FLUIDS RELATED TO ENDOSKARN FORMATION PROCESSES IN THE GUANHÃES AREA, MINAS GERAIS STATE, BRAZIL

MARIA LOURDES SOUZA FERNANDES[1]**, KAZUO FUZIKAWA**[2]**, JOSE MARQUES CORREIA** NEVES[2], **ESSAID BILAL**[3]**, CRISTINA MARIA WIEDEMANN LEONARDOS**[4]

ABSTRACT The Borrachudos Suite consists of a group of A-type granitic bodies intruding Archean and Paleoproterozoic rocks outcropping in the central part of Minas Gerais State. Their age range from 1.77 to 1.67 Ga and the emplacement is related to the opening of the Espinhaco rift. On the eastern border of Morro do Urubu plutonite which is part of the Suite and crops out for an extension of 2 km to the southeast of Guanhães town, occurs a greenish crystalline rock. A continuous transition from Borrachudos granite to these rocks can be observed. Five different alteration stages of transformation are defined on the basis of mineral suites, mineral and total rock chemistry. These features allowed the interpretation of these rocks as endoskarnites. Their microscopy showed the presence of areas with abundant fluid inclusions (FI) in quartz. FI distribution, their morphological and compositional characteristics are the same in all five stages, except that the frequency drops rapidly from stage I to V.

Compositionally the inclusions are carbonic, aqueo-carbonic, and aqueous and they are all associated in parallel planes. Either in the first or second types of FI the carbonic phases present similar microthermometric behavior and values: Th(CO_2)=+27.0 to +29.5°C and Tm(CO_2)=-56.7 to -57.6°C. The latter indicates an almost pure CO_2 which was confirmed by micro-Raman spectroscopy. The former defines the 0.7 to 0.75g/cc isochores, which at 800°C temperature, calculated from amphibole crystallization at magmatic stage as the upper limit for the metassomatic process, indicate a pressure of 3.0 to 3.5 kbar. This range of pressure points to the process having occurred at maximum depth of roughly 10 km. The monophase aqueous inclusions presented Tm(ice)=-1.3°C indicating a solution of low salinity (~2.2wt% NaCl equivalent) which might be even lower as this Tm is dependent on the pressure developed when the fluid is frozen. The three types of inclusions are interpreted as products of post-formational changes of a homogeneous aqueo-carbonic fluid trapped above the solvus of H_2O-CO_2 -NaCl(<~2.6wt%) system. The occurrence of deuteric carbonates and their dissolution by fluids from granites may have been the source of CO_2 in metasomatized rocks.

Keywords: Late Paleoproterozoic anorogenic granites, Borrachudos granite, endoskarn formation, fluid inclusions

INTRODUCTION The term *skarn* is applied to the rocks produced by the replacement of calcite or dolomite marble independent of whether calcic or magnesian silicates are abundant, rare, or, in extreme cases, even present. Replacement of rocks such as hornfels, granites or ultrabasites by calcic or magnesian silicates are also included (Kwak 1987). This concept is also according to Einaudi and Burt (1982), which consider *skarn* to be coarse calc-silicate bodies, occurring in relatively pure carbonates, formed by infiltration or diffusion of metassomatic fluids. They are classified according to the rocks that are replaced. *Exoskarn* and *endoskarn* indicate respectively, replacement of carbonate units and of intrusive rocks in contact zones where the intrusive rock is genetically related to the *skarn* forming fluid.

On the eastern border of the Morro do Urubu plutonite (Fig.l), which is part of Borrachudos Suite outcropping over an extension of 2 km to the southeast of Guanhães town, Minas Gerais state, transition from granite to crystalline greenish rocks can be observed. Progressive transformations of macro and microscopic features as well of mineral and total rock chemistry are present. Such aspects indicate that the so-called Guanhães charnockite (Guimaraes 1987) corresponds to a transformed fraction (autometassomatized) of Borrachudos granite and can be interpreted as an endoskarn. This work presents the results of fluid inclusion studies in quartz, relating their data to the endoskarn formation process.

