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Fluid signature of the shear-zone controlled Veio de Quartzo ore body in the world-class BIF-hosted Cuiabá gold deposit, Archaean Rio das Velhas greenstone belt, Brazil: A fluid inclusion study

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Abstract

The world-class Cuiabá gold deposit of the Archaean Rio das Velhas greenstone belt in Brazil is hosted in banded iron formation containing carbonaceous matter and carbonate, within the reclined, isoclinal Cuiabá fold. Mineralised quartz veins are hosted in andesite in the stratigraphic footwall of the banded iron ores and form some of the more recently discovered ore bodies. Fluid inclusion data of the quartz-vein associated 'Veio de Quartzo' ore body are obtained from five quartz types (Qz1, Qz2, Qz3, Qz5) in gold mineralised V1 shear veins and V2 extensional veins, barren V3 extensional vein arrays and V4 breccia-style veins, all developed during the Archaean D1 event. Three fluid types are distinguished: (i) aqueous fluids of low salinity (1.8–3.8 wt% NaCl equiv.), homogenisation (into liquid) at 220 to 230°C; (ii) aqueous fluids of moderate salinity (5.3–12.7 wt% NaCl equiv.) and homogenisation at 250 to 290°C; and (iii) aqueous-carbonic fluids of moderate salinity (6.0–15.1 wt% NaCl equiv.), with 30–91 mol% CO_2, 8–41 mol% CH_4 and up 28 mol% N_2 and decrepitation (into vapour) at 280 to 310°C. Based on an independent pressure estimate a pressure correction was applied to aqueous fluid inclusions, resulting in minimum trapping temperatures at 360°C for V1 veins, 330°C for V2 veins, 300°C for V3 veins and 270°C for the late-stage V4 veins. Ion chromatography analyses reveal a Br/Cl ratio of 0.7×10^{-3} in Qz1-V1, from 1.4 to 1.5×10^{-3} in Qz2-V2, 0.3 to 0.4×10^{-3} in Qz3-V3 and 0.7 to 0.9×10^{-3}in Qz5-V4 veins. Zinc, Pb and Cu are relatively enriched, with ~ 100 to 1,000 ppm in aqueous and aqueous-carbonic fluid inclusion assemblages in all vein and quartz types, which is similar to other orogenic gold deposits hosted in the Rio das Velhas greenstone belt. The fluid inclusion data are consistent with a model invoking a metamorphic origin for the mineralising fluid. A two-step model of hydrothermal fluid flow and gold enrichment is suggested

to have developed during the Archaean D1 event, with an early, aqueous-carbonic fluid pulse of relatively high temperature (from V1 up to V3) and an evolved, aqueous-carbonic fluid pulse of lower temperature (V4, breccias-style veins).

Introduction

Orogenic lode-gold deposits are hosted in metamorphic terranes that typically contain rocks of lower to upper greenschist facies metamorphic grade (Groves et al. 1998). Textural and structural relationships are commonly well preserved allowing important constraints on the deposit formation. Fluid inclusion studies, summarised by Ridley and Diamond (2000) and Goldfarb and Groves (2015), suggest that ore formation occurred from aqueous-carbonic, CO_2/CH_4 fluids of low to moderate salinities. The source of gold is still debated (Goldfarb and Groves, 2015). As pointed out by Gaboury (2013, 2019), the record of aqueous-carbonic and hydrocarbon gases in fluids from orogenic gold deposits confirms that organic matter-rich sedimentary rocks, containing possible gold-bearing pyrite, could be in part the source for gold in many world-class gold deposits. However, sedimentary rocks only form a small proportion of most Archaean greenstone belts (Goldfarb and Groves 2015). Compositional microanalysis of fluid inclusions using laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS) has the potential to provide new information on the origin and evolution of crustal fluids (Marsala et al. 2013; Rauchenstein-Martinek et al. 2014, 2016; Morales et al. 2016; Wagner et al. 2016; Fusswinkel et al. 2017).

The Quadrilátero Ferrífero (QF) region is one of Brazil's most important gold provinces (Lobato et al. 2001a, b) and hosts a range of Archaean to Cenozoic gold deposits. The most productive deposits are hosted in banded iron formations (BIF) of the Archaean Rio das Velhas greenstone belt (Lobato et al. 2014) (Fig. 1). Some of the largest gold deposits, including Morro Velho, Cuiabá, São Bento and Raposos, are located in the basal unit of this greenstone belt, referred to as the Nova Lima Group (Ladeira 1991; Vieira 1991; Lobato et al. 1998). The Cuiabá deposit, situated ~40 km northeast of Belo Horizonte (Fig. 1), is presently the major gold producer in the QF. The total of the Cuiabá mine's mineral resources, considering measured, indicated and inferred resources is 19.7 million tonnes grading 10.58 g/t Au (AngloGold Ashanti 2018).

Previous fluid inclusion studies of orogenic gold deposits hosted in the Rio das Velhas greenstone belt included those by Xavier et al. (2000), Lobato et al. (2001a, b, c), Ribeiro et al. (2015) and Morales et al. (2016). The study by Xavier et al. (2000) showed that the mineralising fluids were dominantly aqueous with a low salinity (3.0–6.0 wt% NaCl equiv.) and variable concentrations of CO_2 (0–11.4 mol%), CH_4 (1.5–10.2 mol%), subordinate N_2 (0–0.7 mol%) and traces of H_2S and/or HS. The work of Lobato et al. (2001a, b, c) noted the occurrence of aqueous and aqueous-carbonic fluid inclusions with salinities ranging from 1.4 to 12.8 wt% NaCl equiv. and inconsistent volatile compositions of CO_2 (3.5–90.5mol%), CH_4 (64.0–94.5 mol%), N_2 (1.5–21.5 mol%) and H_2S (~1.3 mol%).

This contribution reports on a study conducted to determine the chemistry of the hydrothermal fluids that formed the quartz vein-associated, andesite-hosted ore bodies at the Cuiabá gold deposit. In contrast to previous studies, fluid inclusion assemblages (FIAs) were studied to provide meaningful fluid inclusion data, as well as new geochemical data obtained by LA-ICP-MS. Based on the vein and quartz classification, new fluid inclusion data and spectroscopic investigations provide critical information on the mineralising processes at this world-class deposit.

Geology of the Quadrilátero Ferrífero including the Rio das Velhas greenstone belt

The Quadrilátero Ferrífero (QF) is located in the southern São Francisco Craton (Dorr 1969) and encompasses Archaean gneissic trondhjemite-tonalite-granodiorite (TTG) terranes, Archaean granite-greenstone belts of the Rio das Velhas Supergroup and Proterozoic sedimentary units of the Minas and Espinhaço Supergroups (Dorr 1969; Toledo 1997; Noce 2013). Banded migmatite gneisses make up the largest proportion of the crystalline basement of the QF. They comprise four main lithostructural domains, consisting of 3.2 Ga granitoid gneisses and minor sedimentary rocks, which are intruded by 2.8–2.7 Ga old tonalites, andesites, granites, pegmatites and Proterozoic mafic dikes (Noce et al. 2005; Moreira et al. 2016).

The Rio das Velhas Supergroup contains the Archaean Rio das Velhas greenstone belt (3.0–2.7 Ga; Machado et al. 1989) which comprises the Nova Lima Group at the base and the overlying Maquiné Group (Fig. 1). The greenstone belt rocks are regionally metamorphosed to lower greenschist facies. The lower portion of the Nova Lima Group is composed of lower komatiitic to tholeiitic volcanic rocks interlayered with clastic and exhalative chemical sedimentary rocks (Vieira 1988). The middle mafic and felsic volcanic rocks are interlayered with carbonaceous sedimentary rocks and BIF with felsic volcaniclastic rocks on the top. Clastic sedimentary rocks interlayered with mafic and felsic volcaniclastic rocks form the upper portion of the Nova Lima Group (Fig. 1). Radiometric ages (U-Pb-SHRIMP) of detrital zircons yield a minimum age of 2.74 Ga for the volcaniclastic rocks (Schrank and Machado 1996; Lobato et al. 2001a).

The Paleoproterozoic Minas Supergroup (2.6-2.1 Ga; Babinski et al. 1991) represents a continental margin sequence and comprises clastic and chemical sedimentary rocks. More recently, however, Cabral et al. (2012) dated zircons (U-Pb LA-ICP-MS) from a volcanic layer within the Minas Supergroup iron formation and proposed a 2.65 Ga Neoarchaean age for the deposition of these rocks.

Geology of the Cuiabá gold deposit

The Cuiabá deposit is an Archaean (U-Pb SHRIMP age of 2672±14 Ma on monazite; Lobato et al. 2007) gold deposit, presently exploited in an underground mine. The host rock succession was first defined by Vial (1980) and consists of volcanic, volcaniclastic and sedimentary rocks that form part of the Nova Lima Group (Ladeira 1991).

At Cuiabá, the lowermost stratigraphic unit is characterised by alternating units of chloritised, mafic volcanic and pelitic rocks, which are carbonate and sericite altered (Figs. 2c, ESM-1), as well as interbedded lenses of carbonaceous pelite. The volcanic and pelitic rocks are overlain by the Algoma-type Cuiabá BIF. The Cuiabá BIF consists of rhythmic alternation of dark, white and ocher-coloured, millimeter- to centimeter-thick bands, rich in carbonaceous matter and fine-grained quartz and carbonate (ESM-1). Its lower portion is typically banded and rich in Fe-carbonate and carbonaceous matter. The upper portion, separated by a 15-cm-thick mafic volcanic unit, is a highly deformed ferruginous chert also containing carbonaceous matter. Overlying these chemical sedimentary rocks, is an upper mafic volcanic unit that displays a similar mineralogical composition as the lower, chloritised mafic volcanic rocks. Metamorphosed andesite at Cuiabá consists of albite, epidote, zoisite (clinozoisite), quartz, actinolite, carbonate and chlorite (Vieira 1991). The rocks are characterised by a light green colour and a fine grain size and are massive or foliated (ESM-1). The absence of hornblende indicates that peak metamorphic conditions did not exceed the greenschist-amphibolite facies transition (Spear 1995). This mineral assemblage is characteristic of metamorphic temperatures of 350 to 450°C and is stable over a large pressure range of up to 4 kbars (Spear 1995). The stratigraphic column is completed by a ~1000-m-thick section of volcaniclastic rocks (Vieira 1991; Lobato et al. 1998; Xavier et al. 2000).

Structural setting

The rocks at the Cuiabá deposit underwent at least three deformation events (Ribeiro-Rodrigues et al. 2007). The first two, D1 and D2, developed under ductile to ductile-brittle conditions of SE-NW-directed compressive stress, with tectonic transport from SE to NW. The brittle-ductile D3 structures formed due to E-W-oriented compressive stress (Ribeiro-Rodrigues et al. 2007). All lithological units are overprinted by a pervasive axial planar foliation that is locally mylonitic (S_m= 135/45). They show a prominent mineral stretching lineation (LS = 126/22–35) indicated by the preferred orientation of elongated sericite, carbonates and sulphide minerals. Late, northwest-verging, sigmoidal thrust faults reactivated pre-existing structures and caused folding, boudinage and rotation of the host rocks of the Cuiabá deposit (Vitorino 2017).

