

Tin Content of Biotites from the Afu Younger Granite Complex, Central Nigeria

E. G. IMEOKPARDIA

Department of Geology, University of Ibadan, Ibadan, Nigeria

Abstract

The Sn content, determined by electron microprobe, of 36 biotites from granitic rocks of the Afu Complex ranges from 50 to 1,000 ppm and averages 500 and 150 ppm for biotites from mineralized and barren granites, respectively. These results show that the Sn content of biotites associated with mineralization is three times greater than the Sn content of biotites from barren granites. Thus, the possibility of differentiating between mineralized and unmineralized granite on the basis of the Sn content of biotite is suggested.

The relationship of the tin content of the biotites to that of the rock is nearly constant at approximately 10:1. The biotites have less than 40 percent of the amount of tin than the granites have. The concentration of tin in the biotites appears to be a function of the chemical evolution of the granites. Sn may increase in the biotites with decreasing oxygen fugacity and temperature of crystallization. The low oxygen fugacity and low temperature of crystallization seem due largely to the high concentration of F, Rb, and other volatile elements in the magma.

Introduction

THE possible relationship between the presence or absence of tin mineralization in or near a particular granitic intrusion and the tin content of the granitic rock has been the subject of numerous publications. Tin deposits around the world are known to be closely associated with granitic rocks and related effusives. This spatial and probable genetic relationship is considered to be one of the best examples of ore-rock association (Stanton, 1972).

On the basis of this association several workers have demonstrated that granitic rocks productive in tin may contain higher than normal concentrations of tin; this fact may be a good indicator of their ore-bearing potential.

Geochemical attempts to characterize tin-bearing granites have taken two lines of investigation. The first has been to determine the absolute tin concentration of the rock and that of the constituent minerals (particularly the micas) in order to determine if there is a relationship between a particular granite as tin bearing and the tin content of the whole rock or mineral. The second approach has been the consideration of the distribution of other elements in both the whole rock and the constituent minerals.

During magmatic crystallization tin probably exists as Sn^{+4} or Sn^{+2} and as such it may isomorphously substitute for Fe^{+3} , Fe^{+2} , Mg^{+2} , or Li^+ (Goldschmidt, 1954; Ringwood, 1955a, b) because of similarities in ionic radius and ionic potential (Taylor, 1965) or it may accumulate in the residual silicate melts. It is to be expected that in granitic rocks the major portion of the tin content may be included in the mafic fraction of the rock, where structural sites for substitution exist. If the only mafic mineral present is biotite, it

can be tentatively assumed that a significant proportion of the tin content is contained in this mineral.

Groves (1972), as a result of a study on some granitic rocks from Tasmania, noted that biotites associated with tin-bearing granites are considerably higher in Sn content than those from the tin-poor granites. Similar conclusions have been drawn by several other workers (Barsukov, 1957; Jedwab, 1955; Bradshaw, 1967; Ivanova, 1963).

The present study attempts what is believed to be the first search for such a relationship in the Afu Younger Granite Complex, Nigeria. It is also the first published study using the electron microprobe on rocks from this complex.

Biotites from the various biotite granite phases of the Afu Complex have been analyzed as part of a study of the geochemistry of the rocks. Some of these granite phases are associated with tin-tungsten mineralization and this paper deals with the accumulation of tin in the biotite as a prelude to determining if there is any difference between mineralized and barren granites.

Geologic Setting and Petrography

The Afu Younger Granite Complex is the southernmost of the Nigerian ring structures (Fig. 1) emplaced 144 ± 2 m.y. ago (Bowden et al., 1976). The complex is elliptical in outline and about 50 km in maximum diameter. It shows broad similarities to the other younger granite complexes emplaced during the Early to Late Jurassic (Jacobson et al., 1958; Macleod et al., 1971).

The Afu Complex is made up of high-level anorogenic granites—mainly biotite granites (units 4-11, Fig. 2)—and minor quartz porphyry emplaced within

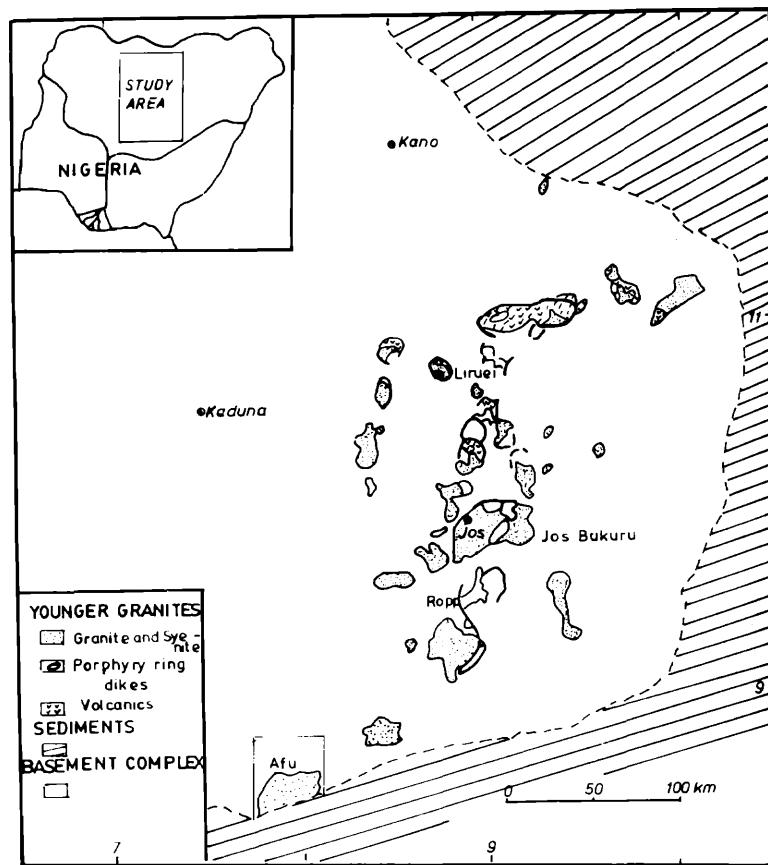


FIG. 1. Location of the Afu Younger Granite Complex, central Nigeria, and generalized geologic map of the ring complexes in Nigeria.

Precambrian-Paleozoic basement gneisses and older granites but exposed beneath the Cretaceous-Recent sedimentary cover of the lower Benue Valley to the south (Fig. 2).

Petrographically the biotite granites which are the prevailing rock types are composed mainly of quartz, K-feldspar, albite, and biotite. Fluorite, zircon, cryolite, magnetite, and hematite are the most commonly observed accessory minerals. Cassiterite, columbite, thorite, and monazite may also be present as accessory minerals.

The average modal composition of the biotite granites is 30 to 35 percent quartz, 42 to 56 percent K-feldspar, 5 to 20 percent albite, and about 2 to 5 percent biotite (Table 1). Generally any single intrusive phase of biotite granite shows a good consistency in mineral composition, although the degree of albitization varies considerably. The modal percentage of albite increases from the early biotite granites to the latest ones, which may be due to albitization or large-scale exsolution phenomenon.

Also the early biotite granites appear to be more biotite rich than the late biotite granites (Table 1).

