STYLES OF HYDROTHERMAL ALTERATION AND GOLD MINERALIZATION ASSOCIATED WITH THE NOVA LIMA GROUP OF THE QUADRILÂTERO FERRÍFERO: PART II, THE ARCHEAN MESOTHERMAL GOLD-BEARING HYDROTHERMAL SYSTEM

LYDIA MARIA LOBATO* & FREDERICO WALLACE REIS VIEIRA**

INTRODUCTION
The objective of this paper is dual. Firstly, we intend to provide a thorough review of the critical knowledge base regarding hydrothermal alteration and mineralization processes associated with Archean, mesothermal gold deposits. Secondly, this knowledge base is applied to the context of mesothermal, lode-gold mineralizations in the Quadrilátero Ferrífero, Minas Gerais, Brazil. Thereby, a state-of-the-art integration of hydrothermal alteration and gold mineralization conditions in the Quadrilátero Ferrífero is presented, as well as a critical evaluation of the generalized, gold-mineralizing, fluid conditions.

By far the greatest number of mineral deposits has been formed by precipitation from hydrothermal solutions (Skinner and Barton 1973). Hydrothermal ore deposits form because a hot, aqueous solution carrying metal and other components precipitates minerals in ore traps due to physico-chemical disequilibrium between rocks and fluid (Skinner 1997). Fluids travelling through rocks result in mineral reactions that accommodate such severe disequilibrium, generating new - hydrothermal mineral associations.

Hydrothermal alteration is a chemical replacement of original minerals in a rock by new minerals where a hydrothermal fluid delivers the chemical reactants and removes the aqueous reaction products. It is a function of variations of temperature, pressure and, most importantly, fluid composition (Reed 1997, Rose and Burt 1979). This chemical interaction between wallrocks and hydrothermal solutions is certainly a major factor in the precipitation of many ores. An understanding of hydrothermal alteration is therefore of value, because it provides insights into the chemical alterations and their effects on the ore body itself. Hence, alteration haloes provide a much wider exploration target than the deposits themselves, and are regularly used by most exploration companies in their search for ore deposits in other parts of the world. Suggested slight variations in temperatures and pressure calculations may have important implications for the physical and chemical conditions of ore formation (Reed 1997). Predictive insights regarding orobed geometry and grade can thereby be inferred.

The usefulness of hydrothermal alteration, both as a guide to ore and as an indicator of the character of solutions associated with ore deposition, has been recognized for a long time (Rose and Burt 1979). The significance of wallrock alteration was initially pointed out in the late 1940’s by way of the recognition of the association of ore with zones of metasomatism, silification and chloritization.

Since then, the improvements in analytical techniques have broadened the knowledge on the subject via studies in the fields of lithogeochemistry, isotope geochemistry, and fluid inclusions, among others. The fields of isotope and fluid inclusions studies have been of utmost importance in unraveling fluid-rock interaction in fossil and recent geothermal systems and sea-floor deposits. They have also established the role that magmatic, meteoric and metamorphic fluids play in ore deposit models (Appleyard and Guha 1991).

Hydrothermal alteration assemblages display zonal patterns that reflect, from the ore zone to the least altered host rock, progressive rock buffering. Hence, alteration haloes provide a much wider exploration target than the deposits themselves, and are regularly used by most exploration companies in their search for ore (c.f. abstracts in Walton and Jambor 1998).

The study of hydrothermal alteration associated with gold deposition in Archean, mesothermal deposits has received a lot of attention in the literature in the last ten years. Efforts to focus on the alteration assemblages rather than the chemical reactions and their effects on the ore body itself.

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**HYDROTHERMAL ALTERATION AND RELATED ORE DEPOSITS**

Over the past five decades students of ore deposits have come to accept that most ore minerals are concentrated within the permeable conduit of adequately conditioned fluids into porous rock systems. Porosity and permeability may be primary properties of deposition or secondary functions of structural ground preparation (e.g. Bursnall 1989). The concept formed the basis to establish the hydrothermal model applied to mineral deposits, for which the revision by Appleyard and Guha (1991) is an excellent source.

Both the geological setting of hydrothermal mineral deposits and the minerals concentrated within them vary widely. Ore traps are sites where appropriate combinations of structural, chemical, and physical conditions force ore mineral pre-cipitation reactions. The fluid that arrives at the ore trap is not the same as the “primary” or “source” fluid, such as magmatic brine or heated seawater, because wallrock reaction along the transport pathway changes fluid composition (Reed 1997). The keys to most questions related to the genesis of hydrothermal ore deposits are (1) the source(s) and the physical and chemical characteristics of the ore-forming fluid; (2) the nature of the hydrothermal aquifer and the hydrodynamic force that controls a solution’s flow; (3) the mechanisms for dissolving and transporting ore-forming components; and (4) the causes of precipitation from the fluid (Skinner 1997). The source(s) is (are) usually not confidently identified, ranging from the so-called “unknown” source to magmatic, metamorphic, sedimentary (or connate) and meteoric. The influence of wallrock composition on mineral deposition is primarily related to the physical properties of various host rocks in their abilities to sustain variations in permeability regimes (Meyer and Hemley 1967).

Pre-tectonically emplaced ores can experience remobilization and substantial geochemical modification by fluids generated during tectonism and metamorphism. This diverges from the formerly accepted hypothesis that the source of the hydrothermal fluids was considered to be purely magmatic, either plutonic or volcanic. These conclusions resulted from the reformulation of models involving the occurrence of carbonate alteration, resulting from reaction of wallrock with CO₂-rich fluids. In the Archean deposits, the alteration assemblages vary according to parent lithological units but always reflect the transition of CO₂ from the fluid to the rock. Components other than CO₂ and gold added to the altered rock are K₂O, H₂O, S and As with other elements introduced from the mineralization, such as NaCl, Li, Rb, Sr, and Cs. However, some local deposits differ in the degree of this component (Meyer and Hemley 1967).

Wallrock alteration is an important associate of hydrothermal ore deposits because the processes of ore deposition are the same processes that characterize wallrock alteration assemblages (Susak 1984). The mineralogical and chemical changes brought about by reactions of the mineral constituents of rocks with circulating solutions within the host rocks of orebodies are common features of a diversity of ore systems. Just as common are the regular zonal patterns, which reflect changes in the composition of the fluid with time (Skinner 1997). These conclusions resulted from the reformulation of models then applied to massive sulfide and lode-gold-type deposits (Appleyard and Guha 1991).

**Alteration Assemblages**

At greenschist to sub-amphibolite facies conditions, there is commonly a wide zone of pervasive carbonate alteration with a central core of ankerite, ferro dolomite or dolomite (less magnesite) grading out into fringes rich in calcite, commonly with associated chlorite. In the strongly mineralized zone, there are normally K-micas, biotite, sericite (less commonly V- or Cr-bearing micas), but these may be absent in Al-poor rocks such as banded iron formation (BIF). In addition, albite and less commonly K-feldspar may be present in volcanic or intrusive host rocks in specific deposits. Quartz veining and silicification are variably developed, and tourmaline may be locally abundant.

Mesothermal, lode-gold deposits are typically hosted by mafic volcanic rocks and by banded iron-formation (BIF) (Phillips et al. 1984). Gold resides within sulfides (mainly pyrite) that replace iron in the altered wallrock immediately adjacent to quartz veins. The alteration assemblages differ in det all from one deposit to another, reflecting different fluid compositions and primary rock types. Despite the variety, the assemblages are remarkably consistent in consisting of pyrite ± pyrrhotite ± arsenopyrite, sericite (or biotite), chlorite, albite and Fe-Mg-Ca carbonates. However, the mineralogy may vary depending on the degree of regional metamorphism and the duration of ore mineralization.

