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COEXISTENT MUSCOVITE AND PARAGONITE IN PELITIC SCHISTS[1]

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ABSTRACT

Basal spacings of 42 pairs of coexistent muscovite and paragonite fit the regression equation

$$d(002)_{2M}(\text{paragonite}) = 12.250 - 0.2634\, d(002)_{2M}(\text{muscovite}) \pm 0.006, \text{ in Å}.$$

The spacings of individual mica pairs closely reflect the metamorphic grade as deduced from independent petrographic evidence (Table 1); the spacings of either white mica, in single-mica rocks, therefore, may be used to monitor the minimum metamorphic grades of these rocks.

The scatter of the measured points about the fitted curve exceeds uncertainties of observation. The scatter could be due to several causes: (1) only partial attainment, or total lack of chemical equilibrium between the two micas, (2) different mica polymorphs in the various samples, (3) the presence of mixed-layering in one or both micas, and (4) failure to take other components in the micas into account. Among these, the last explanation is the most likely. In particular, the presence of the component $CaAl_2Al_2Si_2O_{10}(OH)_2$ in paragonite should lead to excessively large spacings in the coexistent muscovite.

Available chemical analyses of white micas having good *x*-ray data that are close to the binary $KAl_2AlSi_3O_{10}(OH)_2$-$NaAl_2AlSi_3O_{10}(OH)_2$(Mu-Pa) yield a regression equation

$$d(002)_{2M} = 10.034 - 0.427N_{Pa} \text{ (in Å)}$$

where N_{Pa} is the mole fraction of Pa. This equation is consistent with the spacing-spacing regression relation given above. With the aid of intrinsic structure factor calculations for the binary system, based on Radoslovich's atomic coordinates, the two equations make it possible to compute the compositions of coexistent muscovite and paragonite which cannot be mechanically separated. Use of this extrapolatory procedure enables one to obtain improved basal spacing—composition regression relation for this system. Data currently available indicate that the volume behavior of the binary system is non-ideal, and the solvus is asymmetrical with the critical point near $N_{Pa}0 \approx .8$.

Paragonite may be unstable in sedimentary environments because more hydrous assemblages of equivalent chemical composition have been observed. Theoretically, formation of this mineral in schists should be most favoured between the upper biotite and the lower kyanite zones of metamorphism. However, upon prograde metamorphism of a quartzose schist, reaction among chlorite, albite and muscovite may lead to a second episode of paragonite formation just prior to the decomposition of paragonite into the anhydrous assemblage plagioclase-kyanite.

INTRODUCTION

The compositions of coexistent muscovite and paragonite have been studied in recent years by a number of petrologists (Eugster and Yoder,

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[1] Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. d(002)$_{2M}$ DATA ON CAEXISTENT PARAGONITE AND MUSCOVITE

No.	Locality	Muscovite, Å	Paragonite, Å	Difference	σ_i[1]	Other minerals in the assemblage	Metamorphic zone	Ref.
1	Petersburg Pass, U. S. 2, west of Williamstown Mass.	9.987	9.623	0.364	+ .003	choritoid-chlorite-quartz	biotite	3
2	Danby, Vermont	9.981	9.623	0.358	+ .002	—	biotite	1
3	"Ben Slide" near Herrick Mt., Ira, Vermont	9.975	9.623	0.352	0	quartz-chlorite-rutile	biotite	1, 3
4	Egremont, Mass.	9.968	9.637	0.331	+ .012	chloritoid-quartz-biotite(?)	biotite	3
5	Mt. Alander, Mt. Washington, Mass.	9.963	9.629	0.334	+ .003	chloritoid-chlorite-quartz-ilmenite-tourmaline	biotite	3
6	Copake, N. Y.	9.959	9.622	0.337	− .005	chlorite-quartz	biotite	3
7	Lincoln Mtn., Vermont	9.959	9.632	0.327	+ .004	almandine-chloritoid-chlorite-ilmenite-quartz	almandine	3
8	Mt. Ashley, Mt. Washington, Mass.	9.957	9.627	0.330	0	chloritoid-chlorite-quartz	almandine	3
9	Pittsfield, Mass.	9.956	9.625	0.331	− .002	chlorite-quartz-hematite	biotite(?)	3
10	Mt. Ashley, Mt. Washington, Mass.	9.955	9.626	0.329	− .002	chloritoid-chlorite-quartz	almandine	3
11	Heartwellville, Vt. (Harvard Univ. Coll. no. 9791)	9.950	9.623	0.327	− .006	chlorite-chloritoid-plagioclase-almandine-magnetite-quartz	almandine	1, 3
12	Hager Mtn., N. C.	9.948	9.632	0.316	+ .002	quartz	almandine(?) kyanite(?)	3, 5
13	Plymouth, Vermont	9.948	9.644	0.304	+ .014	—	almandine	1
14	Ludlow, Vermont	9.948	9.646	0.302	+ .016	—	almandine	1
15	Stratton, Vermont	9.947	9.626	0.321	− .004	—	almandine	1
16	Mt. Plantain, Mt. Washington, Mass.	9.946	9.628	0.318	− .002	chloritoid-chlorite-quartz	almandine	3
17	Pinney Hollow Plymouth, Vt.	9.945	9.626	0.319	− .004	chloritoid-chlorite-quartz	biotite(?) almandine(?)	3
18	Pittsfield, Vt.	9.943	9.627	0.316	− .004	ankerite-chlorite-quartz	almandine	1, 3
19	E. of Mt. Everett, Mt. Washington, Mass.	9.942	9.622	0.320	− .009	chlorite-ilmenite-tourmaline-quartz	almandine	3

[1] Actual distance from point to regression line, in Å.