The composition of the Odegi albite granite (unit 11, Fig. 2) which forms a small unit at the center of the complex is made up of 35 percent quartz, 34 percent albite, 25 percent orthoclase, 2 percent biotite, and 4 percent accessory zircon, cryolite, and columbite. Thorite, monazite, and xenotime are less abundant. It probably represents a portion of the Odegi biotite granite (unit 8, Fig. 2) which was highly reworked by postmagmatic fluids as reflected by its distinctive geochemical patterns.

The quartz porphyry is composed of large crowded phenocrysts of orthoclase, up to 1 cm in maximum dimension, and rare brown pyroxene, set in a finer grained groundmass of interlocking alkali feldspar, quartz, green amphibole, and altered fayalite. The groundmass is granophytic in texture, with a complex graphic intergrowth of quartz and feldspar. Accessory minerals include iron oxides, zircon, and allanite.

Geochemical Characteristics of the Granites

Table 2 shows the average composition of the intrusive units of biotite granite. The major element variations among the biotite granite phases are not

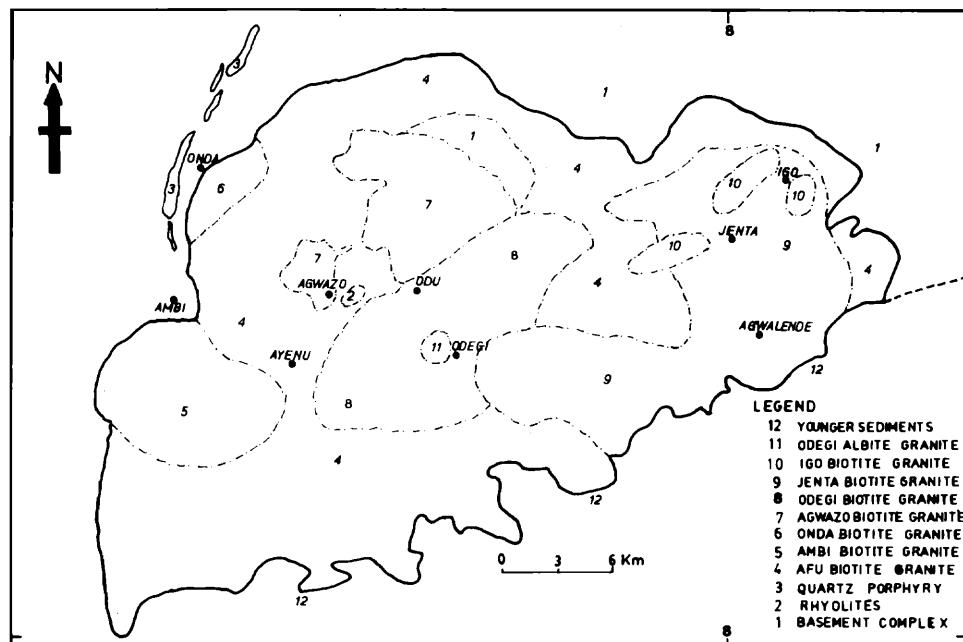


FIG. 2. Geologic sketch map of the Afu Younger Granite Complex. Units 4 through 7 are barren biotite granites; units 8 through 11 are tin-bearing biotite granite phases.

significant (Table 2), a feature which is typical of rocks from the younger granite province of Nigeria. However, compared with the average granites of Nockolds (1954) they may be regarded as high silica alkali granites.

In terms of normative composition all the biotite granites are peraluminous with corundum in the norm and are also closely grouped over the low-temperature minimum of the feldspar-quartz cotectic of the albite-orthoclase-quartz normative diagram of Tuttle and Bowen (1958).

Furthermore, the compositions of the feldspars are very near the end members of albite and orthoclase, indicating reequilibrium at perhaps unusually low temperatures. In fact the application of the compositions of the feldspars to the determinative curves of Whitney and Stormer (1977) yields a 1-kb crystallization temperature range of 600° to 350°C for the various phases in the Afu Complex.

The average concentrations of trace elements for these intrusive units (Table 2) indicate that the Sn, Nb, W, Li, Rb, F, Zn, Th, and Y values are above the average values for low Ca granites (Turekian and Wedepohl, 1961), whereas the Ba, Sr, and Mn values are lower than the average low Ca granites of Turekian and Wedepohl (1961). The mean value of Sn for the biotite granites is 26 ppm which is more than eight times the world average value of 3 ppm for low Ca granites (Turekian and Wedepohl, 1961). Nb, Th, and Y show similar distribution patterns and are closely associated with tin mineralization (Imeokparia, 1982).

The Odegi albite biotite granite shows enhanced levels of Sn, Th, Zr, Nb, Li, and F (Table 2); this probably indicates that an alkaline volatile fluid was associated with this granite phase.

Pertinent geochemical contrasts between barren and mineralized granites in the Afu Complex are summarized in Table 3. Olade (1980) has defined barren granites as those that may contain a certain amount of tin but do not give rise to tin mineralization and mineralized granites as those that contain anomalous tin and give rise to economic tin mineralization. The Afu tin-bearing granites are characterized by higher concentrations of Sn, Nb, W, Li, F, Rb, Th, U, and Y than the barren granites. Thus, they are exceedingly fractionated rocks and are similar to most tin-bearing granitic rocks (Hesp, 1971; Flinter, 1971; Tischendorf, 1973).

The Afu mineralized granites also show the highest degree of variability in their trace element content, which is regarded as a reflection of mineralization (Beus and Gregorian, 1975). The considerably enhanced Li and F values in the mineralized granites may in part reflect the genetic association of these granites with Li- and F-rich greisens and albitized granites. K/Rb and Ba/Rb ratios are also considerably lower in the mineralized granites, suggesting that Rb is considerably enriched during postmagmatic processes related to mineralization.

Method of Biotite Investigation

A total of 36 samples from the Afu Complex was selected for biotite analysis. Rock samples were pol-

TABLE I. Modal Analyses of Rocks from the Afu Younger Granite Complex

Sample no.	Early biotite granite phase												Late biotite granite phases											
	Afu				Ambi				Onda				Agbarzo											
	110	23	105	101	103	104	119	120	121	113	67	58	60	59	9	3°	4°	6°	51°	93	107	108		
Quartz	33.00	34.50	34.25	34.02	33.36	34.21	35.45	35.40	35.54	83	67	58	60	59	9	3°	4°	6°	51°	93	107	108		
Orthoclase (microperthite)	54.81	55.20	55.06	56.54	56.58	56.56	53.60	54.58	54.03	35.16	34.96	35.53	35.42	35.12	34.62	36.43	37.56	37.50	36.50	34.61	34.51	35.06		
Albite (oligoclase)	6.71	5.00	6.40	6.02	6.37	5.68	6.55	6.20	7.00	2.80	2.45	2.00	2.20	3.00	1.50	2.50	3.24	2.40	2.15	1.50	2.92	3.00	2.90	
Biotite	4.71	4.58	3.60	3.02	3.32	3.20	4.00	3.50	2.97	Iron oxide	0.10	0.11	0.10	0.12	0.20	0.15	0.22	0.24	0.12	0.22	0.20	0.10	0.20	
Iron oxide	0.22	0.40	0.20	0.24	0.20	0.11	0.14	0.10	0.20	Zircon	0.50	0.30	0.45	0.11	0.12	0.21	0.11	0.12	0.11	0.12	0.11	0.11	0.11	
Zircon	0.05	0.02	0.04	0.05	0.05	0.03	0.15	0.10	0.15	Fluorite + cryolite	0.40	0.50	0.60	0.10	0.30	0.30	0.10	0.81	1.42	1.20	2.50	0.15	0.40	0.05

