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Author(s):

Argapadmi, Windeati; Toth, Eniko R.; [Fehr, Manuela](#) ; [Schönbächler, Maria](#); [Heinrich, Christoph A.](#)

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**Silver isotopes as a source and transport tracer for gold:
A reconnaissance study at the Sheba, Fairview and New
Consort gold mines in the Barberton Greenstone Belt, Kaapvaal
Craton, South Africa**

**Windeati Argapadmi, Eniko R. Toth, Manuela A. Fehr,
Maria Schönbächler, Christoph A. Heinrich**

Institute for Geochemistry and Petrology (IGP)
Department of Earth Sciences, ETH Zurich
Clausiusstr. 25, 8092 Zürich, Switzerland

Corresponding author: heinrich@erdw.ethz.ch

Abstract

Silver isotopes are a potential tracer for understanding the geochemical enrichment process of gold, which is a mono-isotopic element occurring in metallic form with silver as a significant alloy component. This study applies high-precision measurements of silver isotope ratios to two of the oldest world-class hydrothermal gold vein deposit from the Meso-Archean (3.4-3.1 Ga) Barberton greenstone belt on the Kaapvaal craton in South Africa. Of particular interest is the question whether silver isotopes might be suitable to trace the origin of the world's largest gold deposits that occur in the Witwatersrand basin overlying the granite – greenstone basement of the craton, and to test whether this giant sedimentary gold accumulation might be derived from hydrothermal precursors in the greenstone belts.

Published structural-geological and geochronological results show that the hydrothermal gold deposits formed late in the tectono-metamorphic history of the Barberton greenstone belt, after major crustal deformation but possibly synchronous with widespread potassic granite magmatism. Geological documentation and mine sampling at the New Consort, Fairview and Sheba mines confirm the structurally late introduction of gold into veins and As-rich sulfide replacement orebodies. Own studies highlight the late structural control on gold precipitation, but also the stratabound nature of gold orebodies close to the stratigraphic contact between older mafic to ultramafic submarine lavas (the Onverwacht Group) and overlying carbonaceous siltstones and greywackes (the Fig Tree Group). This stratigraphic contact is marked by a former submarine-exhalative chert, which is itself mineralized (the 'Consort Bar' at New Consort), or barren but highly veined (at Sheba and Fairview mines).

Chemical and isotopic analyses were performed on native gold from the Barberton gold mines, from other hydrothermal gold deposits and from carbon-leader type ores from the Witwatersrand, and of native silver from various epithermal silver deposits. All native gold samples contain significant (1-12 wt%) Ag, but only trace levels of other metals such as Cu or Hg. Stepwise leaching experiments show that native gold is the main carrier of silver, even in arsenopyrite-rich disseminated gold ores from Barberton. Different gold samples from Barberton yield $\epsilon^{109}\text{Ag}$ values (differences in $^{109}\text{Ag}/^{107}\text{Ag}$ relative to NIST SRM 978a in parts per 10^4) from -4.2 ± 0.4 to $+3.6 \pm 0.4$, encompassing almost the entire range of reported terrestrial Ag isotope variations including all of the native silver ores.

Remarkably, the three studied samples from New Consort all have very negative $\epsilon^{109}\text{Ag}$ values, whereas the two samples from Sheba have variably positive $\epsilon^{109}\text{Ag}$ values. The systematic difference between the two neighboring deposits in the Barberton greenstone belt is unlikely to reflect a different source of fluids and dissolved metal components. Both deposits formed at a similar stage in the tectono-metamorphic history of the region, and both are associated with the same meta-chert layer, which we interpret as a master channelway for post-orogenic hydrothermal fluids. More likely, the isotopic difference is due to isotope fractionation related to the reduction of dissolved Ag^+ complexes in the ore fluid to native metal, Ag^0 in the gold alloy. By analogy with other elements (C, S, Fe, Cu) we assume that the more oxidized species (Ag^+ and its complexes) are enriched in the heavier isotope compared with the reduced metal, Ag^0 . As the ore fluid flows from an inferred source in the granitoid basement (e.g., the widespread post-magmatic K-rich granite intrusions) to the high-temperature and contact-proximal New Consort deposit, isotopically light (low $\epsilon^{109}\text{Ag}$) silver is precipitated by partial reduction, leaving a fraction of isotopically heavier silver in solution. Subsequent precipitation of the remaining Ag^+ to Ag^0 will produce gold with isotopically heavy silver, as observed at Sheba.

This reconnaissance study indicates that Ag isotopes may be a useful monitor for gold and silver transport and ore deposition, but are unlikely to be a direct source tracer for the ultimate origin of precious metals, contrary to initial expectations from native silver ores.

