

Chemical composition and physical properties of lithium-iron micas from the Krušné hory (Erzgebirge), Czechoslovakia and Germany. Part B: Cell parameters and optical data

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SUMMARY. Unit-cell dimensions and refractive indices of lithium-iron micas decrease with decreasing iron and increasing lithium. Indices β and γ as well as parameters a and b can be used to estimate the composition of lithium-iron micas but basal spacing and $2V_\alpha$ are poor indicators of composition.

The chemical composition of natural lithium-iron micas from the Krušné hory and the Erzgebirge along the Czechoslovak-German border was discussed in Part A of this study (Rieder *et al.*, 1970). It was concluded that the composition and crystallography of these micas fit best the series siderophyllite-polyolithionite. The compositions were expressed by the ratio $A' = LR/(LR + 'Fe')$. In this expression, LR is the subscript value of Li or octahedral R^{3+} (whichever is the smaller) in the crystallochemical formula, 'Fe' is the sum of the values in the formula of Fe^{2+} and Mn^{2+} . A' therefore defines the position of a particular mica on the siderophyllite-polyolithionite join. This paper deals with the correlation between composition, cell dimensions, and refractive indices.

Cell parameters. A standard non-integrating Buerger precession camera was used with Mo- $K\alpha$ and Cu- $K\alpha$ radiations. Row spacings were measured according to the procedure proposed by Buerger (1964) and converted into cell data. High accuracy of the process was ensured by calibration of the camera with analytical-grade sodium chloride with $a = 5.6402 \text{ \AA}$ at 26°C (Swanson and Fuyat, 1953) and natural quartz from Lake Toxaway, New York, with $a = 4.9131 \pm 0.0002 \text{ \AA}$, $c = 5.4047 \pm 0.0003 \text{ \AA}$, $V = 112.982 \pm 0.007 \text{ \AA}^3$ at $23 \pm 2^\circ \text{C}$ (Huebner, 1967). Films were corrected for shrinkage or expansion by measuring the distance between two pairs of fiducial dots recorded on every photograph.

Single-layer cell data for the micas studied are summarized in a table available from the Department of Mineralogy, British Museum (Natural History), London, S.W. 7.

Plots of a and b against A' (figs. 1, 2), outline near-linear trends that slope steeply towards the lithium-rich compositions. a and b can be used to estimate the composition

