GEOCHEMICAL BEHAVIOUR OF Rb, Ba, Pb, Ti, Mn AND Zn DURING PROGRESSIVE CHLORITIZATION OF GRANITIC BIOTITES

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ABSTRACT

Evaluation of Rb, Ba, Pb, Ti, Mn, Zn, K/Rb, K/Ba, K/Pb, Ti/Fe, Mn/Fe and Zn/Fe data, obtained by X-ray fluorescence methods, for five chloritized biotites shows that, during progressive chloritization of granitic biotites: (*a*) Rb, Ba and Pb contents decrease, (*b*) Mn increases, (*c*) Ti and Zn remain nearly constant, (*d*) the amounts of Rb and Ba leached are greater, relative to their major-element associate, K, (*e*) Pb and K are proportionately leached, and (*f*) Fe is enriched relative to Ti, but is depleted relative to Zn. The results emphasise the need for great caution when interpreting whole-rock trace-element data in petrological studies.

INTRODUCTION

THE importance of biotite as a rock-forming silicate, and its pre-eminence in Rb-Sr and K-Ar geochronology, have motivated numerous studies, in the past, on its physical and chemical properties. The distribution and behaviour of some major- and minor-elements in biotites, during specific igneous and metamorphic processes, have also received attention.

The alteration of biotite to chlorite under hydrothermal conditions is well known, and common in many granitic rocks. This process, also referred to as chloritization, has been studied from a petrographic angle[1,2]. However, to the best of my knowledge, there has not been any attempt in the past to define the geochemical behaviour of some interesting minor-elements present in granitic biotites, when subjected to progressive chloritization. This paper, therefore, is intended to fill the gap, and considers: (1) the effect of chloritization on three large cations of the potassium type (Rb^+, Ba^{2+} and Pb^{2+}) and three ferromagnesian cations (Ti^{4+}, Mn^{2+} and Zn^{2+}) that commonly occur in granitic biotites, in measurable amounts, and (2) the geochemical behaviour of these six cations in relation to their major-element associates, K^+ for Rb^+, Ba^{2+} and Pb^{2+}, and Fe for Ti^{4+}, Mn^{2+} and Zn^{2+}.

METHODS OF STUDY

Analytical techniques.—Rb, Ba, Pb, Ti, Mn, Zn, K and Fe in five biotites, chloritized to varying degrees, from a magmatic granitic series of the 2·7 b.y. old Giants Range batholith of north-eastern Minnesota, U.S.A., on the southern margin of the Canadian shield (Viswanathan and Sims[3]), were analyzed by non-destructive X-ray fluorescence spectrometry. A Norelco apparatus equipped with a tungsten tube, LiF and EDDT analyzing crystals, gas flow proportional counter, and a chart recorder was used. The characteristic radiations measured were RbK_α, $BaL_{\beta 1}$, $PbL_{\beta 1}$, TiK_α, MnK_α, ZnK_α, KK_α and FeK_α. Four analyzed biotites R 2267, R 2312 (Dr. Paul Weiblen, personal communication), SP 109A and CN 27 (Phinney[4]; Turekian and Phinney[5]), and the new U.S.G.S., rock standards G-2, GSP-1, AGV-1, PCC-1, DTS-1, and BCR–1 (Flanagan[6]) were used for deriving working curves. Precision, expressed as the coefficient of variation, is within 10% for Rb, Ti, Zn and Fe, within 15% for Ba, Mn and K, and within 20% for Pb.

Data evaluation.—The geochemical behaviour of Rb, Ba, Pb, Ti, Mn and Zn, and of certain critical ratios involving the major-element associates of these cations, K/Rb, K/Ba, K/Pb, Ti/Fe, Mn/Fe and Zn/Fe, are evaluated as functions of an "Increasing Intensity of Chloritization" (I.I.C.). A suitable parameter to represent I.I.C. is the potassium contents of chloritized biotites, for the hydrothermal alteration of biotite, $K_2(Mg, Fe^{2+})_{6-4}(Fe^{3+}, Al, Ti)_{0-2}[Si_{6-5}Al_{2-3}O_{20}](OH, F)_4$, to chlorite, $(Mg, Al, Fe)_{12}[(Si, Al)_8O_{20}](OH)_{16}$, involves the removal of K. Thus, biotites that are strongly chloritized contain lower K than slightly chloritized biotites. The relevant data are presented in Table I.

