutions multiples dans la série tennantite-tétraédrite. *Soc. franç. Minéral. Crist. Bull.* **97**, 241-250.
- _____ & _____ (1975): Influence des principales substitutions sur le paramètre cristallin dans la série tennantite-tétraédrite. *Soc. franç. Minéral. Crist. Bull.* **98**, 152-158.
- GUNST, R.F. & MASON, R.L. (1980): *Regression Analysis and its Application*. Dekker, New York.
- HALL, A.J. (1972): Substitution of Cu by Zn, Fe and Ag in synthetic tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. *Soc. franç. Minéral. Crist. Bull.* **95**, 583-594.
- INDOLEV, L.N., NEVOYSA, G.G. & BRYZGALOV, I.A. (1971): New data on the composition of stibnite and the isomorphism of Cu and Ag. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **199**, 115-118.
- JOHAN, Z. & KVACEK, M. (1971): La hakite, un nouveau minéral du groupe de la tétraédrite. *Soc. franç. Minéral. Crist. Bull.* **94**, 45-48.
- JOHNSON, M.L. & BURNHAM, C.W. (1985): Crystal structure refinement of an arsenic-bearing argentian tetrahedrite. *Amer. Mineral.* **70**, 165-170.
- JOHNSON, N.E., CRAIG, J.R. & RIMSTIDT, J.D. (1986): Compositional trends in tetrahedrite. *Can. Mineral.* **24**, 385-397.
- KALBSKOPF, R. (1972): Strukturverfeinerung des Freibergits. *Tschermaks Mineral. Petrog. Mitt.* **18**, 147-155.
- KAPLUNNIK, L.N., POBEDIMSKAYA, E.A. & BELOV, N.V. (1980): Crystal structure of schwartzite ($\text{Cu}_{4.4}\text{Hg}_{1.6}$) $\text{Cu}_6\text{Sb}_4\text{S}_{12}$. *Sov. Phys. Dokl.* **25**, 506-507.
- KVACEK, M. (1977): Se-bearing tetrahedrite from Bukov (deposit of Rozna, W. Moravia, CSSR). *Acta Univ. Carol. Geol.* **4**, 233-237.
- LIND, I.L. & MAKOVICKY, E. (1982): Phase relations in the system Cu-Sb-S at 200°C, 10⁸ Pa by hydrothermal synthesis. Microprobe analyses of tetrahedrite - a warning. *Neues Jahrb. Mineral. Abh.* **145**, 134-156.
- LUCE, F.D., TUTTLE, C.L. & SKINNER, B.J. (1977): Studies of sulfosalts of copper. V. Phases and phase relations in the system Cu-Sb-As-S between 350° and 500°C. *Econ. Geol.* **72**, 271-289.
- MACHATSCHKI, F. (1928a): Formel und Kristallstruktur des Tetraedrits. *Norsk Geol. Tidsskr.* **10**, 23-32.
- _____ (1928b): Präzisionsmessungen der Gitterkonstanten verschiedener Fahlerze. Formel und Struktur derselben. *Z. Krist.* **68**, 204-222.
- MAKOVICKY, E. & SKINNER, B.J. (1979): Studies of the sulfosalts of copper. VII. Crystal structures of the exsolution products $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{13.8}\text{Sb}_4\text{S}_{13}$ of unsubstituted synthetic tetrahedrite. *Can. Mineral.* **17**, 619-634.
- MASKE, S. & SKINNER, B.J. (1971): Studies of the sulfosalts of copper. I. Phases and phase relations in the system Cu-As-S. *Econ. Geol.* **66**, 901-918.
- MONTGOMERY, D.C. & PECK, E.A. (1982): *Introduction to Linear Regression Analysis*. Wiley, New York.
- MOZGOVA, N.N., TSEPIN, A.I. & OZEROVA, N.A. (1980): Arsenic schwartzite. *Dokl. Acad. Sci., USSR, Earth Sci. Sect.* **239**, 143-146.
- _____, _____, _____, BORTNIKOV, N.S. & TRONEVA, N.V. (1979): Mercury-containing tetrahedrite-tennantite. *Zap. Vses. Mineral. Obshchest.* **108**, 437-453 (in Russ.).
