A GEOCHEMICAL STUDY OF NIOBIUM DISTRIBUTION, AND OF Nb-Ti AND Nb-Zr RELATIONS IN SOME PHYLLOSILICATES

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ABSTRACT

Nb, Ti, and Zr concentrations in 21 polygenetic biotites and 4 muscovites were measured by X-ray fluorescence spectrometry. Within a single granitic terain, late-magmatic biotites have higher Nb contents (45–65 ppm; mean, 53 ppm) and lower Ti/Nb ratios (114–280; mean, 206) than early-magmatic biotites (Nb: 30–46 ppm; mean, 37 ppm; Ti/Nb: 278–524; mean, 342). Metasomatic biotites have lower Nb (20–41 ppm; mean, 29 ppm) and higher Ti/Nb (208–841; mean, 478) than magmatic biotites (Nb: 30–65 ppm; mean, 44 ppm; Ti/Nb: 114–524; mean, 284). Muscovites contain higher Nb (63–74 ppm; mean, 66 ppm) than biotites (Nb: 20–65 ppm; mean, 36 ppm). Nb^{5+} in biotites is found to substitute for Zr^{4+}, making the geochemical association Nb-Zr as significant as the more commonly accepted Nb-Ti coherence.

INTRODUCTION

STUDIES of niobium abundances in common rock-forming silicates are of considerable scientific and practical importance. The ability of the small, highly charged Nb^{5+} ion ($r = 0 \cdot 69$ Å) to form anionic complexes in silicate melts, sensitive to dynamothermal and chemical variations during rock formation, makes this rare pentavalent cation (crustal abundance, 21 ppm[1]) a very useful petrologic tracer. Furthermore, the possibility that Nb^{5+} can get dispersed as a diadoch in the "spacious" structures of the micas, substituting for crystal-chemically favourable cations (those with high charge having ionic radii close to $0 \cdot 70$ Å, *e.g.*, $Ti^{4+}_{r=0 \cdot 68}$), is an important factor that determines whether or not a rock body is likely to contain commercially recoverable discrete niobium ores.

PURPOSE

Investigations of niobium distributions in common rock silicates, and of variations in critical ratios of geochemically coherent elements involving niobium (*e.g.*, $Nb^{5+}/Ta^{5+}_{r=0 \cdot 68}$; Nb^{5+}/Ti^{4+}; $Nb^{5+}/Sn^{4+}_{r=0 \cdot 71}$; $Nb^{5+}/Zr^{4+}_{r=0 \cdot 79}$; $Nb^{5+}/Mo^{6+}_{r=0 \cdot 62}$; $Nb^{5+}/W^{6+}_{r=0 \cdot 62}$), are generally lacking. This paper, therefore, presents and discusses *Nb, Ti, and Zr* data obtained for biotites and muscovites from polygenetic granitic rocks, with three main objectives: (1) to determine if Nb contents, and Ti/Nb ratios of micas, formed by diverse processes, but sampled from a single petrographic region, differ substantially from one another, (2) to understand the nature of Nb-Ti and Nb-Zr relations in granitic micas, and (3) to find if biotite Nb, and Ti–Nb data can be used as discriminants between granitic magmatites/metasomatites/anatexites.

INVESTIGATIVE TECHNIQUES

Sample selection.—Eighteen biotites from granitic rocks of diverse origins (7 magmatic, 9 metasomatic, and 2 anatectic), three biotites from metamorphic rocks, and four granitic muscovites were selected for study. The magmatites and metasomatites range in composition from granite to leucogranite, and the anatexites range from tonalite to sub-trondhjemite; the metamorphites are volcaniclastic metagreywacke. The samples are from the western part of the $2 \cdot 7$ billion year old Giants Range batholith of northeastern Minnesota, U.S.A.[2]. The origins of the rocks, as stated, are based on the author's detailed studies of field relationships, petrography and petrochemistry[3], oxygen-isotope geochemistry[4,5], rubidium[6], strontium[7], lead[8], and zinc[9] geochemistry.