As with either introduction or redistribution of SiO₂, and more locally CO₂ and gold added to the altered rock are K₂O, H₂O, S and As with other elements introduced from the mineralization, such as NaCl, Li, Rb, Sr, and Cs. However, some local deposits differ in the degree of this component (Meyer and Hemley 1967).
Fluid to Rock Dynamics In the review by McCuaig and Kerrich (1994), examples of different districts are used to highlight the mineralogical composition of alteration zones surrounding lode-gold deposits. The hydrothermal alteration assemblages surrounding quartz-dominated veins in fluid conduits, such as shear zones, faults or fracture systems reflect open chemical- and isotopic-system behavior. The metasomatic interaction of fluids with conduit wallrocks occurs during upward advection through the crust, as the fluids approach chemical, isotopic and thermal equilibrium.

The alteration reflects an intricate interplay between rheological behavior, fluid dynamics and chemical and isotopic exchange, involving 1) the tectonic regime; 2) composition of host lithological units; 3) composition of the hydrothermal fluid; 4) temperature; and 5) pressure.

The alteration due to fluid to rock interaction occurs by two main processes: 1) infiltration of fluids along local structural discontinuities, such as open fractures and microcracks. This varies from the scale of laterally extensive quartz veins to that of the migration of fluids along mineral grain boundaries; and 2) diffusion of ions through static pore fluids. The dominance of one over the other is controlled by the balance between permeability of the conduit and the diffusion rates along grain boundaries in the wallrock. However, in the case of gold systems, infiltration rates are greater than those of diffusion (Ridley 1990).

The mineralogical composition of alteration assemblages associated with lode-gold deposits is varied. The zones are observed: 1) with increasing distance orthogonally away from fluid conduit(s); 2) between host lithological units of differing bulk composition; and 3) regionally with temperature and pressure of formation. Zones perpendicular to fluid conduits are the commonest. They may range from millimeters to decimeters, or more, in thickness, and are identified by the presence of diagnostic mineral assemblages. Inner (proximal) zones reflect fluid-dominated (unbuffered), metasomatic reactions. Zones distant from veins reflect a decreasing gradient of fluid to rock ratio, as well as chemical gradients, and represent progressive infiltration of the fluid into the wallrock. Boundaries between alteration zones may be knife sharp or gradational over centimeters to meters. Sharp boundaries are common in proximal alteration zones. Diffuse boundaries predominate in distal alteration zones. The most distal alteration zones grade into the least-altered regional metamorphic assemblages.

The greatest complexity occurs mainly in the inner alteration zones due to narrow zone widths and the episodic nature of deformation and fluid infiltration, which act in concert with regional metamorphism. Alteration zone boundaries are complex crosscutting relationships. These zones are progressive in nature, such that proximal alteration zones overprint their distal counterparts. Within a single, host-rock type, there is little variation parallel to the fluid conduits. However, a fluid conduit in a single deposit that transects two lithological units of contrasting bulk composition will have different mineral assemblages in the different lithological units. Within a single lithological unit in any given deposit, the alteration zones may be traced parallel to the fluid conduits, both down dip and along strike, for hundreds of meters showing little variation in mineralogical composition within individual zones. This indicates relatively isochemical conditions of vein emplacement and metasomatism.

Distal alteration zones are generally ubiquitous throughout the hydrothermal system, but innermost alteration zones may be restricted to fault-fault or fault-lithological contacts, dilatational flexures in structures, or other such areas of extremely high fluid flux. Alteration holds information on intensive (P, T, X CO2, etc.) and extensive (fluid flux, mass of ore or gangue) properties of the larger hydrothermal system (McCuaig and Kerrich 1994).

Hydrothermal Alteration Conditions The P-T environment is reasonably well constrained for deposits in the greenschist facies, with deposition occurring in the range of T = 300 to 350°C and P = 1 to 3 kbar. For these deposits, the hydrothermal mineral assemblages can completely overprint metamorphic assemblages; both are characteristic of the greenschist facies, but the former does not necessarily reflect retrograde conditions (Phillips 1991, Robert and Sheahan 1991). Wallrock alteration thus post-dates peak metamorphism. Together with gold mineralization, the alteration can be associated with a regional tectono-metamorphic event (Groves and Foster 1993).

Det aided studies of gold alteration envelopes in mafic and ultramafic host rocks have shown that the zoning of mineral assemblages reflects a decrease in CO2 of the fluid away from the ore. It has been shown that decreasing CO2:H2O ratio in the fluid controlled the development of four distinct progressive alteration phases from the gold-bearing zone outward (Dubé et al. 1987). This hydrothermal alteration pattern can be derived from a single fluid with a higher initial CO2:H2O ratio, evolving as a result of interaction with host rocks.

The nature of the ore fluids has been deduced from fluid inclusion studies of quartz veins interpreted to be synchronous with, or slightly post-dating, the main stage of gold mineralization. They indicate that for most deposits, gold mineralizing fluids were rich in CO2-H2O, generally with 10-25 mol % CO2 of relatively low salinity (typically 3-6 vol. % NaCl equivalent), and moderate density (0.3-0.9 g/cm3, typically 0.8). The fluid is considered to have been near neutral to slightly alkaline and mainly reducing, with small (1, commonly 0.1 mol %) concentrations of CH4 having been detected, although oxidized fluids have also been recorded. A. similar concentration of Na is also present. Minimum 18O compositions: Conditions are 200-400°C (mainly 250-350°C) and 0.5-4.5 kbar (mainly 0.8-3 kbar).

Various degrees of phase separation are recorded, but it is only rarely that saline aqueous fluids are recognized. Water dominates the ore fluids (75-90 mol %), whereas CO2 usually constitutes 3-10 mol % of the gases most commonly detected are CO2, H2S, H2 and CH4, and also the relatively reactive species N2, He and Ar. Stable-isotope data for quartz, carbonate and sulfide from various deposits are also remarkably similar. The range of calculated 818O values of the ore fluids, based on the isotopic composition of the dominant type of vein quartz, are typically between 4.5 and 7‰. These values are compatible with either a magmatic or a metamorphic derivation (see revisions by Groves and Foster 1993, Hodgson 1993, De Ronde et al. 1997, and references therein). As mentioned by Groves (1993), there is an increasing body of fluid-inclusion and stable-isotope evidence to sup-
port the involvement of surface waters in upper levels (lower- or sub-greenschist) settings.

**Origin Of Archean Mesothermal Gold Deposits** Research into the origin of gold deposits has probably attracted more hypotheses throughout history than any other mineral-deposit type, and deposits of such a different character (Herrington et al. 1997). There is a broad consensus of an epigenetic origin for Archean gold deposits. Despite this, gold-rich, sulfide-BIF mineralizations have been used to provide evidence for syngenic origin (Frlpp 1976, in Kerrich 1993). This was later refuted by Phillips et al. (1984), who related their origin to the propensity of these very iron-rich rocks to fix sulfide alteration.