° Odegi albite granite

TABLE 2. Average Composition of Intrusive Units, Afu Younger Granite Complex

	Early phases			Late phases			Odegi albite biotite granite
	Afu	Ambi	Onda	Agwarzro	Odegi	Jenta	Igo
Major elements							
SiO ₂	72.90	73.42	74.48	75.80	74.90	75.65	76.20
TiO ₂	0.32	0.16	0.05	0.10	0.08	0.06	0.05
Al ₂ O ₃	12.41	13.10	13.16	12.60	12.35	12.41	12.14
Fe ₂ O ₃	1.80	0.72	0.46	0.55	0.45	0.43	0.49
FeO	1.71	1.79	1.03	0.64	0.82	0.81	0.71
MgO	0.34	0.21	0.18	0.08	0.04	0.05	0.04
CaO	0.89	0.73	0.63	0.51	0.50	0.56	0.52
Na ₂ O	4.11	4.18	4.53	4.40	4.67	4.76	4.30
K ₂ O	4.94	5.19	5.26	4.93	5.25	4.74	5.82
P ₂ O ₅	0.04	0.03	0.02	0.01	0.01	trace	3.77
Trace elements							
Rb	132 (190-450)	375 (320-520)	398 (320-450)	565 (350-725)	654 (420-1,500)	738 (420-1,150)	844 (400-1,000)
Ba	343 (160-625)	142 (100-200)	105 (30-180)	157 (140-165)	65 (20-184)	72 (5-160)	57 (5-120)
Sr	30 (10-70)	18 (8-40)	6 (2-101)	16 (5-25)	8 (2-20)	7 (2-20)	7 (2-20)
Li	24 (4-44)	58 (16-116)	130 (60-196)	41 (20-72)	163 (24-300)	227 (44-884)	230 (68-720)
F	2,440 (900-5,000)	3,780 (1,800-4,080)	4,850 (1,080-6,900)	3,560 (2,080-5,200)	11,900 (1,800-34,000)	11,800 (2,560-32,000)	8,510 (3,200-19,000)
Ga	35 (24-59)	35 (27-42)	33 (26-42)	39 (33-42)	41 (19-54)	50 (32-65)	50 (34-60)
Mn	298 (84-608)	128 (52-204)	88 (172-120)	125 (60-232)	108 (41-180)	119 (42-220)	97 (60-312)
Zn	229 (44-444)	67 (32-132)	111 (58-120)	119 (72-184)	129 (44-192)	207 (48-586)	98 (56-268)
V	20 (10-45)	16 (8-20)	12 (8-20)	21 (18-28)	18 (8-23)	15 (5-20)	18 (8-22)
Sn	12 (2-30)	28 (5-30)	16 (5-25)	37 (20-50)	40 (5-55)	74 (10-470)	50 (10-180)
W	133 (18-400)	220 (120-400)	120 (56-200)	109 (72-120)	205 (72-500)	239 (72-900)	674 (60-1,080)
Nb	76 (29-116)	104 (70-200)	150 (112-200)	91 (48-136)	265 (88-709)	253 (80-500)	160 (30-200)
Element ratios							
K/Rb	139	117	96	76	72	62	50
Ba/Rb	1.00	0.38	0.25	0.29	0.14	0.10	0.09
Rb/Sr	14	24	83	58	96	164	148

Range of trace elements in parentheses

ished and their biotites analyzed by a Cambridge Stereoscan electron microprobe with an accelerating voltage of 15 kV, a sample current of 20 μ A, and a beam diameter of about 2 μ .

Analyses were performed using two of the four spectrometers in the series: Fe, Mg; Na, K; Si, Ca; Al, Ti; Mn, Cr; and Sn, F. Indexed biotite grains in the polished thin sections were occupied at 6 to 10 points to give the corresponding individual analyses. Pure metal standards were used for Sn, Fe, and Cr. Wollastonite was used as a standard for Ca and Si, jadeite for A and Na. Synthetic standards were utilized for K (microcline), F (LiF), and Mg (synthetic MgO). Rhodonite was used for Mn and rutile for Ti. Quantitative analytical data were processed by computer through a modified version of the ZAF correction program MAGIC IV written by Colby (1968 and unpub. rept.) as reviewed by Beaman and Isasi (1970). The precision obtained for the data is within twice the standard deviation of the mean, suggesting that the mean variation displayed by the data is real.

Chemistry of the Biotites

The major element concentrations and structural formulas of the analyzed biotites are given in Table 4A and B.

The major element chemistry of the micas shows them to be typical granite biotites. Plotted in the Al_2O_3 -total iron-MgO diagram the biotites fall in the field of coexistence with either muscovite or hornblende (Nockolds, 1947) and in the magmatic field defined by Gokhale (1968).

The biotites are all rich in Fe and low in Mg. The relationship between Fe and Mg in the biotites showed two possible trends. Whereas in the barren biotites there is a negative correlation ($r = -0.56$) between Fe and Mg, in the tin-bearing or mineralized biotites a positive correlation ($r = 0.56$) exists between Fe and Mg. The antithetic relationship of the two oxides in the barren biotites confirms the simple substitution of Fe^{+2} and Mg^{+2} in the octahedral site of the biotite (annite) and may reflect a crystallization of other ferromagnesian minerals before the crystallization of the biotite. The pattern of behavior in the mineralized biotites may be attributed to leaching of both Fe and Mg by mineralizing fluids or substitution for both by octahedral Al.

TiO_2 shows a decreasing value from 4.77 wt percent in the Afu biotites to 0.19 wt percent in the albitized Odegi biotites.

The biotites associated with mineralization generally have a lower TiO_2 content (2.15 – 0.19 wt %) relative to the barren ones (4.77 – 1.55 wt %), which may be a reflection of a lower crystallization temperature for the mineralized biotites.

The mineralized biotites are also strongly enriched in F, Al, and Si with respect to biotites from the

TABLE 3. Means, Ranges, and Coefficient of Variation (C.V.) of Trace Elements in Tin-Mineralized and Tin-Barren Granites, Afu Complex

	Tin-mineralized granites (n = 106)		Tin-barren granites (n = 74)	
	Mean and range	C.V. %	Mean and range	C.V. %
Sn	54 (5-470)	98	17 (2-50)	59
Nb	229 (30-1,208)	94	92 (29-200)	41
Rb	793 (400-2,750)	50	351 (190-725)	28
Zr	234 (100-2,440)	121	241 (150-420)	28
Y	240 (88-520)	34	170 (30-420)	48
Th	55 (19-425)	72	39 (20-60)	27
Sr	8 (2-12)	140	24 (2-80)	68
Ba	63 (5-184)	62	226 (30-625)	49
Ga	49 (19-84)	22	35 (23-59)	22
Zn	177 (44-696)	72	127 (32-444)	65
Mn	106 (40-312)	41	189 (52-608)	64
Ti	395 (30-807)	38	648 (285-1,145)	29
V	15 (5-23)	23	18 (8-45)	39
La	78 (20-780)	112	79 (35-240)	46
Ce	277 (68-500)	27	293 (143-400)	20
Li	222 (24-992)	77	48 (4-196)	98
F	11,196 (1,800-160,000)	152	2,995 (900-6,900)	41
W	325 (28-1,680)	96	142 (18-400)	72
Pb	43 (15-100)	33	36 (12-70)	38
U	22 (2-235)	163	10 (2-30)	57

barren rocks. They probably also contain significant amounts of Li, because Jacobson et al. (1958) reported 0.77 to 1.88 wt percent Li_2O in the biotites from the Zn-Sn-mineralized Liruei Complex.