The Cuiabá fold is an anticline with the rock succession inverted along the north limb (Fig. 2a). The N116° fold axis plunges from 35° in the upper portion to 12° below level 18. The plunge direction controls the geometry of the mineralised ore bodies. Studies by Vial (1980), Toledo (1997), Ribeiro-Rodrigues (1998) and Ribeiro-Rodrigues et al. (2007) considered the Cuiabá fold as a tubular structure, plunging southeast at 30º. Recently published data for the nearby Lamego gold deposit (Fig. 1) suggests that its fold geometry, which is comparable to that of the Cuiabá fold, represents a reclined, isoclinal, cylindrical and rootless fold (Martins et al. 2016).

Gold mineralisation

Gold mineralisation at Cuiabá is contained in six main BIF-hosted ore bodies (> 4 g/t Au) referred to as Balancão, Canta Galo, Fonte Grande, Fonte Grande Sul (FGS), Serrotinho and Galinheiro (Fig. 2a). These ore bodies represent sulphide-rich segments of the Cuiabá BIF grading laterally into non-economic or barren iron formation. Quartz vein-hosted ore bodies are named Veio de Quartzo (VQZ), Galinheiro Footwall (GAL FW), Serrotinho Footwall (SER FW) and FGS Footwall (FGS FW) (Fig. 2). The three main mineralisation styles are: (i) stratabound-replacement with locally massive ores, commonly in BIF, (ii) disseminated in volcanic and sedimentary rocks, related to hydrothermal alteration in shear zones and (iii) quartz-carbonate-sulphide veins related to shear-zones in volcanic and sedimentary rocks (Ribeiro-Rodrigues et al. 2007).

Decreases in gold grade from over 60 g/t Au to values below the detection limit of the fire assay in sulphide-poor portions always indicate transitions from sulphide-rich to -poor BIF. Gold, ranging in size from 10 to 80 µm, is intergrown with pyrite, pyrrhotite and arsenopyrite. It occurs in fractures or along grain boundaries of pyrite and arsenopyrite. Pyrite is the most common sulphide and accounts for >90% by volume of all sulphides. Most of the pyrite forms porous grains that may be zoned, displaying As-rich centres.

The Fonte Grande Sul ore body is located in the SE closure of the Cuiabá fold (Fig. 2a). It is the largest and highest grade ore body in the deposit. Resources are calculated at 4.91 million tonnes grading 13.87 g/t Au, with additional reserves of 0.8 million tonnes grading 8.11 g/t Au (AngloGold Ashanti 2018). The thickness of the ore body varies between 4 and 6 m. The mineralised BIF is intensely sulphidised (ESM-1), folded and disrupted, containing generally disseminated and massive ores that lack banding.

The recently discovered VQZ ore body (Fig. 2a) has significant gold grades associated with andesite-hosted quartz-rich shear veins and is located between levels 9 and 17 in the southeastern part of the Cuiabá fold hinge (Fig. 2b). Mineralisation is predominantly controlled by a strike-slip, oblique shear zone, with native gold hosted in quartz-rich shear veins and disseminated sulphide minerals in hydrothermally altered country rocks. The Au grade reaches up to ~500 g/t due to the presence of free coarse gold (Vitorino 2017).

Hydrothermal alteration studies at Cuiabá were carried out by Vieira (1988, 1991), Ribeiro-Rodrigues (1998) and Lobato et al. (1998, 2001a,b). These authors showed that the carbonaceous pelites are only locally altered by sulphide-quartz-carbonate veinlets and that the Cuiabá-BIF is strongly sulphidised. Mafic volcanic rocks are overprinted by pervasive alteration, where distal alteration comprises an assemblage of chlorite, carbonate±sericite and sulphide minerals, intermediate alteration is characterised by an assemblage of carbonates, chlorite, quartz, plagioclase and sulphide minerals and the proximal alteration is composed of quartz, sericite, sulphide minerals and free gold.

Materials and methods

Quartz vein samples for fluid inclusion analyses were taken from drill cores CBABSD007 and CBABSD009 intersecting the VQZ ore body at Level 17 (Fig. 2c) and underground exposures of shear and extensional veins of the andesite-hosted VQZ ore body at Level 15 of the Cuiabá mine (Figs. 2b; 3g-i).

The fluid inclusion study was carried out on vein quartz of the S_m (mylonitic foliation)-related mineralised quartz-sulphide and barren quartz veins. Nine doubly polished thick sections were prepared and petrographically mapped in transmitted light. Four of them were chosen for microthermometry. Measurements were conducted using a Linkam THMSG 600 heating and freezing stage with a T95 temperature programmer at the Laboratory of Metallogeny, Institute of Geoscience, at the Federal University of Minas Gerais, Brazil. The stage was calibrated with synthetic inclusions. All measurements were collected by predetermined temperature profiles that include a sequence of step-by-step continuous heating or cooling rates. Heating sequences have been performed slowly to prevent decrepitation. Calculated salinity (wt% NaCl equiv.), bulk composition of all FIAs, as well as pressure and temperature values to construct isochores, were obtained using the MacFlinCor program (Brown and Hagemann 1995). Eutectic temperatures of aqueous FIAs range between –45 and –35°C, indicating a mix of different salts (Borisenko 1977; Goldstein and Reynolds 1994). For measured FIAs that show final ice-melting temperatures above the eutectic for H_2O-NaCl (<–21.2°C), the equation of state by Bodnar and Vityk (1994) was used for the H_2O-NaCl-(KCl) system. In the case of clathrate melting temperatures, (Tm_{Clath}) the equation of Jacobs and Kerrick (1981) for the H_2O-CO_2-CH_4-NaCl was applied due to the presence of CO_2 and/or CH_4. Measurement of homogenisation temperatures of the CO_2 phase (Th_{CO2}) is limited to inclusions larger than 10 µm. The $Th_{TOT(L-V)}$ were obtained from Qz2 of V2 extensional veins and V3 extensional vein arrays, as well as Qz5 from V4 late-stage veins. Measurements on various aqueous-carbonic FIAs with probably higher proportions of volatile phases (CH_4, H_2S, N_2) did not allow salinity calculations with Tm_{Clath} above 10 to 16°C.

Raman spectroscopy investigations were carried out at the Institute of Engineering at the Federal University of Minas Gerais, Brazil. Raman spectra were obtained using a Jobin Yvon/Horiba LABRAM-HR 800 spectrograph equipped with a He-Ne laser (632.8 nm) and linked to a N_2 liquid cooled CCD (charge coupled device) detector. The excitation and collection of the scattered light was achieved using an Olympus BHX microscope focused on single fluid inclusions at high magnification (50x or 100x objectives). Acquisition times varied between 10 and 30 s depending on the background fluorescence of the fluid inclusions. Laser-Raman analyses were applied to several types of aqueous and aqueous-carbonic FIAs in different quartz types. Complex gas mixtures of CO_2, CH_4, N_2 and a limited set of solutes have been detected within each non-aqueous phase at ambient P-T conditions. Data processing of all Raman spectra was conducted using the software Labspec 5. Semiquantitative determination of gas species (CO_2, CH_4 and N_2) and their relative abundances (in mol%) used the method of Burke (2001). Wavelength-dependent relative Raman scattering cross sections (σ532 nm) for each gas species were determined by interpolation from Burke (2001). The instrumental efficiency for all components was set to 0.92 in all calculations based on Garofalo et al. (2014). Uncertainties in calculated mole fractions of species present in the carbonic phase of the inclusions are within 20% relative.

Ion chromatography was performed on quartz samples of the andesite-hosted quartz shear and extensional veins at the School of Earth and Environment, University of Leeds. Quartz samples were reduced to a grain size of 0.5–1 mm and contaminant minerals removed by picking under a binocular microscope. Quartz types of V1 and V2 veins were separated. However, mixing of several fluid inclusion populations contained in the quartz cannot be ruled out. Samples and duplicates were cleaned three times with 18.2 MΩ Milli-Q water. Dry samples were crushed to a fine powder in an agate pestle and mortar and 7 mL of water was added to redissolve the contents of the fluid inclusions. The solution was filtered through a 0.2 μm nylon filter to remove any particles. Cl^-, Br^- and SO_4^{2-} were determined by using ion chromatography. The leachates were analysed for cations such as Na^+, K^+ and Li^+ by atomic emission spectroscopy. As the amount of fluid inclusions leached is unknown, molar ratios are used.

Laser ablation ICP-MS analyses on FIAs trapped in quartz of shear and extensional veins were conducted at the School of Earth and Environment, University of Leeds. The calibration was performed using the standard NIST 610. Fluid inclusion and standard measurements were conducted by using the GeoLas Q Plus excimer laser (ArF, 193 nm, Microlas, Göttingen, Germany). The optical system permits visual observation of the ablation process through a built-in LED source and CCD camera. The material liberated during the ablation is carried by He, purging the ablation cell, into the Agilent 7500 quadrupole mass spectrometer. An octopole reaction cell was used for analyses of ^{40}Ca and ^{56}Fe. A detailed description of the LA-ICP-MS procedure is given in Allan et al. (2005). Elements including Na, K, Ca, Mg, Mn, Fe, Cu, Zn, Sr, Ag, Ba, Pb, As and Au were analysed. Arsenic and Au were measured separately for each vein type to avoid signal interference. Data reduction was conducted with the Matlab based SILLS program (Guillong et al. 2008). LA-ICP-MS intensity ratios for fluid inclusions were normalised to Na and converted to concentration ratios by external calibration against NIST 610 standard reference material.

For the determination of Na concentration, the average salinity of each FIA was used. The analytical error of LA-ICP-MS measurements and data processed required the use of average salinity values for each analysed FIA. Detection limits vary according to inclusion volume, but for most elements were between 1 and 10 ppm.

The Cuiabá quartz veins

In Cuiabá, the quartz veins hosted in andesite can be classified as (i) fault-fill, (ii) extensional (oblique-extensional) and (iii) breccia veins according to the criteria of Passchier (2001) and Robert and Poulsen (2001) (Table 1; adapted from Vitorino, 2017). Vein types are also subdivided based on their crosscutting relationships, relative chronology and mineralogical composition into V1 to V4 vein systems (Table 1). According to Vitorino (2017) all vein types are related to Archaean D1 brittle-ductile shear zones and located in the mineralised zones VQZ, SER FW and FGS FW. Shear veins are most common in the studied VQZ ore body.

The VQZ ore body (Fig. 2a, b) is made-up of four vein types (Table 1) with the following vein classification based on the structural model proposed by Vitorino (2017). Both shear and extensional veins show a similar paragenesis, but differ in terms of relative proportions of quartz types, carbonate, sulphide and accessory minerals (Table 1).

Vein type classification

Shear veins (V1), the most abundant in the VQZ ore body, were emplaced during D1 shearing and are parallel to slightly oblique to the main mylonitic S_m foliation (Fig. 3a). They extend ~30 to 50 m along strike and are up to 30 m in thickness. Their long axis coincides with the mineral lineation Lmin1. They mainly consist of anhedral, smoky quartz (Qz1; Fig. 3g), minor granoblastic, milky quartz (Qz2), ankerite, sericite, chlorite and albite and contain fragments of host rocks. Accessory minerals are pyrite, pyrrhotite, chalcopyrite, sphalerite and native gold. Wall rock fragments show ductile deformation, are typically sericite-altered and sulphide-rich and may contain significant gold.

