INTRODUCTION
Caxias is a small primary gold deposit located in the São Luís Craton, northern Brazil (Fig. 1), along with several others small deposits and showings. This region has been the focus of intermittent alluvial mining since the second half of 17th century. Petrographic, geochemical, geochronological and fluid inclusion studies were carried out in the Caxias and Areal deposits (Klein 1998). This paper presents a characterization of the fluids of the northern sector of the Caxias gold mineralization, based on microthermometric and Raman spectrographic studies. Genetic considerations about this Au mineralization are done as well, supported by the fluid inclusion data.

GEOLOGICAL SETTING AND CHARACTERISTICS OF THE MINERALIZATION
Three major geotectonic units are recognized in the Gurupi region (Cardani et al. 1968, Abreu 1990, Pastana 1995): a stable area, a mobile zone, and sedimentary covers (Fig. 1). The stable area corresponds to the Paleoproterozoic São Luís Craton (SLC). It is bordered by the Neoproterozoic Gurupi Shear Belt. Proterozoic and phanerozoic sedimentary basins cover the former geotectonic units. The SLC comprises dominant granitoids of the Tromai Suite and minor supracrustal rocks from the Aurizona Group. The met aluminous, calc-alkaline Tromai granitoids have trace elements patterns comparable with modern, subduction-related, volcanic arc granites (Pastana 1995, Klein 1998).

The Caxias gold mineralization occurs in two different host rocks (Klein 1998): in the northern sector (N-CX) the mineralization is hosted by a small intrusion of a fine-grained tonalite, with strong chloride (+ carbonate, sericite, epidote, pyrite, sphalerite) alteration, in the southern sector (S-CX) the host-rocks are quartz-sericite- and biotite-chlorite-schists from the Aurizona Group (Fig. 2), with pyrite dissemination. In both areas, mineralization is spatially related to a steeply-dipping, meter wide, N15-25E-trending, dextral, transparent shear zone. Gold occurs disseminated in the hydrothermal altered rocks and in crosscutting quartz veins, especially at the contact of quartz and chlorite grains.

FLUID INCLUSION STUDY
This paper presents the fluid inclusion (FI) data from the northern sector of the Caxias mineralization. Quartz is largely the dominant mineral phase in the veinlets (>90% vol.), which also contain pyrite, carbonate and chlorite. Quartz grains are xenomorphic, limpid and range from 0.4 to 2 mm in size. Slight to moderate undulatory extinction, localized mortar texture, and deformation lamellae are observed, suggesting weak ductile deformational processes.

Sample preparation and microthermometric measurements were carried out following the procedures outlined by Roedder (1984) and Shepherd et al. (1985). Microthermometry was performed with Chaixmeca heating-freezing stages in the fluid inclusion laboratories at the Universidade Federal do Rio Grande do Sul and Universidade Federal do Pará. Raman analyses were performed at the Universidade Federal Minas Gerais on a Dilor Raman microscope with a multichannel detector and the 514.53-nm line of an Ar laser. Instrumental settings were kept constant during the analyses.

Fluid inclusion description and classification
Based on relative phase proportions in the fluid inclusions at room and subzero temperatures, three types of fluid inclusions have been identified.

Type I One-phase carbonic (CO2) fluid inclusions are clear to dark, mainly irregular in shape and their sizes vary between 6 and 30 mm. Small proportions (<10%) of petrographically and microthermometrically undetectable H2O may be admitted in these inclusions. They are the least frequent of all three types and are randomly distributed in the transparent domains of the host quartz. Most of the time they are associated with type II inclusions (Fig. 3); few are isolated and they are seldom seen in the same domain with type III inclusions.

Type II H2O-CO2 liquid inclusions are the dominant type averaging 13 mm in size. Most inclusions are two-phase at room temperature, and may nucleate a third phase (vapor CO2) on cooling. The volumetric proportion of the CO2-rich phase was optically estimated, varying from 15 to 75%. They present random distribution, often clustered and coexisting with the type I inclusions (Fig. 3), and are rarely associated with type III FI.

Type III are two-phase aqueous (H2O liquid + vapor) fluid inclusions, having characteristic clear appearance with sizes ranging from 5 to 27 mm and shapes varying from irregular to rounded or ellipsoidal. Rare daughter minerals have been observed and the degree of filling is constant (0.90-0.95). Most of the inclusions are confined to healed fractures, sharp trails and three-dimensional arrays. Only few of them occur isolated or associated with type II fluid inclusions.

