Table 1. Crystal data of deamino-6-seleno-oxytocin with deamino-oxytocin.

Form	Unit cell dimensions					Space group	Measured density (D_m) (g/cm³)
	a (Å)	*b* (Å)	*c* (Å)	*β* (deg)	*V* (10^3 Å³)		
			Deamino-6-seleno-oxytocin				
Wet	27.1	9.1	23.0	102.2	5.54	*C*2	1.36
			*Deamino-oxytocin**				
Wet	27.3	9.07	23.1	102.4	5.60	$P2_1$	1.305
Dry	28.1	9.43	24.5	124.0	5.38	*C*2	1.328

*Data from (*1*).

of a more substantial size (0.5 by 0.08 by 0.03 mm) have been secured from an ethanol-water mixture. These crystals are monoclinic laths, elongated along the *b*-axis, lying on (001). Preliminary x-ray photographic studies with CuKα radiation showed that the unit cell dimensions (Table 1) of these crystals are comparable to those of the "wet" form of deamino-oxytocin (*1*). In addition, the density of these crystals, determined by flotation, is compatible with that of the "wet" form of deamino-oxytocin. Nevertheless, the analogs crystallize in different space groups: deamino-6-seleno-oxytocin in *C*2 and deamino-oxytocin in $P2_1$. However (*1*) the diffraction pattern of "wet" deamino-oxytocin showed marked pseudo face-centering related to the space group *C*2. In fact, a comparison of the diffraction patterns of all three principal planes and two general planes of the crystals of these analogs showed such similarity that we believe that the overall conformations of both peptide molecules are alike.

In contrast to the "wet" crystals of deamino-oxytocin, those of the selenium analog do not lose crystal water upon prolonged exposure to air or upon soaking in xylene, as manifested by the constancy of the unit cell dimensions and of the diffraction pattern. Therefore the collection of intensity data is facilitated.

Avian vasodepressor assays (*5*) reveal that the biological activities remained unchanged during x-irradiation, indicating that deamino-6-seleno-oxytocin is essentially stable to x-rays.

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Estimating Proportions in Petrographic Mixing Equations by Least-Squares Approximation

Abstract. *Petrogenetic hypotheses involving fractional crystallization, assimilation, or mixing of magmas may be expressed and tested as problems in least-squares approximation. The calculation uses all of the data and yields a unique solution for each model, thus avoiding the ambiguity inherent in graphical or trial-and-error procedures. The compositional change in the 1960 lavas of Kilauea Volcano, Hawaii, is used to illustrate the method of calculation.*

Fractional crystallization, assimilation, and mixing of magmas are often cited in petrographic literature as important mechanisms by which compositional variation in igneous rock series is produced. Graphical constructions or trial-and-error calculations (*1, 2*) have sometimes been used to test the ability of the proposed mechanism to produce the observed compositional changes. Consistent symbolic formulation of the problem shows at once that it fits readily into the framework of least-squares approximation. As in the graphical and trial-and-error methods, the objective of the least-squares analysis is to determine whether an assumed residual liquid might be derived from an assumed parent magma by removal or addition of components which have the compositions of mineral phases or contaminants such as wall rock or xenolith material. Although graphical or trial-and-error solutions are restricted to problems having only three or four components, this very serious limitation does not apply to the least-squares solution.

In this discussion x_{ij} is the observed amount of the *i*th oxide in the *j*th component, where $i = 1,n$, and $j = 1,k$; y_i is the observed amount of oxide *i* in the composition to be approximated; $\hat{b}_j$ is the estimated amount of component *j* required; and $\hat{y}_i$ is the estimated amount of oxide *i*.

For each of the *n* oxides we may thus write a linear equation containing one term in y_i and *k* terms in $b_j x_{ij}$, or, in matrix notation

$$\mathbf{XB} = \mathbf{Y} \tag{1}$$

where

$$\mathbf{X} = \begin{bmatrix} x_{11} & x_{12} & x_{13} \cdots & x_{1k} \\ x_{21} & x_{22} & x_{23} \cdots & x_{2k} \\ x_{31} & x_{32} & x_{33} \cdots & x_{3k} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ x_{n1} & x_{n2} & x_{n3} \cdots & x_{nk} \end{bmatrix} \tag{2a}$$

$$\mathbf{B}' = [b_1, b_2, b_3 \cdots b_k] \tag{2b}$$

and

$$\mathbf{Y}' = [y_1, y_2, y_3 \cdots y_n] \tag{2c}$$

where **B′** and **Y′** are, respectively, the transposes of the column vectors **B** and **Y**.

Interpretations of the results of conventional subtraction diagrams or their numerical analogues (*3*) are rarely free of ambiguity. Usually the number of oxides (*n*) is considerably greater than the number of components (*k*), but graphical and numerical procedures proposed thus far require that the number of oxides used in any solution be equal to or less than *k*.

Using any of these methods, the petrologist must work with no more than *k* of the *n* rows of Eq. 1 in any particular solution; each solution thus ignores at least $(1 - k/n)$ of the available information. Any of the unused rows of Eq. 1 which are linear combinations of those used in a solution are redundant; any which are not redundant are contradictory; that is, they are not satisfied by the solution. The number of contradictory solutions obtainable from a particular set of data rapidly becomes excessive, for k rarely exceeds 5, but n varies from 8 to 11, depending on whether MnO, TiO_2, and P_2O_5 are regarded as essential constituents in a complete silicate analysis. If, for example, $k = 5$ and $n = 8$ there will be $8!/5!3! = 56$ possible sets of oxides upon which to base graphical subtraction diagrams or their numerical counterparts. Barring singularity, which should be quite uncommon, each of these sets will yield an exact solution—that is, one in which $(y_i - \hat{y}_i) = 0$ to within rounding error—for each of the oxides used.