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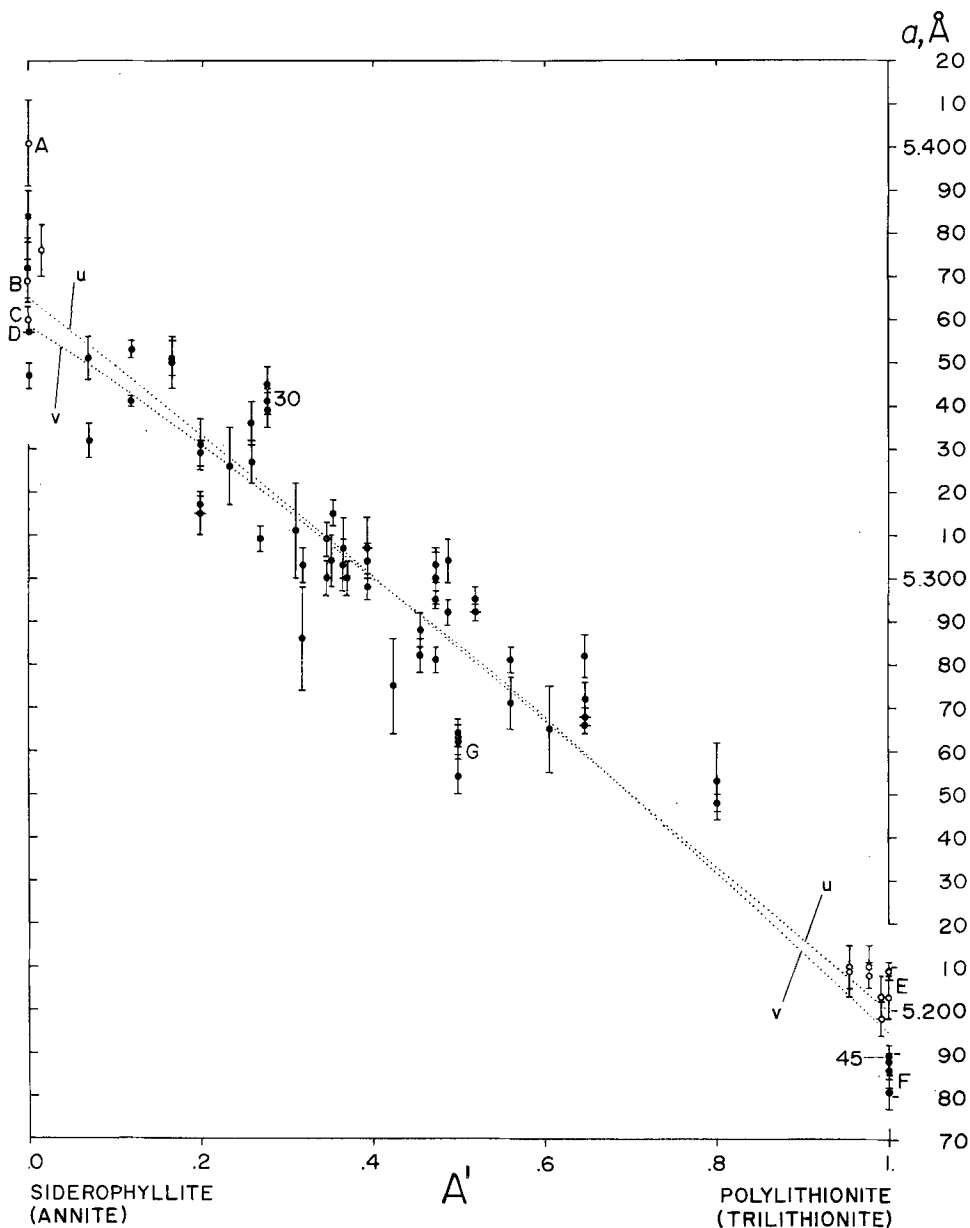


FIG. 1. Parameter a (b of $2M_2$) of natural lithium-iron micas plotted against A' . Letters C, E, F, G refer to samples in deposited table. A, B—refined powder data for synthetic annites (Wones, 1963); D—single-crystal data for sample no. 44 (Ross *et al.*, 1966). Cell parameters for sample no. 45 from Munoz, 1966. Ordered micas are shown by solid circles, micas with other structures by open ones. The dotted lines are regression curves for all data (u: $a = -0.003A'^2 - 0.161A' + 5.365$) and for data for ordered micas (v: $a = -0.023A'^2 - 0.132A' + 5.358$); sample no. 30 was not considered in either case.

