

## An interpretation of the hydroxyl contents of biotites and muscovites

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**SUMMARY.** The net cationic charge of the octahedral and tetrahedral layers was calculated from the analyses of 100 biotites and 93 muscovites and compared to the observed hydroxyl contents (OH+F+Cl). The correlation coefficient between these parameters of  $-0.96$  for biotites and  $-0.82$  for muscovites demonstrates that the hydroxyl content in these micas varies in response to cationic substitutions. Thus substitutions in micas involve cation-hydroxyl replacement couples in addition to other modes previously recognized. Tetrasilicic phlogopite,  $K_2Mg_6Si_8O_{22}(OH)_2$ , which is related to phlogopite by the substitution  $Al^{3+}+H^+ = Si^{4+}$  was synthesized but is not a stable phase under the conditions investigated. This mica crystallizes as a 1M polymorph with  $a = 5.289(2) \text{ \AA}$ ,  $b = 9.151(3) \text{ \AA}$ ,  $c = 10.247(3) \text{ \AA}$ ,  $\beta = 100^\circ 4(2)$ .

Exchange reactions, such as  $Al^{3+}+H^+ \rightleftharpoons Si^{4+}$ , between phlogopite and pyroxenes at depth may provide a mechanism for release of  $H^+$  within the mantle.

THE chemical complexity of micas has been long recognized. Detailed studies of the compositional variation of micas have shown that the complexity results from various ionic substitutions in the octahedral, tetrahedral, and inter-layer cation sites. The mica structure can accept many cations through isomorphous substitution or coupled cationic replacements in both the octahedral and tetrahedral sheets.

Involvement of the anionic component of micas with cationic changes has been proposed by several authors. Rinne (1924), Larsen *et al.* (1937), and Eugster and Wones (1962) showed that hydroxyl-deficient biotites are produced by oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  with the concomitant loss of hydrogen to maintain charge neutrality. The hydroxyl content of micas has been studied in considerable detail by Foster (1964) and Rimsaite (1964, 1970). From the analyses of 65 phlogopites and biotites, Foster found that the (OH, F) content ranges from 5.52 to 0.96 (from structural formulae calculated on the basis of 24 (O,OH,F)). Both Rimsaite and Foster noted that a large percentage of micas are hydroxyl deficient ( $OH+F < 4$ ) but concluded that the amount of  $Fe^{3+}$  within the structure was quantitatively insufficient to account for the observed  $OH^-/O^{=}$  ratios. Rimsaite (1970) proposes that hydroxyl-deficient micas are produced through oxidation of ferrous iron or loss of water or both through subsequent heating. Foster (1964) suggests that the  $OH^-/O^{=}$  ratio may be controlled by the oxygen fugacity of the crystallization environment.

Attempts to synthesize the amphibole potassic magnesio-richterite resulted in the formation of a mica of unusual composition. The mica has the formula  $K_2Mg_6Si_8O_{22}(OH)_2$  and may be termed tetrasilicic phlogopite. The hydroxyl-deficient nature of

this phase led to the further study of the relationships between cationic substitutions and the (OH,F) contents of natural micas.

*Conditions of synthesis.* The mica was synthesized using an oxide-carbonate mix, consisting of reagent grade  $\text{KHCO}_3$ ,  $\text{MgO}$ , and  $\text{SiO}_2$ . Usually 40 mg of starting material plus 1 to 2 mg of water were sealed in noble metal capsules. Larger proportions of water produced noticeable leaching of  $\text{K}_2\text{O}$  and  $\text{SiO}_2$  from the solid phases. Standard hydrothermal techniques were employed. All temperatures and pressures are considered accurate to within  $\pm 5^\circ\text{C}$  and  $\pm 20$  bars respectively.

In runs of 72 to 96 hours' duration, 100 per cent yields of the mica were obtained routinely from starting material of the composition  $\text{K}_2\text{O} \cdot 6\text{MgO} \cdot 8\text{SiO}_2$  plus excess water. Thus the stoichiometry of the starting material requires that the mica have the formula  $\text{K}_2\text{Mg}_6\text{Si}_8\text{O}_{22}(\text{OH})_2$ , and be related to phlogopite by the substitution  $\text{Al}^{3+} + \text{H}^+ = \text{Si}^{4+}$ . With the octahedral sites fully occupied by divalent magnesium, the charge imbalance caused by the Al-Si replacement is restored by the conversion of one hydroxyl ion per 12 (O,OH) to oxygen. Synthetic tetrasilic micas with the composition  $\text{K}_2\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_4$  and  $\text{K}_2\text{Fe}_5\text{Si}_8\text{O}_{20}(\text{OH})_4$  have been reported by Seifert and Schreyer (1965) and by Sabatier and Velde (1970) respectively. In these two phases, Al is replaced by the substitution  $0.5\text{R}^{2+} + \text{Al}^{3+} \rightleftharpoons \text{Si}^{4+}$  and the micas retain a normal hydroxyl content.

