

General Expressions of the Chemical Compositions of the Fine Micas and Chlorites.

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1. General expression

The chemical compositions of so-called fine micas, such as sericite⁽¹⁾, hydro-mica⁽²⁾, hydro-muscovite⁽³⁾, secondary mica⁽⁴⁾, glimmerton⁽⁵⁾, potassium bearing clay minerals⁽⁶⁾, illite⁽⁷⁾, glauconite and celadonite⁽⁸⁾, have been discussed by several authors, but these discussions had no basis on the standpoint of crystal structures. On the other hand, the crystal structure of mica, such as muscovite, was determined and the general formula of mica has been shown to be as follows⁽⁹⁾:



(Where X : K, Na, Ca ; Y : Al, Fe^{III}, Fe^{II}, Mg, Mn, Cr, Ti, Li, V, etc. ;
Z : Si, Al)

This formula has not been adapted to the chemical compositions of the fine micas above enumerated. The writer re-examined the chemical compositions of the fine micas by the general structural formula of mica, that is, the writer summarized the accurate and already reported chemical compositions of fine micas (Table 1. 2), and from these, the writer calculated X, Y, and Z of the formula above described, and values of X, Y, and Z thus calculated were plotted on the triangular diagram as shown in Fig. 1, (a), and (b).

(1) E. V. Shannon, *U. S. Natl. Museum Bull.*, **131** (1926), 367; J. Jakob, C. Friedlaender and E. Brandenberger, *Schweiz. Mineralog. u. Petrog. Mitt.*, **13** (1933), 74; P. Niggli, *ibid.* **13** (1933), 84; J. Jakob, *Z. Krist.*, **69** (1929), 511; B. Kotô, *J. Coll. Sci. Imp. Univ. Tokyo*, **2** (1888), 89.

(2) W. S. Bradley, *Econ. Geol.*, **15** (1920), 236; R. E. Somer, *J. Wash. Acad. Sci.*, **9** (1916), 113; A. Brammhall, *Mineralog. Mag.*, **24** (1937), 507.

(3) G. Nagelschmidt, *Z. Krist.*, **97** (1937), 514.

(4) G. M. Schwartz and R. J. Leonard, *Am. J. Sci.*, **11** (1926), 262.

(5) K. Fndell, U. Hofmann, and E. Maegdefrau, *Zement*, **24** (1935), 625.

(6) C. S. Ross and P. E. Kerr, *J. Sed. Petr.*, **1** (1913), 59.

(7) R. E. Grim, R. H. Bray and W. F. Bradley, *Am. Mineral.*, **22** (1937), 813.

(8) Recently it has been shown that the types of glauconite and celadonite are similar in their X-ray powder patterns to those of micas. J. W. Gruner, *Am. Mineral.*, **20** (1935), 699; E. Maegdefrau and U. Hofmann, *Z. Krist.*, **97** (1937), 514.

(9) Ch. Mauguin, *Comp. rend. Acad. Sci. Paris*, **185** (1927), 238; **186** (1928), 879, 1131; L. Pauling, *Proc. Nat. Acad. Sci. U. S. A.*, **16** (1930), 123; W. W. Jackson and J. West, *Z. Krist.*, **76** (1931), 211; W. L. Bragg, "Atomic Structure of Minerals," 1937, 213.

Table I. (Sericite).

	(1)	(2)***	(3)***	(4)	(5)	(6)
SiO ₂	46.58	50.39	50.05	45.64	47.14	53.01
TiO ₂	0.42	0.14	1.81
Al ₂ O ₃	37.46	29.74	30.11	33.59	37.13	34.70
Fe ₂ O ₃	0.80	1.61	1.47	1.96	0.64	tr.
Cr ₂ O ₃
FeO	0.38	0.43	0.38
MnO	0.01	0.01	0.10
CaO	tr.	0.00	0.00	0.00	0.71	0.27
MgO	1.16	2.40	2.49	2.33	0.17	0.50
Na ₂ O	0.64	2.62	1.97	1.59	0.65	1.01
K ₂ O	6.38	9.97	9.80	8.81	9.98	6.05
H ₂ O(+)	6.06	2.55	3.58	3.89⊗	4.28*	4.67**
H ₂ O(-)	0.30	0.00⊕		
F
Total	99.38*	100.09	100.05	100.10	100.70	100.21

Note: * Ig. loss. ** H₂O. *** analyses on material dried at 110°C.
 ⊗ > 110°C. ⊕ < 110°C.