DISCUSSION

Rubidium.— Fig. 1 (*a*), a plot of Rb contents of chloritized biotites as a function of I.I.C., reveals decrease of Rb with increasing intensity of choritization. The decrease is somewhat gradual in the early stages of alteration, but rather sharp towards the later stages. Fig. 1 (*b*), a plot of K/Rb ratios of chloritized biotites *versus* I.I.C., although not too definitive, indicates an increase of K/Rb ratios with the intensity of chloritization. This suggests that the amount of Rb leached from biotites during progressive chloritization is greater, relative to its major-element associate, K.

TABLE I

*Geochemical data for five chloritized biotites from the Giants Range batholith**

	(1)	(2)	(3)	(4)	(5)
Rb	180	90	135	90	50
Ba	1000	640	440	370	1000
Pb	62	54	97	43	37
Ti	12729	12579	7413	10932	9734
Mn	2950	5550	4750	5100	5450
Zn	650	955	835	1040	835
K	4·65	3·24	2·32	2·03	1·87
Fe	7·12	12·98	11·03	12·56	15·64
K/Rb	258	360	172	226	374
K/Ba	46·5	50·6	52·7	54·9	18·7
K/Pb	750	600	239	472	505
10^3Ti/Fe	180	97	67	87	62
10^3Mn/Fe	41·5	42·8	43·0	40·6	34·9
10^3Zn/Fe	9·1	7·4	7·4	8·3	5·3

* Data for Rb, Ba, Pb, Ti, Mn and Zn, in ppm; for K and Fe, in weight %.