The results of hydrothermal experiments using the bulk composition  $\text{K}_2\text{O} \cdot 6\text{MgO} \cdot 8\text{SiO}_2 \cdot x\text{H}_2\text{O}$  are shown on fig. 1. In direct synthesis experiments, tetrasilic phlogopite is found as the only solid phase at P-T conditions to right of the dashed curve in fig. 1. At temperatures above this curve, the assemblages: forsterite- $\text{K}_2\text{O} \cdot 5\text{MgO} \cdot 12\text{SiO}_2$ - $\text{K}_2\text{O} \cdot \text{MgO} \cdot 3\text{SiO}_2$ -vapour; clino-enstatite- $\text{K}_2\text{O} \cdot \text{MgO} \cdot 3\text{SiO}_2$ -vapour; and forsterite-melt-vapour are produced in well-defined fields. These assemblages are denoted by various symbols in fig. 1. The synthesis experiments are entirely reproducible and the mica persists indefinitely in the absence of other phases. However, the addition of small amounts of the high-temperature  $\text{K}_2\text{Mg}_5\text{Si}_{12}\text{O}_{30}$ -bearing assemblage to previously synthesized batches of the tetrasilic phlogopite in reversibility attempts resulted in the decomposition of

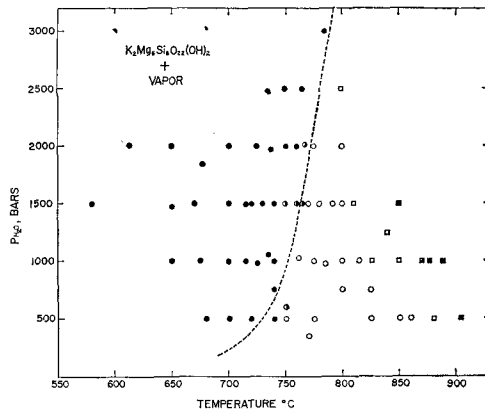


FIG. 1. Hydrothermal run results for the composition  $\text{K}_2\text{O} \cdot 6\text{MgO} \cdot 8\text{SiO}_2 \cdot x\text{H}_2\text{O}$  using an oxide starting material. Solid circles represent formation of tetrasilic phlogopite; open circles represent  $\text{K}_2\text{O} \cdot 5\text{MgO} \cdot 12\text{SiO}_2$ -bearing assemblages; open squares indicate the assemblage enstatite plus  $\text{K}_2\text{O} \cdot \text{MgO} \cdot 3\text{SiO}_2$ ; solid squares represent the forsterite plus glass assemblage. Partially shaded symbols represent the presence of substantial amounts of both high- and low-temperature assemblages. The dashed curve defines the  $\text{P}_{\text{H}_2\text{O}}$ -T field of primary synthesis of the tetrasilic phlogopite.

the mica at temperatures as low as 650 °C and 2000 bars  $P_{H_2O}$ . Below 650 °C the  $K_2Mg_5Si_{12}O_{30}$  compound reacts with vapour to form a mica ( $K_2Mg_5Si_8O_{20}(OH)_4$ ) plus quartz assemblage (Seifert and Schreyer, 1969). Thus it is concluded that the tetrasilicic phlogopite is unstable throughout the range of conditions investigated. However, in view of the low hydroxyl content of this phase, it may be stable under vapour-deficient or vapour-absent conditions.

The phases  $K_2O \cdot 5MgO \cdot 12SiO_2$ , forsterite, and clinoenstatite were identified by standard optical and X-ray powder diffraction techniques. The unit-cell dimensions and refractive indices of the 1:5:12 phase ( $a$  10.22 Å,  $c$  14.15 Å,  $\epsilon$  1.550(2),  $\omega$  1.542(2)) are in good agreement with the data of Roedder (1951) and Khan, Baur, and Forbes (1972).  $K_2O \cdot MgO \cdot 3SiO_2$  was identified optically and its composition verified by microprobe analysis.

TABLE I. Unit-cell parameters of tetrasilicic phlogopite, synthetic Al-phlogopite, and  $K_2Mg_5Si_8O_{20}(OH)_4$

	$K_2Mg_5Si_8O_{22}(OH)_2$	$K_2Mg_5Si_6Al_2O_{20}(OH)_4$ Yoder & Eugster (1954)	$K_2Mg_5Si_8O_{20}(OH)_4$ Seifert & Schreyer (1965)
$a$	5.289(2) Å	5.314	5.256(5)
$b$	9.151(3)	9.204	9.089(8)
$c$	10.247(3)	10.314	10.201(10)
$\beta$	100°4(2)′	99°54′	99°59(10)′
V	488.6(2) Å <sup>3</sup>	496.9(5)	480.9

*Properties of the mica.* The composition of the tetrasilicic phlogopite was confirmed by microprobe analysis of large (40 to 50  $\mu$ ) mica flakes obtained in a run of 58 days' duration. The probe analysis:  $K_2O$  10.37,  $MgO$  30.09,  $SiO_2$  57.52 wt. % is in good agreement with the ideal calculated values of  $K_2O$  11.28,  $MgO$  28.97,  $SiO_2$  57.59 %. A water content of 2.02 wt. % is inferred from the analysis total of 97.98.

At lower temperatures or in runs of short duration, the mica forms extremely fine grained 'clots'. At higher temperatures or pressures or longer run duration, it crystallizes in colourless hexagonal plates ranging in size from 10 to 100  $\mu$ . The mica is biaxial negative with  $2V \approx 10^\circ$ , the refractive indices are  $\alpha$  1.568(2),  $\gamma$  1.586(2). Indices were determined using immersion oils calibrated by means of an Abbe refractor using sodium light.

The unit-cell parameters of the tetrasilicic phlogopite are compared to the cell parameters of synthetic phlogopite (Yoder and Eugster, 1954) and  $K_2Mg_5Si_8O_{20}(OH)_4$  in Table I. The cell dimensions of the mica were determined by a least-squares refinement program described by Evans, Appleman, and Handwerker (1963). The dimensions reported are based on a refinement of at least ten uniquely indexed reflections, calibrated using NaCl ( $a$  5.6402 Å) as an internal standard. The 1M polytype was the only form found throughout the mica synthesis range.