Analytical methods, results, and evaluation.—Nb, Ti, and Zr were analysed by X-ray fluorescence spectrometry. The analytical precision is within 15% for Nb, and within 5% for Ti and Zr. Biotite and muscovite were separated from the rocks using a Frantz isodynamic separator and cleaned under a binocular microscope. The results are presented in Table I. Regression analysis, by the least-squares method, has been employed to evaluate the Nb-Ti and Nb-Zr relations in the samples.

DISCUSSION

Geochmical differences between the polygenetic micas.—Ranges and arithmetic means of Nb contents, and of Ti/Nb ratios, for the polygenetic biotites and muscovites, summarised in Table II, show that:

(1) Biotites from granitic rocks of late-magmatic origin have higher Nb contents (45–65 ppm; mean,

TABLE I

*Nb, Ti and Zr contents, and Ti/Nb ratios of biotites and muscovites from the Giants Range batholith**

	Nb (ppm)	Ti (ppm)	Zr (ppm)	Ti/Nb
Early–magmatic biotites:				
(1)	30	15,724	145	524
(2)	38	10,632	110	280
(3)	46	12,729	180	278
(4)	34	9,734	260	286
Late–magmatic biotites:				
(5)	49	10,932	180	223
(6)	45	12,579	80	280
(7)	65	7,413	150	114
Metasomatic biotites:				
(8)	31	6,439	130	208
(9)	28	15,499	120	554
(10)	41	16,922	100	413
(11)	21	17,671	90	841
(12)	31	10,483	105	338
(13)	25	11,381	40	455
(14)	34	14,226	120	418
(15)	20	13,777	80	689
(16)	35	13,627	243	389
Anatectic biotites:				
(17)	35	8,910	105	255
(18)	41	11,531	130	281
Metamorphic biotites:				
(19)	40	9,884	120	247
(20)	31	7,937	100	256
(21)	37	7,637	120	206
Magmatic muscovite:				
(22)	66	2,170	220	33
Metasomatic muscovites:				
(23)	74	1,123	180	15
(24)	63	1,500	245	24
(25)	63	2,550	230	40

* Analysis by S. Viswanathan at the School of Earth Sciences, University of Minnesota, Minneapolis, U.S.A. Method, X-ray fluorescence.

TABLE II

*Variations in Nb contents and Ti/Nb ratios of polygenetic biotites and muscovites from the Giants Range batholith**

Genetic grouping of biotites**	Range Nb (ppm)	Mean Nb (ppm)	Range Ti/Nb	Mean Ti/Nb
Early–magmatic (4)	30–46	37	278–524	342
Late–magmatic (3)	45–65	53	114–280	206
Magmatic (7)	30–65	44	114–524	284
Metasomatic (9)	20–41	29	208–241	478
Anatectic (2)	35–41	38	255–281	268
Metamorphic (3)	31–40	36	206–256	236
Muscovites (4)	63–74	66	15–40	28
Biotites (21)	20–65	36	114–841	359

* Analysis by S. Viswanathan at the School of Earth Sciences, University of Minnesota, Minneapolis, U.S.A.

Method X-ray fluorescence.

** Numbers in parentheses indicate number of samples analysed.

53 ppm) and lower Ti/Nb ratios (114–280; mean, 206) than biotites from the early-magmatic phases to which they are genetically related (Nb: 30–46 ppm; mean, 37 ppm; Ti/Nb. 278–524; mean, 342).

(2) Biotites from granitic rocks of metasomatic origin have lower Nb contents (20–41 ppm; mean, 29 ppm) and higher Ti/Nb ratios (208–841; mean, 478) than biotites from granitic rocks of magmatic origin (Nb: 30–65 ppm; mean, 44 ppm; Ti/Nb: 114–524; mean, 284).

(3) Biotites from granitic rocks of anatectic origin have Nb contents (35–41 ppm; mean, 38 ppm) similar to those from granitic rocks of early-magmatic origin (30–46 ppm; mean, 37 ppm) but are characterised by lower Ti/Nb ratios (255–281; mean, 268 as against 278–524; mean, 342).