One major problem in developing a consistent model for the formation of all these gold deposits is the above-mentioned, broad range of interpreted formation conditions (Col et al. 1988; Groves 1993). The associated, intense alteration indicates a massive fluid flux, and the simple mineralogical composition of the alteration is perhaps further evidence for a large, open metasomatic system with high fluid flux (Groves 1993). According to the revision by Herrington et al. (1997), the weight of evidence appears to point to a deep, probably metamorphic, fluid source model, despite the indication that mineralization post-dates peak metamorphism. Kerrich (1991) argues that in collisional belts, where crustal thickening is essentially instantaneous, with respect to thermal relaxation, peak metamorphism at 60-km depth may post-date the peak at 10 km by up to 40 Ma. The same author adds that younger ages of mineralization in relation to metamorphism (as much as ~ 100 Ma) may reflect secondary disturbance of the primary ore. The broad range of T and P conditions for deposit formation, discussed by Groves (1993), suggests a very deep crustal level, possibly sub-greenschist-belt source for the gold-bearing fluids, but with some component contributions from other, possibly crustal and ormagmatic sources.

**GOLD-RELATED HYDROTHERMAL ALTERATION WITHIN ROCKS OF THE NOVA LIMA GROUP: WHAT WE KNOW**

The Quadrilátero Ferrifero (QF) is located in the southernmost São Francisco Craton (Almeida and Hasui 1984) in southeastern Brazil. The São Francisco Craton is limited by Brasiliano-age (700-450 Ma) mobile belts, and is constituted by a basement consolidated during the Archean and Eoproterozoic. The geological units of the QF embody: (1) granite-gneissic terranes of Archean age; (2) Archean greenstone belts of the Rio das Velhas Supergroup and other related successions; and 3) Eo- and Mesoproterozoic, metasedimentary units of the Minas Supergroup, the Itacolomi Group and the Espinhaço Supergroup (Dorr 1969).

A more detailed account of the geology of QF region is reviewed by Lobato et al. (1998b, the present volume). Endo (1997) (1997) and Zucchiatti (1998) also provide excellent reviews of the present knowledge of QF geology.

The QF was the most productive gold region in Brazil in the 18th century. The most important gold deposits are located in the northern portion of the QF, embodying for example the Cuiabá, Morro Velho (Grande and Velha), Raposos, São Bento, Faria, Bicalho and Bela Fornas host rocks, which are held by rocks of the Nova Lima Group. Mineralization at Santana is located along the sheared contact between rocks of the Minas Supergroup (Itabira Group) and schists of the Nova Lima Group (see Ladeira 1991).

Lobato et al. (1998b, the present volume) review the styles of hydrothermal alteration and mineralization of epigenetic, structurally-controlled gold deposits in the QF, associated with rocks of the Nova Lima Group. These are the Cuiabá, Jucá Vieira, Raposos, Santana and São Bento deposits. The most important conclusions arising from these investigations incorporate the following most important characteristics:

- **Alteration assemblages replace pre-alteration (metamorphic) associations, pointing to their syn- to post-peak metamorphic development age.** They are dominated by quartz, carbonate, K/Na-mica, feldspar (albite), Fe/Mg-chlorite, pyrite, pyrrhotite, arsenopyrite, ± tourmaline.
- **Pervasive carbonate alteration has a core of Fe-ankrite/ankelite, intermediate ferrodolomite or dolomite grading out into fringes rich in calcite and/or siderite (BIF).** In BIF, carbonate alteration (mostly ankrite) is particularly prominent and sulfide layers are the result of sulfidation of quartz-carbonate-magnetite BIF layers.
- **Mineral reactions of the incipient alteration stage suggest reducing hydrothermal fluid.** The evolution from a carbonate-(advanced stage) to a chloride-dominant (incipient stage) assemblages indicates an initial CO₂:H₂O-fluid, evolved to lower (chlorite) CO₂:H₂O ratios; (4) Unbuffered assemblages in the proximity to ore indicates infiltration of a large volume of external fluid. The zonation of alteration types reflects evolution in the composition of the fluid through interaction with wallrocks. Large fluid volumes under conditions of high shear rate covered the large-scale recrystallization and precipitation along shear-induced permeabilities;
- **S, CO₂, As, Au are added during the alteration, and SiO₂ is either stable or lost. CO₂ addition is constant and the saturation index CO₂/(Ca+Fe₂++Mg+Mn) is useful as a measure of alteration degree;**
- **Gold is closely related to wallrock alteration. Its deposition occurred about sulfide precipitation.** In BIF-hosted mineralizations it must have occurred due to fluid-wallrock sulfidation reactions. This close association suggests that reduced sulfur complexes were the predominant transport mechanism.

**DISCUSSION: INFERRRED CONDITIONS OF HYDROTHERMAL ALTERATION IN THE QUADRILÁTERO FERRIFERO**

This paper reviews the state of the art relating to hydrothermal alteration associated with mesothermal, lode-gold deposits, particularly those hosted by rocks holding mineral assemblages of the sub-amphibolite and greenschist facies of metamorphism. It is shown that the alteration associated with different lithological units imposes varying mineralogical associations in zonal patterns enveloping gold ore. Such associations reflect original fluid composition, and the fluid’s contribution to the regional fluid evolution during rock alteration in structurally controlled pathways. The zonal pattern reflects varying fluid to rock ratios under roughly isothermal conditions.

The deposits described by Lobato et al. (1998b, present volume) are either replacement-dominated (BIF-hosted mineralizations at the Cuiabá, Raposos and São Bento) or disseminated in zones of hydrothermal alteration (carbonate-sericite) associated with quartz veins (e.g. Jucá Vieira and Santana Mines).

The origin of these deposits is controversial and much has been said about their epigenetic versus syngenic attributes (Fleisher and Routhier 1973, Vial 1988, Vieira and Oliveira 1988, Duarte, 1991, Ladeira 1991, among others). It is beyond the scope of this review to dwell on the subject. Identifying a single, coherent model for the mesothermal gold deposits in the QF is a monumental task. It requires an integrated interplay of knowledge relating to regional and local geological information, geochronology, structure, regional geology, petrography and mineralogy, whole-rock geochemistry, radioisogen and stable isotopic signatures, fluid inclusions, geothermometry and geobarometry.

So much of this information is not available yet, but an increasing number of workers are currently contributing to the already voluminous body of existing data, some of which are referenced herein.

We aim to quantify some the critical parameters that brought to bear on the hydrothermal alteration systems associated with the terrain’s gold mineralizations, on the basis of the foregoing review of the state of the art of hydrothermal alteration in Archean, mesothermal, gold-ore systems.

What can we gather about fluid generation and composition, based on the information on hydrothermal alteration and fluid inclusion (and isotopes) studies? How do fluids associated with mesothermal gold deposits in the QF compare to fluids attributed to deposits in similar host rocks in cratons in Australia, Africa, Canada, and India? How could fluid composition have influenced gold deposition? These are the topics we wish to review. By doing so, we aim to contribute effectively to an eventual, integrated model of gold mineralization in the region and elsewhere.