Introduction

Only a small fraction of today's exposed continental crust was stabilized during Archean times, yet more than half of all known and previously mined gold originates from Archean continental crust (Goldfarb et al., 2001; Groves et al., 2005). This over-proportional endowment is dominated by a single ore-forming system, the Witwatersrand basin constituting some 40% of the world's gold, deposited in surficial clastic sediments, affected by placer reworking (Frimmel et al., 2005) of at least partly chemically-precipitated gold (Horscroft et al., 2012; Heinrich, 2015; Frimmel and Hennigh, 2015). Even without this unique sedimentary ore system, Archean crust is over-proportionally endowed with gold, in numerous small to giant hydrothermal deposits that are broadly described as 'lode gold deposits', or as 'orogenic deposits' (Goldfarb et al., 2001). The latter term carries the implication that these hydrothermal deposits were dominantly formed during orogenic processes involving active crustal shortening and regional metamorphism (Groves and Phillips, 1987). Archean lode gold deposits are concentrated in metamorphosed supracrustal host rocks of sedimentary or volcanic origin, known as greenstone belts that are shaped as laterally shortened, steeply-structured keels and are commonly aligned in extensive terranes, such as the Norseman-Wiluna Belt in Western Australia or the Abitibi Belt in Eastern Canada (Percival et al., 2006; Blewett et al., 2010). The greater part of the Archean crust, which exposes high-temperature tonalitic to granitic intrusions and high-grade metamorphic gneisses, is only weakly mineralized at its present erosion level. Reasons for the overproportional gold endowment of Archean crust and the concentration of rich deposits in the greenstone belts were tentatively related to a range of factors including (i) higher thermal energy flux in the early stages of Earth's consolidation (Barley et al., 1998), (ii) a peak in the rate of continental crust generation during the Late Archean (Condie, 1998; Goldfarb et al., 2001; Dhuime et al., 2012), (iii) higher mantle temperatures allowing sulfide-undersaturated ultramafic melting and more efficient gold extraction (Pitcairn, 2011), (iv) the occurrence of these mafic rocks as reactive source for later metamorphic gold mobilization from the lower parts of the greenstone belts (Keays and Scott, 1976; but see: Hofmann et al., 2017), (v) steeper temperature gradients during regional metamorphism leading to a concentration of the largest deposits in the lowest-temperature centre of large greenstone belts (Groves and Phillips, 1987), and (vi) the occurrence of potentially fertile granitoid intrusions including a widespread post-orogenic potassic magma suite, particularly on the Kaapvaal craton (de Ronde et al., 1991; de Ronde et al., 1992; Clemens et al., 2010). None of these hypotheses, however, is well established and broadly recognized as a dominant factor explaining the great Archean gold endowment.

The Paleoarchean Kaapvaal Craton is unique in its gold endowment due to the ~ 3 Ga old Witwatersrand Basin, but it is not as highly endowed with lode gold deposits as Mesoarchean cratons including the Yilgarn Craton of Western Australia and the Superior Province of Eastern Canada (Goldfarb et al., 2001; Groves et al., 2005). Nevertheless, its largest and particularly well-preserved greenstone belt, the Barberton greenstone belt (BGB), hosts several world-class deposits with spectacular gold grades. Other greenstone belts of the Kaapvaal Craton also contain widespread but smaller economic deposits (Foster and Piper, 1993). The Barberton greenstone belt and its surrounding granitic to tonalitic intrusions and gneisses have been subject to intense research, indicating that the complex depositional to tectonometamorphic ('orogenic') history of the region has been completed in an extended period between 3.445 and 3.227 Ga (Robb et al., 1986; de Ronde and de Wit, 1994; Kamo and Davis, 1994; Dziggel et al., 2007; Moyen et al., 2007). Gold mineralization, however, occurred at least 100 Ma after orogeny and structural consolidation of the greenstone belt. It temporally overlapped with or even postdated potassic granitoids and pegmatites, shortly before the establishment of the land surface on which the continental clastic basins including the Witwatersrand basin developed subsequently (de Ronde et al., 1991; Dirks et al., 2013). If magmatic fluids from the ~ 3.1 Ga potassic granitoids were responsible for ore formation, their widespread occurrence on the Kaapvaal Craton implies a major flux of gold to its original land surface. The total quantity of gold deposited in the (now eroded) surficial part of

the craton may have greatly exceeded the comparatively sparse deposits preserved in the small fraction of chemically reactive greenstone belts (Fig. 1).

Gold has a single isotope and is therefore not amenable to direct tracing of its source and chemical reaction history. Silver is a ubiquitous secondary component of metallic gold, the main economic mineral in gold deposits. Silver occurs in solid solution as minor or even major component (electrum) and is potentially the closest proxy to study the origin of gold ores. It has two stable isotopes, ^{107}Ag with a natural abundance of 51.84 % and ^{109}Ag contributing the remaining 48.16%. In this study, Ag isotope variations are reported as relative difference between the Ag isotopic compositions of a sample and a standard (NIST SRM 978a), expressed as

$$\epsilon^{109}\text{Ag} = [({}^{109}\text{Ag}/{}^{107}\text{Ag})_{\text{sample}}/({}^{109}\text{Ag}/{}^{107}\text{Ag})_{\text{standard}} - 1] \cdot 10,000$$

in line with recent studies reporting Ag isotope fractionation (Desaulty et al., 2011; Desaulty and Albarede, 2013) and other isotope proxies investigating isotope fractionation effects (e.g., Teng et al., 2017). In contrast, studies investigating Ag isotope variations in meteorites that are dominated by radiogenic decay of the short-lived isotope ^{107}Pd to ^{107}Ag (half-life of 6.5 Ma; Flynn and Glendenin, 1969) report data as $\epsilon^{107}\text{Ag}$, which is the deviation of the $^{107}\text{Ag}/^{109}\text{Ag}$ ratio from the NIST SRM 978a expressed in parts per 10^4 (e.g. (Chen and Wasserburg, 1990; Schönbächler et al., 2010). Palladium is a siderophile and refractory element during solar and planetary accretion, while Ag is a chalcophile and moderately volatile element. The Pd-Ag isotope system is therefore used to constrain core formation and volatile-element depletion by comparison of meteorite and terrestrial samples (e.g. (Carlson and Hauri, 2001; Schönbächler et al., 2008, 2010). The total variation of $\epsilon^{109}\text{Ag}$ recorded for terrestrial silver ore samples and historic coins ranges from -1.2 to +3.3 with analytical uncertainties of < 0.5 for $\epsilon^{109}\text{Ag}$ (Desaulty et al., 2011; Desaulty and Albarede, 2013). Slightly larger Ag isotope variations of -0.4 to +5.0 for $\epsilon^{109}\text{Ag}$ were reported for 7 native gold samples from Slovakia, Russia and India (Chugaev and Chernyshev, 2012). However, these workers did not remove matrix elements prior to Ag isotope analyses, which can impact on the accuracy of isotope data. So far, little or no geological control exists from diverse terrestrial silver samples, and it is therefore unclear to what extent the natural $\epsilon^{109}\text{Ag}$ variation relates to source differences (including primordial variations), or to mass-dependent isotope fractionation during silver transport and deposition by melts or aqueous fluids.

