

ELECTRON MICROPROBE ANALYSIS OF ZONED MELANITES

CELSE DE BARROS GOMES, *Departamento de Mineralogia e Petrologia,
Universidade de São Paulo, São Paulo, Brasil.*

ABSTRACT

Microprobe traverses were made across four zoned melanites, showing very dark brown cores surrounded by narrow bands bearing lighter colors, from two Brazilian nepheline syenites. The results indicate clearly that the central parts of the crystals are richer in TiO_2 and poorer in SiO_2 and Fe_2O_3 than the margins. No significant variations were registered for Al_2O_3 , CaO, MnO, MgO, Na_2O , and K_2O . The titanium-iron relationship described by Lehtijärvi (1966) and Isaacs (1968) has been found in all the analyzed specimens. A negative correlation between silicon and titanium, only slightly less conspicuous than the former, was also noted. A plot of Ti (total) against Si and Fe atoms in the unit cells of the garnet studied suggests that the addition of Ti is accompanied by the loss of approximately equal amounts of Fe and Si.

INTRODUCTION

As emphasized by many authors, the main problem in relation to the titanian garnets arises from the uncertain role of the titanium ion in the structure. Tetrahedral coordination was primarily suggested by Kunitz (1936), while Zedlitz (1935) came to the conclusion that part of the titanium is octahedrally coordinated. Tarte's (1960) conclusions based on infrared absorption techniques point to a replacement of silicon by titanium. Howie and Wooley (1968) proposed that titanium replaces silicon rather than iron; however, as a result of electron-probe investigations, they considered also the possibility that titanium substitutes for silicon or silicon plus iron. Finally, Isaacs (1968), using microprobe data from zoned titanium-rich garnets, has suggested substitution of titanium for iron. The work of Espinosa (1964), Ito and Frondel (1967), and more recently Dowty and Mark (1968) has also shed some light on the problem.

This paper reports the results of four microprobe traverses across zoned melanites selected from nepheline syenites of the alkaline district of Itapirapuã in the southern part of the State of São Paulo, Brazil (Gomes, in press). Major element, trace element, and mineralogical data on these minerals are given by Gomes *et al.* (1968). Some pertinent information from this paper is as follows: 1. The TiO_2 content in seven analyzed samples ranges from 4.49 to 8.72 percent; 2. high V, Nb, Zr and Y concentrations make up its main spectrographic features; 3. the unit cell parameter increases in proportion to the titanium content; 4. a very intimate relationship with sphene and sodic pyroxene has been noted in all specimens; 5. textural evidence points to formation during late stages of magmatic crystallization. Zoning is a very common feature in these minerals. The dominant pattern displays a deeper color in the central

parts of the crystals than at the edges. In thin section the color is frequently brownish, with intermediate shades ranging from light brown to dark brown. The selected samples exhibit very dark cores, reasonably homogeneous in color, surrounded by narrow bands with lighter colors.

ANALYTICAL TECHNIQUE

The analytical work was carried out with an Applied Research Laboratories electron-probe microanalyser in the Department of Geology and Geophysics, University of California, Berkeley. Instrumental conditions were: accelerating potential 15 kV, specimen current 0.05–0.06 μA , integration time on scalers 20 seconds, and spot size approximately 1 μm . Corrections have been made for instrumental drift, background, mass absorption, secondary fluorescence, and atomic number. The standards used, all natural specimens, were: hedenbergite (Hess #18) for Si and Ca, with values as given by Smith (1966); aenigmatite for Fe, Ti and Na (Kelsey and McKie, 1964); spessartite-almandine garnet for Mn (Pabst, 1938); biotite #3 for K; and almandine garnet #12442 for Al and Mg. The data is believed accurate to ± 2 percent. The traverses were made with step intervals of 3 μm or occasionally 6 μm .

RESULTS

The data obtained for two specimens are plotted on Figures 1 and 2. A photomicrograph of one analyzed melanite, showing the path of the traverse is presented in Figure 3. The average composition for the core and the edge of each specimen, with all the iron calculated as Fe_2O_3 , as well as its chemical formula calculated on the basis of 24 oxygens is given in Table 1. These results indicate clearly that the center of the melanites is richer in TiO_2 and poorer in SiO_2 and Fe_2O_3 than the periphery. Some minor variations also seem to be present, with the inner part of the crystals containing somewhat more MgO and MnO than the borders. An additional variation has been registered in sample C, which exhibits high aluminum in the nucleus. The direct correlation between color of melanite-schorlomite garnets and titanium concentration, with intensity increasing proportionally to this value (Zedlitz, 1935; King, 1965; Howie and Wooley, 1968), has been noted in all the investigated minerals.

