

Ilmenite (high Mg,Mn,Nb) in the carbonatites from the Jacupiranga Complex, Brazil

JOSÉ C. GASPAR

*Instituto de Geociências
Universidade de São Paulo
São Paulo, Brazil CEP 05508*

AND PETER J. WYLLIE¹

*Department of Geophysical Sciences
University of Chicago, Chicago, Illinois 60637*

Abstract

Ilmenite occurs rarely in the carbonatite plug (five separate intrusions) of the Jacupiranga Complex, in the jacupirangite near the contacts, and in the banded reaction zones between carbonatite and jacupirangite. Electron microprobe analyses reveal a wider range of ilmenite compositions than previously reported from carbonatites, as solid solutions in $\text{FeTiO}_3\text{--MgTiO}_3\text{--MnTiO}_3\text{--Fe}_2\text{O}_3$, with high-Nb ilmenites containing up to 3.68 wt.% ($\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$). A group of discrete primary ilmenites from one carbonatite is distinguished by unusually high MnTiO_3 (MnO 15.1–19.6%); ilmenite inclusions in magnetites of the carbonatite intrusions are similar in composition to magnesian ilmenites previously reported; other ilmenites (a few discrete grains, but mainly lamellae with some granules associated with magnetite), have compositions that vary almost completely from FeTiO_3 to MgTiO_3 , with less than 10% Fe_2O_3 . Titanomagnetites (with Nb_2O_5 below detection limits) in jacupirangite have ilmenite lamellae near and within the reaction zones, with Nb_2O_5 increasing ($\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ up to 0.95%) and Fe_2O_3 decreasing in ilmenite as carbonatite is approached. Pentavalent Nb and Ta replace Ti in ilmenite, causing cation deficiency. In coexisting magnetite and ilmenite, MgO and MnO partition preferentially into ilmenite; MgO shows a regular pattern of distribution between ilmenite and magnetite, whereas MnO is distributed irregularly. Coexisting magnetite and ilmenite (with low MgO and MnO) from the reaction rocks give equilibration temperatures of 570–595°C and oxygen fugacities of $10^{-18.5}$ to $10^{-19.5}$ atmospheres. The ilmenites are distinguished from ilmenites in kimberlites by high MnO, very low Cr_2O_3 , and high ($\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$).

Introduction

Valuable petrogenetic information has been obtained from iron–titanium oxide minerals in kimberlites (Boyd and Nixon, 1973; Haggerty, 1975; Mitchell, 1977), but their study in carbonatites has received less attention. Detailed field work on the Jacupiranga carbonatite by one of us (JCG) has provided an unusual opportunity to sample in detail the variations in mineralogy of magnetite and ilmenite through five distinct carbonatite intrusive phases within a single igneous complex. Magnetite is ubiquitous and abundant, but ilmenite is rare. In this paper, we present data for ilmenite and relate the results to magnetite analyses (Gaspar and Wyllie, 1983) to the extent that this is possible.

Recent studies of magnetite and ilmenite in carbona-

tites have been directed toward the question of whether or not there is a petrogenetic relationship between kimberlites and carbonatites (Mitchell, 1979). Boctor and Svisero (1978) and Mitchell (1978) presented analyses of magnetites and ilmenites from the Jacupiranga carbonatite, and concluded that the evidence does not support a genetic relationship between the two rock types. Gaspar and Wyllie (1983) presented a more detailed study of the magnetites from Jacupiranga and, while agreeing with Boctor and Svisero (1978) and Mitchell (1978) that the crustal petrogenesis of kimberlite is very different from that of carbonatites, they pointed out that the genetic links may be forged within the upper mantle, following a scheme summarized by Le Bas (1977, Fig. 24.1).

The Jacupiranga Complex

Improved exposures uncovered by the quarrying and mining operation in the Jacupiranga Complex, together with detailed mapping, has revealed that the central

¹ Present address: Department of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

carbonatite plug is composed not of two intrusions (Melcher, 1966), but of five. The geology of the carbonatites was summarized by Gaspar and Wyllie (1983, Table 1). The five successive intrusions of carbonatite are identified as C_1 to C_5 , from oldest to youngest. There are many alvikite and beforsite dikes; one beforsite dike (B) emplaced in the diffuse contact zone between C_2 and C_3 is treated in this paper. The carbonatites were intruded into jacupirangite (J). At contacts between carbonatite and jacupirangite a banded rock is developed varying in width from 10 cm to more than 2 m. Centimeter-wide bands of carbonate alternate with silicate-rich bands composed mainly of phlogopite, alkali amphibole, magnetite, and veins of carbonate a millimeter or so wide. Magnetite and ilmenite occur only in the silicate-rich bands in these reaction zones.

The occurrence of ilmenite

The occurrence of various forms of ilmenite and their distribution in the different rock types is summarized in Table 1 and described in the Appendix (Figures and Tables in the Appendix have the prefix "A" before the number). Near the banded reaction rock between jacupirangite and carbonatite, the titanomagnetites of the jacupirangite contain ilmenite lamellae. Ilmenite occurs in various forms in the silicate-rich bands of the reaction rock. Ilmenite is rare in the carbonatites.

There are very few discrete crystals of ilmenite with primary appearance. Most ilmenite is associated with magnetite, which is relatively abundant in all rock types encountered, except for the fine carbonate bands in the reaction rocks. The ilmenite occurs as oxidation exsolution lamellae, or as internal or external granules in composite grains with magnetite (Buddington and Lindsley, 1964; Haggerty, 1967a). Some small crystals of ilmenite enclosed within magnetite may be inclusions of primary ilmenite (Haggerty, 1967a).

Ilmenite compositions

The procedures for microprobe analyses of the ilmenites are given in the Appendix. The chemical compositions of ilmenite listed in Table 2 and plotted in Figure 1 confirm that the minerals are solid solutions of $MgTiO_3$, $FeTiO_3$, Fe_2O_3 and $MnTiO_3$. The calculation of Fe^{3+} content is discussed in the Appendix. The analyses of oxidation exsolution ilmenite lamellae from Jacupiranga carbonatites reported by Boctor and Svisero (1978) and Mitchell (1978) are plotted for comparison. These authors noted that the MgO contents were much higher than those of ilmenites from other carbonatite and alkaline rocks. Values in other carbonatites have characteristically less than 1% MgO, except for the 12–15% MgO reported by Boctor and Svisero (1978) which is similar to ilmenite in kimberlites, and 15–24% MgO reported by Mitchell (1978) which is higher than in kimberlitic ilmenites. The high MnO and low Cr_2O_3 contents of the ilmenites distinguish

Table 1. Forms of ilmenite in rocks at Jacupiranga

Ilmenite	Carbonatite	Reaction rock	Jacupirangite
Discrete crystals	C_4 B	RC_1 RC_5	
Inclusions in magnetites	C_1 C_3		
Lamellae		RC_1 RC_3 RC_5	J
Internal granules		RC_3 RC_5	
External granules		RC_1 RC_3 RC_5	

C_1 , C_3 , C_5 , Carbonatite intrusions (Gaspar and Wyllie, 1982).

B, Beforsite dike. J, Jacupirangite.

RC_1 , RC_3 , RC_5 , banded reaction rocks between carbonatite and jacupirangite.

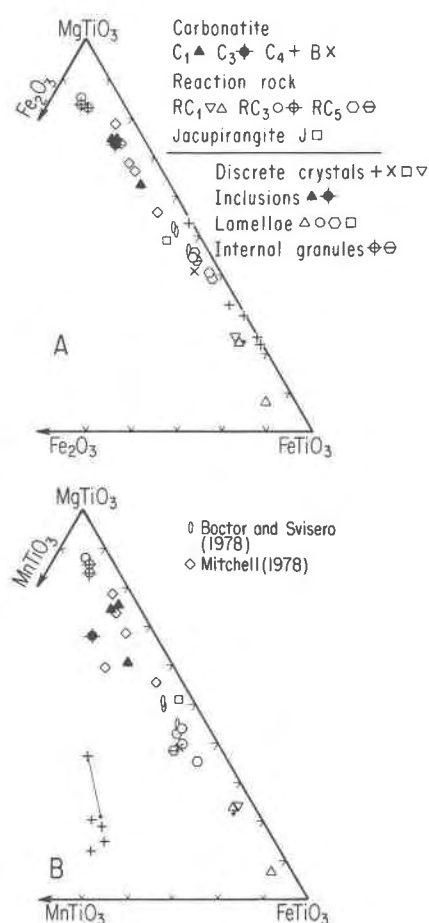


Fig. 1. Ilmenite compositions (mole %) from Jacupiranga carbonatites, jacupirangite, and banded reaction rocks between them. See Table 1 and text for explanation of symbols and ilmenite occurrences. Inclusions, lamellae, and granules are enclosed in magnetite. Symbols with cross (+) superimposed are for ilmenite with high Nb. See Table 2 for analyses. Previous analyses by Boctor and Svisero (1978) and Mitchell (1978) are plotted for comparison. The two dots connected to symbols are rim and core compositions for zoned minerals.