The extensional V2 veins are hosted in andesite and controlled by the compositional banding S_b, occurring either at a high angle or subparallel with respect to the mylonitic S_m foliation (Fig. 3b). They represent the most abundant vein type in the center of the Cuiabá fold and may occur tens to hundreds of meters from the D1 shear zone. Commonly continuous along strike, they can extend for 200 m and range between a few centimetres up to 2 m in thickness. There are mutual cross-cutting relationships between V1 and V2 types. The V2 veins are mainly composed of Qz2, ankerite, sericite, chlorite and minor pyrite, pyrrhotite and chalcopyrite (Fig. 3h).

The V3 extensional vein arrays are at high angle with the mylonitic S_m foliation, having an average thickness from 5 to 30 cm. The V3 extensional vein arrays are mainly composed of euhedral quartz (Qz3) (Fig. 3f inset) and are immersed within the V1 shear veins (Fig. 3c, f; Table 1).

The V4 extensional veins (hereafter designated as V4 late-stage veins) show massive and tabular vein geometries (Fig. 3d, e). Wall rock fragments are located in the inner part of the veins and impose a brecciated structure. These are controlled by flanking structures (flanking folds and flanking shear bands, cf. Passchier 2001) and barren. They mainly consist of Qz5, carbonate (ankerite, calcite) and locally pyrrhotite and pyrite (Fig. 3d, i, Table 1); these sulphides are present as centimetre to up to 10 cm sized agglomerates and locally as well formed grains.

Quartz type classification

Four main quartz types (Qz1, Qz2, Qz3 and Qz5) are discriminated mainly based on morphological characteristics. The Qz1 is typically smoky, anhedral, medium- to coarse-grained, with strong wavy extinction; it is rich in fluid inclusions. The grain boundaries of Qz1 are interlobate (Fig. 4c, d). The polygonal granoblastic, fine- to medium-grained Qz2 developed at the expense of Qz1 (Fig. 4a, c, d), mainly along crystal boundaries. The proportion of fluid inclusions is relatively low compared to Qz1. Vitreous Qz3 is polygonal and shows well defined limits of coarse- to very coarse-grained transparent euhedral crystals that are locally transformed to granoblastic Qz4 (Fig. 4e). The Qz3 and Qz4 contain a moderate amount of fluid inclusions. Qz5 shows similar morphological features to Qz1.

Fluid inclusion data of the VQZ ore body

Fluid inclusion classification and description

The results of detailed petrography constraining the size, shape and L/V phase ratio of fluid inclusions, their occurrence as groups, trails or individual inclusions are provided in Table 2. Emphasis was placed on the identification of FIAs, which are defined as the most finely discriminated fluid inclusion trapping event that can be identified based on petrography (Goldstein and Reynolds 1994). In total, 20 distinct FIAs are observed and numbered (1–20, subscript are indicated by subscript characters). The FIAs in internal trails and three-dimensional groups, with respect to individual quartz grains, are pseudosecondary in nature, whereas trails crosscutting quartz grain boundaries are determined as secondary in origin (Sterner and Bodnar 1984; Wilkinson 2001). Secondary FIAs and FIAs that appear randomly and cannot be constrained with respect to their relative timing of trapping, defined as indeterminate, are not further considered in this investigation.

This study focuses on primary and pseudosecondary FIAs, which are present in all vein and quartz types except Qz4 (Fig. 5, Table 2). Primary and pseudosecondary FIAs are defined by: (i) aqueous-carbonic fluid inclusions, irregular to ovoid-shaped, 5–10 µm, locally up to 15 µm in size and contain about 10 vol.% vapour; and (ii) aqueous fluid inclusions, regular to ovoid shaped, about 5–10 µm in size with about 5–10 vol.% vapour.

Microthermometry results

V1 shear veins

Aqueous fluid inclusions in Qz1 show eutectic temperatures (T_e) between–43 to –39°C; Tm_{ice} between (i) –9.5 and –5.1°C and (ii) –3.5 and–1.1°C. The $T_{DECREP\ (L)}$ ranges between 220 and 250°C (Fig. 6c, Table 3). Salinity values range from (i) 1.8 to 5.6 wt% NaCl equiv. and (ii) 8.1 up to 13.4 wt% NaCl equiv. (Fig. 6a).

Aqueous-carbonic fluid inclusions display Tm_{CO_2} between –61.7 and –58.1°C; Tm_{Clath} between (i) 1.2 and 3.6°C and (ii) 6.1 and 6.6°C; Th_{CO_2} between 25.1 and 30.4°C and $T_{DECREP(V)}$ between 280 and 310°C (Fig. 6c, Table 4). Aqueous-carbonic fluid inclusions indicate salinities ranging from 7.2 to 12.7 wt% NaCl equiv. (Fig. 6c). The bulk density varies between 1.02 and 1.05 g/cm^3.

V2 extensional veins

Aqueous fluid inclusions in Qz2 display T_e between (i) –44 and –42°C and (ii) –45 to –35°C; Tm_{ice} between –5.2 and –3.3°C; $Th_{TOT(L)}$ from 260 to 290°C (FIA 11_D) and $T_{DECREP(L)}$ at 325°C (Fig. 6b). Salinity values range from 5.0 to 8.5 wt% NaCl equiv. (Fig. 6a, Table 3). Aqueous-carbonic fluid inclusions in Qz1 show Tm_{Clath} between 15.1 and 16.8°C and $T_{DECREP(L)}$ from 215 to 275°C (Table 4).

V3 extensional vein arrays

Aqueous fluid inclusions in (i) Qz1 and (ii) Qz2 show T_e between (i) –43 to –39°C and (ii) –39 to–35°C; Tm_{ice} between (i)–8.9 and–7.0°C and (ii) –5.5 and –3.0°C and $T_{DECREP(L)}$ between 190 and 230°C. Average salinities of aqueous fluid inclusions in Qz1 range from 10.5 to 12.7 wt% NaCl equiv. Homogenisation into vapor of FIAs in Qz2 is observed at 220°C and 230°C (Fig. 6b). Average salinities of aqueous fluid inclusions in Qz2 range from 4.9 to 8.5 wt% NaCl equiv. (Fig. 6a). Aqueous fluid inclusions in Qz3 show T_e between –35 to –30°C; Tm_{ice} between –6.3 and –1.8°C; $T_{DECREP(L)}$ between 210 and 270°C with outliers up to 350°C (Table 3). Salinity values for range between 3.0 and 9.5 wt% NaCl equiv. (Fig. 6a, Table 3).

Aqueous-carbonic fluid inclusions in Qz3 show Tm_{CO_2} from –61.0 to –57.2°C; Tm_{Clath} between 0.4 and 6.8°C and $T_{DECREP(V)}$ between 220° and 290°C (Fig. 6c, Table 4). Salinity values of fluid inclusions vary from 6.0 to 10.1, with outliers up to 15.1 wt% NaCl equiv. (Fig. 6a, Table 4). The bulk density of FIAs varies between 1.02 and 1.09 g/cm^3.

V4 late-stage veins

Aqueous fluid inclusions display T_e between –44 and –38°C, with Tm_{ice} ranges between –7.0 and –3.9°C. Homogenisation temperatures (into L) vary from 175 to 195°C (Fig. 6b). Decrepitation temperatures (into L) are observed between (i) 210 and 220°C and (ii) 220 and 260°C (Table 3). Salinity values range between (i) 6.2 and 8.0 wt% and (ii) 8.9 and 10.5 wt% NaCl equiv. (Fig. 6a, Table 3).

Aqueous-carbonic fluid inclusions in Qz5 show Tm_{CO_2} between –61.5 and –59.9°C and Tm_{Clath} between (i) 0.3 and 3.6 and (ii) 6.1 and 8.1°C (Table 4). The Th_{CO_2} was not observed due to the small size of the fluid inclusions. The salinity ranges from 3.7 to 15.1 wt% NaCl equiv. in fluid inclusions in Qz5 (Fig. 6a, Table 4). The bulk density of aqueous-carbonic fluid inclusions ranges from 1.01 up to 1.08 g/cm^3 (FIA 12_B).

Raman spectroscopy

The majority of non-aqueous phases of FIAs in all quartz and vein types are characterised by Raman bands of gaseous components such as CO_2, CH_4 and N_2. Methane shows a constant and single symmetric stretching band at approximately 2909 cm^{-1} (± 5 cm^{-1}) (ESM-3). The presence of CO_2, located at 1281 cm^{-1} (± 3 cm^{-1}) and 1384 cm-1 (± 3 cm^{-1}), was detected in aqueous-carbonic fluid inclusions trapped in Qz1-V1 shear veins (ESM-3). Nitrogen (at 2324 ± 2 cm^{-1}) and dissolved HS^- (at 2574 cm^{-1}) have been recorded only in low intensity in aqueous-carbonic fluid inclusions in Qz3-V3 extensional vein arrays (ESM-3). Aqueous fluid inclusions in Qz2-V2 and Qz2-V3 extensional vein arrays show significant lower amounts of CH_4 and no CO_2. The Raman spectrum of molecular CO_2 shows two strong bands at 1281 cm^{-1} (± 3 cm^{-1}) and 1384 cm^{-1} (± 3 cm^{-1}) (ESM-3).

The calculations of the non-aqueous phase of individual fluid inclusions of FIA 8_{C+E}, in Qz1-V1 shear veins, resulted in 91.4 mol% CO_2 and 8.6 mol% CH_4, whereas the non-aqueous phase of individual fluid inclusions of FIA4_C in Qz3-V3 extensional vein arrays are composed of 30.0 mol% CO_2, 41.0 mol% CH_4 and 28.0 mol% N_2. The FIAs 11_{A-E} in Qz2-V2 extensional veins display CH_4 fluid inclusions only with count rates between 400 and 880.

Trapping conditions

No petrographic evidence for phase immiscibility (cf. Ramboz et al. 1982) has been observed in the samples analysed. Due to the lack of independent pressure estimate and without observing any homogenisation temperature for aqueous-carbonic fluid inclusions, the decrepitation temperatures are interpreted as minimum trapping temperatures (cf. Roedder 1984). In the case of aqueous fluid inclusions, a temperature (pressure) correction can be applied using an independent pressure estimate, the Potter (1977) equation of state and interactive graphs in the MacFlinCor program (Brown and Hagemann 1995). The independent pressure estimate of 1.5 kbars is derived from the metamorphic mineral assemblage that characterises the host rocks in the Cuiabá gold deposit (Vieira 1991; Lobato et al. 2001c). These pressures are interpreted to reflect the approximate pressure conditions at the time of mineralisation, which are compatible with a mesozonal (1–2 kbars at 4–8 km paleodepth level assuming lithostatic pressure conditions) crustal setting for Cuiabá (cf. Hagemann and Brown 1996; Hagemann and Cassidy 2000, Ridley and Diamond 2000).

Homogenisation and decrepitation as well as calculated trapping temperatures of FIAs are shown in Table 5 and Figure 6b/d. A possible indication for phase immiscibility is provided by one aqueous, FIA 2_D, trapped in Qz2-V3 vein. In this assemblage, vapour-rich fluid inclusions all homogenised into vapour at about 220°C (Table 3). The majority of the FIAs in Qz1-V1 shear veins and Qz3-V3 extensional vein arrays decrepitated prior to homogenisation into vapour.

