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Magmatic Hydrothermal Fluids at the Sedimentary Rock-hosted, Intrusion-related Telfer Gold-Copper Deposit, Paterson Orogen, Western Australia: P-T-X Constraints on the Ore Forming Fluids

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Abstract

The Neoproterozoic Telfer deposit, one of Australia's largest gold-copper deposits is located in the Paterson Orogen. Several highly differentiated calc-alkaline to alkali-calcic peraluminous granites intruded the metasedimentary rocks near (5-20 km) Telfer contemporaneous with structurally controlled gold-copper mineralization.

Fluid inclusion assemblages with different fluid inclusion types were identified in samples from a range of different vein types. These inclusion types range from three phase aqueous $L_{aq}+V_{aq}+S_{halite}$, high salinity (≤ 50 wt % NaCl equiv), high temperature ($\leq 460^{\circ}$ C) inclusions to two phase aqueous or two phase aqueous carbonic, low to moderate salinity (2 - 22 wt % NaCl equiv.), moderate to high temperature ($\leq 480^{\circ}$ C) fluid inclusions.

Fluid inclusion trapping mechanisms, and interpreted precipitation mechanisms for gold and copper include: (1) adiabatic cooling between 450 and 200°C in all veins, and (2) locally, fluid phase separation at around 300°C. The trapping pressure of fluid inclusion assemblages trapped during phase immiscibility was calculated to be approximately 1.5 kbars. For fluid inclusion assemblages that lack evidence for phase immiscibility a pressure, at the temperature of final homogenization, of up to 3 kbars was calculated. This high pressure value is interpreted to be related to local fluid overpressure, as a consequence of fault zone movement, in faults and fractures that localized gold at Telfer. Phase immiscibility and gold precipitation was induced during sharp pressure decrease accompanying fault zone movement.

In situ laser ICP-MS analyses of fluid inclusions revealed high trace element contents in all fluid inclusion assemblages. Manganese/Fe ratios of < 0.24 in all vein types suggests that reduced fluids dominated the system, but locally, a switch to more oxidized conditions with Mn/Fe ratios > 0.24 is observed. Given the high temperatures and salinities of up to 480°C and 42 wt % NaCl equiv., Au and Cu were likely transported as chloride complexes. This interpretation is supported by the observation that the highest base metal contents occurs in the highest salinity fluid inclusion.

Potassium/Ca ratios of >1 in most assemblages, the high homogenization temperatures (\leq 480°C) in many fluid inclusion assemblages, and the high trace element contents (e.g., Fe, Mg, K, Na) in most of the fluid inclusion assemblages is compatible with involvement of a magmatic hydrothermal fluid during gold-copper mineralization. This fluid

was probably derived from the coeval granites in the Telfer area and, thus Telfer is interpreted to be a distal, intrusion-related, metasedimentary rock hosted, gold-copper deposit type.

Because of all the arguments mentioned above, Telfer can best be described as an unique intrusion-related, structurally controlled, metasedimentary rock hosted, gold-copper deposit.

Introduction

The Neoproterozoic Telfer gold-copper deposit, Western Australia (Fig. 1), is one of Australia's largest gold deposits with current resources of 15 Moz Au and 0.78 Mt Cu (Newcrest Resources and Reserve Statement, 2014). More than 10 Moz Au have been produced since its discovery in the 1970s, and the start of production in 1975. Gold mineralization is localized in folded and faulted metasedimentary rocks that are located within 10s of km to tin-tungsten bearing, and locally hydrothermally altered granites.

The genetic model for this world-class Au deposit has changed over time from a syngenetic sediment-hosted exhalative (e.g., Turner, 1982) to an epigenetic model with possible input from surrounding Neoproterozoic granitic intrusions (e.g., Goellnicht et al., 1989; Goellnicht et al., 1991; Rowins et al., 1997). Goellnicht et al. (1989) suggested a mix of magmatic and meteoric fluids for the deposit and a granitic gold-copper source. Rowins et al. (1997) modified this model and proposed that granite is the heat source for convection of hydrothermal fluids that may be partly derived from felsic magma, basinal brines, metamorphic fluids, or meteoric water. In this latter model, the sedimentary rocks are interpreted to be the source for the metals by leaching them with these hydrothermal fluids (Rowins et al., 1997).

Most of the gold systems in Western Australia are of the Archean orogenic gold only type (e.g., Yilgarn Craton, Yeats et al., 1999; Hagemann and Cassidy, 2001) and mineralization took place between 2700 and 2600 Ma. The late Neoproterozoic (ca. 640 and 590 Ma) Telfer gold-copper deposit appears, therefore, to be a unique gold deposit in Western Australia in terms of age. Furthermore, only few major gold deposits or districts of

similar age are known worldwide. These deposits are mainly related to the: (1) Pan-African orogenic event (e.g., the gold deposits of the Arabian-Nubian shield); (2) Brasiliano orogeny (e.g., gold deposits of the Brasilia fold belt in Brazil), or (3) Baikalide orogeny (e.g., gold deposits of the Baikal fold belt), although ages for this last group are poorly constrained and may well be much younger (Goldfarb et al., 2001, and references therein). All these major gold events, including the gold mineralization at Telfer, ended a worldwide period lacking major gold mineralization that lasted nearly 1.2 billion years (Groves et al., 2003).

New detailed geochronology has highlighted the coeval nature of Telfer gold mineralization to the regional granites (Schindler, 2014), again implying a relationship between granite emplacement and gold-copper mineralization at Telfer (c.f., Goellnicht et al., 1989; Rowins et al., 1997). We will present a detailed fluid inclusion study of ore forming fluids by microthermometry, laser Raman, and in situ laser ablation inductively coupled plasma mass spectrometry (laser ICP-MS) analyses of Telfer fluid inclusions. The P-T-X-t conditions of the hydrothermal ore forming fluids will put constraints on the genetic model of the Telfer gold-copper deposit and further highlight the important role of the surrounding granites to the process of mineralization.

Regional Geology

Telfer is situated in the northwestern part of the Neoproterozoic Paterson Orogen in Western Australia, a ~2000 km long belt of metamorphosed sedimentary and igneous rocks. The orogen extends from the Australian coast (northwest of Telfer), across the northern and central parts of Western Australia, through central Australia to western Queensland (Bagas, 2004, Fig. 1).

The oldest rocks of the Paterson Orogen are metamorphosed igneous and sedimentary rocks of the Paleoproterozoic Rudall Complex, with metamorphic grades reaching granulite facies conditions (Smithies and Bagas, 1997). The complex is exposed to the south of Telfer and is unconformably overlain by metasedimentary Neoproterozoic rocks of the Yeneena Supergroup that includes the Throssell and Lamil groups (Bagas, 2000).

Meta-sedimentary rocks of the Lamil Group host the mineralization at Telfer. These rocks consist of shallow-marine sandstone, shale, limestone and dolostone (Bagas, 2000), which are thought to have been deposited into an intracratonic basin, a failed rift or into a

pull-apart basin in an extensional strike slip system (Harris, 1987). The age of the Lamil Group is ca. 820 Ma (Bagas, 2003; Bagas and Nelson, 2007). Metamorphic grade is low, generally at greenschist facies conditions immediately around Telfer (Bagas, 2000).

The Lamil Group is divided into the Malu, Puntapunta, and Wilki formations (Bagas, 2000). The Malu Formation is the host for the Telfer gold-copper deposit and includes the Telfer Member at the top of the formation. The Malu Formation consists of quartz-rich sandstone, siltstone, and shale, with the Telfer Member being defined by a higher portion of siltstone and rare carbonate beds transitionally overlain by the Puntapunta Formation (Bagas, 2000).

The Puntapunta Formation transitional overlies the Malu Formation and comprises laminated to thinly bedded dark-grey dolomitic sandstone, dolomitic siltstone, chert, shale, and limestone. The Wilki Formation, the youngest formation of the Lamil Group, consists of silicified sandstone and minor shale (Bagas, 2000).

Several highly differentiated granite bodies intruded the Lamil Group between ca. 640 and 600 Ma. These are named the Mount Crofton Granite, Minyari Granite, Wilki Granite, and O'Callaghans Granite (Fig. 1). The Mount Crofton, Minyari, and Wilki granites are oxidized or magnetite series granites, whereas the O'Callaghans Granite is reduced or an ilmenite series granite. None of these granites are entirely sourced from a mantle-derived magma, but there are different proportions of mantle-derived magma involvement in the melts that formed each of the granites (Schindler, 2014).

Bagas and Smithies (1998) and Bagas (2005) recognized and described multi deformation and metamorphic events in the Paterson Orogen. The earliest deformation events are associated with a continent-continent collision that resulted in crustal thickening (up to ~35 km). The first deformation event recognizable in the Lamil Group around Telfer is the Miles Orogeny, a north-easterly to southwesterly shortening (resulting in open to close folding and faulting) associated with lower greenschist metamorphism (Bagas, 2000; Bagas, 2004).

The Paterson Orogeny is the last event affecting the Lamil Group at ca. 550 Ma. The age is not exactly constrained, but it postdates the deposition of ca. 610 Ma glacigenic sedimentary rocks of the Tarcunyah Group in the Officer Basin to the west of Telfer (Bagas and Smithies, 1998). This orogeny reactivated earlier structures and is also associated with north- to northwest-trending dextral faults indicating south-southwest directed shortening

(Williams, 1992). These structures are probably part of the cross-continental mega-shearing that affected the Paterson Orogen and the Petersmann Orogen between 650 and 550 Ma (Li and Evans, 2011).