Table 2. Ilmenite compositions from Jacupiranga

	1	2	3	4	5	6	7	8	9	10	11	12
TiO ₂	58.2	56.6	58.8	49.1	52.1	52.4	51.7	55.2	57.7	55.4	58.1	51.6
SiO ₂	0.00	0.00	0.02	0.03	0.00	0.02	0.50	0.00	0.00	0.03	0.00	0.11
ZrO ₂	0.02	0.03	0.03	0.03	0.01	0.00	0.03	0.02	0.02	0.02	0.14	0.03
Ta ₂ O ₅	0.00	0.07	0.00	0.00	0.01	0.05	0.05	1.21	0.06	0.07	0.01	0.41
Nb ₂ O ₅	0.14	0.37	0.21	0.00	0.42	0.71	0.32	0.96	1.88	3.36	0.40	3.27
Al ₂ O ₃	0.00	0.02	0.00	0.00	Nd	Nd	0.08	Nd	0.00	0.00	0.00	0.00
Fe ₂ O ₃	7.51	6.55	6.23	6.55	4.79	3.83	5.11	6.87	9.42	9.90	9.74	0.16
FeO	9.77	14.7	10.7	38.6	33.6	33.9	33.6	9.12	5.10	4.31	3.66	21.1
MnO	3.16	4.90	2.24	2.09	2.07	2.19	2.26	7.18	3.41	2.93	2.78	19.6
MgO	21.5	16.8	22.4	1.90	6.28	5.99	6.22	19.0	24.6	24.6	25.8	3.49
CaO	0.78	1.05	0.00	0.12	0.02	0.33	0.11	0.04	0.02	0.00	0.01	0.16
TOTAL	101.08	101.09	100.63	98.42	99.30	99.42	99.98	99.60	102.21	100.62	100.64	99.93
	Cation number (6 oxygens)											
Ti	1.874	1.885	1.894	1.875	1.901	1.912	1.873	1.846	1.816	1.770	1.834	1.914
Si	-	-	-	-	-	-	0.023	-	-	-	-	0.006
Zr	-	-	-	-	-	-	-	-	-	-	0.003	-
Ta	-	-	-	-	-	-	-	0.016	-	-	-	0.006
Nb	0.005	0.005	0.005	-	0.017	0.018	0.006	0.021	0.035	0.066	0.010	0.071
Al	-	-	-	-	-	-	0.006	-	-	-	-	-
Fe ³⁺	0.242	0.218	0.201	0.250	0.175	0.140	0.185	0.230	0.297	0.317	0.307	0.006
Fe ²⁺	0.350	0.543	0.384	1.637	1.366	1.378	1.355	0.339	0.179	0.153	0.128	0.869
Mn	0.118	0.184	0.082	0.088	0.085	0.091	0.093	0.270	0.121	0.105	0.098	0.822
Mg	1.372	1.111	1.431	0.143	0.455	0.435	0.446	1.258	1.535	1.561	1.615	0.258
Ca	0.036	0.051	-	0.006	-	0.018	0.006	-	-	-	-	0.009
TOTAL	3.997	3.997	3.997	3.999	3.999	3.992	3.993	3.980	3.983	3.972	3.995	3.961
	13	14	15	16	17	18	19	20	21	22	23	24
TiO ₂	53.8	50.9	52.1	54.8	52.9	54.5	54.9	54.6	55.4	54.7	54.2	55.0
SiO ₂	0.07	1.18	0.29	0.03	0.00	0.06	0.03	0.05	0.04	0.15	0.02	0.02
ZrO ₂	0.01	0.01	0.01	0.02	0.00	0.01	0.01	0.03	0.02	0.02	0.04	0.00
Ta ₂ O ₅	0.07	0.16	0.35	0.34	0.57	0.01	0.02	0.14	0.04	0.03	0.03	0.00
Nb ₂ O ₅	1.13	2.32	3.14	3.04	2.10	0.43	0.32	0.81	0.53	0.77	0.79	0.00
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.00	Nd	Nd	Nd	Nd	Nd	0.00	Nd
Fe ₂ O ₃	0.00	1.28	0.00	0.32	0.00	1.76	2.24	3.83	3.03	3.19	5.27	6.71
FeO	22.3	19.7	20.6	16.2	20.4	28.5	27.2	24.2	24.6	25.2	24.9	22.6
MnO	17.8	17.9	16.6	15.1	16.6	3.34	2.75	3.92	3.46	3.69	3.88	1.61
MgO	3.97	5.50	4.92	10.3	5.76	9.81	10.8	11.7	12.3	11.6	10.7	14.2
CaO	0.04	0.16	0.33	0.16	0.32	0.08	0.10	0.22	0.00	0.08	0.88	0.01
TOTAL	99.19	99.11	98.34	100.32	98.65	98.30	98.37	99.50	99.42	99.43	100.71	100.15
	Cation number (6 oxygens)											
Ti	1.991	1.868	1.930	1.927	1.948	1.954	1.954	1.913	1.933	1.921	1.891	1.855
Si	0.003	0.056	0.015	-	-	0.003	-	0.003	0.003	0.006	-	-
Zr	-	-	-	-	-	-	-	-	-	-	-	-
Ta	-	-	0.006	0.006	0.006	-	-	-	-	-	-	-
Nb	0.024	0.053	0.071	0.062	0.047	0.006	0.006	0.017	0.011	0.017	0.017	-
Al	-	-	-	-	-	-	-	-	-	-	-	-
Fe ³⁺	-	0.047	-	0.011	-	0.063	0.080	0.134	0.106	0.112	0.184	0.230
Fe ²⁺	0.917	0.804	0.847	0.633	0.841	1.129	1.078	0.944	0.955	0.982	0.965	0.859
Mn	0.743	0.739	0.693	0.599	0.690	0.137	0.111	0.154	0.136	0.146	0.153	0.063
Mg	0.290	0.399	0.361	0.720	0.423	0.691	0.762	0.815	0.850	0.805	0.736	0.963
Ca	0.003	0.009	0.018	0.008	0.018	0.006	0.011	-	-	0.003	0.045	-
TOTAL	3.971	3.975	3.941	3.966	3.973	3.989	3.997	3.991	3.994	3.992	3.991	4.000

1,2,3 - C₁, inclusions.
4 - RC₁, S₂, lamella.
5,6 - RC₁, S₃, core and rim, respectively. Discrete grain.
7 - RC₁, S₄, lamella.
8 - C₃, platy crystal coexisting with pyrite. Both are included in a magnetite.
9, 10 - RC₃, internal granules.
11 - RC₃, lamella.
12, 13, 14, 15 - C₄, discrete grains.
16, 17 - C₄, core and rim respectively of a discrete grain.
18, 19, 20, 21 - RC₅, lamellae.
22 - RC₅, internal granule in the same magnetite of lamella 21.
23 - B, discrete grain in a beforite emplaced in the contact of C₂ and C₃.
24 - J, lamella in the titanomagnetite of the jacupiranga near the C₁ intrusion.
Nd - not determined. Cr₂O₃ present as trace amounts only.

them from kimberlitic ilmenites. The analyses listed in Table 2 and plotted in Figure 1 encompass and extend beyond the range of previously published compositions of ilmenites from Jacupiranga carbonatite.

Niobium and tantalum, with ionic radii similar to that of titanium, have a tendency to enter the structure of ilmenite as a trace element. The first reported values of Nb₂O₅ and Ta₂O₅ from Jacupiranga ilmenites are listed in

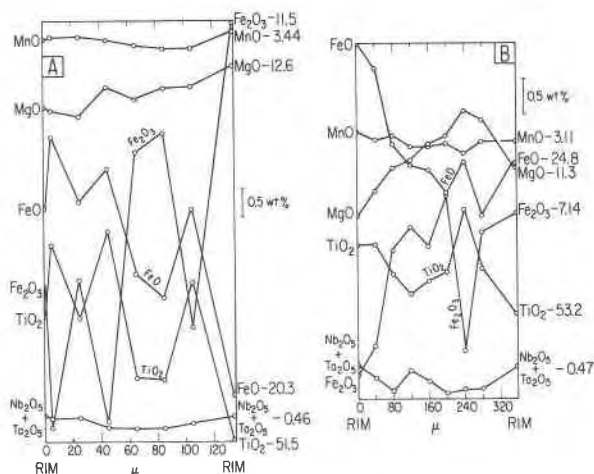


Fig. 2. Electron microprobe traverses along the lengths of ilmenite lamellae in magnetite from the reaction rock of the C_5 intrusion (RC_5). Each point represents a single analysis.