Based on the Th_{TRAP} of aqueous and minimum Th_{TRAP} of aqueous-carbonic FIAs, isochores were calculated for aqueous FIAs 11_{A-E} (5.8 wt% NaCl equiv.) and aqueous FIA 9 (8.5 wt% NaCl equiv.), both trapped in Qz2-V2 extensional vein and from aqueous-carbonic FIA 8_E (7.2 wt% NaCl equiv.). Isochores were calculated based on the equation of state of Bodnar and Vityk (1994) for aqueous FIAs and Jacobs and Kerrick (1981) for aqueous-carbonic FIAs. Using the intersection of the ‘maximum’ isochores of aqueous FIAs 11_{A-E} and aqueous-carbonic FIA 8_E with the crystallisation temperature of 300–390°C for arsenopyrites in the proximal alteration zone (Kresse 2018), an average pressure between 1.1 and 3.2 kbars is estimated (Fig. 6e).

Ion chromatography

The ion chromatography data for all vein types show that fluid inclusions are dominated by Na and K, with lesser amounts of Li (Table 6). Chloride ion (Cl^-) and SO_4^{2-} are the major anions in quartz-hosted fluid inclusions. Significant SO_4 values may be attributed to the presence of sulphides and their subsequent oxidation and/or leaching. Fluid inclusions of the V4 late-stage veins display maximum chloride values of up to 32,600 ppb. Bromide values are variable, but the highest are in fluid inclusions of the V2 extensional veins (Table 6).

Laser ablation ICP-MS

Analytical results for FIAs trapped in quartz from V1, V2, V3 and V4 veins show that Na^+, Ca^{2+}, K^+ and Mg^{2+} are the dominant cations and are discussed for each vein type below. Analyses of As and Au (Fig. 7) were conducted separately in aqueous FIAs trapped in Qz1-V1, Qz2-V2 and Qz5-V4 veins, because of possible interferences with other trace element signals (ESM-4). This data set is discussed separately below. Sodium and K were measured simultaneously. The average LA-ICP-MS concentration data for all FIAs analysed are provided in the ESM-5.

V1 shear veins

Quantitative LA-ICP-MS microanalysis of FIAs yielded one distinct population of data with a signature of Na>K>Ca>Mg (Fig. 8). The solutes of aqueous-carbonic fluid inclusions are elevated in Sr and Ba in comparison to aqueous inclusions (ESM-5). Base metal concentrations are in the order of 60–1,600 ppm (Fig. 8). The maximum Fe concentrations are in the range of 218 to 788 ppm. Manganese concentrations range from 33 to 61 ppm in aqueous fluid inclusions, whereas aqueous-carbonics show a large range from 34 to 111 ppm (ESM-5).

V2 extensional veins

Aqueous fluid inclusions in Qz2-V2 veins have lower K and Na and higher Mg and Ca concentrations in comparison to aqueous and aqueous-carbonic fluid inclusions in Qz1-V1 shear veins. For example, Sr and Ba concentrations are elevated in aqueous fluid inclusions in Qz2 compared to fluid inclusions in Qz1-V1, Qz3-V3 and Qz5-V4 veins (Fig. 8). Base metal concentrations range between 200 and 600 ppm in aqueous fluid inclusions (Fig. 9), with Zn being below detection limit.

V3 extensional vein arrays

Fluid inclusions in Qz3-V3 veins show the dominance of Na-K (Na>K>Ca>Mg). Alkali elements and base metals of fluid inclusions in Qz1 and Qz2 coincide with values of fluid inclusions in Qz1-V1 veins (Fig. 8; ESM-5). Strontium and Ba in aqueous fluid inclusions in Qz1 reach concentrations up to 456 and 327 ppm, respectively (ESM-5). Fluid inclusions trapped in Qz3 yield less Sr and Ba than fluid inclusions in Qz1-V3 veins (ESM-5).

V4 late-stage veins

Aqueous fluid inclusions trapped in Qz5-V4 late-stage veins are characterised by much higher Na concentrations compared to aqueous and aqueous-carbonic fluid inclusions in Qz1-V1, Qz2-V2 and Qz3-V3 veins (Fig. 8). Strontium reaches values up to 342 ppm and Ba up to 93 ppm in aqueous fluid inclusions (Table 8). Base metals display similar ranges compared to the other vein types.

Gold and arsenic concentration data

Figure 7 shows the correlation between As and Au of fluid inclusions trapped in V1, V2 and V4 veins. Aqueous fluid inclusions trapped in Qz1-V1 shear veins, characterised by a salinity range from of 8.1 to 13.4 wt% NaCl equiv., shows a positive correlation of As and Au, yielding two populations. Population A is characterised by relatively low As (20–200 ppm) and low Au (1–15 ppm) concentrations, whereas population B has higher As (up to 369 ppm) and Au concentrations (41 ppm) (Fig. 7; ESM-4). Moderately saline fluid inclusions (4.9 to 8.0 wt% NaCl equiv.) trapped in Qz2-V2 veins show elevated As and Au concentrations (Fig. 7). These FIAs have lower Na concentrations, but an elevated K signature (ESM-4). Laser ICP-MS data of aqueous fluid inclusions trapped in Qz5 with a salinity range from 6.4 to 9.6 wt% NaCl equiv. plot at relatively elevated As and Au concentrations coinciding with the population B of V1 veins (Fig. 7) and a maximum Au value of 56 ppm (Fig. 7; ESM-4).

Discussion

Microthermometry and Raman spectroscopy

The CO_2-CH_4-rich FIAs in shear-related, andesite-hosted quartz veins of the VQZ ore body, Archaean Cuiabá gold deposit (Fig. 2a), indicate three different fluid types: 1) aqueous of low salinity (1.8–3.8 wt% NaCl equiv.), 2) aqueous of moderate salinity (5.3–12.7 wt% NaCl equiv.) and 3) aqueous-carbonic of low to moderate salinity (6.0–15.1 wt% NaCl equiv.) with variable mol% CO_2 (30–91 mol%), CH_4 (8.6–41mol%), N_2 (maximum values of 28 mol%) and trace concentrations of HS^- in the non-aqueous phase.

Many orogenic gold deposits hosted in metasedimentary rocks contain N_2 and/or CH_4 at concentrations similar to that of CO_2 (Bodnar et al. 2014). Overall, fluid inclusion microthermometry and Raman data are comparable to those compiled for metamorphic fluids by Ridley and Diamond (2000), Ribeiro et al. (2015) and Morales et al. (2016). Previous studies on Cuiabá by Xavier et al. (2000) and Lobato et al. (2001a, b) showed low-salinity (3–6 wt% NaCl equiv.), H_2O-CH_4-CO_2 (± N_2+HS) ore-forming fluids. Methane-rich fluid inclusion types are abundant in quartz veins cross-cutting the organic carbon-bearing BIF of the Cuiabá deposit (Lobato et al. 2001c).

Ion chromatography

Three groups of ion chromatography results are depicted in Figure 9a, with the highest Cl/Br ratios (Table 6) corresponding to fluid inclusions in the Qz3-V3 extensional vein arrays (inset in Figure 9a). They all plot to the left of the seawater evaporation line, indicating that during water-rock interaction Na in the fluid was partly exchanged for other cations (Lüders et al. 2005). This Na loss is in agreement with the LA-ICP-MS data, which demonstrates average Na concentration in FIAs decreasing from V1 shear to V2 extensional veins and V3 extensional vein arrays (Fig. 8), with renewed Na increase in FIAs trapped in Qz5-V4 late-stage veins (Figs. 8, 9a). According to Lüders et al. (2005), Marsala et al. (2013) and Rauchenstein-Martinek et al. (2016), leaching of organic-rich sedimentary rocks increases Br and lowers the Cl/Br and Na/Br ratios, characterising data above the seawater evaporation line (as Qz2 of V2 veins; Fig. 9a). Given that in Cuiabá organic-bearing carbonaceous pelites (Fig. 2a) are associated with the Cuiabá BIF, and the Cuiabá BIF itself is containing carbonaceous matter, the low Cl/Br ratios (Table 6) may be interpreted similarly. An alternative for the low Cl/Br ratios is the mobilisation of Br during metamorphic devolatilisation of organic-rich sedimentary rocks (cf. Muramatsu and Wedepohl 1998).

Crush-leach and LA-ICP-MS studies by Leisen et al. (2012) and Fusswinkel et al. (2017) on euhedral fissure and cavity quartz samples from Alpine quartz veins and the Neoarchaean Pampalo orogenic gold deposit, respectively record lower molar Cl/Br ratios (9–150) than those of modern seawater. Low ratios are compatible with metamorphic fluids, whereby higher molar Cl/Br ratios are considered to be typical of magmatic-hydrothermal fluids (Fusswinkel et al. 2017) (500–1,600). In the case of Cuiabá, there is no indication of magmatic activity associated with gold mineralisation. One alternative to explain the moderate fluid salinity (15.1 wt% NaCl equiv.; Tables 3 and 4) and high Cl/Br ratios (Qz3, Fig. 9a inset) would be to invoke an evaporitic source.

For various orogenic gold deposits in Victoria, Australia, Fu et al. (2012) suggested that low-salinity, H_2O–CO_2 fluids, generated during transitional greenschist-amphibolite facies metamorphism of variably altered basalts, preserve their halogen signatures (Br/Cl ratio of $1.3 \pm 0.3 \times 10^{-3}$; Jambon et al. 1995). The Br/Cl ratios in Qz1-V1 shear and Qz5-V4 late-stage veins yield similar ranges (Table 6). The euhedral Qz3 has the comparably lowest Br/Cl ratios (Fig. 9b, Table 6). The Br/Cl ratios of fluid inclusions trapped in Qz1, Qz2 and Qz5 from V1, V2 and V4 veins are compatible with both magmatic and metamorphic fluid sources, as suggested by Böhlke and Irwin (1992) for the Oriental deposit in California (1.2–2.4×10^{-3}).

Similar Br/Cl ratios have been determined for fluid inclusions in samples of post-metamorphic gold quartz veins from the Monte Rosa gold district, NW Italy (Diamond 1993) and the Muruntau gold deposit, Uzbekistan (Graupner et al. 2006).

Major and trace element distribution in fluid inclusions

Most previous workers investigating orogenic gold deposits (Diamond 1993; McCuaig and Kerrich 1998; Ridley and Diamond 2000; Mernagh et al. 2007) have used microthermometric and spectroscopic methods of fluid inclusions to determine the composition of ore-forming hydrothermal fluids. However, there are limited LA-ICP-MS data for fluid inclusions of orogenic gold deposits and/or metamorphic fluids (Marsala et al. 2013; Rauchenstein-Martinek et al. 2014, 2016; Morales et al. 2016, Fusswinkel et al. 2017).