The region surrounding Telfer also contains other important metal accumulations including the polymetallic tungsten-zinc-copper deposit O'Callaghans deposit associated with 640-600 Ma granitic magmatism. The O'Callaghans skarn (78 Mt @ 0.33 WO₃, 0.29 % Cu, 0.5 % Zn and 0.25 % Pb; Newcrest Resources and Reverse Statement, December, 2014), located approximately 10 km south of the Telfer Au-Cu deposit, comprises a sheet-like body of scheelite-wolframite-bearing amphibole-pyroxene-garnet replacement of metasedimentary rocks found immediately above the O'Callaghans granite.

Telfer Deposit Geology

Mineralization at the Telfer gold-copper deposit is located in different vein types hosted by folded and faulted metasedimentary rocks of the Malu Formation of the Lamil Group at the Telfer Dome. The dome, formed during the Miles Orogeny (Bagas, 2004), is a northwest trending structure that is made up of two en-echelon double plunging anticlines, known as the Main and West domes separated by a tight and faulted anticline (Goellnicht et al., 1989; Fig. 2 and 3).

Three different mineralization styles characterize the Telfer gold-copper deposit. There are: (1) bedding concordant (reef-type) veins; (2) discordant veins, crosscutting lithologies; and (3) breccia and stockwork type veins. The term "reefs" is used at Telfer for bedding sub-parallel, concordant and laterally extensive quartz-sulfide-gold or dolomitequartz-sulfide-gold veins with traces of scheelite (Fig. 4a, Fig.5). Average grades of the reefs are between ~5 to ~50 g/t Au and 0.2 % to 1.5 % Cu (Technical report Telfer property, 31st December 2011, newcrest.com.au). The discordant veins are subdivided in northeast trending veins that dip ~45° to the northwest (NE veins), and east-northeast trending veins that dip steeply north-northwest or south-southeast (ENE veins). The former ones consist of quartz-carbonate-sulfide-gold, and the latter ones of carbonate-quartz-sulfide-gold. Carbonates consist of pink to grey dolomite with minor amounts of calcite. Traces of scheelite are found in both sub-types (Fig. 4c, and Fig. 5), together with different accessory minerals (Fig. 6). Gold and copper grades for these veins are similar to those in the reefs.

The mineralized breccia and stockwork type veins are located underground in a subvertical zone parallel to the fold axis of the Main Dome. This zone is called 'vertical stockwork corridor' (VSC). The stockwork type veins consist of dolomite-quartz-sulfide-gold and the breccia type consists of clasts of wallrock with a matrix of dolomite-quartz-sulfidegold (Fig. 4d, and Fig. 5). The exact timing relationship between these different vein types is presently equivocal; Maidment et al. (2010) suggested that the reefs were emplaced first, followed by stockwork and discordant veins. Recent underground mapping has found evidence for mutual crosscutting relationship between the different vein types (pers. comm. John Miller and Geoff Batt). Several pulses of hydrothermal activity formed alternating reefs and discordant veins.

The dominant sulfides in all vein types are pyrite and chalcopyrite with minor amounts of pyrrhotite and trace amounts of different Pb-Zn-Co sulfides. Furthermore, traces of Au-Ag tellurides, xenotime, monazite, tourmaline, and rutile are present in most of the reefs (Rowins et al., 1997). In reefs of upper levels, bornite and chalcocite replace chalcopyrite as a product of supergene enrichment. Gold is present as free gold inclusions in pyrite, as crack infill in pyrite and chalcopyrite, in the lattice of pyrite, as Au-telluride (calaverite) or Au-Ag-telluride (sylvanite), or as electrum inclusions in pyrite (Davies, 2013).

Stratigraphic thickness of the overlying sedimentary rocks implies that the mineralization at Telfer formed beneath a combined rock package up to 5 km thick (Bagas, 2000). Regional lower greenschist facies metamorphism supports that depth estimate, and no higher metamorphic grade rocks are recognized in the proximity of the Telfer deposit. All metasedimentary rocks of the Telfer Dome are affected by hydrothermal sericitization, silicification and lesser carbonate (calcite-dolomite) and tourmaline replacement (Goellnicht et al., 1989), with alteration most intensely developed immediately around the veins and breccias (Rowins et al., 1997). Chlorite alteration is reported as fracture coating and as a subtle pervasive alteration proximal to mineralization. The exact timing relationship of this chlorite alteration is ambiguous and earlier studies suggest that it may not be related to gold-copper mineralization (unpublished Newcrest report, James Maxlow, 2007). Intensity of hydrothermal wallrock alteration also depends on the type of lithology, with argillaceous sandstones and calcareous siltstones showing strong sericite-carbonate alteration and quartz rich sandstone showing strong silica alteration (Rowins et al., 1997).

Timing of mineralization:

Early research work on Telfer in the 1970s and 1980s favored a syngenetic model for mineralization (Tyrwhitt, 1979, 1985; Turner, 1982). However, as deeper levels of the deposit were exposed, it became evident that mineralization was predominantly hosted in structurally controlled sites related to folds and faults (Goellnicht et al., 1989; Dimo, 1990; Goellnicht, 1992; Hewson, 1996; Rowins et al., 1997; Howard et al., 2005). Consequently, an epigenetic origin for the deposit was proposed by Goellnicht et al. (1989) and subsequently expanded on by Rowins et al. (1997).

Published SHRIMP and ID-TIMS U-Pb ages of monazite and xenotime suggest that the Telfer mineralization took place between 659 Ma and 638 Ma, but these results show evidence of isotopic disturbance (Maidment et al., 2010). Furthermore, younger U-Pb ages of around 592 Ma of a monazite sample from the A reef at Main Dome (Fig. 3) are reported as well (unpublished internal company report, Newcrest). These hydrothermal U-Pb ages overlap (including within analytical uncertainty) with the timeframe of magmatism known from the Telfer district. U-Pb zircon geochronology shows that granite emplacement took place between ca. 645 and ca. 600 Ma, with clusters at ca. 630 and a single granite at 600 Ma (the O'Callaghans Granite, Maidment et al., 2010; Schindler, 2014). Although there is a close temporal relationship between the Mount Crofton Granite, Minyari Granite, Wilki Granite, and O'Callaghans Granite, and gold mineralization, Maidment et al. (2010) stated that the lack of a close spatial association (< 5 km) suggests that granite emplacement was potentially not directly involved in the mineralizing system.

Modeling of FALCON gravity geophysical data sets highlight large concealed intrusions, including the O'Callaghans Granite, extending underneath Telfer (Mackey, 2012). This observation, combined with the significant Au-Cu and W-(Sn) association in the district shares many similarities to the better documented intrusions-related deposits in for example the Tintina belt (Thompson et al., 1999; Thompson and Newberry, 2000; Hart et al., 2002).

Past studies of ore forming fluids

The first fluid inclusion study of samples from gold-bearing veins at Telfer was conducted by Collins (1985) followed by Goellnicht (1987). Both authors analyzed samples

from the upper parts of the deposit, and pointed out the complex composition of fluid inclusions with high salinities between 20 and 50 wt % NaCl equiv., and homogenization temperatures between 150 and 440°C. These same studies also reported significant amounts of CO₂ and minor amounts of CH₄. Both authors also reported the similarities of fluid inclusions independent of vein type or location in the deposit. Goellnicht et al. (1989) combined fluid inclusion physicochemistry with Pb-Pb isotopes and trace element analyses of sulfides from the same areas of the Telfer deposit and concluded a strong magmatic fluid input with minor mixing with cooler, less saline meteoric fluids.

Rowins et al. (1997) conducted δ^{34} S isotope and S/Se analyses of pyrite, δ^{13} C and δ^{18} O isotope analyses of carbonates from mineralized veins and barren host rocks, and δ^{11} B isotope and major element analyses on hydrothermal tourmaline. Based on these analyses, they reinterpreted the role of the granite as only providing the heat for driving thermal convection cells. These authors concluded the involvement of basinal brines as the primary ore forming fluid, with leaching of regional sedimentary rocks as the ultimate source of metal and sulfur. Despite this, the δ^{11} B isotopes of hydrothermal tourmaline from Telfer imply mixing of granite-derived boron with marine evaporate, or carbonate-derived and/or clastic sedimentary sourced boron (Rowins et al., 1997).

Petrography

Reef samples

Fluid inclusion observations were made on samples collected from the M50 reef, the 130 reef, and the so called 'mineralized Limey Unit' (see Fig. 3). The M50 reef is located around 500 m below the ground surface between a layer of carbonaceous siltstones in the hanging-wall and calcareous sandstones in the footwall. The thickness of this gold-bearing reef varies from 0.1 to 2.0 m and consists of quartz, pink and grey dolomite, calcite, muscovite, pyrite, chalcopyrite, bornite, and chalcocite, with traces of scheelite, pyrrhotite, sphalerite, cassiterite, tellurobismuthite and other tellurides.

The I30 reef is located around 1000 m below the surface above the Limey Unit, and its thickness varies between ~10 m in the hinge zone to 0.5 m on the flanks of the fold structure of the Main Dome. The reef consists of quartz, white and pink dolomite, calcite,

sulfides, and traces of scheelite and gold. The sulfides in the I30 are mainly pyrite and chalcopyrite with traces of bornite, galena, and stibnite, and very rare bismuth tellurides.