(4) Nb contents and Ti/Nb ratios in anatectic biotites (mean, 38 ppm; 268) are comparable to corresponding data for biotites from their parent metamorphic rocks (Nb: 31–40 ppm; mean, 36 ppm: Ti/Nb: 206–256; mean, 236).

(5) Muscovites have higher Nb contents (63–74 ppm; mean, 66 ppm) and much lower Ti/Nb ratios (15–40; mean, 28) than biotites (Nb: 20–65 ppm; mean, 36; Ti/Nb: 114–841; mean, 359).

Nb-Ti and Nb-Zr relations.—The negative correlation ($r = -0\cdot7321$) observed between Nb and Ti contents of biotites and muscovites considered here (Fig. 1) is opposed to the expected trend,

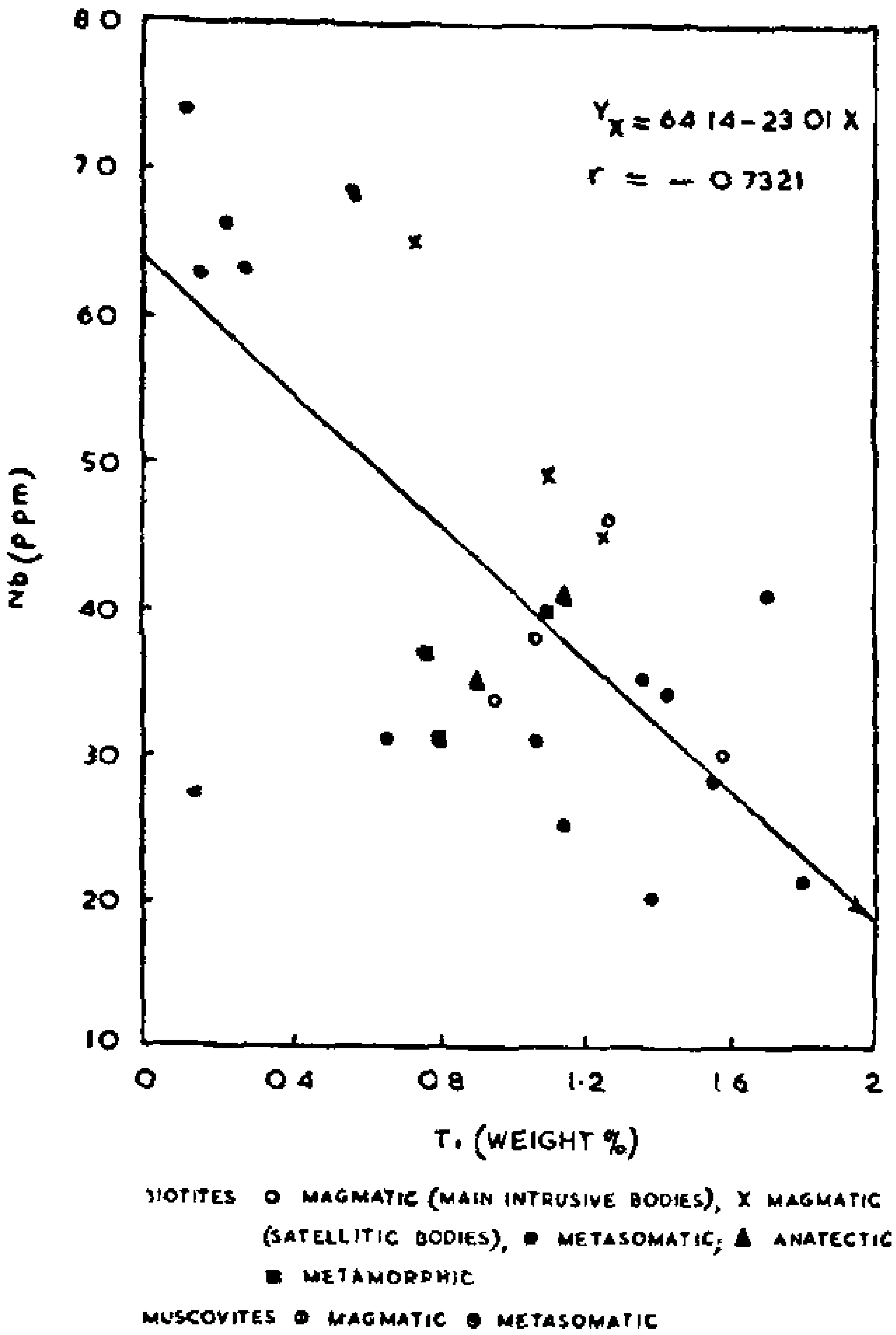

FIG. 1. Nb-Ti relations in polygenetic granitic biotites and muscovites.

for, (*a*) Nb^{5+} and Ti^{4+} are commonly regarded as a pair of geochemically coherent elements[10-13] because of their almost identical ionic radii ($r_{Nb^{5+}} = 0\cdot69$ Å; $r_{Ti^{4+}} = 0\cdot68$ Å) and high charge, and (*b*) Nb is reported to enter the biotite lattice in isomorphous substitution for Ti[14]. The trend obtained in the present study, therefore, suggests that Nb in biotites possibly substitutes for another crystal-chemically favourable cation. The positive correlation ($r = +0\cdot5491$) between Nb and Zr in biotites and muscovites shown in Fig. 2 indicates Zr^{4+} to be this cation. Such a possibility is consistent with crystal-chemical considerations, for, similarities between the ionic radii of Nb^{5+} ($r = 0\cdot69$ Å) and Zr^{4+} ($r = 0\cdot79$ Å), combined with their high charge, permit substitution of one by the other. Thus, the Nb-Zr geochemical association appears to be as significant as the more commonly accepted Nb-Ti coherence.

Discriminant diagrams.—The data obtained in this study permit construction of two diagrams that are potential aids in recognizing granitic rocks of diverse origins, occurring within a single petrographic region, based on the Nb and Ti contents of their constituent biotites. Appropriate discri-