Chemical analysis of FIAs (Fig. 8) shows that the major elements are essentially constant for different FIAs in all vein types, suggesting that fluids were trapped under rock-buffered conditions. Alkali and alkali-earth element concentrations are similar to those obtained from other orogenic gold deposits (Diamond 1993; Wagner et al. 2016). Mono- and divalent cations such as Na, K, Ca and Mg are responsible for lower eutectic temperatures in comparison to fluids containing only Na (Borisenko 1977). Low to moderate salinities, order of abundance Na>K>Ca>Mg, are typical in orogenic gold deposits (Yardley and Bodnar 2014; Ribeiro et al. 2015; Morales et al. 2016). Figure 8 shows a significant Na dominance in all vein types, with Mg and Ca increase in V2 veins (ESM-5). The concentrations of alkali-earth elements Sr and Ba are lower compared to alkali elements, varying among quartz vein types (Fig. 8). Carbonate alteration of andesite may have acted as a predominant process to influence fluid composition, resulting in significant Ca, Ba and Sr concentrations, which further influenced the geochemistry of fluid inclusions in V1 shear, V2 extensional, as well as late-stage V4 veins (Kojonen et al. 1993; McCuaig and Kerrich 1998; Xavier et al. 2000). Alternatively, these elements may have been contributed to the fluid due to interaction with surrounding carbonaceous pelites, containing high contents of Sr (up to 183 ppm) and Ba (up to 279 ppm; Ribeiro-Rodrigues 1998). Sodium and K metasomatism may have also been important, as well as formation of hydrothermal alteration minerals such as sericite that indicates K enrichment in the fluid (Ridley and Diamond 2000; Morales et al. 2016). In general, fluid-rock interaction resulted in Na decrease and Mg increase in V2 relative to V1 and V3 veins (Fig. 10a), whereas Sr increases in V2, V3 and V4 relative to V1 veins (Fig. 10b). A decrease of K from V1 to V2 and elevated Ca relative to Sr and K in V2 veins compared to V1 shear veins (Fig. 10c), can be observed.

Figure 7 shows a continous As increase in FIAs from V1, through V2 and to V4 veins (ESM-3). During the early stage with V1 vein formation, As in hydrothermal fluids fluctuated from relatively low to high values (fields 1 and 2 in Fig. 7). During V2 and V4 formation a fluid richer in As evolved (fields 3, 4 and 5; Fig. 7; ESM-4). It is noteworthy that As-rich pyrite and not arsenopyrite, is the As-bearing sulphide phase of the hydrothermal alteration in the andesite hosting the VQZ ore body (Kresse et al. 2018).

According to Rauchenstein-Martinek et al. (2014, 2016), metamorphic fluids are commonly undersaturated in gold. Fluid inclusions trapped in quartz-tourmaline-carbonate veins of the Sigma orogenic gold deposit show a range between 0.5 and 5.0 ppm Au (Garofalo et al. 2014). The present results display median values from 12 ppm in V1, 7 ppm in V2 and up to 29 ppm Au in the V4 late-stage veins (ESM-4; Fig. 7), suggesting that peak gold precipitation took place during the V1 and V2 vein development. Formation of the pyrrhotite-dominated V4 vein may have resulted from progressive decrease in sulphur fugacity, which enabled pyrrhotite and not pyrite to form in the late stage of hydrothermal alteration. Lower sulphur fugacity conditions may have hindered gold buffering and precipitation during V4 vein formation. Although the lowest Au concentrations (1–4 ppm) are accompanied by low (17 ppm) to high (300 ppm) As concentrations in FIAs of the Qz1-V1 shear veins, all low, intermediate and high Au values (7–14 ppm) in Qz2-V2 extensional veins plot in the intermediate to high As field (80–330 ppm). The Au-As correlation of V4 is highly variable, but the highest Au concentrations (56 ppm) is related to high (120 ppm) As values. During V1 development As was partly supplied to form the early-stage As-rich pyrite only in andesite, but remained in the fluid, i.e., did not precipitate to form arsenopyrite during the V2 and V4 late-stage vein formation, which is evidenced by the absence of arsenopyrite.

Characteristics of the ore-forming fluids

Fluid precipitation processes Aqueous and aqueous-carbonic FIAs trapped in different quartz and vein types in the andesite-hosted VQZ ore body contain a vapour phase of ± 10 vol%, indicating homogenous fluids (miscible) at the time of trapping. Given that only fluid inclusions trapped in aqueous FIA 2_D in Qz2-V2 extensional veins display homogenisation into vapour, but decripitate before final homogenisation, the evidence for intermittent phase immiscibility as a possible fluid precipitation process is equivocal. According to Anderson et al. (1992), a positive correlation between Th_{TOT} and salinity is compelling evidence for fluid mixing of two or more distinct miscible fluids. Based on the distribution of data in Figure 6a-c, the evidence for mixing is vague. Hydrothermal fluids at Cuiabá either unmixed at a deeper crustal level, with the low-density CO_2 vapour-rich fluid inclusions escaping to surface, or alternatively heterogeneous fluids with varying CO_2 and/or CH_4 proportions moved up fault zones and cooled according to the local geothermal gradient.

Evolution of volatiles in veins associated with wall rock reactions Laser Raman data and their quantification show variable amounts of CH_4 (8.6–41 mol%), CO_2(30–91 mol%) and N_2 (28 mol%) in the non-aqueous phase of individual FIAs trapped in Qz1-V1, Qz3-V3 and Qz5-V4 (except CO_2 is lacking in Qz2-V2 veins). Methane and CO_2 trapped in fluid inclusions from gold-bearing veins are common in orogenic gold systems (Ho et al. 1985) and can be explained by either metamorphic reactions involving carbonates with H_2, as well as serpentinisation reactions (Xavier et al. 2000; Gaboury 2013, 2019). Nitrogen, in contrast, is only rarely detected and therefore the significant amount of N_2 in aqueous-carbonic FIAs trapped in the Qz3-V3 extensional vein arrays requires an explanation. Various authors (e.g. Andersen et al. 1993) provided evidence that N_2 can be sourced by: (i) breakdown of organic matter from sedimentary rocks where N_2 can be fixed in K-bearing silicates (mica), (ii) hydrothermal alteration of NH_4^+-bearing silicates and formation of N_2, or (iii) primary N_2 liberated from magma or through metamorphism of the lower crust.

Fluid source Low to moderate salinities (max 15 wt% NaCl equiv.) and moderate to high homogenisation and decrepitation temperatures of up to ~380°C (Fig. 6; Tables 4 and 5) of the ore-forming hydrothermal fluids are compatible with those associated with mesozonal orogenic gold deposits (Ridley and Diamond 2000; Goldfarb and Groves 2015; Groves et al. 2019). Stable isotope data at Cuiabá are consistent with the hydrothermal fluids being dominantly of metamorphic origin (Lobato et al. 2001c) based on: (i) oxygen isotope data on carbonates of the Cuiabá BIF and andesite range between +9 and +10 ‰, which are compatible with metamorphic fluids (Taylor 1987); (ii) $\delta^{34}S$ signature of pyrite and pyrrhotite ranges between 1.4 and 5.6 ‰ (Lobato et al. 2001c; Kresse et al. 2018), indicating a sedimentary sulphur source (Farquhar et al. 2000); (iii) carbon isotope data on carbonate minerals of the Cuiabá BIF and andesite are in the range of 0.7 to-8.5 ‰ and -5.5 to -8.4 ‰, respectively, which are similar to other Archaean greenstone belt-hosted orogenic gold deposits worldwide (De Ronde et al. 1997) and those are interpreted of metamorphic origin. Kresse et al. (2018) conducted sulphur isotope analyses on hydrothermal pyrite and concluded that sedimentary rocks were a significant source for sulphur. Sedimentary rocks make-up much of the local stratigraphy in the Rio das Velhas greenstone belt. Studies on the metasedimentary schist-hosted Macraes orogenic gold deposit in the Otago goldfield by Craw and MacKenzie (2016) have shown that this narrow range in oxygen isotope values is characteristic of hydrothermal fluids that have interacted with schistose host rocks and is widespread in hydrothermal systems throughout the Otago schist belt.

Significance of base metal concentrations

Cuiabá is low in base metal minerals, which is compatible with orogenic gold systems (Phillips and Powell 2010; Goldfarb and Groves 2015). Typical low-salinity metamorphic fluids are unlikely candidates for forming large base metal occurences and have average Zn, Pb and Cu values in the range of 1–10 ppm (Phillips and Powell 2010; Wagner et al. 2016). The FIAs in the Cuiabá vein system have elevated Zn, Pb and Cu concentrations in comparison to sedimentary systems. However, our data are compatible with the predominance of metamorphic fluids.

Anomalous base metal contents are also registered in pyrite hosted in BIF, andesite and carbonaceous pelite within the Cuiabá deposit (Fig. 2) (Kresse et al. 2018), a feature equally reported by Oliver et al. (2015) for the Neoproterozoic Paracatu sedimentary rock (black shale)-hosted orogenic gold deposit. The sulphur isotope ratios obtained for pyrite and pyrrhotite by Kresse et al. (2018) indicate that the metamorphic hydrothermal fluids (Fig. 12) interacted and exchanged chemical components with the sedimentary rocks in the Cuiabá area during their ascent. Two scenarios may be envisaged: equilibration with the wall rocks and -or mixing with basinal brines originating from sedimentary, as suggested by Pb and Sr isotope studies on pyrite at Cuiabá. However, the salinity data are not compatible with this latter hypothesis. Lead isotope analyses of sulphide minerals show a limited spread of data (Lobato et al. 2001b, c), indicating the formation of gold mineralisation during the late Neoarchaean between 2.75 and 2.70 Ga. Although the interpretation of Pb isotope data is uncertain (Lobato et al. 2001c), Pb values may imply a derivation from a mixture of old continental crust and greenstone belt sedimentary rocks (Noce et al. 2007). Existing Sr isotope data ($^{87}Sr/^{86}Sr$) of BIF-hosted pyrite from the Cuiabá deposit support the influence of the continental crust related to the fluid geochemistry (Lobato et al. 2001c). As Archaean fluids are typically characterised by low Sr isotope ratios, the recorded relatively high ratio of 0.707909 may indicate that Sr of the mineralising fluids was derived from the upper continental crust (Lobato et al. 2001a, b; Noce et al. 2007).

The geochemical data set of FIAs at Cuiabá, Lamego and Córrego do Sítio in the QF (Fig. 1) demonstrate that the major and trace element compositions are nearly identical with few discrepancies such as Cu, Pb, Ag and Au (Morales et al. 2016). The Lamego and Córrego do Sítio deposits show elevated base metal concentrations from 100 to 1,000 ppm (Fig. 11; Table7).

The Cuiabá Th_{TRAP} and moderate salinity data obtained in all vein types correlate positively with higher base metal concentrations than typically encountered in orogenic gold deposits (Table 7). Minimum Th_{TRAP} in similar salinity ranges are obtained for Lamego (200–370°C) and Córrego do Sítio (310–395°C) (Ribeiro et al. 2015; Morales et al. 2016).

Taking these data into account (Fig. 11; Table 7), it appears that FIAs trapped in shear and extensional veins at Cuiabá, Lamego and Córrego do Sítio display significant base metal concentrations in comparison to data of metamorphic fluids related to orogenic belts elsewhere (Marsala et al. 2013; Rauchenstein-Martinek et al. 2014, 2016; Wagner et al. 2016) and orogenic gold deposits in general (Fusswinkel et al. 2017).