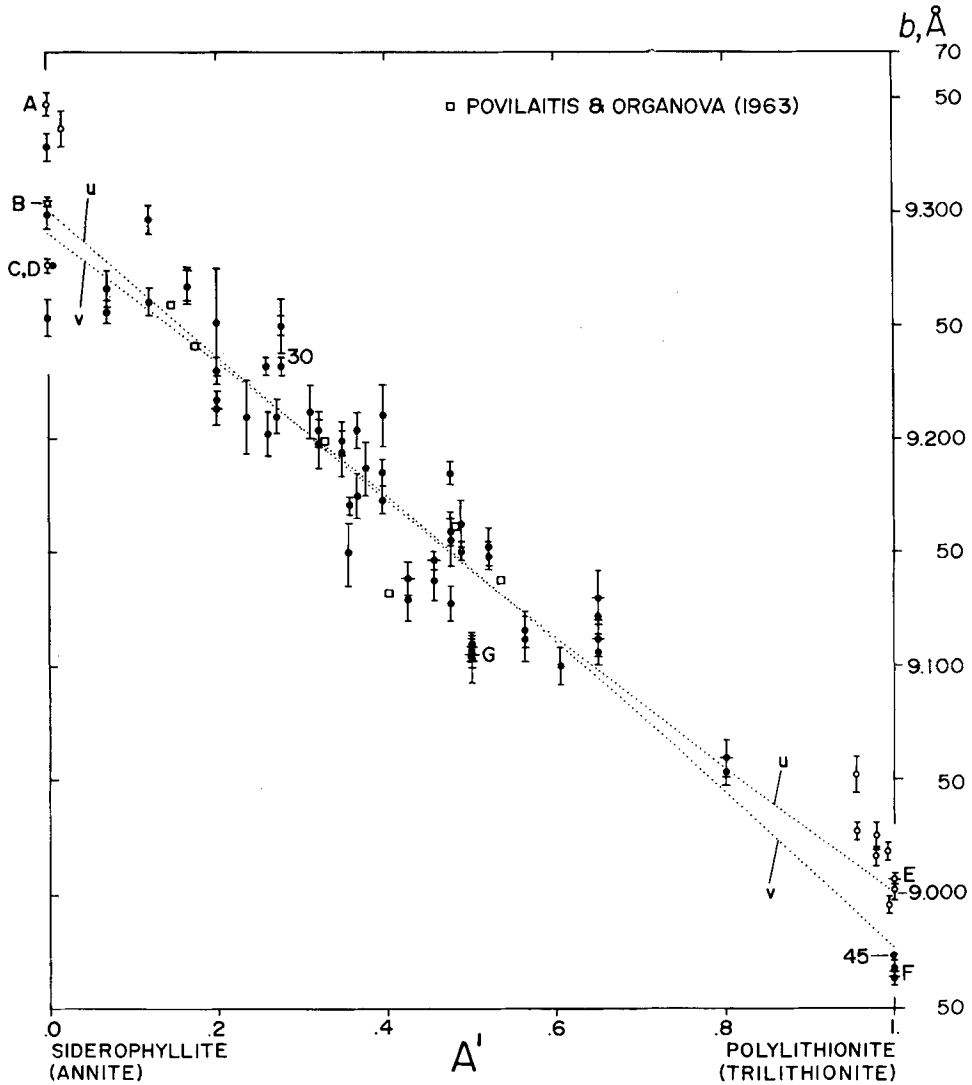


FIG. 2. Parameter b (a of $2M_2$) of natural lithium-iron micas plotted against A' . Data of Povilaitis and Organova (1963) are plotted on the same grid. Symbols as in fig. 1. Regression equations: $u: b = 0.033A'^2 - 0.336A' + 9.301$, $v: b = -0.042A'^2 - 0.274A' + 9.290$; sample no. 30 was not considered in either case.

of lithium-iron micas, but the estimate suffers from some bias. The model of the ordered structure (Rieder, 1968) requires that a and b of ordered micas be smaller than those of disordered micas (annite, trilithionite?). Regression curves for a and b were calculated separately from all data and from the data for ordered micas, and the difference, although statistically not significant, is in the predicted direction.

The plot of A' against d_{00N} , where N is the number of layers in the repeat of a polytype (Rieder, 1968) shows splitting, which can be explained by octahedral ordering of micas on the siderophyllite-polyolithionite join. The large spacings are interpreted as a product of octahedral disorder, the low ones, of octahedral ordering. Like a and b , d_{00N} is bigger for iron-rich micas than for lithium-rich ones, and consequently so is the cell volume V/N . The splitting of d_{00N} invalidates this parameter (and V/N) as an indicator of composition.