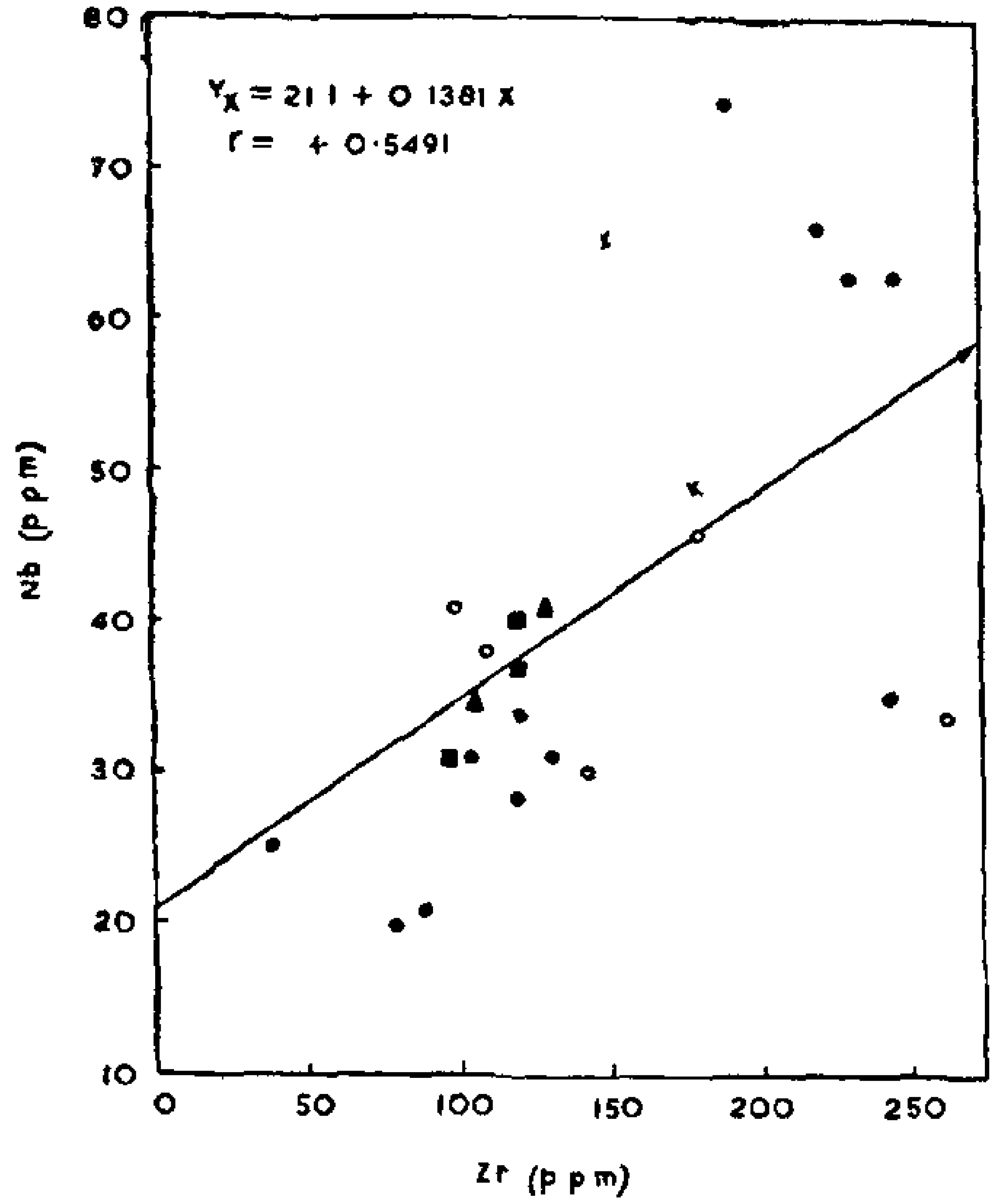

FIG. 2. Nb-Zr relations in polygenetic biotites and muscovites. Symbols as defined in Fig. 1.

