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COEXISTING PYROXENES IN MAFIC AND ULTRAMAFIC ROCKS FROM BARRA VELHA, SANTA CATARINA, BRAZIL

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ABSTRACT — Microprobe data are given for 8 pairs of coexisting clino- and orthopyroxenes from mafic and ultramafic rocks cropping out near the village of Barra Velha, 25 km from the city of Itajaí, Brazil. Those rocks are closely associated to Precambrian migmatites and undifferentiated gneisses. Radiometric data suggest that the whole complex was affected by two metamorphic episodes of granulite (Transamazonian age, ~2 b.y.) and amphibolite (probably of Brazilian age, ~600 m.y.) facies.

Kretz coefficients point to the formation of the Barra Velha pyroxenes under high grade metamorphic conditions. Crystallization trends — indicating a FeO enrichment together with CaO-MgO diminution in clinopyroxenes, and a strong increase in FeO over MgO, in addition to an almost constant CaO content in orthopyroxenes — are consistent with the behavior already observed in pyroxenes from other metamorphic provinces.

INTRODUCTION

Several occurrences of mafic and ultramafic rocks have been found along the coast of the State of Santa Catarina, SE Brazil, in the vicinity of Barra Velha area, approximately 25 km from the city of Itajaí. These bodies were described for the first time by Bartorelli et al. (1969), with additional data on their geology given more recently by Minioli (1972) and Soares (1974). Soares (1975) gives detailed information on mineralogy, petrography, chemistry and general geologic evolution of the mafic and ultramafic bodies.

The area of Barra Velha is characterized mainly by Precambrian migmatites and undifferentiated gneisses; closely associated to them are the mafic and ultramafic bodies. Holocene sediments cover the area in patches.

Gneisses and both homogeneous and heterogeneous migmatites are the main regional lithologies. Dark minerals are predominantly hornblende, biotite, and garnet. Heterogeneous migmatites present a well developed ultramafic paleosome and a granoblastic neosome of granitic to quartz-dioritic composition. Contacts of these rocks with the bodies of granitoid rocks — mainly granodioritic in composition — are undefined and even transitional in places. Small lenses of quartzites and itabirites are found locally. The mafic and ultramafic bodies appear as several elongated outcrops with an apparent general NNW trend, probably defining the erosive remnants of what formerly was a major magmatic body. Petrographically, metapyroxenites and pyroxene meta-hornblendites are dominant. In addition, Soares (1975) also describes other varieties, such as true amphibolites, talc-pyroxene meta-hornblendites, amphibol-

litic gneisses, hornblende-hypersthene gneisses (granulites) and hornblende metagabbros. Texturally, the mafic and especially the ultramafic rocks show a remarkable variation in grain-size and fabric, some samples presenting amphibole crystals up to 15 cm.

Preliminary radiometric dating suggests that the whole complex — mafic and ultramafic rocks as well as migmatites and gneisses — was affected by a high-grade metamorphic event (probably up to granulite facies) of Transamazonian age (about 2 b.y.). Additional evidence indicates that a follow-up under conditions of the amphibolite facies, of probable Brazilian age (~600 m.y.), is responsible both for the development of a second generation of migmatites and the extensive development of talc and amphiboles in the mafic and ultramafic units.

A later event, geologically unrelated to the basement complex, is characterized by small dykes of alkaline rocks (Barra Velha coast and BR-101 Highway), still of uncertain radiometric age (see Minioli, 1972).

Analytical Technique All the analytical data were obtained with an Applied Research Laboratories EMX electron microprobe in the Instituto de Geociências da Universidade de São Paulo. Instrument conditions were as follows: 15 kV accelerating potential, 0.03 μ A specimen current, integration time on scalers 20 seconds, and spot size approximately 1 μ diameter. X-ray quanta (K_{α} radiation) have been simultaneously detected by three linear spectrometers with LiF, ADP, and RAP crystals. The standards used were Ca-rich pyroxene N. 5-118 and orthopyroxene N. 2525. Standard correction procedures were applied for background, drift, and matrix effects by using the appropriate oxide correction factors of Bence and Albee (1968) and Albee and Ray (1970).