GEOLOGY The geology of the Guanhães area (Fig. 1) is dominated by Basal Complex lithologies (Grossi Sad *et al.* 1990, Grossi Sad 1997), consisting of an association of medium to high grade polymetamorphic rocks. Conspicuous in the Basal Complex are the granitic rocks of TTG association attributed to the Guanhães Suite, which are gneissified and migmitized with poorly defined bands. The 2660 Ma age (Rb/Sr in total rock - Miiller *et al.* 1986) is interpreted as the minimum age for the metamorphism related to the Jequie Cycle.

The Guanhães Group (Grossi Sad *et al.* 1990) appears as elongated and isolated islands within the Basal Complex, where metavolcanic rocks, chemical and clastic metasediments, amphibolites, banded gneisses, etc., can be recognized. In the absence of geochronological data these rocks are considered as having an Archaean or lower Proterozoic age.

A series of sub-alkaline granitic bodies of the Borrachudos Suite cuts the Basal Complex and Guanhães Group lithologies. The body outcropping near Dores de Guanhães has an age of 1777 ± 30 Ma, (U/Pb in zircon - Fernandes 2000). Similar ages were obtained in other bodies (Dossin *et al.* 1993, Chemale Jr. *et al.* 1998). Metarhyolites of

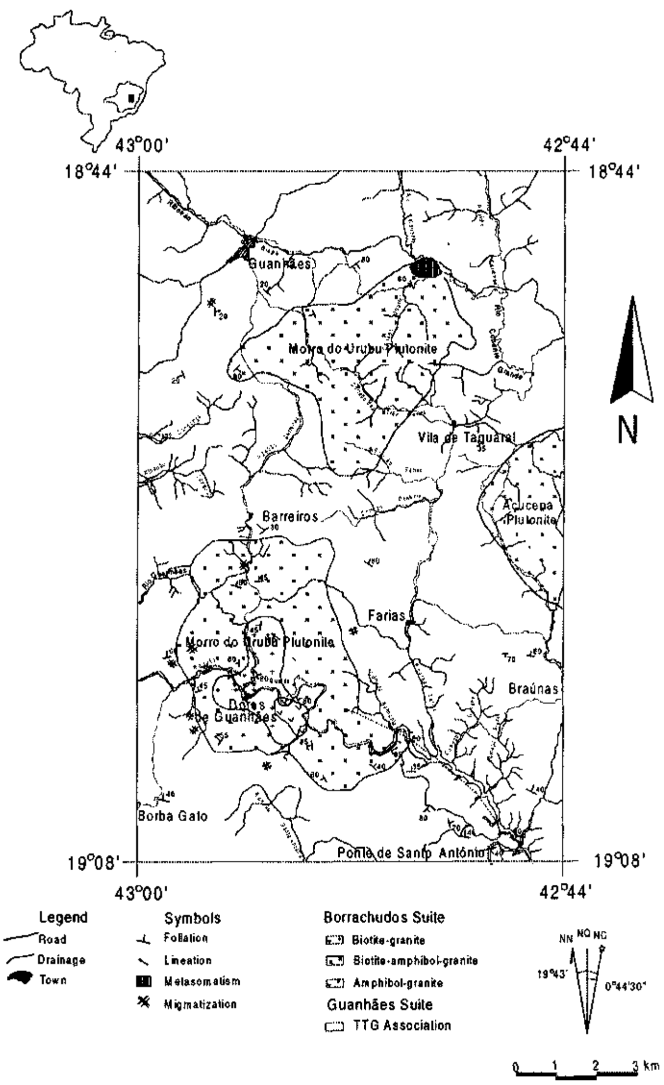

Figure 1 - Lithofacies map of Borrachudos Suite granitoid rocks between Dores de Guanhães and Guanhães, MG (modifiedfrom Fernandes 2000).

1 - CPMTC/IGC-UFMG, Campus Pampulha, 31270-901, Belo Horizonte, MG, Brazil. Iourdes@dedalus.lcc.ufmg.br
2 - CNEN/CDTN, Cidade, Universitária, 31270-010, Belo Horizonte
3 - EMSE, Saint-Etienne, France
4 - UnB, Instituto de Geociências, Brasília, DF

same composition and age (Brito Neves *et al.* 1979, Machado *et al.* 1989) occur in the Serro and Conceicao do Mato Dentro area, westward of Guanhães. Tectonically, they are located in the middle of Espinha?o Supergroup basal units. This age is considered as the minimum age for the opening of the Espinhaco basin.

