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PETROLOGY AND CHEMISTRY OF DIOPSIDIC ROCKS IN GRANULITE TERRAINS FROM THE BRAZILIAN BASEMENT

Riassunto — Intercalazioni e lenti di rocce ricche in diopside sono relativamente frequenti in aree granulitiche precambriane dello scudo continentale Brasiliano. Rocce di questo tipo raccolte vicino a Salvador (Stato di Bahia) sono state studiate dal punto di vista petrografico e chimico. La loro costituzione chimica è caratterizzata da una grande omogeneità e per quanto riguarda alcuni elementi (Al, Ca, Mg, Fe) «inerti» nel metamorfismo, essa può indicare un'origine da sedimenti calcarei impuri attraverso una serie di reazioni caratteristiche dei vari stadi del metamorfismo progressivo. La reazione principale attraverso la quale il diopside può essersi formato sembra essere la seguente: 1 tremolite + 3 calcite + 2 quarzo \rightleftharpoons diopside + 3 CO₂ + 1 H₂O.

Associazioni mineralogiche diverse e localmente presenti (ad es. quella costituita da orneblenda e tremolite) possono essere causate da pressione di CO_2 o pressione totale dei fluidi maggiore o da locali variazioni del materiale originario.

Abstract — Rocks formed dominantly of diopsidic pyroxene occur as lenses, layers and intercalations in Precambrian granulite terrains of the Brazilian basement over all of the State of Bahia. Samples collected near Salvador (Bahia) have been studied petrologically and chemically. Major and minor element compositions reveal a great homogeneity within all of the samples and the more «inert» elements, Al, Ca, Mg, Fe, are consistent with a derivation from carbonate sediments. Petrographic and chemical features, field observations etc., suggest that diopside-rich rocks were formed by progressive regional metamorphism of siliceous dolomites through a series of intermediate steps. The principal diopside-forming reaction would be: 1 tremolite + 3 calcite + 2 quartz ≓ diopside + 3 CO₂ + 1 H₂O. Hornblende-tremolite assemblages are considered to be caused by higher CO₂ total fluid pressure and/or local chemical.

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INTRODUCTION

Major sedimentary formations that have undergone progressive regional metamorphism up to uppermost amphibolite facies are ubuiquitous in the geologic record from the Precambrian to the Mesozoic. Interbedded with the principal rock types (quartzfeldspathic gneiss, hornblende-gneiss, marbles, etc.), are minor amounts of lime-rich silicate rocks. These rocks occur usually as thin layers or lenses and their mineralogy depends on their original composition and the metamorphic conditions. Under amphibolite facies conditions, diopside and/or hornblende are usually the major minerals, accompanied by varying amounts of calcite, tremolite, scapolite and plagioclase.

Owing to their geologic setting, mineralogical and chemical composition, these rocks are usually considered to have been formed by progressive metamorphism of impure carbonate sediments, in particular of siliceous dolomite-limestone material. Dolostones are very common sedimentary rocks recognizable in succession from the Precambrian to the Pleistocene (INGERSON [1962]); they occur normally in beds of variable thickness and purity and vast lateral extent.

On other hand, occurrences of carbonate-bearing rocks or lime-rich rocks in high-grade granulite facies terrains constituted mostly by metasediments are rare and very few papers deal with their petrology and chemistry. The present work reports petrological and chemical studies of diopside-rich rocks interlayered in granulites from the Brazilian Precambrian basement in an area near Salvador, Bahia State.

Occurrences and genesis of diopside-rich rocks in metamorphism

Diopside-rich assemblages may be formed, as is well known, during both progressive regional, and contact metamorphism. An impressive number of studies concerning both these rock-forming processes have accumulated in the literature. For regional metamorphism, the appearance of diopside always marks p-T metamorphic conditions in the range of amphibolite facies. The minerals accompanying diopside may represent intermediate steps in reaction giving diopside as the end product or may be characteristic of particular environmental conditions. For example, the mineral pair diopside-actinolite (accompanied by plagioclase-quartz or plaglioclase-scapolite-quartz) was frequently found to be the most stable assemblage under p-T conditions of amphibolite facies (see f.i. HIETANEN [1963; 1968]; TROMMSDORFF [1966], etc.).