TABLE I

Microprobe Analyses of Orthopyroxenes

	Metapyroxenites					Pyroxene Meta-hornblendite	Hornblende Metagabbros	
	2	8	10	14	21	18	26	28
SiO ₂	51.8	50.7	52.5	52.4	53.3	51.1	50.3	50.1
TiO ₂	0.06	0.14	0.06	0.05	0.12	0.16	0.21	0.13
Al ₂ O ₃	0.82	2.86	1.22	1.32	1.89	2.59	1.64	1.44
Cr ₂ O ₃	0.10	0.13	0.11	0.12	0.09	0.08	0.05	0.03
FeO*	19.2	17.6	16.2	16.3	18.3	18.6	23.7	23.2
NiO	0.14	0.21	0.07	0.07	0.06	0.13	1.69	2.12
MnO	0.76	0.50	0.52	0.56	0.58	0.58	0.90	0.96
MgO	25.2	25.8	27.2	27.1	25.9	24.9	20.0	19.6
CaO	0.49	0.57	0.62	0.53	0.51	0.45	0.73	0.84
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.02
K ₂ O	0.01	0.01	0.01	0.03	0.02	0.02	0.03	0.01
Total	98.57	98.52	98.50	98.48	100.77	98.61	99.29	98.44

Numbers of ions on the basis of 6 oxygens

Si	1.940	1.886	1.936	1.934	1.936	1.906	1.929	1.941
Al ^{IV}	0.036	0.114	0.053	0.057	0.064	0.094	0.071	0.059
Al ^{VI}	—	0.012	—	—	0.017	0.020	0.003	0.006
Ti	0.001	0.004	0.001	0.001	0.003	0.004	0.006	0.003
Cr	0.002	0.004	0.003	0.003	0.002	0.002	0.001	0.001
Fe	0.600	0.549	0.500	0.504	0.555	0.579	0.759	0.749
Ni	0.004	0.006	0.002	0.002	0.001	0.003	0.052	0.065
Mn	0.024	0.016	0.016	0.017	0.017	0.018	0.029	0.031
Mg	1.408	1.431	1.495	1.491	1.400	1.382	1.143	1.127
Ca	0.019	0.023	0.024	0.021	0.019	0.018	0.029	0.034
Na	—	—	—	—	—	—	0.002	0.001
K	—	—	—	0.001	0.001	0.001	0.001	—
Z	1.976	2.000	1.989	1.991	2.000	2.000	2.000	2.000
WXY	2.058	2.035	2.041	2.040	2.015	2.027	2.025	2.017
Ca	0.9	1.1	1.2	1.0	1.0	0.9	1.4	1.7
Mg + Ni	68.7	71.0	73.5	73.4	70.3	69.3	59.4	59.4
Fe + Mn	30.4	27.9	25.3	25.6	28.7	29.9	39.2	38.9
FeO								
FeO + MgO	0.43	0.40	0.37	0.37	0.41	0.43	0.54	0.54
Mg								
Mg + Fe	0.70	0.72	0.75	0.75	0.71	0.70	0.60	0.60
100 Mg								
Mg + Fe + Mn	69.3	71.7	74.3	74.1	70.9	69.8	59.2	59.1

★ All Fe calculated as FeO

CHEMICAL RESULTS

Data for 8 pairs of coexisting clinopyroxene and orthopyroxene are listed in Tables I and II (3 samples are from metapyroxenites, 1 from a pyroxene meta-hornblendite, 2 from hornblende metagabbros) together with their chemical formulae, some differentiation indices and values for the distribution coefficient as proposed by Kretz (1963). Pyroxene crystals are present both as isolated grains, with no apparent signs of recrystallization, or as remnants of retrograde transformations; typically, clinopyroxenes may be totally

or only partially encircled, along grain boundaries, by a green Mg-hornblende, while orthopyroxene may be replaced — along cleavage planes, fractures and rims — by talc and a fibrous tremolite variety. Pyroxene shows neither zoning nor exsolution.