*Cationic charges and hydroxyl content.* Synthesis of the tetrasilicic phlogopite strongly suggests that the hydroxyl contents of natural micas may be related to charge

imbalances caused by cationic substitutions. To determine if any relationships between cation content and hydroxyl content existed, cationic charges were tabulated from published analyses of phlogopites, biotites, and muscovites and compared to the observed hydroxyl contents (OH+F+Cl) of these micas. Using structural formulae calculated on the basis of 24 (O,OH,F), cationic charges were computed for both the octahedral and tetrahedral layers and the inter-layer position. Charge deviations from the ideal values of +12, +30, and +2 were denoted as  $d_o$ ,  $d_t$ , and  $d_i$  respectively. The sum of  $d_o$  and  $d_t$  results in a net charge,  $\Delta$  ( $\Delta = d_o + d_t$ ), for the octahedral and tetrahedral layers. The  $\Delta$  does not measure charge imbalances due to coupled cationic substitutions because these are cancelled in the summation. Structural formulae based on 24(O,OH,F) may introduce some error in cation abundances due to postulated changes in the anion content of micas after dehydroxylation. However, this method was used because alternate means of calculation (Foster, 1960) arbitrarily fix the OH+F content at 4.0 per formula unit and ignore any of the real variations in hydroxyl content.

The  $\Delta$  value was calculated from the structural formulae of 100 natural phlogopites and biotites. These were obtained from the compilations of Deer *et al.* (1962), Butler (1967), Nockolds (1947), Dodge *et al.* (1969), and Nash and Wilkinson (1970). While this is not an exhaustive survey of biotite analyses, it is considered to be a representative sample of both biotite compositions and geologic environments. The values of  $d_i$ ,  $d_o$ ,  $d_t$ , and source of the analysis are given in Table II.

For the 100 samples analysed,  $\Delta$  was found to vary from 2.56 to -0.95. In only one case was  $\Delta$  equal to zero. Since these phases have to be electrostatically neutral,  $\Delta$  may be balanced by either altering the alkali charge or the OH<sup>-</sup>/O<sup>=</sup> ratio within the structure.

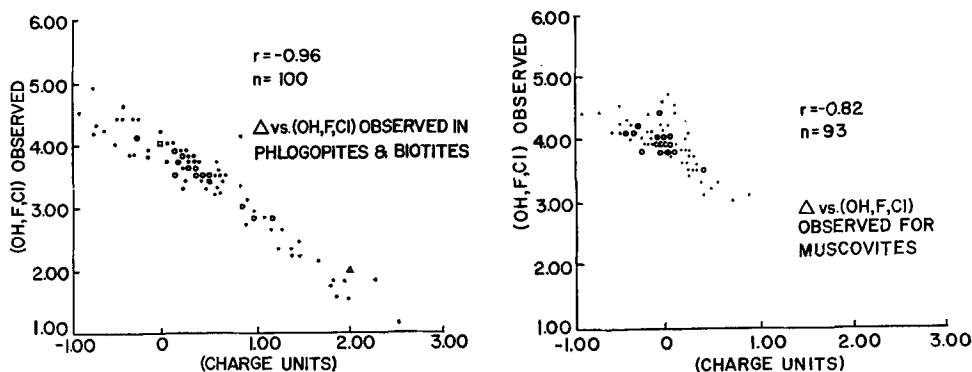
From Table II it is apparent that while  $d_i$  can have substantial magnitude, it is generally much smaller than  $\Delta$  and, to a first approximation, can be considered zero. Thus, because of the constraint of electrostatic neutrality,  $\Delta$  must necessarily be compensated by alteration of the OH<sup>-</sup>/O<sup>=</sup> ratio. The dependence of hydroxyl content on  $\Delta$  was confirmed quantitatively by calculation of linear regressions of  $\Delta$  on observed (OH+F+Cl) contents (hereafter termed (OH)<sub>obs</sub>) and  $\Delta$  versus  $d_i$  by a least-squares regression method for the 100 mica samples discussed above. The correlation coefficient between  $\Delta$  and (OH)<sub>obs</sub> is -0.96, while the correlation between  $\Delta$  and  $d_i$  is 0.06. This means that 91 % of the variation of (OH)<sub>obs</sub> from the ideal value of 4.0 can be interpreted in terms of a dependence on  $\Delta$ . A plot of  $\Delta$  versus (OH)<sub>obs</sub> is shown in fig. 2 where the linear relationship is apparent. The linear regression equation for these data has an intercept value of 4.02(2) at  $\Delta = 0$ , and a slope of -1.03(3). Departures of the data points from a straight line are most probably due to either the alkali charge contribution ( $d_i$ ) or errors in the chemical analysis. Undoubtedly, some of the data represent analyses on micas partially converted to vermiculite or chlorite although care was taken to select only high-quality analyses. Partial alteration or faulty analysis of fluorine, water, or ferrous/ferric ratios must necessarily decrease the correlation between  $\Delta$  and (OH)<sub>obs</sub>. Much of the scatter in figs. 2 and 3 may be attributable to these factors.