The Brasíliano Orogeny marked the end of the Proterozoic in the area, which was responsible for the gneissification of Borrachudos Suite granites. The 620 Ma age (U/Pb in zircon - Fernandes 2000) marks the development of anatectic and syn-tectonic fluids. The 507 Ma age (U/Pb in titanite - Fernandes *et al.* 1999) is in agreement with those obtained by Machado et al.. (1989) and by Bilal *et al* (1998) and may represent the decrease of metamorphism or a late metamorphic pulse related to the post-tectonic extensional regimes. Metamorphic assemblages are not observed in the Borrachudos Suite lithotypes. Except for biotite (Fernandes 2000), the chemical composition of mineral preserve the original anorogenic characteristic signature.

BORRACHUDOS GRANITE IN GUANHÃES AREA In the Guanhães area the Borrachudos granite is represented by medium to coarse grained foliated, pinkish-gray rocks. Amphibole and/or biotite agglomerates mark occur as a down-dip lineation. Under the microscope the rock presents mesoperthitic (Or_{96-91} Ab_{04-09} An_{00}), plagioclase (Ab_{99-88} $Or_{()()}$ An_{00-01}) and quartz. The mam mafic constituents (amphibole and biotite) correspond to hastingstite and annite varieties, respectively. Among accessory minerals zircon, apatite, and magnetite are early crystallized followed by allanite, titanite, and fluorite. The rocks are met aluminous and sub-alkaline subsolvus granites, enriched in Nb, Ga, Y and ETR (except Eu) and presenting high values for Fe/Mg and K/Na ratios.

ENDOSKARNS Northeastwards of this granitic body, nearly 4 km to the east of Guanhães, greenish crystalline rocks considered as charnockitic (Guimaraes 1973, Grossi Sad 1997) and attributed to the Basal Complex occur. Nevertheless, progressive alteration of Borrachudos granite to this rock can be observed. The color changes gradually from pink (unaltered granite) to gray, to green and the granitic structural and textural characteristics are preserved. Over an extension of 2 km a series of mineralogical transformations can be characterized which permitted the separation of five different progressive stages (I to V). Their main characteristics are summarized in Table 1.

Macroscopically, stage I rocks seem unaltered. In thin sections the mineralogy is the same as that of unaltered granite. Plagioclase saussuritization ($Ab_{91}An_{()8}Or_{01}$), crystallization of masses of carbonate, and an intense fracturing can be observed. The amphibole (hastingsite) is characterized by (Fe/Fe+Mg) ratio of 0,056. As mentioned biotite corresponds to annite.

Rocks in stage II are gray. In their paragenesis the appearance of garnet ($Al_{64}Gr_{22}Py_{01}Sp_{13}$) can be noted. The amphibole (Fe/Fe+Mg) ratio is 0,086 and plagioclase has an Ab $An_{l2}Or_{Ql}$ composition.

In stage III the rocks are darker. Biotite disappears and carbonate decreases. Increase in amphibole Fe content (Fe/Fe+Mg = 0,099), plagioclase Ca content (Ab_{86}.An_{12} Or_{Q1}), and the proportion of garnet ($Al_{64}Gr_{22}Py_{00}SP_{14}$) are observed.

Gray-greenish color of rocks marks the stage IV. The composition of plagioclase reaches $Ab_{83}An_{15}Or_{()2}$ and of amphibole (Fe/Fe+Mg) ratio, 0,103.

In stage V the rocks become green resembling charnockites. Here, crystallization of hedenbergitic pyroxene after amphibole, continued presence of garnet ($Al_{67}Gr_{22}Py_{00}Sp_{11}$), amphibole (Fe/Fe+Mg) ratio of 0,123, and plagioclase composition of $Ab_{8l}An_{l7}Or_{01}$ occur.