Microthermometry
TYPE I AND II FLUID INCLUSIONS
Low-temperature measurements indicated most of the carbonic phase melting temperature (TmCO2) close to the CO2 triple point (-56.6°C), and the remaining varying down to -57.5°C. The homogenization point temperature (ThCO2) occurs always to liquid, between -3.2 and 27.7°C and 7.9 and 30.9°C for types I and II, respectively (Fig. 4a), corresponding to bulk densities between 0.7 and 1.0 g/cm3. This wide spectrum of ThCO2 occurs not only in different domains of the host
quartz but also in single clusters (Fig. 3). In type II inclusions, clathrate melting temperatures (Tmclath) always occur below the ThCO₂, showing little variation, with mean and mode around 7.5°C (Fig. 4b). The total homogenization (Tht) also shows a wide range (Fig. 4c), between 205 and 378°C.

**TYPE III FLUID INCLUSIONS** Four eutectic temperatures (Te) were obtained, two around -45°C and the other two around -27°C. The former belongs to inclusions that show ice final melting temperature (Tmice) between -5°C to -10°C (salinities between 7.8 and 13.9 wt. % NaCl equiv.), and final homogenization between 180°C and 242°C. The second group shows Tmice in the range -0.1°C to -7.4°C (0.18 to 11 wt. % NaCl equiv.) and Tht ranging from 124°C to 228°C (Fig. 5).

**Raman spectroscopy** The clustering of TmCO₂ around -56.6°C, with little deviation from its triple point, suggests that the composition of carbonic phase present in types I and II fluid inclusions can be roughly considered as pure CO₂. Notwithstanding, four fluid inclusions were selected for Raman spectroscopy. Although CO₂, N₂, CH and H₂S have been tested, only CO₂ and N₂ were detected. Molar proportions of these two components were calculated using the relative Raman scattering cross-section of 1.21 for CO₂ (N=1), showing N, mostly as traces in the carbonic phase, reaching 5 mole % only in one FI. These results are consistent with the microthermometric data obtained using the experimental CO₂-N₂ system phase diagram of Kerkhof and Thiery (1994).

**DISCUSSION AND CONCLUSIONS** The dominant group of CO₂-bearing fluid inclusions (types I and II) is considered the most precocious, and may represent primary FI. Constraints in bulk properties of these two types of CO₂-bearing fluids (P-T-V-X-|O₂) were given by combined microthermometric and Raman microspectrometric data. The composition was estimated according to...
Ramboz et al. (1985) or Holloway (1981), when the molar fraction of CO₂ in the carbonic phase is 100%. For type I fluid inclusions the presence of 5% H₂O, undetected by common petrography and microthermometry, and absence of salts have been assumed. The resulting bulk composition of the types I and II FI is XH₂O: 55 to 95 mol %, XCO₂: 6 to 45 mol %, XN₂: 0 to 2 mol %. Salinities, derived from Thclath in type II FI, are in the 0.2 to 9.8 wt. % NaCl equiv. range, with a strong mode in 5% (mean 4.5%). Bulk densities, obtained from ThCO₂ are in the range 0.761 to 1.006 g/cm³. This compositional range is compatible with metamorphic fluids produced by dehydration and decarbonization of greenstone sequences.

Type II fluid inclusions show highly variable ThCO₂ and ThT. This behavior may result from leakage related to heating (Shepherd et al. 1985), deformation (Wilkins and Barkas 1978), entrainment under pressure fluctuation (Robert and Kelly 1987), or fluid immiscibility (Ramboz et al. 1982). The highly variable CO₂/H₂O ratios have been used as evidence of phase separation and heterogeneous trapping (Ramboz et al. 1982), fluid mixing (Cassidy and Bennett 1993), or H₂O loss (Crawford and Hollister 1986). The coexistence of chemically and physically contrasting fluids (in this study, the carbonic and aqueous-carbonic FI) is an evidence that they are cogenetic and contemporaneous. This characteristic has been also attributed to successive mixing of different fluids (Pichavant et al. 1982), heterogeneous trapping (Ramboz et al. 1982), and post-entrainment modifications with variable loss of H₂O (Crawford and Hollister 1986).

Although some post-entrainment modification may have affected the CO₂-bearing FI, as evidenced by the weak ductile deformation in host quartz, this was not the dominant process that led these populations of FI to acquire the described characteristics. Besides, it is not evident in the salinity x ThT diagram for types II and III FI (Fig. 6) the vertical tendencies that are typical of necking-down and leakage by heating. Therefore, it is considered that the features presented by these fluid inclusions are characteristic of an immiscible or heterogeneous state, which may be attained by opposite processes such as mixing and unmixing (phase separation). Considering the characteristics and fluid properties displayed by the CO₂-bearing FI, the criteria of Ramboz et al. (1982) for fluid immiscibility, and the close distribution between the two FI types, the inclusions may be considered as cogenetic. Therefore, the contemporaneous and heterogeneous trapping requirements are satisfied. Regarding the homogenization, the type II inclusion homogenize all to H₂O, while the final homogenization of the type I inclusions could not be detected. But, as this type I FI is CO₂-rich (estimated H₂O volume % is only 5 %) and as no bubble shrinking was observed, it must be supposed that the homogenization occurred to liquid CO₂. These features, besides the lack of a compositional continuum (ThT versus % NaCl correlation; Fig. 6) suggest that the immiscible state was probably attained by phase separation, although a mixing process cannot be totally discarded.

