THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF

THE MINERALOGICAL SOCIETY.

No. 113. June, 1926. Vol. XXI.

# *On the chemical classification of the mica group.*

## *II. The basic micas.*

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[Read January 19, 1926.]

IN the first part of this paper[2] it was shown that the acid section of the mica group could be divided into two main series, the potash micas and the lithia micas. The molecular ratio of potash to silica was 1 : 6 and the micas were therefore represented as salts of an acid characterized by this value. The present section contains the result of a similar investigation of the basic micas, especially biotite and phlogopite; here again it will be seen that the grouping $K_2O \cdot 6SiO_2$ is present throughout. For comparison of the molecular composition, the analyses of the basic micas have been recalculated in molecular ratios, $(Si,Ti)O_2$ being made equal to 600 according to the method already used for the acid micas. To economize space, however, figures have not been tabulated for the older analyses, but the values for $R_2O_3$ and RO, which are the only 'solid' variables when the ratio $K_2O \cdot 6SiO_2$ is fixed, have been

[1] Communicated by permission of the Director.

[2] A. F. Hallimond, Min. Mag., 1925, vol. 20, pp. 305-318.

plotted in fig. 5. This diagram renders it possible to ascertain at once those published analyses which approximate to a given composition; similarly, any new analysis can be classified and compared with earlier data. The analyses used in this paper are (1) the biotites and phlogopites cited by Dana,[1] (2) those given by H. E. Boeke (complete analyses later than 1890),[2] (3) a number of recent analyses by W. Kunitz and others; ratios for these are tabulated at the end of the paper.

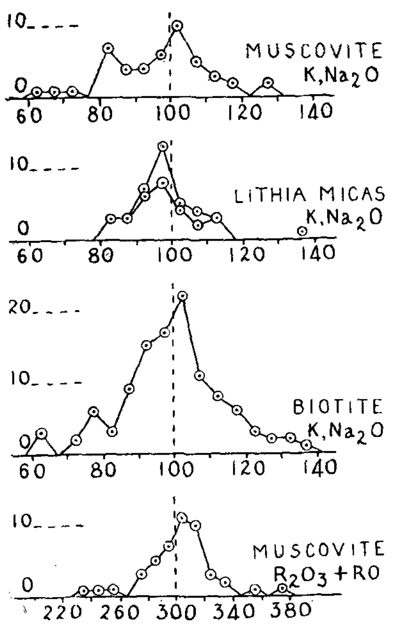



FIG. 3.[4] Frequency diagrams showing the incidence of $R_2O$-values in the published analyses of muscovite, lithia micas, and basic micas; also the incidence of values for $RO+R_2O_3$ in muscovite ($SiO_2$ = 600). The upper line for lithia micas includes a few analyses not listed in Part I. The ordinates represent the number of analyses occurring in each division of the base-line.

*Ratio of $SiO_2$ to $K_2O$.*—While the first part of this paper was in the press a discussion of the mica group was published by A. N. Winchell,[3] who assigns formulae with the ratios $K_2O \cdot 6SiO_2$ (phlogopite), $K_2O \cdot 5SiO_2$ ('eastonite'), and $K_2O \cdot 8SiO_2$ ('phengite'). It is of special interest, therefore, to examine what proportion of the mica analyses deviate from the ratio $K_2O \cdot 6SiO_2$. This is conveniently done by means of frequency diagrams (fig. 3), in which the base-line is divided into compartments, corresponding with intervals of, say, 60–65, 65–70, 70–75, &c., in the value for $R_2O$, when $SiO_2 = 600$. Above each compartment an ordinate is drawn representing the number of analyses for which the $R_2O$-value falls within the interval. The resulting points yield a curve showing the relative frequency of analyses for the respective values of $R_2O$. Three

[1] Dana's 'System of Mineralogy', 6th ed., 1892, pp. 630, 631, 633.

[2] H. E. Boeke, Neues Jahrb. Min., 1916, vol. 1, pp. 89–95. [Min. Abstr., vol. 1, p. 245.]

[3] A. N. Winchell, Amer. Journ. Sci., 1925, ser. 5, vol. 9, pp. 309-327, 415–450, diagram p. 321. [Min. Abstr., vol. 3, p. 12.]