Sedimentary rocks may be considered as an essential source of gold and fluids (Pitcairn et al. 2006; Large et al. 2011), whereby the BIF-surrounding carbonaceous pelite may represent a possible source for base metals (Fig. 2a). Large et al. (2011) indicated that metalliferous black shales are commonly enriched in metals including Mo, V, Ni, Cr, Zn, As, Cu and Pb. Xavier et al. (2000) and Lobato et al. (2001b) show the relevance of carbonaceous pelite and fluid-rock interactions for some Rio das Velhas greenstone-belt-hosted deposits. Morales et al. (2016) highlights the carbonaceous pelites at the Córrego do Sítio district and Cuiabá deposits as a partial sources of metals; however, these units only amount to a minor portion of their rock packages. Whole-rock geochemical analyses of carbonaceous pelites at Cuiabá yield Zn values up to 630 ppm, Pb in the order of 56 ppm and As reach up to 162 ppm (Ribeiro-Rodrigues 1998). Andesite reveals Zn, Pb and As concentrations of 218 ppm, 16 ppm and 15 ppm, respectively. Gold concentrations in carbonaceous pelites and andesite are between 8–10 ppb. Based on data of Baltazar and Zucchetti (2007), Martins et al. (2016) calculated an approximate thickness of 5,550 m of clastic, clastic-chemical and volcaniclastic sedimentary rocks, making the Rio das Velhas a sedimentary-rich greenstone belt. The Archaean Cuiabá orogenic gold deposit is over- and underlain by these thick sequences of lithologically variable, supracrustal sedimentary rocks. Sedimentary rocks composed of widespread turbidites (Burwash-Wash Formations; Taylor and McLennan 1985) also dominate similar Archaean terrains, such as the Yellowknife Supergroup (Helmstaedt and Padgham 1986). These contrast with other volcanic-dominated greenstone belts and associated orogenic gold deposits (Anhaeusser 2014).

Cuiabá vein and fluid model

The proposed model for hydrothermal fluid flow and precipitation of metals, including gold, at the Cuiabá deposit is based on the detailed investigation of the andesite shear-zone-hosted quartz veins and the physico-chemical constraints obtained by the present fluid inclusion investigation. We propose a two-step hydrothermal model that involves the development of: 1) V1 to V3 veins by an early-stage, aqueous-carbonic, high temperature fluid, with minimum Th_{TRAP} at 290°C (Qz2-V3) to a maximum Th_{TRAP} at 360°C (Qz1-V1) and 2) breccias-style V4 veins, which formed by an evolved, late-stage, aqueous-carbonic, low temperature fluid with a mean Th_{TRAP} at 260°C. The evolution of the vein system, including the hydrothermal fluids and gold mineralisation, is illustrated in Figure 12 and given in the following section. Overall, the two-step hydrothermal fluid model is interpreted to reflect four pulses of hydrothermal fluids during the evolution of the paleohydrothermal system. Fluid pulse 1 to 3 relate to the first hydrothermal stage, whereas fluid pulse 4 relates to the second hydrothermal stage (Fig. 12). The first hydrothermal stage contains:

Pulse 1 An early, first hydrothermal fluid pulse is represented by Na-K-rich, aqueous and aqueous-carbonic FIAs of low and moderate salinity with $CO_2 > CH_4$ (N_2 free) (Fig. 12). These oxidised fluids have base metal contents between 60 to 1,600 ppm and median As and Au values of 64 ppm and 12 ppm, respectively. They are trapped in Qz1-V1 shear and Qz1-V2 extensional veins (the veins with visible gold), with mean Th_{TRAP} between 350 and 380°C. These temperatures are similar to the arsenopyrite formation temperature between 300 and 390°C (Kresse 2018).

Pulse 2 The second hydrothermal fluid pulse is represented by aqueous FIAs of moderate-salinity (Fig. 12). These are Mg-Ca-Sr-Ba-rich and Na-K-poor, with base metal contents between 200 and 600 ppm and median As (125 ppm) and medium Au (7 ppm) values. These are trapped in Qz2-V2 extensional veins with Th_{TRAP} ranging from 290 to 360°C.

Pulse 3 The third hydrothermal fluid pulse is base metal rich and represented by Na-K-Ca-rich, aqueous and aqueous-carbonic FIAs of low and moderate salinity and $CH_4 > CO_2 = N_2$ (Fig. 12). The base metal content ranges from 300 to 1,500 ppm and FIAs trapped in Qz3-V3 extensional vein arrays have Th_{TRAP} between 290 and 340°C.

The second hydrothermal stage includes:

Pulse 4 The forth hydrothermal pulse is characterised by aqueous and aqueous-carbonic FIAs of low and moderate salinity (Figs. 6, 12). It is Na-K-rich, displays elevated Ca, Sr and Ba values and shows base metal contents between 100 and 1,000 ppm with very high median As (290 ppm) and Au (29 ppm) values. Pulse 4 fluids are trapped in Qz5-V4 extensional, breccias-style veins with significant lower Th_{TRAP} between 240 and 270°C when compared to the other fluid pulses.

The low to moderate saline, aqueous-carbonic fluid of Pulse 1 is suggested to represent the main mineralising fluid in V1 shear and V2 extensional veins, which led to gold precipitation. Since fluid inclusions in V1 shear veins, as well as in V2, V3 and V4 extensional veins, are very similar with regards to compositional types and physico-chemical conditions, the fluid chemistry probably did not change significantly from the first (Pulses 1–3) to the second (Pulse 4) hydrothermal stage during the Archaean deformation history. The Au concentration in FIAs trapped in each vein type (Qz1-V1 shear, Qz2-V2 extensional, Qz5-V4 late-stage veins) suggest the following: 1) an early precipitation of Au as native gold from a Na-K-As-rich hydrothermal fluid due to intermittent phase immiscibility at depth and/or partial mixing and 2) a late-stage Au-bearing Na-K-As rich hydrothermal fluid, which was not able to precipitate gold in pyrrhotite-rich V4 late-stage veins probably due to insufficient total concentration of sulphur ($m_{\sum S}$).

Conclusions

The detailed investigations on hydrothermal fluids in the different vein types at Cuiabá revealed the following:

1. The Cuiabá quartz veins, hosted in the footwall andesite of the Veio de Quartzo ore body, encompass V1 shear, V2 extensional (V1 and V2 with visible gold), V3 extensional vein array and V4 extensional (breccias-style) veins. An early-stage, anhedral Qz1 evolves to a granoblastic Qz2 and a late-stage, euhedral Qz3 during a first hydrothermal stage, which is represented by V1, V2 and V3 veins. The breccia-style V4 veins are interpreted to be related to a second hydrothermal stage, during which the anhedral Qz5 develops, bearing morphological and fluid inclusion characteristics similar to Qz1.

2. Microthermometric data show that the ore-forming fluid have the signature of typical orogenic gold fluids, i.e., low- to moderate-salinity (4.0–10.0, locally up to 15 wt% NaCl equiv.) containing variable amounts of CO_2, CH_4, N_2 and minor HS^-.
3. The geochemical data in FIAs display the following fluid-rock interactions inbetween quartz veins: (i) Na decreases in V2 relative to V1 and V3 veins; (ii) Sr increases in V3 and V2 relative to V1; (iii) K continously decreases from V1 to V4; and (iv) Ca is relatively higher to Na and K concentrations in V2 in comparison to V1, V3 and V4.
4. Possible intermittent phase immiscibility as well as heterogeneous entrapment resulting from intermittent partial mixing of two or more ore fluids may be considered as the principal fluid processes leading to the formation of the Cuiabá orogenic gold deposit.
5. A distinction to the typical orogenic gold fluids is the Cu, Zn and Pb enrichment encountered in fluid inclusions of Cuiabá, which are also similar to other deposits hosted in the Rio das Velhas greenstone belt (Lamego and Córrego do Sítio). These values, in the range of 100 to 1,000 ppm, may have been caused by interaction with: (i) metalliferous black shales and (ii) the (meta) sedimentary rocks that dominate the Rio das Velhas greenstone belt.
6. The fluid inclusion results provide an opportunity to classify shear and extensional veins and help identifying the evolution of the fluids forming the different vein types in the orogenic gold deposits of the QF. The similar geochemical affinity of the Cuiabá veins, hosted in the footwall andesite, suggest they are all part of the same hydrothermal event. This event is characterised by two main stages, with the first displaying changing physico-chemical parameters due to fluid-rock reactions and fluid dynamic processes. This is particularly apparent in the recorded Au concentrations of FIAs trapped in the main hosts for the mineralisation of the VQZ ore body (Qz1-V1 shear and Qz2-V2 extensional veins), but also in the Qz5-V4 late-stage veins, which may represent a paragenetically late and second Archaean hydrothermal fluid stage.

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Figure captions

Fig. 1 Geological map of the Quadrilátero Ferrífero region. The inset shows the location of the Quadrilátero Ferrífero in Brazil (modified after Baltazar and Zucchetti 2007)

Fig. 2 Geology of the Cuiabá mine. **a** Geological map of the Cuiabá mine, Level 11, with location of the main orebodies**. b** Geological map of the VQZ orebody at Level 15. **c** Lithostratigraphic section of sampled drill cores with corresponding gold grades in ppm) (information provided by AngloGold Ashanti). Legend in **b** also valid for **a**. Abbreviations: BIF-hosted orebodies: FGS-Fonte Grande Sul, SER-Serrotinho, BAL-Balancão, GAL-Galinheiro, GAL EXT-Galinheiro extenção, DDO-Dom Domingos, CGA-Canta Galo, SUR-Surucu. Quartz vein-hosted ore bodies: VQZ-Veio de Quartzo, GAL FW-Galinheiro Footwall, Gal QTZ-Galinheiro Quartzo, SER FW-Serrotinho Footwall, FGS FW-Fonte Grande Sul Footwall; VIA-Viana

Fig. 3 Photographs of quartz veins, hand specimen and drill core sections of the andesite-hosted quartz veins forming part of the Veio de Quartzo ore body (after Vitorino 2017). **a** V1 shear vein, indicating pinch- and swell structure (Level 15, VQZ ore body). **b** V2 extensional vein (Level 15, VQZ ore body). **c** V3 extensional vein arrays within V1 shear vein (Level 15, VQZ ore body). **d** V4 extensional late-stage veins (Level 15, VQZ ore body). **e** Hand specimen of V1 shear veins consisting of Qz1 (Level 15). **f** Drill core sections of V2 extensional veins (Qz2)(drill core CBABSD07, Level 17). **g** Hand specimen of V4 extensional veins (Qz5) (Level 15). **h** Stope view and sample location of V3 extensional vein arrays consisting of Qz3 (Level 15, VQZ ore body)

Fig. 4 Photomicrographs of quartz types. **a** Qz1 and Qz2 of V1 shear veins (transmitted light) (sample 009_7). **b** Qz1 and Qz2 of V1 shear veins (transmitted light, crossed nicols) (sample 009_7). **c** Intergrowth of all quartz types of V1 shear and V3 extensional vein arrays (transmitted light) (sample FICU01). **d** Qz5 of V4 late-stage veins (transmitted light) (sample QZL_1).