The mineralized Limey Unit is between 5 and 10 m thick and is slightly different to the first two reefs mentioned above, as it displays a replacement style rather than a real vein. The unit consists of sandstone and interstitial carbonate infill (Maxlow, 2007) and in the mineralized area this unit is replaced by a dolomite-muscovite-sulfide assemblage. The main sulfide is pyrite with minor chalcopyrite and traces of scheelite, stibnite, and very rare bismuth tellurides.

Fluid inclusions: All carbonate samples have only rare fluid inclusions. Limited two phase liquid and vapor inclusions were observed in dolomite and three phase inclusions, with most probably halite daughter crystal, were observed in only one sample of dolomite. Microthermometric measurements could not be conducted because all these inclusions decrepitated upon freezing and heating. Fluid inclusions in quartz are abundant and three different types of inclusions were identified based on observation at room temperature (Table 1): (1) Aqueous two phase liquid (L_{aq}) and vapor (V_{aq}) inclusions, most of them being liquid rich with ~10 vol % vapor; (2) three phase inclusions with $L_{aq}+V_{aq}$ and one (halite) or more crystals (S), again liquid rich with around 10 vol % vapor and up to 15 vol % solids. The second solid was identified as calcite with laser Raman analyses; and (3) two phase inclusions with L_{ag} and carbonic vapor (V_{carb}) or three phase inclusions with L_{ag} + carbonic liquid (L_{carb}) + V_{carb}, both being mostly rich in aqueous liquid with the carbonic phase occupying around 10 vol %. Rare vapor-rich two phase Lag+Vcarb inclusions were observed with up to 95 vol % vapor. The focus of this investigation was on fluid inclusions that either occur as internal trails in single quartz crystals, not crosscutting grain boundaries or that occur as internal clusters (Fig. 7a and b), implying a primary or pseudosecondary origin. Only quartz crystals that are in textural equilibrium with sulfides of the main gold stage, paragenetic stages 2 and 3 (Fig. 6) or in textural equilibrium with visible gold (Fig. 7b) were chosen. These inclusion types are trapped in the following assemblages: (1) assemblages that contain three phase L_{aq}+V_{aq}+S_{halite} fluid inclusions only; these assemblages form in clusters or internal trails (Fig 6a); (2) assemblages that contain L_{ag}+L_{carb}+V_{carb} fluid inclusions and form clusters or internal trails. Commonly, the carbonic phase is only identified during freezing runs; (3) assemblages that contain $L_{aq}+V_{aq}+S_{halite}$ inclusions together with vapor rich $L_{aq}+V_{carb}$ inclusions, trapped in clusters (Fig. 7b); and (4) assemblages with $L_{aq}+V_{aq}$ fluid inclusions only, located in internal trails only.

The upper reef (M50 reef) contains more aqueous fluid inclusions than carbonic inclusions, whereas the lower reefs (I30 reef and mineralized Limey Unit) had more carbonic fluid inclusions and less aqueous inclusions. Cathodoluminescence images did not reveal any important growth zonation in the single fluid inclusion assemblages.

Discordant vein samples

Both types of discordant veins were sampled, which are typically located in deeper parts of the main Telfer deposit. Samples were taken from different levels of the underground mine, from around 900 m to >1000 m below the surface and also from diamond drill cores intersecting these veins at similar depth. The sampled east-northeast trending veins are up to 0.85 m wide, and consist of quartz, grey and pink dolomite, pyrite, chalcopyrite, minor muscovite and traces of cassiterite, galena, sphalerite, stannite and gold. The sampled northeast trending veins are similar in width and consist of pink dolomite, quartz, pyrite, chalcopyrite, minor muscovite, scheelite and galena, and traces of cassiterite, sphalerite, stannite, tellurobismuthite and gold.

Fluid inclusions: Fluid inclusions in carbonates are uncommon, but are abundant in quartz for both discordant vein types. Furthermore, some fluid inclusions trapped in scheelite were observed. The host quartz and scheelite crystals are in textural equilibrium with sulfide-gold mineralization (Fig. 4c). The same three fluid inclusion types as in the reef samples (Table 1), and a fourth inclusion type, with three phases $L_{aq}+V_{carb}+S_{halite}$, liquid rich with around 10 vol % vapor and up to 15 vol % solids, was identified in samples from discordant veins. Identical fluid inclusion assemblages occur in both discordant and reef samples, only assemblages that contain $L_{aq}+V_{aq}+S_{halite}$ inclusions together with vapor rich $L_{aq}+V_{carb}$ inclusions (assemblage type 3), are absent in the discordant veins. Instead, fluid inclusion assemblages only (Fig. 4) which are located in clusters (type 5) occur in samples from the discordant veins. As in samples from the reefs, CL images did not show any zonation within the single quartz grains.

Stockwork samples

Samples from the VSC were collected from diamond drill core intersecting the VSC at a depth of ~ 1000 m below surface. The samples consist of pink dolomite, quartz, pyrite, chalcopyrite and minor muscovite. Traces of sphalerite, stannite, and pyrrhotite are present in the veins and the matrix of breccia.

Fluid inclusions: As in all other vein types and samples, fluid inclusions in the dolomite are very rare; even in quartz there are less inclusions than in samples from any other vein type. Three different fluid inclusion types were identified in the quartz (Table 1): (1) two phase $L_{aq}+V_{carb}$ (type 3), all of them are liquid rich with the vapor being around 10 vol %; (2) three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions (type 2), and (3) three phase $L_{aq}+V_{carb}+S_{halite}$ fluid inclusions. Both of the latter fluid inclusion types have the same proportions of liquid, vapor and solid as in samples from the reefs. The fluid inclusion assemblages in samples from the VSC contain only one fluid inclusion type. Again, CL did not show any growth zonation in the host quartz grains, which are in textural equilibrium with the mineralization.

Results

Microthermometry and laser Raman analyses

Many of the following homogenization temperatures (Th_{LV-V}), dissolution temperature of halite (Tm_{halite}), and salinities calculated from Tm_{halite}, are only minimum values, as many of the inclusions decrepitated before Th_{LV-L}, Tm_{halite} or both, and, therefore, these temperatures represent decrepitation temperatures (T_{decrep}). The range of these temperatures for all different fluid inclusion assemblage types and vein types is provided in Table 2, and illustrated in Figure 8 which also shows the amount of decrepitated fluid inclusions.

Fluid inclusion assemblage type 1: Fluid inclusion assemblages that contain $L_{aq}+V_{aq}+S_{halite}$ ($\pm S_{calcite}$) inclusions only are highly saline (31 to 50 wt % NaCl equiv.) for all vein types with the highest salinities observed in the reefs and in the discordant ENE veins. Eutectic temperature was between -65 and – 55°C, indicating a mix of different salts, for example NaCl-KCl-CaCl₂-MgCl₂ and possibly including FeCl₃ or other rare metal chlorides (c.f., Roedder, 1984; Goldstein and Reynolds, 1994; Goldstein, 2001). This very low eutectic

temperature may also represent a metastable phase transition instead of true first melting, so the implications for salt composition has to be taken with care (e.g., Bakker and Baumgartner, 2012). The eutectic temperature in samples from the VSC was slightly higher, around -35°C and may indicate a more simple salt composition, for example only NaCl-KCl-MgCl₂ in the VSC.

More than half of these inclusions have final homogenization by halite dissolution (36 out of 62, including some inclusions that decrepitated after vapor homogenization, but before Tm_{halite}). Fifteen fluid inclusions decrepitated before either halite dissolution or vapor bubble disappearance and only eleven exhibited final homogenization by vapor disappearance. Trapped calcite crystals, identified by laser Raman analyses, are interpreted to be accidently trapped, as no change in size (i.e., dissolution) upon heating was observed. This interpretation is further corroborated by the solubility of calcite that decreases with increasing temperature at the T-X_{salinity} conditions measured for these inclusions (Fein and Walther, 1987; Caciagli and Manning, 2003). Although no carbonic phases (e.g., CO₂, CH₄) could be identified at room temperature or during freezing runs, laser Raman analyses revealed CO₂ (< 8 mol %), minor CH₄ (< 6 mol %) and locally traces of N₂ (< 0.1 mol %) in the gas phase of many of these inclusions. The mole fraction of CH₄ in the vapor phase (X_{CH4}) varies from zero to 0.85, but generally inclusions that contain CO₂ and CH₄ have a X_{CH4} of less than 0.60. The Th_{final} of fluid inclusions in assemblages with L_{ag}+V_{ag}+S_{halite} (±S_{calcite}) inclusions only has a wide spread, ranging from 215 to 454°C. Vapor homogenization temperature into liquid range from 143 to 440°C. There is no distinguishable difference in salinities and homogenization temperatures for fluid inclusions trapped in samples from shallow depth (500 m below present surface) or deeper levels (at 1000 m below present surface). Fluid inclusion data reported from Goellnicht et al. (1989) for very shallow levels, < 100 m below the present surface, suggest a similar P-T-X range to the results presented here, although there is no detailed subdivision in single fluid inclusion assemblages reported in this publication.

Fluid inclusion assemblage type 2: The assemblage type 2 contains $L_{aq}+V_{carb}$ fluid inclusions only and there are several subgroups (based on large difference in the salinities of these inclusions). The first subgroup was only identified in samples from the discordant ENE veins and has very low salinity (< 0.1 wt % NaCl equiv), no first and final ice melting could be identified in these inclusions and the salinity was calculated from clathrate melting at +10°C.