Optical data. The refractive indices β and γ were measured by the double-variation method as modified by Melka (1961) and together with $2V_\alpha$ are given in table I and figs. 3 and 4. Because different flakes were used for $2V$ and refractive index measurements some discrepancies occur such as $\beta \neq \gamma$ when $2V_\alpha = 0$.

Like the cell parameters, refractive indices increase with increasing 'Fe' proportion in the octahedral sheet (see also Kunitz, 1924). The spread of points in fig. 3 does not suggest that refractive indices vary with octahedral order or disorder. Indices β and γ are easy to measure and their unbiased relation to composition makes them a valuable means of estimating composition. For this purpose, a second-order regression of composition on indices β , γ was calculated as well as 95 % confidence limits (fig. 3).

The plot of $2V_\alpha$ against composition (fig. 4) suffers from a large scatter. $2V_\alpha$ increases with increasing lithium, but the relationship (observed by Kunitz, 1924, and by Sitnin and Razina, 1963) is obscured by twinning and polytypism, which lower the axial angle.

Optical adjustments of the mica crystals before X-raying verified that the β of the untwinned monoclinic structures is parallel to the b axis except for crystals of $2M_1$ from one sample (41), whose optic axial plane is perpendicular to (010), as in muscovite. The $2V_\alpha$ of this sample falls into two groups, both of which are lower than the $2V_\alpha$ of micas with similar composition (fig. 4). The orientation of the optic axial plane and the size of the $2V_\alpha$ indicate the unusual character of this lepidolite.

Discussion. X-ray and optical data for synthetic lepidolites and X-ray data for some synthetic ferruginous micas have been obtained because few natural micas of such compositions are available. Data for synthetic fluor-zinnwaldite (labelled G in figs. 1 and 2) are also included for comparison. Figs. 2 and 3 include the data on lithium-iron micas given by Povilaitis and Organova (1963). In both figures, their data are in a reasonable agreement with ours.

Optical data for micas from Zinnwald and Altenberg as given by Gottesmann (1962) are plotted in fig. 3, and outline a markedly different trend although our micas 1, 16, 22, 23, and 35 come from the same localities. It is impossible to explain the difference although it is tempting to ascribe it to anomalies in Gottesmann's analyses: two of them are anomalously high in silica and all five too high in alumina. It is not possible to decide whether the analyses are in error or whether all represent unusual micas.

In Part A of this study, the composition of mica no. 30 was shown to be either unusual or contaminated. Contamination with common greisen minerals such as quartz or topaz does not affect the ratio A' , and so the fact that the cell parameters

TABLE I. Optical data for natural lithium-iron micas arranged in order of increasing values of $A' = LR/(LR + 'Fe')$

| Sample no. | A' | β | γ | $2V_a$ | Sample no. | A' | β | γ | $2V_a$ |
|------------|-------|---------|----------|--------------------------------|------------|-------|------------------|----------|-------------------------------|
| 44 | 0.000 | — | 1.662 | < 5° | 29 | 0.362 | — | 1.610 | 9° 30' ± 1° |
| 12 | 0.013 | — | 1.647 | < 5° | 9 | 0.372 | 1.601 | 1.603 | { 28° 27° 24'* |
| 8 | 0.068 | — | 1.634 | { 0°* 15° | 35 | 0.395 | — | 1.593 | 21° ± 2° |
| 7 | 0.121 | — | 1.631 | { 10° 4° 14'* | 38 | 0.425 | — | 1.601 | 28° ± 1° 30' |
| 18 | 0.167 | — | 1.626 | 17° | 40 | 0.456 | — | 1.595 | 27° ± 1° |
| 13 | 0.199 | 1.613 | 1.615 | { 17° 30' ± 2° 30' 22° 34'* | 5 | 0.472 | — | 1.603 | { 26° 30' ± 30' 28° 54'* |
| 31 | 0.199 | — | 1.627 | < 5° | 37 | 0.488 | 1.593 | 1.595 | 31° 30' ± 1° |
| 2 | 0.234 | — | 1.618 | < 5° | 15 | 0.517 | — | 1.595 | 39° 30' ± 30' |
| 23 | 0.259 | 1.610 | 1.611 | { 5° 34'* | 16 | 0.560 | 1.584 | 1.588 | { 27° 30' 28° 15' ± 1° 30' |
| 3 | 0.267 | — | 1.616 | { 18° ± 1° 8° | 1 | 0.604 | { 1.574 1.578 | 1.576 | 32° |
| 30 | 0.278 | — | 1.626 | 14° 30' ± 1° 30' | 22 | 0.645 | 1.576 | 1.580 | { 29° 38' ± 1° 22'* |
| 4 | 0.311 | — | 1.605 | { 13° 8° 17'* | 17 | 0.799 | 1.578 | 1.579 | { 36° 36° 20' ± 40' |
| 6 | 0.316 | — | 1.601 | { 6° < 1° 06'* | 41 | 0.956 | 1.552 | 1.554 | { 28° 30' ± 30' 22° ± 1° |
| 33 | 0.349 | — | 1.602 | 0° | 43 | 0.977 | 1.553 | 1.555 | 35° ± 30' |
| 10 | 0.350 | 1.601 | 1.602 | { 25° 30°* | 42 | 0.992 | 1.551 | 1.553 | 35° 30' ± 30' |
| 14 | 0.352 | — | 1.624 | — | | | | | |