(1) The Carrol-Driscoll Mine, Idaho. E. V. Shannon, *U. S. Natl. Museum, Bull.*, **131** (1926), 367.

(2) Werkkanals des Rheinkraftwerks, Albdruk-Dogern. Occurs in gneiss. Coarse grains accumulated by water dressing. J. Jakob, C. Friedlaender and E. Brandenberger: *Schweiz. Mineralog. u. Petrog. Mitt.*, **13** (1933), 74; P. Niggli: *Schweiz. Mineralog. u. Petrog. Mitt.*, **13** (1933), 84.

(3) As (2), fine grains.

(4) Campra bei Olivone, Kanton Tessin. Fine scales in sericite-biotite schist, forming nests partly. J. Jakob: *Z. Krist.*, **69** (1929), 511.

(5) The Hitachi Mine, Ibaragi Prefecture. K. Seto: *J. Japan. Assoc. Mineral. Petrol. Econ. Geol.*, **1**. (1929), 124.

(6) Ōtakisan in Tokushima Prefecture. B. Kotô: *J. Coll. Sci. Imp. Univ. Tôkyô*, **2** (1888), 89.

From these figures the following general facts are recognized:

(1) The plotting points of the colourless fine micas such as sericite, hydro-mica, secondary mica, illite, etc., and the plotting points of the chemical compositions of glauconite and celadonite fall in the same area. (Fig. 1, (a), (b)).

(2) The fine micas have, as a rule, less X(K, Na, Ca) and more Y(Al, Fe''', Fe'', Mg, etc.) than muscovite (M), and such fluctuation is largest in illite. (Fig. 1, (a)).

(3) From Fig. 1 (b) the differences in the chemical compositions of glauconite and celadonite are not clearly shown.

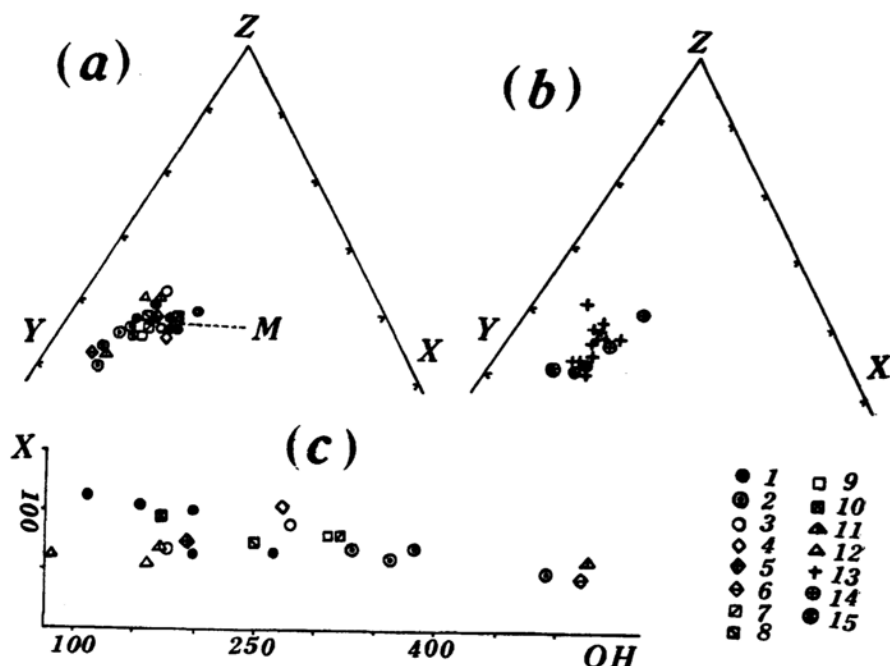


Fig. 1. 1, Sericite; 2, Illite; 3, Phengite; 4, Alurgite; 5, White mariposite; 6, Hydro-mica; 7, Hydro-muscovite; 8, Secondary muscovite; 9, Damourite; 10, Gilbertite; 11, Micas altered from spodumene; 12, Micas reported by E. Maegdefrau and U. Hofmann; 13, Glauconite; 14, Celadonite; 15, "Grünerde" (by K. Hummel); *M*: Mean value of the chemical compositions of muscovite (by W. Kunitz, *Neues Jahrb. Mineral. Geol.*, Beilage-Band, A, 50 (1924), 365.)