The present study was motivated by initial reconnaissance of silver ore samples, possibly indicating globally distinct source provinces (Carlson and Hauri, 2001; Desaulty et al., 2011), and by the specific hope that Ag isotopes in hydrothermal ores from the Kaapvaal craton might yield a tracer to elucidate the source and/or low-temperature depositional mechanisms for gold in the Witwatersrand. However, the results reported here show that silver isotopes in primary gold from two adjacent and genetically linked deposits in the Barberton greenstone belt span the entire range of terrestrial $\epsilon^{109}\text{Ag}$ reported in the literature, indicating that this variation is more likely due to stable isotope fractionation during hydrothermal transport and precipitation, rather than by an isotopic variation in the source of the precious metals.

Figure 1. Location and overview map of the Kaapvaal Craton composed dominantly of tonalitic to granitic gneisses and intrusions (crosses), widely dispersed but volumetrically minor greenstone belts (black) and overlying Archaean continental basins including Pongola and Witwatersrand (stippled), partly covered by late Archaean to Phanerozoic strata (white; simplified from Zeh and Gerdes, 2012).

Geological Background: Gold on the Kaapvaal Craton

The geological record of the Kaapvaal craton starts with the submarine extrusion of the mafic to ultramafic lavas, the Onverwacht Group in the Barberton greenstone belt at 3286 ± 29 Ma, overlapping within dating uncertainty with ages in excess of 3.3 Ga from the earliest gneisses (Dziggel et al., 2010, and references therein). The submarine lavas and mafic intrusions were altered by sub-seafloor hydrothermal activity, causing mobilization and depletion of their initially perhaps elevated gold content (Hofmann et al., 2017). Exhalative chert marks the top of the lavas, at a disconformity to the overlying Fig Tree Group, which is a thick sequence of turbiditic and organic-rich siltstones and sandstones deposited in a marine setting. It shallow upward to near-shore sandstones and continental conglomerates of the overlying Moodies Group (3225 ± 3 Ma; Dziggel et al., 2010). Felsic volcanoclastics dated at 3256–3259 Ma overlap in age with the earliest granitic to tonalitic intrusions along the outer contacts of the Barberton greenstone belt and elsewhere on the Kaapvaal Craton, and with the earlier phase (3250 ± 30 Ma) of tonalite gneisses of the poly-phase Stentor pluton (Kamo and Davis, 1994; Dziggel et al., 2010; Fig. 2). Major crustal shortening involving terrain accretion, thrusting and complex folding largely shaped the present geometry of the Barberton greenstone belt around 3227–3230 Ma. This orogenic event included high-pressure amphibolite facies metamorphism and the emplacement of large intrusions of the tonalite – trondhjemite granitoid (TTG) suite, e.g., the 3227 Ma Kaap Valley pluton (Kamo and Davis, 1994; Dziggel et al., 2010; Fig. 2). De Ronde and de Wit (1994), Dziggel et al. (2007), Schoene et al. (2008) and Dirks et al. (2009; 2013) explain this orogenic D2 phase by large-scale accretion synchronous with orogen-parallel extension, dated by igneous zircons and metamorphic titanite to between 3260 and 3225 Ma.

The next craton-scale event did not start until ~100 million years later, with the widespread emplacement of potassium-rich granitoid magmas and the concurrent or later formation of major gold deposits in the Barberton region. A porphyry dyke with a zircon age of 3126 Ma predates gold mineralization at Fairview mine (Dziggel et al., 2010; see also Fig. 2C). More widespread and voluminous granitoid plutonism occurred around 3100 Ma and is speculated to relate to a magmatic arc, whose tectonic accretion occurred some 200–300 km to the N and W along the edge of the Kaapvaal Craton (de Ronde et al., 1991; Fig. 1). Regionally, clastic sedimentary basins including those overlying the Pietersburg Greenstone Belt as well as the Pongola and Witwatersrand basins contain detrital zircons demonstrating surface exposure and erosion of arc-related or anorogenic granites with a prominent age peak at 3150 to 3000 Ma (Poujol et al., 2003; Dziggel et al., 2007). Close to the Barberton

Greenstone belt, this granitoid event formed several intrusions of potassic granite: the coarse porphyritic Nelspruit Batholith and the fine-grained Hebron Pluton at 3106 ± 3 Ma and 3014 ± 3 Ma respectively; a late intrusive phase (3107 ± 5 Ma) in the otherwise older Stentor gneiss dome; and large granite intrusions SW of the Barberton greenstone belt (Mpuluzi Batholith and 2 other plutons, all dated at ~ 3107 Ma by reliable zircon U-Pb TIMS ages; Zeh and Gerdes, 2012; Zeh et al., 2013). The Nelspruit batholith, mapped in detail by Robb et al. (1983), mostly consists of coarse porphyritic granite (Fig. 3G), but also comprises late stocks of fractionated pegmatitic and aplitic, and locally stockwork-veined granites such as the Berlin pluton (Fig. 3I) located just N of the map boundary in Figure 2A.