TABLE 4A. Major Element Content of Biotites (weight percent), Afu Complex (Barren Rocks)

Specimen no.	1 Cl-110-A	2 Cl-91-A	3 Cl-89-A	4 Cl-86-A	5 Cl-105-A	6 Cl-101-AM	7 Cl-103-AM	8 Cl-119-ON	9 Cl-120-ON	10 Cl-121-ON	11 Cl-123-A	12 Cl-104-AM	13 Cl-09-AG
SiO ₂	34.64 ± 0.50	32.63 ± 0.29	35.94 ± 0.60	39.58 ± 0.77	35.76 ± 1.37	35.11 ± 0.60	37.14 ± 1.15	35.10 ± 0.99	34.72 ± 1.69	34.46 ± 0.78	35.45 ± 0.50	38.75 ± 0.60	34.79 ± 0.50
Al ₂ O ₃	11.55 ± 0.24	12.93 ± 0.86	11.71 ± 0.40	17.89 ± 0.78	12.29 ± 0.57	15.28 ± 0.73	14.68 ± 1.00	18.58 ± 0.95	14.93 ± 1.06	14.34 ± 0.97	12.10 ± 0.78	14.01 ± 0.40	14.57 ± 0.24
Fe as FeO	36.74 ± 1.08	34.26 ± 0.82	28.91 ± 0.75	24.01 ± 0.98	32.06 ± 1.12	29.32 ± 0.12	29.42 ± 1.80	26.92 ± 1.04	34.31 ± 1.44	34.71 ± 0.98	32.68 ± 1.01	29.33 ± 0.75	31.19 ± 1.08
MgO	1.23 ± 0.08	2.15 ± 0.20	6.35 ± 0.89	4.91 ± 0.61	3.05 ± 0.20	2.47 ± 0.84	2.95 ± 0.70	0.02 ± 0.02	0.05 ± 0.03	0.05 ± 0.03	3.19 ± 0.08	3.16 ± 0.05	2.49 ± 0.03
CaO	0.00	0.03 ± 0.01	1.65 ± 0.25	0.12 ± 0.10	0.00 ± 0.0	0.05 ± 0.00	0.06 ± 0.04	0.01 ± 0.05	0.00	0.00	0.00	0.04 ± 0.01	0.00
Na ₂ O	0.14 ± 0.07	0.08 ± 0.01	0.42 ± 0.03	0.07 ± 0.02	0.09 ± 0.10	0.15 ± 0.19	0.08 ± 0.09	0.21 ± 0.09	0.12 ± 0.07	0.12 ± 0.06	0.13 ± 0.05	0.07 ± 0.05	0.05 ± 0.02
K ₂ O	8.74 ± 0.28	8.01 ± 0.50	6.95 ± 0.60	6.54 ± 1.58	8.89 ± 1.22	8.96 ± 0.12	8.47 ± 1.11	9.58 ± 0.13	9.04 ± 0.59	9.05 ± 0.60	9.39 ± 0.70	9.34 ± 0.36	8.94 ± 0.24
TiO ₂	4.77 ± 0.74	4.06 ± 0.20	3.33 ± 0.30	1.91 ± 0.67	2.98 ± 0.30	2.49 ± 0.85	2.87 ± 0.67	1.55 ± 0.76	2.13 ± 0.64	2.23 ± 0.50	3.09 ± 0.54	3.10 ± 0.48	2.74 ± 0.64
MnO	1.01 ± 0.30	0.63 ± 0.05	0.50 ± 0.02	0.60 ± 0.30	0.58 ± 0.12	0.65 ± 0.20	0.62 ± 0.16	0.65 ± 0.20	0.62 ± 0.20	0.63 ± 0.14	0.60 ± 0.03	0.65 ± 0.01	0.65 ± 0.01
F	0.23 ± 0.14	0.61 ± 0.06	0.39 ± 0.03	0.51 ± 0.31	0.32 ± 0.09	0.70 ± 0.13	0.61 ± 0.05	2.94 ± 0.31	0.94 ± 0.38	2.23 ± 0.27	0.35 ± 0.01	0.80 ± 0.13	0.69 ± 0.14
Sn	0.02 ± 0.01	0.005 ± 0.005	0.01 ± 0.02	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.02	0.01 ± 0.01	0.04 ± 0.02	0.02 ± 0.02	0.02 ± 0.01	0.01 ± 0.02	0.01 ± 0.01	0.02 ± 0.01
Total	98.87	95.40	96.16	96.05	95.19	95.91	95.60	96.88	97.85	96.68	99.24	96.12	
Fe _{total} /(Fe _{total} + Mg)	0.97	0.94	0.84	0.93	0.93	0.92	0.93	0.99	0.998	0.99	0.92	0.904	0.926

Structural formulas (calculated on the basis of 22 oxygens)

Si	5.652	5.839	5.616	6.179	5.810	5.750	5.874	5.751	5.712	5.716	5.751	5.994	5.761
Al(IV)	2.183	2.161	2.156	1.821	2.190	2.250	2.126	2.249	2.288	2.284	2.289	2.006	2.239
Al(VI)	0.00	0.123	1.472	0.163	0.666	0.611	1.339	0.608	0.520	0.065	0.549	0.560	
Ti	0.585	0.569	0.392	0.224	0.364	0.308	0.341	0.191	0.264	0.278	0.377	0.360	0.336
Fe	5.013	4.653	3.712	3.292	4.359	4.015	3.892	3.693	4.723	4.815	4.434	3.794	4.252
Mg	0.229	0.681	1.476	0.443	0.738	0.603	0.695	0.004	0.013	0.012	0.772	0.729	0.599
Mn	0.138	0.088	0.066	0.083	0.080	0.089	0.086	0.089	0.086	0.088	0.083	0.089	
Ca	0.000	0.013	0.276	0.020	0.009	0.009	0.010	0.002	0.000	0.000	0.000	0.006	0.000
Na	0.043	0.009	0.128	0.021	0.028	0.047	0.025	0.066	0.038	0.043	0.023	0.015	0.14
K	1.818	1.937	1.286	1.296	1.844	1.657	1.709	2.003	1.897	1.915	1.944	1.843	1.858

TABLE 4B. Major Element Content of Biotites (weight percent), Afu Complex (Mineralized Rocks)