The final homogenization temperature of this group is between 200 and 485°C. The second subgroup has low to moderate salinities (8 - 17 wt % NaCl equiv.) and a wide spread of Th_{LV-L} from as low as 150°C up to 365°C. The third group has moderate salinities (~20 wt % NaCl equiv.) with homogenization temperatures slightly lower than the previous two groups (157 - 260°C). The lowest temperatures are from fluid inclusions trapped in scheelite in the discordant ENE veins. Homogenization temperature for quartz hosted inclusions of the third subgroup range from 232 to 260°C. Both of the latter two subgroups are present in all different vein types at Telfer. In addition to CO₂, all fluid inclusions from this assemblage type have small amounts of CH₄ (up to 13 mol %, with an average of 2 mol %) indicated by Tm_{CO2} between -59.8 and -57.0°C and confirmed by laser Raman analyses. No other gas species was identified in addition to CO₂ and CH₄. No eutectic temperatures were observed in any of the samples.

Fluid inclusion assemblage type 3: Fluid inclusion assemblage type 3 is only present in the reef samples and comprises two different types of fluid inclusions. The three phase L_{aq}+V_{aq}+S_{halite} inclusions have minimum salinities between 36 and 42 wt % NaCl equiv. with all inclusions decrepitating before Tm_{halite}. The decrepitation temperatures for these fluid inclusions range from 285 to 340°C. Eutectic temperature of these inclusions is between -60 and -68°C, again indicating the involvement of complex metal chlorides (c.f., Roedder, 1984; Goldstein and Reynolds, 1994; Goldstein, 2001). Laser Raman revealed between 15 and 83 mol % CO₂ and between 17 and 85 mol % CH₄ in the vapor phase of these inclusions which was not observed during freezing measurements. The two phase carbonic fluid inclusions in these assemblages have very low salinities (~ 1 wt % NaCl equiv), all are vapor rich with around 95 vol % vapor phase and have decrepitation temperatures (no final homogenization temperature could be obtained) of 275°C. Very low Tm_{CO2} of -67.5 to -66.0°C and laser Raman analyses revealed large amounts of CH₄ (up to 66 mol %) and traces of N₂ in these vapor rich inclusions. The homogenization temperature of the carbonic phase (Th_{CO2}) in these inclusions is extremely low with temperatures of -56.4 to -52.2°C, calculated density of the carbonic phase is therefore relatively low with values between 0.44 and 0.55 g/cm³. No eutectic temperatures were observed for this fluid inclusion type.

Fluid inclusion assemblage type 4: Fluid inclusion assemblage type 4 with $L_{aq}+V_{aq}$ inclusions only is only present in samples from discordant NE trending veins or in the mineralized Limey Unit. The inclusions in the reef sample are moderately saline with 21 wt

% NaCl equiv. and have Th_{LV-L} from 240 to 241°C. No eutectic temperature was observed for these inclusions. The inclusions in the discordant veins are less saline (10 - 14 wt % NaCl equiv.) and have low eutectic temperatures (-60 to -55°C), and a wider spread of Th_{LV-L} from 143 to 343°C.

Fluid inclusion assemblage type 5: Fluid inclusion assemblage type 5 was only observed in samples from the discordant ENE veins and from the VSC. The main difference from the fluid inclusion assemblage type 1 is the higher amount of CO₂ and CH₄ in the vapor phase in the assemblage type 5 inclusions, which made observation of the carbonic phase transitions possible with an optical microscope. The assemblage type 5 inclusions have a salinity of 31 to 35 wt % NaCl. The Th_{final} for fluid inclusions from these assemblages are between 180 to 325°C, and as in all other cases described so far, decrepitation is quite common so real salinities and real homogenization temperatures may well be in the same range as in assemblage type 1 inclusions. Again no eutectic temperature could be observed.

Laser Ablation ICP-MS analyses

Results from 105 three phase $L_{aq}+V_{aq}+S_{halite}$ and 45 liquid rich two phase $L_{aq}+V_{aq}$ fluid inclusions hosted in quartz and 9 liquid rich two phase $L_{aq}+V_{carb}$ inclusions hosted in scheelite, were used for the determination of the major and trace element composition (Na, Mg, K, Ca, Mn, Fe, Cu, Zn, Sr, Ba, Pb) and the results of another 46 $L_{aq}+V_{aq}+S_{halite}$ and 18 $L_{aq}+V_{aq}$ fluid inclusions, hosted in quartz, for the determination of the As, Mo, Ta, W, and Au content of the ore forming fluid. The analytical results for all the different fluid inclusion types are given in Table 3. As the results do not show a normal distribution, we do not use average and standard deviation values, but refer to median, minimum and maximum values instead. Analyses of fluid inclusions in dolomite did not provide acceptable results due to contamination of the host mineral by several unidentified mineral inclusions. In addition, there was also no reliable microthermometry data for these inclusions. The high Ca content of scheelite masked the Ca content of the fluid inclusions trapped in scheelite, so no reliable results for Ca in fluid inclusions from scheelite were obtained. As scheelite can also contain several hundreds to thousands ppm Sr (e.g., Bell et al., 1989), the Sr content of the fluid inclusion is also obscured by the Sr content of the host mineral. Most of the fluid inclusions in any vein type are Na dominated with K/Na and Ca/Na ratios of < 0.3. Only three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions from one of the discordant ENE veins are strongly enriched in Ca with a median Ca/Na ratio of 0.59 and a median (K+Ca)/Na ratio of 0.87 (Tab. 3). These samples contain several inclusions with solid halite and calcite. As stated above, however, calcite is not regarded as a true daughter crystal, but is interpreted as an accidentally trapped phase. Therefore, analyses of inclusions containing a calcite crystal were discarded and the Ca/Na ratio of 0.59 represents the real fluid ratio from inclusions without accidentally trapped calcite. The only fluid inclusions strongly enriched in K were detected in samples from the M50 reef with a median K/Na ratio of 0.63 and median (K+Ca)/Na ratio of 0.95 (Table 3).

Most of the inclusions, irrespective of the vein type, are enriched in Fe with a maximum value of ~48,000 ppm for the high salinity inclusions. Three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions from samples from the reefs have relatively high Mn values up to ~12,000 ppm. Manganese/Fe median ratios are <0.24 for all polyphase fluid inclusions containing solids and for two phase $L_{aq}+V_{aq}$ or $L_{aq}+V_{carb}$ inclusions hosted in quartz from both discordant vein types and the VSC. Two phase $L_{aq}+V_{carb}$ inclusions in quartz from the I30 reef have an extreme high median Mn/Fe ratio of 0.92 and two phase $L_{aq}+V_{carb}$ inclusions in scheelite from the discordant ENE veins have high median Mn/Fe ratios of 0.31. The overall high values of K, Ca, Mg, and Fe are in accordance with the commonly very low T_e measured during freezing runs that suggests a NaCl-KCl-MgCl₂ ± CaCl₂ ± FeCl₃ fluid composition.

The Cu, Zn, and Pb values of the fluid inclusions are on average four, eight, and six times higher, respectively, in the analyzed three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions than in the two phase $L_{aq}+V_{aq}$ or $L_{aq}+V_{carb}$ inclusions (all values reported here for Cu, Zn, and Pb are median values of each inclusion type and vein type). Copper values are highest in $L_{aq}+V_{aq}+S_{halite}$ fluid inclusions hosted in quartz from both types of the discordant veins and in some of the reef samples with median values up to 3199 ppm (Tab. 2, Fig. 9). Three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions in quartz from the VSC and in scheelite from the discordant ENE vein have much lower Cu values between 191 and 249 ppm. Two phase $L_{aq}+V_{aq}$ or $L_{aq}+V_{carb}$ fluid inclusions have the highest Cu values with up 621 ppm in samples from the I30 reef and, similar to the multi phase inclusions, the lowest values of < 23 ppm in scheelite from the vein the vein the discordant ENE vein, with no copper detected in fluid inclusions in quartz from this vein at all. Zinc values are highest in the three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions in quartz of the I30

reef with 5731 ppm and three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions in scheelite from the discordant ENE vein with 2029 ppm. The Zn values of three phase $L_{aq}+V_{aq}+S_{halite}$ fluid inclusions in the other veins are between 464 and 1151 ppm. For two phase $L_{aq}+V_{aq}$ or $L_{aq}+V_{carb}$ fluid inclusions, the highest Zn values are in inclusions in quartz of the discordant ENE vein with 313 ppm and the other veins have Zn values between 113 and 290 ppm for the two phase $L_{aq}+V_{aq}$ or $L_{aq}+V_{aq}+S_{halite}$ inclusions. The Pb content is again highest for three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions from the I30 reef with a median value of 1151 ppm followed by three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions in quartz and scheelite of the ENE trending discordant veins with 567 and 819 ppm, respectively. Two phase $L_{aq}+V_{aq}$ or $L_{aq}+V_{carb}$ inclusions of all vein types have again lower values of Pb between 56 ppm for the VSC and I30, and 176 ppm for inclusions from quartz of the discordant ENE veins.