[4] Figs. 1-2 were given in Part I of this paper.

such curves are shown in the figure, the first two being for the potash and lithia micas given in the first part of this paper, while the third represents the basic micas now plotted. The ratio $K_2O . 5SiO_2$ requires the value 120 $R_2O$, while $K_2O . 8SiO_2$ requires 75, and it is at once clear that few analyses contain $R_2O$ in these proportions; the majority lie close to the value 100 and are symmetrically grouped in a manner which suggests that the deviations are due to accidental causes. The fourth curve in fig. 3 shows a similar distribution of the values for $R_2O_3 + RO$ in muscovite; these were shown in Part I to approximate to the simple value 300. Taken together, the four curves offer very strong

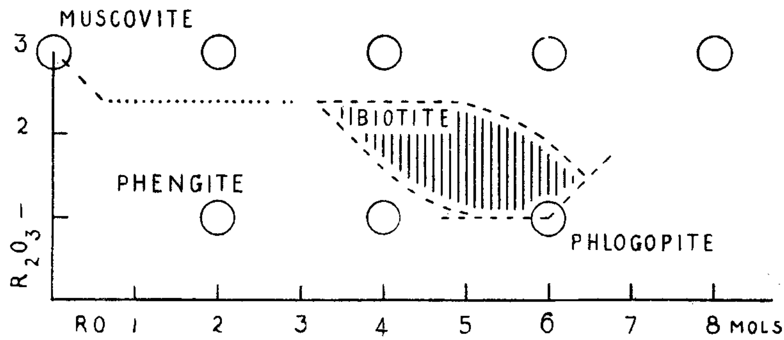



Fig. 4. Relation of acid to basic micas. Type $K_2O . mRO . nR_2O_3 . 6SiO_2 . 2H_2O$. General diagram showing the limits of composition for muscovite and biotite; circles indicate the compounds derivable from graphical formulae based on trisilicic acid.

support to the view that both acid and basic micas are essentially compounds of the constant group $K_2O . 6SiO_2$.

*Relation of muscovite to biotite.*—Fig. 1 in Part I of this paper showed the composition of the muscovite group, the co-ordinates being the molecular proportions of RO and $R_2O_3$ when $SiO_2 = 600$. Fig. 5 is a similar diagram for the biotites. The two figures represent on a large scale portions of a general diagram for the muscovite-biotite group. This general diagram is shown in fig. 4, which summarizes the chemical relations of the two species. Only five analyses, tabulated on p. 33, fall in the space between biotite and muscovite, so that there is under normal conditions a wide gap in the range of solid solution.

*Basicity of the micas in relation to that of the parent rocks.*—The micas, with their widely varied range of RO-content, have presumably formed from silicate melts or solutions with a corresponding range of composition. Beginning with melts of an acid character (pegmatites) nearly free from RO, we have, first, pure muscovite passing over into phengitic muscovite as the content of RO increases. In this way nearly one-third of the alumina may be replaced by RO. Further increase in RO results in the discontinuous addition of a substantial amount of RO to form the most acid members of the biotite group. 'Phase-rule' considerations would require that these acid biotites should be capable of co-existence with the corresponding muscovite, and they are indeed derived almost without exception from the granites and gneisses, rocks in which the two minerals often crystallize side by side. The range of micas from the granites and intermediate rocks extends about half-way across the biotite area, the remainder being occupied by vein micas, phlogopites, and a few micas from the basic rocks. Thus the chemical composition of the micas closely reflects their mode of origin.

*The biotite group.*—Fig. 5 represents very completely the chemical data for this section. Out of 119 analyses of biotite and phlogopite, only the five above mentioned lie outside the area of the figure and six others (p. 33) are omitted because of exceptional alkali-content. All the remainder lie within or very close to the area bounded by the broken lines. This area is therefore taken to represent approximately the normal limits of composition for the biotite group. Recent analyses are scattered fairly uniformly over the whole area, but there is need to supplement the existing data toward the top right and the bottom left corners. The latter contains three very interesting micas (nos. 201–203) from minette, kersantite, and syenite-porphyry, rocks which might be expected to yield biotites of exceptional composition. A rather sparse interval between biotite and phlogopite has now been bridged by recent analyses, so that the whole group seems to be a continuous series as regards composition. Micas usually called phlogopite comprise not only minerals of the accepted formula, but also a number represented by points toward the right of the area, with higher content of $R_2O_3$. 'Anomite' occurs in the centre of the area as well as on the phlogopite side, but a distinction based on the passage of 2V through zero does not seem to warrant making this a separate species. Lepidomelane, a term sometimes applied to dark ferrous micas, but usually to micas rich in ferric oxide, must certainly include a number of oxidized materials. The composition is well exhibited in the tables given by Doelter. On account of the frequency of alteration, the lepidomelanes given by Dana have not been plotted, but there can be no doubt that a few oxidized micas will have been included in fig. 5. Kunitz suggests that in most analyses some of the