Table 2. The primary ilmenites (#12 to 17, Table 2) are distinguished from the lamellae ilmenites and most of the granules and inclusions by their relatively high niobium (1–3.4% Nb_2O_5). Three other ilmenites have Nb_2O_5 values within the same range: two internal granules from the silicate-rich layers of the banded reaction zone associated with carbonatite C_3 (#9 and 10, Table 2), and an inclusion of ilmenite within magnetite from carbonatite C_3 (#8, Table 2). Detailed discussion of Nb and Ta in the ilmenites is presented in the Appendix.

The primary ilmenites in carbonatite C_4 are distinguished from all others by their extremely high MnO contents (16–20%), together with high Nb_2O_5 (1.1–3.4%). The largest of these niobium–manganoan-ilmenites was analyzed at core and rim, and the zoning plotted in Figure 1 shows an increase in Fe/Mg from core to rim (analyses 16 and 17 in Table 2). These ilmenites also contain less Fe_2O_3 than the other ilmenites (Fig. 1A).

The compositions of the ilmenite inclusions in magnetites of carbonatites C_1 and C_3 are geikielites, plotting in Figures 1A and B in approximately the same area as the exsolution lamellae analyzed by Mitchell (1978). The discrete ilmenite crystal from the beforosite dike (B, Table 1) is a magnesian ilmenite plotting in Figure 1 close to the exsolution lamellae analyzed by Boctor and Svisero (1978). The ilmenite lamellae in magnetite from the jacupirangite near contacts with carbonatite (Table 1, J; Table 2, #24) coincide closely in Figures 1A and 1B with the lamellae in magnetite from the carbonatite analyzed by Boctor and Svisero (1978). The lamellae from jacupirangite are distinguished from the lamellae in reaction rock by lower MnO, however, as illustrated clearly in Figure 3.

Ilmenite occurs in several forms in the silicate-rich layers of the reaction rocks developed between jacupirangite and carbonatites (Table 1, Appendix). The lamellae and low-niobium internal and external granules exhibit a

wide variation in Mg/Fe. They are ilmenite–geikielite solid solutions, varying almost from one end-member to the other. The reaction band RC_3 contains examples of high-niobium granules (#9 and 10 in Table 2) and low-niobium lamellae (#11 in Table 2). These ilmenites contain an average of 85% $MgTiO_3$ (Fig. 1). Small discrete crystals of ilmenite occur in the silicate-rich layers RC_1 and RC_5 (Table 1). The analysis from RC_1 (#5–6, Table 2) is relatively low in MgO, in common with the associated low-niobium lamellae (#4 and 7, Table 2).

Figure 2 shows the results of analytical profiles along two lamellae in the reaction rock produced by the C_5 intrusion. The profile in Figure 2A is from a lamella extending from one edge to the other of the magnetite host, and that in Figure 2B is from a lamella that begins and ends inside the magnetite grain. These are compositionally similar to RC_5 lamellae.

Sympathetic variation of FeO and TiO_2 , and antipathetic variation of the latter two with Fe_2O_3 , is documented in Figure 2A. In Figure 2B the same behavior occurs except for the first and the last measurements, which show FeO and Fe_2O_3 varying together indicating the involvement of magnetite, because the beam spot was very near the end of the lamella. In Figure 2B, MgO decreases toward the rims of the lamella, but in Figure 2A it increases slightly from one rim to the other. ($Nb_2O_5 + Ta_2O_5$) and MnO vary little, but there is a perceptible tendency of enrichment toward the rims.

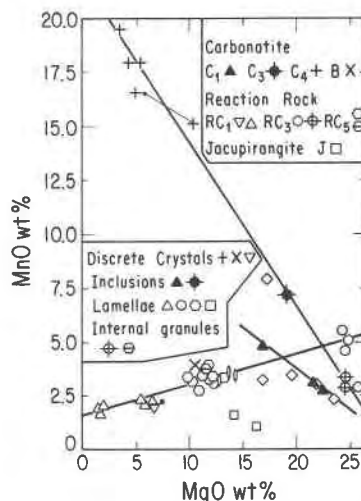


Fig. 3. Variation of MnO and MgO in ilmenites from the Jacupiranga rocks (see Fig. 1; additional points for partial analyses are also plotted). Note the contrast between sympathetic variation for the lamellae, and antipathetic variation for high-Nb discrete crystals from C_4 and the inclusions and granules from C_3 and RC_3 . The previous analyses of lamellae in magnetites from the carbonatites lie close to the line for the lamellae (Boctor and Svisero, 1978), or straddle this line (Mitchell, 1978).

Relationships between MgO and MnO in ilmenites

Figure 1 illustrates the almost continuous chemical variation from ilmenite to geikielite among individual grains. The discrete primary ilmenites from carbonatite C₄ are distinguished from the main trend by much higher MnTiO₃ (Fig. 1B), and lower Fe₂O₃ (Fig. 1A). The ilmenite lamella in magnetite from the jacupirangite (near the contact with carbonatite) is distinguished from the main trend by somewhat lower MnTiO₃ (Fig. 1B), and slightly higher Fe₂O₃ compared with other ilmenites with similar Mg/Fe (Fig. 1A). Distinctions among the different types of ilmenite are clearer in Figure 3, which shows the absolute contents of MnO and MgO. Figure 3 illustrates results from several partial analyses, in addition to the complete analyses listed in Table 2 and plotted in Figure 1.

The low-niobium lamellae and granules from the silicate-rich layers of the banded reaction rocks define a straight line illustrating sympathetic variation of MnO with MgO. The low MnO contents of the lamellae in magnetites from jacupirangite locate them well below this line. A second relationship is suggested by the line connecting the C₄ analyses with the other three high-niobium ilmenites associated with carbonatite C₃. This relationship is antipathetic, in contrast with that connecting the low-niobium lamellae and granules. There are three ilmenite inclusions in magnetite from carbonatite C₁ which could represent primary ilmenite (solid triangles in Fig. 3). A straight line connecting these three analyses suggests an antipathetic relationship among them, similar to that connecting the high-niobium ilmenites, but diverging from it.

The analyses in Figure 3 indicate that the ilmenites in the carbonatite intrusions define composition variation lines trending in the same general direction as zoning in primary discrete ilmenites (from C₄). These trends differ significantly from the sympathetic variation line defined by the low-niobium lamellae and granules in the silicate-rich layers of the reaction zones.

Contact relationships involving Nb and Fe³⁺

As illustrated in Figures 1, 3, and A1, the ilmenite lamellae produced by oxidation exsolution from titanomagnetites in jacupirangite have compositions distinct from the ilmenites in the carbonatites, and from the variety of ilmenites in the silicate-rich layers of the banded reaction zones between jacupirangite and carbonatites. For example, the ilmenite in jacupirangite (#24, Table 2) is one of only two ilmenites analyzed with no detectable niobium and tantalum. The other is a lamella in the reaction zone of carbonatite C₁.

The influence of carbonatite on the composition of ilmenite in jacupirangite, and in silicate-rich bands of the reaction rocks between jacupirangite and carbonatite, was explored by sampling across the transition from jacupirangite through the reaction zone towards the car-

bonatite intrusion C₁ (Fig. 4). A small intrusive carbonatite vein (distinct from carbonate-rich layers in the banded rock) cuts the reaction rock and has a distinctive effect on the ilmenite composition.

The ilmenites S₁ and S₂ are lamellae in magnetites on each side of the boundary between jacupirangite and the reaction rock. Ilmenite S₄ is from the reaction rock nearly 10 cm away from the contact. The textures (following the summary by Haggerty, 1976a) are as follows: S₁—trellis with fine lamellae; S₂ and S₄—trellis and sandwich type with large lamellae. The titanomagnetites in the jacupirangite a few centimeters from the contact are homogeneous, optically (Gaspar and Wyllie, 1983). These textures indicate that there is an increase in degree of oxidation exsolution from magnetite within the silicate rock, from jacupirangite towards the carbonatite contact. Figure 4 illustrates that the increasing oxidation exsolution is accompanied by increase in Nb and decrease in Fe³⁺ contents of the ilmenites.