Arsenic was detected in two $L_{aq}+V_{aq}$ inclusions of the discordant NE veins with again a wide spread from 33 to 155 pm. Three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions had measureable As, in a total of 16 inclusions from all different vein types, except from the I30 reef. Inclusions in quartz from the M50 reef have the highest single value of As of 1584 ppm although the median values for all vein types are more homogenous with a range from 119 to 167 ppm. This highest value may represent the analyses of a sub-micron arsenopyrite inclusion. No As was detected in the three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions of the I30 reef.

Both Mo and W were detected in rare inclusions in quartz. Five two phase $L_{aq}+V_{aq}$ fluid inclusions from the NE trending discordant veins show some W with values between 20 and 466 ppm. No other vein type has two phase $L_{aq}+V_{aq}$ or $L_{aq}+V_{carb}$ inclusions containing W. Three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions have, in general, more W, with the highest values observed for the M50 reef with a maximum value of 6158 ppm and a median value of 4734 ppm. The other analyzed fluid inclusions show median values between 25 and 100 ppm (for the different vein types). Molybdenum was detected in two three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions from the M50 reef and these two values have an extremely wide spread from 3 to 2666 ppm. This high value is believed to be an outlier as no other Mo was detected in any fluid inclusion and may represent a sub-micron molybdenite grain.

Discussion

Fluid source and metal transport

Since the discovery of the Telfer gold-copper deposit, the genetic model of the deposit, and consequently the metal and fluid source, has been debated. Earliest studies proposed an exhalative origin (Tyrwhitt, 1979; Turner, 1982). A variation on this, whereby the Middle Vale reef, one of the first discovered reefs, was considered to have formed as an evaporite horizon that was subsequently replaced by quartz-sulfide assemblages, was proposed by Royle (1985, unpublished Newmont Australia company report). Structural observations combined with fluid-inclusion studies implicated magmatic fluids in the formation of the ore-assemblage (Goellnicht, 1987). It was concluded that magmatic fluids from the regional granitoids had mixed with cooler connate/formational waters, and had precipitated in structurally controlled, and compositionally favorable, sites in the Telfer Dome (Goellnicht, 1987; Goellnicht et al., 1989). Subsequently, the role of the granites was downplayed, suggesting that they acted more as heat sources to convectively circulate connate/contact-metamorphic fluids that scavenge elements from the sedimentary sequence (Rowins, 1994).

Magmatic versus basinal brine fluid source: The high salinities of up to 50 wt % NaCl equiv., the high homogenization temperatures and decrepitation temperatures of up to ~450°C, and the presence of CO₂–CH₄ in the ore forming hydrothermal fluids are common in granite-associated tin-tungsten-copper and gold deposits (e.g., Wilkinson, 2001; Baker, 2002) and less commonly in porphyry copper systems (e.g., Roedder, 1984; Ulrich et al., 1999), both of which are clearly associated with magmatic activity and magmatic fluids (Fig. 10). Although the high amounts of CO₂ and CH₄ are not common in typical porphyry copper deposits (Wilkinson, 2001), these carbonic species have been reported in some more reduced porphyry deposits, including the San Anton porphyry gold-copper deposit in Mexico as well as in some smaller prospects near the Telfer deposit (Rowins, 2000). The lower temperature, lower salinity fluid inclusions (assemblage types 2 and 5 at Telfer) are commonly found in orogenic lode gold deposits (Fig. 10b). The high content of major elements (Na, Mg, K, Ca, Fe), including base metals (Mn, Cu, Zn, Pb) in all fluid inclusion assemblages are compatible with the characteristic composition of magmatic hydrothermal

fluids provided by Yardley (2005). The only other 'typical' fluid source for these highly saline fluid inclusions would be basinal brines. However, according to Yardley (2005) and Wilkinson (2001) typical basinal brines have lower Fe, Mg, and K content and generally higher Ca content than the fluid inclusion assemblages at Telfer.

According to Haynes and Kesler (1988), fluids with K/Ca ratios > 1 are mainly characteristics of magmatic derived hydrothermal fluids. The K/Ca ratios at Telfer are > 1 for all fluid inclusion assemblages and vein types except for the highly Ca enriched type 1 assemblages from the ENE trending discordant veins. The lower K/Ca ratios of < 1 for fluid inclusion assemblages with three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions from these discordant veins cannot easily be explained by a completely different fluid source or mixing with non-magmatic fluid at a later or early paragenetic stage. The metal budget, homogenization temperature and total salinity of the veins with lower K/Ca ratios are similar to other veins which have the higher K/Ca ratios. However, the lower K/Ca ratios are compatible with fluid-rock interaction (c.f., Baker et al., 2004), for example, buffered by the calcareous wall rocks at Telfer. This explanation appears more plausible than calling upon a different (unidentified) fluid source or fluid type.

Oxidation state of ore forming fluid: Bottrell and Yardley (1991) proposed that the Mn/Fe ratio in fluids reflects the oxidation state of a hydrothermal fluid provided that it equilibrated with chlorite. As there are only minor amounts of chlorite in veins or in the wall rocks at Telfer and the exact timing of this chlorite alteration is ambiguous, this ratio is only used as an approximation of the oxidation state. Most of the fluid inclusion assemblages have fluid Mn/Fe ratios < 0.24 and are interpreted to be originated from a reduced fluid (Bottrell and Yardley, 1991). Pyrrhotite inclusions in pyrite observed as part of detailed petrographic work (Davies, 2013) and the high CO₂-CH₄ content of some Telfer inclusions support the reduced nature of the ore forming fluids relative to the fayalite-magnetitequartz buffer (FMQ, c.f., Tomkins, 2010) at the high temperatures reported. The only fluid inclusion assemblages with higher Mn/Fe ratios are type 2 assemblages with two phase L_{aq} + V_{carb} inclusions in quartz from the I30 reef with high median Mn/Fe ratios of 0.92 and type 2 assemblages in scheelite from the discordant ENE veins with median Mn/Fe ratios of 0.31, both indicating that these trapped fluids were more oxidizing than the other fluid inclusions (e.g., Bottrell and Yardley, 1991; Baker et al., 2006). The granites around Telfer that are spatially and temporally related to gold-copper mineralization at Telfer are mainly

oxidized relative to FMQ, except for the O'Callaghans granite which is reduced relative to the FMQ (Schindler, 2014). The more reduced state of the ore forming fluid would imply a change of oxidation state from the source (the granites) to the trap (Telfer deposit) except for the fluid that has been potentially sourced from the O'Callaghans Granite and, therefore, an interaction of the magmatic fluids with the sedimentary rocks surrounding the deposit.

Gold transport: The higher concentration of Cu, Pb, Fe in the high salinity, three phase $L_{aq}+V_{aq}+S_{halite}$ fluid inclusions that are present in all veins at Telfer, supports a hypothesis that metals, such as Au and Cu, were transported as chloride complexes. High temperature X-ray absorption spectroscopy has shown that natural polyphase brine fluid inclusions trapped in granites similar to those in the Telfer district, has copper as $[CuCl_2]^-$ at magmatic temperatures (between 200 and 700°C, Berry et al., 2009). Given the high temperature (plus 450°C), and saline nature of the Telfer fluid inclusions, it is inferred that chloride was the dominant anion for the transport of copper, and by association of gold and copper, there is strong evidence that the gold was transported as a chloride complex at Telfer as well.

The high K/Ca ratio (> 1), the medium- to high-trapping temperatures, the high salinities, and the high major and trace element content of the ore forming fluid are consistent with typical magmatic fluids and shows that there was a strong magmatic input in the Telfer gold-copper system. Whether the metals are leached from sedimentary rocks, derived directly from the granitic magmas and/or deep seated mafic/ultramafic magmas is still unclear. Goellnicht et al. (1989) preferred the granites of the Telfer area as a fluid and metal source. Based on C, O, B, Pb and S-isotope data, Rowins et al. (1997) suggested that the sedimentary rocks around Telfer are the source for the metals that were leached by basinal brines. Goellnicht (1992) and Rowins et al. (1997, see Fig 4 therein) agree that the range of Pb isotope values from different sulfides of the mineralized veins at Telfer show that a mixture of magmatic fluids, derived from the Mount Crofton, Minyari, Wilki, and O'Callaghans granites, reacted with the sedimentary rocks of the Lamil Group that surrounds the granites and the Telfer gold-copper deposit. Although Rowins et al. (1997) favor a sedimentary source for metal, sulfur, and fluid, they stated that the range of δ^{34} S from sulfides in the Mount Crofton Granite (δ^{34} S of 1.8 and 2.0 ‰) is within the range of δ^{34} S from sulfides associated with gold-copper mineralization at the Telfer deposit (δ^{34} S between – 4.0 and 9.3 ‰). Therefore, they concluded that a magmatic derived fluid, which

interacted with regional sedimentary rocks, cannot be excluded as a source for the mineralizing fluids. Similar interpretations are valid for δ^{11} B values (Rowins et al., 1997) of hydrothermal ore fluids calculated from tourmaline boron isotope composition at Telfer (δ^{11} B between -9.0 to -1.6 ‰). These values are interpreted to be either the result of: (1) fluid-rock interaction between magmatic derived fluids with light δ^{11} B (-14.2 to -13.2 ‰ for the Minyari Granite, Rowins et al., 1997) and sediment-derived fluids with heavy δ^{11} B (> 10 ‰ for marine carbonates or evaporates, c.f., Bast et al., 2014), or (2) entirely derived from clastic sedimentary rocks of the Lamil Group. Rowins et al. (1997) emphasize, however, that the geochemical composition of tourmaline at Telfer (dravitic) favors a derivation from the clastic sedimentary rocks of the Lamil Group. In addition, the significant lateral distance between granites and Telfer (> 5 km) suggests interaction between the magmatic fluid and the sedimentary rocks along the pathway.