Thin layers of diopside-rich or wollastonite-rich rocks can be frequently observed (see for example BURNHAM [1959]) as transition rocks produced by exchange reactions between siliceous rocks and marbles. In this case whether diopside or wollastonite predominates, seems to depend essentially upon the chemical composition (i.e. magnesian content) of the original sediments.

Diopside-plagioclase assemblages represent another stable assemblage in amphibolite facies, although they may be transformed into hornblende-rich asseblages when physico-chemical conditions change slightly (SMITHSON et al. [1971]).

Diopside-rich rocks are, furthermore, the common product of high-grade progressive contact metamorphism of calcareous sediments. In such a metamorphism, as in regional metamorphism, several zones can be distinguished and a number of authors, beginning with Bowen [1940] and TILLEY [1951], have investigated the equilibrium reactions characterizing the various zones. Detailed observations of these reactions show that many phenomena characterizing regional metamorphism (type of phases, intermediate products, etc.) will be reproduced on a smaller scale in contact metamorphism. For example, high-grade contact metamorphism of impure dolomite produces diopside- and forsterite-rich assemblages which pass through an intermediate stage of tremolite formation (see for example COOPER [1957]; COMPSTON [1960]): similar series of reactions, as it will be seen later, characterize regional metamorphism of such a sediments.

GEOLOGICAL SETTING AND PETROLOGY OF DIOPSIDE-RICH ROCKS FROM BAHIA

Diopside-rich rocks here investigated occur in Precambrian granulite terrains of the Brazilian basement in a cratonic area (S. Francisco craton) which forms a large part of the Bahia State. All the samples analyzed except one (UB ITA) were collected in a limited area near the town of Salvador. Sample UB ITA comes from a granulite terrain from Western Bahia which probably has passed through the same geologic history as those of Salvador.

Petrology and chemistry of the granulites of Salvador are reported in previous works (FUJIMORI [1968]; FUJIMORI and ALLARD [1966]: SIGHINOLFI and FUJIMORI [1972]). Great variations over short distances in mineralogical assemblages characterize the granulites of Salvador. They form a typical charnockite series which consists of strictly alternating rocks ranging in composition from acid to basic. The paragenetical complexity within a given rock type leads FUJIMORI [1968] to tuggest the intervention of polymetamorphic events repeatedly reaching medium-high pressure granulite facies conditions. Basic or ultrabasic rocks occurring in minor amounts interlayered with the main granulite types consist of diopside-rich rocks and hypersthene-bronzite-rich lenticular bodies (bronzitites). Diopside-rich rocks occur as layers or lenses of varying thickness (from a few cm to 10 m) and lateral extent (up to a hundred m). Their homogeneity distinguishes these rocks from other granulites. No mineralogical zoning within the layers from the contact to the center exists and the presence of foreign material is apparently only represented by local pegmatitic veins generally discordant with the main structure. Well defined neoformation of biotite, K-feldspar (and quartz) appears to be related to such mobilizates. The colour of the rocks is fairly uniform light-green to almost white in some cases. Diopside always occupies more than 70% of the whole rock and in most cases exceeds 95%. Plagioclase is Ca-rich (An₆₀) and is present in practically all the samples accompanied by a small amount of biotite, hornblende, tremolite and scapolite. Green spinel, sphene, apatite and opaque minerals are sporadically present. Quartz occurs in discrete amounts in three sahples. Diopside is almost colorless and granular. The straight smooth contacs between grains makes a typical mosaic texture, but interpenetrating contacts also occur mostly in portions where other minerals are present. Basal parting is common and $z \wedge c$ is about 40°. Inclusions of plagioclase with shard-like shapes occur in some samples and very minute possible fluid inclusions are very common. Biotite is reddish yellow and strongly pleochroic in most cases, but an almost colorless phlogophite type is also found. The contact between biotite and diopside is straight, and in some samples the biotite crystals are not cut by main shearing planes. This indicates for some biotites a neoformation