FLUID INCLUSIONS (FI): MICROSCOPY, MICROTHERMOMETRY, AND MICRO-RAMAN SPECTROSCOPY Microscopy of FI thin sections showed abundant FI in quartz specially in stage I. Here three compositionally different FI types can be observed: carbonic, aqueo-carbonic, and aqueous. The carbonic ones can be separated into two groups according to their size and shape: one group of smaller FI (10 μm) with regular shape (polyhedral) and a second group of larger FI (36 u.m) with irregular shape.

The polyhedral FI are two phased at room temperature (Fig. 2a) presenting large distribution along parallel planes, indicating their secondary formation, or even if they contain primary fluids they are products of post-entrapment changes (Roedder 1984, chapter 3). CO_2 homogenized mostly to liquid between +27,Oand+29,5°C (Th) (Fig. 3a). The melting of CO_2 (Tm_{CO2} occurred between -56,7and-57,6°C (Fig. 3b), which is very close to their triple point indicating, therefore, a fluid of almost pure CO_2 composition.

The irregular carbonic inclusions (Fig. 2b) are less frequent and are associated to the polyhedral ones. Homogenization occurs either to liquid or to vapor phases within the same range of temperatures as the polyhedral inclusions (+27,7and+29,7°C - Fig. 3a). The few

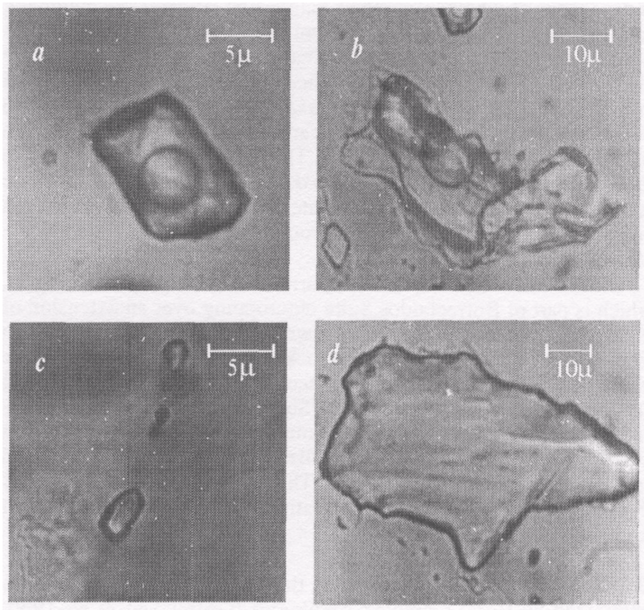

Figure 2 - FI photomicrographs: (a) Stage I: two-phased polyhedral carbonic inclusion; (b) Stage I: two-phased irregular carbonic inclusion; (c) Stage IV: assemblage of one-phase carbonic inclusions at room temperature (~-25° C); (d) Stage V: irregular carbonic inclusion containing very low density CO_2.

Table 1 - Mineralogy of endoskarns.

	Stage I	Stage II	Stage III	Stage IV	Stage V
Plagioclase	$Ab_{91}An_{08}Or_{01}$	$Ab_{87}An_{12}Or_{01}$	$Ab_{86}An_{13}Or_{01}$	$Ab_{83}An_{15}Or_{02}$	$Ab_{81}An_{17}Or_{01}$
Biotite	Annite	Annite	-	-	-
Amphibole	Hastingsite-hastingsitic hornblende	Hastingsite-hastingsitic hornblende	Hastingsite-hastingsitic hornblende	Hastingsite-hastingsitic hornblende	Hastingsite-hastingsitic hornblende
(Fe/Fe+Mg) amph	0,056	0,086	0,099	0,103	0,123
Garnet	-	$Alm_{64}Gr_{22}Py_{01}Sp_{13}$	$Al_{64}Gr_{22}Py_{00}$ Sp_{14}	Not analysed	$Al_{67}Gr_{22}Py_{00}$ Sp_{11}
Pyroxene	-	-	-	-	Hedenbergite