Specimen no.	¹ Cl-93-OD	² Cl-107-OD	³ Cl-108-OD	⁴ Cl-20-J	⁵ Cl-69-J	⁶ Cl-77-J	⁷ Cl-73-J	⁸ Cl-83-J
SiO ₂	39.91 ± 0.56	35.60 ± 0.65	34.84 ± 0.64	35.93 ± 1.36	41.67 ± 0.98	35.83 ± 1.19	33.94 ± 0.74	35.20 ± 0.60
Al ₂ O ₃	13.05 ± 1.85	15.02 ± 0.36	18.58 ± 0.66	15.13 ± 0.85	19.82 ± 0.86	17.26 ± 0.80	15.93 ± 0.90	19.06 ± 0.76
Fe as FeO	30.87 ± 3.05	32.16 ± 0.67	28.75 ± 1.07	28.87 ± 1.05	23.02 ± 0.78	30.00 ± 2.13	30.11 ± 0.97	28.66 ± 0.98
MgO	0.73 ± 0.40	0.12 ± 0.02	0.20 ± 0.02	0.02 ± 0.01	0.05 ± 0.02	0.06 ± 0.01	0.28 ± 0.03	0.19 ± 0.02
CaO	0.01 ± 0.02	0.00	0.00	0.04 ± 0.09	0.00	0.00	0.00	0.00
Na ₂ O	0.24 ± 0.12	0.21 ± 0.05	0.23 ± 0.10	0.29 ± 0.11	0.07 ± 0.01	0.12 ± 0.10	0.17 ± 0.05	0.19 ± 0.12
K ₂ O	8.91 ± 1.18	9.41 ± 0.11	9.41 ± 0.28	8.83 ± 1.16	9.64 ± 0.28	9.44 ± 0.14	9.56 ± 0.10	9.62 ± 0.26
TiO ₂	1.87 ± 0.34	2.15 ± 0.21	1.88 ± 0.27	1.26 ± 0.25	0.83 ± 0.16	1.41 ± 0.26	2.60 ± 0.78	1.61 ± 0.44
MnO ₂	0.50 ± 0.05	0.63 ± 0.06	0.47 ± 0.05	0.65 ± 0.04	0.55 ± 0.01	0.60 ± 0.02	0.62 ± 0.20	0.52 ± 0.05
F	2.69 ± 0.98	2.74 ± 0.74	2.36 ± 0.62	3.09 ± 0.63	4.03 ± 0.90	4.82 ± 0.66	2.32 ± 0.27	3.21 ± 0.32
Sn	0.04 ± 0.02	0.04 ± 0.01	0.04 ± 0.03	0.04 ± 0.01	0.05 ± 0.04	0.04 ± 0.02	0.03 ± 0.01	0.04 ± 0.02
Total	98.82	98.08	96.76	94.10	99.73	99.10	95.56	98.30
Fe _{total} /(Fe _{total} + Mg)	0.980	0.997	0.995	0.99	0.998	0.998	0.992	0.995
Structural formulas (calculated on the basis of 22 oxygens)								
Si	6.270	5.810	5.640	6.054	6.315	5.778	5.665	5.648
Al(IV)	1.730	2.190	2.360	1.946	1.685	2.222	2.335	2.352
Al(VI)	0.771	0.699	1.185	1.055	1.855	1.099	0.799	1.253
Ti	0.231	0.264	0.228	0.159	0.095	0.173	0.326	0.195
Fe	4.199	4.389	3.891	4.073	2.918	4.098	4.203	3.845
Mg	0.175	0.029	0.048	0.005	0.012	0.016	0.069	0.046
Mn	0.065	0.087	0.064	0.089	0.076	0.083	0.087	0.075
Ca	0.002	0.000	0.000	0.007	0.000	0.000	0.001	0.000
Na	0.075	0.068	0.071	0.080	0.019	0.037	0.053	0.060
K	1.667	1.959	1.942	1.896	1.863	1.968	2.036	1.970

TABLE 4B—(Continued)

Specimen no.	9 G1-113-J	10 G1-55-I	11 G1-57-I	12 G1-58-I	13 G1-59-I	14 G1-60-I	15 G1-62-I	16 G1-64-I
SiO ₂	35.88 ± 1.21	34.30 ± 0.80	36.37 ± 1.73	35.77 ± 0.73	37.51 ± 2.57	42.24 ± 0.56	36.79 ± 2.33	37.25 ± 2.16
Al ₂ O ₃	16.67 ± 0.41	17.77 ± 0.38	19.47 ± 0.28	18.00 ± 0.66	19.03 ± 1.39	19.62 ± 0.66	17.45 ± 1.18	18.42 ± 0.91
Fe as FeO	29.30 ± 2.13	29.54 ± 1.09	27.98 ± 0.80	28.10 ± 1.53	26.25 ± 3.78	20.64 ± 1.00	29.93 ±	27.59 ± 2.85
MgO	0.04 ± 0.02	0.30 ± 0.09	0.28 ± 0.02	0.17 ± 0.03	0.16 ± 0.08	0.08 ± 0.02	0.07 ± 0.02	0.05 ± 0.01
CaO	0.00	0.00	0.02 ± 0.01	0.00	0.00 ± 0.00	0.00	0.00	0.00
Na ₂ O	0.19 ± 0.10	0.14 ± 0.06	0.17 ± 0.03	0.23 ± 0.08	0.27 ± 0.14	0.14 ± 0.02	0.14 ± 0.08	0.20 ± 0.07
K ₂ O	9.47 ± 0.16	9.41 ± 0.29	9.47 ± 0.13	9.46 ± 0.15	9.10 ± 1.18	8.84 ± 0.56	9.83 ± 0.32	9.79 ± 0.24
TiO ₂	1.49 ± 0.15	2.39 ± 0.30	1.14 ± 0.27	1.58 ± 0.36	1.46 ± 0.73	0.18 ± 0.01	1.31 ± 0.74	1.20 ± 0.51
MnO ₂	0.30 ± 0.01	0.63 ± 0.02	0.47 ± 0.02	0.62 ± 0.01	0.30 ± 0.05	0.30 ± 0.01	0.63 ± 0.03	0.60 ± 0.03
F	2.89 ± 0.59	2.89 ± 0.25	1.86 ± 0.20	3.37 ± 0.63	3.55 ± 1.29	5.52 ± 0.67	3.40 ± 0.20	3.55 ± 0.50
Sn	0.05 ± 0.02	0.06 ± 0.03	0.05 ± 0.02	0.06 ± 0.02	0.05 ± 0.05	0.10 ± 0.09	0.05 ± 0.02	0.04 ± 0.02
Total	96.28	99.43	98.51	97.36	97.73	97.66	97.41	98.03
F _{total} /(F _{total} + Mg)	0.999	0.990	0.995	0.995	0.995	0.996	0.998	0.998

Structural formulas (calculated on the basis of 22 oxygens)

Si	5.878	5.594	5.76	5.797	5.928	6.213	5.965	5.918
Al(IV)	2.122	2.406	2.240	2.203	2.072	1.787	2.035	2.082
Al(VI)	1.097	1.010	1.395	1.236	1.472	1.616	1.298	1.369
Ti	0.184	0.293	0.135	0.193	0.174	0.019	0.160	0.143
Fe	4.015	4.030	3.711	3.808	3.472	2.515	3.695	3.666
Mg	0.009	0.072	0.065	0.40	0.038	0.018	0.016	0.013
Mn	0.036	0.087	0.076	0.087	0.036	0.037	0.087	0.083
Ca	0.000	0.001	0.004	0.000	0.009	0.018	0.000	0.001
Na	0.061	0.043	0.046	0.071	0.084	0.040	0.045	0.062
K	1.979	1.958	1.914	1.955	1.836	1.660	2.033	1.984

TABLE 4B—(Continued)