Enstatite content in orthopyroxenes varies from 69 to 74% in metapyroxenites and pyroxene meta-hornblendite, but is significantly lower, clustering around 59%, in hornblende metagabbros. Al₂O₃ is not distributed homogeneously throughout the series, ranging from 0.82 to 2.86% in the different samples, and bears no apparent rela-

TABLE II

Microprobe Analyses of Clinopyroxenes

	Metapyroxenites				Pyroxene Meta-hornblendite		Hornblende Metagabbros	
	2	8	10	14	21	18	26	28
SiO ₂	52.3	51.1	51.7	51.8	52.1	51.7	51.5	50.8
TiO ₂	0.16	0.33	0.18	0.13	0.20	0.33	0.09	0.23
Al ₂ O ₃	1.24	4.01	1.91	1.67	2.36	2.02	1.94	3.50
Cr ₂ O ₃	0.22	0.30	0.18	0.14	0.09	0.25	0.04	0.04
FeO*	6.11	6.04	5.08	5.45	5.47	6.04	8.14	7.09
NiO	0.52	0.15	0.08	0.11	0.09	0.23	1.27	1.88
MnO	0.19	0.15	0.19	0.16	0.19	0.14	0.25	0.39
MgO	15.0	14.5	15.5	15.1	14.8	14.4	13.4	13.1
CaO	23.3	23.6	23.1	23.5	23.6	23.6	22.1	21.7
Na ₂ O	0.47	0.29	0.48	0.41	0.29	0.37	0.22	0.38
K ₂ O	0.01	0.01	0.02	0.03	0.02	0.01	0.02	0.01
Total	99.51	100.47	98.42	98.50	99.21	99.08	98.97	99.11

Numbers of ions on the basis of 6 oxygens

Si	1.952	1.884	1.937	1.945	1.939	1.936	1.948	1.919
Al ^{iv}	0.048	0.116	0.063	0.055	0.061	0.064	0.052	0.081
Al ^{vi}	0.006	0.058	0.021	0.018	0.042	0.025	0.034	0.074
Ti	0.004	0.009	0.005	0.003	0.005	0.009	0.002	0.006
Cr	0.006	0.009	0.005	0.004	0.002	0.007	0.001	0.001
Fe	0.190	0.186	0.159	0.171	0.170	0.189	0.257	0.223
Ni	0.015	0.004	0.002	0.003	0.002	0.006	0.038	0.057
Mn	0.005	0.005	0.006	0.005	0.005	0.004	0.007	0.012
Mg	0.836	0.798	0.864	0.844	0.820	0.802	0.756	0.729
Ca	0.930	0.935	0.929	0.945	0.940	0.947	0.895	0.876
Na	0.033	0.021	0.034	0.029	0.020	0.027	0.016	0.027
K	—	—	0.001	0.001	0.001	—	0.001	—
Z	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
WXY	2.025	2.025	2.026	2.023	2.007	2.016	2.007	2.005
Ca	47.1	48.5	47.4	48.0	48.5	48.6	45.8	46.2
Mg + Ni	43.1	41.6	44.2	43.0	42.4	41.5	40.7	41.4
Fe + Mn	9.9	9.9	8.4	8.9	9.0	9.9	13.5	12.4
FeO	0.29	0.29	0.25	0.26	0.27	0.29	0.38	0.35
FeO + MgO	0.29	0.29	0.25	0.26	0.27	0.29	0.38	0.35
Fe Mg x 100	22.7	23.3	18.4	20.3	20.7	23.5	33.9	30.6
Mg	0.81	0.81	0.84	0.83	0.83	0.81	0.75	0.76
Mg + Fe	0.81	0.81	0.84	0.83	0.83	0.81	0.75	0.76
K _D	0.54	0.61	0.55	0.60	0.52	0.54	0.51	0.46

* All Fe calculated as FeO

tionship with the FeO/(FeO + MgO) ratio (Fig. 1). CaO concentration, as expected, is very low, from 0.45 to 0.62% in orthopyroxene of the ultramafic rocks, and increasing slightly to about 0.73 – 0.84% in hornblende metagabbros. These results are quite consistent with values quoted in the literature for orthopyroxenes of other metamorphic provinces.

Clinopyroxenes from ultramafic rocks are very homogeneous in composition (Table II), an anomaly is the exceptionally high Al₂O₃ content of sample 8. Clinopyroxenes

from metagabbros are characterized by higher FeO and less MgO-CaO; an expressive feature seems to be their relatively high NiO and Na₂O contents. These pyroxenes are therefore diopsides (those from the ultramafics) and salites (the ones from the metagabbros) (cf. Deer et al., 1963). Al₂O₃ values are consistently higher than those found in orthopyroxenes – as is normally the case in pairs – varying from 1.24 to 4.01%, and again unrelated to concomitant changes in FeO and MgO (see Fig. 1).