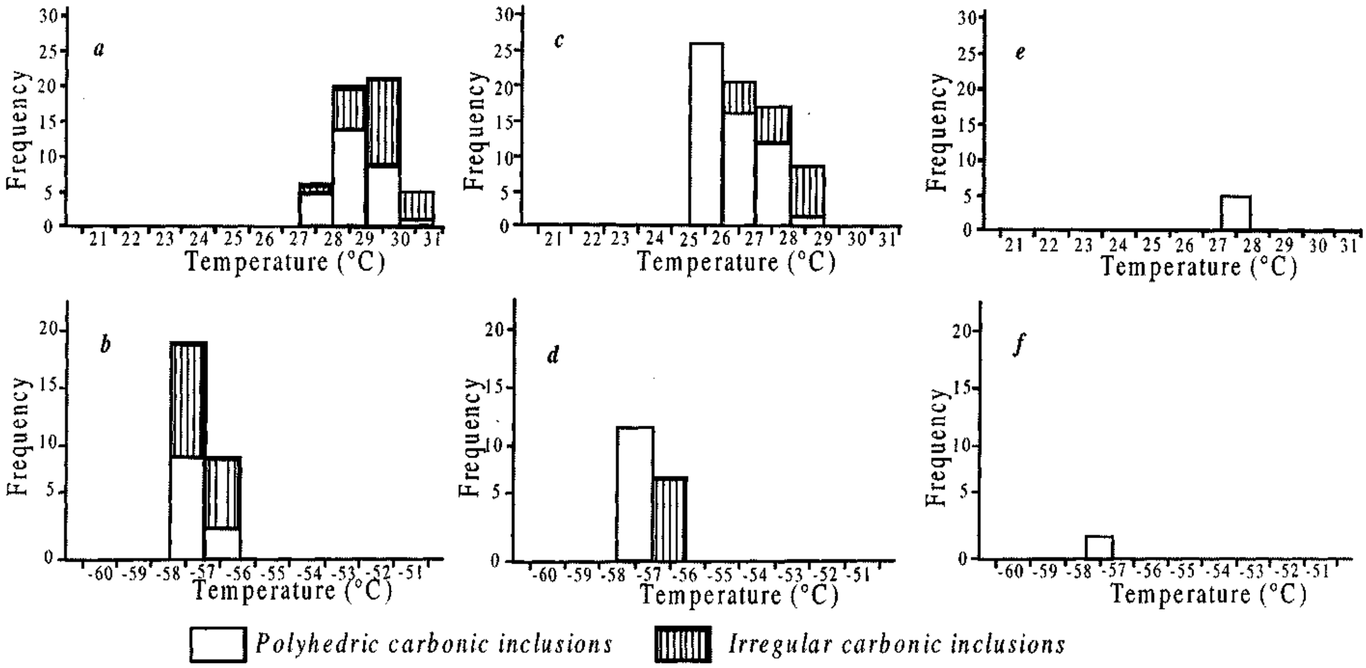

Figure 3 - Thco₂ and Tmco2 histograms of polyhedral and irregular carbonic inclusions: Stage I = (a) and (b); Stage II = (c) and (d); Stage III = (e) and (f).

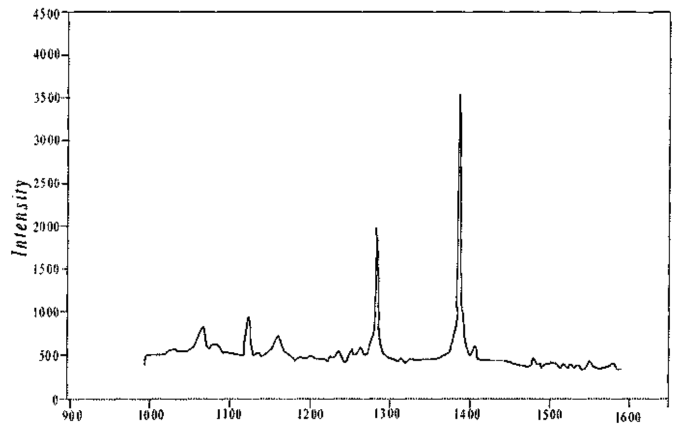

Figure 4 - Micro-Raman spectrums of stage I carbonic inclusion indicating CO_2.