Pegmatites are exposed in the New Consort mine (Figs. 2b, 3H) and are thought to be the magmatic rocks most closely related to gold mineralization (Robb et al., 1983). They are barren and only weakly deformed. An approximate age of 3040 Ma was obtained by Rb-Sr and Sm-Nd dating of a pegmatite in the New Consort mine (Otto et al., 2007; Dziggel et al., 2010). Harris et al. (1993) present a texturally and analytically convincing and concordant TIMS U-Pb age for titanite associated with loellingite – arsenopyrite – pyrrhotite mineralization of 3027 ± 8 Ma and a decay-constant corrected amphibole Ar-Ar date of 3040 Ma in the same sample. These pegmatite mineral ages almost overlap and are taken by Dziggel et al. (2010) to indicate that gold mineralization at New Consort occurred well after the large-scale potassic granite event. However, some resetting from an older age closer to ~ 3100 Ma cannot be excluded in our opinion, nor unambiguously separated from a hydrothermal rutile age of 3084 ± 18 Ma from the Fairview mine (Dziggel et al., 2010) or approximate zircon U-Pb ages from ore-related porphyries by LA-ICPMS (de Ronde et al., 1991). It is clear, however, that the gold mineralization in the Barberton Greenstone belt is not related to prograde metamorphism of the greenstones and metasediments, but postdates contractional orogeny by 120-180 Ma years. Temperatures during gold mineralization increased with proximity to the intrusive contacts, from the Sheba mine in the interior of the greenstone belt ($\sim 300^\circ\text{C}$; de Ronde et al., 1992) to New Consort in intimate contact with intrusive pegmatites and closer to Stentor and Nelspruit granites (grading from 520 to 600°C ; Otto et al., 2007). Nevertheless, this gradient in mineralization temperature is similar to the much earlier regional-metamorphic gradient from greenschist facies to amphibolite facies conditions during the peak orogenic event (D2; Dirks et al., 2013).

Figure 2. Map of the northwestern keel of the Barberton Greenstone Belts with the location of major gold mines (A; simplified from Otto et al., 2007, Dziggel et al., 2010, Dirks et al., 2013). Section lines P-Q and X-Y in (A) mark the location of cross-sections (B, C, simplified from mine data; PLC 2014). Maps and sections emphasize the location of most economic mineralization near the stratigraphic contact between the Onverwacht Group and the Fig Tree Group, marked by a primary quartzite inferred to be a former exhalative chert. The New Consort mine is located closer to the basal contact of the greenstone belt that is intruded by pegmatites inferred to be fractionates of late-stage potassic granites including the Nelspruit Granite; mineralization occurs on both sides of the meta-chert horizon locally known as 'Consort Bar' (section B; P-Q in map A). The cross-section through the Sheba mine area (C; X-Y in map A) shows the highly deformed (folded and faulted) chert contact between the Onverwacht metavolcanics and Fig Tree metasediments, which we interpret as master channelways for ore-forming fluids forming replacement orebodies in metasediments and high-grade veins in the metavolcanics (for precise locations of the composite mine sections see Argapadmi, 2015).

The Barberton gold deposits: Geology and sampling

The Barberton gold deposits are structurally controlled by late brittle-ductile reactivation of earlier thrusts and faults, but also stratabound to the vicinity of carbonaceous metasediments (PLC, 2014). The three largest deposits are located close to the contact between Onverwacht Group mafic lavas and carbonaceous mudstones of Fig Tree Group (Foster and Piper, 1993; Williams, 1997). Our sampling (Table 1; Figs. 3, 4) was based on two weeks of underground mapping and core logging together with mine geologists. Detail maps of sampling areas are documented in Argapadmi (2015).

New Consort is a type example of post-orogenic hypozonal gold deposits that formed late in the tectonometamorphic history of Precambrian greenstone belts (Kolb et al., 2015). New Consort formed well after regional thrusting, metamorphism and the associated tonalite magmatism (Dziggel et al., 2007; Otto et al., 2007). Most of the mineralization is stratabound to within or close proximity of a ~ 4 m wide zone of fuchsite – biotite and sulfide-bearing quartzite, called the Consort Bar (Foster and Piper, 1993). Gold mineralization is characterized by pyrrhotite + arsenopyrite + loellingite ± chalcopyrite ± pyrite, with biotite + hornblende + fuchsite ± garnet forming the dominant alteration assemblages (Otto et al., 2007). A vertical mineral zonation in the mine indicates a steep temperature gradient from the orebodies towards the syntectonic intrusive contacts (3040 ± 84 Ma by Rb–Sr; Harris et al., 1993), consistent with the interpretation that granitic magmatism and mineralization are broadly coeval (Otto et al., 2007; Kolb et al., 2015).