TABLE 1—(*Continued*)

No.	Locality	Muscovite, Å	Paragonite, Å	Difference	σ_i^{1}	Other minerals in the assemblage	Metamorphic zone	Ref.
20	Same as no. 17	9.942	9.627	0.315	− .004	quartz-chlorite	biotite(?) almandine(?)	3
21	Täschtal, Zermatt, Switzerland	9.942	9.637	0.305	+ .006	kyanite-quartz	kyanite	2
22	NE of Stark Mtn., Fayston, Vt.	9.941	9.622	0.319	− .009	chlorite-quartz	almandine(?) kyanite(?)	3, 6
23	Athens, Vt.	9.941	9.632	0.309	0	—	kyanite	1
24	West Townshend, Vt.	9.940	9.644	0.296	+ .012	—	kyanite	1
25	Londonderry, Vt.	9.939	9.626	0.313	− .006	—	almandine	1
26	E. of Mt. Everett, Mt. Washington, Mass.	9.938	9.632	0.306	0	chlorite-quartz-albite-almandine-apatite-tourmaline	almandine	3
27	Harmonyville, Vt.	9.938	9.632	0.306	0	—	almandine	1
28	Jamaica, Vt.	9.937	9.625	0.312	− .008	—	staurolite	1, 3
29	Glebe Mtn., Vt.	9.937	9.625	0.312	− .008	chlorite-almandine-quartz-epidote-ilmenite-magnetite	almandine	1, 4[2]
30	Salisbury, Conn.	9.934	9.628	0.306	− .005	chlorite-almandine-staurolite-quartz-ilmenite-tourmaline	staurolite	3
31	East Jamaica, Vt.	9.933	9.630	0.303	− .004	—	staurolite	1
32	Chester, Vt.	9.933	9.631	0.302	− .003	—	kyanite	1
33	Townshend, Vt.	9.931	9.629	0.302	− .005	—	kyanite	1
34	Grafton, Vt.	9.925	9.639	0.286	+ .003	—	kyanite	1 4
35	Bear Mtn., Salisbury, Conn.	9.924	9.633	0.291	− .003	almandine-chlorite-quartz	staurolite	3
36	Cavendish, Vt.	9.922	9.638	0.284	+ .001	—	kyanite	1
37	Simpsonville, Vt.	9.919	9.641	0.278	+ .004	—	kyanite	1
38	Gassetts, Vt.	9.918	9.640	0.278	+ .002	—	kyanite	1, 3
39	Mte. Campione, Switzerland (Harvard Univ. (Coll. no. 10489)	9.892	9.649	0.243	+ .004	kyanite-staurolite-biotite-quartz	staurolite	1, 3
40	Zillertal, Switzerland (USNM 104643)	9.891	9.648	0.243	+ .003	kyanite-staurolite-biotite-quartz	staurolite	3
41	Pizzo Forno, Switzerland	9.888	9.647	0.241	+ .001	—	staurolite	1
42	Willis Mtn., Va.	9.832	9.660	0.172	0	kyanite-quartz	kyanite	3

[2] Measurements by Zen. Differ slightly from the values reported by Rosenfeld *et al.*, 1958.

Ref.: 1. Rosenfeld *et al.*, 1958.
2. Zen *et al.*, 1964.
3. This report; data measured by Zen except point 7, measured by Albee.
4. Rosenfeld, 1956.
5. Zen, 1961.
6. Cady *et al.*, 1962.

1954a,b, 1955; Rosenfeld *et al.*, 1958; Chatterjee, 1962). This interest was generated, in part at least, by the discovery that paragonite is a common rock-forming mineral in highly aluminous pelitic schists of low to medium grades of metamorphism. Because the basal spacings of the coexistent muscovite and paragonite pairs show progressive changes according to the grade of metamorphism (Rosenfeld *et al.*, 1958), and because basal spacings are readily measured, these parameters promise to offer a sensitive and continuous method to monitor the grades of metamorphism of a large group of rocks.

The volume behavior of the muscovite-paragonite solid-solution series presents another interesting problem. The volume-of-mixing effect has been studied for the alkali feldspars of high thermal state (Donnay and Donnay, 1952) and for a portion of the plagioclase series (Smith, 1956). Paragonite and muscovite belong to a chemical system similar to the feldspars, and it would be petrologically interesting to compare the volume behavior of these solution systems. The crystal structures of paragonite and muscovite are nearly identical. Their *a* and *b* dimensions are approximately the same; the largest dimensional change in this solid solution series is in the basal (001) spacings. Therefore, the values of these basal spacings, when measured on samples of known chemical composition, give a first approximation to the volume behavior in this system.

This paper represents the results of some new *x*-ray measurements on the muscovite-paragonite pair. Combined with similar data in the literature, a linear regression curve can be fitted. Such a curve leads to provisional conclusions on the volume properties of the system; the curve is also useful in yielding minimum measures of the metamorphic grades of rocks that contain only one of these micas.

Because coexisting paragonite and muscovite commonly occur in intimate physical mixtures, it is very difficult to get single-phase separates of these two minerals in amounts adequate for chemical analyses. Consequently, only scanty data exist on the correlation between the *x*-ray spacings and chemical compositions for this two-phase system. A method has been devised whereby the phase compositions in such mixtures can be estimated in partial concentrates. The method involves a combination of extrapolation of data on mixtures, and successive approximation by means of calculated *x*-ray diffraction intensities. It is hoped that the application of this method will aid the eventual construction of a good working curve for the correlation of spacings and chemical compositions; such a curve is essential to the understanding of the subsolidus behavior of this system.

EXPERIMENTAL (E. Z. AND A. L. A.)

Values for the basal spacings of muscovite and paragonite were measured on powder samples, using a diffractometer and Cu/Ni radiation.[1] The instrumental constants used were: scale factor, 4; multiplier, 1; time constant, 4 seconds; slits, 1° and 0.003″; scanning speed, $\frac{1}{4}°$ or $\frac{1}{8}°$ per minute; chart speed, $\frac{1}{2}$ inch per minute. The (10.1) peak of quartz was commonly used as an internal standard: its position was calibrated against a primary thorite standard whose cubic cell dimensions have been measured carefully by Frondel (1955) and Skinner (1957). For samples whose muscovite spacings overlap the (10.1) peak of quartz, either the primary thorite or secondary fluorite standard was used.

For a few samples, it was practical to measure the spacings of the $(0010)_{2M}$[2] peaks, for which $K\alpha_1$ and $K\alpha_2$ are resolved. For most samples, however, one of the two mica phases was in small amounts, and the low intensities of the (0010) lines made their precise measurement impossible. For these samples, therefore, the $(006)_{2M}$ lines were used. Because the diffraction lines of the internal standards used all lie close to the chosen mica lines, the use of low-angle lines is not believed to add errors to the results. The peaks were scanned repeatedly in up-angle direction and the results were averaged. The peak position is defined as that of the median line, measured at a number of intensity levels, and extrapolated to the noise level. This method gives spacing values reproducible to 0.001 Å; the individual uncertainty to be assigned to the $(002)_{2M}$, therefore, is ±0.003 Å due to measurement scatter alone.