character. Scapolite occurs in small amounts in most of the samples. It occurs as inclusions in diopside and also as an interstitial mineral between pyroxene grains. Their prismatic to anhedral grains show birifringence around 0.028, so the scapolite is a meionite-rich member with high CO3 content. Cordierite is another possible minor component of diopside-rich rocks but very difficult to identify due to the reduced grain size. Tremolite type amphibole is almost colorless to slightly greenish and pleochroic. It occurs both as small irregular inclusions in diopside and sometimes as large crystals showing smooth contacts with diopside grains. Epidote (and few biotites and hornblendes) is clearly formed from diopside and plagioclase, probably in retrograde metamorphic reactions. Most of the carbonates occur as inclusions in diopside crystals, occupying shearing and fractures planes. So the carbonate may be a later surface alteration product. Finally, it must be remarked that at the contacts of the diopside-rich layers or sometimes interstratified within them, very thin concordant layers of hornblende-diopside- and diopside-hypersthene- bearing rocks frequently occur.

CHEMICAL DATA

Table 1 reports chemical data relative to 16 samples of diopsidic rocks and 3 samples of surrounding granulites. To investigate genetic relationships between the metamorphic skarns and possible sedimentary starting materials, some elements (Al, Mg, Ca, Fe) known to be relatively «inert» in metamorphic metasomatic reactions, have been considered. Plotting the samples on an Al₂O₃-CaO-(FeO+MgO) diagram (Fig. 1) in which compositional fields for various sedimentary rock types were delimited (based on the work of WAHLSTROM and KIM [1959]), we can see that all the samples fall in a very limited area, at the boundary between the limestone-dolomite field and the field for lime-silicate rocks in amphibolite facies. This compositional homogeneity could lead one to think that the diopside-rich assemblage was achieved through a fixed sequence of chemical reactions between chemical constituents of the original sedimentary rocks, with negligible amounts of material exchanged with an outside source. These were also the conclusions drawn by COOPER [1957] from a study of diopside--rich rocks formed by high-grade contact metamorphism.

	TABLE 1 - Analytical results (samples UB 2, UB 10 and UB 15: granulite country rocks).	alytical res	ults (samp	les UB 2, l	UB 10 and	UB 15: grav	ulite count	'ry rocks).		
	UB 1	UB 3	UB 4	UB 5	UB 6	UB 7	UB 8	UB 9	UB 11	UG 12
SiO_2	47.44	48.45	50.20	64.47	53.83	51.92	50.56	49.11	48.71	50.80
TiO_2	0.40	0.27	0.34	0.01	0.14	0.20	0.20	0.36	0.41	0.22
AI_2O_3	7.80	5.81	6.50	4.26	4.12	4.15	5.17	6.25	10.30	6.56
${\rm Fe}_2{ m O}_3$	2.76	1.43	1.77	0.36	0.22	1.08	0.09	1.93	0.93	0.86
FeO	2.52	2.26	1.90	0.62	1.44	1.64	3.22	2.14	2.47	2.36
MnO	0.141	0.130	0.130	0.029	0.093	0.111	0.124	0.121	0.084	0.104
MgO	14.04	14.19	14.21	9.58	13.76	14.56	14.28	14.02	10.93	13.31
CaO	23.46	25.51	24.32	18.52	24.32	24.61	25.29	24.53	24.30	24.72
Na_2O	0.25	0.22	0.33	0.46	0.44	0.23	0.23	0.32	0.36	0.37
$K_{2}O$	0.38	0.34	0.13	1.98	0.70	0.04	0.02	0.29	0.64	0.09
${\rm H_{2}^{-}0^{+}}$	1.24	1.37	1.10	0.62	0.98	0.64	0.70	1.51	1.67	1.32
Total	100.43	99.98	100.93	100.91	100.04	99.18	99.88	100.88	100.80	100.71
Total Fe	5.56	3.94	3.88	1.05	1.82	2.90	3.66	4.30	3.67	3.48
(as $Fe_{2}O_{3}$)										
Li ²	26	29	15	7	13	14	11	19	26	25
Cr	23	38	46	122	18	26	30	35	41	26
Ni	16.2	16.8	18.6	4.3	5.4	10.4	16.4	15.5	46.0	8.8
Cu	7	L	6.5	5	4	6.5	9	9	9.2	6.1
Zn	57	30	35	25	44	29	37	42	81	06
Rb	45	7.5	8.5	70	35	4	2.5	7.5	31	9
Sr	37	62	65	69	51	39	22	90	315	190
Pb	14	18	19	13	17	15	14	15	18	19
Trace elements: ppm.	pm.									