The Consort Bar at level 51 consists of foliated biotite - amphibole bearing quartzite of ~ 8 m thickness, containing minor sulfides in stringers aligned with foliation (Fig. 3D), comprising 5% chalcopyrite, 15% pyrrhotite, and 80% needle-shaped arsenopyrite aligned with but overgrowing the foliation on the microscale. Gold in this high-grade ore is present as small particles attached to the sulfides. Coarser visible gold for isotope analysis was found in the same outcrop in a near-foliation-parallel quartz vein similar to the small veinlets shown in Figure 3D (sample C21). A second sample C11 originating from the same level and ore zone was obtained from mine geologists without detailed outcrop documentation. It was investigated because of its high grade and abundance of sulfides, which are dominantly euhedral arsenopyrite crystals of up to 1 cm (80% of total rock), anhedral and finer-grained pyrrhotite (20%) and minor chalcopyrite, in a matrix consisting of 20% silica-rich minerals including quartz, albite, biotite and tourmaline (Figs. 3F). Gold occurs as mm-sized particles in the matrix, and as abundant microscopic metal inclusions in the arsenopyrite (Fig. 4C).

Sheba and Fairview are structurally linked deposits mined from the same access. They host high-grade gold on both sides of the meta-chert horizon consisting of green, black and white interlayers of fine-grained quartzite. Coarse visible gold occurs together with minor pyrite in high-grade quartz ± carbonate veins cutting previously carbonated, metamorphosed and boudinaged mafic to ultramafic lavas of the Zwartkoppie Member of the uppermost Onverwacht Group (Fig. 3A). Disseminated gold also occurs as native metal inclusions or disseminated between arsenopyrite and pyrite in black metasediments (shales and greywackes) of the lowermost Fig Tree Group. Sulfides locally form impregnations around veins, following the metamorphic foliation without being deformed themselves (Fig. 3C, 4B). Apart from this regional to mine-scale stratabound control, ore zones crosscut stratigraphy, earlier thrusts and isoclinal folds at mine to sample scale, as indicated in Figures 2C, 3 and 4A. The dominantly brittle structures associated with mineralization are consistent with the lower temperature of mineralization, approximating greenschist-facies conditions with chlorite stable, only a little pyrrhotite and no loellingite. Large-scale structures are interpreted to be extensional (Otto et al., 2007; Kolb et al., 2015). Textural and microchemical observations confirm the late introduction of main economic Au with second generation of volumetrically minor undeformed pyrite (Fig. 4A), compared to early arsenical pyrite containing a minor fraction of invisible and refractory gold (de Ronde et al., 1992).

Samples from Sheba and Fairview include a spectacular but typical high-grade specimen S0 from Sheba mine. It consists of black, coarsely crystallized quartzite similar to massive recrystallized parts of the meta-chert at the Zwartkoppie (ZK) orebody and is cut by gold-filled fractures and irregular veins with comparable volume fractions of native gold, pyrite and finer-grained white quartz. The vein minerals are undeformed except for undulose extinction of quartz in transmitted light, and stained pyrite shows delicate growth banding in reflected light (Fig. 4A). Sample S6 from the ZK orebody at level 36 was taken ~ 5 m below the footwall of the chert marker horizon, which here is 5 m wide, steeply SSW dipping, and cut by a vertical N-S striking altered felsic dyke (Argapadmi, 2015). The footwall consists of bright green former metabasalt rich in quartz, fuchsite and carbonate. Abundant early carbonate and cherty quartz veins are boudinaged and aligned into a strong metamorphic foliation. Irregular but largely undeformed quartz – carbonate veins containing free gold but very little sulfide (pyrite) cut this foliation and all earlier veins (sample S6 is a hand-picked gold particle from a vein next to the one shown in Fig. 3A). Two samples from Fairview are lower-grade disseminated gold ores in metasediments of the Fig Tree Group, located above the chert marker. Sample FC is an exploration core of the MRC (Main Reef Chert) orebody, showing intense local sulfide dissemination along quartz – carbonate veins (Fig. 3C) in the immediate hanging wall of the intensely fractured chert marker (Fig. 3B). Predominant arsenopyrite and lesser pyrite follow the metamorphic foliation but are, like the vein itself, largely undeformed (Fig. 3C, 4B). Sample F4 has lower sulfide content but equally undeformed arsenopyrite needles, disseminated in Fig Tree Group metagreywacke from the Commitment Reef, a structural zone in the hanging wall of the chert marker (sampled at 42 level; Argapadmi, 2015).

The role of *siliceous cherts*, as likely products of exhalative magmatic-hydrothermal activity related to the Onverwacht submarine lavas, has initially given rise to the notion of syngenetic gold mineralization forming the Barberton deposits (de Ronde et al., 1992). The spatial association of orebodies to the vicinity of the chert horizons is evident, but is not widely stressed in more recent publications that demonstrated the structurally late introduction of gold. Nevertheless, the chert horizon or Consort Bar may be a decisive feature controlling the deposition of gold in the Barberton gold mines, because metamorphosed cherts can be sites of preferred fluid flow and focussing during hydrothermal gold transport. Even un-recrystallized marine cherts away from any ore deposit are characterized by intense veining, and detailed $\delta^{18}\text{O}$ studies by ion microprobe have shown that they largely exchanged their oxygen with a focussed flux of metamorphic or possibly magmatic fluid (Marin-Carbonne et al., 2011). Figure 3 shows that the meta-chert is full of brittle (Fig. 3B; Sheba) or brittle-ductile veins (Figs. 3D, E; New Consort). The meta-chert is commonly recrystallized to a coarse, macroscopically black quartzite, such as the wall rock of the gold - pyrite vein of sample S0 shown in Figure 4A.