The influence of carbonatite is clearly displayed by the analysis of S₃ near the small intrusive carbonatite vein. There is no magnetite in the silicate-rich layer containing S₃, and the ilmenite occurs as discrete, anhedral to subhedral crystals. The core composition has higher Nb and lower Fe³⁺ than S₂ and S₄, and the same trend is illustrated from core to rim of the zoned S₃ ilmenite. Thus, the carbonatite vein produced the same trend of increasing Nb and decreasing Fe³⁺ in ilmenite as that developed in the reaction rock from the jacupirangite contact towards the carbonatite contact (S₁—S₂—S₄).

The decrease in Fe³⁺ in ilmenite caused by proximity to carbonatite indicates lower oxygen fugacity in carbonatite magma than in the silicate country rocks. Furthermore, as discussed in connection with Figure A2, it appears that each carbonatite intrusion is characterized by different oxidation conditions.

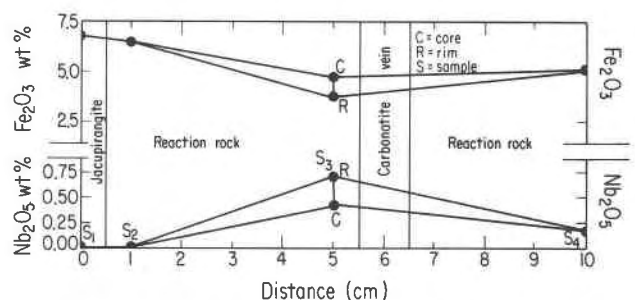


Fig. 4. Nb₂O₅ and Fe₂O₃ contents of ilmenites in a traverse across reaction zone RC₁, with jacupirangite to the left, and C₁ sovite to the right. The reaction rock is cut by a narrow carbonatite vein. S₁, S₂ and S₄ are lamellae and S₃ is a discrete, zoned crystal. See Table 2. The same points are plotted in the area J-RC₁ of Fig. 7.

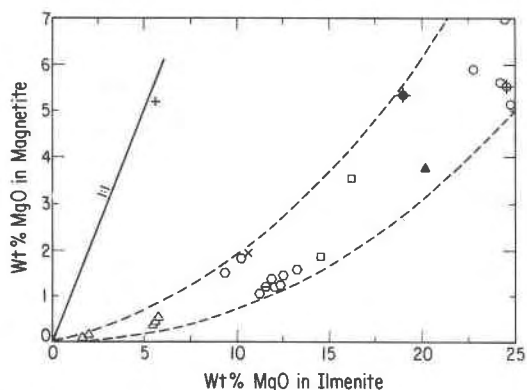


Fig. 5. Distribution of MgO between ilmenite and coexisting magnetite in Jacupiranga rocks. A general trend favoring ilmenite is evident, except for the C₄ discrete crystals (+) that plot near a 1:1 line. See Figures 1 and 3 for symbols. The compositions of ilmenite are from Table 2, and of magnetite from Gaspar and Wyllie (1983).

Coexisting ilmenite and magnetite

Magnetites in the carbonatites and associated rocks of Jacupiranga have compositions in the magnesioferrite-magnetite series very close to Fe₃O₄ (Gaspar and Wyllie, 1983). The most common occurrence of ilmenite is as oxidation exsolution lamellae in the magnetite. There are also composite grains with internal and external ilmenite granules which could be interpreted as either primary crystals or as products of oxidation exsolution (Haggerty, 1976a), and there are possibly primary inclusions of ilmenite enclosed in magnetite along with other minerals. Discrete primary ilmenite crystals are rare.

The partitioning of Mg

Figure 5 compares the MgO content of ilmenites and magnetites coexisting in the same rocks. The abundant ilmenite lamellae have probably equilibrated with the coexisting magnetite host, but in other examples the magnetite and ilmenite need not represent equilibrated mineral pairs. Most points plotted represent analyses of specific coexisting minerals, but some represent the average of ilmenites in one rock plotted against the average of magnetites in the same rock. Except for the discrete primary ilmenites in carbonatite C₄, all points lie within a broad trend illustrating strongly preferential concentration of MgO into the ilmenites (note the 1:1 ratio line). This behavior is consistent with the experimental data of Pinckney and Lindsley (1976). There is nothing in this figure that allows distinction between equilibrated intergrown mineral pairs, and the coexisting assemblages of magnetite and possible primary ilmenite in any of the rocks, except for the carbonatite C₄. In C₄, the average of the primary ilmenites (very rich in MnO, Fig. 3) contains almost the same amount of MgO as the average magnetite in the rock.

The ranges of values given by Boctor and Svisero

(1978) and Mitchell (1978) for MgO in ilmenite and magnetite compositions from Jacupiranga carbonatites overlap our values plotted within the band in Figure 5.

The partitioning of Mn

Figure 6 compares the MnO content of ilmenites and magnetites coexisting in the same rocks, and shows the preference of Mn for the ilmenite structure. Haggerty (1976b) reviewed the extensive work on the crystal chemistry of Mn substitution in magnetite and ilmenite, and reported the universal agreement that Mn is strongly partitioned towards ilmenite, regardless of whether ilmenite is primary, or the result of oxidation exsolution. Except for the extreme enrichment of MnO in the carbonatite C₄, there is nothing in Figure 6 to distinguish the distribution in carbonatites from that in the reaction zone rocks.

The ranges of values given by Boctor and Svisero (1978) and Mitchell (1978) for MnO in ilmenite (2.2–3.5%, with one at 7.9%) and magnetite (0.5–1.2%) compositions from Jacupiranga carbonatites, defines an area consistent with the values in Figure 6.

Haggerty (1976b, Fig. Hg-41C) divided the field equivalent to Figure 6 into areas showing the generalized distribution of MnO as a function of rock type. His boundaries between areas for (A) tholeiites, (B) rhyolites, (C) granites, and (D) granodiorites, monzodiorites, pegmatites and syenites are reproduced in Figure 6. The Jacupiranga minerals straddle the areas for the extrusive and intrusive acidic rocks. The irregular distribution of MnO between magnetite and ilmenite in the same rock indicates that the two minerals were not produced by simple exsolution in equilibrium with each other.

Petrogenetic considerations

Gaspar and Wyllie (1983) concluded on the basis of field relationships and magnetite compositions that the carbonatites were magmatic, that the oldest carbonatite,

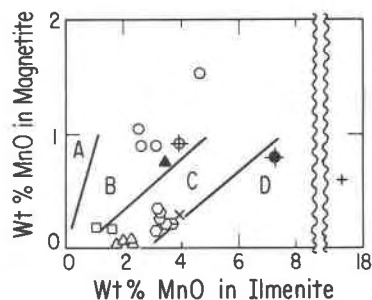


Fig. 6. Distribution of MnO between ilmenite and coexisting magnetite in jacupiranga rocks. (Table 2 for ilmenites; Gaspar and Wyllie, 1983, for magnetites). The areas defined by Haggerty (1976b) are: A - tholeiites, B - rhyolites, C - granites, and D - granodiorites, monzonites, pegmatites, and syenites. Most of the Jacupiranga minerals spread across the ranges B and C for rhyolites and granites. See Figures 1 and 3 for symbols.

C₁, was derived from a source somewhat different chemically from the magmas precipitating the successively younger carbonatites, and that C₃, C₄, and C₅ represent a continuum in time and magmatic evolution. Other conclusions related to the transformation products of jacupirangite titanomagnetites in the banded reaction zones, and the source of the beforseite dikes, will be reviewed along with the following discussion of the petrogenetic evidence from ilmenites.

Petrogenetic interpretations based on the ilmenite are more complicated than those based on magnetite, both because the ilmenite has more varied forms and occurrences and also because of the rarity of ilmenite.

Significant chemical variations among the ilmenites involve the substitution of Mn for Mg (Figs. 1 and 3), and the range of Nb and Ta (Figs. A1 and A2). Figure 3 shows an antipathetic relationship between MgO and MnO in sovites. The Nb₂O₅ contents of ilmenites in jacupirangite and carbonatite are quite different, and Nb₂O₅ plays a role in the compositions of ilmenites in the banded reaction rocks (Fig. 4). The content of Ta₂O₅ is generally small compared with that of Nb₂O₅. The ilmenite compositions are compared in Figure 7 in terms of (MgO + MnO) versus (Nb₂O₅ + Ta₂O₅).

Ilmenites from the sovites (C) in Figure 7 plot in an area separated from that of the other ilmenites. Because of the antipathetic relationship between MgO and MnO (Fig. 3), despite the significant difference in composition between the primary discrete manganoan ilmenites of C₄ and the ilmenite inclusions within magnetite from C₁ and C₃, all of the ilmenites from sovites occupy a band between about 22% and 26% (MgO + MnO).