The results of the measurements are given in Table 1, and plotted in Fig. 1. Where the information is available, the mineral assemblages of the samples are listed in Table 1. The data points could be fitted to a line, $y=ax+b$; because neither the muscovite nor the paragonite spacings could be considered as more nearly "correct," the true distance-to-the-point least-square line was calculated. The equation is

$$y = 12.250 - 0.2634x, \pm 0.006 \text{ (in Å)} \tag{1}$$

where $y = d(002)_{2M}$ for paragonite and $x = d(002)_{2M}$ for muscovite and where the values of a and b are computed by the relations

$$a = \cot \omega$$
$$b = (\Sigma y_i + \cot \omega . \Sigma x_i)/n$$

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[1] Some of the data published by Rosenfeld *et al.* (1958) were measured by Rosenfeld using a somewhat different technique and internal standard (diamond). We have cross-checked our results by measuring the same sample by the two methods and there appears to be no discrepancy within the limits of experimental errors.

[2] This notation will be used throughout this paper. Thus $(0010)_{2M}$ refers to the 10th-order basal reflection reckoned on the basis of the 2M polymorph.

and

$$\omega = \tfrac{1}{2}\,\text{arc cot}\left\{\left[\Sigma x_i^2 - \Sigma y_i^2 - \frac{(\Sigma x_i)^2}{n} + \frac{(\Sigma y_i)^2}{n}\right]\Big/2\left[\Sigma x_i y_i - \frac{1}{n}\Sigma x_i \Sigma y_i\right]\right\}.^{1}$$

DISCUSSION OF THE CURVE (E. Z.)

The data of Fig. 1 and Table 1 show a good correlation between the spacings and the metamorphic grades. In general, the mica pairs with the lowest paragonite spacings (and correspondingly the highest muscovite spacings) occur in rocks which are in the biotite or even the chlorite zone of metamorphism, although these rocks do not actually have biotite in the mineral assemblage. The muscovite and paragonite spacings approach each other as the metamorphic grade passes through the biotite, the almandine, the staurolite, and finally into the kyanite zone. This convergence of spacings was pointed out by Eugster and Yoder (1955) and by Rosenfeld *et al.* (1958).

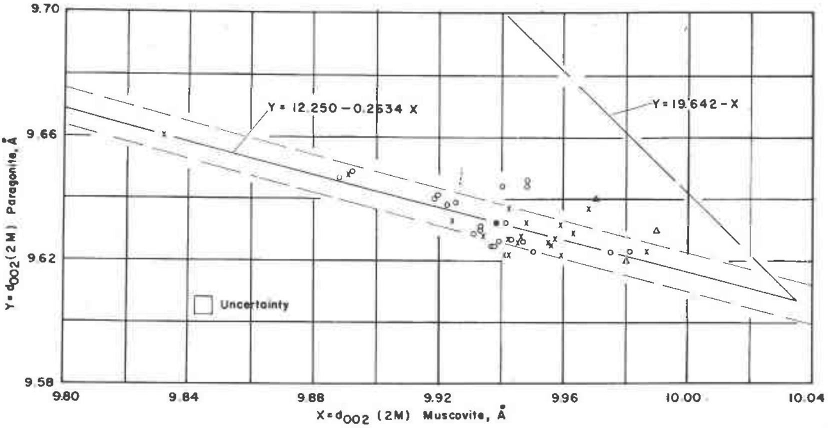

FIG. 1. $(002)_{2M}$ spacings of coexisting muscovite and paragonite. The light dashed lines give the width of one standard deviation according to equation (1). The heavy dashed line, of slope −1, would be obeyed if the spacings were linear functions of the interlayer composition in the binary system Mu-Pa, and if the solvus were symmetrical; the location of this curve is given by equation (2). Crosses, new data; circles, data from Rosenfeld *et al.* (1958); triangles, data from Chatterjee (1962), which were not used in the least-square computations.

The point for sample 42 is especially interesting, because it shows the closest approach of the two mica spacings. The sample occurred as small

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[1] Conway (1945, p. 588) also derived an equation for the same least-square procedure using the correlation coefficient and standard deviations as independent variables.

scaly booklets on kyanite blades from a quartz-kyanite rock at Willis Mountain, Virginia; the rock was described by Espenshade and Potter (1960, p. 10, 39) who first reported paragonite from this general area. Because of the small amount of the sample, chemical analysis was not possible, nor were the spacings measured with as much precision as were the others. Nonetheless, the point falls almost exactly on the regression line. Although the position of the point suggests that the grade of metamorphism of the rock was considerably higher than that of any of the other samples, the associated mineral assemblage is clearly that of the kyanite zone. The apparently higher metamorphic grade may be partly deceptive. The solvus of the muscovite-paragonite pair presumably closes with rising metamorphic grade. Therefore, one would expect the rate of mutual approach of the basal spacings of the two micas to increase as the grade rises; at higher metamorphic grades the basal spacings should become increasingly sensitive to small differences in the grades of metamorphism.

If the curve in Fig. 1 is a true representation of the measured points, then measurements of the basal spacings of either a muscovite or a paragonite, in a rock which carries only one of these white micas, would give a minimum estimate of the probable metamorphic grade, because a mica of that composition should break down into two phases at a lower metamorphic grade.

If the molar volume in the paragonite-muscovite system is ideal with respect to the Na/K ratio, but the *a* and *b* dimensions are constant, and if in addition the solvus is symmetrical, then the points in Fig. 1 should all lie on a straight line with a slope of -1; the location of the line, however, would depend on the basal spacings of the pure end-members. Figure 1 shows that the departure of the points from the 45° line is systematic and large; the difference between the regression line and the 45° line is much greater than could be accounted for by errors of observation.

The assumption of fixed *a* and *b* dimensions is incorrect even for micas that lie entirely within the binary system $KAl_2AlSi_3O_{10}(OH)_2$ and $NaAl_2AlSi_3O_{10}(OH)_2$ (Mu and Pa, respectively, in this paper). Radoslovich and Norrish (1962, p. 608) gave for muscovite $b = 8.995$ Å, and for a paragonite synthesized by H. S. Yoder, $b = 8.90$ Å. An analyzed paragonite from Zermatt, Switzerland (Zen *et al.* 1961) yielded $b = 8.89$ Å. Burns and White (1963) reported, on the basis of some leaching experiments, that the *b*-dimension of muscovite is sensitive to the nature and amount of the interlayer atoms. The *a* and *b* dimensions contract with increasing Na substitution for K, apparently because of the smaller size of the Na atoms. However, exactly how the *b* dimension changes in detail as a function of the interlayer composition is unknown. It seems improbable that this factor should just suffice to make the volume of mixing zero in the binary system, and we tentatively conclude that the solvus is asymmetrical and/or the volume behavior is non-ideal.