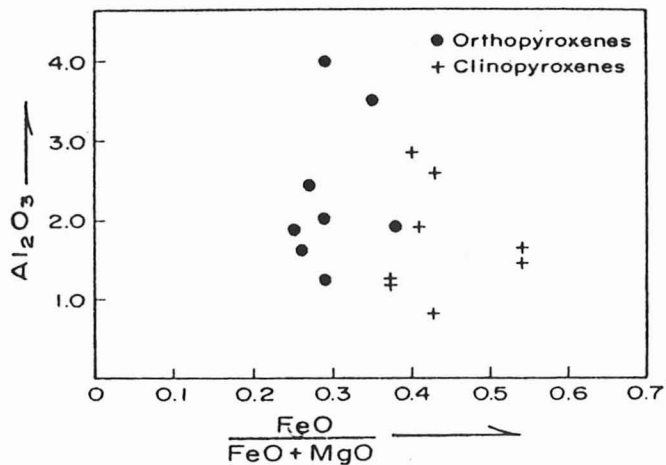


Fig. 1 Plot of Al_2O_3 against the $\frac{\text{FeO}}{\text{FeO}+\text{MgO}}$ ratio.

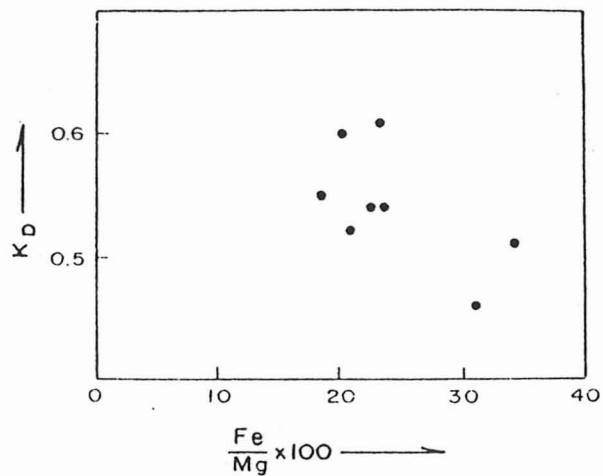


Fig 3 Plot of K_D against the $\frac{\text{Fe}}{\text{Mg}} \times 100$ ratio.

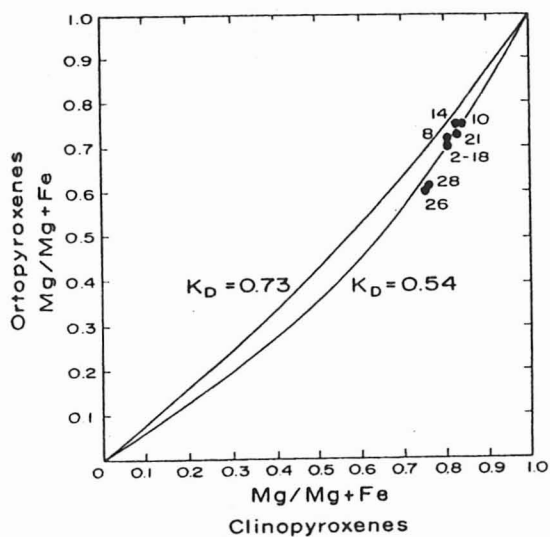


Fig. 2 Kretz coefficients for the Barra Velha pyroxenes. Upper ($K_D = 0.73$) and lower ($K_D = 0.54$) distribution curves represent igneous and metamorphic fields respectively (Kretz, 1963).

PETROLOGICAL CONSIDERATIONS

The Kretz coefficients for the Barra Velha pyroxenes, ranging from 0.46 to 0.61, are listed for the 8 pyroxene pairs in Table II. Figure 2 shows how the K_D figures for our pyroxene pairs plot close to the distribution curve representing high-grade metamorphic conditions, as established by Kretz in his original publication; the only exception are the figures for sample 28. On the other hand, Figure 3 shows a rather poor correlation between K_D and Fe/Mg ratios, a fact that probably indicates the importance of original rock composition in the determination of K_D values.

Both the low values of the K_D coefficients as well as their rather narrow spread suggest that mafic and ultramafic rock are the products of parallel geologic evolutions, recrystallizing first under conditions of the granulite facies and being later on subjected to amphibolite facies metamorphism, without being however totally destroyed or changed in their chemical characteristics during that second event.