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(continued)
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TABLE

	UB 13	UB 14	UB 17	UB 18	UB 19	Ca ITA	Average	UB 2	UB 10	UB 15
SiO	50.45	46.76	50.19	49.34	49.64	63.51	51.60	68.93	68.03	59.81
ZiO2	0.20	0.48	0.29	0.42	0.32	0.15	0.27	0.51	0.59	0.71
$\tilde{Al_{2}O_{3}}$	5.68	8.45	7.12	10.10	9.92	2.93	6.57	14.49	14.94	17.72
${\rm Fe}_2{ m O}_3$	1.00	2.80	1.26	2.27	1.44	0.55	1.30	1.53	1.56	1.97
FeO	1.97	2.46	3.43	1.58	2.88	4.28	2.32	1.85	1.76	4.81
MnO	0.074	0.152	0.179	0.150	0.125	0.198	0.121	0.027	0.040	0.105
MgO	14.87	12.92	12.30	11.55	11.39	9.59	12.84	1.03	0.92	2.98
CaO	24.22	25.64	24.23	22.81	23.91	18.07	23.65	2.65	2.67	5.73
Na_2O	0.29	0.16	0.28	0.25	0.17	0.55	0.31	2.49	3.26	3.11
K_2^{0}	0.59	0.11	0.14	0.14	0.11	0.07	0.36	5.22	5.33	2.43
H_{2}^{-0+}	1.16	1.00	0.86	2.42	1.04	0.48	1.15	0.36	0.26	0.11
Total	100.49	100.93	100.28	100.98	100.94	100.38		60.66	00.36	99.48
Total Fe	3.19	5.53	5.07	4.02	4.64	5.30	3.88	3.58	3.51	7.31
(as Fe_2O_3)										
Li	25	21	30	26	24	10	20			
Cr	24	38	20	35	94	50	42			
Ni	11	11.5	12	36	19	6.6	15.9			
Cu	15	7.5	9	11.6	8.5	7	7.4			
Zn	92	98	91	81	79	113	64			
Rb	61	10	6	6	6	5	19.8			
Sr	190	47	150	165	145	33	104			
Pb	19	20	17	17	21	11	17			

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Considering other major elements, we can see large variations in silica and potassium. Silica variation could be due of course to the original quartz content but, because high silica and potassium contents appear frequently in the same sample (as in the case of UB 5 sample), we can argue that enrichment of both elements could probably have occurred through metasomatic reactions with the surrounding potassium-rich rocks (see Table 1). The presence of clear late formed biotite and K-feldspar occurring in the diopside-rich rocks accounts for that phenomena.



Fig. 1 - Al-Ca-(Mg+ferrous Fe) diagram. The areas outlined for the various sedimentary rock types redrawn from WAHLSTROM and KIM [1959]. Dashed area: compositional field of the Bahia diopside-rich rocks. Area with partial contours: rough compositional field for calc-silicate rocks in amphibolite facies (from the data of WAHLSTROM and KIM [1959]; WINCHESTER [1972]; WINCHESTER and LAMBERT [1970] etc.).