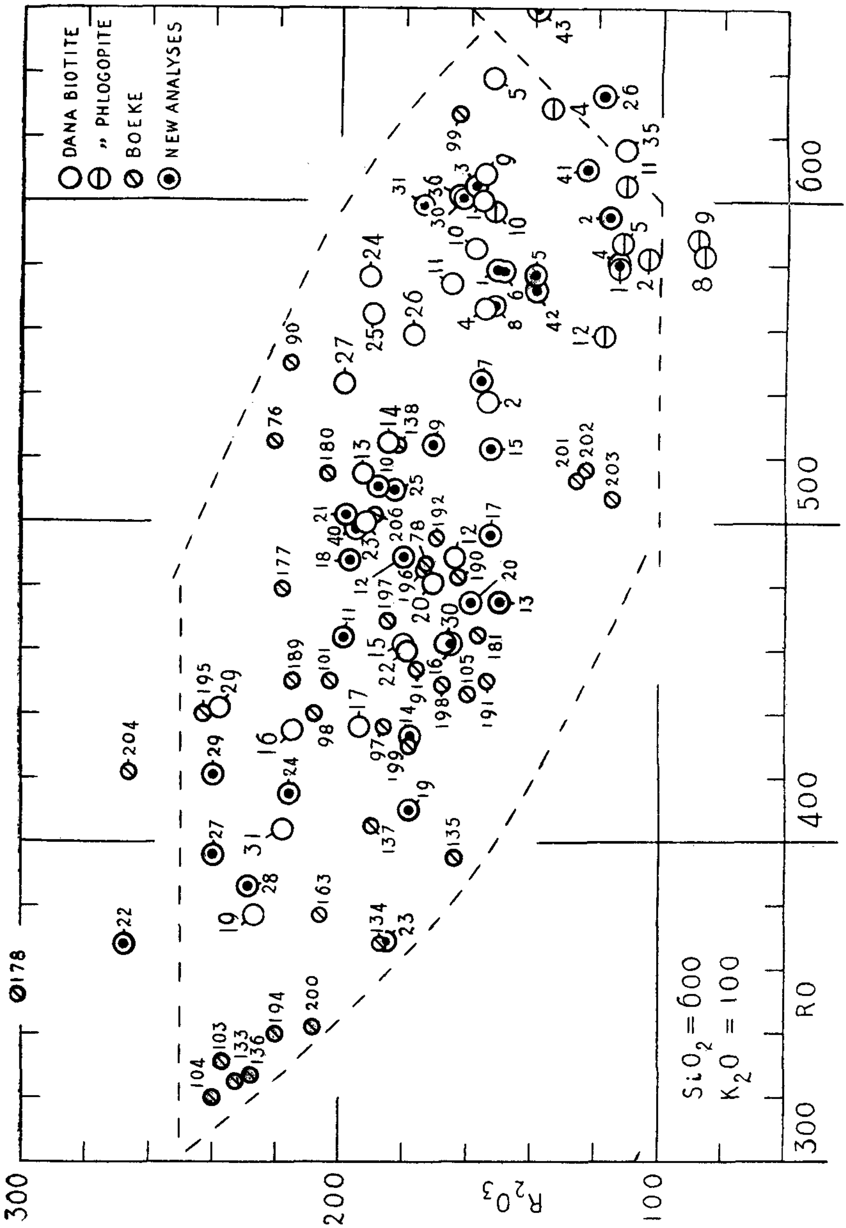
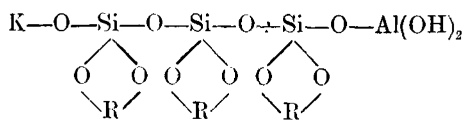