Assuming the gold content of the sedimentary rocks around Telfer averages 2 ppb (Goellnicht, 1992) and that the leaching and subsequent precipitation efficiency of the gold was 100 %, a volume of around 140 km³ is needed to account for the (minimum amount of) 25 Moz of gold mineralization at the Telfer deposit. Applying the same variables for the granites assuming an average gold value for the Mount Crofton, Wilki and Minyari granites of 1 ppb (Schindler, 2014), an estimated volume of around 290 km³ of granite is needed to deliver the gold at Telfer. With the O'Callaghans Granite having single samples with much higher gold values (up to 80 ppb, Schindler, 2014), a much smaller overall rock volume would be needed. However, if the efficiency of leaching and precipitation of gold was reduced to, for example, 60 % for sedimentary rocks and granites, approximately 380 km³ and 815 km³, respectively, would be necessary to account for the gold. As the most realistic value is probably between the two assumed values used above, both sources for gold are feasible and consequently none of them can be excluded. Therefore, the exact metal source for metals at the Telfer gold-copper deposit is presently considered to be equivocal and cannot be defined by fluid inclusion data alone.

Trapping conditions

Determination of the true trapping conditions of the formation of Telfer mineralization was made difficult due to the common decrepitation of fluid inclusions on

freezing or heating. Fluid inclusions that were trapped in a single phase field and were not affected by post entrapment modifications should have similar Th_{final} and salinities within a given assemblage (Lecumberri-Sanchez et al., 2012). It is also difficult to determine, whether the multiphase $L_{aq}+V_{aq}+S_{halite}$ inclusions have consistent Th_{LV-L} and Tm_{halite} in a single assemblage because they commonly decrepitated before either Th_{LV-L} or Tm_{halite} were reached. However, on the basis of visual estimation of the phase proportions during heating and before decrepitation, we assume a similar Th_{LV-L} or Tm_{halite} for inclusions within one assemblage and entrapment in a single phase field.

Schmidt and Bodnar (2000) determined that the solvus for inclusions with a composition of 40 wt % NaCl equiv and 10 mol % CO₂ is above 2kbar. This composition described by Schmidt and Bodnar (2000) is similar to the composition of inclusions found in samples from Telfer deposit, explaining the high internal pressures and decrepitation before final homogenization. The pressure at final homogenization for inclusions with final homogenization by halite dissolution was calculated using the equation of Lecumberri-Sanchez et al. (2012), and reaches values > 3 kbar for some inclusions, which is outside of the range of application of the equation.

Fluid inclusion assemblage type 3 shows clear evidence for fluid immiscibility using the criteria of Ramboz et al. (1982); (1) the liquid-rich high salinity and the vapor-rich less saline inclusions were trapped contemporaneously, (2) the liquid-rich inclusions homogenize most likely into liquid, whereas the vapor-rich inclusions homogenize most likely into vapor, and (3) both fluid inclusion types have similar decrepitation temperatures (Tab. 2). For these fluid inclusion assemblages the homogenization temperature is the trapping temperature, so no pressure correction is necessary. For all other fluid inclusion assemblages that do not display evidence for phase immiscibility a pressure correction would be necessary to obtain true trapping temperatures. Nevertheless, no independent pressure or temperature estimation based on mineral thermobarometry for the Telfer gold-copper deposit is currently available due to the lack of appropriate minerals.

The high pressure at the point of homogenization of high salinity fluid inclusions with final homogenization by halite dissolution exceeds lithostatic or hydrostatic pressure for paleo-depths of approximately 5 km for the Telfer deposit (based on the estimated stratigraphic thickness of overlying sedimentary rocks). Therefore, no pressure temperature correction was applied for these fluid inclusion assemblages.

Precipitation mechanism and fluid dynamics

The overpressure mentioned above can be best explained by ascending hydrothermal fluids in an active fault reaching a less permeable zone where fluid pressure builds up. The fluid overpressure at one point can trigger the failure of faults with a rapid decrease in pressure leading to phase separation of the ore forming fluid and precipitation of metals (c.f., Sibson et al., 1988; Wilkinson and Johnston, 1996). Fluid inclusion assemblage type 3 represents fluid inclusions trapped during phase separation of ascending hydrothermal fluids during fault failure (Fig. 11). The trapping pressure of these fluid inclusions is lower than from inclusions from the other assemblage types. Similar trapping mechanisms have been reported by Wilkinson and Johnston (1996) for gold mineralization in western Ireland. Mapping at Telfer revealed structures such as horizontal extension and shear veins with dilatant jogs along bedding plane (Hewson, 1996, Miller and Batt, pers. comm.) which are compatible with fluid pressure fluctuations and potential unmixing. All type 3 fluid inclusion assemblages are from samples of the reefs; none of these assemblages were identified in the discordant veins or in the VSC. Evidence for phase immiscibility caused by sudden pressure drop was therefore only observed in the reefs, whereas the pressure drop in the discordant veins or the VSC was apparently not large enough to result in unmixing of the fluid, but still may have led to a adiabatic cooling of the fluid and precipitation of gold.

Most of the other fluid inclusions assemblages show a vertical trend on a binary Th_{final} versus salinity diagram or a trend along the halite saturation curve for inclusions with final homogenization by halite dissolution (Fig. 10a, b), which is indicative of fluid cooling (c.f., Wilkinson, 2001). This cooling might have been adiabatic cooling caused by changes in pressure, as mentioned above, and also a result of interaction between the hot hydrothermal fluid and the ambient temperature of the surrounding host rocks during the hydrothermal alteration processes.

Given that similar fluid inclusion assemblages are present in all vein types at Telfer, it is suggested that fluid cooling was the dominant factor for ore precipitation with minor fluid unmixing observed only in the reefs. No evidence for mixing of different fluids could be identified in any vein type or any fluid inclusion assemblage type (Fig. 10).

Absolute timing and global context

Although Telfer is a gold-copper deposit and not a gold-only deposit, it shares more geological and chemical features with intrusion related gold deposit than with other goldcopper deposits like iron-oxide-copper gold (IOCG) and porphyry gold-copper deposits.

The age of the Telfer deposit in comparison to gold and gold-copper deposits worldwide, and especially in Western Australia, is rather unique. After a period of around 1,200 m.y. (after the Paleoproterozoic gold mineralization at Pine Creek – Tanami, Australia, and the Trans-Hudson gold mineralization, USA) with no major gold mineralization (Groves et al., 2003), the Telfer gold-copper deposit marks the beginning of a new period or era of gold mineralization. The other major gold deposits (e.g., in the Arabian-Nubian shield, or the Brasilia fold belt) also dated to have formed in the Neoproterozoic are all hosted in major orogenic belts and are mostly classified as classic orogenic gold deposits (Goldfarb et al., 2001). Typical intrusion–related gold deposit formed during the late Neoproterozoic. The geotectonic setting and age of the granites, related to the gold-copper mineralization at Telfer, is also unique in Australia (Schindler, 2014). Schindler (2014) proposed a post collisional intraplate setting for the emplacement of the granites in the Telfer region.

According to Baker (2002), intrusion-related gold deposits have different dominant fluid inclusion types depending on the depth of formation: (1) shallow deposits (< 5 km) have fluid inclusions with high temperatures and high salinities as well as low salinity CO₂ fluid inclusions, whereas (2) deep deposits (> 5 km) have many low salinity CO₂ inclusions that are rarely postdated by saline aqueous fluid inclusions (e.g., Jilau deposit, Tajikistan, 2 -14 wt % NaCl equiv., Cole et al., 2000). For example, the Kori Kollo deposit in Bolivia and the Shotgun deposit in Alaska, two shallow deposits formed < 2 km depth, have both similar ranges in homogenization temperatures and salinities as Telfer, although only the Shotgun deposit contains CO₂ bearing fluid inclusions. The Timbarra deposit in Australia and the Jilau deposit in Tajikistan are examples of deep intrusion-related gold deposits which formed > 7 km depth. Both have a similar range in homogenization temperatures, only show CO₂ inclusions but lack high salinity inclusions (Baker, 2002, and references therein) which are characteristic for the Telfer deposit. Importantly fluid inclusions at the Telfer gold-copper deposits are compatible with both, shallow and deep ore environments, thus underlining the unique composition of the ore forming fluids at the Telfer deposit.

Another major difference between Telfer and other intrusion-related gold deposit (Table 4) is the distance between intrusions, interpreted to be the hydrothermal fluid source (and potentially metals?), and the depositional site. The examples listed in Table 4 are all hosted within or proximal (< 3 km) to the intrusion. In contrast, Telfer is located > 5 km away from the intrusions that are interpreted to be the fluid and potentially the metal source. Furthermore, typical intrusion-related gold deposits do not contain significant amounts of copper (< 100 ppm Cu, Thompson et al., 1999); in contrast, at Telfer copper is an economically important by product (reefs contain 0.2 % to 1.5 % Cu, Technical report Telfer property, 31st December 2011, newcrest.com.au).