Data on trace elements show that, except in a few cases (chromium in samples UB 5 and UB 19 and rubidium in K-rich samples), a quite homogeneous distribution occurs in all the samples. For purpose of comparison, Table 2 reports the average elemental contents commonly accepted for carbonate sediments and concentration ranges in other genetically possible materials. Concerning the effective value of such comparisons, it must be emphasized that it is extremely hard to estimate average abundances of minor elements in carbonate rocks, these values particularly depending on the non carbonate materials which may have been added through a number of different processes. Nevertheless, for some elements for which reliable data are available a fairly good agreement exists between averages in diopside-rich rocks and carbonate sediments: this is the case for Ni, Cu and Pb. For all trace elements (except strontium) like for most of main constituents (alumina, iron, titania etc.), a slight but definite concentration increase in diopside-rich rocks in relation to carbonate sediments can be observed. At this point COOPER [1957], studying progressive contact metamorphism of carbonate rocks, pointed out that the reactions that produce the release of carbon dioxide and formation of denser minerals (like diopside), besides producing a strong decrease in the total volume (more than 30%) imply variations (in general positive) in the absolute content of some elements. This fact must be taken into account in comparing chemical analyses of the unmetamorphosed and metamorphosed facies of a carbonate rock.

The sole element present in diopside-rich rocks in markedly lower levels that in carbonate sediments is strontium. At this point it must be noted that depletion of strontium in carbonate rocks seems to characterize every recrystallization process of primary crystallized carbonate, both in the sedimentary environment and during metamorphic recrystallization (see ROBINSON [1971]).

PETROGENETIC CONSIDERATIONS

The transformation of calcareous sedimentary rocks into diopside-rich asseblages stable at high temperature-pressure conditions involves a complete decarbonization process that takes place progressively during regional metamorphism. In the last few years the equilibrium conditions for some of the reactions which occur during the metamorphism of siliceous dolomites have been determined experimentally (METZ and WINKLER [1963]; METZ [1966, 1967, 1970]; WINKLER [1967]; METZ, PUHAN and WINKLER [1968]).

A complete list of reactions and some experimental data on the equilibrium conditions in the system CaO-MgO-SiO₂-CO₂-H₂O is given by TURNER [1967] and by METZ and TROMMSDORFF [1968]. Considering regional metamorphism, the reactions which take place at the lower metamorphic grade lead essentially to the formation of talc, tremolite (and calcite) through reactions of the type:

- (1) 3 dolomite + 4 quartz + 1 $H_2O \rightleftharpoons 1$ talc + 3 calcite + 3 CO_2
- (2) 5 dolomite + 8 quartz + 1 $H_2O \ge 1$ tremolite + 3 calcite + 7 CO_2
- (3) 2 dolomite + 1 talc + 4 quartz \approx 1 tremolite + 4 CO₂

METZ and PUHAN [1970], dealing with the experimental investigation of reaction (1), demonstrate that the temperature of formation of talc and calcite depends to a considerable extent on the composition of the CO_2 -H₂O-gas phase. At low total fluid pressure (P_f less than 1,000 bars) talc and calcite appear over the whole temperature range between about 350 and 490 C (i.e. in the field of the albite-epidote-hornfels facies). At higher total fluid pressure (more than 3,000 bars) and at medium CO_2 -concentrations, talc and calcite appear at about 550 C.