2. Relation between (OH) and (K, Na, Ca) of the fine micas.

Next the writer compared the content of (OH)⁽¹⁰⁾ and that of X(K, Na, Ca) as shown in Fig. (1), (c). It is shown, from Fig. 1, (c), that the content of (OH) is roughly inversely proportional to the content of X(K, Na, Ca). The writer also compared the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the content of X(K, Na, Ca), but no fixed ratio has been found between these values.

In the chemical compositions of glauconite and celadonite, we could not recognize the fixed ratio between the values of (OH) and X(K, Na, Ca), or (OH) and the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$.

3. $\text{R}_2\text{O}_3/\text{RO}$ in glauconite and celadonite.

In Fig. 1, (a) and (b), the differences between the chemical compositions

(10) It is a very difficult problem to solve the state of the water in the crystal structures of such fine micas. In the chemical analyses reported in literatures, the water contents are described in various forms, such as $\text{H}_2\text{O}(+)$ and $\text{H}_2\text{O}(-)$ or only as H_2O or as ignition loss. Generally the content of $\text{H}_2\text{O}(-)$ is small, and the writer used the value of $\text{H}_2\text{O}(+)$ when the content of water is described separately as $\text{H}_2\text{O}(+)$ and $\text{H}_2\text{O}(-)$, and in other cases, he used the total content of water or ignition loss.

Table 2.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO ₂	52.58	58.90	53.22	56.79	47.29	53.47	40.79	46.54	46.54
TiO ₂	25.29	1.28	0.17
Al ₂ O ₃	23.56	25.28	21.19		31.31	32.36	29.98	36.37	30.39
Fe ₂ O ₃	2.30	1.22	1.59	1.19	0.79	8.07	0.72	4.42
FeO	5.76	0.37	0.42	2.48	0.36	2.98
Mn ₂ O ₃	0.87
MnO	0.18	0.72
CaO	0.65	0.65	0.07	0.69	0.17	0.45	0.22	0.35
MgO	2.43	1.49	6.02	3.29	2.38	2.71	0.50	0.94
Na ₂ O	1.37	0.34	0.17	0.88	0.44	0.38	0.46	1.44
K ₂ O	9.52	5.73	11.20	8.92	4.07	7.68	3.47	8.06	5.57
H ₂ O(+)	5.94*	4.14*	5.75*	4.72*	9.92**	4.07*	9.34	6.83*	5.31**
H ₂ O(-)									
					1.88		1.20		
F	0.02	0.58
Total	100.44	99.86	99.99	100.84	(100.26)	(100.16)	(100.15)	100.25	98.52

Note: *H₂O; **Ig. loss; †Ig. loss on material dried at 110°C; ††Ig. loss on material

(1) Phengite (Wildschapbachtal). "Doelter's Handbuch der Mineralchemie", II, Part 2 (1917), 428.

(2) Phengite (Witticher Tal). "Doelter's Handbuch der Mineralchemie", II, Part 2 (1917), 428.

(3) Alurgite. (A manganese mine at St. Marcel, Piemont, Italy). S. L. Penfield, *Z. Krist.*, **25** (1896), 277.

(4) White mariposite (The Josephine Mine, Bear Valley, California). W. L. Hillebrand, *U. S. Geol. Survey Bull.*, **167** (1900), 74. Cr₂O₃: none.

(5) A. micaceous mineral altered from spodumene (The Etta mine, South Dakota), G. M. Schwarz and R. J. Leonard, *Am. J. Sci.*, **11** (1926), 262. Li₂O: 0.28.

(6) A micaceous mineral altered from spodumene (Branchville, Connecticut). G. J. Brush and E. S. Dana, *Z. Krist.*, **5** (1881), 210. Li₂O: 0.04.

(7) Hydro-mica (North Carolina). W. S. Bailey, *Econ. Geol.*, **15** (1920), 236.

(8) Hydro-muscovite. G. Nagelschmidt, *Z. Krist.*, **97** (1937), 514. Li₂O: tr.

(9) Secondary muscovite (Spreckstein). "Doelter's Handbuch der Mineralchemie", II, Part 2 (1917), 426.

Table 2. (Continued).