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

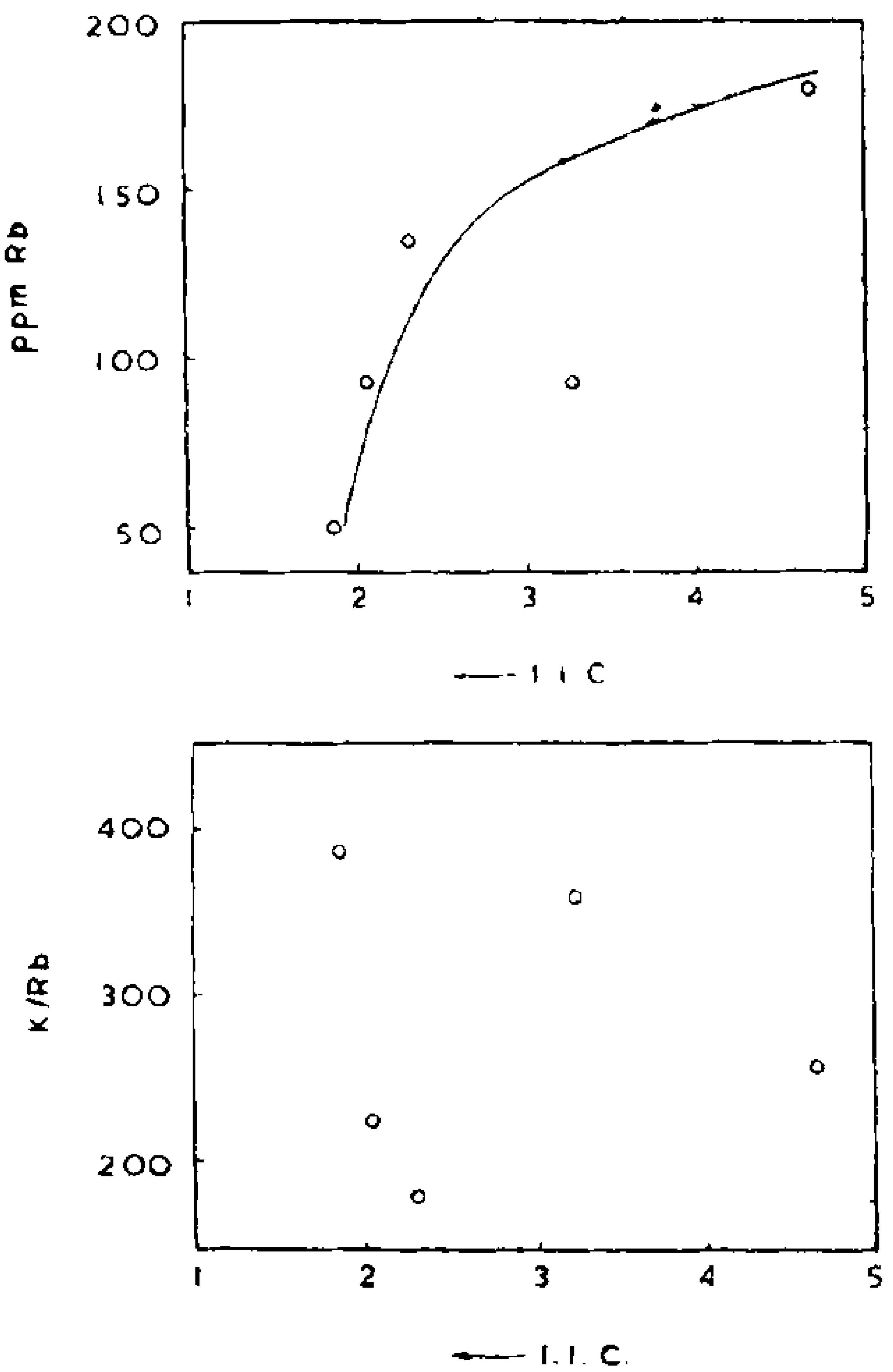

FIG. 1 (*a*), Rb in chloritized biotites as a function of increasing intensity of chloritization (I.I.C.). (*b*) K/Rb ratios of chloritized biotites as a function of increasing intensity of chloritization (I.I.C.).

Barium.—Fig. 2 (*a*), a plot of Ba contents of chloritized biotites as a function of I.I.C., shows a distinct and progressive decrease of Ba with the intensity of chloritization. Fig. 2 (*b*), a plot of