For definition of A' see text. Sample numbers refer to those in Rieder *et al.* (1970), where their localities and chemical analyses are given. Refractive index measurements refer to sodium light and are accurate to within ±0.001 except 41, 42, and 43 which are ±0.002, while $2V$ measurements are in white light on a universal stage except for those marked * which were measured with an optic axial angle goniometer in sodium light.

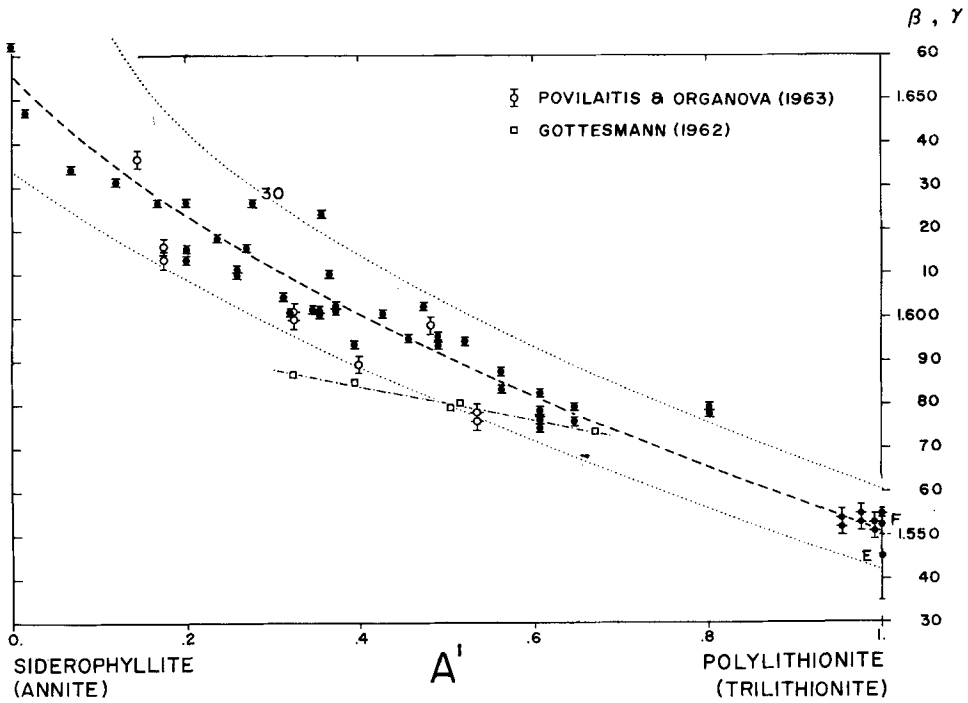


FIG. 3. Refractive indices β , γ of natural lithium-iron micas (solid circles) plotted against A' . The dashed line is a corresponding regression curve ($A' = 46.182(\beta, \gamma)^2 - 157.686(\beta, \gamma) + 134.478$). The correlation coefficient is a highly significant -0.980 . The dotted lines are drawn at $\pm 2S$ about the regression line and serve for prediction of composition (A' ratio) from refractive indices β , γ . $S^2 = s^2 + \text{var } u_p(x)$, where s^2 is variation about the regression and $\text{var } u_p(x)$ is variance of a point on the regression (for formulas see, for example, pp. 250-1 of Guest, 1961). On the same grid are plotted the data of Povilaitis and Organova (1963) and Gottesmann (1962). The dash-and-dot line is a linear regression line for Gottesmann's (1962) data.

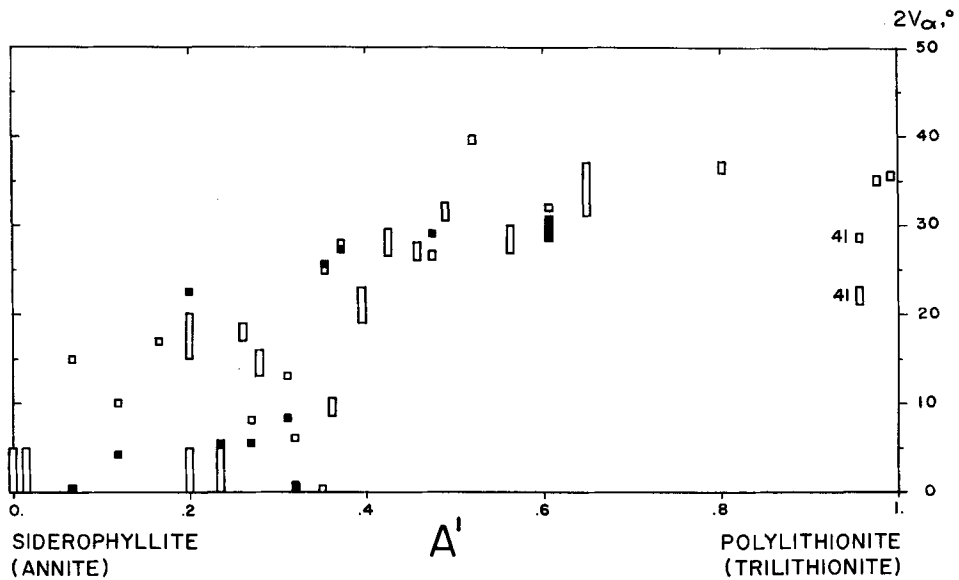


FIG. 4. $2V_{\alpha}$ of natural lithium-iron micas plotted against A' . Universal stage measurements are shown by open rectangles, optic-axial-goniometer measurements, by solid ones.

and refractive indices of no. 30 do not fall in line with those of the remaining micas on the plots shows that this mica is genuinely different from other lithium-iron micas studied.

Cell data for two crystals from samples nos. 14 and 17 deviated substantially from the trends in figs. 1 and 2. Cell data for other crystals from those samples are 'normal', thus proving compositional heterogeneity of the samples. The cell data of the crystal from sample no. 14 are close to those of a muscovite (reflections $06l$ with l even are strong, like those of a muscovite). If this muscovite is an intrinsic constituent of sample no. 14 and in equilibrium with the lithium-iron mica, it indicates a miscibility gap between muscovite and micas on the siderophyllite-polyolithionite join. Cell parameters of one crystal from sample no. 17 correspond to those of a lithium-iron mica richer in iron. Data for these crystals were not plotted in figs. 1 and 2, but are available in the deposited table. These two cases demand that even cell data that appear normal be interpreted with caution.

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