The antipathetic titanium-iron relationship, as seen in Figures 1 and 2, is in agreement with the recent conclusions reached by Lehigh (1966) and Isaacs (1968). As a result of electron-probe microanalysis of zoned titanium-rich garnets, they have shown that titanium varies inversely with iron in those minerals. The symmetrical behavior of the titanium and iron curves, each the mirror image of the other, in all the graphs constitutes very strong evidence that titanium is occupying the iron position in the structure. However, it should be noted that the silicon variation is also opposite to that of titanium, which seems to suggest that titanium replaces silicon too, and therefore is filling up the tetrahedral sites. This point of view is at variance with the results of Isaacs (1968), who found that the little variation in the silicon was not related to titanium. Ap-

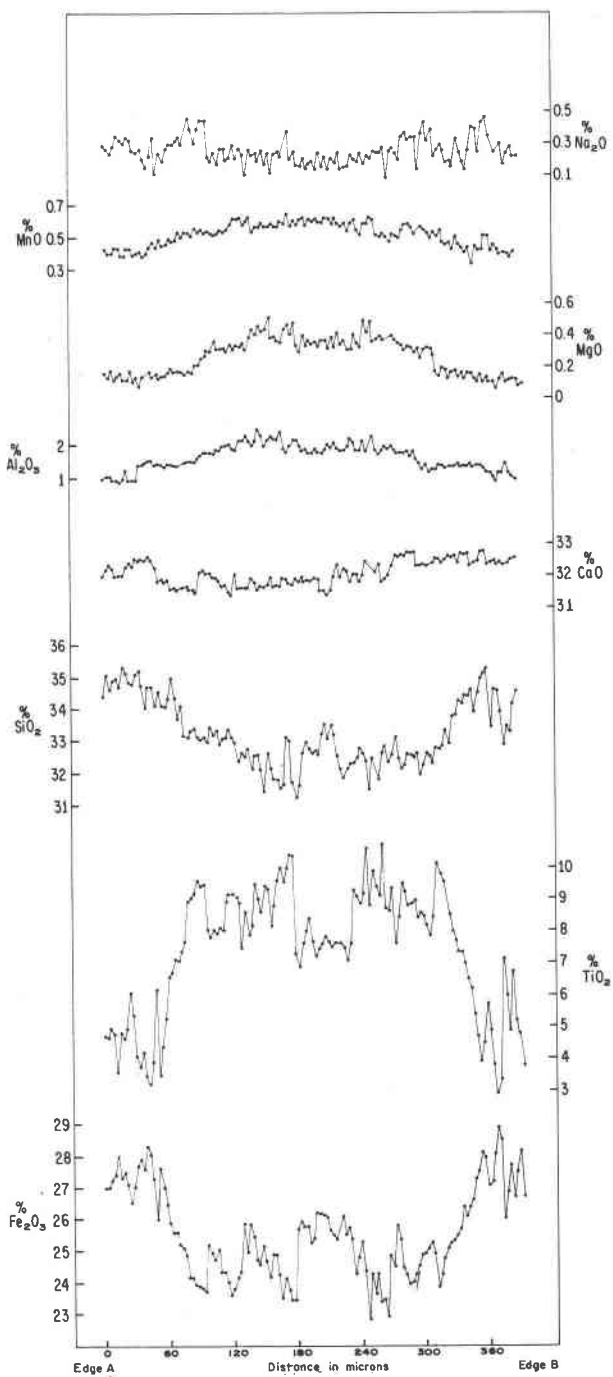


FIG. 1. Microprobe traverse across Specimen C at 3 μ m intervals.