Several authors (Howie, 1955; Davidson, 1968; Giardi, 1974) have used the crystallization trends of pyroxenes in metamorphic rocks, though still little understood, to

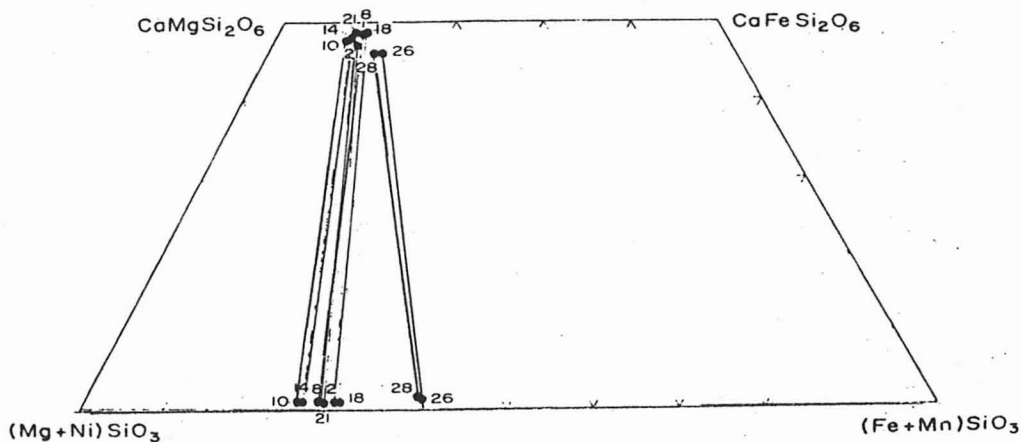


Fig. 4 Chemical composition of coexisting clino- and orthopyroxenes as given by the weight percent of the end-members $\text{CaSiO}_3 : (\text{Mg} + \text{Ni})\text{SiO}_3 : (\text{Fe} + \text{Mn})\text{SiO}_3$.

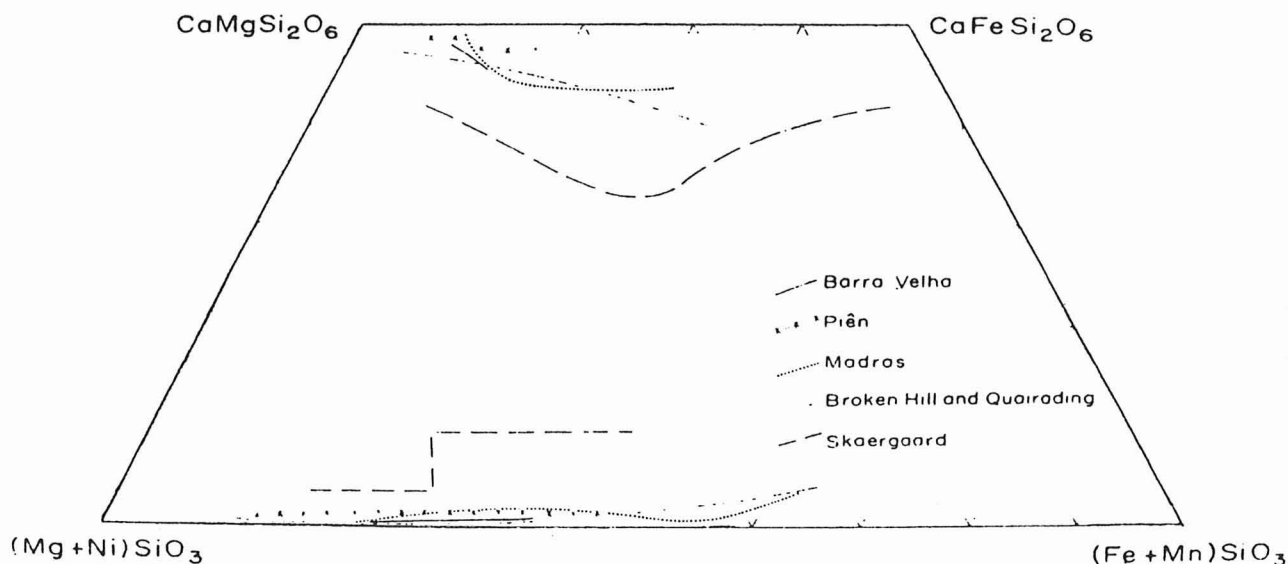


Fig. 5 Crystallization trends of pyroxenes from the Skaergaard intrusion (data from Brown, 1957; Brown and Vincent, 1963) and from the metamorphic provinces of Madras (Howie, 1955), Broken Hill and Quairading (Davidson, 1968), Piên (Girardi, 1974), and Barra Velha.