TABLE II. Cation charge parameters, observed hydroxyl content  $(OH)_o$ , and calculated hydroxyl content  $(OH)_c$  for phlogopite and biotites.  $(OH)_c$  has been derived from the expression  $(OH)_c = 4.0 - \Delta$ .  $d_1$ ,  $d_o$ ,  $d_t$ , and  $\Delta$  are defined in the text. The source of the analysis is identified at the head of each data section with Table and analysis number given in the left-hand column

No.	$d_1$	$d_o$	$d_t$	$\Delta$	$(OH)_c$	$(OH)_o$	No.	$d_1$	$d_o$	$d_t$	$\Delta$	$(OH)_c$	$(OH)_o$
Deer <i>et al.</i> (1962)							Dodgo <i>et al.</i> (1969)						
10-2	0.40	-0.06	-0.41	-0.47	4.47	4.02	1-HL4	-0.16	1.08	-0.39	0.69	3.31	3.46
10-3	0.15	0.50	-0.65	-0.15	4.15	4.00	1-MT1	-0.12	0.85	-0.48	0.37	3.63	3.75
10-4	0.17	0.98	-0.47	0.51	3.49	3.32	1-HL9	-0.14	1.34	-0.40	0.94	3.06	3.18
10-5	-0.22	1.15	-0.28	0.87	3.13	4.22	1-SL18	0.03	0.98	-0.38	0.60	3.40	3.35
10-6	-0.52	0.86	-0.26	0.60	3.40	3.80	1-Bcc13	-0.05	1.11	-0.46	0.65	3.35	3.68
10-7	0.06	2.19	-0.48	1.71	2.29	2.16	1-WV1	-0.21	0.73	-0.48	0.25	3.75	4.01
10-8	-0.08	1.32	-0.10	1.22	2.78	2.98	1-SL32	-0.23	1.09	-0.43	0.66	3.34	3.59
10-9	-0.01	0.10	-0.21	-0.11	4.11	3.91	1-MT4	-0.20	0.85	-0.49	0.36	3.64	3.84
10-10	0.25	2.25	-0.18	2.06	1.94	1.63	1-MP617	-0.22	0.72	-0.42	0.30	3.70	3.90
10-11	0.19	1.30	1.00	0.30	3.70	3.50	1-BCa20	-0.03	0.92	-0.40	0.52	3.48	3.53
10-12	0.39	-0.04	-0.44	-0.48	4.48	4.09	1-MG1	-0.13	0.74	-0.47	0.27	3.73	3.87
12-1	0.17	2.01	-0.14	1.87	2.13	1.93	1-KR	-0.19	0.47	-0.31	0.16	3.84	4.02
12-2	-0.04	1.34	-0.21	1.13	2.87	2.90	1-MT	-0.03	0.90	-0.38	0.52	3.48	3.50
12-3	0.31	0.89	-0.69	0.20	3.80	3.55	1-BP1	-0.10	0.35	-0.37	-0.02	4.02	4.10
12-4	0.20	2.77	-0.21	2.56	1.44	1.23	1-BC12	0.01	0.96	-0.30	0.66	3.34	3.31
12-5	0.05	0.91	-0.66	0.26	3.74	3.72	1-FD3	-0.20	0.77	-0.36	0.41	3.59	3.78
12-6	-0.02	1.70	-0.38	1.32	2.68	2.69	1-BP2	0.00	0.70	-0.31	0.39	3.61	3.62
12-7	0.12	1.99	0.02	2.01	1.99	1.87	1-MG3	-0.12	0.52	-0.51	0.01	4.00	4.08
12-8	0.18	0.28	-0.11	0.17	3.83	3.64	1-FD13	-0.12	1.27	-0.41	0.86	3.14	3.40
12-9	0.14	0.75	-0.67	0.08	3.92	3.80	Butler (1967)						
12-10	-0.12	1.91	-2.30	-0.39	4.39	4.51	4-5	-0.18	0.81	-0.50	0.31	3.69	3.87
12-11	-0.20	2.34	-0.03	2.31	1.69	1.88	4-6	-0.12	0.88	-0.54	0.34	3.66	3.73
12-12	0.35	-0.03	-0.27	-0.30	4.30	3.94	4-7	-0.07	0.76	-0.54	0.22	3.78	3.84
12-13	0.20	-0.24	-0.07	-0.31	4.39	3.89	4-8	-0.08	0.85	-0.46	0.39	3.61	3.66
12-14	-0.02	-0.22	0.03	-0.19	4.20	4.23	4-9	-0.15	0.75	-0.57	0.18	3.82	3.98
12-15	0.07	0.04	-0.05	-0.01	4.01	4.10	4-10	0.30	0.66	-0.64	0.02	3.98	4.28
12-16	-0.26	-0.59	0.21	-0.38	4.38	4.64	4-11	-0.04	0.77	-0.57	0.20	3.80	3.84
13-1	0.26	-0.26	-0.43	-0.69	4.69	4.43	4-12	-0.13	1.10	-0.60	0.50	3.50	3.63
13-2	-0.08	0.53	-0.53	0.00	4.00	4.06	4-13	-0.18	0.81	-0.52	0.29	3.71	3.89
13-3	-0.04	1.07	-0.46	0.62	3.38	3.42	4-14	-0.18	0.89	-0.54	0.35	3.65	3.87
13-4	-0.30	0.85	-0.58	0.27	3.73	4.03	4-15	-0.12	1.07	-0.54	0.53	3.47	3.59
13-5	-0.20	1.22	-0.60	0.62	3.38	3.58	4-16	-0.26	0.46	-0.72	-0.26	4.26	4.51
13-6	0.30	0.75	-0.51	0.24	3.75	3.45	4-17	-0.12	0.92	-0.56	0.36	3.64	3.74
13-7	-0.29	0.18	-0.91	-0.73	4.73	5.01	4-18	-0.21	0.70	-0.59	0.11	3.89	4.07
13-8	-0.16	1.69	-0.49	1.20	2.79	2.93	4-19	-0.20	0.70	-0.59	0.10	3.90	4.09
13-9	-0.01	0.98	-0.65	0.32	3.68	3.68	4-20	-0.10	1.02	-0.56	0.46	3.54	3.59
13-10	0.27	1.25	-0.58	0.68	3.32	3.59	4-21	-0.09	1.14	-0.62	0.52	3.48	3.57
13-11	-0.06	0.92	-0.60	0.32	3.68	3.74	4-22	-0.31	0.59	-0.76	0.17	4.27	4.46
13-12	-0.01	0.99	-0.66	0.33	3.67	3.66	Nockolds (1947)						
13-13	-0.17	1.01	-0.68	0.33	3.67	3.83	3-49	0.26	1.67	-0.23	1.44	2.56	2.27
13-14	-0.03	1.56	-0.67	0.88	3.12	3.15	3-40	0.17	1.35	-0.36	0.99	3.01	2.87
13-15	0.26	-0.64	0.05	-0.59	4.59	4.32	4-53	0.25	2.13	-0.19	1.94	2.06	1.63
13-16	-0.07	0.84	-0.66	0.18	3.82	3.86	4-54	0.25	1.97	-0.14	1.83	2.17	1.78
Nash & Wilkinson (1970)							4-55	0.20	2.09	-0.65	1.44	2.56	2.40
SS3	0.06	1.38	-0.38	1.00	3.00	2.93	4-62	-0.20	0.91	0.01	0.92	3.09	2.81
SS11	-0.08	1.45	-0.42	1.03	2.97	2.99	4-61	0.16	-0.64	-0.09	-0.73	4.73	4.27
SS29	0.04	0.88	-0.34	0.54	3.46	3.42	4-60	-0.18	1.31	-0.10	1.21	2.79	2.95
Dodge <i>et al.</i> (1969)							5-3	0.13	1.81	-0.51	1.30	2.70	2.39
1-FD12	0.01	1.01	-0.58	0.43	3.57	3.58	5-4	0.12	2.13	-0.63	1.50	2.50	2.26
1-HL29	-0.01	0.94	-0.55	0.39	3.61	3.61	5-5	0.34	-0.59	-0.31	-0.90	4.90	4.65
1-FD20	-0.02	0.95	-0.63	0.32	3.68	3.67	5-11	0.18	-0.11	-0.84	-0.95	4.95	4.79
							5-12	-0.03	2.03	-0.53	1.50	2.50	2.49