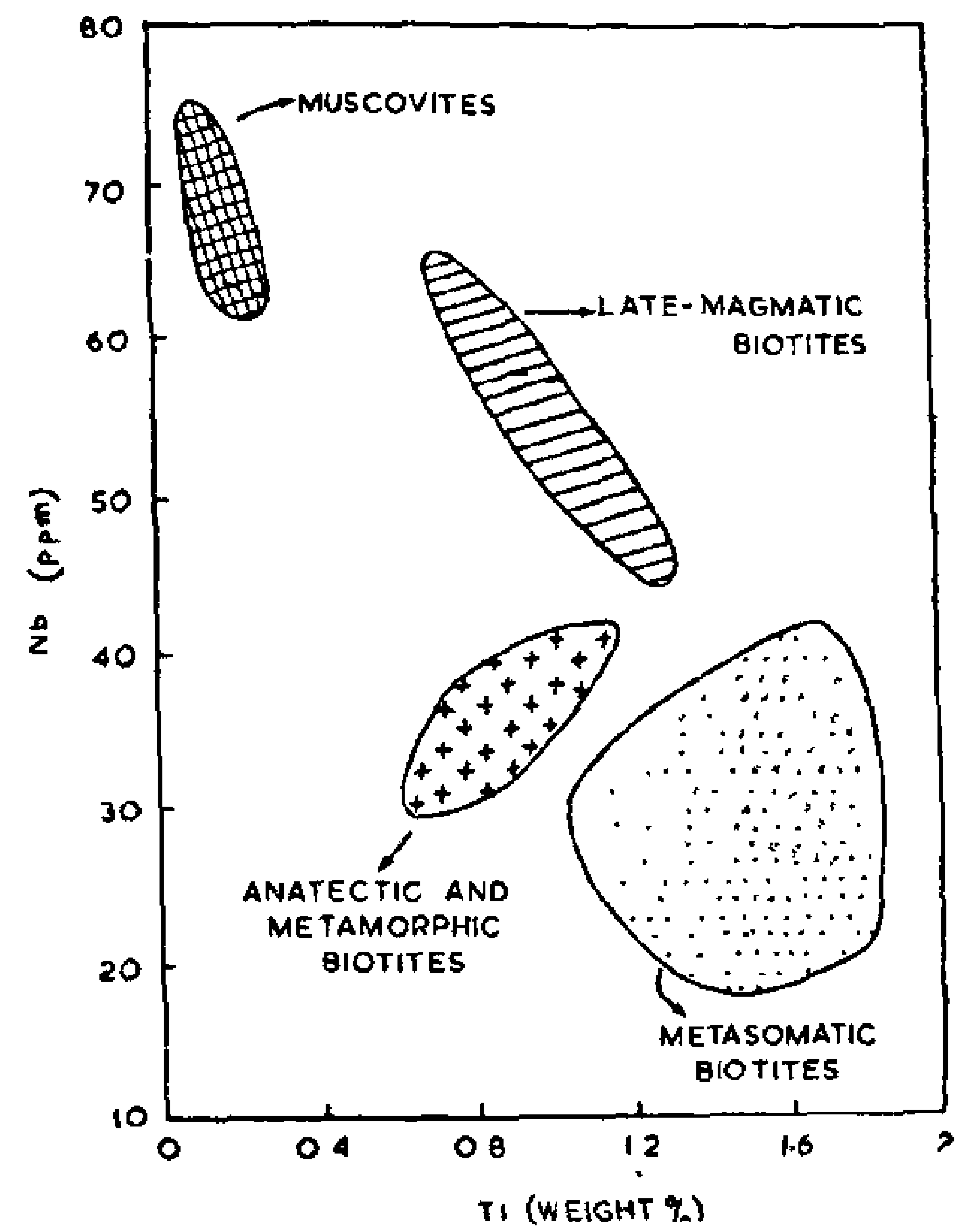

FIG. 3. Discriminant diagram for polygenetic granitic rocks based on the Nb and Ti contents of their constituent biotites.

minant fields for late-magmatic, metasomatic, and anatectic granitic rocks are defined in Fig. 3, a plot of $(Nb)_{biotite}$ *versus* $(Ti)_{biotite}$. Figure 4, wherein $(Ti/Nb)_{biotite}$ is plotted against $(Ti)_{biotite}$ helps to distinguish magmatic granites from metasomatic granites.