Compared to other gold-copper deposit types such as IOCG and porphyry goldcopper), Telfer displays significant geological and chemical differences, but also shares some typical geological features of these deposit types. For example, IOCG and porphyry goldcopper deposits show similar ore forming fluid properties as described here for the Telfer gold-copper deposit. Both deposit types have high temperature and high saline ore forming fluids and both types are clearly related to magmatic processes (e.g., Groves et al., 2010; Sillitoe, 2010). Similar ore forming fluids are reported from reduced porphyry copper-gold deposits (Rowins, 2000), although high concentrations of CO₂ and CH₄, as described in this paper, are uncommon in IOCG and porphyry deposits.

Nevertheless, large alteration zones, commonly on a regional scale, which are typical features of porphyry deposit and IOCGs (e.g., Groves et al., 2010; Sillitoe, 2000), are not present at Telfer. Furthermore, the mineralization style at Telfer (all gold is hosted by quartz veins and only minor in breccias, no disseminated mineralization in the host rock at all) is different to typical porphyry or ICOG deposits and metal zonation is absent at Telfer. Hydrothermal iron oxides are rarely present at Telfer compared to typical IOCG's.

Conclusions

Detailed study of fluid inclusions from all of the different veins at the Telfer deposit revealed an uncommon mix of ore forming fluids for intrusion-related and structurally controlled gold as well as IOCG or porphyry gold-copper deposits. Saline, carbonic fluid

inclusions were trapped in five different fluid inclusion assemblages: (1) three phase $L_{aq}+V_{aq}+S_{halite}$ inclusions only, (2) two phase $L_{aq}+V_{carb}$ or three phase $L_{aq}+L_{carb}+V_{carb}$, (3) three phase $L_{aq}+V_{aq}+S_{halite}$ together with vapor rich $L_{aq}+V_{carb}$, (4) three phase $L_{aq}+V_{carb}+S_{halite}$ only, and (5) $L_{aq}+V_{aq}$ only. These assemblages reveal trapping conditions from P \leq 1.5 kbar up to 3 kbar and T \leq 150 to \geq 480°C and all of these assemblages seem to have played an important role during the process of gold-copper mineralization.

The large range in homogenization temperatures combined with a restricted range in salinity suggests that the main precipitation mechanism was cooling caused by fluid rock interaction as well as decrease in pressure (Fig. 10). Based on the contemporaneous trapping of immiscible fluids, phase immiscibility is suggested to have been, at least locally, an additional mechanism promoting ore deposition at the Telfer gold-copper deposit. Evidence of immiscibility was predominantly found in the reefs and was not observed in the deeper discordant or stockwork veins. No evidence for mixing of a hot magmatic and a cool meteoric fluid was found anywhere in mineralized veins in the deposit. Immiscibility of hydrothermal fluids that circulated in the reefs is suggested to have been the result of fault failure triggered by fluid overpressure, which caused a sudden pressure drop (c.f., Wilkinson and Johnston, 1996; Cox, 2005; Fig. 11). This mechanism can explain the large range of pressures reported above.

Laser ICP-MS analyses of in situ fluid inclusions revealed that the fluid had high concentrations of Na, K, Mg, Fe, Mn, Pb, Zn, and Cu for all analyzed fluid inclusion assemblages containing three phase $L_{aq}+V_{aq}+S_{hallte}$ inclusions, with the highest Pb-Zn concentrations for assemblages from the I30 reef. High concentrations of Na, K, Mg, Ca, for all assemblages with two phase $L_{aq}+V_{aq}$ inclusions were also revealed. The Mn/Fe ratio for all aqueous fluid inclusion assemblages is < 0.24, indicating reduced conditions during entrapment of the fluids. The only difference was observed in fluid inclusions trapped in the I30 reef, which also represents the deepest sampled reef. Here the fluid inclusion assemblages contain two phase aqueous carbonic $L_{aq}+V_{carb}$ fluid inclusions and have Mn/Fe ratios > 0.24 and, therefore, were seemingly more oxidized than any other vein type at Telfer. Furthermore, the strongest enrichment in base metals (Pb-Zn) for the I30 reef may be a sign of late fluids circulating through this deeper reef, whereas the upper M reefs were already "sealed" at the time these fluids circulated through the deeper reefs. The K/Ca ratio is > 1 for most fluid inclusion assemblages except for assemblages with aqueous three phase

 $L_{aq}+V_{aq}+S_{halite}$ fluid inclusions from the ENE trending discordant vein set, which show a strong enrichment in Ca.

A dominantly magma-derived reduced fluid with K/Ca ratio of > 1 transported the gold and copper in chloride complexes (Williams-Jones et al., 2009), for which cooling and/or pressure fluctuation is a much more efficient depositional mechanism than for Au transported as a bisulfide complex. The evidence presented is compatible with a magmatic origin of the hydrothermal ore fluids. The source of the metals (i.e., gold and copper) remains enigmatic. Nevertheless, the strong magmatic signature of the ore fluid suggests that, at least partly, gold and copper are sourced from the surrounding granites.

Similar fluid inclusion assemblages with similar P-T-X conditions found in all different Telfer vein types are interpreted to reflect a similar fluid from the same source affecting the entire deposit. Metal budget and mineralogy, as well as homogenization temperature and total salinity of fluid inclusions of the veins with K/Ca ratio < 1 is similar to veins with higher K/Ca ratios > 1. Therefore, the differences in major and trace element content of the ore forming fluid is rather reflecting fluid – wall rock interaction depending on the different host lithology than reflecting different fluid sources for the different vein types.

In summary, the Neoproterozoic Telfer gold-copper deposit shares many of the geological and geochemical features observed in intrusion-related gold and IOCG or porphyry gold-copper deposits but has also some significant differences (Table 4). Because of all the arguments mentioned above, Telfer can best be described as an unique intrusion-related, structurally controlled, metasedimentary rock hosted gold-copper deposit.

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Figure captions:

Fig. 1: (A) Geology of the northwestern Paterson Orogen including location of the other main ore deposits in the Paterson Orogen: the sedimentary-replacement copper (cobalt) Nifty deposit, and the unconformity-related Kintyre uranium deposit (modified after Bagas and Nelson, 2007); (B) Geology of the Telfer area, with the location of the main granite bodies, Mount Crofton Granite, Minyari Granite, Wilki Granite, and O'Callaghans Granite; also showing the line through the Telfer gold copper deposit for the cross section in Figure 3 (modified after Langsford, 2000).

Fig. 2: Geological overview of the Telfer gold-copper deposit, cross section line for Figure 3 indicated (modified after Batt, 2012)

Fig. 3: Schematic cross-section through the Telfer West and Main Dome showing major reefs; discordant NE and ENE veins only shown as sketch as they are out of this 2D plane; red star indicates approximate sample location (modified after Batt, 2012).

Fig. 4: Photo plate of the different mineralization styles at the Telfer gold-copper deposit; (A) underground exposure of the M50 reef with strong hydrothermal sericitisation in the footwall; (B) drill core sample of discordant NE vein; no dolomite in this sample; quartz and pyrite with inclusions of chalcopyrite (not visible in hand sample); (C) underground exposure of discordant ENE veins; intense hydrothermal sericitisation at the contact of the vein to the wall rock visible; (D) drill core sample of the VSC mineralization; strongly brecciated host rock with matrix of quartz, dolomite, and pyrite; Dol = dolomite, Qtz = quartz, Py = pyrite, Cpy = chalcopyrite, Sche = scheelite.

Fig. 5: Photographs of all samples used for fluid inclusion studies.

Fig. 6: Paragenetic sequence of the Telfer gold-copper deposit; quartz with fluid inclusions for this study was taken from the main gold stage.

Fig. 7: Examples of representative fluid inclusion assemblages; (A) Sample from I30 reef with fluid inclusion assemblage type 1, three phase $L_{aq}+V_{aq}+S_{halite}$ fluid inclusions only; (B) sample from the M50 reef showing assemblage type 3, three phase $L_{aq}+V_{aq}+S_{halite}$ fluid inclusions together with vapor rich two phase $L_{aq}+V_{carb}$ inclusions.

Fig. 8: (A) Histogram of Th_{final} (Th_{LV-L}, T_{decrep}, and Tm_{halite}) for all analyzed fluid inclusions from assemblage type 1, three phase L_{aq}+V_{aq}+S_{halite} fluid inclusions only, all inclusions have Th_{final} between 220 and 450°C except one outlier at lower temperature; small diagram at the bottom shows the results for non decrepitated inclusions (same for B-D; (B) histogram of salinity in wt % NaCl equiv for all analyzed fluid inclusions from fluid inclusion assemblage type 1, three phase L_{aq}+V_{aq}+S_{halite}; (C)) Histogram of Th_{final} (Th_{LV-L}, T_{decrep}, and Tm_{halite}) for all analyzed fluid inclusions from assemblage type 2, L_{aq}+Vc_{arb} fluid inclusions only; majority of inclusions have Th_{final} at around 250°C with some showing lower and higher temperature; (D) histogram of salinity in wt % NaCl equiv for all analyzed fluid inclusions from assemblage type2, L_{aq}+Vc_{arb} inclusions only.

Fig. 9: Laser ICP-MS results as whisker box plots for all different vein types analyzed; 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; black circle: mean; black line: median; circle: outlier > 1.5*Q3-Q1; triangular: extreme outlier > 3*Q3-Q1; (C) results for two phase $L_{aq}+V_{aq}$ inclusions; (B) results for multiphase $L_{aq}+V_{aq}+S_{halite}$ inclusions.