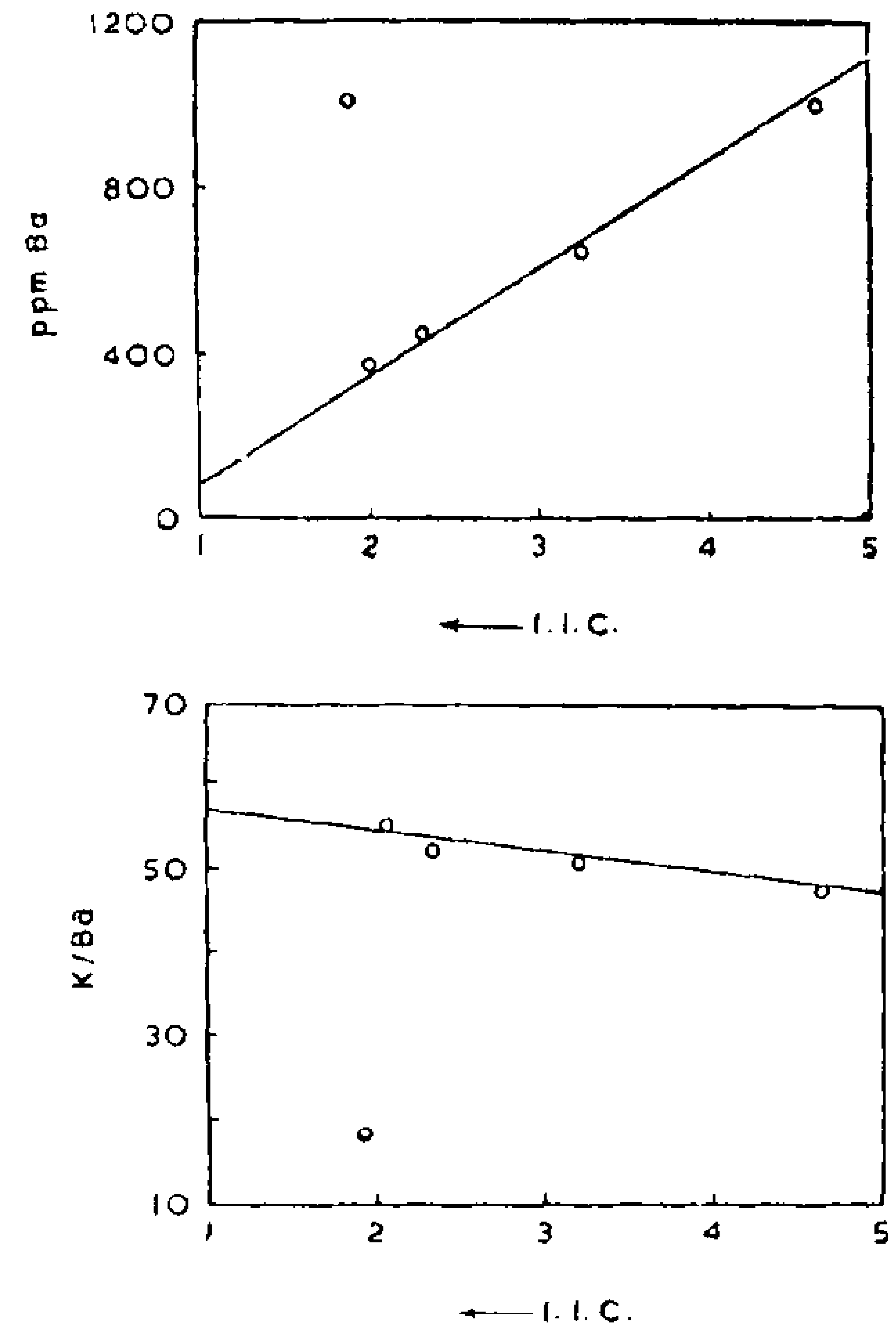

FIG. 2 (*a*), Ba in chloritized biotites as a function of increasing intensity of chloritization (I.I.C.). (*b*) K/Ba ratios of chloritized biotites as a function of increasing intensity of chloritization (I.I.C.).

K/Ba ratios of chloritized biotites *versus* I.I.C., indicates a definite increase of K/Ba ratios with the intensity of chloritization. This suggests that the amount of Ba leached from biotites during progressive chloritization is greater, relative to its major-element associate, K.

Lead.—Fig. 3 (*a*), a plot of Pb contents of chloritized biotites as a function of I.I.C., reveals a progressive decrease of Pb with the intensity of chloritization. Fig. 3 (*b*), a plot of K/Pb ratios of chloritized biotites *versus* I.I.C., shows that the K/Pb ratios decrease linearly with the intensity of chloritization. This suggests that both Pb and its major-element associate, K, are proportionately leached from biotites during the alteration.

Titanium.—It is commonly observed that chlorite pseudomorphs after biotite are peppered with sphene granules. The Ti required to develop sphene clearly is contributed by the pre-existing biotite. This suggests that the Ti content of chlori-