The Nb₂O₅ content of the sovite ilmenites increases with the age of the intrusions, from C₁ (<0.5% Nb₂O₅), to C₃ (0.96% Nb₂O₅), to C₄ (1.13–3.27% Nb₂O₅), which is consistent with the geochemical concentration of incompatible element Nb into successive liquids during differentiation. Similarly, there is an increase in the MnO content of the sovite ilmenites with increasing age of the intrusions, C₁, C₃, and C₄ (Fig. 3). According to the results for sovite ilmenite C₁ and C₃–C₄ in Figure 3, increasing MnO appears to be accompanied by decreasing MgO.

The ilmenite in the beforseite dike (B) has essentially the same composition as ilmenite lamellae in the reaction zone RC₅, as shown by the areas for RC₅ in most diagrams (Fig. 1, 3, A1, 5, 6, and 7), but it is distinguished from most of the lamellae by its higher Nb₂O₅ (Fig. A1 and 7).

Gaspar and Wyllie (1983) concluded, on the basis of magnetite compositions in carbonatite C₅, a beforseite dike B₅ emanating from it, and in dolomite-rocks in the contact zone between carbonatites C₂ and C₃, that the dolomitic rocks could be related. This conclusion now extends to the beforseite dike B, because of the compositional similarity between the ilmenites in beforseite B and reaction rocks RC₅.

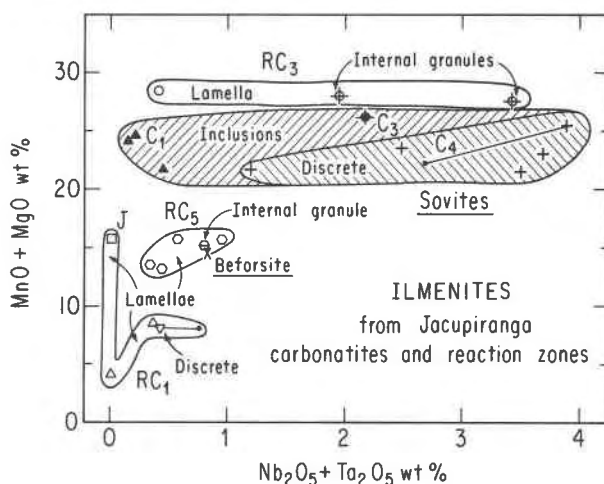


Fig. 7. The variation of (MnO+MgO) and (Nb₂O₅+Ta₂O₅) in ilmenites, combining results in Figs. 3 and A1. See Figures 1 and 3 for symbols, and Table 2 for analyses. Distinct ranges exist for ilmenites from the sovites, and from RC₁, RC₃, and RC₅. High (Nb₂O₅+Ta₂O₅) occurs only in ilmenites with high (MnO+MgO).

Ilmenite in the jacupirangite (J) is distinguished from all ilmenites in the carbonatites, and all but one in the banded reaction rocks, by the absence of detectable (Nb₂O₅ + Ta₂O₅), as shown in Figure A1, A2, 4, and 7.

More than 90% of the ilmenites in the silicate-rich bands of the banded reaction rocks (RC) are lamellae, produced by oxidation exsolution from the titanomagnetite of the jacupirangite country rock. The titanomagnetites of the jacupirangite have characteristic size and shape that are preserved within the banded rock through a few centimeters, until recrystallization and exsolution alters them. However, as demonstrated by the fact that the magnetites enclosing the lamellae contain more MnO than the starting titanomagnetite (Gaspar and Wyllie, 1983), despite the fact that MnO should partition strongly into the coexisting ilmenite (see Fig. 6), the process cannot be simply one of oxidation exsolution. Fluids or magmas involved in the generation of the banded rocks must cause chemical changes in addition. This is confirmed by the Nb₂O₅ and Ta₂O₅ contents of the ilmenites in the banded reaction zones (Figs. A1, 4, and 7).

The changes in Nb₂O₅ and Fe₂O₃ occurring across the contact between jacupirangite and banded reaction rock RC₁ were illustrated in Figure 4. The compositions of minerals S₁, S₂, S₄, and zoned S₃ from Figure 4 occupy the area J-RC₁ in Figure 7. Within the banded reaction rock RC₁, as a contact with carbonatite is approached, the ilmenite lamellae in the original jacupirangite lose Fe₂O₃ (Fig. 4), gain MnO (Fig. 3), lose MgO (Table 2, Fig. 7), and gain Nb₂O₅ and Ta₂O₅ (Figs. 4 and 7). The direct role of carbonatite is indicated by the zoning in the RC₁ discrete ilmenite in Figure 7 (S₃ in Fig. 4), where zoning

shows enrichment in $(\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5)$, and depletion in Fe_2O_3 .

Ilmenites in the reaction rocks RC_3 (Fig. 7) are ferroan geikielites with MgO contents higher than those of any other ilmenites analyzed in this complex (Fig. 1, Table 2), and nearly twice as high as the MgO in jacupirangite ilmenite. Their MnO contents are only slightly higher than those of the RC_1 ilmenites. Their magnetite hosts contain much more MgO than the titanomagnetite in the nearby jacupirangite (Fig. 5). The lamellae contain about the same amount of Nb_2O_5 as those in the RC_1 zone, but internal granules of ilmenite with otherwise similar composition are greatly enriched in $(\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5)$ (Fig. 7).

Magnetites enclosing ilmenite granules in the RC_3 zone may or may not enclose lamellae, as well. When both are present, they retain their respective low- and high-Nb as shown for the examples plotted in Figure 7. It is clear that these internal granules are not the end-products of progressive exsolution. The involvement of fluids or magmas in the transformation and recrystallization of the banded reaction rocks RC_3 appears to have been much more extensive than in the other examples studied. According to the available data, the internal granules crystallized as primary crystals in a medium rich in magnesium and niobium, and these were enclosed by magnesian magnetites which subsequently exsolved lamellae of ilmenite with lower concentrations of niobium.

The lamellae of ilmenite in RC_5 occupy a limited area in Figure 7. The one internal granule analyzed has essentially the same composition as the lamellae. In this example, in contrast with that described for RC_3 , the internal granule was apparently produced by the same process as that generating the lamellae. The increase in $(\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5)$ and MnO compared with the ilmenite in the jacupirangite confirms that here, as in the other banded reaction zones, the process of exsolution is accompanied by significant chemical reactions.

Temperatures and oxygen fugacity

The oxide pairs in most of the occurrences cannot be used to estimate temperatures and oxygen fugacities by the Buddington-Lindsley method because the ilmenites contain too much MgO and MnO (Buddington and Lindsley, 1964). Only the ilmenites S_2 and S_4 from the banded reaction rock RC_1 shown in Figure 4 are suitable. Using the graph of Spencer and Lindsley (1981), the results obtained are for S_2 , $f\text{O}_2 = 10^{-18.5}$ and temperature = 595°C , and for S_4 , $f\text{O}_2 = 10^{-19.5}$ and temperature = 570°C . S_2 and S_4 plot, respectively, slightly above and below the NNO buffer. As expected from the Fe_2O_3 content of these ilmenites, $f\text{O}_2$ is lower for S_4 than for S_2 . The decreasing Fe_2O_3 in the ilmenites from the jacupirangite towards the carbonatite C_1 , and the same effect of the carbonatite vein on nearby ilmenite, as shown in Figure 4 (S_3), indicate that the carbonatite has even lower oxygen fugacity than that estimated for the jacupirangite contact.

Prins (1972) estimated temperatures of $540\text{--}575^\circ\text{C}$ and $f\text{O}_2$ from 10^{-23} to 10^{-24} from exsolved ilmenites of carbonatites from Galapo and Oldonyo Dili. From intrinsic $f\text{O}_2$ measurements for minerals in carbonatites from Oka, Friel and Ulmer (1974) determined a temperature of $710 \pm 15^\circ\text{C}$, and $f\text{O}_2$ of $10^{-17.1} \pm 10^{-0.5}$. These data from other carbonatites correspond approximately to the FMQ buffer.