The final step of decarbonization, corresponding to the formation of diopside, may occur according to a number of reactions, as reported by TURNER [1967], three of the most significant of these were recently experimentally studied by METZ [1970]. They are:

- (4) 1 tremolite + 3 calcite + 2 quartz \geq 5 diopside + 3 CO₂ + 1 H_2O
- (5) 1 tremolite + 3 calcite \rightleftharpoons 4 diopside + 1 dolomite + 1 CO₂ + + 1 H₂O
- (6) 1 dolomite + 2 quartz \rightleftharpoons 1 diopside + 2 CO₂

The temperature of formation of diopside for all these reactions (analogous to tremolite in the earlier decarbonization step) depends to a great extent on the fluid phase composition and the total fluid phase pressure. Fig. 2 gives the schematic representation of these interdipendences for reactions (4) and (6). Petrographic

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evidence and experimental data (METZ [1970]) suggest that during regional metamorphism diopside is formed almost exclusively by reaction (4). On the basis of these considerations we must discuss the petrogenesis of diopside-rich granulite rocks starting with a mineralogical assemblage of tremolite, calcite and quartz.

At least two possibilities can be explored depending on the temperature and pressure conditions (i.e. metamorphic grade) at which the reaction started and finished.

a) Formation of diospide started and was completed with consequent complete decarbonization at relatively low temperature (in the range of amphibolite facies). The CO_2 phase separated can be al least partially retained *in situ* or can escape completely from the system. Complete retention is very unlikely because of the very high CO_2 fugacity at these temperatures (see MAJUMDAR and RUSTUM Roy [1956]). In the case of partial retention of CO_2 calc silicate carbonate-bearing rocks can be formed and such rocks are indeed commonly dispersed in amphibolite facies terrains.

Extremely low temperatures of diopside formation, corresponding to very low CO_2 pressure (Fig. 3), are not to be expected in the process because the formation of tremolite, consuming H₂O and liberating CO_2 , is the preceeding reaction at lower temperatures. Liberation of water according to reaction (4) makes possible the formation of hydrated minerals like biotite and hornblende stable at T-p amphibolite facies conditions. Progressive metamorphism in granulite facies, as in the case considered here, would presumably do not affect diopside stability and the sole reactions which can occur consist of partial dehydration reactions and recrystallization of earlier formed biotite and hornblende.

b) Reaction (4) was not completed in the amphibolite facies but transformation of tremolite-bearing assemblages to diopside continues and is completed in granulite facies. The temperature of final diopside formation is higher and the minimum temperature will depend on total fluid pressure and particularly on the CO_2 partial pressure (Fig. 2 and 3).

All the components of the fluid phase tend to escape from the system but while CO_2 presumably will be completely lost, because of the disproportionate increase in the fugacity of CO_2 relative to that for H₂O with increasing temperature (MEL'NIK [1972]), a large part of water will still remain. This agrees also



Fig. 2 - Schematic representation of the intersecting bivariant equilibrium surfaces of reactions (4) and (6) in the temperature-CO₂ partial pressure (X_{CO2}) -total fluid pressure (P_f) diagram (from METZ [1970]).

with that normally encountered in progressive contact metamorphism (see for example SHIEH and TAYLOR [1969]).

Now, if we consider that reaction (4) causes the release of water also during granulite metamorphism, it would be expected that the total dehydration of the diopside-rich assemblages would be delayed or not reached (depending on the final conditions of metamorphism) at the same time as other dehydration reactions normally occurring in high-grade metamorphism (i.e. biotite-garnet, hornblende-pyroxene etc.) were completed. The final consequence of this would be the presence of hydrated minerals (like biotite and hornblende) coexisting with diopside in larger amounts in diopside-rich layers than in the surrounding granulites. This is in effect what occurs in the case here examined (see H_2O data in Table 1) and this, together with other observations (tremolite relicts present in most of the samples, part of the biotite and hornblende clearly in equilibrium with diopside etc.)



Fig. 3 - Equilibrium data for reactions (4) and (6) on a diagram P_{f} -temperature. Dashed area: range of equilibrium temperatures for X_{CO2} values from 0.1 to approx. 1.0 (from METZ [1970]).

seems to indicate that complete decarbonization of the calcareous sediments was not totally achieved before the material underwent granulite facies metamorphism.