The correlation of  $d_i$  with the observed (OH+F) is  $-0.22$  and therefore approximately 5 % of the OH variation is attributable to  $d_i$ . This is in contrast to margarites where Deer *et al.* (1962) have suggested that the hydroxyl content varies in response to changes in the alkali content.

The relationship between  $\Delta$  and hydroxyl content was also examined for a group of 93 muscovites. The formulae, all calculated on the basis of 24(O,OH,F), were obtained from the data of Deer *et al.* (1962), Foster (1964), Muller (1966), Bloss



FIGS. 2 and 3: FIG. 2 (left). Hydroxyl content variation (OH,F,Cl) versus net octahedral-tetrahedral charge,  $\Delta$ , for 100 phlogopites and biotites. The larger circles indicate multiple points. The location of the  $K_2Mg_6Si_8O_{22}(OH)_2$  phase is shown by a triangle, that of  $K_2Mg_5Si_8O_{20}(OH)_4$  (Seifert and Schreyer, 1965) by a square. FIG. 3 (right). Hydroxyl content variation (OH,F,Cl) versus net octahedral-tetrahedral charge,  $\Delta$ , for 93 muscovites. The large circles indicate multiple points.

*et al.* (1959), and Butler (1967). Values of  $d_i$ ,  $d_o$ ,  $d_t$ , and  $\Delta$  are given in Table III. The relationship between  $\Delta$  and  $(OH)_{obs}$  is shown in fig. 3. The correlation coefficient of  $-0.82$  is somewhat less than the correlation of the same parameters in biotites, but again demonstrates a very strong dependence of (OH,F) on  $\Delta$ .

*Discussion.* Charge imbalance, caused by cationic substitutions in biotites and muscovites, can be balanced in a variety of ways. In addition to simple isomorphous replacements in biotites, Gower (1957) has proposed substitutions of the type  $(Mg, Fe^{2+})^{[6]} + Si^{[4]} \rightleftharpoons Al^{[4]} + Al^{[6]}$  where the numbers in the square brackets refer to the coordination number of the cation. Seifert and Schreyer (1971) have demonstrated a unique coupled substitution of the type  $Mg^{[6]} + Mg^{[4]} \rightleftharpoons Si^{[4]}$ . In addition, Seifert and Schreyer (1965) showed by the synthesis of the mica  $K_2Mg_5Si_8O_{20}(OH)_4$  that octahedral vacancies can be a means to balance charge inequalities caused by cationic substitutions.