Pegmatites largely crosscut the mineralized zones at New Consort, and our observations at the footwall ore body confirm that the 3 m wide dyke shown in Figure 3H is barren, but altered and boudinaged adjacent to zones of high-grade gold mineralization. These and other observations are consistent with a source of the gold-mineralizing fluids outside the greenstone belt, most likely associated with the post-orogenic potassic granite magmatism.

Chemical conditions of gold deposition are not the main focus of this paper, but any mechanism must involve reduction of aqueous Au^+_{aq} together with Ag^+_{aq} to metallic gold or electrum. Agangi et al. (2014) take anomalous $\Delta^{33}\text{S}$ evidence (mass-independent sulfur isotope fractionation) of pyrite in the Barberton gold ores as evidence for an atmosphere-derived source of sulfur involved in Au-complexation and ore deposition. However, the anomalous $\Delta^{33}\text{S}$ values were mostly found in inclusion-rich pyrite crystals. Thin hydrothermal overgrowths that might equate to the inclusion-free, unambiguously gold-associated pyrite generation (similar to those in Fig. 4A) seem to lack a clear $\Delta^{33}\text{S}$ anomaly (figure 4 of Agangi

Figure 3. Post-orogenic rock features in slab photographs, arranged by inferred tectono-metamorphic position from bottom (granitoids) to top (interior of greenstone belt), and by greenstone belt stratigraphy from left (footwall) to right (hangingwall). The top row A – C from the Sheba and Fairview mines, located in the interior of the Barberton greenstone belt, shows dominantly brittle structures and fluid channelways which were active under greenschist facies metamorphic conditions, including black quartz – ankerite veins rich in free gold cutting sea-floor-altered and boudinaged meta-ultramafics of the Onverwacht Group (A), the chert marker with well preserved sedimentary-exhalative lamination cut by a dense network of brittle quartz veins (B), and disseminated arsenopyrite – pyrite ores that locally form intense sulfide impregnation haloes following the low-grade metamorphic foliation of the carbonaceous meta-siltstones of the Fig Tree Group (C).

The second row D – F shows samples from the New Consort mine located closer to the outer contact of the Barberton Greenstone Belt, with dominantly brittle-ductile structures formed under amphibolite facies conditions. Mineralized lithologies include, in equivalent stratigraphic position from left to right, biotite-altered amphibolites derived from mafic volcanics of the Onverwacht Group containing arsenopyrite along foliation planes and abundant, variably re-folded quartz veinlets (D; next to sample C21) at the lower contact of the chert marker consisting of re-folded quartz veins in a biotite and fuchsite bearing quartzite (the Consort Bar, E). F: Exceptionally gold- and sulfide-rich sample of euhedral arsenopyrite with pyrrhotite + biotite + albite in an altered possibly metasedimentary rock (sample C11).

The bottom row G – I shows a typical outcrop surface of equigranular granite of the Nelspruit Batholith with pegmatoidal K-feldspar sweats (G), a pegmatite sample from the Footwall Lens of the New Consort mine (H; see Fig. 2B), and a late stock of fine-grained aplitic to porphyritic Berlin granite (I), the latest phase intruding the Nelspruit Granite and cut by a dense stockwork of quartz veins. All scale bars = 1 cm. Abbreviations (also for Fig. 4): ab = albite; ank = ankerite ($\pm$ calcite); asp = arsenopyrite; bio = biotite; g = gold; ksp = potassium feldspar; po – pyrrhotite; py = pyrite; trm = tourmaline; qz = quartz.

Figure 4. Photomicrographs of textural relationships of gold and sulfides, demonstrating the late timing of gold and As-S-rich mineralization. A: Bonanza-grade gold – pyrite – quartz sample S0 showing that gold precipitated together with euhedrally growth-zoned pyrite and fine-grained quartz in a vein cutting coarse-grained black quartz (Sheba mine; mixed cross-polarized transmitted light and reflected light on stained pyrite surface).

B: Photomicrograph of Figure 3C, showing the wall of a carbonate vein (upper right) cutting foliated black meta-siltstone of the Fig Tree Group, with undeformed pyrite and arsenopyrite crystals encroaching on the metamorphic foliation of the sedimentary wall rock (sample FC, reflected light; cf. Fig. 3C).

C. Detail of high-grade sulfide-rich ore from Figure 3F, showing arsenopyrite crystals enclosing small gold inclusions, in a matrix of albite (ab), quartz (qz), biotite (bio), tourmaline (trm), pyrrhotite (po) and free gold flakes (g) reaching 2 mm in size (sample C11, mixed reflected and plain-polarized transmitted light).

et al., 2016). We infer that the anomalous sulfur isotope data reflect early seafloor alteration and are unrelated to gold mineralization. Indeed the low abundance of pyrite and its textural occurrence indicate that gold in the Barberton deposits was not dominantly precipitated by de-sulfidation of iron-rich silicates (Phillips and Groves, 1983). More likely, gold was precipitated by fluids meeting a reducing environment, as indicated by the intimate association of native gold with abundant arsenopyrite (e.g. Fig. 4C; see Heinrich and Eadington, 1986) and by the stratabound nature of high-grade gold orebodies to the contact zone between lavas against variably carbonaceous sedimentary rocks. A conspicuous and unusual feature of most veins and the recrystallized chert in the Sheba and Fairview mines is the deep black color of quartz, the cause of which has not been ascertained. We speculate

that it may be due to submicroscopic graphite particles that could reflect hydrothermal mobility of reduced carbon (e.g. CH₄), consistent with CH₄ and hydrocarbons detected in dominantly H₂O-CO₂-rich fluid inclusions (de Ronde et al., 1992; even though these authors propose fluid phase separation as the dominant precipitation process). Irrespective of the chemical driving force for high-grade gold ore deposition, the unavoidable reduction of Au as well as Ag during metal precipitation will be important for the discussion of Ag isotope variations.