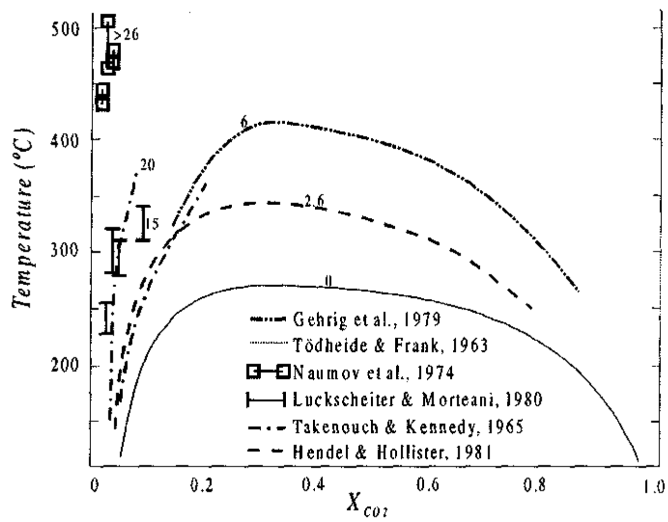

Figure 5 - Phase diagram of CO_2-H_2O-NaCl system (Numbers near each curve indicate NaCl concentration).

homogenizations to the vapor phase were always observed on the larger inclusions suggesting partial loss of fluid. Solid CO_2 also melted at similar temperatures (-56,9and-57,3°C - Fig. 3b). Nficro-Raman spectroscopy (Fig. 4) indicated CO_2 as the sole fluid component confirming the microthermometric data.

Aqueo-carbonic inclusions occur associated to the described inclusions in lesser proportion. They present irregular shape, average size of 24 jam, and three phases at room temperature (H_2O_{liq}. + CO_{2liq} + CO_{2vap}). T_{hco2} and T_{mCO2} are similar to that obtained for both types of CO_2 -tearing inclusions.

In the midst of carbonic and aqueo-carbonic inclusions, occur small (10 μm), one-phase, irregular sand aqueous inclusionslusions. The non-nucleation of new solid phases during criometry and Tm_{ICE} . around -1,3°C indicates a solution of low salinity for the last type or inclusions.

Finally, there are numerous aqueous, one phase, irregularly shaped and larger sized secondary inclusions, distributed along planes different to the previous ones. They are probably later than the metassomatic process and have not been investigated.

FI in stage II keep the same morphology and distribution characteristics and the same composition as well (Fig. 3cand3d). The only difference is the much lower frequency in their number.

In stage III, most inclusions are empty. They present similar features described for FI in stage V. Few microthermometric data (Fig. 3f) obtained on carbonic and aqueo-carbonic inclusions are concordant with those of previous stages.

In stages IV and V, the FI are usually one-phased (Fig.2c) with deep dark appearance. Freezing tests did not show any change even at temperatures below -150°C, indicating that the cavities are probably empty. This observation was further supported with the study of inclusions like those of fig. 2d where the presence of remaining fluid could be noticed only at irregularities of the cavity. Criometry confirmed this fluid as being CO_2, which melted at -57„7°C.

DATA INTERPRETATION AND FI GENESIS The Tm_{CO2} between -56.7 and -57.6° C is a strong evidence of practically pure CO„ which has been confirmed with micro-Raman spectroscopy (Fig. 4). This carbonic phase being an almost pure CO_2 fluid, their $Th_{co2(liq3)}$ between + 27and+ 29.5° C define isochores of 0.7 to 0.75 g/cm densities. For a temperature of 800°C obtained for the crystallization of amphibole during the magmatic stage (Fernandes *et al.* 1995) these isochores indicate pressures of 3,0 a 3,5 kbar (Roedder 1984). As metasomatism is related to the emplacement of granitic body these P-T conditions would reflect the upper limit possible to the process.

Aqueo-carbonic inclusions with low density CO_2 which homogenize to vapor phase are considered as products of post-entrapment modifications where partial loss of fluids occurred. The aqueous phase may have been present in a lesser amount in the original fluid considering the lower frequency of aqueous and aqueo-carbonic inclusions. Tm.,e of-1,3° C point to a solution of low salinity (-2,2 wt % NaCl equivalent). Temperatures of metasomatism, which culminated in pyroxene (hedenbergite) crystallization, must have been higher than the solvus of H_2O-CO,- NaCl (2,6 wt %) system (Fig. 5 - Hendel and Hollister 1981, in Hollister and Crawford 1981). This system would represent reasonably well the fluid composition of inclusions as the microthermometry and the micro-Raman spectroscopy indicated almost pure CO_2 and salinity below 2.6 wt% NaCl equivalent.