It remains to discuss the petrogenesis of the tremolite-hornblende-bearing assemblages present as thin layers interbedded between the diopside-rich rocks and other granulite rock types. Two

	(a)	(b)	(c)	(d)	(e)	(f)
Li	20	5		0.6-45.5	4	
Cr	42	11		15.6-59.3	56-220	32
Ni	15.9	20	7.2-13.5	16-130	22-80	9
Cu	7.4	4		20-160	46-55	8
Zn	64	20		147-5600		
Rb	19.8	3		18.6-113		
Sr	104	610	420-490	62-1440	100-410	14
Pb	17	9	7-2-13.5	11-210		

 TABLE 2 - Some trace element data in diopside-rich rocks and in parental materials (values in ppm).

(a) Average trace element content for the diopside-rich rocks from Bahia.

- (b) Average trace element content for sedimentary carbonate rocks (Turekian and Wedepohl, 1961).
- (c) Some concentration ranges in sedimentary carbonate rocks (Graf, 1962).
- (d) Some concentration ranges in dolostones (Weber, 1964).
- (e) Some concentration ranges in diopsidic hornfels (Challis, 1965).
- (f) Trace element contents in diopsides form amphibolite facies calc-silicate rocks (Hietanen, 1972).

possibilities can be explored to explain the persistence of such assemblages stable under lower T-p metamorphic conditions within granulite assemblages: a) Local variation in the fluid phase composition and/or in the total fluid pressure (greater P_{CO2} and/or total pressure); b) Local compositional variation of the original material (for example lower Ca/Mg ratio) favouring the persistence of tremolite-hornblende assemblages in spite of diopside: this has also been pointed out by LOOMIS [1966] and HIETANEN [1972]. Although nothing definite can be concluded, since it is very hard to imagine significant variations over very limited distances in the fluid phase at very high and presumably homogeneous T-p conditions, the hypothesis of a major influence of local chemical variations in the original material must be preferred.

CONCLUSIONS

From the preceeding observations the following conclusions can be drawn:

a) The diopside-rich rocks occurring in lenses and thin layers in granulite terrains from the Brazilian Precambrian basement are of a homogeneous chemical composition particularly in some major relatively «inert» components. Their bulk chemistry (major and trace elements) agrees well with the hypothesis that these rocks were formed by high-grade metamorphism of lime-rich sediments, probably siliceous dolomites.

b) Major variations in major and trace elements occur only for elements, like silica, potassium and rubidium, known to be easy «migratile» elements in high-grade metamorphism. Variations regarding these elements, at least partially, may be ascribed to metasomatic reactions with surrounding potassium-rich rocks. Late formation of biotite and K-feldspar in the diopside-rich rocks can be regarded as a product of these reactions.

c) Progressive metamorphism of siliceous dolomites leads to diopside-rich end products through a series of reactions involving the formation of tremolite and calcite in the intermediate steps. The principal diopside-forming reaction is:

1 tremolite + 3 calcite +2 quartz \rightleftharpoons 5 diopside + 3 CO₂ + 1 H₂O

d) Two hypotheses concerning the timing of this reaction, i.e. if the reaction was exausted totally in amphibolite facies or has been continued in granulite facies conditions, were explored. Much evidence seems to indicate that complete decarbonization was achieved only during granulite facies metamorphism.

f) Hornblende-tremolite assemblages, characterizing thin layered rocks within the diopside-rich lenses, are interpreted as products of incomplete diopside-forming reactions, due to local chemical variations of the original material.

ANALYTICAL METHODS

Both major and trace element determinations were made by atomic absorption spectroscopy using a 303 Mod. Perkin Elmer

spectrophotometer unit and 165 chart recorder. Major elements were analyzed (analyst Sighinolfi) using the decomposition procedure suggested by BERNAS [1968] and modified in some details. $HClO_4$ -HF decomposition, as described by SIGHINOLFI [1972] was used for trace elements. Instrumental conditions for most elements are reported by SIGHINOLFI [1969]. Constant accuracy checks were carried out on USGS silicate standards.

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