Type III (aqueous) FI show two different eutectic temperatures, reflecting compositional differences. The assemblage with the lowest Te is Cu-rich (~NaCl, ~MgCl₂) and has no association with the CO₂-bearing inclusions. The group with Te around -27°C is Na-rich (~KCl), is seldom associated with types I and II and has salinities in the same range of the type II FI. Although the Na-rich FI could be regarded as part of the phase separation process, their much lower ThT, their rather constant phase proportions, and the fact that they are mostly confined to healed fractures preclude this hypothesis. Thus the origin of this fluid, as well as the Cu-rich fluid, is ascribed to a later fluid infiltration event.

As the heterogeneous trapping of immiscible or partially immiscible fluids was suggested, the isochores intersection method (Roedder and Bodnar 1980) could be used for temperature and pressure determination of fluid entrapment. However, this procedure requires density contrasts to produce isochores with different and intersecting slopes, which is not the case here, where type I and II FI have similar density ranges. Therefore, bulk composition isochores, calculated from fluid inclusion data combined with geothermometry of hydrothermal chlorites from the host microtonalite (Klein 1998), bracketed the P-T conditions between 262°C and 307°C and 1.6 kb and 3.7 kb (Fig. 7). These conditions are compatible with crustal depths of the brittle-ductile transition and beginning of the greenschist facies metamorphism.

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Figure 3-Distribution of types I and II fluid inclusions in the N-Caxias deposit, showing variable CO₂/H₂O phase ratios (A and B) and CO₂ homogenization temperature (B). Type III inclusions are late (see text for explanation).
Figure 4-Histograms showing microthermometric data of type I and type II fluid inclusions from N-Caxias. a: CO₂ homogenization temperature (ThCO₂); b: clathrate melting temperature for type II inclusions (Tmclath); c: total homogenization temperatures for type II inclusions (Tht).

Figure 5-Histograms showing the microthermometric data of type III fluid inclusions of N-Caxias. a: ice melting temperature (Tmice); b: final homogenization temperature (Tht).

Figure 6-Salinity versus final homogenization plot for type II (triangles) and III (asterisks) fluid inclusions.

Figure 7-P-T grid for N-Caxias mineralization. Isochores labeled A and B cover the density range of type II fluid inclusions. Isochores C and D cover the density range of type I fluid inclusions. A limit of 262-397°C is given by the chlorite geothermometer. The stippled area represents the P-T conditions for gold mineralization at N-Caxias.
Oxygen fugacities were calculated for the P-T-X range obtained from FI data, according to the equation of Ohmoto and Kerrick (1977), considering the equilibrium $C + O_2 = CO_2$, and using the fugacity coefficient of Ryzhenko and Volkov (1971). Values of log $fO_2$ obtained through this procedure range from -29.8 to -34.2, and are similar to those reported for Archean lode-gold deposits by Groves and Foster (1991).

The last point to deal with is the source and the role of the nitrogen on the volumetric and compositional properties of the CO2-bearing fluid inclusions. Hydrothermal alteration of K-bearing minerals, such as feldspars and micas and the breakdown of organic matter present in sediments are possible sources of N2 (Kreulen and Schuiling 1982, as feldspars and micas and the breakdown of organic matter present in sediments are possible sources of N2).}

Andersen et al. 1993). As the concentration of N2 is low, the only noticed influence was a small lowering of the carbonic phase melting temperature, while no relationship of its presence and the CO2 density (ThCO2) was observed.

Concluding, the geological setting, mineralogical, structural style, besides P-T-X-fO2 characteristics derived from fluid inclusions, suggest that this low-salinity, reduced, aqueous-carbonic fluid, responsible for the gold mineralization in the northern sector of the Caxias deposit, is similar to the ore-bearing metamorphic fluids postulated for mesothermal gold mineralization hosted by shear zones and granite-greenstone sequences in several Precambrian cratons worldwide.

References


Cordani U.G., Melcher G.C., Almeida F.F.M. de 1968. Outline of the Precambrian sediments are possible sources of N2 (Kreulen and Schuiling 1982, as feldspars and micas and the breakdown of organic matter present in sediments are possible sources of N2).}

References


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