**Fluid Inclusion and Isotopic Studies**

The studies by Godoy (1994) for the Raposos Mine identify three types of fluid inclusions, based on microthermometric and spectroscopic studies using Raman. Type I inclusions are abundant in the ore and composed of H₂O, CH₄, N₂, CO₂, with a smaller proportion of CO₂. Type II contains 3% CO₂, has H₂O and CO₂, and has NaCl, with lesser CH₄. Type III is an aqueous, saline fluid. Type I is interpreted as the initial, more reducing, mineralizing fluid. Type II is related to carbonate alteration (probably evolved from I) and type III to late, brittle deformation structures. The fluids of gold mineralization at 350 °C and 400 °C, respectively, take into consideration type I inclusions and temperatures of formation for arsenopyrite and chlorite. Phase separation between a liquid and a gas is also indicated by Godoy (1994).
Fluid inclusions in mineralized and barren quartz veins in the São Bento Mine have been studied by Alves et al. (1992), Alves (1995) and Alves et al. (1997). These studies indicate the presence of $H_2O + CO_2$ (H$_2$O-rich) and CH$_4$ (± HS-)-fluids which were possibly related to Au transport and deposition. CH$_4$ is the predominant gas phase of type 2 (CH$_4 + N_2 \pm$ HS-) inclusions, considered to be representative of the most primary fluid signature.

Type 1 inclusions are aqueous, nitrogenous and carbonic, and their evolution from la to lc indicates a path from least (primary) to most evolved fluid composition. There is a decrease in the carbonic phase from 10-15% to 5% (la to lc). This phase in inclusions la is CH$_4$-rich (molar volume of 50%), with a CO$_2$-equivalent density of 1.05 g/cm$^3$, and minimum T and P of ~300°C and 3.2 kb, respectively. The path of fluid evolution is indicated by CO$_2$-rich (>88.1%) inclusions (types Ib and c), with lower CO$_2$-equivalent density of 0.76 g/cm$^3$ and lower minimum T and P, around ~200°C at 1 kb. The most evolved fluid composition, identified in association with white mica, is practically pure CO$_2$. The carbonic phase also contains N$_2$ and HS-, and more rarely H$_2$S. Their aqueous phase has a salinity in the range of 3.4 to 5.0 vol. % NaCl equivalent. Salinities estimated for most other deposits worldwide are typically 1-10 vol. % NaCl equivalent.

Carbonic species in aqueous-carbonic fluids associated with lode-gold deposits range in ~10-30%. CO$_2$ varies from almost pure to mixtures containing near-equal proportions of CO$_2$ and CH$_4$ (Mikucki and Ridley (1995)). Alves et al. (1997) indicate similar values. In la inclusions CO$_2$ varies from approximately 42 to 73%, CH$_4$ from 10 to 40% and N$_2$ from almost nothing to 29%. In lc inclusions CO$_2$ varies from approximately 17 to 88%, CH$_4$ from none to 46% (mostly around 10 to 15%) and N$_2$ from 6 to 59%. The evolution from an initially reducing fluid to a more oxidizing condition is interpreted by Alves (1995) as resulting from varying $\delta^13C$, via reactions such as CH$_4 + 2$O$_2 \rightarrow CO_2 + 2$H$_2$O. The presence of both HS- and more rarely H$_2$S, suggests that at least some of the fluid evolutionary path involved a near-neutral pH. A possible immiscibility between type-2 and type-1 fluids is also indicated.

Fluid inclusion studies in the Cuiabá Mine are reported by Toledo et al. (1998). Proximal zones contain predominantly aqueous, with a bubble occupying 10-15 vol. % of the inclusion cavity. The fluids were then homogeneous (not immiscible) at the time of trapping. The gas is composed solely of CH$_4$ and CO$_2$ is subordinate. Raman microspectroscopy confirmed the presence of CH$_4$ and CO$_2$, and revealed peaks for N$_2$ and traces of H$_2$S-HS-. Salinity values for the aqueous phase were constrained between 5.9 and 8.0 wt% eq. NaCl. The authors suggest that evolution of both CH$_4$ and CO$_2$ resulted from hydrolysis of the carbonate matter with consequent sharp decrease in $\delta^13C$, (see O$_2$ and S evolution in QF).

DeWitt et al. (1994) studied the gas composition of fluid inclusions from a variety of quartz veins at São Bento and showed that most formed in place from silderite-rich BIF during regional metamorphism. Ladeira (1980) determined oxygen isotope values for quartz from lapa seca, as well as for schists hosting gold in the Morro Velho Mine. In a variety of rock types, oxygen values vary from 15.86 to 17.36‰, within similar ranges for whole-rock $\delta^18O$ of schists. The author indicates that the values suggest isotopic equilibrium with submarine fluids, relating to a syenogenic, exhalative hydrothermal alteration. Vial et al. (1987) re-interpret these results and propose the lapa seca to be a suite of volcanic and volcaniclastic rocks, metamorphosed and hydrothermally altered.

Carbonate isotopic studies in metapelites indicate an organic origin for carbon. The results vary from -18‰ to -12‰ at the Raposos Mine (Godoy 1994), to -20 to -25‰ at the Morro Velho and Cuiabá Mines (Fernandes et al. 1994).

Carbon isotope values (Godoy 1994) in carbonate from various rock types at the Raposos Mine indicate two main groups of distinct isotopic ratios. Values around zero for mafic rocks not affected by hydrothermalism, and from -4 to -6‰ for mineralized, hydrothermally altered BIF, mafic and ultramafic rocks. According to this author, the former values are compatible with isotopic equilibrium with submarine fluids, whereas the latter suggest carbonates formed in the presence of fault-controlled hydrothermal fluids. The author hence interpreted the results originating from metamorphic processes of thermodynamic consequences.

Hydrothermal Alteration and Controls of Fluid to Rock Interaction

The alteration assemblages described by Lobato et al. (1998b), the present volume) are the result of mineral reactions between host rocks and the infiltrating, ore-forming fluid (Vieira 1991a, Pereira 1995, Junqueira 1997, among others). They reflect conditions of formation ranging from low to high fluid to rock ratios. Although these reactions do not reproduce the complex hydrothermal processes in all their details, they can be used to infer the controls of fluid to rock interaction, particularly for the case of metamorphosed mafic and ultramafic wallrocks.

The incipient stage of alteration of these rocks is dominated by the formation of hydrous minerals (chlorite, talc). Carbonate is also important, but its proportion is significantly augmented only in the advanced stages of alteration.

Alteration assemblages of the incipient stage of alteration vary according to changes in $X_{CO_2}$ under isothermal conditions, fully compatible with temperature calculations for these systems (see next section). Hydrothermal reactions involving carbonate formation from metamorphic albite are dependent on $X_{CO_2}$ and $K_f$/NaF. Under conditions of low $X_{CO_2}$ this reaction is dependent on small changes of $X_{CO_2}$ at high $X_{CO_2}$ it is more sensitive to variations of $K_f$/NaF.

In spite of the indicated fluctuations in $X_{CO_2}$, typical alteration assemblages for the incipient stage can be interpreted to reflect differences mainly in the chemical composition of the parental rocks. The development of alterations zones containing larger proportions of carbonate, muscovite (~paragonite) and albite characterize an advanced hydrothermal alteration stage, involving addition of CO$_2$ and Na from the fluid, with resultant H$_2$O and H$^+$ loss. They are a consequence of the replacement of chlorite and initial carbonates. Zones of carbonate-white mica alteration depend on $X_{CO_2}$, and activities of K$^+$ and Na$^+$ (see discussion about pH variation and Mikucki and Ridley 1993, Fig. 1). Sulfdation is intimately related to these zones, and occurred when part of the iron of chlorite reacted with sulfur from the fluid.

The progressive hydrothermal alteration of the Al-poor BIF is not well constrained. Nevertheless, it is clear from textural observations at the Raposos Mine (Lobato et al. 1998a) that progressive replacement of siderite and magnetite by ankerite and pyrrhotite is concomitant, although ankerite, together with some siderite, seems to appear first. Carbonate and sulfide alterations are recurrent. Pyrite and arsenopyrite overgrow pyrrhotite. Rare chlorite appears when pyrrhotite appears. Small amounts of euhedral albite and muscovite bands are present in the advanced stage of sulfide substitution (gold-rich ore).

