

Barian-titanian biotites in nephelinites from Oahu, Hawaii¹

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Abstract

Late-magmatic biotites in nephelinites from Oahu, Hawaii contain unusually high amounts of BaO (up to 20 weight percent) and TiO₂ (up to 14 weight percent) and are markedly low in SiO₂ (21 to 28 weight percent) and K₂O (2 to 6 weight percent). As BaO content increases, SiO₂, K₂O, and MgO decrease and FeO and Al₂O₃ increase. Atomic substitution schemes indicate that Ba substitutes entirely for K, Na, and Ca in interlayer sites; Al compensates for tetrahedral Si deficiencies; and Ti is probably limited to octahedral substitution for Mg and Fe. Tetrahedral occupancy by Ti appears unlikely, although undetermined Fe³⁺ may compensate for tetrahedral deficiencies. A substitution scheme of the type $K + 3(Mg,Fe) + 3Si = Ba + 2Ti + 3Al$ is suggested.

Numerous samples of nephelinite from cores of the Honolulu Volcanic Series, Nuuanu Valley, Oahu, Hawaii (Diamond Drill Hole #48; Wentworth, 1951) contain barium-titanium-rich biotites as a late magmatic phase. Other igneous occurrences have been noted previously (Thompson, 1977; Wendlandt, 1977, and others), but hitherto none have been reported from Hawaiian nephelinites, and none are as high in BaO (up to 20 weight percent) and TiO₂ (up to 14 weight percent) as the ones here described.

Ba-Ti biotites in the nephelinites occur as tiny (70 × 100 μm maximum) subhedral plates or laths. They are usually found within vesicles, and less commonly as smaller groundmass grains. They are reddish-brown in color, and exhibit dark-brown pleochroism, which may be attributed to high amounts of titanium and/or ferric iron, and show no optical zoning. The biotites are associated with nepheline, pyroxene (titan-augite), zeolite (primarily phillipsite and thomsonite), and, more rarely, apatite and carbonate.

Biotites from five samples were analyzed (Table 1; sample nos. refer to depth from surface) with an ARL EMX-SM electron microprobe, using natural and synthetic standards of similar composition. Data were corrected for background, drift, mass absorption, and secondary fluorescence (Keil, 1967; Bence and Albee, 1968).

Individual biotites from Oahu are relatively homogeneous. Compositional zoning was observed in only one grain, showing a decrease in BaO and FeO outward, with concomitant increases in SiO₂, K₂O, and MgO. Grain-to-grain inhomogeneities within single samples probably reflect biotite crystallization from isolated magmatic fluids of slightly different bulk compositions. Sample-to-sample compositional variations may be related similarly, since BaO and TiO₂ contents of respective host lavas show no correlation with those of the biotites. The biotites in different samples exhibit a wide compositional range (Fig. 1) with SiO₂, K₂O, and MgO decreasing linearly with BaO content, whereas FeO and Al₂O₃ increase, similar to the zoning trend observed in the single biotite grain mentioned above. Semi-quantitative microprobe determinations indicate that the biotites contain trace amounts of Rb (0.05 weight percent, or less) and Sr (up to 0.16 weight percent).

Calculated structural formulae (Table 1) indicate that the biotite structures incorporate unusual amounts of Ba²⁺ and Ti⁴⁺ and are markedly deficient in Si⁴⁺. A plot of Ba vs. the K+Na+Ca available for 12-fold interlayer sites shows that Ba may be assigned entirely to interlayer sites, on a 1:1 basis (Fig. 2). The resulting charge imbalance is offset by coupled substitution of the type $Ba^{2+} + Al^{3+} = K^{+} + Si^{4+}$ (Wendlandt, 1977). Further tetrahedral substitution of Al³⁺ may result from the substitution scheme $Mg^{2+} +$

¹ Contributions to the mineral chemistry of Hawaiian rocks VII.

Table 1. Selected microprobe analyses (weight percent oxides) of Ba-Ti-rich biotites

	1	2	3	4	5	6	7
SiO ₂	24.2	21.1	22.8	22.4	26.2	33.4	33.6
TiO ₂	14.1	13.1	13.5	13.5	13.2	3.04	2.45
Al ₂ O ₃	16.8	17.6	16.8	16.4	16.0	16.1	14.1
FeO ^a	9.8	13.2	12.6	16.2	12.5	5.40	16.1
MgO	11.3	8.1	8.8	6.0	9.4	21.9	14.4
CaO	0.23	0.21	0.08	0.07	0.19	0.15	0.07
Na ₂ O	0.57	0.28	0.39	0.30	0.44	0.05	0.36
K ₂ O	4.3	2.32	3.2	2.32	4.1	7.38	6.48
BaO	14.5	20.5	17.7	18.5	14.6	8.62	7.32
TOTAL	95.8	96.3	95.9	95.7	96.6	96.9 ^b	95.5 ^c