Comparison with ilmenites from other carbonatites and from kimberlites

Mitchell (1978) compiled analyses of ilmenites from carbonatites, kimberlites, and other rocks, with results reproduced in Figures 8A and 8C. Our figures are slightly modified compared with Mitchell's diagrams, with some additional analyses plotted. We have expanded the area for ilmenite from Jacupiranga to enclose three analyses of ilmenite lamellae and a discrete crystal, presented by Boctor and Svisero (1978). The additional points near the Jacupiranga area are for ilmenite lamellae from Russian carbonatites (Garanin *et al.*, 1980). The compositions of ilmenites from carbonatites in and near the area A are defined by the points plotted in Figures 8A and C. These

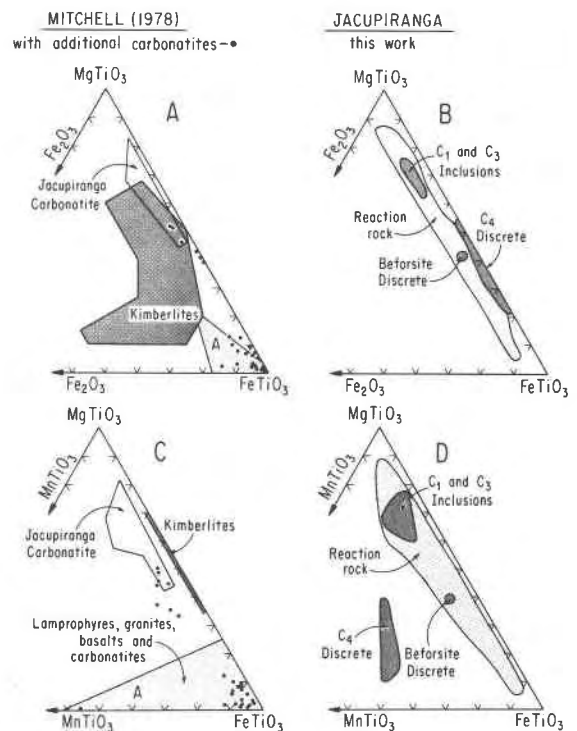


Fig. 8. A, C. Ilmenite compositions in carbonatites, kimberlites, and other rocks from Mitchell (1978) with carbonatite ilmenites plotted as dots. Mitchell (1978) used carbonatite results from Prins (1972) and McMahon and Haggerty (1976). Additional dots are from Secher and Larsen (1980) and Garanin *et al.* (1980). B, D. New analyses of Jacupiranga ilmenites based on points plotted in Figures 1A and B.

points include some of those plotted by Mitchell, together with additional analyses from the literature. With one exception (high MnTiO₃), these cluster near the FeTiO₃ corner.

Mitchell (1978) reported that the magnesian ilmenites from the Jacupiranga carbonatite differ from those of other carbonatites, and from kimberlites. Ilmenites from Jacupiranga overlap with those from kimberlites in Figure 8A, but they are distinguished in Figure 8C by their higher Mn content.

The ranges of ilmenite compositions in carbonatites according to previous studies (Figures 8A and C) is now considerably expanded by the new analyses from Jacupiranga carbonatites reported in this paper. The individual analyses plotted in Figure 1 have been grouped in Figures 8B and D for comparison with Mitchell's (1978) compilation. Ilmenites from the carbonatite intrusions and the befsite dike occupy three distinct areas, whereas the ilmenites from the banded reaction rocks between carbonatite and jacupirangite occupy a large range of compositions extending parallel to the geikielite-ilmenite axis, almost from one extreme to the other. The ilmenite inclusions from intrusions C₁ and C₃ plot within the range previously identified for Jacupiranga by Mitchell (1978) in Figures 8A and C. The reaction rock area extends beyond the Jacupiranga carbonatite range, and connects it with the other carbonatite range identified by Mitchell (1978) in area A of Figures 8A and C. The ilmenite in the befsite dike is centrally placed within the reaction rock area, between the two carbonatite areas of Figures 8A and C.

The discrete primary ilmenites from intrusion C₄ have distinctive compositions. They occupy an area with less Fe₂O₃ and considerably more MnTiO₃ than any of the other Jacupiranga ilmenites. In addition, they are less magnesian than the ilmenites previously reported from Jacupiranga. The C₄ ilmenites approach the composition of the ferroan pyrophanite reported from the Oka carbonatite by McMahan and Haggerty (1976). This discrete crystal with composition near Il₄₀Py₅₀Hem₁₀ (the dot near the middle of the MnTiO₃-FeTiO₃ axis in Figure 8C) differs from all other reported ilmenites from carbonatites.

Except for the carbonatites from Jacupiranga, Russia, and Oka, ilmenites from carbonatites cluster around the FeTiO₃ corner of Figure 8. The ilmenite compositions extend from FeTiO₃ toward MgTiO₃ and MnTiO₃, with characteristically low Fe₂O₃ and Cr₂O₃. All analyses so far published contain less than 10 mole % Fe₂O₃. Cr₂O₃ is usually less than 0.1% (Mitchell, 1979).

Magnesian ilmenites are rare, and Mitchell (1978) noted that their occurrence in the Jacupiranga carbonatites is unusual. Magnesian ilmenites are characteristically found in kimberlites, which are distinguished from carbonatite ilmenites by their low MnO (<1.0%, Figure 8C), and high Cr₂O₃ (0.1-2.5%, Mitchell, 1979).

According to Garanin *et al.* (1981), the average Nb₂O₅

and Ta₂O₅ contents of ilmenites from kimberlites are, respectively, 0.22% and 0.16%, compared with values for ilmenites from carbonatites of 1.11% and 0.13%. They concluded that the higher contents of Nb₂O₅ and Ta₂O₅ distinguished ilmenites of carbonatites from those of kimberlites. Our results for Nb₂O₅ and Ta₂O₅ for the Jacupiranga ilmenites (Table 2) are consistent with this conclusion.

These results for ilmenite from the Jacupiranga carbonatite and banded reaction rocks extend the known range of compositions for carbonatites, without changing the chemical criteria for distinction between ilmenites from carbonatites and kimberlites. The variety of compositions promises more general petrogenetic interpretations when the study of other minerals in the carbonatites is completed.

Acknowledgments

We thank Serrana S/A de Mineração, G. C. Melcher, and V. A. V. Girardi for making possible the field work of JCG, I. M. Steele for invaluable assistance with microprobe analyses, and J. V. Smith for assistance with the microprobe. Financial support was provided by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) PROC 201.158/80 and PROC 40.1410/81, Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) PROC 80/470 and PROC 81/0168-8, and the Earth Science Division of the National Science Foundation Grants EAR 76-20410, and EAR 81-08599.

References

- Boctor, N. Z. and Svisero, D. P. (1978) Iron-titanium oxide and sulfide minerals in carbonatite from Jacupiranga, Brazil. *Carnegie Institution of Washington Year Book*, 77, 876-880.
- Boyd, F. R. and Nixon, H. (1973) Origin of the ilmenite-silicate nodules in kimberlites from Lesotho and South Africa. In P. H. Nixon, Ed., *Lesotho Kimberlites*, p. 254-268. Lesotho National Development Corporation, Maseru.
- Buddington, A. F. and Lindsley, D. H. (1964) Iron-titanium oxide minerals and synthetic equivalents. *Journal of Petrology*, 5, 310-357.
- Carmichael, I. S. E. (1967) The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contributions to Mineralogy and Petrology*, 14, 36-64.
- Friel, J. J. and Ulmer, G. C. (1974) Oxygen fugacity geothermometry of the Oka carbonatite. *American Mineralogist*, 59, 314-318.
- Garanin, V. K., Kudryavtseva, G. P. and Lapin, A. V. (1980) Typical features of ilmenite from kimberlites, alkali-ultrabasic intrusions, and carbonatites. *International Geology Review*, 21, 1025-1050.
- Gaspar, J. C. and Wyllie, P. J. (1983) Magnetite in the carbonatites from the Jacupiranga Complex, Brazil. *American Mineralogist*, 68, 195-213.
- Haggerty, S. E. (1975) The chemistry and genesis of opaque minerals in kimberlites. *Physics and Chemistry of the Earth*, 9, 295-307.
- Haggerty, S. E. (1976a) Oxidation of opaque mineral oxides in basalts. In D. Rumble, III, Ed., *Oxide Minerals*, p. Hg1-Hg100. Mineralogical Society of America.
- Haggerty, S. E. (1976b) Opaque mineral oxides in terrestrial