Analytical methods

Six gold grains from the New Consort and Sheba mines were selected for Ag isotope analyses based on detailed field observations and sample characterization. In addition, 4 native gold samples from other deposits (Witwatersrand carbon-leader type ores; orogenic quartz vein deposits of Mt. Charlotte in the Archaean Yilgarn Craton and Brusson in the Alps) and 6 samples of native silver from various hydrothermal ore deposits were investigated for comparison (see Table 1). The native silver and gold grains (except the smallest grains C11-1, W-VAAL and W-CLR) were washed with acetone and water from a Millipore system before they were digested in aqua regia. Two bulk rock samples from the Fairview mine (F4 ~ 0.7 g; FC ~ 1 g) rich in disseminated sulfides and a handpicked arsenopyrite crystal (C11-2 ~ 0.06 g) from the New Consort mine were also investigated. These three samples were powdered and leached in order to isolate any gold from sulfide and silicate phases and to test for the potential presence of Ag in other minerals. First, sulfides were leached with 7 M HNO₃. Gold was then liberated from the sample residue with aqua regia, followed by a third digestion step for silicates with concentrated HNO₃ - HF. Except for the native Ag ores, major and trace element concentrations were measured on an Element XR inductively coupled plasma mass spectrometer (ICPMS). Concentrations were determined using synthetic standard solutions for external calibration. The native gold samples had Ag concentrations between 1 and 12 wt.%, which was sufficient for Ag isotope analysis. The native Ag ores were checked on an Axiom MC-ICPMS for purity. Only the Cliff Mine sample (NMNHR164237) contained detectable Cu (Ag/Cu >4), while all other native silver samples contained > 99% Ag.

Sample aliquots containing ~ 500 ng Ag were selected for Ag isotope analyses, except for sample C11-2 that only comprised a total of 100 ng Ag which was still sufficient for high-precision Ag isotope analysis. Silver was isolated from matrix elements using anion-exchange chromatography following procedures of Schönbachler et al. (2007). Samples were loaded in 0.5 M HCl onto 1.25 ml of AG1-X8 (100-200 mesh) resin. Matrix elements were eluted with 0.5 M HCl, 0.001 M HCl and 0.5 M HNO₃, followed by elution of Ag with 0.5 M HNO₃. Native Ag ores were not passed through the ion exchange procedure, except for the Cliff Mine sample (NMNHR164237) to remove the Cu.

Silver isotopes were measured using a Neptune Plus multiple-collector ICPMS (MC-ICPMS) at ETH Zürich using wet plasma. The exceptions are the native Ag ore samples, which were analysed on an Axiom MC-ICPMS at DTM, Carnegie Institution of Washington, Washington (DC). Samples and NIST SRM 978a Ag standards were analysed at intensities that yielded ca. 1×10^{11} A signal for ¹⁰⁷Ag and ¹⁰⁹Ag (20 ppb solution for the Neptune MC-ICP-MS). The solutions were doped with NIST SRM 3138 Pd solution to yield ¹⁰⁶Pd/¹⁰⁷Ag ratios of 1. Palladium isotopes were used for external mass bias correction of Ag isotope using ¹⁰⁸Pd/¹⁰⁵Pd = 1.18899 (Schönbachler et al., 2007) and the exponential law. Cadmium interferences on mass 108 were monitored and corrected using ¹¹¹Cd. Samples were monitored for Nb and Zr, because the latter can produce significant oxide interferences on Ag and Pd isotopes (Ek et al., 2017). Silver isotope data are reported relative to the NIST SRM 978a Ag standard as $\epsilon^{109}\text{Ag} = [(^{109}\text{Ag}/^{107}\text{Ag})_{\text{sample}} / (^{109}\text{Ag}/^{107}\text{Ag})_{\text{NIST SRM 978a}} - 1] \cdot 10^4$.

Repeat analyses of solution S0-1 (Table 1) display a reproducibility of 0.44 (2 standard deviations) for $\epsilon^{109}\text{Ag}$ and this is taken as the estimated uncertainty for all Au samples. Similar or even better reproducibility's were obtained from multiple flakes ($n \leq 3$) of the native silver samples, which yielded standard deviations between 0.17-0.41 (2 σ ; Table 1). For

single analyses, an uncertainty of 0.5 (2σ) was adapted based on repeat analyses on Cody Shale obtained on the same instrument (Schönbächler et al., 2007).

Blanks were ≤ 0.1 ng Ag yielding a relative blank contribution of less than 0.1 %. The accuracy of the Ag isotope procedures (ion exchange chemistry and Ag isotope analyses) was verified using an artificial sample that consisted of a mixture of 9.2 μg Au and 500 ng NIST SRM 978a Ag standard. It yielded an Ag isotope composition identical to the unprocessed standard ($\epsilon^{109}\text{Ag} = 0$) with $\epsilon^{109}\text{Ag} = -0.12 \pm 0.44$. Aliquots of NIST SRM 978a Ag standard passed through the ion exchange procedure displayed slight Ag isotope fractionation compared to the unprocessed standard with $\epsilon^{109}\text{Ag} = -0.48 \pm 0.24$. This effect is small compared to the reproducibility of sample analyses ($\epsilon^{109}\text{Ag} = \pm 0.44$) and much smaller than the significant range in $\epsilon^{109}\text{Ag}$ observed between natural samples.