Fig. 5 Representative FIAs of all vein types, Veio de Quartzo ore body. **a-d** Qz1-V1 shear veins with small-sized, two-phase aqueous (FIA8$_A$) and aqueous-carbonic(FIA8$_C$) grouped FIAs. **e-g** Qz2-V2 and Qz2-V3 extensional veins showing, two-phase, aqueous, FIAs (FIA 2$_E$, FIA 11$_A$, FIA 11$_C$). **h-j** Qz3-V3 extensional vein arrays displaying two-phase, grouped aqueous fluid inclusion (FIA4$_A$) and two-phase, individual, aqueous-carbonic fluid inclusions (FIA 4$_C$) and internal trail of two-phase, aqueous fluid inclusions (FIA 6). Photomicrographs taken under transmitted light

Fig. 6 Box and whisker plots of salinity (a), Th$_{TOT}$ (b), T$_{DECREP}$ (c) and Th$_{TRAP}$ (d) for analysed FIAs. The central box is the middle 50% of the data from 25% quartile (Q1) to 75% quartile (Q3); whiskers are extreme values that are not outliers. Circles indicate outlier values. Isochore diagram (d) of aqueous and aqueous-carbonic FIAs. The range of P$_{min}$ and P$_{max}$ are calculated based on the intersection points with the mean Th_{TRAP} and calculated arsenopyrite formation temperature (Kresse 2018). The bluish area indicates metamorphic greenschist facies conditions (Spear 1995)

Fig. 7 Gold vs. As plot showing low to moderate saline, aqueous two-phase FIAs trapped in Qz1-V1 shear, Qz2-V2 extensional and Qz5-V4 late-stage veins. Error bars (SD) are given in both directions (dashed lines). The arrow indicates the development of increasing Au and As concentrations in fluid inclusions of Qz1-V1 shear veins, through Qz2-V2 extensional veins to maximum Au values of Qz5-V4 late-stage veins. A and B represent populations of V1 shear veins

Fig. 8 Laser ablation ICP-MS results in ppm as whisker box plots for all different vein types analysed. Qz1-V1 shear, Qz2-V2 extensional, Qz3-V3 extensional vein arrays, Qz5-V4 late-stage veins. The central box is the middle 50% of the data from 25% quartile (Q1) to 75% quartile (Q3); whiskers are extreme values that are not outliers. Circles indicate outlier values

Fig. 9 Crushed-leach ion chromatography in fluid inclusions trapped in vein quartz of the andesite-hosted Veio de Quartzo ore body. **a** Cl/Br vs. Na/Br molar ratio.Qz2V2 veins lie close to the seawater evaporation line, whereas those of the Qz3-V3 far above this line (inset), indicating that significant locally exchange of Na for other cations has taken place. Precipitation or dissolution of halite produces a trajectory parallel to the 1:1 line (inset). The field for the ultramafic-hosted Pampalo orogenic Au deposit (Fusswinkel et al. 2017), of low salinity, aqueous fluids of Alpine quartz veins (Leisen et al. 2012) is also shown. Note that analyses are not charged balanced and therefore data plot well to the left of the line in diagram. **b** Br/Cl (× 1,000) molar ratio vs. Cl concentration**.** Greyish band shows the range of mantle/magmatic fluid ratios based on values by Jambon et al. (1995)

Fig. 10 Normative plots of alkali and alkali-earth elements of LA- ICP-MS analyses from aqueous and aqueous-carbonic FIAs of V1 shear, V2 extensional, V3 extensional vein array and V4 late-stage vein. **a** Na-Mg-K, **b** Ba-K-Sr **and c** Ca-K-Sr. The Na- and K-rich fluid (V1 shear veins) evolved to a Mg-Sr-Ca-rich and Na-poor fluid (V2 extensional veins). New Na- and K-rich fluid is related to the V4 late-stage vein. The V3 extensional vein arrays, immersed in the V1 shear vein type, show similar composition to V1

Fig. 11 Correlation plot of Zn-Pb and Zn-Cu concentrations of different types of crustal fluids in comparison with fluid inclusion LA-ICP-MS data of the andesite-hosted quartz veins at the Cuiabá deposit. References: Lamego orogenic Au deposit and Córrego do Sítio orogenic Au district (Morales et al. 2016), El Teniente and Butte Porphyry Cu-Mo deposit - magmatic hydrothermal fluids (Klemm et al. 2007), Bingham Canyon Porphyry Cu-Au deposit - magmatic hydrothermal fluids (Seo et al. 2012), Central Alps - metamorphic fluids (Rauchenstein-Martinek et al. 2014, 2016) - granite-hosted smoky quartz fissure vein, Binn Valley - Mixed metamorphic-evaporitic fluids (Klemm et al. 2004). Low-temperature-saline brines of sediment-hosted Pb-Zn deposits (Wilkinson et al. 2009). Range of crustal fluids from Yardley (2005). Abbreviation: QV = quartz vein, CP = carbonaceous pelite, MG = metagreywacke, MD = mafic dike

Fig. 12 Schematic evolution model of the Cuiabá veins and VQZ orebody, including FIAs characteristics of mineralised Qz1-V1 shear vein, Qz2-V2 and Qz3-V3 extensional vein, corresponding to the first hydrothermal stage; Qz5-V4 late-stage vein of the second hydrothermal stage. The schematic reproduction of a photomicrography of quartz type evolution shows Qz1, Qz2 and Qz3. The Qz4 is considered as a recrystallisation product of Qz3 in V3 extensional vein arrays

Electronic Supplementary Materials

ESM-1: Photographs of mineralised host rocks at Cuiabá. **a** Sampled drill core section of sulfidised andesite (Level 17 of the Fonte Grande Sul ore body, drill core 03A, 1414.70–1414.84). **b** Sampled drill core section of sulfidised carbonaceous pelite

(Level 17 of the Fonte Grande Sul ore body, drill core 009, 1378.24–1378.40). **c** Sampled drill core section of sulfidised BIF ((Level 17 of the Fonte Grande Sul ore body, drill core 03A, 1619.6–1619.85). **d** Stope view of sulfidised BIF (Level 15, Galinheiro ore body)

ESM-2 Examples of representative FIAs of V3 and V4 vein types of the Veio de Quartzo ore body. **a-c** Qz3-V3 extensional vein arrays displaying an internal trail of two-phase, aqueous fluid inclusions (FIA 6) and two-phase, isolated aqueous-carbonic fluid inclusion (FIA 4_B). **d-g** Qz5-V4 late-stage veins, showing two phase, grouped, aqueous fluid inclusions (FIA 12_A), individual aqueous-carbonic fluid inclusions (FIA 12_B) and two phase, grouped, aqueous fluid inclusions (FIA 14). Photomicrographs taken under transmitted light

ESM-3 Raman spectra of individual fluid inclusions. **a** Raman spectra of FIAs trapped in Qz1-V1 shear veins. **b** Raman spectra of FIAs trapped in Qz3-V3 extensional vein arrays

ESM-4 Arsenic and gold composition (in ppm) of aqueous fluid inclusions trapped in quartz of V1 shear, V2 extensional and V4 late-stage veins measured by laser ablation-inductively coupled plasma-mass spectroscopy

ESM-5 Average laser ablation-inductively coupled plasma-mass spectroscopy concentration data (in ppm) for aqueous and aqueous-carbonic FIAs trapped in quartz (Qz1, Qz2, Qz3 and Qz5) of the andesite hosted shear and extensional quartz veins, Veio de Quartzo ore body

Table 1 Classification of the Cuiabá quartz veins (adapted after Vitorino 2017)

Vein type Classification after Passchier (2001) and Robert and Poulsen (2001)	**Vein system**	**Controlled by**	**Mineralogical composition**		**Vein geometry**
			Main	***Accessory***	
Fault-fill	V1 (shear)	S_m	Qz1, Qz2, cb, ser, chl, plg	py, po, cpy, sph, free gold	Folded, pinch and swell, boudins
a- Extensional b- Oblique extensional c- Fault-fill	V2 (a, b, c) (extensional)	S_b	Qz2, Qz1, cb, ser, chl	py, po, cpy, (free gold)	Tabular and folded; boudins and sigma shapes
Extensional vein array	V3 (extensional)	S_m	Qz3, Qz4	-	En-echelon
Extensional and brecciated	V4 (late-stage, extensional)	Flanking and cross-cutting S_m	Qz5, cb	py and po	Tabular and massive

Abbreviations: qz = quartz, cb =carbonate, ser = sericite, chl = chlorite, plg =plagioclase, py = pyrite, po = pyrrhotite, cpy = chalcopyrite, sph = sphalerite

Table 2 Summary of FIAs and their characteristics (e.g., chemical system, L/V ratio, shape, size and occurrence) based on quartz and vein types[1]

Vein type	**Sample ID**	**Qz type**	**FIA**	**N**	**Chemical system**	**L/V ratio**	**Shape**	**Size**(in μm)	**Occurrence**
V1 shear veins	009_7	Qz1	7	5	aq	10	Ovoid shaped and negative crystal	5–10	Grouped
		Qz1	8_A	5	aq	10	Irregular to ovoid shaped	5–10	Grouped
		Qz1	8_B	3	aq	10	Irregular to ovoid shaped	5–10	Grouped
		Qz1	8_C	4	aq-carb	10	Irregular to ovoid shaped	5–10	Grouped
		Qz1	8_D	2	aq	10	Irregular to ovoid shaped	5–10	Grouped
		Qz1	8_E	2	aq-carb	10	Irregular to ovoid shaped	5–10	Grouped
	007_2	Qz1	10	3	aq-carb	10	Negative crystal	5–10	Isolated

V2 extensional veins		Qz2	9	5	aq	10	Regular to ovoid shaped	5–10	Isolated
		Qz2	11A	7	aq	10	Regular to ovoid shaped		Grouped
		Qz2	11B	3	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	11C	5	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	11D	8	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	11E	5	aq	10	Regular to ovoid shaped	5–10	Grouped
V3 extensional vein arrays	FICU01	Qz1	1A	4	aq	10	Irregular to ovoid shaped	5–10	Grouped
		Qz1	1B	7	aq	10	Irregular to ovoid shaped	5–10	Grouped
		Qz2	2A	5	aq	10*	Irregular to ovoid shaped	5–10	Grouped
		Qz2	2B	4	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	2C	4	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	2D	3	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	2E	6	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	2F	4	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	2G	7	aq	10	Regular to ovoid shaped	5–10	Grouped
		Qz2	3	6	aq	10	Regular	5–10	Isolated
		Qz3	4A	3	aq	10	Regular	5–15	Grouped
		Qz3	4B	1	aq-carb	10	Regular to ovoid shaped	5–15	Isolated
		Qz3	4C	2	aq-carb	10	Regular	5–15	Isolated
		Qz3	4D	3	aq-carb	10	Ovoid shaped to irregular	10–20	Isolated
		Qz3	5A	5	aq	10	Irregular	5–15	Grouped
		Qz3	5B	4	aq	10	Irregular	5–10	Isolated
		Qz3	6	5	aq	10	Regular to ovoid shaped	5–15	Internaltrail
V4 late-stage veins	QZL_1	Qz5	12A	6	aq	10	Regular to ovoid shaped	10–20	Grouped
		Qz5	12B	2	aq-carb	10	Regular to ovoid shaped	10–15	Isolated
		Qz5	13	4	aq	10	Irregular	10–15	Isolated
		Qz5	14	7	aq	10	Regular ovoid shaped	10–15	Grouped
		Qz5	15	5	aq	10	Regular	5–15	Grouped
		Qz5	16A	6	aq	10	Ovoid shaped to irregular	10–15	Isolated
		Qz5	16B	5	aq	10	Ovoid shaped to irregular	5–15	Grouped
		Qz5	16C	2	aq-carb	10	Ovoid shaped to irregular	5–15	Isolated
		Qz5	16D	3	aq	10	Ovoid shaped to irregular	10–15	Grouped
		Qz5	17A	2	aq	10	Ovoid shaped	5–10	Grouped
		Qz5	17B	2	aq-carb	10	Ovoid shaped	10–15	Isolated
		Qz5	18	8	aq	10	Ovoid shaped to irregular	5–15	Grouped
		Qz5	19	2	aq	10	Ovoid shaped to irregular	5–10	Isolated
		Qz5	20	8	aq	10	Ovoid shaped to irregular	5–15	Grouped

Abbreviations: Qz = quartz, N=number

[1] Sample FICU01 mainly consists of Qz3, but also describes Qz1 and Qz2, both corresponding to the V1 shear vein type.