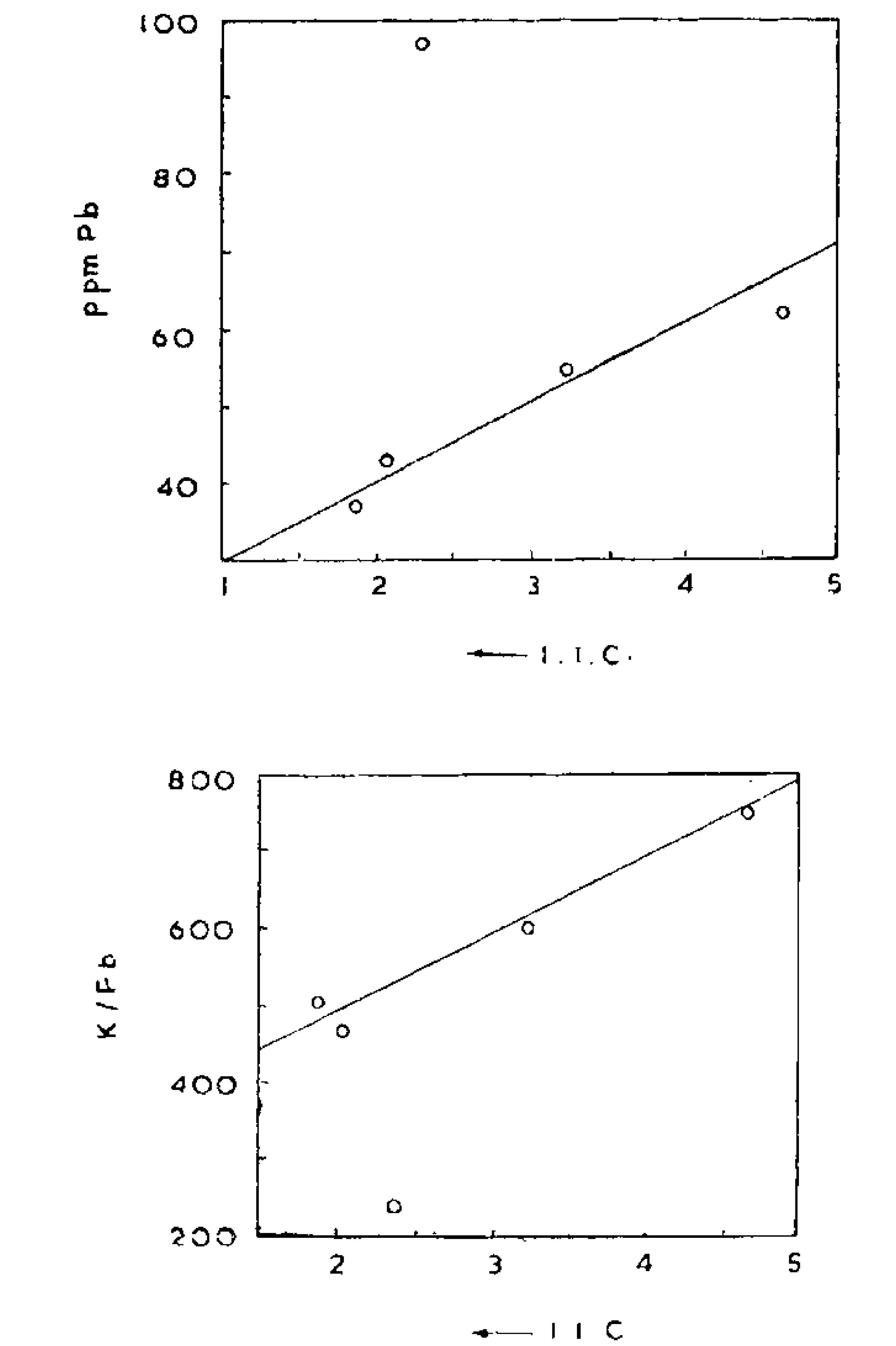

FIG. 3 (*a*), Pb in chloritized biotites as a function of increasing intensity of chloritization (I.I.C.). (*b*) K/Pb ratios of chloritized biotites as a function of increasing intensity of chloritization (I.I.C.).