- igneous rocks. In D. Rumble, III, Ed., *Oxide Minerals*, p. Hg101–Hg300. Mineralogical Society of America.
- Heinrich, E. Wm. (1966) *The Geology of Carbonatites*. Rand McNally and Company, Chicago.
- LeBas, M. J. (1977) *Carbonatite–Nephelinite Volcanism*. John Wiley and Sons, London.
- McMahon, B. M. and Haggerty, S. E. (1976) Oka carbonatite complex: oxide mineral zoning in mantle petrogenesis. *Geological Society of America, Abstracts with Programs*, 8, no. 6, 1006.
- Melcher, G. C. (1966) The carbonatites of Jacupiranga, São Paulo, Brazil. In O. F. Tuttle and J. Gittins, Eds., *Carbonatites*, p. 169–181. John Wiley and Sons, New York.
- Mitchell, R. H. (1977) Geochemistry of magnesian ilmenites from kimberlites in South Africa and Lesotho. *Lithos*, 10, 29–37.
- Mitchell, R. H. (1978) Manganoan magnesian ilmenite and titanian clinohumite from the Jacupiranga carbonatite, São Paulo, Brazil. *American Mineralogist*, 63, 544–547.
- Mitchell, R. H. (1979) The alleged kimberlite–carbonatite relationship: additional contrary mineralogical evidence. *American Journal of Science*, 279, 570–589.
- Pinckney, L. R. and Lindsley, D. H. (1976) Effects of magnesium on iron–titanium oxides (abstr.). *Geological Society of America Abstracts with Programs*, 8, 1051.
- Prins, P. (1972) Composition of magnetite from carbonatites. *Lithos*, 5, 227–240.
- Reed, S. J. B. (1973) Principles of X-ray generation and quantitative analysis with the electron microprobe. In C. A. Andersen, Ed., *Microprobe Analysis*, p. 53–81. John Wiley and Sons, New York.
- Secher, K. and Larsen, L. M. (1980) Geology and mineralogy of the Sarfartôq carbonatite complex, southern West Greenland. *Lithos*, 13, 199–212.
- Spencer, K. J. and Lindsley, D. H. (1981) A solution model for coexisting iron–titanium oxides. *American Mineralogist*, 66, 1189–1201.
- intrusions C₁, C₃, and C₅; rocks of the banded zones from intrusions C₂ and C₄ were not surveyed.
- At least 90% of the ilmenite in the banded rocks consists of lamellae apparently produced by oxidation exsolution from magnetite, with textures varying from trellis to sandwich (Buddington and Lindsley, 1964). There are in addition composite grains with internal or external granules of ilmenite (Buddington and Lindsley, 1964), which could have been derived either through continuation of the process that produced the lamellae, or by the inclusion of primary ilmenite crystals within magnetite (Haggerty, 1976a). The magnetites of banded rock RC₁ contain lamellae only, or lamellae and external granules of ilmenite. The magnetites of RC₃ and RC₅ contain lamellae only, lamellae and internal granules, or lamellae plus internal and external granules.
- There are discrete crystals of ilmenite in the groundmass of amphibole and phlogopite of the banded rocks from RC₁ and RC₅. They are anhedral to subhedral prismatic grains varying in size from about 3 μm up to 1 mm. Approaching the contact with carbonatite C₁, in RC₁, they become larger and less abundant. Those that were too small to be analyzed successfully could be identified by the electron microprobe.

Ilmenite in carbonatites

Discrete ilmenite crystals well removed from the more abundant magnetite occur in the sovite intrusion C₄. They form elongated prisms with lengths from 0.1 mm to 1 mm, and have the appearance of primary crystals.

Only a few ilmenite grains are likely candidates for a primary origin, e.g.: 10 μm to 30 μm long ilmenite with associated dolomite inclusions in magnetite grains from the C₁ sovite (#1, 2 and 3, Table 2), 0.6 mm long ilmenite intergrown with a pyrite inclusion in a 1.5 mm magnetite from the C₃ sovite (#8, Table 2), and a 0.1 mm ilmenite in the beforite dike in the diffuse contact zone between intrusions C₂ and C₃ (dike B of Gaspar and Wyllie, 1983, Table 1; #23, Table 2). This could be a primary ilmenite, but its position very close to a much larger anhedral magnetite grain (4 mm diameter) makes it suspect.

We found no ilmenites in the Jacupiranga carbonatites comparable with those described by Mitchell (1978) and Boctor and Svisero (1978), whose samples were collected at a higher level in the carbonatite plug, before the quarry surface was lowered to the horizon of the present mapping and collection. Both papers refer to apatite–magnetite–phlogopite carbonatite, with large rounded olivine crystals, which resemble but may not correlate with the carbonatite C₁ described by Gaspar and Wyllie (1983, Table 1, Fig. 10).

According to Mitchell (1978), ilmenite occurs exclusively as oxidation exsolution lamellae within large magnetite crystals. According to Boctor and Svisero (1978), ilmenite occurs as exsolution lamellae in magnetite, or as subhedral crystals enclosed in magnetite, or as aggregates of tabular crystals at the interface between magnetite and the carbonate minerals (calcite and dolomite). These textures correspond to the lamellae, internal granules, and external granules in Table 1 for the ilmenite occurring in the banded reaction rocks.

Analytical procedure

Microprobe analyses were carried out in the ilmenites using an ARL/EMX automated electron microprobe operated at 15 kv and 1.0 μA beam current. Data were corrected by a modified Magic IV computer program. Standards used were diopside glass (for Ca, Si and Mg); Fe metal (for Fe); synthetic rutile (for Ti);

*Manuscript received, June 18, 1982;
accepted for publication, March 18, 1983.*

Appendix

The occurrence of ilmenite

The occurrence of the various forms of ilmenite in the different rock types, summarized in Table 1, is described in more detail below.

Ilmenite in jacupirangite

The jacupirangite contains anhedral crystals of titanomagnetite with maximum diameter 1 mm. Up to 1 cm from the contact between jacupirangite and the banded reaction rock, the titanomagnetite exhibits progressive development of ilmenite lamellae, producing the typical trellis intergrowth described by Buddington and Lindsley (1964).

Ilmenite in the silicate-rich bands of the reaction rocks

The carbonate rocks of the banded reaction zone contain neither magnetite nor ilmenite. Magnetite and ilmenite occur in the silicate bands of the reaction zones bordering carbonatite

Table A1. Corrected values of FeO and Fe₂O₃ for ilmenites

	1	2	3	5	6	8	9	10	11
FeO ^a	9.77	14.7	10.7	33.6	33.9	9.12	5.10	4.31	3.66
FeO ^b	9.70	14.6	10.6	33.5	33.7	8.62	4.60	3.38	3.52
Fe ₂ O ₃ ^a	7.51	6.55	6.23	4.79	3.83	6.87	9.42	9.90	9.74
Fe ₂ O ₃ ^b	7.67	6.71	6.39	4.95	3.99	7.35	10.1	11.0	9.90

	12	14	16	17	18	19	20	21	22	23
FeO ^a	21.1	19.7	16.2	20.4	28.5	27.2	24.2	24.6	25.2	24.9
FeO ^b	20.1	19.0	15.3	19.8	28.4	27.2	24.0	24.5	24.9	24.6
Fe ₂ O ₃ ^a	0.16	1.28	0.32	0.00	1.76	2.24	3.83	3.03	3.19	5.27
Fe ₂ O ₃ ^b	1.28	1.92	1.28	0.64	1.92	2.40	4.15	3.19	3.35	5.43

a--values from Table 2.

b--corrected values considering the cation deficiency resulting from the presence of pentavalent Nb₂O₅ and Ta₂O₅.

Numbers are the same as the analyses in Table 2. Analyses 4, 7, 13, 15 and 24 remain unchanged after correction.

synthetic enstatite with 10 wt.% Al₂O₃ (for Al); synthetic glass with 0.65 wt.% MnO (for Mn); natural baddeleyite (for Zr); Nb metal (for Nb) and Ta metal (for Ta). The detection limit for minor elements calculated according to Reed (1973) is near 0.02 wt.%. The accuracy of the analyses is $\pm 5\%$ of the amount present for concentrations below 2 wt.% and $\pm 2\%$ of the amount present for major elements, except for Nb and Ta where the use of metal standards for low concentrations (<4 wt.%) leads to much larger errors, especially for concentrations below 1 wt.%. Long count times (100 seconds) were used for better accuracy in Nb and Ta analyses.

The method used to calculate Fe³⁺ is discussed below. Mn was assumed to be Mn²⁺, following custom (Haggerty, 1976b).

The data presented in Table 2 are averages. The results presented for lamellae may represent one lamella or may be the average of 2 or 3 lamellae chemically similar to each other, where 2 to 3 points were analyzed in each one. If the chemical features of a lamella are distinct, its results are presented separately. All the other results represent individual crystals where 2 to 6 points were measured. Many grains were too small for complete analyses, but the results of satisfactory partial analyses have been plotted in some figures, in addition to the values tabulated. Many grains were tested for Cr₂O₃, but its concentration was too low to merit attempts at useful analyses. The distinction between low- and high-Nb ilmenites was established by an extensive search of many grains using the display of the energy dispersive system (EDS).

Nb and Ta contents

The high values of Nb₂O₅ were noted in connection with Table 2 and Figure 3. Nb₂O₅ and Ta₂O₅ contents are compared in Figure A1.