If equation (1) applies to the entire Mu-Pa system, then it should yield the basal spacing of the end member paragonite when that of the end-member muscovite is known. This latter value remains unsettled even for the $2M_1$ polymorph. As will be discussed in a later section, however, we estimate a spacing value of d = 10.034 Å for the $(002)_{2M}$ of Mu_{100} muscovite. Equation (1) then gives d = 9.607 Å for the $(002)_{2M}$ of Pa_{100} paragonite. The paragonite value is the same as the average of the values, 9.637 Å and 9.575 Å, respectively for synthetic and extrapolated natural paragonite (Pa_{100}), obtained by H. P. Eugster (written communication, 1963; according to Eugster the value reported by Eugster and Yoder (1954a) should be for d $(001)_{2M}$, not for *c* as reported).

The scatter of the measured points about the regression line in Fig. 1 exceeds observational uncertainties and must be explained. Five possible explanations are offered.

(1) Some of the muscovite-paragonite pairs are out of mutual chemical equilibrium. If this be true, however, the basal spacings of the associated mica pairs should show no consistent relation. The overall trend of Fig. 1 shows that this explanation by itself is inadequate.

(2) At least some of the muscovite-paragonite pairs may exist in partial, metastable equilibrium. For instance, it may be that the chemical potential of only one of the independent components is equilibrated in the two phases. The situation is graphically represented in Fig. 2. In Fig. 2A is shown the mean molar Gibbs free energy curve of a binary two-phase system that shows a simple solvus. At a particular set of external conditions (temperature, total pressure, a_{H_2O}), the stable pair of phases is given by *a* and *d*, which possess a common tangent on the curve. Portions of the curve to the left of *a* and to the right of *d* represent stable one-phase assemblages. The segment of the curve *a–d* is not realized at stable equilibrium. However, the parts *a–b* and *c–d*, where the curve is concave upward (and thus stable against local fluctuations), are realizable in metastable equilibria; the part *b–c* is truly unstable. The corresponding behavior of the values of the chemical potential of each component is depicted in Fig. 2B, which is adopted from Prigogine and Defay (1954, p. 241). At stable 2-phase equilibrium (points *a* and *d*), the values of the chemical potential of each component are equal in the two phases. If, however, only one of the components is equilibrated (a situation that may be realized, for example, in some ion-exchange reactions), then the value of this chemical potential could be higher or lower than that at stable equilibrium. Thus, if N denotes the mole fraction and α and β de-

note the two phases, Fig. 2B shows that the above situation corresponds to the coupled statements

$$N_1^\alpha > N_1^\alpha \text{ (stable)}; N_1^\beta > N_1^\beta \text{ (stable)},$$

where $N_1^\alpha + N_2^\alpha = 1$, $N_1^\beta + N_2^\beta = 1$, and subscripts "1" and "2" are interchangeable indices.

It is of course possible to achieve metastability by other mechanisms, which may or may not be reflected by scatter of points in Fig. 1. For instance, the system might undergo order-disorder transitions in the interlayer and/or tetrahedral cation positions. Radoslovich (1960) suggested that the tetrahedral positions of muscovite belong to two subsets of equal abundance; on the basis of the dimensions of the tetrahedra he calculated that one of these sets is occupied by Si only where the other set is populated by Al and Si with equal density. It seems likely that order-disorder of Al and Si could occur in this subset, or even between the two sets, which may or may not remain distinct within the Pa-Mu binary (indeed, the existence of two sets of tetrahedral sites is not established for paragonite). Radoslovich's work indicates that an order-disorder process between the subsets should be accompanied by rotation of the tetrahedra and therefore by changes in the basal spacings. At this time, however, nothing more can be said on this subject.

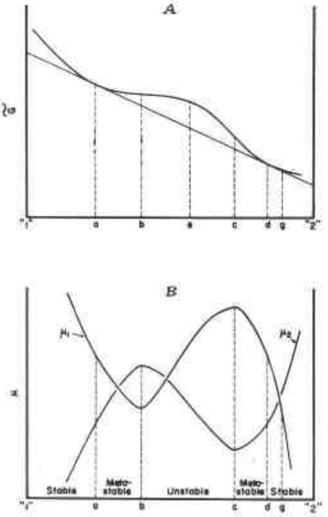

FIG. 2. Schematic representation of (A), the molar mean Gibbs free energy in a two-component system showing a miscibility gap and (B), the chemical potentials μ_1 and μ_2, of the two components corresponding to this function. Long dashed line: common tangent connecting the stable pair of phases, *a* and *d*. Other symbols are explained in the text.

(3) One or both phases of some coexistent mica pairs shown in Fig. 1 may not be a 2M polymorph. Yoder and Eugster (1955, p. 244) showed that the value of the fundamental 10 Å spacing of synthetic muscovite (Mu_{100}) depends on the stacking sequence: these authors report values of

$d_{001}=10.066$ Å, $d_{002}=10.007$ Å, and $d_{003}=9.996$ Å, respectively for the 1M, 2M and 3T polymorphs. Presumably variations of this sort are also shown by the end-member paragonite and for micas with intermediate compositions. Among the coexistent micas here reported, only sample 7 has been established to be of the 2M-polymorph. While most of the natural muscovite and paragonite samples (Eugster and Yoder, 1954a; Yoder and Eugster, 1955; Hurst, 1957; Zen *et al.* 1960) from metamorphic rocks are of the 2M type, it is obviously not safe to rule out the effect of stacking polymorphism in the scatter of points shown in Fig. 1.

(4) Cook and Rich (1962, p. 592) suggested that in some soils from weathered phyllites in Virginia, random mixed layering may occur in micas of the system Mu-Pa. Such a mixed-layer mineral, if verified, would be difficult to treat theoretically because we are not certain whether mixed-layer minerals represent solutions or simple mechanical mixtures (Zen, 1962). If mixed layering does occur, however, it obviously would affect the basal spacings. We have noted for a few samples a weak peak situated about half way between the strong $(006)_{2M}$ reflections of muscovite and the coexistent paragonite; the weak peak might be a phase (a regular 1:1 mixed layer?) in this system, but this point cannot be verified. Because the basal spacings of muscovite and paragonite here reported all show integral higher and lower order reflections, errors due to the effect of mixed layering are unlikely.

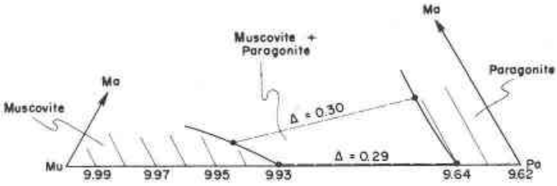

FIG. 3. Effect of addition of small amounts of the Ma component on the basal spacings of coexistent muscovite and paragonite. For a given paragonite spacing, that of muscovite would be greater in a Ma-bearing system than in a Ma-free system.