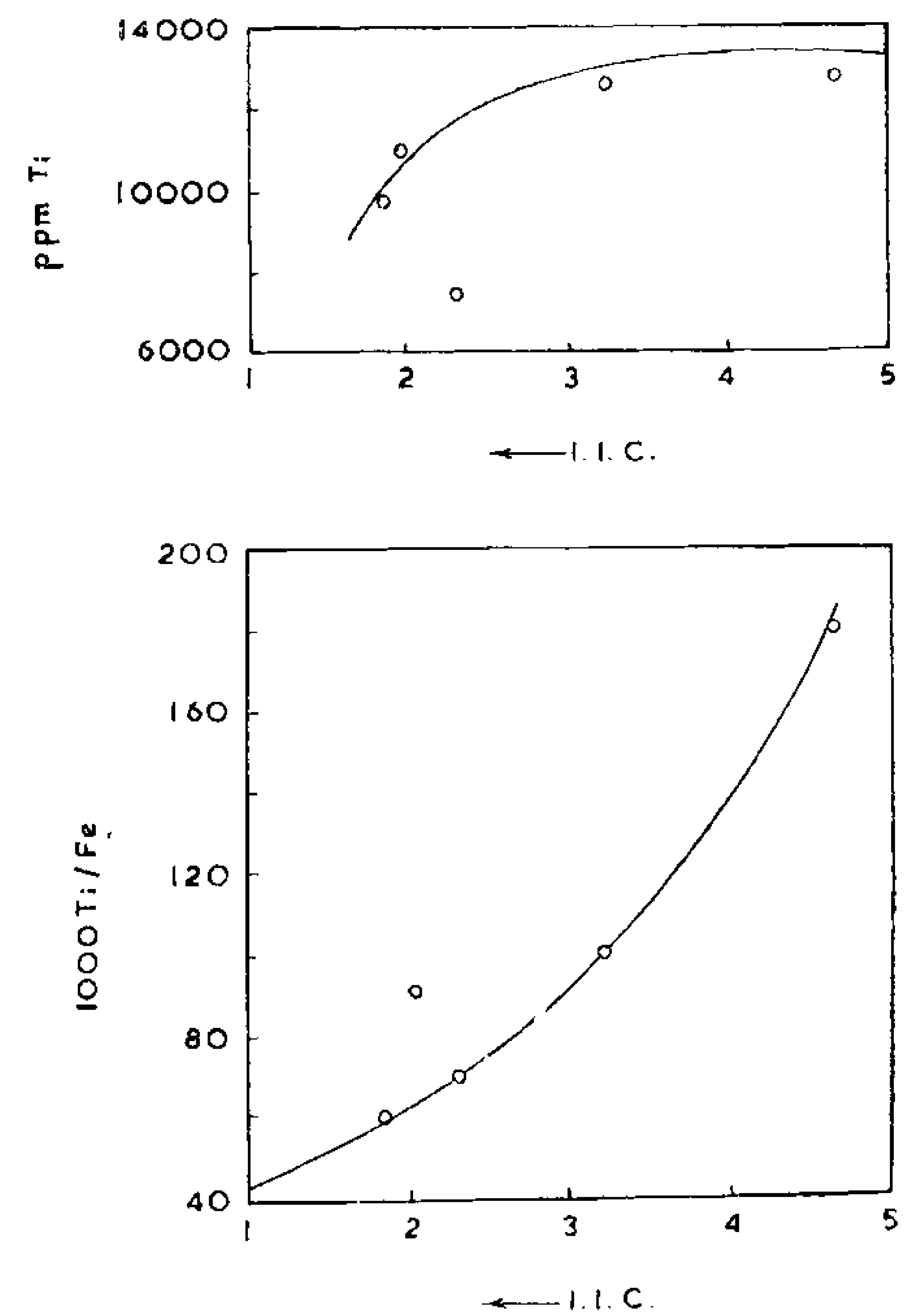

FIG. 4 (*a*), Ti in chloritized biotites as a function of increasing intensity of chloritization (I.I.C.). (*b*) Ti/Fe ratios of chloritized biotites as a function of increasing intensity of chloritization (I.I.C.).

tized biotites should be more or less similar to that of their parent biotites. Data from the present study confirm this prediction, although there is a tendency for a slight decrease of Ti during progressive chloritization (Fig. 4 *a*). The Ti/Fe ratio is also observed to decrease (Fig. 4 *b*), which suggests Fe enrichment relative to Ti during chloritization of biotites.

Manganese.—Fig. 5 (*a*), a plot of Mn contents of chloritized biotites as a function of I.I.C., reveals distinct increase of Mn with the intensity of chloritization. This is probably due to the addition of Mn from the chloritizing solutions. No meaningful conclusions can be drawn from the plot of Mn/Fe ratios of chloritized biotites *versus* I.I.C. (Fig. 5 *b*).

Zinc.—Fig. 6 (*a*), a plot of Zn contents of chloritized biotites as a function of I.I.C., shows that the Zn content is in the same range, or is somewhat higher than that of unchloritized or little chloritized biotites. The decrease of Zn/Fe ratios, during progressive chloritization (Fig. 6 *b*), suggests Fe depletion relative to Zn.

SIGNIFICANCE OF THE RESULTS

Some of the results reported here emphasise the need for great caution when interpreting whole-rock trace-element data in petrological studies that involve application of critical-element ratios such as K/Rb and K/Ba. Biotite, an important mineral in granitic and migmatitic suites, when present in substantial amounts, exerts a powerful control on the total trace-element content of these rocks (*e.g.*, Rb, Ba, Pb, Zn). Insufficient attention to the effects of even a slight degree of chloritization of biotites, on trace-element distributions, could lead to misinterpretations and erroneous conclusions, as demonstrated in the following example :

Consider a granitic rock that contains 20% quartz, 40% plagioclase, 20% K-feldspar (K_2O = 16·9% ; Rb = 200 ppm), 15% biotite (K_2O = 8·4% ; Rb = 800 ppm), and 5% accessory minerals. Simple geochemical calculations would show that such a rock has 3·85% K, and 160 ppm Rb,