FIG. 5. The basic micas. Molecular proportions of RO and $R_2O_3$ ($SiO_2$ = 600). Type $K_2O . mRO . nR_2O_3 . 6SiO_2 . 2H_2O$.

water has been reduced by FeO during ignition, so that the values for $H_2O$ tend to be too low. This would not affect the determination of ferrous iron, but Kunitz further suggests that a similar reaction has taken placein the mica after crystallization, and that all the iron was originally in the ferrous state. If the small amounts of ferric iron shown in most biotites were transferred to the RO group, the left-hand boundary of the biotite area would be somewhat narrowed, but the general character of the area would remain the same. There seems no reason, however, to believe that the natural melts are so deficient in oxygen as this assumption would imply, and it is more probable that the average fresh biotite is substantially in the condition in which it crystallized. The state of oxidation of iron and titanium will be discussed later in relation to the molecular volumes.

*Chemical formulae.*—In Part I the acid micas were referred to hexasilicic acid on account of the symmetry and convenience of the structural formulae. Similarly, the basic micas could be regarded as mixtures of a series of compounds of the type $K_2O \cdot mRO \cdot nR_2O_3 \cdot 6SiO_2 \cdot 2H_2O$, as indicated along the co-ordinate axes of fig. 4. Upon consideration of the most basic phlogopites, however, there appear reasons for preferring the half-formulae with $KSi_3$ as the common nucleus, similar to that given below. Possible trisilicic compounds are represented in fig. 4 by circles. According to the trisilicate scheme, the basic micas are essentially a series of mixtures extending from phlogopite, $\frac{1}{2}(K_2O \cdot 6RO \cdot R_2O_3 \cdot 6SiO_2 \cdot 2H_2O)$ towards a biotite $\frac{1}{2}(K_2O \cdot 4RO \cdot 3R_2O_3 \cdot 6SiO_2 \cdot 2H_2O)$. The series is extended laterally by the presence of other analogous compounds and is terminated at the acid end by the transition to muscovite. As the RO increases the series as a whole exhibits an increasing degree of substitution of $R_2O_3$ accompanied by an increasing addition of RO, so that the points extend down a rather oblique line on the diagram.

Biotites are easily represented graphically by a hexasilicate formula like that already given for protolithionite (Part I, p. 315), putting alumina or RO in place of lithia. Phlogopite, however, could only be represented by substituting RO for the water attached to the alumina, and this water is certainly not displaced. With trisilicic formulae, on the other hand, the valency available for the bases is greater; phlogopite can then be written



and from this the most basic micas on the right of fig. 5 are derived by putting $2(AlO_2R)$ or a similar group in place of R.

*Basic Micas. Analyses recalculated to molecular proportions when* $(Si,Ti)O_2 = 600$.

*Table III. Recent analyses.*

| No. | | | $R_2O_3$. | RO. | $(K,Na)_2O$. | $H_2O$. | $F_2$. | $H_2O + F_2$. | V (obs.)[1] | V (calc.) | Diff. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Kunitz,[2] 1 | ... | 151 | 578 | 105 | 325 | — | 325 | 323 | 312 | 11 |
| 2 | ,, 2 | ... | 114 | 595 | 83 | 55 | 119 | 174 | 299 | 300 | −1 |
| 3 | ,, 3 | ... | 158 | 605 | 100 | 120 | 65 | 185 | 313 | 319 | −6 |
| 4 | ,, 4 | ... | 113 | 580 | 89 | 42 | 92 | 134 | — | — | — |
| 5 | ,, 5 | ... | 139 | 577 | 103 | 137 | 52 | 189 | 310 | 307 | 3 |
| 6 | ,, 6 | ... | 149 | 578 | 114 | 162 | 42 | 204 | 316 | 311 | 5 |
| 7 | ,, 7 | ... | 156 | 544 | 108 | 175 | — | — | — | — | — |
| 8 | ,, 8 | ... | 152 | 567 | 100 | 152 | 44 | 196 | 309 | 311 | −2 |
| 9 | ,, 9 | ... | 171 | 524 | 109 | 167 | — | — | 309 | 312 | −3 |
| 10 | ,, 10 | ... | 188 | 511 | 110 | 171 | 4 | 175 | 319 | 317 | 2 |
| 11 | ,, 11 | ... | 199 | 464 | 99 | 217 | — | — | 315 | 314 | 1 |
| 12 | ,, 12 | ... | 180 | 489 | 101 | 239 | — | — | 314 | 310 | 4 |
| 13 | Grout,[3] 1 | ... | 150 | 475 | 94 | 62 | — | — | 300 | 296 | 4 |
| 14 | ,, 2 | ... | 178 | 433 | 63 | 160 | — | — | 298 | 301 | −3 |
| 15 | ,, 3 | ... | 153 | 523 | 89 | 59 | — | — | 300 | 304 | −4 |
| 16 | ,, 4 | ... | 226 | 462 | 73 | 67 | — | — | 301 | 300 | 1 |
| 17 | Seidel,[4] 1 | ... | 153 | 496 | 133 | 228 | — | — | 334 | 300 | 34 |
| 18 | ,, 2 | ... | 197 | 488 | 90 | 199 | — | — | 320 | 317 | 3 |
| 19 | ,, 3 | ... | 178 | 410 | 117 | 161 | — | — | 311 | 298 | 13 |
| 20 | ,, 4 | ... | 159 | 475 | 128 | 187 | — | — | 333 | 300 | 33 |
| 21 | ,, 5 | ... | 198 | 502 | 98 | 237 | — | — | 324 | 320 | 4 |
| 22 | ,, 6 | ... | 268 | 368 | 132 | 253 | — | — | 359 | 327 | 32 |
| 23 | Pilipenko[5] | ... | 185 | 369 | 100 | 190 | — | — | 305 | 294 | 11 |
| 24 | Stanley[6] | ... | 216 | 415 | 95 | 126 | 19 | 145 | 303 | 313 | −10 |