It is implicit in these replacement models that any perturbations of the ideal cationic charge in one layer will be electrostatically balanced by adjustment of the cationic charge in the other layer. The data presented above, however, demonstrate that the hydroxyl group (OH,F,Cl) in phlogopites, biotites, and muscovites varies in response to net cationic charges and hence cationic substitutions. Thus cation-hydroxyl couples must be considered as well as the replacement models discussed above. Micas

TABLE III. Cation charge parameters, observed hydroxyl content and calculated hydroxyl content for muscovites. See Table II for complete explanation.

No.	$d_i$	$d_o$	$d_t$	$\Delta$	(OH) <sub>o</sub>	(OH) <sub>o</sub>	No.	$d_i$	$d_o$	$d_t$	$\Delta$	(OH) <sub>o</sub>	(OH) <sub>o</sub>
<b>Butler (1967)</b>							<b>Muller (1966)</b>						
3-1	-0.04	-0.56	0.49	-0.07	4.07	4.12	3-46	-0.16	-0.56	-0.32	-0.88	4.88	4.50
3-2	-0.01	-0.30	0.35	0.05	3.95	3.93	3-53	-0.06	0.16	-0.14	0.02	3.98	4.00
3-3	-0.04	-0.27	0.37	0.10	3.90	3.94	3-59	-0.01	-0.21	-0.04	-0.25	4.25	3.92
3-4	-0.07	-0.12	0.33	0.21	3.79	3.87	<b>Foster (1964)</b>						
3-5	-0.02	-0.22	0.27	0.05	3.95	4.03	4-6	0.14	-0.44	-0.24	-0.68	4.68	4.50
3-6	0.01	-0.29	0.32	0.03	3.97	3.96	4-7	-0.10	0.06	0.06	0.12	3.88	4.00
3-7	0.06	-0.39	0.37	-0.02	4.02	3.97	4-8	-0.10	-1.84	-0.10	-1.94	5.94	6.10
3-8	-0.04	0.08	0.37	0.45	3.55	3.63	4-10	-0.04	-0.34	-0.06	-0.40	4.40	4.40
3-9	-0.03	-0.38	0.30	-0.08	4.08	4.09	4-12	0.08	0.06	-0.10	-0.04	4.04	3.98
3-10	-0.07	-0.15	0.21	0.06	3.94	4.04	4-13	0.04	0.14	-0.10	0.04	3.96	3.94
3-11	-0.06	-0.07	0.52	0.45	3.55	3.60	4-15	0.20	0.38	0.16	0.54	3.46	3.26
3-12	-0.03	-0.24	0.31	0.07	3.93	3.85	4-16	-0.06	-0.20	0.20	0.00	4.00	4.70
3-13	-0.06	-0.44	0.33	-0.11	4.11	4.17	4-18	0.10	-0.26	0.02	-0.24	4.24	4.12
3-14	-0.05	-0.01	0.38	0.37	3.63	3.65	4-21	0.16	-0.30	-0.06	-0.36	4.36	4.08
3-15	0.05	-0.32	0.31	-0.01	4.01	3.94	4-22	0.16	-0.38	-0.02	-0.40	4.40	4.22
3-16	-0.14	-0.52	0.05	-0.47	4.47	4.62	4-23	0.06	-0.12	-0.06	-0.18	4.18	4.16
3-17	0.00	-0.25	0.19	-0.06	4.06	4.03	4-24	-0.20	0.06	-0.12	-0.06	4.06	4.30
3-18	-0.10	-0.04	0.12	0.08	3.92	4.00	4-25	0.22	-0.12	0.06	-0.06	4.06	4.48
3-19	-0.07	-0.24	0.31	0.07	3.93	4.01	4-26	0.14	0.36	0.06	0.42	3.58	3.42
3-20	-0.01	-0.19	0.25	0.06	3.94	3.96	4 27	0.12	-0.30	0.14	0.16	4.16	4.04
3-21	-0.06	-0.11	0.21	0.10	3.90	3.94	4 28	0.08	0.00	0.02	0.02	3.98	4.10
3-22	-0.10	0.12	0.13	0.25	3.75	3.89	4-29	0.04	0.20	0.14	0.06	4.06	4.52
<b>Deer et al. (1962)</b>							4-30	0.10	0.02	0.00	0.02	3.98	3.86
5-1	-0.13	-0.02	0.09	0.07	3.93	4.14	4-31	0.02	0.12	0.04	0.08	3.92	3.90
5-2	-0.02	-0.19	0.05	0.24	3.76	4.06	4-32	-0.04	-0.02	0.06	0.04	3.96	4.34
5-3	0.29	-0.64	0.09	-0.55	4.55	4.22	4-34	0.12	-0.32	0.12	-0.20	4.20	3.98
5-4	-0.03	-0.21	0.21	0.00	4.00	4.04	4-36	0.15	-0.32	0.00	-0.32	4.32	4.20
5-5	0.79	-0.55	-0.09	-0.64	4.64	3.86	4-37	0.01	-0.20	0.08	-0.12	4.12	4.14
5-6	0.18	-0.48	0.03	-0.45	4.45	4.26	4-38	0.14	-0.06	0.12	0.06	3.94	4.78
5-7	-0.11	0.67	0.27	0.94	3.06	3.17	4-39	0.04	-0.42	0.04	-0.38	4.38	4.22
5-8	0.05	0.03	0.27	0.30	3.70	3.65	4-40	0.07	-0.04	0.08	0.04	3.96	3.90
5-9	-0.03	-0.69	0.54	-0.15	4.15	4.20	4-42	0.02	-0.18	0.08	-0.10	4.10	4.04
5-10	-0.01	-0.53	1.42	0.89	3.11	3.11	4-43	-0.22	-0.10	0.18	0.08	3.92	4.10
5-11	-0.09	-0.66	0.75	0.09	3.91	4.00	4-44	0.02	-0.14	0.18	0.04	3.96	3.94
5-12	-0.50	-1.25	0.89	-0.36	4.36	4.92	4-46	-0.12	0.18	0.16	0.34	3.66	3.78
5-13	0.04	-0.57	0.60	0.03	3.97	3.92	4-51	-0.14	0.66	0.28	0.94	3.06	3.16
5-14	-0.09	-0.05	0.15	0.10	3.90	4.02	4-52	0.12	0.06	0.22	0.28	3.72	3.48
5-15	-0.01	-0.31	-0.04	-0.35	4.35	4.30	4-53	0.12	-0.07	0.30	0.23	3.77	3.70
<b>Bloss et al. (1959)</b>							4-55	0.04	0.06	0.28	0.34	3.66	3.64
Brazil	-0.02	-0.32	0.00	-0.32	4.32	4.24	4-56	-0.14	0.07	0.22	0.28	3.71	4.16
S. Dakota	-0.06	-0.26	-0.02	-0.28	4.28	3.94	4-58	0.02	-0.23	0.24	0.01	3.99	4.22
India	+0.08	-0.36	0.06	-0.30	4.30	4.28	4-58	-0.08	-0.18	0.22	0.04	3.96	4.02
<b>Muller (1966)</b>							4-60	0.02	-0.14	0.36	0.22	3.78	3.70
3-2	-0.21	0.19	-0.14	0.05	3.95	3.89	4-61	-0.10	-0.16	0.28	0.12	3.88	4.56
3-4	-0.09	0.03	-0.02	0.01	3.99	3.99	4-63	-0.14	-0.24	0.38	0.14	3.86	4.50
3-5	-0.08	-0.67	-0.37	-1.04	5.04	4.65	4-64	-0.08	-0.26	0.56	0.30	3.70	3.78
3-17	-0.05	-0.27	-0.23	-0.50	4.50	4.26	4-65	-0.02	0.00	0.36	0.36	3.64	3.74
3-44	-0.08	0.19	-0.14	0.05	3.95	3.88	4-66	-0.16	-0.56	0.76	0.20	3.80	4.48
							4-67	-0.24	-0.30	0.60	0.30	3.70	3.92
							4-68	0.00	0.06	0.56	0.62	3.38	3.36
							4-70	-0.08	-0.70	0.72	0.02	3.98	4.12