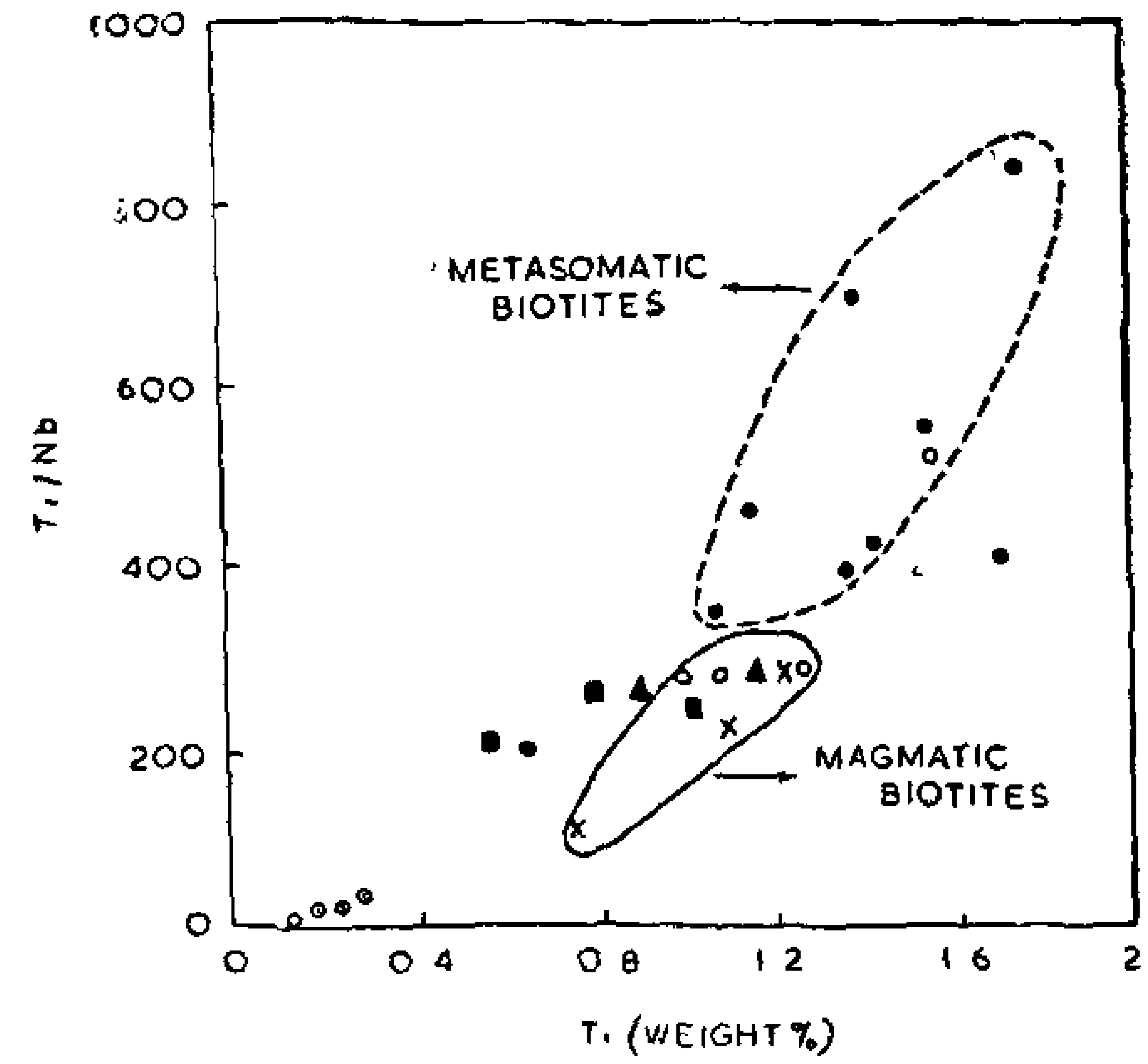

FIG. 4. Discriminant diagram for magmatic and metasomatic granites based on the Ti/Nb ratios and Ti contents of their constituent biotites. Symbols as defined in Fig. 1.

CONCLUSIONS

(1) Biotites from granitic rocks of late-magmatic origin have higher Nb contents and lower Ti/Nb ratios than biotites from the early-magmatic phases to which they are genetically related.

(2) Biotites from granitic rocks of metasomatic origin have lower Nb contents and higher Ti/Nb ratios than biotites from granitic rocks of magmatic origin.

(3) Muscovites have higher Nb contents and lower Ti/Nb ratios than biotites.

(4) In the biotites considered here, Nb^{5+} is found to substitute for Zr^{4+}, thus making the Nb-Zr geochemical association as significant as the more commonly accepted Nb-Ti coherence.

ACKNOWLEDGEMENTS

I am very thankful to Dr. Paul Sims for useful discussions and financial support; Drs. Paul Weiblen and Tibor Zoltai for guidance in X-ray fluorescence spectrometry; Mr. K. K. Dar and the late National Professor Dr. D. N. Wadia for encouragement.

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SYNTHESES OF SOME NEW THERAPEUTIC N-*p*-BROMOPHENYL-N′-2-(SUBSTITUTED) BENZOTHIAZOLYL GUANIDINES

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AMONG a series of mono and *bis* diguanides showing antibacterial activities prepared by Rose and Swain[1-2], one compound, chlorhexidine B.P.C. (Hibitane), has found practical use as an antibacterial agent in medicinal and veterinary practice. Encouraging antibacterial properties *in vitro* against *Mycobacterium tuberculosis* have been reported in several biguanide derivatives[3-4]. The heterocyclic diguanidine derivatives[5] have been found to be active to mice when administered. These activities have also been found in many thiazole compounds[6].

Antibacterial activity against *Esch. coli* and *Staph. aureus* of some N-aryl-N′-2-(4, 5, 6-methyl)