Fig. 10: Salinity versus final homogenization temperature of fluid inclusions from all different vein types at Telfer. High salinity fluid inclusions plotting above the halite saturation curve have final homogenization by vapor disappearance (L – V) whereas the sample plotting on the saturation curve have final homogenization by halite dissolution. (A) results from not decrepitated inclusions, single fluid inclusion assemblages are circled, arrows indicating cooling trends, the main precipitation mechanism at Telfer; (B) results of all analyzed fluid inclusions including the once that decrepitated; decrepitation is indicated by black arrows; grey fields showing typical range of fluid inclusion data for different deposit types, compositions for these deposits exist outside the boxes, should be taken as guidance values (grey fields after Wilkinson, 2001); (C) T_{decrep} versus salinity of the fluid inclusion

assemblage 3, $L_{aq}+V_{aq}+S_{halite}$ fluid inclusions together with vapor rich $L_{aq}+V_{carb}$ inclusions; all of these inclusions decrepitate before final homogenization; inset of phase diagram showing fluid immiscibility for the same sample pair at 500 °C and 1.5 kbar (after Pichavant et al., 1982)

Fig. 11: trapping pressure (kbar) versus trapping temperature for several different fluid inclusion assemblage types; inset (A) represents the isochors used to determine the trapping pressure for the I30 reef $L_{aq}+V_{carb}$ inclusions (isochores calculated after Kerrick and Jacobs, 1981) and inset (B) showing isochors of high salinity $L_{aq}+V_{aq}+S_{halite}$ with Th_{final} by halite dissolution (isochores calculated after Lecumberri-Sanchez et al., 2012); (C) fluctuation fluid pressure, building up before the failure and sudden drop at the time of failure (after Cox, 2005).

Table 1: Summary table showing details of all samples used for further analyses.

Table 2: Results of microthermometry of fluid inclusions from all different vein types; results shown here are not for single fluid inclusion assemblages but rather for the whole assemblage type; variations with single assemblages are much smaller.

Table 3: Results of laser ICP-MS of single fluid inclusions; Salinity is the average salinity which was used for calculating the major and trace element content of the inclusion. Results on single fluid inclusion do not show a normal distribution, therefore only minimum, maximum and median is shown here.

Table 4: Overview of intrusion-related gold deposits worldwide (modified after Thompson et al., 1999; Baker, 2002) (Long et al., 1992; Boiron et al., 1995; Morávek, 1995; McCoy et al., 1997; Smith et al., 1999; Cole et al., 2000; Mustard, 2001; Selby et al., 2002)

Appendix

Analytical Methods

Samples from different ore bodies, vein types, and mineralization styles, and from different depth levels of the Telfer gold-copper deposit were analyzed as part of this study. Fluid inclusion petrology was completed on thirteen double polished sections at the University of Western Australia. A transmitted light microscope was used for detailed mapping of fluid inclusion assemblages following the definition of Goldstein and Reynolds (1994) prior to any further analyses. Primary or pseudosecondary fluid inclusions as defined by Roedder (1984) were investigated during this study. Sample discs, with a 5 mm diameter, of eleven sections with suitable fluid inclusions and containing representative FIAs were cut from the sections using an ultra sonic disc cutter at the Centre for Microscopy, Characterisation and Analysis (CMCA) at the University of Western Australia (UWA). Exact sample location and geological details are given in Table 1. Cathodoluminescence (CL) images of the areas containing the mapped FIAs were taken using the TESCAN VEGA3 SEM at CMCA to examine possible growth zonation within the single quartz grains.

Microthermometry

Microthermometric observations were completed using a Linkam THSMG 600 heating and freezing stage mounted on an Olympus BX53 microscope. The Linkam stage was controlled via the PC software Linksys32. A synthetic CO_2 -H₂O inclusion standard (Tm_{CO2}=-56.6°C) was used for calibration of low temperatures. A synthetic H₂O inclusion standard was used for calibration of ice melting (Tm_{ice} = 0.0°C) and for calibration of homogenization temperatures (Th_{H2O} = 374.1°C). Accuracy of measurements is ±0.1°C for temperatures between -190°C and 0.0°C, above 0.0°C accuracy is ±1.0°C.

Salinity (expressed as wt % NaCl equiv.), density, isochores, and homogenization pressure were calculated from low temperature phase changes and final homogenization temperatures into liquid for inclusions without halite daughter crystal using the computer program "MacFlincor" (Brown and Hagemann, 1995) and the equation of state from Bodnar and Vityk (1994) and Kerrick and Jacobs (1981). The equations of Thiery et al. (1994) were used to calculate CO₂ - CH₄ ratios based on melting temperature of the carbonic phase.

Salinity, density, and homogenization pressure for fluid inclusions containing halite daughter crystals was calculated based on halite dissolution temperature and the final homogenization temperature with HokieFlincs_H2O-NaCl (Steele-MacInnis et al., 2012) and the equation of state by Lecumberri-Sanchez et al. (2012), Sterner et al. (1988), and Atkinson Jr (2002).

Laser Raman analyses

Vapor phases and unknown solid phases of single inclusions where analyzed using laser Raman at Geoscience Australia and at Virginia Polytechnic Institute and State University. The detection limits are dependent upon the instrumental sensitivity, the partial pressure of each gas, and the optical quality of each inclusion. Raman detection limits are estimated to be around 0.1 mol % for CO₂, O₂ and N₂, and 0.03 mol % for H₂S and CH₄ (Wopenka and Pasteris, 1986) and errors in the calculated gas ratios are generally less than 1 mol %.

At Geoscience Australia, laser Raman spectra of fluid inclusions were recorded on a Dilor© SuperLabram spectrometer equipped with a holographic notch filter, 600 and 1800 g/mm gratings, and a liquid N2 cooled, 2000 x 450 pixel CCD detector. The inclusions were illuminated with 514.5 nm laser excitation from a Melles Griot 543 Series argon ion laser, using 5 mW power at the samples, and a single 30 second accumulation. A 100X Olympus microscope objective was used to focus the laser beam and collect the scattered light. The focused laser spot on the samples was approximately 1 μ m in diameter. Wavenumbers are accurate to ± 1 cm⁻¹ as determined by plasma and neon emission lines. For the analysis of CO₂, O₂, N₂, H₂S and CH₄ in the vapor phase, spectra were recorded from 1000 to 3800 cm⁻¹ using a single 20 second integration time per spectrum.

At Virginia Polytechnic Institute inclusions were analyzed using a JY Horiba LabRam HR (800 mm) high-resolution Raman spectrometer attached to an Olympus optical microscope with 50x and 80x long-working-distance objectives. Excitation was provided by a 514.529 nm (green) Laser Physics 100S-514 Ar⁺ laser. The laser output was 50 mW at the source and <10 mW at the sample. The slit width was set to 150 μ m, the confocal aperture was set at 400 μ m and 600 grooves/mm gratings were used. The position of each measured

Raman line and peak areas were determined after baseline correction using Gaussian/Lorentzian peak fitting.

Inclusions were analyzed using three 30-second accumulations within a scanning range of ~1000-4000 cm⁻¹. Specific attention was focused in the regions for CO₂ (the Fermi diad at ~1285 and 1388 cm⁻¹), CH₄ (~2917 cm⁻¹), N₂ (~2331 cm⁻¹), H₂S (~2611 cm⁻¹) and H₂O (~3000 - 3700 cm⁻¹). Relative amounts of volatile species were calculated based on Placzek's polarisability theory using instrument efficiency factors determined using gas mixtures of known composition. Additional details concerning the methods used are provided by Lin et al. (2007) and Fall et al. (2011).

Laser ablation ICP-MS

Major and trace element composition of fluid inclusions were analyzed by laser ablation ICP-MS at the University of Leeds, UK. A Lambda Physik 193nm ArF Excimer laser coupled to an Agilent 7500c ICP-MS Quadrupole with an octapole reaction cell to eliminate any interference of ⁴⁰Ar⁺ and ⁴⁰Ar¹⁶O⁺ on ⁴⁰Ca⁺ and ⁵⁶Fe⁺, respectively, was used for the analyses. Details on the exact analytical methods can be found in Allan et al. (2005). An optical system that allows observation of the laser ablation process was used and it is described in detail by Gunther et al. (1997). The standard NIST610 was analyzed as external calibration standard with Na as the internal standard element. The Na concentration of inclusions from salinities calculated by microthermometry was used to calculate the concentrations of the other analyzed elements. As fluid inclusions typically decrepitated during heating of microthermometry measurements, salinity was calculated on different fluid inclusions to those analyzed with laser. The MATLAB based software package "SILLS" (Guillong et al., 2008) was used to calculate the trace element content (in ppm) of single inclusions from the raw data. Following isotopes were analyzed during the measurements: ²³Na, ²⁴Mg, ³⁹K, ⁴⁰Ca, ⁵⁵Mn, ⁵⁶Fe, ⁶³Cu, ⁶⁶Zn, ⁸⁸Sr, ¹³⁷Ba, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb. In a separate analysis routine, another set of fluid inclusion in the same samples with same composition (based on petrography and microthermometry) and from same inclusion assemblages were analyzed for following elements: ²³Na, ⁷⁵As, ⁹⁵Mo, ¹⁸¹Ta, ¹⁸²W, and ¹⁹⁷Au to allow for a longer dwell time on the Au peak as the concentrations were very low and this enable a more accurate analyses.