may become hydroxyl-deficient through substitutions of the type  $\text{Al}+\text{H}^+ \rightleftharpoons \text{Si}$ ,  $\text{Al}+\text{H}^+ \rightleftharpoons \text{Ti}$ ,  $M^{2+}+2\text{H}^+ \rightleftharpoons \text{Ti}$ , or  $\text{Fe}^{2+}+\text{H}^+ \rightleftharpoons \text{Fe}^{3+}$ . Similarly hydrogen may be added to the mica by the substitutions  $\text{Si} \rightleftharpoons \text{Al}+\text{H}^+$ ,  $\text{Al} \rightleftharpoons M^{2+}+\text{H}^+$ ,  $M^{2+} \rightleftharpoons 2\text{H}^+$  or  $M^{2+} \rightleftharpoons \text{Li}+\text{H}^+$ . Cation-hydroxyl couples were first proposed by Gruner (1933) in discussing the isomorphism of kaolinite and anauxite.

In the trioctahedral micas,  $d_0$  is generally positive and varies from +2.25 to -0.60. The tetrahedral layer usually is undercharged due to the presence of Al in excess of the ideal Al:Si ratio of 1:3. Variation in the  $d_t$  value is between +0.20 and -1.00.  $\Delta$  was found to range within the limits of +2.50 to -1.00.

In contrast,  $d_0$  in muscovites is usually negative and was found to vary from +0.66 to -1.85.  $d_t$  is generally positive and has a slightly larger range of +1.42 to -0.37 as compared to +0.20 to -1.00 for biotites. This suggests larger amounts of  $\text{Si}^{4+}$  in the tetrahedral layer as compared to biotites. The negative  $d_0$  values indicate a deficiency of  $\text{Al}^{3+}$  in the octahedral layer or replacement of Al by divalent cations or both.

A comparison of figs. 2 and 3 shows that the range of (OH,F) contents is considerably larger for the trioctahedral micas than for muscovites. The lowest (OH,F) value for muscovite was 3.11 as compared to 1.23 for biotite. Trioctahedral micas tend to be OH deficient, only 25 % have (OH,F) > 4.0, while 52 % of the muscovites contain an excess of OH.

In muscovite, the oxygen atoms bonded to one tetrahedral group and two octahedral Al atoms could be additional hydroxyl positions, where the H-atom is pointing into an octahedral void. In phlogopites and biotites, this is not possible since all octahedral sites ideally are occupied. In the trioctahedral micas, additional hydrogen must be bonded to oxygen atoms on the basal surface, which are co-ordinated to two tetrahedral cations, and are thus fully charge saturated. These sites are less favourable than the proposed muscovite site because of Pauling bond strength considerations (Baur, 1970; Forbes, 1969). This may be the reason that a larger percentage of muscovites are OH-rich as compared to phlogopites and biotites. The correlation between  $\Delta$  and (OH,F)<sub>obs</sub> in fig. 2 is noticeably poorer for hydroxyl contents greater than 4.0 and may suggest a randomness in the positions of additional hydroxyl ions in the trioctahedral micas.