Phillips et al. (1984) relate the pervasive nature of sulfidation in BIF to their very iron rich composition. Hence, the mineral transformations in BIF are sensitive to $X_{CO_2}$ and most importantly to $K_f$. Nevertheless, the presence of albite and white mica also suggest some dependence on $Q_{f}$/NaF and $Q_{f}$/Mg.

As indicated, wallrocks tend to have similar gross mineral assemblages, regardless of the original chemical composition of the parental rocks. Proximal zones of hydrothermal alteration reflect fluid-dominated (unbuffered), metamorphic reactions. This suggests that the original mineralogical and chemical composition adapted to the composition of the infiltrating fluid. On the other hand, hydrothermal alteration zones distant from ore reflect low gradient fluid to rock ratio, as well as chemical gradients.

The incipient and more advanced stages of alteration can be interpreted in terms of gradual evolution of the composition of a relatively uniform, external fluid through interaction with wallrocks.

Hydrothermal Alteration and Fluid Composition

Mikucki and Ridley (1993) discuss ore fluid composition and fluid's compositional evolution of Archean lode-gold deposits at different metamorphic grades. Considering the wealth of information on the lode-gold deposits in the QF much can be inferred in light of these authors' thermodynamic interpretations.

Mikucki and Ridley (1993) show that deposits characterized by pyrite-anterite, dolomite and albite alteration, with pyrite and arsenopyrite, range from 250 to 350°C. Those with ankerite, dolomite, calcite, quartz, biotite and albite alteration, with pyrite, pyrrhotite and arsenopyrite are in the 320 to 420°C temperature bracket.

The temperature (T) and pressure (P) brackets suggested for some of the QS mesothermal deposits are taken from fluid inclusion studies and arsenopyrite geothermometry, the results of which are having already been presented. Arsenopyrite thermometry carried out in the Cuiabá Mine indicates that the T of alteration was from 250°C.

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to 520°C and gold deposition occurred between 270-300°C (Ribeiro-Rodrigues 1998).

The gold deposits described by Lobato et al. (1998b, the present volume) can be envisaged in the P-T regime of the greenschist to sub- amphibolite metamorphic facies.

**MAJOR COMPONENTS** Relatively CO₂-rich, aqueous ore fluids have long been recognized as characteristic of sub- amphibolite facies lode-gold deposits (Dubé et al. 1987).

Estimates of $X_{\text{CO}_2}$ of the initial ore fluid from both thermodynamic and fluid inclusion measurements indicate a range of 0.05-0.25. Variations in CO₂ gradients control alteration-zoning patterns in lode-gold deposits.

Mikucki and Ridley (1993, Fig. 1) show that in the case of an ultramafic composition (A- least altered, ultramafic host rock), zones of progressive carbonate alteration encompass associations with B-talc-chlorite, C- biotite, D- fuchsite (gold-bearing zone). Log (cocaoa) for A is ~ 0.05-0.25, for B it is ~ 0.40-0.8, for C ~ 1.1-1.2 and for D Log (~3×4H₂O) is about 1.2 to 1.4. The X$_{\text{CO}_2}$ values of 0.10 to 0.25 overlap the C to D alteration assemblages. These values refer to T of 350°C and total pressure $P = P_{\text{CO}_2} + P_{\text{H}_2\text{O}} = 2$ kb.

Major-component evolution in OF gold-mineralizing fluids In BIF-hosted mineralizations such as those at Raposos and São Bento, sulfide fluid inclusions in the advanced stage of alteration (chloritization, pyrrhotite, arsenopyrite) of quartz-carbonate (mostly siderite)-magnetite layers. Sulfdiation is accompanied mainly by strong carbonate (ankerite) alteration (Pereira Martins 1996, Junqueira 1997, Ribeiro-Rodrigues 1998). Other aspects of BIF alteration include restricted development of sericite, albite and epidote in the case of Cuiabá, carbonaceous matter was also involved (see below).

This mineral assemblage suggest a H₂O-CO₂-H₂S fluid (see also Phillips et al. 1984). Estimates of the initial fluid composition also indicate the presence of higher than usual CH₄ and NaCl, attesting the reducing, slightly saline fluid character (Godoy, 1994, Alves 1995, Toledo et al. 1998).

The recurrent nature of carbonate-sulfide alteration suggests fluctuations in the $\frac{a_{\text{CO}_2}}{a_{\text{H}_2\text{O}}}$ ratio. At Raposos, sulfide alteration seems to dictate the shear-dominated, gold-mineralizing zones thereby indicating an increase in the fluid $a_{\text{CO}_2}/a_{\text{H}_2\text{O}}$ ratio with the advancement of hydrothermal alteration.

Subordinate gold mineralization in mafic metavolcanic and metasedimentary rocks is also epigenetic, syn-tectonic. At Raposos, alteration zones of metamafic and meta-ultramafic rocks enveloping ore involve initial breakdown of epidote and/or actinolite, with nucleation of chlorite and Fe-carbonates plus sulfides (Junqueira 1997). This indicates that a incipient stage of alteration, having evolved from an initial reducing fluid, characterized by a higher CO₂:H₂O ratio, typical of the advanced stage.

The mineralogical composition of meta-ultramafic alteration zones at the Raposos Mine (Lobato et al. 1998b, the present volume, Fig. 7a) are similar to zones A to D described by Mikucki and Ridley (1993). They also imply an increase in fluid $a_{\text{CO}_2}/a_{\text{H}_2\text{O}}$ ratio similar to $a_{\Sigma S}/a_{\Sigma S}$ variations with the advancement of the alteration and proximity to ore.

The Jucá Vieira and Santana mineralizations also fall within the epigenetic model that Hodgson (1993) classifies as shear-related, mafic- or sediment-hosted disseminated sulfides. Gold is closely related to wallrock alteration and is simultaneously enriched in zones of carbonate, sericite, and tourmaline alteration (mainly Santana Mine), together with quartz and sulfides (Menezes 1996, Pereira 1996). As in the case of the Raposos Mine too, Vieira (1991a) and Pereira (1996) propose an H₂O-CO₂ fluid. It varies from a predominantly H₂O-dominated fluid in the incipient stage of alteration (chloritization) to a higher CO₂:H₂O ratio in the most advanced stages of hydrothermal alteration.

**OXIDATION STATE ($f_O^2$) AND TOTAL SULFUR CONTENT ($a_{\Sigma S}$)** Redox reactions tend to occur when two phases with different oxidation states come in contact. Redox conditions of alteration assemblages vary between lode-gold deposits. Most deposits that contain pyrite ± arsenopyrite ± pyrrhotite formed from relatively reduced ore fluids, with the highest redox potential of the ore fluid. Fluids of the majority of ore deposits studied to date display log $f_{O^2}$ in the range 0.5-3, above the CO₂—CH₄ stability curve. Total sulfur concentration in the ore fluids are in the range of ~ 10⁻²²⁻³⁻ H₂S, with a trend towards lower sulfur contents at lower temperatures. With buffer reactions in log $f_{O^2}$ and $a_{\Sigma S}$ for deposits in the 350°C and 2 kb range. The 'oxidized' fluid field emulates some of the largest gold camps currently known (e.g. the Golden Mile, Kalgoorlie).
On the other hand, the presence of carbonaceous matter with no magnetite in the Cuíabá BIF may in part explain the predominance of pyrite (and rare pyrrhotite) during sulfidation. As shown by Toleda (1997), the carbonaceous matter is oxidized to Fe-carbonate. Aggregates of pyrite (± arsenopyrite) substitute carbonates (siderite and Mn-ankerite) in various pulses of fluid to rock interaction. Pyrrhotite, chalcocite and sphalerite are subordinate. The oxidation of carbonaceous matter in Cuíabá may have been related to the interaction with a fluid similar to that which reduced magnetite to produce sulfides and carbonate (Raposos). The presence of carbonate haloes separating carbonaceous matter from pyrite (Toleda 1997, Fig. 80) suggests that O2 buffering might have given way to widespread carbonate development, and subsequent relative increase in aΣ2. Under higher aΣ2 conditions the Fe-carbonate to pyrite transformation occurred.