(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)⊕	(18)⊕
45.72	48.96	50.10	51.22	47.21	52.23	44.01	51.65	50.30
.....	0.50	0.53	0.37	0.64	tr.	tr.
37.17	30.96	25.12	25.91	21.47	25.85	26.81	21.67	32.80
2.18	5.12	4.59	10.73	4.04	11.99	6.20	0.00
.....
.....	2.24	1.52	1.70	1.24	0.00
.....
0.05	0.26	0.35	0.16	0.21	0.60	0.11	0.00	0.55
2.00	1.97	3.93	2.84	3.62	2.69	2.43	4.48	1.95
1.44	1.65	0.05	0.17	0.33	0.07	0.31	0.52
6.69	8.47	6.93	6.09	5.78	6.56	4.78	6.08	6.72
6.79*	3.83*	6.82†	7.49†	10.99††	7.88†	9.19†	6.44	6.98
....	1.04
102.04	99.38	100.44	100.70	100.01	100.55	100.03	98.07	99.82

dried in air; ⊕Chemical; analysis is of 105°C dried material.

(10) Damourite (Fen Norway). "Doelter's Handbuch der Mineralchemie", II, Part 2 (1917), 422.

(11) Gilbertite (Ehrenfriedersdorf). "Dana's System of Mineralogy", 1914, 618.

(12) Illite (Maquoketa (Ordovician) shale, near Gilead, Calhoun County, Illinois). $H_2O(+)$: 7.18; $H_2O(-)$: 1.90. R. E. Grim, R. H. Bray and W. F. Bradley, *Am. Mineral.*, 22 (1937), 813.

(13) Illite (Pennsylvanian underclay, near Fithian, Vermilion County, Illinois). $H_2O(+)$: 7.14; $H_2O(-)$: 1.45. Ref. as (12).

(14) Illite (IV b horizon of Clarence soil, Ford County, Illinois). $H_2O(+)$: 6.17; $H_2O(-)$: 3.80. Ref. as (12).

(15) Illite (Cretaceous shale, near Theles, Alexander County, Illinois). $H_2O(+)$: 7.88; $H_2O(-)$: 1.13. Ref. as (12).

(16) Illite (Pennsylvanian shale, near Petersburg, Menard County, Illinois). $H_2O(+)$: 8.03; $H_2O(-)$: 2.33. Ref. as (12).

(17) Mica in marl. Small amount of quartz is included in the analysed sample. E. Maegdefrau and U. Hofmann, *Z. Krist.*, 98(1938), 31.

(18) Mica in liparite. Sarospatak, North-east of Mt. Hegyalja. Ref. as (17).

Table 3.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO ₂	51.55	51.38	51.63	51.25	50.75	51.27	53.58	48.66	48.5
TiO ₂	tr.	tr.	tr.	tr.	tr.	tr.	0.07
Al ₂ O ₃	4.03	4.25	5.01	4.44	6.65	5.45	8.17	8.46	9.0
Fe ₂ O ₃	22.17	23.82	23.09	22.22	21.64	23.14	18.27	18.80	20.0
FeO	3.54	2.91	2.75	3.62	3.41	2.85	2.87	3.98	3.1
MnO	tr.	tr.	tr.	tr.	tr.	tr.	tr.
MgO	3.86	3.23	3.71	3.53	3.23	3.97	2.95	3.56	3.7
CaO	0.69	0.55	0.35	0.62	0.57	0.49	0.89	0.62	0.4
Na ₂ O	0.55	0.78	0.68	0.94	0.75	0.28	0.94	none	1.5
K ₂ O	7.03	6.82	6.75	6.95	6.92	6.80	5.64	8.31	6.2
P ₂ O ₅	0.03	tr.	0.02	tr.	tr.	tr.	tr.
CO ₂
H ₂ O(+)	6.62*	6.62*	6.25*	6.23*	6.02*	6.00*	6.53*	4.62	7.3**
H ₂ O(-)								1.94	
Total	100.07	100.36	100.24	99.80	99.94	100.25	99.91	98.95	99.67

Note: *H₂O; **Ig. loss; *** chemical analysis of 105°C dried materials;

(1)-(7) Glauconite from Japan (after T. Yagi) "Glauconite." (in Japanese).

(8) Glauconite. J. W. Gruner, *Am. Mineral.*, **20** (1935), 699; with CO₂, total 99.08.

(9) Glauconite. H. Schneider, *J. Geol.*, **35** (1927), 296.

Table 3. (Continued).