Specimen no.	17 CI-3-AB°	18 CI-4-AB°	19 CI-6-AB°	20 CI-51-AB°	21 CI-152-AB°	22 CI-111-IG	23 CI-67-J
SiO	46.05 ± 0.84	39.71 ± 1.06	45.05 ± 0.70	43.45 ± 0.62	44.99 ± 1.0	35.60 ± 0.95	35.72 ± 1.05
Al ₂ O ₃	17.86 ± 0.20	13.82 ± 0.83	18.43 ± 0.46	15.66 ± 0.52	16.81 ± 0.70	17.21 ± 0.19	19.38 ± 0.18
Fe as FeO	15.20 ± 1.08	29.08 ± 2.03	13.94 ± 0.56	15.66 ± 0.78	15.05 ± 0.78	30.05 ± 1.08	24.54 ± 1.75
MgO	0.01 ± 0.02	0.00	0.02 ± 0.01	0.00	0.00	0.04 ± 0.02	0.10 ± 0.03
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.17 ± 0.03	0.22 ± 0.12	0.22 ± 0.02	0.21 ± 0.02	0.21 ± 0.01	0.18 ± 0.13	0.24 ± 0.17
K ₂ O	10.08 ± 0.24	9.27 ± 0.07	10.12 ± 0.19	9.84 ± 0.20	10.20 ± 0.22	9.34 ± 0.18	9.31 ± 0.90
TiO ₂	0.10 ± 0.02	0.19 ± 0.04	0.22 ± 0.02	0.24 ± 0.01	0.14 ± 0.02	1.82 ± 0.10	1.14 ± 0.73
MnO ₂	trace	trace	trace	trace	trace	0.65 ± 0.03	0.30 ± 0.01
F	6.78 ± 0.46	4.91 ± 1.30	6.62 ± 0.54	6.77 ± 0.62	5.91 ± 0.52	3.40 ± 0.34	7.21 ± 0.34
Sn	0.06 ± 0.01	0.04 ± 0.01	0.04 ± 0.03	0.08 ± 0.05	0.07 ± 0.03	0.03 ± 0.02	0.05 ± 0.02
Total	91.59	97.26	94.65	91.91	93.38	97.73	97.81
Fe _{total} /(Fe _{total} + Mg)	0.999	1.000	0.999	1.00	1.00	0.999	0.998

- Albited rocks

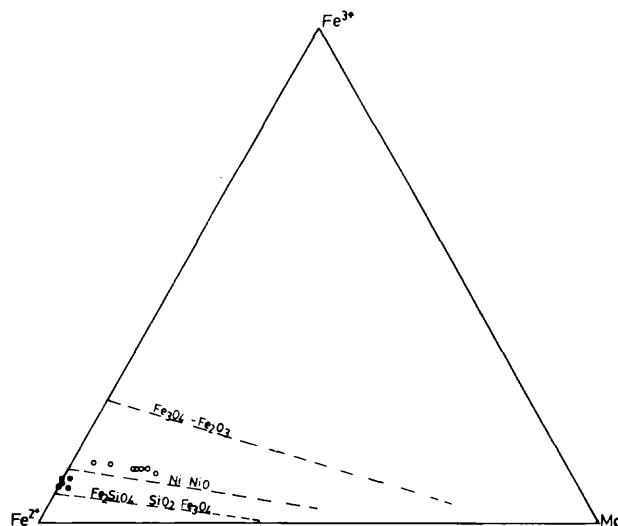


FIG. 3. Fe^{+3} - Fe^{+2} -Mg diagram of the Afu Complex biotites. Dashed lines = compositions of biotites in the system $\text{KFe}_3^{+3}\text{AlSi}_3\text{O}_{12}(\text{H}^{-1})$ - $\text{KFe}_3^{+2}\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ - $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ (after Wones and Eugster, 1965). Circles = barren biotites; dots = mineralized biotites.

The mica from the mineralized rocks, particularly from the albited rocks, has an approximate composition between muscovite and Fe-Al celadonite, $\text{KFeAlSi}_4\text{O}_{12}\text{H}_2$. Velde (1965, 1972), from experimental studies of micas of similar compositions, indicated that this mica in an F-free system (which the mineralized rocks are not) at 2 kb would be stable only below 200°C.

The $\text{Fe}_{\text{total}}/(\text{Fe}_{\text{total}} + \text{Mg})$ ratios of all the biotites are within the range of 0.92 to 1.00 except for sample 89 from the Afu biotite granite which is 0.84. The values of this ratio are greater than 0.95 (maximum 0.99+) for all the biotites associated with mineralization. The trend of the Afu Complex biotites within the compositional triangle Fe^{+3} - Fe^{+2} -Mg rather closely parallels Wones and Eugster's (1965) estimated composition of biotite solid solutions in the ternary system $\text{KFe}_3^{+3}\text{AlSi}_3\text{O}_{12}(\text{H}^{-1})$ - $\text{KFe}_3^{+2}\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ - $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ which are stable at oxygen fugacities controlled by individual buffer equilibria (Fig. 3). The correlation suggests that compositions of the biotites from the barren phases are defined by oxygen fugacities slightly greater than those of the N1-N10 buffer or below those of the hematite-magnetite buffer (Wones and Eugster, 1965). However, those from the mineralized rocks plot below those of N1-N10 buffer biotites.

Thus, the biotite compositions suggest that oxygen fugacities of the Afu magmas were defined by buffer reactions during crystallization, that is, f_{O_2} decreased with decreasing temperature. Volatiles were important constituents of the fluid phase as indicated by

the high contents of Rb, Li, and F in the rocks. The presence of Li and/or B may add to the effect of F alone on the solidus temperature, as the presence of either element also reduces solidus temperatures by partitioning strongly into the melt and modifying it structurally (Chorlton and Martin, 1978; Wyllie and Tuttle, 1964).

The relatively high iron magnesium ratios in the tin-bearing phases are in accordance with the suggested low temperature of the mineralizing fluids.

The Sn Content of the Biotites

The results obtained from microprobe analysis of the biotite samples are plotted on a generalized map of the complex (Fig. 3). The values range from 50 to 1,000 ppm Sn and average 500 ppm for the biotites from the tin-mineralized granites and 150 ppm for the biotites from the barren rocks.

The mean Sn content of biotites from the barren samples is higher than the average values of 67 and 64 ppm given by Jedwab (1955) and Groves (1972) for unmineralized biotites from France and Australia, respectively. Similarly the results are significantly higher than those reported for some Russian biotites (Barsukov, 1957; Ivanova and Butuzova, 1968) and British biotites (Bradshaw, 1967). The high Sn values in the biotites of barren granites compared with biotites from most other granitic rocks of similar composition may be a reflection of the general high background content of Sn and the potential ore-bearing potential of the complex.

The mean Sn content in biotites of the mineralized granites (500 ppm) is significantly higher at the 95 percent level than those from the barren samples. Groves (1972) reported a similar average content of 556 ppm in biotites from mineralized rocks in the Blue Tier batholith of Tasmania. Similar high Sn values in biotites from mineralized granites have been documented by Rattigan (1963), Putman and Burnham (1963), Ivanova (1963), and Bradshaw (1967), in spite of differences in analytic techniques.

Two areas of relatively higher Sn content can be outlined (Fig. 4): the area around Odegi and the northeastern parts of the Afu Complex (Jenta and Igo areas). South and west of Odegi, the biotites have a low Sn content corresponding to areas devoid of mineralization.