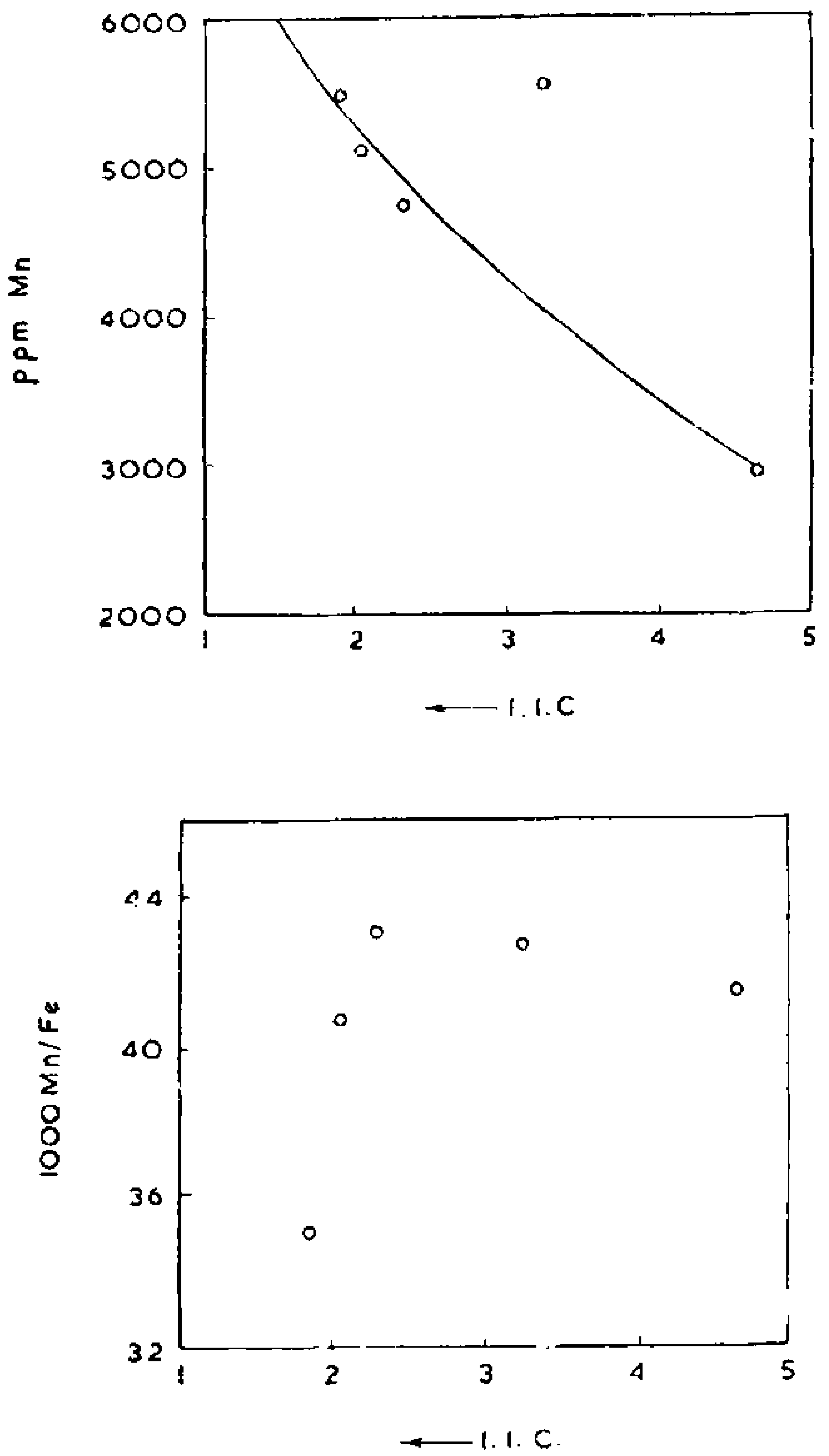

FIG. 5 (*a*), Mn in chloritized biotites as a function of increasing intensity of chloritization (I.I.C.). (*b*) Mn/Fe ratios of chloritized biotites as a function of increasing intensity of chloritization (I.I.C.).