This agreement is purely tautological, however, showing only that the set chosen is one for which a solution exists. If oxide i is not used as control in any of a set of graphical solutions (or row i of Eq. 1 is not used in the analogous calculations), each $\hat{y}_i$ obtained is an estimate of y_i, though a rather indirect one. Presumably, an objective comparison of the quality of these estimates could be developed. In most practical situations, however, there is little reason for preferring one set of variables to another, and a method yielding a single solution based on all the data would be preferable to one yielding many different but not independent solutions, each based on only part of the available information. The least-squares approximation does in fact give a single solution based on all the data, and our choice of notation makes it obvious that the problem can be formulated as one in least-squares approximation (*4*). Premultiplication of Eq. 1, the equations of condition, by the transpose of **X** gives the normal equations

$$\mathbf{X'XB} = \mathbf{X'Y} \qquad (3)$$

and premultiplication of the normal equations by the inverse of $[\mathbf{X'X}]$ yields the desired solution, namely

$$\hat{\mathbf{B}} = [\mathbf{X'X}]^{-1}\mathbf{X'Y} \qquad (4)$$

There is only one such solution, and it exists only when $n \geqq k$; the inequality denotes the common situation, in which graphical methods and their numerical analogues fail to yield unique solutions. If we now substitute $\hat{\mathbf{B}}$ from Eq. 4 in the left side of Eq. 1 and perform the indicated multiplication, we obtain a vector $\hat{\mathbf{Y}}$ which is the least-squares approximation of **Y**; that is, the elements of $\hat{\mathbf{Y}}$ are those which minimize the quantity

$$S = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \qquad (5)$$

the sum of squares of the residuals.

Table 1. Composition of 1960 lava glass E of Kilauea Volcano, Hawaii. Column A represents an estimate of oxide weight percentages, $\hat{\mathbf{Y}}$, and parent magma (glass D) and mineral weight percentages, $\hat{\mathbf{B}}$, based on graphical constructions. Column B gives the analogous weight percentages obtained from the least-squares calculation. Column C is the actual chemical analysis of glass E, **Y**. Graphical estimates and all data used in the least-squares calculation are from Murata and Richter (*2*, p. 17, Table 5, columns 1, 4, 5, 6, 7, and 8).

Oxide	A	B	C
	Oxides		
SiO_2	50.75	50.89	50.96
$Al_2O_3 + Cr_2O_3$	13.50	13.63	13.58
FeO	12.60	12.56	12.45
MgO	5.78	5.77	5.77
CaO	9.84	9.89	9.77
Na_2O	2.65	2.67	2.60
K_2O	.74	.74	.72
TiO_2	3.57	3.56	3.58
P_2O_5	.38	.38	.39
MnO	.19	.19	.18
Sum	100.00	100.28	100.00
	Parent magma and mineral proportions		
Basalt glass D	123.30	123.07	
Augite	−10.00	−10.02	
Plagioclase	−11.00	−10.46	
Olivine	− 2.30	− 2.30	
Sum	100.00	100.29	
	Sum of squares of oxide residuals		
$\Sigma(\hat{y}_i - y_i)^2$	.0812	.0396	

Results obtained thus far provide a convenient, consistent, and intuitively appealing summary or description of the data. If the analysis is to be carried further, allowance must be made for the fact that the elements of **Y** are not known to be either homogeneous in variance or uncorrelated. Knowledge or reasonable assumption about the elements of the (true or theoretical) covariance matrix of the y's is indispensable if the sample statistics are to provide meaningful estimates of the errors attaching to the elements of $\hat{\mathbf{Y}}$ and $\hat{\mathbf{B}}$. Reasonable assumptions about the relative magnitudes of the parent variances of **Y** may sometimes be made, but a priori information about its covariances is nearly always inadequate, if not entirely lacking. In its absence the least-squares approximation must serve primarily as a scheme for data reduction.

Compositional changes in the lava of Kilauea Volcano during the 1960 eruption have been investigated by Murata and Richter (*2*) with the aid of graphical constructions. They demonstrated that removal of suitable amounts of clinopyroxene, plagioclase, and olivine from their assumed parent magma (*2*, Table 5, glass D) could yield a liquid having the composition of their assumed residual liquid (*2*, Table 5, glass E). This composition and the proportions of parent magma and minerals required to generate it are given in column A of Table 1. For the least-squares solution, the columns of matrix **X** (Eq. 1) represent the chemical compositions of glass D, clinopyroxene, plagioclase, and olivine; the dependent vector **Y** is the chemical composition of glass E to be determined by least-squares approximation. The vector of weight fractions ($\hat{\mathbf{B}}$) is obtained from Eq. 4 and substituted in the left side of Eq. 1 to yield the least-squares estimate $\hat{\mathbf{Y}}$.

The result (column B, Table 1) is in excellent agreement with that of Murata and Richter. Such close agreement should not be expected in every comparison, and least-squares solutions differing markedly from graphical solutions or nonnumerical expectations are to be anticipated. The principal advantage of the least-squares solution is not that it agrees or disagrees with earlier work, but that it utilizes all the data in a systematic and widely accepted fashion. In other procedures, inadequacies of the model are confounded with uncertainties arising from the fact that only a part, usually a small part, of the available information contributes to any particular solution. In contrast, a least-squares calculation that does not give a satisfactory solution is a clear indication that the underlying model is at fault.

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