(5) The muscovite-paragonite pair may not belong to the simple binary system Mu-Pa: certainly nautral paragonite and muscovite always contain other components. One of the most important of these is the component Ma, $CaAl_2Al_2Si_2O_{10}(OH)_2$. Available data suggest that, analogous to the feldspars, the solubility of Ma in muscovite is inconsiderable, but is important in paragonite (Rosenfeld *et al.* 1958; Rosenfeld, 1956). The basal spacing of margarite is close to that of paragonite; addition of Ma to paragonite, therefore, probably does not drastically affect its basal spacing. However, as shown in Fig. 3, at a given metamorphic

grade a muscovite in equilibrium with a Ma-rich paragonite should contain less Pa than one in equilibrium with a Ma-free paragonite. Addition of limited amounts of Ma to the system thus should result in large basal spacings for muscovite while affecting the spacing of paragonite but little. In Fig. 1, this fact would be expressed by having such points lying to the right of and above the regression curve, or some lower line parallel thereto.[1]

Besides the component Ma, other components might also contribute to the deviations of the basal spacings. Radoslovich and Norrish (1962, p. 611), in extrapolating the basal spacings of muscovite as a function of the Fe^{2+}, Fe^{3+}, Mg and Ti contents, implied this effect. More explicitly, Ernst (1963) suggested that the presence of the phengitic component, which he defined as $K(Mg, Fe^{2+})_{.5}Al_{1.5}Si_{3.5}Al_{.5}O_{10}(OH)_2$, leads to abnormally low basal spacings. If the mica contains normal octahedral but deficient tetrahedral Al, the fact could be reflected in alkali deficiency and would lead to changed basal spacing. Lastly, if H_3O^+ occurs in the interlayer position (Table 2, sample J), this fact too should be reflected in the values of the basal spacings. How these several effects contribute to the scatter of the empirical points unfortunately remains totally unassessable.

Despite these many uncertainties, the very large departure of the regression curve from the line of unit slope (Fig. 1) suggests that, if variations of the dimensions in the *ab* plane can be ignored, then the volume relations in the system must be strongly non-ideal. Extrapolation of equation 1 suggests that the critical point of the solvus in the binary system should be near a composition corresponding to $d(002)_{2M} \sim 9.70$ Å; the solvus is strongly asymmetrical.

Much of the present uncertainty could be removed if a composition-basal spacing curve were available, for then it would be possible to compute approximately the volume-of-mixing effect. With such a curve, moreover, one would be able to compute directly a diagrammatically correct solvus by the use of equation 1, and thus to deduce the nature of the "binary" solvus.

Construction of a Composition—Basal Spacing Curve
(E. Z. and A. L. A.)

A preliminary linear regression curve for the binary two-phase system is here presented; this curve employs nine good chemically analyzed micas available to us which also have superior to fair *x*-ray cell dimension

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[1] If this be the sole or major cause for the scatter of points in Fig. 1, then the least-square procedure would not be justified. This contingency, however, is here cheerfully ignored.

data. In addition, the curve made use of three points of considerably lower reliability. The addition of these three points, however, does not significantly affect the regression constants.

The data used for the least-square curve are given in Table 2. The equation is:

$$d(002)_{2M} = 10.034 - 0.427\ N_{Pa}, \text{ in Å} \tag{2}$$

The equation predicts a value for end-member muscovite of 10.034 Å and for end-member paragonite of 9.607 Å[1]. The data are plotted in Fig. 4.

One purpose of constructing a d-N curve (perhaps rather prematurely) is to enable us to obtain further data by a method of successive approximation. The method is particularly designed for use on 2-phase mixtures which defy complete mechanical separations; it is now briefly outlined.

For a given sample, several partial separates of muscovite and paragonite are obtained. These samples contain no other phase with K, Na and Ca, and differ from one another in the relative proportions of the two mica phases but not in the compositions of the individual phases. The fulfillment of this last condition is verified by *x*-ray spacing measurements, noting the absence of any unusual features such as line broadening and line splitting that might indicate complications. The intensities of the $(004)_{2M}$ or the $(006)_{2M}$ lines of both micas in each mixture are repeatedly measured at the peak values and the average values are recorded. Finally, each mixture is chemically analyzed for potassium, sodium and calcium.

Next, curves relating the intrinsic $(004)_{2M}$ and $(006)_{2M}$ structure factors and the $(002)_{2M}$ basal spacings are computed for the binary system. In making the computation, the atomic coordinates in the c^* direction, z_i, in the 2:1 layer, are those given by Radoslovich (1960) for the Spotted Tiger Mine muscovite, with its corresponding lattice spacing and composition of the interlayer atoms. The atomic scatter factors are used for the elements in the 2:1 layer; the values for the proper $\sin\theta/\lambda$ $(=\frac{1}{2}d)$ are interpolated from the International Tables (1962). For the elements in the interlayer position, the ionic scatter factors are used.

For micas other than the sample from the Spotted Tiger Mine, a further approximation is necessary because it is not known how the z_i's vary, in terms of absolute distances, with the interlayer composition. Such variations surely must occur because the values of d(010) change from 8.995 Å for muscovite to 8.89 Å for paragonite (for margarite it is 8.92 Å, according to Radoslovich and Norrish, 1962); presumably the z_i's increase with decreasing *b* dimensions, but in an unknown manner. These

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[1] The equation is not affected by adding the stipulation that equation (1) should be obeyed.