(10)	(11)	(12)***	(13)	(14)	(15)***	(16)	(17)	(18)	(19)
48.12	49.42	49.10	53.61	49.11	55.30	54.30	54.84	54.22	46.65
.....	nb.	nb.	tr.	0.73
9.16	10.23	19.30	9.56	8.03	10.90	5.08	3.52	3.70	17.92
19.10	16.01	7.52	21.46	20.05	6.95	14.77	12.64	12.50	10.09
3.47	3.00	2.87	1.58	3.05	3.54	4.82	4.90	4.75	4.25
.....	tr.	0.09	0.24	0.19	0.07
2.36	3.78	2.71	2.87	3.18	6.56	6.05	6.65	6.98	1.63
0.76	0.31	0.98	1.39	0.87	0.47	0.80	0.89	0.84	1.26
0.22	0.26	0.00	0.42	0.66	0.00	3.82	0.39	0.44	0.69
7.08	7.91	7.50	3.49	6.97	9.38	4.85	7.00	6.90	3.91
.....	0.04
.....	1.66
5.28⊗	} 8.08* }	} 6.07 } }	} 5.96* }	} 8.05* }	} 5.21 } }	} 5.64* }	} 9.62* }	} 99.9* }	5.07
4.78⊕									5.86
100.33	99.00	96.05	100.34	99.97	98.31	100.22	100.69	100.51	99.83

⊗ > 105°C; ⊕ < 105°C.

(10) Glauconite. A. F. Hallimond, *Mineralog. Mag.*, **19** (1922), 330.

(11) As (10); quartz: 0.80%.

(12) Glauconite. E. Maegdefrau and U. Hofmann, *Z. Krist.*, **98** (1938), 31.

(13) Glauconite. Mean value of the chemical compositions of glauconite collected by "Challenger". W. H. Twenhofel, "Principles of Sedimentation", 1939, 401.

(14) Mean value of 12 analyses of glauconite reported by A. F. Hallimond, *Mineralog. Mag.*, **19** (1922), 330.

(15) Celadonite W. E. Maegdefrau and U. Hofmann, *Z. Krist.*, **98** (1938), 31.

(16) Celadonite. A. Lacroix, *Bull. soc. franç. minéral.*, **39** (1916), 93.

(17) Mean value of celadonite from Scotland. W. H. Twenhofel, "Principles of Sedimentation", 1939, 401.

(18) Mean value of the chemical analyses of celadonite reported by F. Heddle and L. Fermor, *Rec. Geol. Survey, India*, **58** (1926), 141, 330.

(19) "Grünerde". K. Hummel, *Chem. Erde*, **6** (1931), 468.

of glauconite and celadonite are not clearly shown. The writer showed the difference as follows. From the accurate chemical compositions (Table 3) of glauconite and celadonite⁽¹¹⁾, the writer calculated the values of R_2O_3 ($Al_2O_3 + Fe_2O_3$) and $RO(FeO + MgO)$ as $SiO_2 : 2.00$ and plotted them on Fig. 2. (c). From this figure, it is clearly shown that R_2O_3/RO is less than 1 in celadonite, while, the ratio is larger than 1 in glauconite.

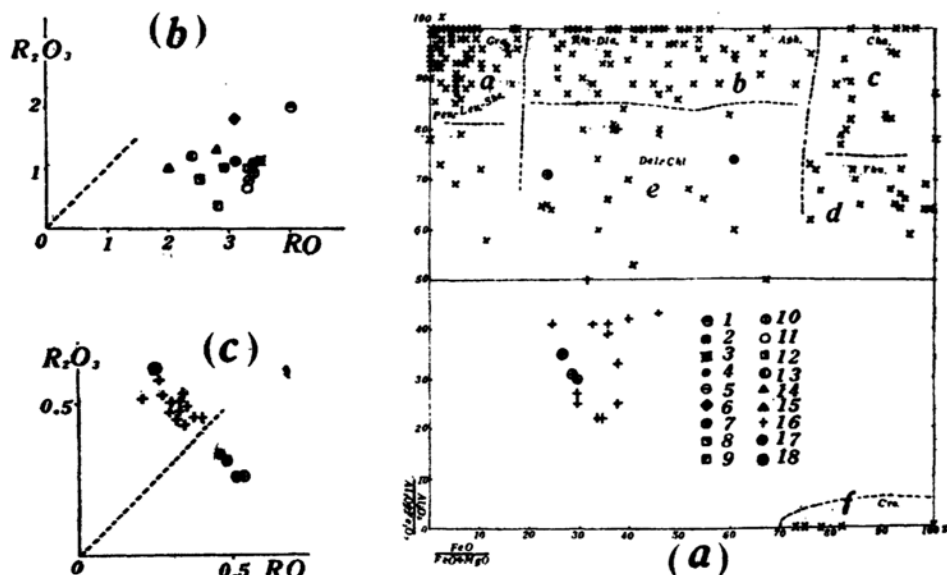


Fig. 2. Diagrammatic expression of the chemical compositions of chlorites, glauconite, celadonite and "Grünerde". \times : chlorites.