A parallel can be traced between Cuíabá and the carbonate-dominated, hydrothermal alteration at the Kerr-Addison Mine, Canada (Kishida and Kerrich 1987). The deposit lies in a fault zone, with host rocks to the north containing magnetite as opposed to the more reducing conditions to the south, indicated by the presence of graphite. Along the fault interface, interaction with the same fluid oxidized carbon and reduced Fe+2 of magnetite, both reactions producing Fe-carbonates (ankerite and ferro-dolomite). The authors indicate that XCO2, defined as CO2/(CO2 + H2O + CH4), is also a function of aΣ2, which may be controlled by either the infiltrating fluid or by reaction with the wallrocks. The aΣ2 of the incoming fluid then controlled the proportion of CO2 in the fluid in contact with graphite-bearing wallrocks (graphite oxidation). There is preferential gold concentration south of the fault, suggesting that its precipitation was controlled by the oxidation state of the fluid.

Pyrrhotite development is also constrained by the tectonic regime. At the Raposos Mine, gold-bearing sulfide zones are preferentially associated respectively with D1 and D2 structures of Vieira and Oliveira (1988). These zones are interpreted as resulting from different tectonic conditions by Vieira (1987b), with pyrrhotite forming in tensional zones, and pyrite + arsenopyrite in dilational zones (Type-1 and -2 mineralization styles, respectively) in different, time-unrelated deformational phases. Pyrrhotite also dominates shearzones in Cuíabá (Toleda 1997).

Our integrated observations suggest that such styles of sulfide enrichment were conditioned by the fluid evolutionary history and tectonic structures, but are not related to any specific timeframe. From the borders of zones dominated by pyrrhotite (Type-1 mineralization style), fractures developed and advanced into BIF banding, where subhedral to anhedral pyrite and arsenopyrite grew (Type-2 mineralization style). However, the first few centimeters of such fractures are filled by pyrrhotite that is immediately followed by the former two sulfides. Streaks containing all three sulfides (± chalcopyrite) can be cut by trails of similar composition, suggesting two to three similar sulfide generations. As suggested by Toleda (1997), the presence of pyrrhotite-filled fractures, and indicates that there are variations in the mineral composition of some hydrothermal phases (cf. Emmermann 1989). Pyrite ± arsenopyrite and pyrrhotite fill cracks in deformed (“mylonitic”) crystals, thus containing regions of oxygen isotope variations because of a temperature increase. He correlates the increase in pyrrhotite with conditions prevailing in mineralizations close to the Kerr-Addison Mine, located at the northwestern outcrop of the OP. In this zone, the deposition of pyrite associated with garnet, pyrrhotite and other sulfides indicates higher temperature than that characteristic of the gold deposits described by Lobato et al. (1998b, the present volume). In the case of the São Bento Mine, the increase in pyrrhotite with depth has also been interpreted as resulting from a temperature augmentation (Marchetto 1997). A similar trend in the sulfide and phyllosilicate mineral compositions is described for the alteration at the Hollinger-Mcintyre and Sigma deposits, in Canada (Hodgson 1993). This change alongside with other mineralogical variations is consistent with increasing T and/or decreasing volatile fugacities in the hydrothermal fluid with depth.

Consistently, studies of fluid inclusions (Robert and Kelly 1987) and of oxygen isotopes (Kishida and Kerrich 1987) show no systematic variation in T with depth, corroborating the notion that the alteration is roughly isothermal (McCuiga and Kerrich 1994). Vertical zonation of wallrock alteration is not common in individual lode-gold deposits, though reported (see Groves 1993). Most lode-gold deposits are characterized by alteration assemblages commensurate with the ambient metamorphic P-T conditions (Clark et al. 1989). Pyrite ± arsenopyrite + magnetite + chlorite ± carbonate (1988) also predominate in the hydrothermal alteration processes. In higher T deposits iölldingite, magnetite and ilmenite appear, plagioclase is oligoclase-andesine and amphibole develop. In the absence of detailed T calculations for varying depth levels in the OP gold mines, an alternative explanation lies with the evolution in fluid composition. We suggest that the changes in mineralogical composition with depth, exemplified at Morro Velho and São Bento, is related to changes in fluid fugacity (buffering). As depicted in Figure 1, pyrrhotite formation in preference to pyrite is a function of aΣ2, and aΣ2 is controlled by the evolution of pyrrhotite (accessory) and sphalerite (primary). As already pointed out, the initial fluid was relatively reducing and its aΣ2 and aΣ3 were controlled by the pyrrhotite-pyrite pair in the presence of arsenopyrite, hence slightly above the CO2-Ch4 stability curve (Figure 1). In the T range estimated, the stability of pyrite and pyrrhotite is a function of aΣ2. However, at higher aΣ2, pyrrhotite is stable up to the point of failure, Pfluid in the fault and/or shear zone are higher than in the adjacent wallrocks, driving fluid out of this zone and promoting interaction with wallrocks. Following failure and valve breach, there is a decrease in Pfluid that is transiently lower than in the wallrocks. This causes reacted fluids to migrate back into the fault zone where they can mix with primary ore fluids and promote Au deposition.

Hydrothermal precipitation is enhanced by major Pfluid reduction. Because the pressure drops from extreme fault-valve behavior are potentially so large, phase separation of CO2 becomes likely in a mixed CO2-H2O fluid, even at considerable depth (Sibson 1990b). Phase separation plays a very important role in gold precipitation (Phillips and Powell 1992). Variations in the mineral composition of some hydrothermal phases with depth are registered in various mines. They can also be alternatively explained as reflecting fluid evolution due to variations in volatile fugacities. This could be the case regarding pyrrhotite increase in Morro Velho and São Bento Mines. Vieira (1986) interprets this variation because of a temperature increase. He correlates the increase in pyrrhotite with conditions prevailing in mineralizations close to the Kerr-Addison Mine (Ponta and Fauna), located at the northwestern outcrop of the OP. In this zone, pyrrhotite increases with depth and associated with garnet, pyrrhotite and other sulfides indicates higher temperature than the deposits described by Lobato et al. (1998b, the present volume). In the case of the São Bento Mine, the increase in pyrrhotite with depth has also been interpreted as resulting from a T augmentation (Marchetto 1997). As already pointed out, the initial fluid was relatively reducing and its aΣ2 and aΣ3 were controlled by the pyrrhotite-pyrite pair in the presence of arsenopyrite, hence slightly above the CO2-Ch4 stability curve (Figure 1). In the T range estimated, the stability of pyrite and pyrrhotite is a function of aΣ2. However, at higher aΣ2, pyrrhotite is stable up to the point of failure, Pfluid in the fault and/or shear zone are higher than in the adjacent wallrocks, driving fluid out of this zone and promoting interaction with wallrocks. Following failure and valve breach, there is a decrease in Pfluid that is transiently lower than in the wallrocks. This causes reacted fluids to migrate back into the fault zone where they can mix with primary ore fluids and promote Au deposition.