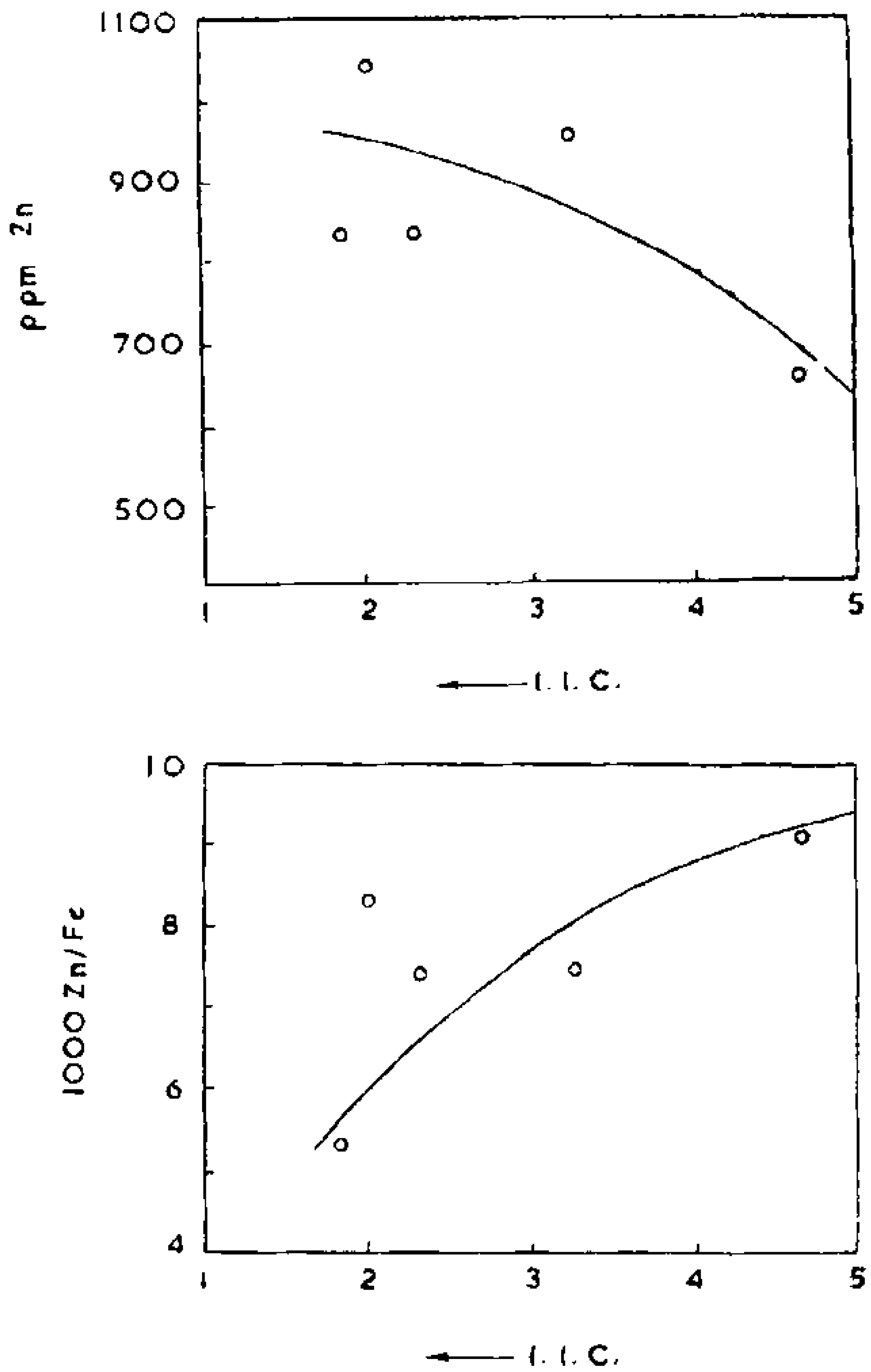

FIG. 6 (*a*), Zn in chloritized biotites as a function of increasing intensity of chloritization (I.I.C.). (*b*) Zn/Fe ratios of chloritized biotites as a function of increasing intensity of chloritization (I.I.C.).

giving a whole-rock K/Rb ratio of 241—a normal value for a granitic rock. If, on the other hand, the biotite of this rock is chloritized even to a slight extent, it is reasonable to expect, in the light of the results reported here with respect to rubidium, that the initial K_2O and Rb contents of the biotite can decrease to 3·0% and 200 ppm. In this case, calculations would show that the rock contains 3·18% K and 70 ppm Rb, giving a whole-rock K/Rb ratio of 454—an anomalously high value for a crustal granitic rock. Thus, what otherwise constituted a perfectly normal granitic rock would get misinterpreted as being abnormal, if sufficient attention is not paid to the problem of trace-element behaviour during progressive chloritization of biotites.

The biotite structure is "spacious" and capable of accommodating numerous trace-elements that fulfil certain crystallochemical requirements. It is, therefore, essential to carry out more studies of the geochemical behaviour of trace-elements, other than those reported here, during progressive chloritization of biotites.

ACKNOWLEDGEMENTS

Dr. Paul Sims for stimulating discussions and financial assistance; Dr. Tibor Zoltai and Dr. Paul Weiblen for their inspiring lectures on, and guidance in, X-ray fluorescence techniques; Mr. K. K. Dar and the late National Professor Dr. D. N. Wadia, for their encouragement.

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