gather petrological information. A representation of pyroxene composition from our Tables I and II in Ca-Mg (+Ni)-Fe (+Mn) triangle shows a consistent trend that, no doubt, reflects a crystallization path (Fig. 4). The Ca-rich phase follows a trend of FeO enrichment coupled to CaO and MgO depletion, while the coexisting Ca-poor counterpart plot along a straight line, almost parallel to the basal En-Fs boundary; clinopyroxenes start at about $Wo_{48}En_{44}Fs_8$ and go to about $Wo_{46}En_{41}Fs_{13}$ — thus presenting a rather narrow compositional range — whereas the coexisting orthopyroxenes stretch from around $Wo_1En_{74}Fs_{25}$ to $Wo_2En_{59}Fs_{39}$.

Thus, the pyroxenes from Barra Velha duplicate the behavior already observed in pyroxenes from the Madras province (Howie, 1955) and from Broken Hill and Quairading (Davidson, 1968), namely: a) in clinopyroxenes, FeO enrichment together with CaO-MgO diminutions; b) in orthopyroxenes, a relatively stronger increase in FeO over MgO, in addition to an almost constant CaO content (Fig. 5). This low concentration of the large Ca cation suggests a long period of crystallization, enough to account for a complete exsolution (Howie, 1955).

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REFERENCES

- Albee, A.L., and Ray, L. (1970) — Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates, and sulphides. *Anal. Chem.*, 42: 1408-1414.
- Bartorelli, A., Minioli, B., and Kawashita, K. (1969) — Nota preliminar sobre rochas ultrabásicas de Itajuba, SC. *An. XXIII Congr. Bras. Geol.*, pp. 243-246, Salvador, Ba.
- Bence, A.E., and Albee, A.L. (1968) — Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.*, 76: 382-403.
- Brown, G.M. (1957) — Pyroxenes from the early and middle stages of fractionation of the Skaergaard intrusion, East Greenland. *Min. Mag.*, 31: 511-543.
- Brown, G.M., and Vincent, E.A. (1963) — Pyroxenes from the late stage of fractionation of the Skaergaard intrusion, East Greenland. *J. Petrol.*, 4: 175-196.
- Davidson, L. R. (1968) — Variation in ferrous iron-magnesium distribution coefficients of metamorphic pyroxenes from Quairading, Western Australia. *Contr. Miner. and Petrol.*, 19: 239-259.
- Deer, W.A., Howie, R.A., and Zussman, J. (1963) — *Rock forming minerals*, Vol. II, Chain Silicates. Longmans, London.
- Girardi, V.A.V. (1974) — *Petrologia do complexo básico-ultrabásico de Piên, PR*. Livre Docência Thesis. Instituto de Geociências, Universidade de São Paulo (unpublished).
- Howie, R.A. (1955) — The geochemistry of the charnockites series of Madras, India. *Trans. Royal Soc. Edinburgh*, 62: 725-769.
- Kretz, R. (1963) — Distribution of magnesium and iron between orthopyroxenes and calcic pyroxenes in natural assemblages. *J. Geol.*, 71: 773-785.
- Minioli, B. (1972) — *Aspectos geológicos da região litorânea Piçarras-Barra Velha, SC*. D. Sc. Thesis, Instituto de Geociências, Universidade de São Paulo (unpublished).
- Soares, R.M.C. (1974) — *Petrografia das Rochas Ultramáficas e Relações com Rochas Metamórficas e Migmatíticas Associadas na Região de Barra Velha, SC*. XXVIII Congr. Bras. Geol., Bol. 1: 341-343, Porto Alegre (Abs.).
- Soares, R.M.C. (1975) — *Petrologia do Complexo Máfico-Ultramáfico de Barra Velha, SC*. M. Sc. Thesis. Instituto de Geociências, Universidade de São Paulo (unpublished).