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Figure 1 - After Mikucki and Ridley (1993; Fig. 5). Log \( f_O^2 \) versus \( a(ZS) \) diagram for 350°C, 2 kb and \( \Sigma SO^2^- = 10^{2.5} \). Patterned areas are likely \( f_O^2 \) and \( a(ZS) \) conditions for typical sub-amphibolite fades gold deposits. Stability boundaries for Fe-sulfide and Fe-oxide phases are shown as heavy solid lines; light solid lines and dashed lines show reaction boundaries for Cu- and As-bearing phases, and carbonate phases (at \( \chi CO_2 = 0.25 \)), respectively. Heavy dashed lines are important aqueous redox buffers. Ore fluid conditions for ‘reduced’ greenschist fades lode-gold deposits are limited by the assemblage pyrite ± pyrrhotite ± arsenopyrite ± siderite, and fluid inclusion constraints that suggest \( CO_2/H_2O > 1.0 \). Fluids associated with mesothermal gold deposits of the QF, described by Lobato et al. (1998b, the present volume), belong to this group. Those for ‘oxidized’ greenschist-fades deposits are limited by pyrrhotite-chalcopyrite ± hematite ± magnetite stability, which together with isotopic evidence suggest combined sulfate species exceed sulfide contents. As = arsenic met al; Apy = arsenopyrite; Bn = bornite; Ccp = chalcopyrite; Hem = hematite; Mag = magnetite; Po = pyrrhotite; Py = pyrite; Sd = siderite.

Influence on gold deposition from reduced gold-bearing, sulfur complexes (see below).

**pH CONDITIONS AND IONIC COMPONENTS** Ore-fluid pH can be estimated taking into account the alteration involving white micas ± albite. For likely low ore fluid salinities, \( pH \) values thus vary over the restricted range of 5.2 to 6.2 (Figure 3), that is from near-neutral to slightly alkaline in nature (neutral \( pH = 5.2 \) at 350°C, 2 kb).

Common components in ore-forming fluids are \( Na^+ \), \( K^+ \) and \( Ca^{2+} \). Fluid composition can be inferred by observation of Figure 3, at varying \( pH \) values. Activities of \( Na^+ \) are roughly one order of magnitude greater than those of \( K^+ \), supporting inference from fluid inclusion studies that \( Na^+ \) is the dominant cation (Mikucki and Ridley 1993).

**pH evolution in QF gold-mineralizing deposits** In all deposits described by Lobato et al. (1998b, the present volume), development of both \( K/Na-mica \) and varying amounts of albite plagioclase, in the presence of carbonates, must have reflected small variations in \( \chi CO_2 \), and in the activities of \( K^+/H^+ \) and \( Na^+/H^+ \), particularly in the case of metamorphosed mafic and ultramafic rocks. This infers a near-neutral to slightly alkaline original fluid. Because these reactions release \( H^+ \), near-neutral to slightly acid conditions may have prevailed in the more advanced stages of hydrothermal alteration.

At Jucã Vieira, reactions involving the formation of paragonite + quartz and paragonite + ankerite from chlorite are cation consuming, with \( H^+ \)-release. \( H^+ \) is also released from the paragenetic relative transformation. These reactions suggest that under fluid-dominated conditions a near-acid fluid may in fact have evolved (Pereira 1996).

In metamafic rocks at Raposos, the replacement of metamorphic albite by sericite suggests interaction with a \( CO_2 + K^+ \)-rich fluid, evolving into a \( H_2O + Na^+ \) fluid responsible for hydrothermal albite generation. Chlorite + calcite are replaced by sericite + Mg-siderite + quartz, suggesting reaction with a \( CO_2 + K^+ \)-rich fluid and \( H^+ \) release. In the advanced stage of hydrothermal alteration of meta-ultramafic rocks, the replacement of calcite + quartz by ankerite + albite (± Mg-Fe-chlorite) can be envisaged through the reaction with a \( CO_2 + Na^+ \) fluid and \( H^+ \) release (Junqueira 1997).

In Santana, the replacement of biotite by either chlorite or muscovite involves hydrolysis reactions with \( K^+ \) release. Chlorite, on the other hand, consumes \( K^+ \) to give way to muscovite, again suggesting slight fluctuations in the fluid \( K^+/H^+ \).

Carbonate alteration is widespread in all deposits. As in the case of deposits discussed elsewhere (Kishida and Kerrich 1987), carbonate precipitation reactions lead to fluid acidification. Variations in \( pH \) are however minimal considering that hydrolysis reactions involving hy-
Evidence for cooling of the fluid is brought about by data from Alves (1995) for the Santo Bento Mine, with a variation from ~300°C at 3.2 kb to ~200°C at 1 kb. Slight variations in the fluid $f_O_2$ are particularly important in the case of Fe-bearing host rocks (BIF and lapa seca). Sulfidation of Fe-rich wallrocks has been demonstrated as an efficient gold deposition mechanism, mainly in the case of many large replacement ore bodies like those hosted by BIF and lapa seca (see Phillips et al. 1984, McCraig and Kerrich 1994 for discussion). Not only do sulfides replace original carbonate and magnetite, but they also replace advanced-stage carbonates, suggesting multiple pulses of sulfide nucleation. The oxidation of sulfur $S_0$ to form pyrite $(S^2_0)$ provides a driving force to reduce aurous complexes of gold. Pyrrhotite formation can also reduce Au but tends to be less effective.

Since intense K$^+$ and CO$_2$ metasomatism is plentiful, some pH reduction has been deduced. The reduction in pH strongly enhances gold precipitation. pH influence seems to have been particularly important in the case of the Jucá Vieira (Pereira 1996) and Santana gold deposits. The evolution to a near-acid fluid resulting from widespread K/Na-mica development at Jucá Vieira may have been in part responsible for gold precipitation.

CONCLUSIONS The first part of this paper reviews the state of the art relating to hydrothermal alteration associated with mesothermal, lode-gold deposits, particularly those hosted by rocks of Archean greenstone belts holding mineral assemblages of the sub-ambibolite and greenschist facies of metamorphism. The most critical points embrace the following conclusions:

1. Structurally hosted, mesothermal, lode-gold deposits in metamorphic terranes constitute a single, coherent group of epigenetic protolith or met al deposits;

2. The study of hydrothermal alteration associated with Archean, lode-gold mineralizations focused on the sub-ambibolite to green-schist facies group of deposits. These studies show that a central core of Fe-carbonate (ankerite) grades out into fringes rich in calcite and chlorite. Ore zones normally have higher K$^+$/H$^+$ and activities of (Mg$^{2+}$Fe$^{2+}$)/(H$^+$)$_2$ in the fluid to rock interaction. Interestingly, whereas pyrite alteration is more common where chlorite alteration occurs, pyrrhotite predominates in zones of Fe-carbonate alteration indicating a pattern of moderately high K$^+$/H$^+$ conditions for the latter.