Structural Formulae Based on 22 Oxygens

Si	3.984	3.677	3.907	3.921	4.304	5.056	5.34
Ti	1.744	1.722	1.733	1.733	1.631	0.345	0.29
Al	3.260	3.619	3.382 ¹	3.376	3.100	2.868	2.63
Fe ^d	1.353	1.925	1.801	2.376	1.710	0.684	2.13
Mg	2.780	2.103	2.233	1.564	2.294	4.942	3.42
Ca	0.041	0.039	0.015	0.013	0.033	0.025	0.01
Na	0.182	0.095	0.129	0.102	0.140	0.014	0.11
K	0.906	0.517	0.693	0.545	0.866	1.424	1.32
Ba	0.937	1.402	1.184	1.270	0.939	0.511	0.46
Cation Sum	15.187	15.009	15.083	14.940	15.017	15.879 ^e	15.78 ^f

1. Nuuanu Valley, Oahu; Sample 48-80
2. Nuuanu Valley, Oahu; Sample 48-112
3. Nuuanu Valley, Oahu; Sample 48-143
4. Nuuanu Valley, Oahu; Sample 48-163
5. Nuuanu Valley, Oahu; Sample 48-271
6. Barium phlogopite inclusion in monticellite. Highwood Mountains, Montana; Wendlandt (1977)
7. Barian Biotite, Alban Hills leucitite, Central Italy; Thompson (1977)

- ^a All Fe given as FeO
- ^b Includes 0.04 MnO, 0.03 P₂O₅, 0.05 Cr₂O₃ and 0.03 Ni
- ^c Includes 0.37 MnO and 0.22 Cr₂O₃
- ^d Formulae calculation based on 2Fe³⁺ 2+
- ^e Includes 0.005 Mn and 0.005 Cr
- ^f Includes 0.05 Mn and 0.02 Cr

$2\text{Si}^{4+} = \text{Ti}^{4+} + 2\text{Al}^{3+}$ (Robert, 1976), where Ti^{4+} substitutes octahedrally for Mg^{2+} (and Fe^{2+}). A 1:1 correspondence between Si and Al (Fig. 3) indicates that Al^{3+} is restricted to tetrahedral sites. Assigning Al^{3+} entirely to tetrahedral sites does not compensate for all Si^{4+} deficiencies; Fe^{3+} or Ti^{4+} may account for the remainder, although the existence of tetrahedral Ti^{4+} is controversial (Hartman, 1969). Robert (1976) has shown that tetrahedral Ti^{4+} occupancy is not apparent in high Ti-micas. Likewise, Forbes and Flower (1974) have demonstrated that with increasing titanium content in micas, octahedral substitution occurs according to the substitution scheme $\text{Ti}^{4+} = 2\text{R}^{2+}$, giving rise to a net octahedral deficiency. Such an octahedral deficiency is apparent in the Oahu biotites, since structural cation sums (Table 1) are consistently about 1.0 atomic units lower than expected

for ideal biotite stoichiometry. A summary representation of substitutions occurring in the Oahu biotites may be given as:



When the Oahu biotite data are plotted according to this proposed substitution scheme, the data exhibit a near ideal 1:1 linear trend (Fig. 4).

The unusual biotite compositions reflect the chemical character of the host nephelinites. They are highly undersaturated and enriched in alkalis, volatiles, and light rare-earth elements. High in both Ba and Ti, the Oahu biotites allow the simultaneous evaluation of the structural substitutions proposed for high-Ba phlogopites (Wendlandt, 1977) and synthetic high-Ti micas (Robert, 1976; Forbes and Flower, 1974). The present study indicates that the