The Sn content of biotites of the partially greisenized granite and greisen veins average 300 and 100 ppm, respectively. These values seem to be lower than those of the associated primary biotites of the unaltered mineralized granites and may indicate leaching by hydrothermal fluids and subsequent deposition in veins. The extraction of tin from biotite has also been noted by Tischendorf et al. (1971). This is believed to be one of the several modes for Sn concentration

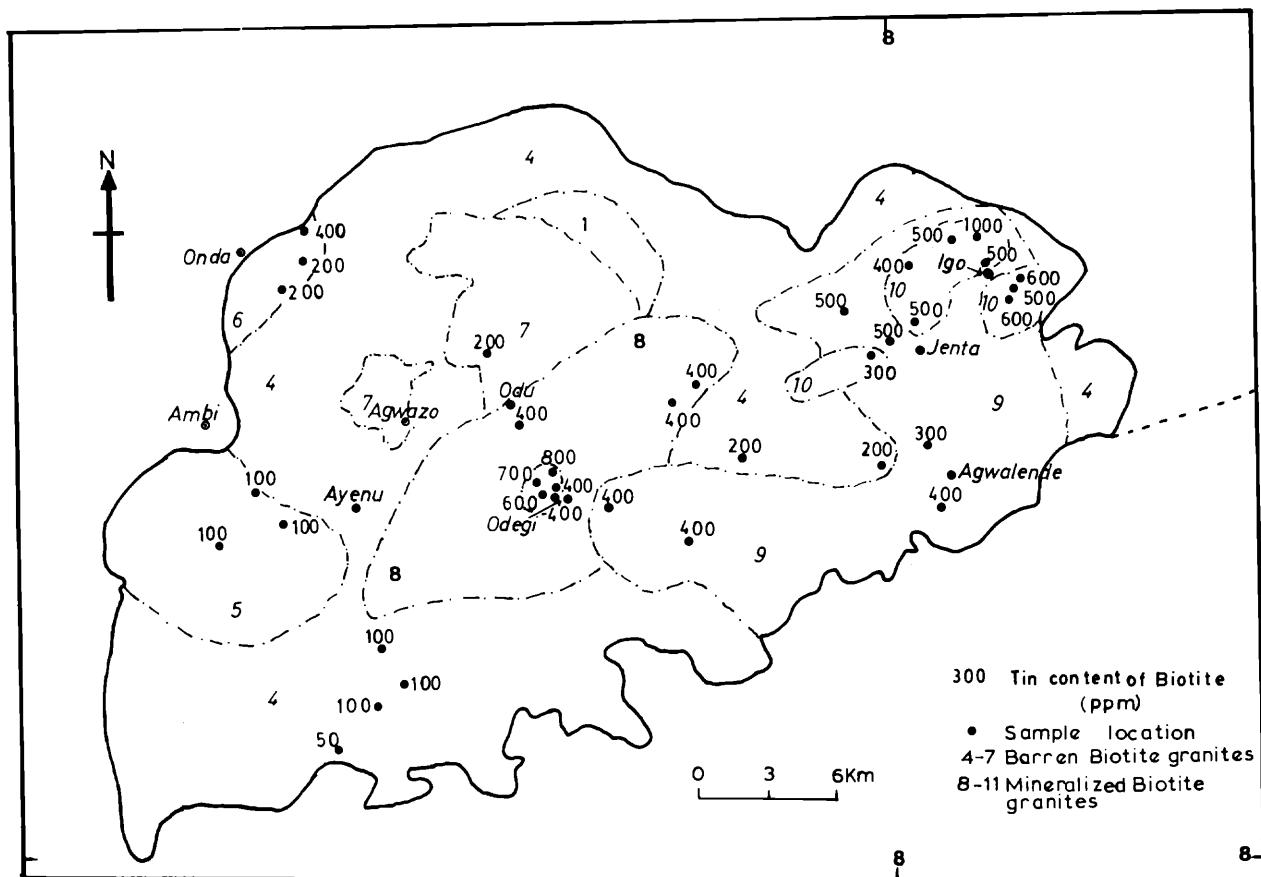


FIG. 4. Sn content of biotites plotted on a generalized map of the Afu Complex. Units 4 through 7 are barren phases; units 8 through 11 are mineralized phases; unit 1 is the basement complex.

in veins and fractures. According to Tischendorf (1973) tin and other elements are set free when dark micas are altered to form sericite or chlorite by late or postmagmatic processes. These elements are subsequently made available for mineralization in the veins.

Figure 5 shows the dependence of the amount of tin present in the biotite samples on the concentration of these biotites in the granite. A negative correlation ($r = -0.56$) is observed, and it is shown that there is a distinction between mineralized and nonmineralized granites. There is also a significant positive correlation ($r = +0.77$) between the Sn in biotite as a percentage of total Sn and the modal percent of biotite.

The combination of the positive correlation between tin in granite and biotite ($r = +0.60$) and the negative correlation between tin in granite and the modal percentage of biotite (Fig. 6) indicates that higher quantities of tin are concentrated in smaller amounts of the biotite. However, the amount of Sn in the mineralized granites is such that the tin-rich biotites contain a smaller percentage of the total Sn

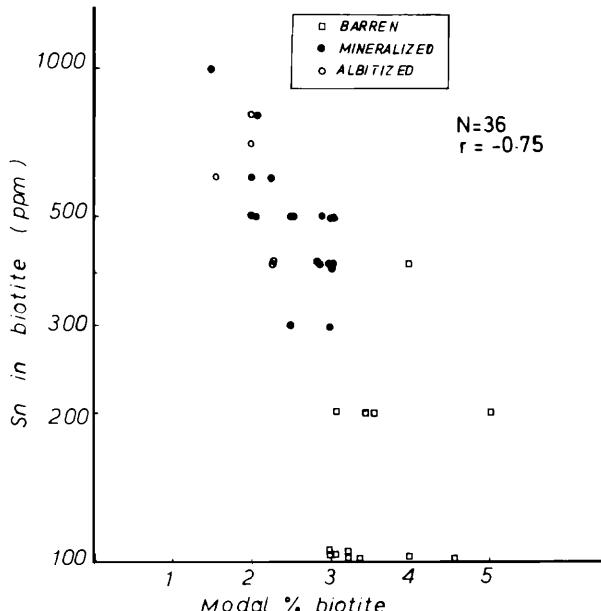


FIG. 5. Plot of Sn in biotite against the modal percent of biotite in barren (squares), mineralized (dots), and albitized (circles) rocks.

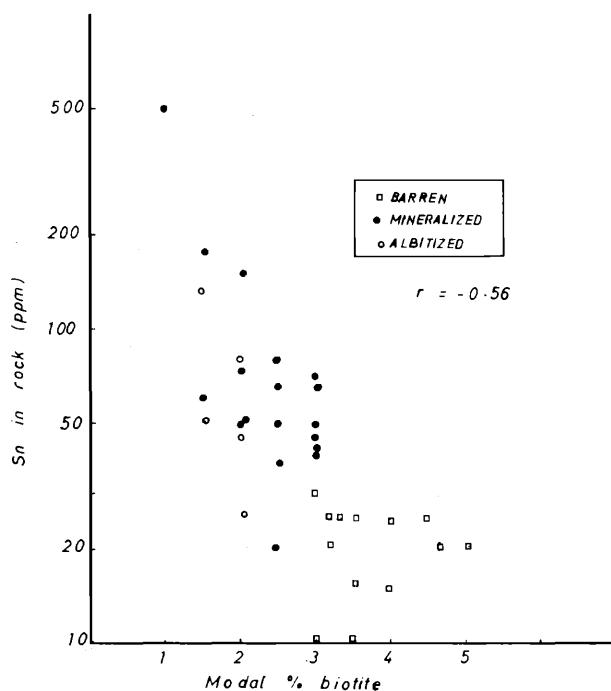


FIG. 6. Plot of Sn in granite against the modal percent of biotite in barren (squares), mineralized (dots), and albitized (circles) rocks.

than do the biotites of the barren granites. Hence, the high Sn content of biotite reflects possible mineralization.