[1] These values, for the molecular volumes, will be dealt with in a later part of the paper. Tables I–II were given in Part I.

[2] W. Kunitz, Neues Jahrb. Min., 1924, Beilage-Band 50, p. 386. [Min. Abstr., vol. 2, p. 424.]

[3] F. F. Grout, Amer. Min., 1924, vol. 9, p. 161. [Min. Abstr., vol. 3, p. 53.] Potash seems to be replaced by lime in nos. 14, 15, and 16.

[4] P. Seidel, Diss. Univ. Zürich, 1906. Refs. 4–8 are cited in Zeits. Krist., 1923, vol. 57, pp. 416–421.

[5] P. P. Pilipenko, Izvestiya Univ. Tomsk, 1915, no. 63, pp. 553–554. [Min. Abstr., vol. 2, p. 109.]

[6] E. R. Stanley, Trans. Roy. Soc. South Australia, 1916, vol. 40, pp. 268–271. [Min. Abstr., vol. 1, p. 70.]

*Table III (continued)*:

| No. | | $R_2O_3$. | RO. | $(K,Na)_2O$. | $H_2O$. | $F_2$. | $H_2O+F_2$. | V (obs.). | V (calc.). | Diff. |
|---|---|---|---|---|---|---|---|---|---|---|
| 25 | Thomassen [7] | 183 | 510 | 102 | 53 | 3 | 56 | — | — | — |
| 26 | Eckermann [8] | 118 | 633 | 110 | 100 | 73 | 173 | 311 | 307 | 4 |
| 27 | Harwood [9] ... | 240 | 394 | 97 | 251 | 18 | 269 | — | — | — |
| 28 | ,, [10] ... | 229 | 386 | 93 | 212 | 19 | 231 | — | — | — |
| 29 | ,, [11] ... | 240 | 421 | 106 | 195 | 25 | 220 | — | — | — |
| 30 | Vincent [12] ... | 162 | 601 | 104 | 52 | 68 | 120 | 326 | 320 | 6 |
| 31 | Ginzburg [13] ... | 174 | 599 | 96 | (ign.) 6 | — | — | — | — | — |
| 32 | Jakob,[14] 1 ... | 151 | 658 | 101 | 291 | — | — | 332 | 324 | 8 |
| 33 | ,, 2 ... | 134 | 650 | 96 | 186 | — | — | 327 | 316 | 11 |
| 34 | ,, 3 ... | 124 | 594 | 101 | 254 | — | — | 320 | 304 | 16 |
| 35 | ,, 4 ... | 182 | 587 | 104 | 252 | — | — | 328 | 326 | 2 |
| 36 | ,, 5 ... | 121 | 600 | 101 | 189 | — | — | 330 | 302 | 28 |
| | | (180) | (481) | | | | | | (309) | (21) |
| 37 | ,, 6 ... | 206 | 545 | 113 | 213 | — | — | 327 | 329 | −2 |
| 38 | ,, 7 ... | 104 | 670 | 98 | 262 | — | — | 314 | 305 | 9 |
| | | (119) | (639) | | | | | | (309) | (5) |
| 39 | ,, 8 ... | 97 | 669 | 92 | 169 | — | — | 310 | 302 | 8 |
| | | (126) | (611) | | | | | | (307) | (3) |
| 40 | Eckermann [15] | 195 | 498 | 100 | 183 | 7 | 190 | 316 | 318 | −2 |
| 42 | ,, ... | 123 | 610 | 108 | 144 | 67 | 211 | 313 | 305 | 8 |
| 43 | ,, ... | 139 | 572 | 78 | 99 | 56 | 155 | 295 | 307 | −12 |
| 44 | ,, ... | 139 | 660 | 82 | 117 | 78 | 195 | 332 | 318 | 14 |