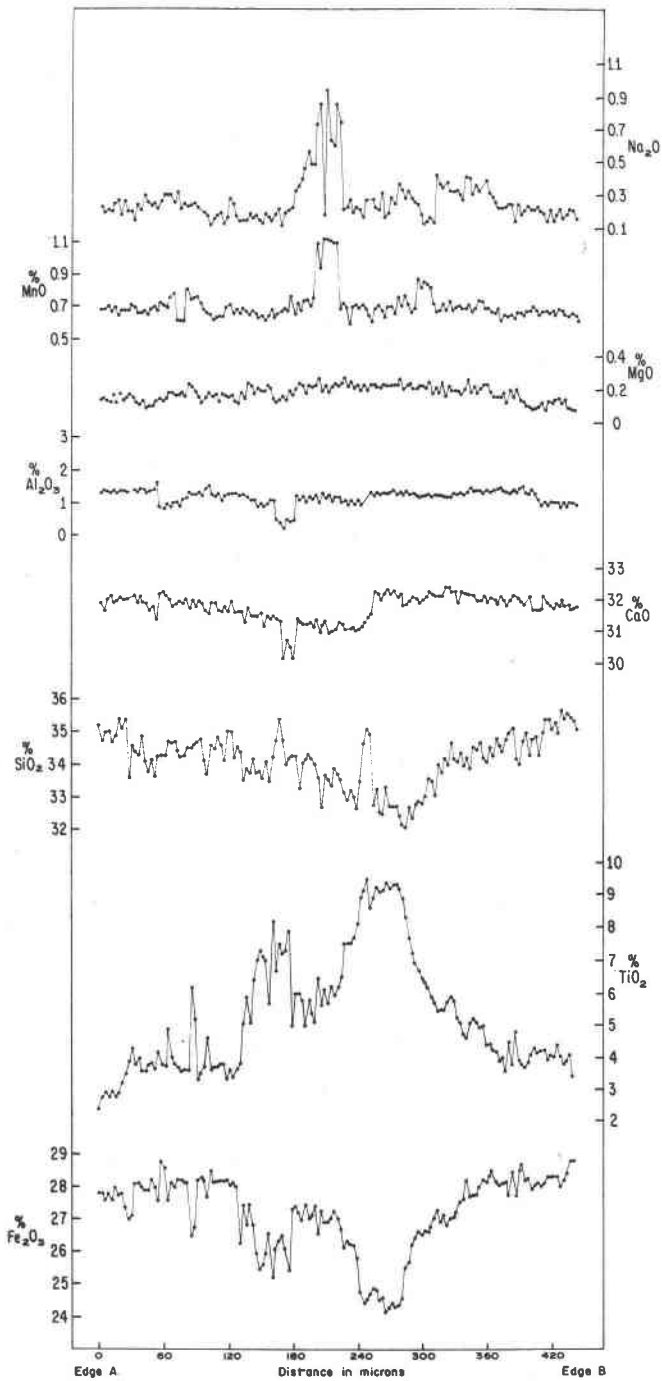


FIG. 2. Microprobe traverse across Specimen D at 3 μm intervals.

parent contradictions take place if the above conclusions are compared with those furnished by Howie and Woolley (1968). According to these authors, the iron-titanium relationship does not hold invariably in the melanites, and, indeed, the inverse correlation between silicon and titanium seems to be the more usual and fundamental.

The calcium varies slightly along the traverses, but it appears to be unrelated to the titanium and iron contents. Except for sample C, the aluminum is constant; in C the observed changes are not related to titanium and iron. Magnesium and manganese behave in a similar fash-

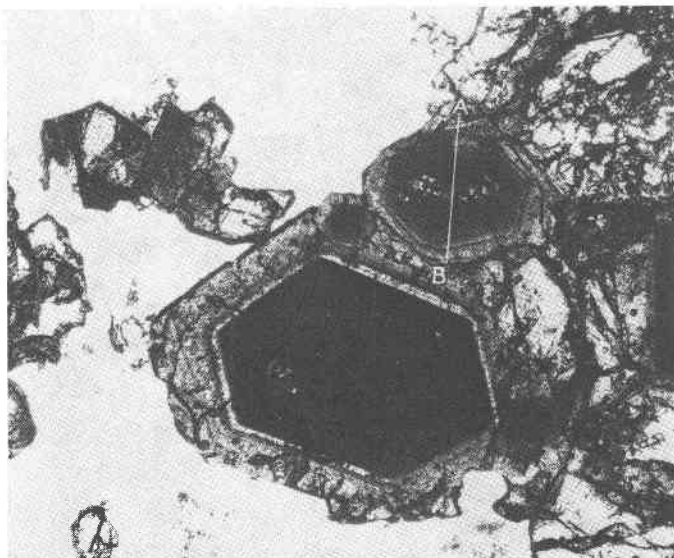


FIG. 3. Photomicrograph of Specimen D showing the path of the traverse.

ion, although the second element can occasionally reach unusual high concentrations (Fig. 2). This fact is attributed to the existence of fine cracks in the mineral, which apparently allows a local manganese enrichment. The sodium trend is somewhat irregular, with the variations apparently related to inclusion effects instead of other reasons.