TABLE 2. DATA ON ANALYZED PARAGONITE AND MUSCOVITE

No.	Mineral	Locality	$d(002)_{2M}$	K/(K+Ca +Na)	Reference and comments
A	Paragonite	Zermatt, Switzerland	9.623	0.05	Zen *et al.*, 1960; good single-phase material.
B	Paragonite	Synthetic	9.637	0.00	H. P. Eugster, written communication to Zen, 1963.
C	Muscovite	Gassets, Vermont	9.918	0.61	Rosenfeld *et al.*, 1958; good single-phase material. Minor Fe^{2+} and Mg ignored.
D	Muscovite	Methuen, Ontario	9.95_0	0.91	Hurlbut, 1956
E	Muscovite	Spotted Tiger Mine, Australia	10.007	0.94_2	Radoslovich, 1960. No Ca analysis reported but presumably Ca is absent (E. W. Radoslovich, 1963, oral communication).
F	Muscovite	Synthetic	10.042	1.00	H. P. Eugster, written communication to Albee, 1960 (differs from value in Yoder and Eugster, 1955).
G	Muscovite	Macon Co., N. C. (USNM no. 18203)	9.985	0.92	This report; detailed data to be published elsewhere.
H	Muscovite	Lincoln Mtn., Vt. no. LA10K)	9.950	0.81	This report; detailed data to be published elsewhere.
I	Muscovite	Salisbury, Conn.	9.927	0.73_7	This report; detailed data to be published elsewhere.
Three less reliable points:					
J	Paragonite	Gassetts, Vermont	9.640	0.11	Rosenfeld *et al.*, 1958. *X*-ray data are good but chemical analysis on material with about 12% muscovite contamination; correction, based on relative intensities of the diffraction lines, is approximate.
K	Paragonite	Lincoln Mtn., Vermont (LA10p)	9.640	0.17	*X*-ray data good. Chemical data based on the extrapolation procedure described in this paper, using F^2 weighting. Unweighted $N_{Mu}=0.16$.
L	Muscovite	Lincoln Mtn., Vermont (LA10p)	9.960	0.75	Same comment as above; unweighted $N_{Mu}=0.75$.

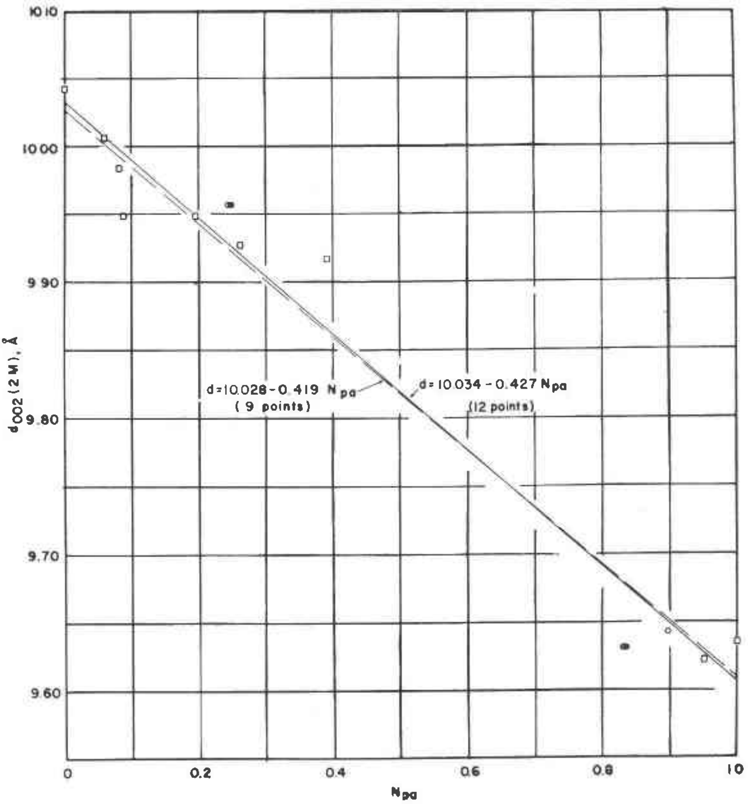

FIG. 4. Regression curve between the $(002)_{2M}$ spacings and compositions of analyzed muscovite and paragonite, reckoned in terms of the components Mu and Pa. Solid line, regression using all 12 points (F^2-weighted; Table 2). Long dashed line, regression using only the 9 superior points. The regression curve for the 12 points, weighted but with the constraint of equation (1), is identical with the solid line given. Squares represent the nine superior analyses; circles, the three less precise analyses. Open circles are the weighted extrapolated compositions, solid circles are the unweighted extrapolated compositions. Please notice that the spacing plot for sample K is slightly in error.

increases in z_i cannot be simply prorated (by assuming, for instance, constant volume for the 2:1 layer), because it would imply large distortions for the coordination polyhedra, as pointed out to Zen by E. W. Radoslovich (1963, oral comm.). Fortunately, however, the F^2 value is not sensitive to small changes in z_i, especially if these changes are in the same direction, because the corrections tend to cancel one another. In the absence of a better guide, therefore, we simply assumed that the 2:1 layers remained rigid in the binary system and the z_i coordinates, in absolute distances, possess the values given by Radoslovich.

The calculated d(002) – $F^2(004)$ and d(002) – $F^2(006)$ curves are given in Figs. 5 and 6; these curves are used to translate the relative intensities of the two micas in their mixtures to relative amounts of the two phases. The relative amounts are then plotted against the bulk composition, K/(K+Na+Ca); when extrapolated to zero muscovite and zero paragonite, they give estimates of the compositions of each phase. The validity of the method depends on the correctness of the F^2 computations, as well as on the reliability of the *x*-ray intensity measurements and on the extrapolation procedure (see Appendix for additional comments). The problem of preferred orientation on the *x*-ray slide is not serious as both phases have a platy habit and only highly oriented mounts are used. However, even for oriented samples, the *x*-ray technique probably cannot detect micaceous phases in amounts less than 3% (Zen, unpubl. data) and so this much error is intrinsic. Nonetheless, at this stage even such crude measures are useful.

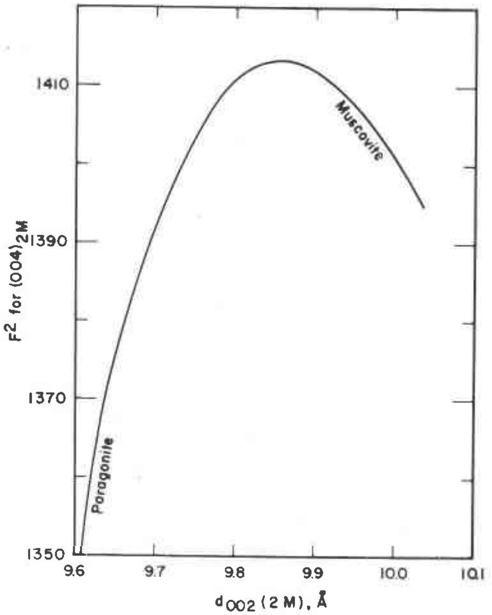

FIG. 5. Calculated $F^2(004)_{2M}$ as a function of the d spacings of $(002)_{2M}$ for muscovite and paragonite in the binary system Mu-Pa. Radoslovich's (1960) atomic coordinates are used; the curve is also consistent with equations (1) and (2). See text for further details.