3. Deposits are typically hosted by mafic volcanic rocks and by banded iron-formation (BIF). Gold resides within sulfides (mainly pyrite $\pm$ pyrrhotite $\pm$ arsenopyrite) that replace iron minerals in the altered wallrock immediately adjacent to quartz veins;

4. Differences in alteration assemblages from one deposit to another reflect different fluid compositions and primary rock types;

5. Inner (proximal) zones reflect fluid-dominated (unbuffered), metasomatic reactions. Zones distant from veins reflect a decreasing gradient of fluid to rock ratio. They represent progressive infiltration of the fluid into the wallrock;

6. Gold mineralizing fluids were CO$_2$-H$_2$O-rich, of relatively low salinity (0.05-0.25 wt % NaCl equivalent), and moderate density (0.3-0.9 g/cm$^3$). They were near neutral to slightly alkaline and mainly reducing, with small concentrations of CH$_4$ although oxidized fluids have also been recorded;

7. Typical temperature and pressure were 300 to 350°C and 1 to 3 kb, respectively. Minimum gold depositional conditions were 200-400°C (mainly 250-350°C) and 0.5-4.5 kb (mainly 0.8-3 kb);

8. Estimates of $X_{CO_2}$ of the initial ore fluid indicate a range of 0.05-0.25, increasing with the advancement of alteration. CO$_2$ gradients controlled alteration-zoning patterns under isothermal conditions;

9. Log $O_2$ in the range of 0.5-3 above the CO$_2$-CH$_4$ stability curve. Total sulfur concentration was in the range of ~10 to $10^5$ ppm;

10. The pH of solutions was near neutral to slightly alkaline.

Conclusions of mineral assemblages in a series of deposits associated with rocks of the Nova Lima Group, Quadrilátero Ferrífero region of Minas Gerais, Brazil, are presented by Lobato et al. (1998b, the present volume). In the second part of the present paper, the hydrothermal alteration of such deposits is scrutinized. To achieve this objective published detailed information on fluid composition for other similar deposits and fluid inclusion data for the QE are combined. It has been shown that:

1. For metamafic and meta-ultramafic rocks, alteration assemblages of the incipient stage of alteration vary according to changes in $X_{CO_2}$ under isothermal conditions. If albite and/or white mica is involved, reactions are also dependent on $a(K/Na)$;

2. Stages of advanced hydrothermalism in carbonate-white mica assemblages depend on activities of K$^+$ and Na$^+$;

3. The least-altered chlorite-dominated, and the most-altered carbonate-dominated alteration assemblages suggest a shift from a pre-

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Figure 3 - After Mikucki and Ridley (1993; Fig. 3). Stability relationships for Na-K aluminosilicates as a function of fluid composition at 350°C and 2 kb. The shaded area is the field of fluid compositions for most sub-ambibolite fades Archean gold ore-fluids, including the deposits described in this paper. pH contours are for 3% (long-dashed lines) and 1% (short-dashed lines) Na$_2$CO$_3$. Data from Bowers et al. (1984) and Shock and Helgeson (1988). $Ab =$ albite; $Kfs = K$-feldspar; $Kin = kaolinite; Pg = paragonite.

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The increase in pyrrhotite with depth at the Morro Velho Mine is also marked by the appearance of biotite and reduction in the amount of chlorite in hydrothermally altered rocks surrounding ore (Vieira 1988). Biotite to chlorite transformation at 300°C is a function of variations in the K$^+$/H$^+$ and (Mg$^{2+}$Fe$^{2+}$/H$^+$) activities of the fluid (Beane 1994). Alternatively to the temperature increase at depth, discussed by some authors (see also Lobato et al. 1998b, the present volume), we suggest that biotite development at the expense of chlorite may reflect increase in these ratios in the fluid, again owing to fluid to rock interaction. Interestingly, whereas pyrite alteration is more common where serumization occurs, pyrrhotite predominates in zones of Fe-carbonate alteration indicating a pattern of moderately high K$^+$/H$^+$ conditions for the latter. In fact, Mikucki and Ridley (1993) mention a pH range of 5.8 to 6.8 for fluids responsible for the biotite-ankerite association at Kambalda (Australia).

Fluid Evolution and Implications for Gold Transport and Deposition The close association between gold mineralization and sulfides in all deposits suggests that reduced sulfur complexes were the predominant transport mechanism. Microtextural studies indicate that gold deposition occurred simultaneously with sulfide precipitation due to fluid-wallrock sulfidation reactions.

Studies of gold transport in ore-depositing environments have shown that sulfide complexes of gold are of major importance in the near-neutral region of pH, at $a_{CO_2}$ no higher than ~300°C (Seward 1993). Gold solubility as a reduced sulfur complex (Au(HS$^-$_2)) is also affected by variations in $f_O_2$ and $a_{CO_2}$, particularly by increasing fluid $f_O_2$ and decreasing $a_{CO_2}$. Thioarsenide complexes are also important (Romberg 1986). Saturation of gold in the fluid decreases in response to lower $f_O_2$ and particularly lower sulfur activity until the fluid becomes gold-saturated. Only once gold-saturation is approached, will extensive gold deposition proceed (Phillips and Powell 1992).

Gold deposition is a function of physico-chemical changes in the fluid that will lead to removal of gold from solution by destabilizing gold complexes. This can be achieved by variations in the fluid due to (1) cooling; (2) oxidation; (3) reduction; (4) pH variation, (5) lowering $a_{CO_2}$; (6) lowering of pressure, with phase separation; (7) solution mixing; (8) wallrock alteration. Interplay of these factors may have played a role in gold deposition in the deposits described in the QE.
dominantly predominantly H2O-rich fluid in the incipient stage (chloritization) to a higher CO2/H2O ratio in the most advanced stages of hydrothermal alteration.

4 - In metamorphic rocks, slight variations in O2 and PH2O are demonstrated by mineral reactions. An initially reducing fluid was buffered to somewhat higher O2 via reaction with original metamorphic epidote, and later to lower O2 due to chlorite oxidation. An initially near-neutral to slightly alkaline fluid evolves to slightly acid conditions due to reactions that release H+.

5 - The progressive hydrothermal alteration of the Al-poor BIF shows that original siderite and magnetite are-recurrently replaced by ankerite and sulfides. Chlorite appears when pyrite/hornblende forms. Some albite and muscovite are present in the advanced stage (gold-rich ore). This indicates that buffering of fluid O2, a2s and an2s controlled BIF alteration, which was much less sensitive to activities of K+H+ and Na+H+.

6 - Based on mineral transformations, it is concluded that ore fluid Xan2s, a2s, O2 and pH values are similar to those postulated for deposits elsewhere. The assemblage pyrite + arsenopyrite = pyrrhotite formed from a reducing fluid with O2 above or near that of the CO2/CH4 redox buffer.

7 - Significant amounts of sulfur were added during BIF alteration. Considering the relatively sulfur-rich, reducing nature of the original fluid, interaction with magnetite and siderite in the incipient stage of alteration must have provided the conditions necessary to buffer the incoming fluid O2. Hence, the capacity of the mineral assemblage to buffer the incoming fluid O2 determined (1) the a2s (and an2s) in the fluid reacting with the minerals, and thereby (2) the sulfide paragenesis in physical space, in chemical space and over geological time.

8 - Variations in a2s can also be deduced from the gold-associated alteration in BIF. Shear zones are occupied mainly by pyrrhotite, whereas pyrite and arsenopyrite occur as discrete bedded-replacement zones in BIF. These variations can also be interpreted as a result of varying Pfluid conditions of a somewhat reducing, sulfur-rich fluid;...