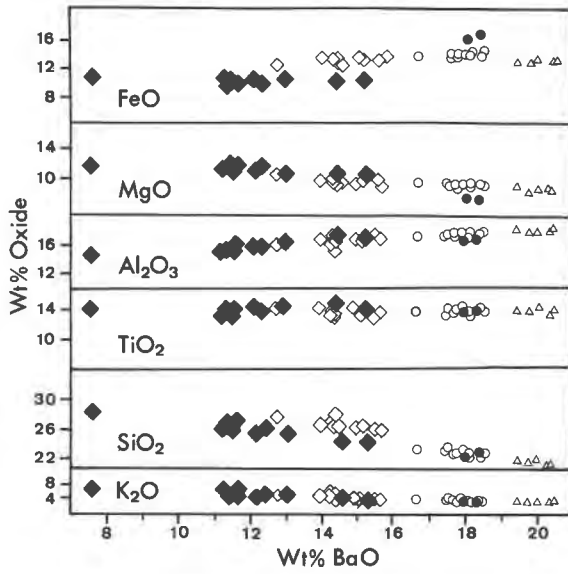


Figure 1

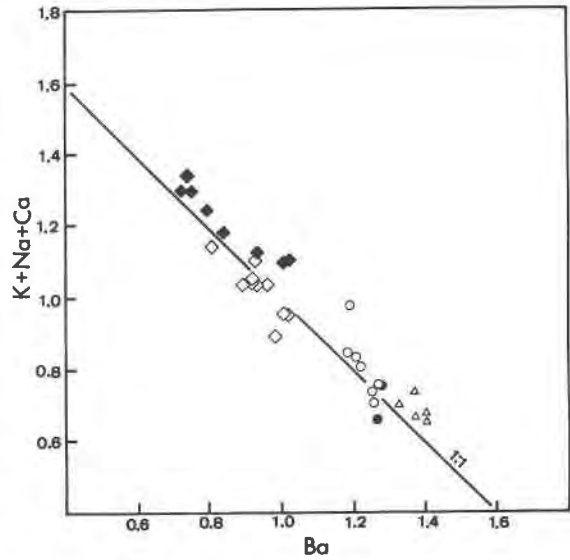


Figure 2

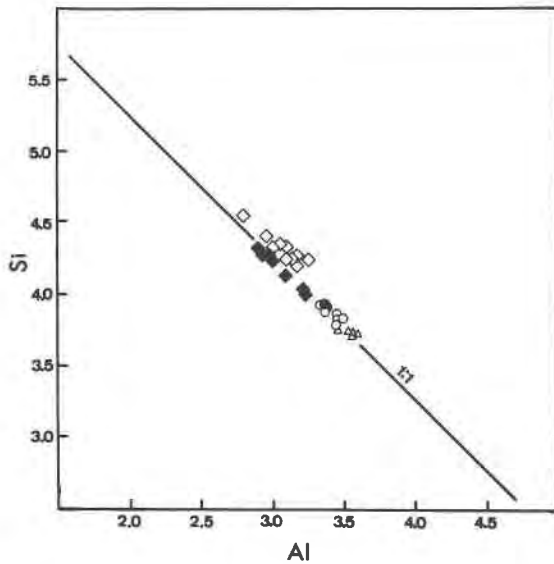


Figure 3

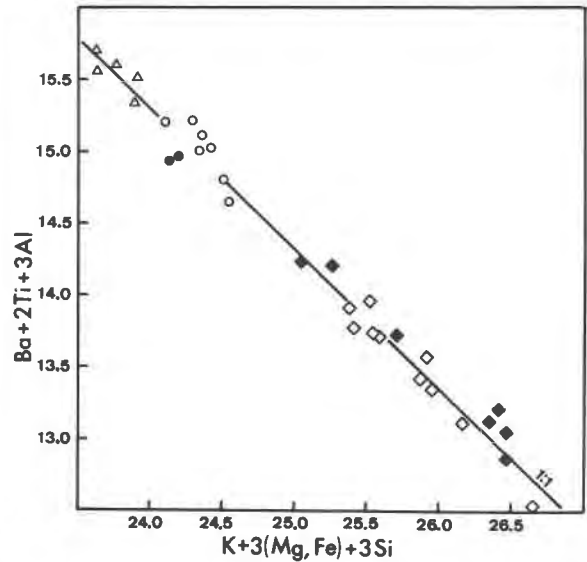


Figure 4

◆ = 48-80 △ = 48-112 ○ = 48-143 ◇ = 48-163 ● = 48-271

Fig. 1. BaO variation diagram of Oahu biotites showing a linear decrease of MgO, SiO₂, and K₂O, and concomitant increase of FeO and Al₂O₃.

Fig. 2. Plot of atomic proportions of interlayer cations showing 1:1 variation of Ba with remaining cations. For the 1:1 reference line, the sum of interlayer cations = 2.

Fig. 3. Plot of atomic proportions of tetrahedral cations, Si vs. Al, showing 1:1 correspondence.

Fig. 4. Plot of atomic proportions according to the substitution scheme $K + 3(Mg,Fe)^{2+} + 3Si^{4+} = Ba^{2+} + 2Ti^{4+} + 3Al^{3+}$, showing near 1:1 correspondence.

substitution schemes of Wendlandt, Robert, and Forbes and Flower are appropriate to the Oahu biotites.

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References

- Bence, A. E. and A. L. Albee (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.*, 76, 382-403.
- Forbes, W. C. and M. J. F. Flower (1974) Phase relations of titanphlogopite, $K_2Mg_4TiAl_2Si_8O_{20}(OH)_4$: a refractory phase in the upper mantle? *Earth Planet. Sci. Lett.*, 22, 60-66.
- Hartman, P. (1969) Can Ti^{4+} replace Si^{4+} in silicates? *Mineral. Mag.*, 37, 366-369.
- Keil, K. (1967) The electron microprobe x-ray analyzer and its application in mineralogy. *Fortschr. Mineral.*, 44, 4-66.
- Robert, J. L. (1976) Titanium solubility in synthetic phlogopite solid solutions. *Chem. Geol.*, 17, 213-227.
- Thompson, R. N. (1977) Primary basalts and magma genesis. III. Alban Hills, Roman comagmatic province, central Italy. *Contrib. Mineral. Petrol.*, 60, 91-108.
- Wendlandt, R. F. (1977) Barium-phlogopite from Haystack Butte, Highwood Mountains, Montana. *Carnegie Inst. Wash. Year Book*, 76, 534-539.
- Wentworth, C. K. (1951) *Geology and Ground-water Resources of the Honolulu-Pearl Harbor Area Oahu, Hawaii*. Board of Water Supply, City and County of Honolulu, Honolulu, Hawaii.

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