The high-Nb, discrete, primary ilmenites from carbonatite C₄ and that from the beforosite dike illustrate a sympathetic trend of increasing Ta₂O₅ with increasing Nb₂O₅ contents, with the slope of the variation line increasing for the highest values of Nb₂O₅ (up to 3.27%). The zoned ilmenite shows decrease of Nb₂O₅ and increase of Ta₂O₅ from core to rim. Another ilmenite from a carbonatite intrusion, the primary inclusion in magnetite from C₃, has relatively high Nb₂O₅ (0.96%) and extremely high Ta₂O₅. It contains 1.21% Ta₂O₅ (average of three measurements, 1.11%, 1.14%, and 1.39%) compared with the next highest value of 0.57%. The two other high-Nb ilmenites, internal granules from the reaction zone of intrusion C₃, have Nb₂O₅ reaching 3.36%, but their somewhat lower Ta₂O₅ places them below the chemical variation curve in Figure A1.

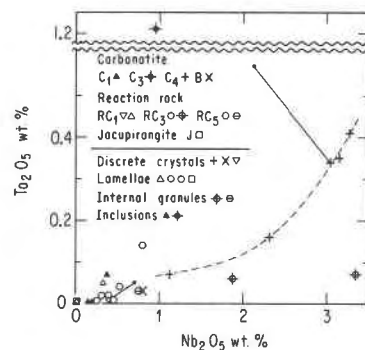


Fig. A1. Variation of Nb₂O₅ and Ta₂O₅ in ilmenites from the Jacupiranga rocks (see Fig. 1). Note the very high Ta₂O₅ in the C₃ inclusion, the trend for primary discrete ilmenites from C₄, and the contrasted zoning for one of them.

The low-Nb ilmenite lamellae and granules in magnetites from the reaction zones, and the inclusion in magnetites of carbonatite intrusion C₁, are restricted to a limited range with less than 0.81% Nb₂O₅ and less than 0.1% Ta₂O₅. There is no detectable Nb₂O₅ or Ta₂O₅ in the ilmenite lamellae in a magnetite from the jacupirangite (#24, Table 2), and in one magnetite from the reaction zone of C₁ (#4, Table 2).

Figure A2 shows the effect of substitution of Ti by (Nb+Ta). For ilmenite with composition RTiO₃ and a trace of SiO₂, but without Nb or Ta, the (Ti+Si) cations should total 2.0 (Zr is not significant in these ilmenites). The line drawn through the value of 2.0 represents 1:1 substitution of (Ti+Si) by (Nb+Ta). The primary ilmenites from the C₄ carbonatite plot very close to this line. The variation from core to rim of the zoned crystal also follows this antipathetic substitution line.

For the ilmenite associated with each carbonatite intrusion, a different line can be drawn through the analyses, each parallel to the C₄ line, representing 1:1 substitution. The fit of points to the substitution lines is good for C₃, fair for C₅, and for C₁ the linear relationship is poor but the position between the lines for C₃ and C₅ is established. The intersection points of these lines with the (Ti+Si) axis give the sums of the cations (Ti+Si) corresponding to the structure without Nb and Ta. Intersection numbers less than 2.00 are caused by replacement of (Ti+Si) by some other cation. According to the analyses in Table 2, the only available cation for this site (except for minute traces of Zr) is Fe³⁺. Variation of Fe₂O₃ in the ilmenites is illustrated in Figure 1A, but Figure 1A does not reveal the distinctive oxidation states implied in Figure A2 for the rocks associated with each carbonatite intrusion.

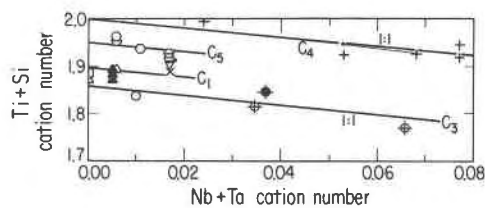


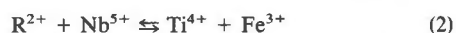
Fig. A2. The substitution of Ti by (Nb+Ta) in ilmenites from Jacupiranga rocks (see Figs. 1 and A1, and Table 2). The ilmenites from each intrusion and its associated reaction rock plot close to specific 1:1 substitution lines.

The fact that the compositions for all three types of ilmenite associated with the carbonatite C₃ (low-Nb lamellae and high-Nb granules in the reaction rock, and an inclusion in magnetite of the carbonatite) lie on the same substitution line in Figure A2 suggests that the oxidation conditions are specific for the C₃ intrusion. The different positions of the substitution lines for ilmenites associated with intrusions C₁, C₅, and C₄ indicate less substitution of Fe₂O₃ in these ilmenites. The points for the ilmenite in jacupirangite and in the beforite dikes are close to the line labeled C₁, representing relatively high substitution of Fe³⁺.

Assuming the normal oxidation state for both Nb and Ta (pentavalent), reactions for substitution of these elements in ilmenite may be proposed. Two possible reactions are:



and:



If Reaction (1) occurs, for each pair of pentavalent cations that enters the structure of ilmenite, one divalent cation position will become vacant.

The ideal ilmenite structure based on six oxygen atoms should have cations totalling 4.00. As seen in Table 2, only the ilmenite from jacupirangite reaches this value; all others exhibit a cation deficiency, suggesting that the substitution of Nb and Ta for (Ti+Si) occurs mainly according to Equation (1). The total cation numbers from Table 2 are plotted as open circles in Figure A3 against the weight per cent of combined Nb₂O₅. The crosses represent the cation deficiency calculated on the basis of Equation (1), allowing one cation deficiency for each two (Nb+Ti) cation numbers from Table 2. The crosses define a good straight line representing the cation deficiency as a function of weight per

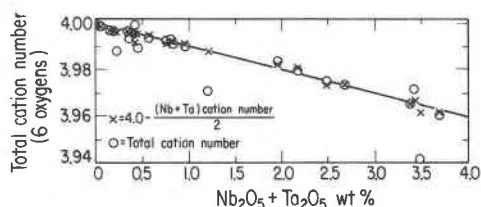


Fig. A3. The measured (circles, Table 2) and calculated (X) total cation numbers from ilmenites from the Jacupiranga rocks decrease as Nb and Ta are substituted into the sites normally occupied by Ti.

cent (Nb₂O₅+Ta₂O₅). The circles fit the line fairly well also, with a few values falling well below the line. We conclude that the cation deficiency is reasonably explained by the substitution of these elements in ilmenite as Nb⁵⁺ and Ta⁵⁺, as indicated in Equation (1).

If (Nb+Ta) is plotted against Fe³⁺, an antipathetical relation between them is suggested for ilmenites from C₁ and C₄, but not for ilmenites from C₃ and C₅. Equation (2) might be responsible in part for the substitution mechanism of Ti and Nb and Ta in ilmenites from C₁ and C₄.

The straight line in Figure A3 gives an empirical method for estimating the cation deficiency in ilmenite, according to the formula:

$$\text{cation deficiency} = \text{weight per cent (Nb}_2\text{O}_5+\text{Ta}_2\text{O}_5)/100.$$

The cation deficiency in these ilmenites is dominated by the abundance of niobium, and this empirical equation would need modification for ilmenites with higher Ta₂O₅.

Calculation of Fe³⁺

The amount of Fe³⁺ listed for the ilmenites in Table 2 was calculated following the method of Carmichael (1967), which consists of combining all the divalent cations with the molecular proportions of (TiO₂+SiO₂), with sufficient FeO added to make the ratio 1:1. The excess FeO is calculated as Fe₂O₃. We added Nb₂O₅ and Ta₂O₅ to the sum (TiO₂+SiO₂) because these cations replace Ti in the ilmenites (Fig. A2). Consequently one divalent cation was combined to each molecule of Nb₂O₅ and Ta₂O₅. However the results in Figure A3 suggest that Equation (1) plays an important role in these ilmenites, indicating that values of Fe³⁺ should be calculated considering the crystal chemistry and cation deficiency consequent on the presence of Nb and Ta. If Equation (1) is assumed, the calculation of Fe³⁺ is then conducted as if no Nb or Ta were present. This is because each one of the molecules Nb₂O₅ and Ta₂O₅ causes one divalent vacant position (one divalent cation was combined to each of these molecules).

The recalculated values for FeO and Fe₂O₃ disregarding Nb and Ta are compared in Table A1 with the calculated values listed in Table 2. For the ilmenite with the highest content of (Nb₂O₅+Ta₂O₅) (Table 2, #12) the difference in calculated Fe₂O₃ content is 1.12 wt.% (Table A1). For the point representing this analysis in Figure 1A, for example, this represents a variation of only 2% towards the Fe₂O₃ corner. As only few ilmenites present similar variations, the distribution of points in figures would not be changed significantly by the new values.