Hesp (1971) found that some biotites held less than 45 percent of the total-rock tin; in high tin granites, this fell to 10 to 20 percent. In this study, biotites from high tin granites hold less than 40 percent of the available tin at most, while biotites from the barren granites hold as much as 80 percent of the available tin. It would therefore appear that much of the tin in the Sn-poor granites is located in the silicate fraction.

The incidence of a high Sn content of biotites and rocks of the late phases may reflect a progressive concentration of Sn in the melts and the solidified granites, thus producing high Sn concentrations in the rocks and biotites. Alternatively, the high Sn content of biotites from these late phases may indicate decreased availability of substitution sites within the rock (Blaxland, 1971). However, as suggested by Groves (1972), the high tin content of biotite appears to be due to a normal distribution of tin between liquid and crystals in the residual tin-rich liquid.

Many workers have suggested that the amount of Sn present in biotite may relate directly to the biotite composition. Hesp (1971) noted a strong resemblance between the behavior of Sn and Fe^{+2} , Fe^{+3} , and Ti^{+4} and considered that it could be substituted with Ca^{+2} .

Hesp (1971) and Levashev et al. (1971) found a negative correlation between Sn and Ti and attributed this to the greater degree of covalency of the Sn-O bond relative to the Ti-O bond and hence to the greater electronegativity of Sn. There are also negative correlations between total iron and Sn and between $\text{Fe}^{+2}/\text{Fe}^{+3}$ and Sn (Rattigan, 1964).

In this present study Sn is negatively correlated with Fe_{total} ($r = -0.65$)/Ti ($r = -0.57$) but positively with $\text{Fe}_{\text{total}}/\text{Fe}_{\text{total}} + \text{Mg}$ ($r = 0.68$). Hesp (1971) found a similar relationship between Sn and the iron-magnesium ratio ($\text{Fe}_{\text{total}}/(\text{Fe}_{\text{total}} + \text{Mg})$). This relationship may imply that the Sn content of biotite increases with low f_{O_2} and low temperatures as indicated by the iron/magnesium ratio (Wones and Eugster, 1965). The oxygen fugacity of the magma was not controlled externally but has been defined by buffer equilibria and consequently is a function of magma composition and temperature. Thus, the Sn content of the biotites was by and large a function of the processes that led to the increase in the activity of tin during the crystallization of the rocks.

Discussion

The results of this study indicate that biotites from the tin-bearing granites of the Afu Complex have higher Sn contents than biotites from the barren granites. The areas of biotite with high Sn contents generally coincide with regions of known mineralization and mining. This then raises the question as to the nature of the relationship of the biotite granites to processes of ore deposition.

In the younger granite province, it is well established that the biotite granites are genetically as well as spatially related to tin mineralization (Falconer, 1912; Williams et al., 1956; Macleod et al., 1971; Bowden and Kinnard, 1978). However, despite this close genetic association between tin mineralization and biotite granites, only a small proportion of these granites are mineralized—even within the same intrusive complex where they are considered consanguineous and similar in mode of crystallization and major element composition (Bowden and Turner, 1974).

Thus, the ability to yield economic concentrations of tin most probably depends dominantly on the geochemical nature of the magma and the character of the related postmagmatic processes (Beus and Gregorian, 1975). If tin mineralization is a product of ore-forming fluids developed during the evolution of the host intrusions, then there is a high probability that this may be reflected in the trace element contents and their distribution patterns in both the rocks and minerals.

Imeokparia (1980) has given both petrographic and

geochemical evidence to show that the ore-forming fluids were locally derived from magma in the normal course of magmatic crystallization.

It is believed that tin is accepted into the biotite lattice in amounts indicating equilibrium between biotite and the parent granitic liquid. This is reflected in the significantly high positive correlation between Sn in biotite and Sn in rock ($r = 0.60$). However, the tin anomalies in biotite provide a more sensitive and extensive indication of associated tin mineralization than those in the whole-rock samples. The distribution patterns of Sn in whole-rock samples are generally erratic, and individual samples may have a relatively high or low Sn content owing to the mode of occurrence of Sn as either dispersed or fracture-controlled mineralization.

The high Sn content of biotites might suggest some correlation with cations occupying octahedral positions in the biotite lattice, but, as pointed out by Groves (1972), the negative correlations obtained in this study between Sn, and Fe and Ti are not those predicted for a selective substitution of Sn for Fe and Ti from a consideration of ionic radius coordination number, ionization potential, and electronegativity (Hamaguchi and Kuroda, 1970).

It is believed that the change in composition of the mineralized biotites appears to be a result of chemical evolution of the granites and hydrothermal processes with later fluids having increased Fe/Mg activity ratios and probably related increases in the volatile contents. The tin content of the biotites may also reflect the same processes and may only be indirectly related to the biotite composition.

Tauson (1967) has noted that the substitution of Sn in the biotite lattice is influenced largely by the fluorine content. F (Bailey, 1977) and Rb (Glyuk et al., 1977) are apparently capable of lowering the granite solidus by several hundred degrees, and it is probable that, in the case of the granite phases associated with mineralization, their combined effects along with other volatile elements have led to a final crystallization temperature of 500°C or lower and low oxygen fugacities. The positive correlation between F and Sn ($r = +0.86$) in the biotites suggests significant association of these two elements in the magma (Imeokparia, 1981).

Whatever processes are responsible for the concentration of Sn in biotites, it is obvious that a significantly high Sn content in the biotites is only associated with mineralized granites. It may be argued therefore that igneous biotites generally have a low Sn content unless mineralization is associated with the host rock. Thus, it is possible to distinguish between a normal and abnormal concentration of tin in biotite, which might be useful in geochemical exploration.

Conclusions

The results of this study show the possibility for the use of Sn abundance in biotite as an exploration tool. Biotite from mineralized intrusions is on the average relatively enriched in Sn and contains generally three times the Sn content of barren biotite. The Sn content of the biotite is probably dependent on the f_{O_2} , temperature of crystallization, and volatile content of the magma. It may increase with a decrease of temperature and f_{O_2} and an increase in the volatile content.

Various empirical formulas relate the tin content of the biotite to the chemical and modal composition of the granite. The biotite contains less than 40 percent of the tin content of the granite, although it may be more than this in the tin-poor granite. A high tin content of granite corresponds to a high tin content of biotite, a low modal percentage of biotite, and a low percentage of total tin held in biotite.

Hydrothermal alteration involving greisenization leads to leaching of Sn from biotite. The leached materials are probably deposited in the veins of the mineralized zones by migrating solutions.

Acknowledgments

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