So, although there are three types of FI - carbonic, aqueo-carbonic, and aqueous - the fluid must have been trapped under conditions above the solvus of the mentioned system and must have, therefore, been homogeneous. Modifications such as divisions (successive necking downs), migrations and shifts occurred following heterogenization of the fluid trapped in inclusions and must have led to the formation of three compositionally different types of inclusions. Planar distribution of inclusions, similar Th_{CO2} and Tm_{CO2} in both carbonic and aqueo-carbonic inclusions from all alteration stages, and highly variable CO_2/H_2O ratios are indicative of the mentioned process.

DISCUSSION The presence of carbonic inclusions in metasomatized rocks and its absence in unaltered granite, coupled with the occurrence of deuteric carbonate in the former lithologies, permit to relate the carbonic fluid to the metassomatic process. From the standpoint of the regional geodynamic evolution, the metassomatic process can be related to the granitic emplacement of the Brasíliano event.

Martinez (1992) investigated, under the light of FI data, an abrupt transition from porphyroid granites to charnockites and enderbites during the Brasíliano event. Nevertheless, the limited occurrence of metassomatites on the border zones of granites, the existence of zones of contact metamorphism between Borrachudos granite and carbonate levels in itabirite, the similarities between the observed mineralogical transformations and of those described by Bilal (1991) for Mata Azul (Goias) anorogenic granites, favor the interpretation as endoskarnites. One possibility for the origin of this carbonic fluid would be the dissolution of the host-carbonated levels by solutions from the granite. In a convective process, the fluid would return to the granite with altered composition, enriched in CO_2, Ca, Fe and Mn, among others.

According to Einaudi and Burt (1982), endoskarns show a mineral-zoning pattern, which reflect progressive addition of Ca to the protolith. They are more widespread in places where the metassomatic fluids have used limestones as channel-ways and where intense fracturing occurs rendering the rocks highly permeable. In deeper terrains, where the plutons are less fractured and fluid circulation is more restricted, endoskarns form only narrow zones in the near intrusive contact zone. This seems to be the case of the rocks under present study.

In this sense the fluid would be genetically related to the emplacement of the granite.

Acknowledgements To FAPEMIG (Grants # 787/92 and 10467 95); FINEP(Grant # 65/94/0135/00), Centre de Pesquisas Prof. Manoel Teixeira da Costa (IGC-UFMG), Laboratorio de Inclusoes Fluidas (CDTN-CNEN), Laboratorio de Espectrografia micro-Raman (Depto. Fisica-UFMG), CAPES/COFECUB (Grant n° 162/94), James . Vieira Alves for statistical treatment of microthermometric data, and to two referees from RBG are acknowledged for their comments and suggestions.

References

Bilal E. 1991. *Étude de deux massifs de la province granitique stannifere de I 'Etat de Golds (Bresil) et des formations metassomatiques associees aux minéralisations en Sn et Be.* Ecole Nationale Superieure des Mines de Saint-Etienne. Doctoral thesis, 382 p.

Bilal E., Marciano V., Correia Neves J.M., Fuzikawa K., Riffel B.F., Nalini H.A., Fernandes M.L.S., Nasraoui M. 1998. Alteration hydrothermale des monazites-Ce des pegmatites du district de Santa Maria de Itabira (Minas Gerais, Bresil). *C. R. Acad. Sci. Paris.,* 326:693-700

Brito Neves B.B., Kawashita K., Delhal J. 1979. A evolução geocronológica da Cordilheira do Espinhaco: novos dados e integra9ao. *Rev. Bras, de Geoc.,* 9:71-85

Chemale Jr. F., Quade H., Schmus W.R. van. 1998. Petrography, geochemistry and geocronology of the Borrachudos and Santa Barbara metagranites, Quadrilatero Ferrifero, Brazil. *Zbl. Geol. Paliiont. Teill,* 739-750