The close association between titanium, iron, and silicon in the analyzed melanites is emphasized by Figure 4. This has been constructed using only data from sample C, with the unit formula calculated on the basis of 24 oxygens. The plot of the atomic proportions of Ti (total) against Si and Fe indicates clearly that titanium is replacing both elements in the melanite structure.

In the structural formulae of Table I, all Fe has been assigned conven-

TABLE 1. CHEMICAL COMPOSITION OF ZONED MELANITES

	Specimen A		Specimen B		Specimen C		Specimen D	
	Edge	Core	Edge	Core	Edge	Core	Edge	Core
SiO ₂	34.17	32.25	34.26	32.71	34.44	32.80	34.70	33.65
TiO ₂	4.00	8.43	4.73	8.26	4.68	8.45	3.91	6.82
Al ₂ O ₃	1.25	1.34	1.22	1.20	1.19	1.82	1.22	1.12
Fe ₂ O ₃	29.05	25.93	27.99	25.69	27.39	24.78	28.03	26.30
MnO	0.39	0.41	0.23	0.30	0.43	0.56	0.68	0.74
MgO	0.21	0.29	0.19	0.23	0.19	0.30	0.14	0.21
CaO	31.36	31.44	31.61	31.66	32.31	31.05	31.85	31.65
Na ₂ O	0.18	0.32	0.26	0.34	0.29	0.25	0.22	0.31
K ₂ O	—	—	—	—	0.02	—	—	0.01
Total	100.61	100.41	100.49	100.39	100.87	100.91	100.75	100.81

		Number of Ions on the Basis of 24 (O)			
Si	Z	5.712	5.452	5.660	5.440
Ti		0.044	0.312	0.110	0.206
Al		0.244	0.236	0.230	0.354
				6.00	6.00
Ti	Y	0.457	0.720	0.467	0.845
Al		—	—	—	—
Fe ⁺		3.640	3.210	3.376	3.082
				3.85	3.93
				—	—
Mn		0.055	0.042	0.059	0.079
Mg		0.052	0.047	0.027	0.075
Ca	X	5.617	5.653	5.689	5.676
Na		0.058	0.110	0.092	0.080
K		—	—	—	—
				5.783	5.608
				—	0.172
				6.00	6.00
				0.217	0.220
				0.489	0.653
				0.019	—
				3.502	3.288
				4.01	—
				—	3.94
				0.096	0.104
				0.035	0.052
				5.687	5.652
				0.070	0.100
				—	—
				—	—
				5.89	5.91
				—	—

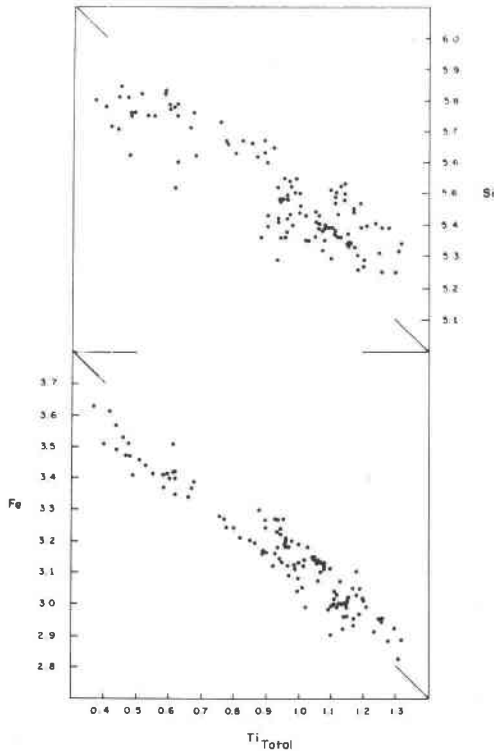


FIG. 4. Plot of the number of ions of Ti (total) against Fe and Si. Data taken from Specimen C, with the chemical formula calculated on the basis of 24 oxygens. The diagonal line represents the slope for the 1:1 replacement.

tionally to the *Y* position, with the result that Ti apparently occurs in both *Z* and *Y* sites. If some Fe in fact occurs in the *Z* position (*cf.*, Dowty and Mark, 1968), then Ti could conceivably all be located in *Y*. The variability of the zoned melanites in the present samples clearly involves substitution of Ti for both Fe and Si. For specimen C (Fig. 4), the replacement scheme involves a small amount of Al in addition and is approximately $0.2 \text{ Al}^{3+} + 1.0 \text{ Ti}^{4+} = 0.7 \text{ Fe}^{3+} + 0.6 \text{ Si}^{4+}$. In all four cases the ratio of replaced Fe atoms to replaced Si atoms is slightly greater than one.

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