The estimates obtained by this technique could be used to improve the original d-N curve, and a second cycle of refinement initiated, and so on. As a measure of the convergence of the iterative method, the compositions of coexistent muscovite and paragonite from sample LAlOp were derived this way, as detailed in the Appendix. The regression curve obtained by using the crude intensity ratios as direct measures of the relative phase amounts is identical with equation (2).

Equations (1) and (2) can be combined to yield directly the compositions of the coexistent micas, irrespective of the volume behavior of the system. Figure 7 gives the results, if we assume that the equations are applicable throughout the binary system, without the intervention of phase transformations. The curve terminates at $N_{Pa} \approx 0.8$, which corresponds to the critical point on the solvus. For comparison, the corresponding curve based on the assumption of a linear d-N curve and a symmetrical solvus (very nearly corresponding to the model used by Eugster and Yoder, 1955) is given as the dashed line. The direction of asymmetry of our curve seems reasonable, because it should be easier to put a small atom (Na) into a large hole than the converse. The asymmetry is in the same direction, and of comparable magnitude, as that for the alkali feldspars reported by Orville (1963, p. 220).

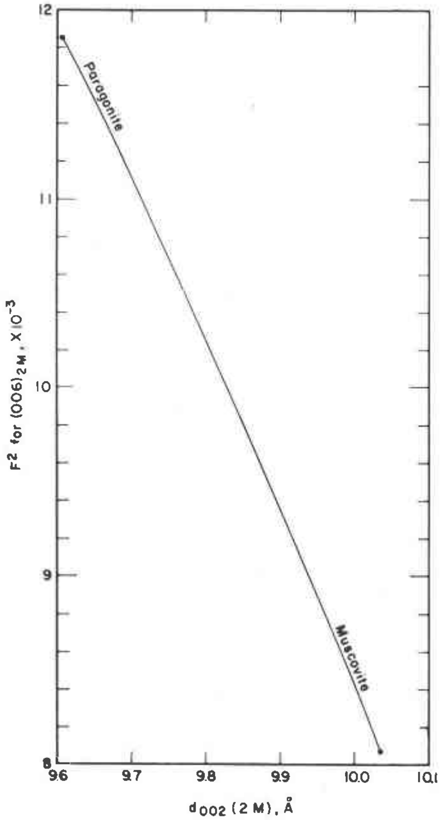

FIG. 6. Calculated $F^2(006)_{2M}$ as a function of the d spacing of $(002)_{2M}$. The other stipulations are identical with those for Fig. 5.

Comments on the Stability Range of Paragonite in Metamorphic Rocks (E. Z.)

Only a few comments on the petrologic relations of paragonite will be made. The theoretical aspects of the phase relations of paragonite in the system $KAlO_2$-$NaAlO_2$-Al_2O_3, in the presence of quartz and at arbitrary values of the intensive variables T, P_T, and a_{H_2O}, have been examined by Thompson (1961).

In soils and unmetamorphosed sedimentary rocks, paragonite is rare, although muscovite (illite) is nearly ubiquitous. Cook and Rich (1962) reported paragonite from kaolinitic soils in Virginia, and Bannister (1943) reported paragonite (brammallite) from some shales in Wales. Although neither illite nor brammallite truly belongs to the simple binary system Pa-Mu, these minerals probably are the same *phases* as muscovite and paragonite, respectively, and are not separated therefrom by miscibility gaps or alternative assemblages.

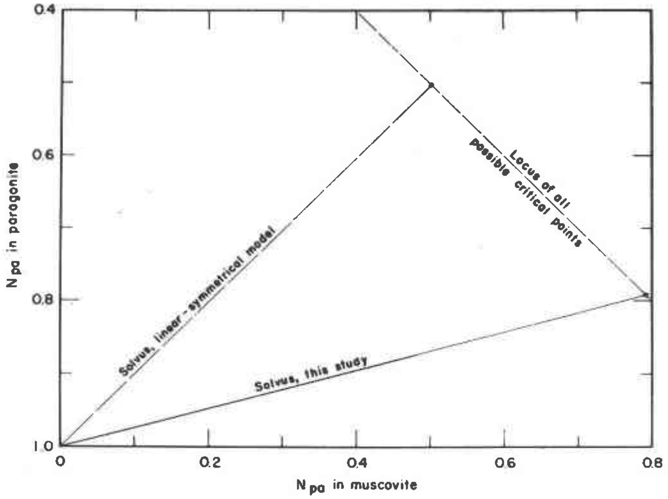

FIG. 7. Compositions of coexistent muscovite and paragonite according to equations (1) and (2). The curve terminates at $N_{Pa} \approx 0.8$, which is the critical point on the solvus. For comparison, the comparable curve assuming a symmetrical solvus and linear relation between basal spacing and Mu/(Mu+Pa) is given as the dashed line; the critical point on the solvus would be at $N_{Pa} = 0.50$.

Apart from these samples, the lowest grade rocks which carry paragonite, to our knowledge, are chloritoid-bearing phyllites of the biotite zone, reported on here and by Albee (1957), Zen (1960) and Cady *et al.*

(1962). The lack of paragonite in lower grade rocks may be real, because the extensive literature on the clay mineralogy of sediments and sedimentary rocks, with rare exceptions, does not mention paragonite. Zen (1960, p. 152) suggested that in quartz-bearing rocks the lower limit of stability for this phase might be given by the alternative assemblage, kaolinite+albite, found in many such rocks (see, for instance, Coombs, 1954, p. 81); the latter represents a more hydrous assemblage. Na-montmorillonite might be part of another possible alternative assemblage to paragonite; however, this cannot be strictly true because montmorillonite in sedimentary rocks generally belongs to more complex chemical systems.

Paragonite becomes unstable at a lower temperature than does muscovite under comparable conditions (Eugster and Yoder, 1954b, p. 112); this agrees with the commonly observed assemblage kyanite-muscovite-sodic plagioclase in schists. Everything else being equal, rocks in the almandine and low-kyanite zones of metamorphism might be expected to be the most likely hosts to paragonite.