[7] L. Thomassen, Vidensk. Schrift. I. Mat.-naturw. Kl., Kristiania, 1920–1921, no. 9, p. 295.

[8] N. Sahlbom, Geol. För. Förh. Stockholm, 1922, vol. 44, pp. 383–385. [Min. Abstr., vol. 1, p. 396.] The figures given are for the analysis completed by Eckermann (see ref. 15 below).

[9] H. F. Harwood, Min. Mag., 1923, vol. 20, p. 23.

[10] Biotite from Dartmoor granite; unpublished analysis included by courtesy of Messrs. A. Brammall and H. F. Harwood.

[11] H. F. Harwood, Min. Mag., 1924, vol. 20, p. 203.

[12] Phlogopite from Twinnge, Burma; unpublished analysis included by courtesy of Mr. H. C. G. Vincent (analyst).

[13] I. I. Ginzburg, Min. Abstr., 1925, vol. 2, p. 466.

[14] J. Jakob, Zeits. Krist., 1925, vol. 61, p. 157. [Min. Abstr., vol. 2, p. 423.] Lithia and fluorine do not seem to have been estimated. Except in nos. 5, 7, 8, iron and manganese are assigned to sesquioxide, since this brings the total nearer to 100. The use of the total in this way does not appear reliable and the values given in brackets have been calculated to show the result of regarding the (Fe,Mn) as sesquioxide throughout. Most of these analyses lie on the extreme right in fig. 5, but they have not been plotted on account of this uncertainty.

[15] H. Eckermann, Tschermaks Min. Petr. Mitt., 1925, vol. 38, p. 281. [Min. Abstr., vol. 3, p. 81.] Small amounts of $Li_2O$ are included with $R_2O_3$. Manganese

*Table IV. Basic micas not plotted in fig. 5.*

| | $R_2O_3$. | RO. | $(K,Na)_2O$. | $H_2O$. | $F_2$. | $H_2O + F_2$. |
|---|---|---|---|---|---|---|
| 1. *Micas with high alkalis.* | | | | | | |
| Boeke, 193 ... | 195 | 449 | 136 | 230 | — | — |
| ,, 205 ... | 145 | 424 | 135 | 182 | — | — |
| ,, 207 ... | 226 | 442 | 130 | 266 | — | — |
| 2. *Micas with low alkalis.* | | | | | | |
| Boeke, 146 ... | 218 | 508 | 51 | 153 | — | — |
| ,, 179 ... | 235 | 515 | 61 | 272 | — | — |
| ,, 176 ... | 242 | 370 | 64 | 148 | — | — |
| 3. *Micas intermediate between biotite and muscovite.* | | | | | | |
| Dana, 18 ... | 278 | 203 | 93 | 86 | 111 | 187 |
| ,, 21 ... | 322 | 296 | 111 | 268 | 7 | 275 |
| ,, 32 ... | 303 | 255 | 97 | 265 | — | — |
| Boeke, 80 ... | 213 | 228 | 125 | 121 | — | — |
| ,, 100 ... | 145 | 280 | 92 | 136 | — | — |

is not stated, and it seems possible that small amounts of that element may have been included with MgO. No. 43 contains also CaO (30 units) and BaO (7 units); the crystals were not transparent in bulk. See also no. 26, ref. 8, above.