Table 3 Summary of microthermometry results and calculated salinity values of aqueous FIAs trapped in quartz of andesite-hosted veins[1]

Sample ID	Vein type	Quartz type	FI phase	FIA	N	Min-Max Tm$_{ice}$	Min-Max Th$_{TOT}$[°C]	Min-Max T$_{DECREP}$ [°C]	Min-Max salinity [wt% NaCl equiv.] (average salinity value)
009_7 3e	V1 shear veins	Qz1	Laq + Vaq	8_{A}	5	–3.5 to –1.1	-	220 to 250 (into L)	1.8 to 5.6 (3.8)
009_7 3b		Qz1	Laq + Vaq	8_{B}	3	–3.4	-	230 to 240	5.4
009_7 3b		Qz1	Laq + Vaq	8_{D}	4	–9.5 to –5.2	-	-	8.1 to 13.4 (12.4)
009_73a		Qz1	Laq + Vaq	7	5	–5.8 to –4.2	-	235 to 245	6.4 to 8.9
007_2 1a	V2 extensional veins	Qz2	Laq + Vaq	9	5	–5.2 to –3.3	-	325	5.0 to 8.5 (6.7)
007_2 1		Qz2	Laq + Vaq	11_{A}	7	–4.1 to –3.5	260 to 290 (into L)	-	4.5 to 6.6 (5.8)
		Qz2	Laq + Vaq	11_{B}	3			-	
		Qz2	Laq + Vaq	11_{C}	4			-	
007_2 3		Qz2	Laq + Vaq	11_{D}	8	–5.0 to –3.0	250 to 270 (into L)	-	4.9
		Qz2	Laq + Vaq	11_{E}	5		230 to 250 (into L)	-	8.0
FICU4a	V3 extensional vein arrays	Qz3	Laq + Vaq	4_{A}	3	–4.9 to –2.9	-	270	4.8 to 7.8 (6.6)
FICU3a		Qz3	Laq + Vaq	6	5	–6.2 to –3.9	-	350	6.2 to 9.5 (8.3)
FICU3b		Qz3	Laq + Vaq	5_{A}	5	–2.2 to –1.8	-	210/220/230	3.0 to 3.6
FICU3c		Qz3	Laq + Vaq	5_{B}	4	–6.3	-	-	9.2
FICU4d/e		Qz2	Laq + Vaq	3	6	–5.5 to –3.3	220 to 225 (into L)	270 to 320	5.5 to 8.5 (5.8)
FICU2a		Qz2	Laq + Vaq	2_{A}	5	–3.0	-	-	4.9
FICU2b		Qz2	Laq + Vaq	2_{B}	4	–4.0 to –3.8	220 to 230 (into L)	-	6.1 to 6.4 (6.2)
FICU2c		Qz2	Laq + Vaq	2_{C}	4	–4.2	-	-	6.7
FICU1a		Qz2	Laq + Vaq	2_{D}	3	–5.5 to –3.3	220 (into V)	-	5.8 to 8.5 (7.2)
FICU1b		Qz2	Laq + Vaq	2_{E}	6	–3.6 to –3.5	-	-	5.6 to 5.8
FICU1c		Qz2	Laq + Vaq	2_{F}	4	–3.5 to –3.1	-	-	5.0 to 5.6 (5.3)
FICU1d		Qz2	Laq + Vaq	2_{G}	7	–4.6 to –3.2	-	-	5.3 to 7.1 (6.5)
FICU1		Qz1	Laq + Vaq	1_{A}	4	–8.0 to –7.0	-	190 to 230	10.5 to 11.7 (11.0)
FICU1f			Laq + Vaq	1_{B}	7	–8.9 to –7.0	-		10.5 to 12.7
QZL 1a	V4 late-stage veins	Qz5	Laq + Vaq	12_{A}	6	–5.1 to –3.9	-	250 to 260	6.2 to 8.0
QZL 1a		Qz5	Laq + Vaq	13	4	–6.7 to –5.6	-		8.7 to 10.1 (9.4)
QZL 1b		Qz5	Laq + Vaq	14	7	–5.1 to –2.4	-	220 to 240	3.9 to 8.0 (7.0)
QZL 1c		Qz5	Laq + Vaq	15	5	–6.3 to –5.5	175 (into L)	-	8.5 to 9.6 (9.1)
QZL 2a		Qz5	Laq + Vaq	16_{A}	6	–7.0 to –5.8	-	-	8.9 to 10.5 (9.6)
QZL 2a		Qz5	Laq + Vaq	16_{B}	5	–6.4 to –4.0	195 (into L)	-	6.4 to 9.7 (8.2)
QZL 2a		Qz5	Laq + Vaq	16_{D}	3	–4.4 to –4.3	-	-	6.8 to 7.2
QZL 2b		Qz5	Laq + Vaq	17_{A}	2	–4.9	190 (into L)	210	7.7
QZL 3		Qz5	Laq + Vaq	18	8	–6.3 to –4	-	210 to 220	6.4 to 9.6 (7.9)
QZL 3g		Qz5	Laq + Vaq	20	8	–5.5 to –3.2	190 (into L)	215	5.2 to 8.5 (7.6)
QZL 3f		Qz5	Laq + Vaq	19	2	–2.2 to –1.5	-	-	2.5 to 3.6 (3.0)

Notes: Numbering of FIA's starts with FIA 8 in V1 shear veins due to preparation progress

[1] Sample FICU1 mainly consists of Qz3, but is in conjunction with Qz1 and Qz2 of V1 shear vein

Table 4 Summary of microthermometry results and calculated clathrate salinity values of aqueous-carbonic FIAs trapped in quartz of andesite-hosted veins

Sample ID	Vein type	Quartz type	FI type	FIA	N	Min-Max Tm$_{CO2}$	Min-Max T$_{C}$ [°C]	Min-Max Th$_{CO2}$	Min-Max T$_{DECREP}$ [°C]	Min-Max salinity [wt% NaCl equiv.]
009_7 2	V1 shear veins	Qz1	Laq + Vcarb	8_{C}	4	–61.7 to –58.1	1.2 to 3.6	25.1 to 30.4	-	9.3 to 12.7
009_7 2		Qz1	Laq + Vcarb	8_{E}	3	–61.1 to –59.1	6.1 to 6.6	29.4 to 30.1	280 to 310 (into V)	7.2
007_2 2	V2 extensional veins	Qz1	Laq + Vcarb	10	3	-	15.2 to 16.8	-	215 to 275	-
FICU4b	V3 extensional vein arrays	Qz3	Laq + Vcarb	4_{B}	1	–57.4	6.8	-	-	6.0
FICU4c		Qz3	Laq + Vcarb	4_{C}	2	–57.4	0.4 to 3.6		-	9.2 to 15.1
FICU4c		Qz3	Laq + Vcarb	4_{D}	3	–61.0 to –57.2	3.0 to 6.5	28.4 to 30.1	220 to 290 (into V)	6.5 to 10.1 (8.2)
QZL 2b	V4 late-stage veins	Qz5	Laq + Vcarb	16_{C}	2	-	6.1 to 7.0	-	-	5.7 to 7.2 (6.4)
QZL 2c		Qz5	Laq + Vcarb	17_{B}	2	-	7.7 to 8.1	-	-	3.7 to 4.4
QZL 1a		Qz5	Laq + Vcarb	12_{B}	2	-	0.3 to 3.6	-	-	11.0 to 15.1

Table 5 Homogenisation, decrepitation and trapping temperatures based on pressure (temperature) correction of FIAs. Th_{TRAP} from 300 to 360°C have a similar range as those of the arsenopyrite formation temperature (300–390°C) obtained from geothermometry in BIF-hosted arsenopyrite (Kresse 2018).

Vein type	FIA	Homogenisation temperature	Trapping temperature (*decrepitation temperature)
Qz1-V1	FIA 8_{A-B}	-	220–250°C*
	FIA 8_{E}	-	280–310°C*
Qz2-V3	FIA 2	220–230°C	290–300°C
	FIA 3	220–225°C	290–295°C
Qz2-V2	FIA 11_{A-E}	230–290°C	300–360°C
Qz3-V3	FIA 4_{D}	-	220–270°C*
Qz5-V4	FIA 15	175°C	245–265°C
	FIA 16_{B}	195°C	
	FIA 17_{A}	190°C	
	FIA 20	190°C	

Table 6 Ion chromatography analyses of fluid inclusions of quartz vein types of the andesite-hosted VQZ ore body

	V1 shear veins (Qz1)			V2 extensional veins (Qz2)		V3 extensional vein arrays (Qz3)		V4 late-stage veins (Qz5)	
Na	2120	2480	1010	7950	6680	7760	7040	9080	5240
K	525	894	426	2560	2410	2860	2770	3420	2450
Li	1	1	1	3	2	2	2	2	2
Cl	8550	10800	4750	22700	19400	29300	23800	32600	21000
Br	14	18	8	71	65	25	17	61	34
SO_4	4130	n.d.	4660	661	677	n.d.	n.d.	1770	1120
M ratio Na/K	6.8	4.7	4	5.3	4.7	4.6	4.3	4.5	3.6
M ratio Cl/Br	1410	1370	1360	715	662	2580	3210	1180	1380
M ratio Br/Cl ($x10^{-3}$)	0.7	0.7	0.7	1.4	1.5	0.4	0.3	0.9	0.7
M ratio Cl/SO_4	5.6	-	2.8	93.2	77.3	-	-	49.8	50.6
M ratio Na/Br	539	487	443	386	352	1050	1470	508	531

Notes: Data are given in ppb; n.d. = not detected, M=molar; analysed values do not represent true concentrations in fluid inclusions.

Table 7 Median base metal concentrations and corresponding average salinity of aqueous and aqueous-carbonic FIAs of orogenic gold deposits in the QF and Telfer Cu-Au deposit

Deposit	Quartz veins	Average salinity [wt% NaCl equiv.]	Median base metal concentrations [ppm]		
			Cu	**Zn**	**Pb**
Cuiabá – VQZ ore body	Qz1-V1 shear veins	9.3	864	637	190
		5.4	373	632	150
		2.7	312	292	62
		11.8	729	720	253
	Qz2-V1 shear veins	5.6	488	350	188
	Qz2-V2 extensional veins	6.6	501	-	403
	Qz3-V3 extensional vein arrays	5.8	474	-	286
		7.0	496	1540	342
		9.2	1020		977
	Qz5-V4 late-stage veins	3.2	545	190	214
		6.2	286	274	152
		8.0	443	644	186
Lamego, Cabeça de Pedra ore body	BIF hosted Qv	2.4	176	313	29
		3.7	174	575	49
	CP hosted Qv	9.8	446	2430	257

		10.4	527	2340	191
Córrego do Sítio, Carvoaria Velha deposit	CP hosted Qv	5.8	1310	376	213
		8.6	583	435	280
	MG hosted Qv	4.5	465	449	103
	MD hosted Qv	15.0	2880	365	103
Telfer Intrusion-related Cu-Au deposit, Australia	Aqueous-carbonic FIAs	10.0	621	328	196
		15.0	-	354	405
	Aqueous FIAs	10.0	171	272	44
		14.5	1270	378	1200

Notes: Lamego and Corrego do Sitio dataset (Morales et al. 2016), Telfer (Schindler et al. 2016). Abbreviations: CP=carbonaceous pelite, MG=metagreywacke, MD=mafic dike, Qv=quartz vein