In the schists reported in this paper, biotite is rare. Outstanding exceptions are the three samples from Switzerland (Table 1, nos. 39, 40, 41). These samples significantly do not have albite or chlorite. A reaction that could give rise to the observed assemblage is:

$$\begin{array}{cccc} \text{3 chlorite} & +\ \text{8 albite} & +\ \text{5 muscovite} & =\ \text{8 paragonite} \\ 3Mg_5Al_2Si_3O_{10}(OH)_8 & 8NaAlSi_3O_8 & 5KAl_3Si_3O_{10}(OH)_2 & 8NaAl_3Si_3O_{10}(OH)_2 \\ & +\ \text{5 biotite} & +\ \text{9 quartz} & +\ 4H_2O \\ & 5\ KMg_3AlSi_3O_{10}(OH)_2 & 9\ SiO_2 & 4H_2O \end{array}$$

where for simplicity the phases are supposed to be pure end-members. The reaction to the right represents a net dehydration and thus is prograde. The left-hand assemblage is common among schists in the almandine zone. The reaction is of course multivariant because the phases in reality represent complex solutions; nonetheless, in rocks of appropriate mineralogical composition, upon progressive metamorphism, a late episode of paragonite formation at the expense of chlorite and albite (or the $NaAlSi_3O_8$ component of a plagioclase) seems plausible. As paragonite so far has not been reported from rocks of much higher metamorphic grade than these samples from Switzerland, this reaction apparently occurs shortly before paragonite becomes intrinsically unstable.

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APPENDIX (A.L.A.)

The compositions of coexisting muscovite and paragonite were derived for sample no. LAlOp (no. 7 in Table 1) from the Lincoln Mountain quadrangle, Vermont (Cady *et al.* 1962) by the method outlined in this paper. The rock is an almandine-chloritoid-chlorite-muscovite-paragonite-quartz-ilmenite schist, which contains no feldspar. The coexistent muscovite and paragonite occur in distinctly different sizes (Rosenfeld, 1956); this fact enabled the partial separation of the two phases in the following manner. The nonmagnetic portion of the rock was sieved; paragonite was concentrated in the finer fraction. Further concentration of paragonite from these finer fractions was achieved by panning and differential settling in water or in acetone. The various processes did not affect the basal spacing of either phase.

TABLE 3. CHEMICAL AND *X*-RAY INTENSITY DATA ON VARIOUS MIXTURES FROM SAMPLE LA10P [ANALYST: A. D. MAYNES]

Wt. %	No. 31	No. 32	No. 33	No. 34	No. 35	No. 36	No. 37	No. 38
Na_2O	1.45	2.60	2.70	2.07	2.06	1.93	3.60	3.20
K_2O	4.15	4.77	4.24	2.39	4.28	5.09	4.42	3.26
CaO	1.34	0.15	0.22	0.37	0.26	0.12	0.08	0.21
P_2O_5		0.17	0.19		0.14	0.11	0.09	0.42

Atom-per cent Na/(Na+K)[=Pa/(Pa+Mu)]:
37.5 45.3 49.2 56.9 42.2 36.6 55.3 59.9
Intensity ratio: I $(004)_{2M}$ (muscovite)/I $(004)_{2M}$ (paragonite), and average deviation from the mean.
3.57±.12 1.78±.04 1.39±.06 0.821±.044 2.62±0.15 4.0±0.2 .938±.035 .704±.042
Mole-per cent of phases, paragonite/(paragonite+muscovite), corrected by calculated F^2 values:
22.4±0.7 36.6±0.5 42.6±1.0 55.7±1.4 28.2±0.1 20.5±0.9 52.4±0.9 59.4±1.5

Each *x*-ray intensity ratio, given in Table 3, is the average of measurements on ten acetone smear-mounts, scanned in both up- and down-angle directions. The $(004)_{2M}$ intensities were used for the micas of sample LA10p, because the (10.1) line of quartz interferred slightly with the muscovite $(006)_{2M}$ peak. The relative amounts of the two phases were converted from the raw intensity ratios by using the calculated F^2 values, corresponding to the observed $(002)_{2M}$ spacings, as outlined in this paper. Because the ratio $F^2(004)_{2M}$(paragonite)/$F^2(004)_{2M}$(muscovite) is near unity (Fig. 5), this conversion is insensitive to uncertainties in the F^2 curve.

The chemical data on the 8 mixtures used in the procedure are given in Table 3 and

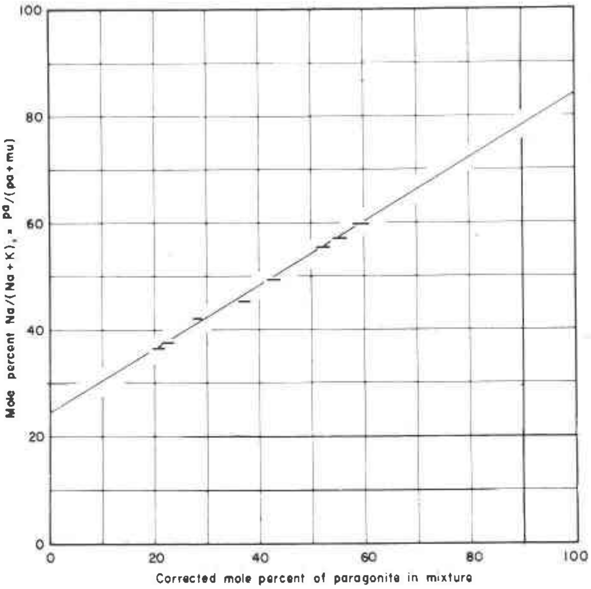

FIG. 8. Least-square line relating the chemical compositions of different fractions of sample LA10p (no. 7 in Table 1) to the fractions of paragonite in the mixtures. These fractions were calculated from the x-ray intensities of the $(004)_{2M}$ lines and weighted by the structure factors. CaO in the analyses was ignored because this component was probably entirely in the apatite inclusions. Widths of the bars give the probable errors in intensity measurements.

Fig. 8. Mixtures 31–36 were originally analyzed only for Na_2O, K_2O and CaO. Because of its high CaO content, mixture 31 was then ground extremely fine, and centrifuged in a liquid of 3.3 density. The heavy fraction consisted predominantly of apatite with subsidiary tourmaline. Because of this fact, the other mixtures were analyzed for P_2O_5.[1] Mixture 37 was centrifuged to remove apatite before it was chemically analyzed; interestingly this mixture has the lowest CaO and P_2O_5 content. There is enough P_2O_5 in all the mixtures which were analyzed for this component, to account for all the CaO as fine-grained apatite inclusions (see also Jaeger, 1962, p. 5303). It is, of course, conceivable that both CaO and P_2O, are actually components in the mica phases; however, if so, there should be a direct correlation between the CaO content and the amount of paragonite in the mixtures, while in fact the correlation is poor. For the present purposes, therefore, we have simply ignored the CaO content in the extrapolatory procedure.

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[1] Unfortunately, not enough of mixture 31 remained for a new CaO determination.

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