Dossin I.A., Dpssin T.M., Charvet, J., Cocherie A., Rossi P. 1993 - Single-zircon dating by step -wise Pb-evaporation of Middle Proterozoic Magmatism in the Espinhaco Range, Southeastern Sao Francisco Craton (Minas Gerais, Brazil). In: SBG. Simp. Craton Sao Francisco, 2, Salvador, *Anais,* 39-42

Einaudi M.T. & Burt D.M. 1982. Terminology, Classification, and Composition of Skarn Deposits. *Econ. Geol.* 77(4): 745-753

Fernandes M.L.S. 2000. *O Granito Borrachudos entre Guanhães e Dores de Guanhães, MG: genese e evolucdo.* Inst. de Geociências, Universidade Federal do Rio de Janeiro. Doctoral thesis, in prep.

Fernandes M.L.S., Bilal E., Correia Neves J.M., Giret A., Vasconcelos K. - 1995 - Estimativa das condifoes de cristalizafao do Granito Borrachudos na regiao de Dores de Guanhães, MG. In: SBG, Nucleo Minas Gerais. Simp. Geol. MG, 8, Diamantina, *Resumos Expandidos,* 64-66

Fernandes M.L.S., Bilal E., Wiedemann C.M., Correia Neves J.M., Lemos E.E. 1999. "O registro da deformacao Brasíliana em um corpo da suite Borrachudos aflorante na regiao de Dores de Guanhães, MG: evidencia geocronologica. In: SBG Simp. Nac. Est. Tect., 7, Le^ois, *Anais,* 34-37

Grossi Sad J.H., Chiodi Filho C., Santos J.F., Magalhaes J.M.M., Carelos P. 1990. Duas suites granfticas do bordo sudeste do craton Sanfranciscano, em Minas Gerais: petroqui'mica e potencial met alogenetico. In: SBG: Congr. Bras. Geol.,36, Natal, /lna/.v 4:1836-1848

Grossi Sad J.H. 1997. Geologia da Folha de Guanhães. In: Grossi Sad J.H., Lobato L., Soares-Filho B., Pedrosa Soares A.C. (coord. e ed.). *Projeto Espinhaco em CD-ROM (texto, mapas e anexos).* Belo Horizonte, COMIG - Companhia Mineradora de Minas Gerais, 2317-2435

Guimaraes D. 1973. Ocorrencia de charnockito hiperitico entre Guanhães e Virginopolis, MG. In: *Notas geocronologicas e petrográficas.* Belo Horizonte. S.ed., 34p.

Hendel E.M. & Hollister L.S. 1981. An empirical solvus for CO2-H2O-2.6Wt% salt. *Geochim. Cosmochim. Acta,* 45:225-228

Kwak T.A.P. 1987. *W-Sn skarn deposits.* Amsterdam, Elsevier, 451 p.

Machado N., Schrank A., Abreu F.R. de, Knauer L.G., Abreu P.A.A. 1989 Resultados Preliminares da geocronologia U/Pb na Serra do Espinha90 Meridional. Anais do V In: SBG/Nucleos Brasília e Minas Gerais, Simp. Geol. MG, 5, e Simp. Geol. Brasília, I, Belo Horizonte, *Ana is,* 171-174

Martinez N.A. 1992. *Evolução e genese das rochas granuliticas e charnocklticas da regiao de Mangalo, MG: Uma proposta a partir do estudo de inclusoesfluidas.* Institute de Geociências. Universidade Federal de Minas Gerais., Belo Horizonte. Master thesis , lOOp

MullerG., Hohndorf A., Lauenstein H.J., Lenz, H. 1986. Petrological and geochemical data on high-metamorphic Archean Bif-bearing rock sequence near Guanhães, Minas Gerais, Brazil. *Geol. Jb.D.,79:3-20*

Roedder E. 1984. *Reviews in Mineralogy: Fluid Inclusions.* Mineralogical Society of America, v. 12, 644p.

Contribution IGC-044
Received January 28, 2000
Accepted for publication May 23, 2000