- (a) Pen.-Leu.-She.-Gro. area: Penninite, Leuchtenbergite, Sheridanite, Grochaultite, etc.
 (b) Rip.-Dia.-Aph. area: Ripidolite, Diabantite, Aphrosiderite, etc.
 (c) Cha. area: Chamosite.
 (d) Thu. area: Thuringite.
 (e) Del. area: Delessite, Chloropite, (Cinochlore, Prochlorite), etc.
 (f) Cro. area: Cronstedite.

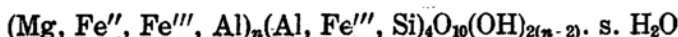
1, Amesite; 2, Aphrosiderite; 3, Bavalite; 4, Chamosite; 5, Cinochlore; 6, Cronstedite; 7, Daphnite; 8, Delessite; 9, Diabantite; 10, Leuchtenbergite; 11, Penninite; 12, Ripidolite; 13, Sheridanite; 14, Strigovite; 15, Thuringite; 16, Glauconite; 17, Celadonite; 18, "Grünerde" (by K. Hummel).

4. General expression of the chemical composition of chlorites.

About the chemical compositions of chlorites, the excellent generali-

(11) T. Yagi, *J. Japan. Assoc. Mineral. Petrol. Econ. Geol.*, 3 (1930), 119 (a Japanese); J. W. Gruner, *Am. Mineral.*, 20 (1935), 699; W. H. Twenhofel, "Principles of Sedimentation," 1939, 401; H. Schneider, *J. Geol.*, 35 (1927), 296; A. F. Hallimond, *Mineralog. Mag.*, 19 (1922), 330; 13 (1298), 68; K. Hummel, *Chem. Erde*, 6 (1931), 468; E. Maedgenfrau and U. Hofmann, *Z. Krist.*, 98 (1938), 31; L. L. Fermor, *Rec. Geol. Survey, India*, 58 (1926), 141, 330; A. Lacroix, *Bull. soc. franç. minéral.*, 39 (1916), 93.

zation was reported by J. Orcel⁽¹²⁾. The crystal-structural formula of chlorite has been discussed recently by H. Berman⁽¹³⁾ to be as follows.



Namely the half of (Al, Fe''') replaces a part of Si and the other half of (Al, Fe''') replaces a part of (Mg, Fe'') and it was shown that the various ratios of RO/R₂O₃, Al₂O₃/R₂O₃, and FeO/RO produce many species of chlorite well known. The writer tried a general expression of the chemical compositions of chlorites by above three ratios. First the chemical compositions of chlorite are expressed by the ratio of R₂O₃/RO (where SiO : 200) in Fig. 2, (b). It is clearly shown from Fig. 2, (b) that the ratio of R₂O₃/RO is less than 1 in chlorites. Next the chemical compositions of the main chlorites are plotted in the diagram by the ratio of Al₂O₃/R₂O₃ and the ratio of FeO/RO as shown in the Fig. 2, (a). It is clearly shown, from Fig. 2, (a) that all the chemical compositions of chlorites are plotted in the area of Al₂O₃/R₂O₃ ≥ 50 % (except cronstedite), and the chlorite area may be divided into as follows.

(a) Mg-Al chlorite area...penninite, leuchtenbergite, sheridanite, grochauite, etc.

(b) Al-Fe''-Mg chlorite area...ripidolite, diabantite, aphrosiderite, etc.

(c) Fe''-Al chlorite area...chamosite.

(d) Fe'''-Al-Fe'' chlorite area...thuringite.

(e) Fe'''-Fe''-Al-Mg chlorite area...delessite, chlororite, clinochlore, prochlorite, etc.

(f) Fe'''-Fe'' chlorite area...cronstedite.

For the sake of comparison, the chemical compositions of glauconite and celadonite are plotted in the Fig. 2, (a). As well shown from Fig. 2, (a), the plotted points of the chemical compositions of glauconite and celadonite ordinarily fall in the area of Al₂O₃/Fe₂O₃ ≤ 50 %.

Conclusion.

The writer tried a generalization of the chemical compositions of fine micas (including glauconite and celadonite) and chlorites and also tried a general expression of these chemical analyses to show some chemical characteristics of these minerals.

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Tokyo University.*

(12) J. Orcel, *Bull. soc. franç. minéral.*, **50** (1927), 75.

(13) H. Berman, *Am. Mineral.*, **22** (1937), 378.