- OEN, I.S., BURKE, E.A.J. & KIEFT, C. (1973): Bismuthian tennantite from Mangualde, Portugal. *Neues Jahrb. Mineral. Monatsh.*, 43-46.
- PATRICK, R.A.D. & HALL, A.J. (1983): Silver substitution into synthetic zinc, cadmium and iron tetrahedrites. *Mineral. Mag.* **47**, 441-451.
- PAULING, L. & NEUMANN, E.W. (1934): The crystal structure of binnite, $(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$, and the chemical composition and structure of minerals in the tetrahedrite group. *Z. Krist.* **88**, 54-62.
- RAABE, K.C. & SACK, R.O. (1984): Growth zoning in tetrahedrite-tennantite from the Hock Hocking mine, Alma, Colorado. *Can. Mineral.* **22**, 577-582.
- RILEY, J.F. (1974): The tetrahedrite-freibergite series, with reference to the Mount Isa Pb-Zn-Ag orebody. *Mineral. Deposita* **9**, 117-124.
- ROJKOVIC, I. & KRISTIN, J. (1978): Dependence of some physical properties of tetrahedrites on their chemical compositions in the Rudnany deposit. *Geol. Zb. (Slov. Acad. Vied.)* **29(2)**, 295-306.
- SACK, R.O. & LOUCKS, R.R. (1985): Thermodynamic properties of tetrahedrite-tennantites: constraints on the interdependence of the Ag \leftrightarrow Cu, Fe \leftrightarrow Zn, Cu \leftrightarrow Fe and As \leftrightarrow Sb exchange reactions. *Amer. Mineral.* **70**, 1270-1289.
- SHIMADA, N. & HIROWATARI, F. (1972): Argentian tetrahedrites from the Taishu-Shigekuma mine, Tsushima Island, Japan. *Mineral. J.* **7**, 77-87.
- SUGAKI, A., SHIMA, H. & KITAKAZE, A. (1975): Experimental study on argentian tetrahedrite. *Tohoku Univ. Sci. Rep., 2nd ser., Spec. Vol.* **7** (T. Takeuchi Mem. Vol.), 63-72.

- TATSUKA, K. & MORIMOTO, N. (1973): Composition variation and polymorphism of tetrahedrite in the Cu-Sb-S system below 400°C. *Amer. Mineral.* **58**, 425-434.
- _____ & _____ (1977): Tetrahedrite stability relations in the Cu-Fe-Sb-S system. *Amer. Mineral.* **62**, 1101-1109.
- TIMOFEYEVSKIY, D.A. (1967): First find of Ag-rich freibergite in the USSR. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **176**, 148-151.
- TSEPIN, A.I., MOZGOVA, N.N., BORTNIKOV, N.S. & VYAL'SOV, L.N. (1979): Zinc-bearing fahlore. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **247**, 150-153.
- _____, NOVGORODOVA, M.I. & DMITRIYEVA, M.T. (1977): First find of goldfieldite in the USSR. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **234**, 156-158.
- VASIL'YEV, V.I. & LAVRENT'YEV, YU.G. (1973): Mercury-bearing tennantite. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **218**, 111-113.
- WEISBERG, S. (1985): *Applied Linear Regression*. Wiley, New York.
- WUENSCH, B.J. (1964): The crystal structure of tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. *Z. Krist.* **119**, 437-453.
- _____, TAKEUCHI, Y. & NOWACKI, W. (1966): Refinement of the crystal structure of binnite, $\text{Cu}_{12}\text{As}_4\text{S}_{13}$. *Z. Krist.* **123**, 1-20.
- YUI, S. (1971): Heterogeneity within a single grain of minerals of the tennantite-tetrahedrite series. *Soc. Min. Geol. Japan, Spec. Issue 2, Proc. IMA- IAGOD 1970*, 22-29.
- YUSHKIN, N.P. (1978): New cadmium variety of tetrahedrite. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **242**, 149-152.

Received May 22, 1986, revised manuscript accepted August 12, 1986.