The presence of water as a free phase within the mantle has been suggested as an important factor in mantle processes such as partial melting and genesis of volatile-rich magmas. Formation of a volatile phase has been assumed to result from the decomposition of hydrous phases such as phlogopite (Kushiro *et al.*, 1967), amphibole (Oxburgh, 1964), and titanoclinohumite (McGetchin *et al.*, 1970; Merrill, 1970). However, consideration of the cation-hydroxyl substitution model suggests an alternate means of producing volatiles. Modreski and Boettcher (1970) have found that  $\text{Al} \rightleftharpoons \text{Si}$  exchange occurs between coexisting phlogopite and enstatite at high pressures. If the hydroxyl group is involved in the exchange, through the substitution  $\text{Al}^{3+}+\text{H}^+ = \text{Si}^{4+}$ , one hydrogen ion is released for every Al ion lost to enstatite. Similarly this type of exchange may occur between phlogopite and diopside as well. Several other cation-hydroxyl couples resulting in the liberation of hydrogen



are readily conceived. Thus hydrogen may be produced as the result of solid-state processes, without the requirement of total decomposition and consequently dehydration of hydrous phases.

*Acknowledgements.* The author is grateful to Drs. W. H. Baur, J. H. Carman, and R. B. McCammon for their constructive criticisms of this paper.

#### REFERENCES

- BAUR (W. H.), 1970. *Trans. Amer. Cryst. Assoc.* **6**, 125.  
 BLOSS (F. D.), SHEKARCHI (E.), and SHELL (H. R.), 1959. *Amer. Min.* **44**, 33 [M.A. 14-345].  
 BUTLER (B. C. M.), 1967. *Journ. Petrology*, **8**, 233 [M.A. 18-276].  
 DEER (W. A.), HOWIE (R. A.), and ZUSSMAN (J.), 1962. *Rock Forming Silicates*, **3**. Sheet Silicates. London (Longmans).  
 DODGE (F. C. W.), SMITH (V. C.), and MAYS (R. E.), 1969. *Journ. Petrology*, **10**, 250 [M.A. 21-58].  
 EUGSTER (H. P.), and WONES (D. R.), 1962. *Ibid.*, **3**, 82 [M.A. 16-52].  
 EVANS (H. T.), APPLEMAN (D. E.), and HANDWERKER (D. W.), 1963. *Progr. Amer. Crystallogr. Assoc. Ann. Meet.* **42**.  
 FORBES (W. C.), 1969. *Amer. Min.* **54**, 1399 [M.A. 21-126].  
 FOSTER (M. D.), 1960. *U.S. Geol. Surv. Prof. Pap.* **354-B**.  
 ——— 1964. *Ibid.* **474-F**.  
 GOWER (J. A.), 1957. *Amer. Journ. Sci.* **255**, 142.  
 GRUNER (J. W.), 1932. *Zeits. Krist.* **83**, 75.  
 KHAN (A. A.), BAUR (W. H.), and FORBES (W. C.), 1972. *Acta Cryst.* **B28**, 267.  
 KUSHIRO (I.), SYONO (Y.), and AKIMOTO (S.), 1968. *Earth Planet. Sci. Lett.* **3**, 197.  
 LARSEN (E. S. Jr.), GONYER (F. A.), and IRVING (J.), 1937. *Amer. Min.* **22**, 898 [M.A. 7-31].  
 MCGETCHIN (T. R.), SILVER (L. T.), and CHODOS (A. A.), 1970. *Journ. Geophys. Res.* **75**, 255 [M.A. 70-3336].  
 MODRESKI (P. J.) and BOETTCHER (A. L.), 1970. *Progr. Ann. Meet. Geol. Soc. Amer., Milwaukee*, 626.  
 MULLER (G.), 1966. *Contr. Min. Petr.* **12**, 59 [M.A. 18-193].  
 NASH (W. P.) and WILKINSON (J. F. G.), 1970. *Ibid.* **25**, 241 [M.A. 21-348].  
 NOCKOLDS (S. R.), 1947. *Amer. Journ. Sci.* **245**, 401.  
 OXBURGH (E. R.), 1964. *Geol. Mag.* **101**, 1 [M.A. 17-524].  
 RIMSAITE (J.), 1964. *Beitr. Min. Petr.* **10**, 152 [M.A. 17-191].  
 ——— 1970. *Contr. Min. Petr.* **25**, 225 [M.A. 70-2533].  
 RINNE (F.), 1924. *Verh. Akad. Wiss. Leipzig*, **76**, 261.  
 ROEDDER (E. W.), 1951. *Amer. Journ. Sci.* **249**, 81, 224.  
 SABATIER (H.) and VELDE (B.), 1970. *Progr. Ann. Meet. Geol. Soc. Amer., Milwaukee*, 671.  
 SEIFERT (F.) and SCHREYER (W.), 1965. *Amer. Min.* **50**, 1114 [M.A. 17-474].  
 ——— 1969. *Contr. Min. Petr.* **22**, 190.  
 ——— 1971. *Ibid.* **30**, 196.  
 WONES (D. R.), 1963. *Amer. Min.* **48**, 1300 [M.A. 16-560].  
 YODER (H. S.) and EUGSTER (H. P.), 1954. *Geochimica Acta*, **6**, 157.

[Manuscript received 26 April 1971]