Geochemical results

Silver isotope compositions of the native gold samples from Barberton are compared in Figure 5 with the additional samples of gold and silver from other deposits (Table 1) and a summary of other high-quality Ag isotopic data for terrestrial materials in the literature. The isotopic data from native Ag ores cover an $\epsilon^{109}\text{Ag}$ range from -3.7 to +2.0. These data supersede those published in the abstract of Hauri and Carlson (2001). The $\epsilon^{109}\text{Ag}$ data from the Barberton gold deposits vary over an even greater range of 7.9 ϵ , encompassing the range for native silver deposits and the entire variation that was previously reported from terrestrial samples including historic silver coins (Desaulty et al., 2011; Desaulty and Albarede, 2013), with the only exception of an anomalously Ag-enriched weathered basalt from Hawaii ($\epsilon^{109}\text{Ag} \sim +10$; Schönbächler et al. 2007). Barberton values extend from well below the near-zero $\epsilon^{109}\text{Ag}$ of the Allende chondrite (Schönbächler et al. 2007, 2008, Theis et al. 2013) to values well above estimates of the bulk silicate Earth composition ($\epsilon^{109}\text{Ag} = +2.2 \pm 0.7$) based on fresh basalts (Schönbächler et al., 2010).

Figure 5. Variation of $\epsilon^{109}\text{Ag}$ in gold and silver metal samples, in comparison with published data from common terrestrial rocks (Schönbächler et al., 2007; Schönbächler et al., 2008; 2010; see Table 1; Desaulty et al., 2011; Theis et al., 2013). The anomalous basalt value is from a highly weathered and unusually Ag-enriched sample (Schönbächler et al., 2007).

Even though the number of analyses is limited, our data show that $\epsilon^{109}\text{Ag}$ is consistently negative in the samples from the New Consort mine and include the most negative value ever reported, whereas those from Sheba are consistently positive, only topped by the gold sample from the Archean quartz vein stockwork of Mount Charlotte (Western Australia). Other gold samples fall between these extremes, with the gold samples from two carbon-leader type orebodies of the Witwatersrand gold field (Vaal Reef; Carbon Leader Reef Meier et al., 2009; Heinrich, 2015) both falling close to $\epsilon^{109}\text{Ag} \sim 0$.

Minor components present in gold metal include Fe, Cu at the level of a few 100 ppm, variable Hg from tens of ppm in Barberton gold rising to higher values in the likely lower-temperature orogenic gold deposits (Mt Charlotte and particularly Brusson; Figure 6 and 7). Gold also contains up to a few ppm Pt but significantly less Pd (<1 ppm). The two isotopic groups of negative $\epsilon^{109}\text{Ag}$ in New Consort and positive $\epsilon^{109}\text{Ag}$ at Sheba do not correlate with any of the chemical variables in metal composition.

The disseminated gold ore samples from Fairview did not yield enough Ag for isotope analysis, but they provide an important test on the mineralogical occurrence of Ag in these more complex ores. Stepwise leaching experiments were performed to determine Ag potentially hosted in minerals other than native gold, notably as solid solution in arsenopyrite. Figure 7 shows that the first step of leaching of the variably sulfide-rich samples dissolves all pyrite, pyrrhotite and arsenopyrite, as shown by the open squares in Figure 7A at the start of the dashed arrow tracks. At the same time, a corresponding quantity of a few to a few tens of percent of Fe are dissolved (Fig. 7B). The nitric acid leach steps liberate very small amounts of Ag, close or below the detection limit of the concentration measurements. The next leach step with aqua regia yields slight (FC, F4) to significant (C11-2) Ag concentration, which in the latter sample is associated with measurable gold dissolution. This represents an unknown mixture of gold from the rock matrix and gold from the numerous inclusions in arsenopyrite (Fig. 4C). The isotopic composition of the aqua regia leach step ($\epsilon^{109}\text{Ag} = -3.94 \pm 0.44$) overlaps within analytical uncertainty with the macroscopic gold flake obtained from the same sample (C11-1; $\epsilon^{109}\text{Ag} = -4.22 \pm 0.44$), and also has similar chemical composition although these analyses were close to the limit of quantification. Final dissolution of the residue by a hydrofluoric-nitric acid mixture is dominated by residual silicates, as shown by the high Al concentrations liberated from micas, plagioclase and tourmaline (Fig. 7D). The absence of Ag from the first and the third leach step shows that Ag is indeed dominantly residing in metallic gold, whereas sulfides contribute little to the total Ag budget, even in samples containing $10^4 - 10^5$ times higher sulfide contents in the bulk ore compared to Au. Although Au was not measured to the same limits of detection, our results also indicate that most of the Ag-rich gold in our samples occurs as native metal, rather than as solid solution component in arsenopyrite or pyrite. This shows that Ag is precipitated by the same process of reduction from an aqueous M^+_{aq} complex to native metal, M^0 , just like Au, implying that silver isotopes are indeed a suitable proxy for the behavior of gold in hydrothermal systems.

Figure 6. Variation of $\epsilon^{109}\text{Ag}$ (A), Cu content (B) and Hg contents (C) plotted against the content of silver as the only major component of native gold in the studied samples.

Figure 7. Relationships between silver concentrations (horizontal axis) and S+As, Fe, Ca+Mg and Al concentrations (vertical axes, all measured relative to total weighed-in solid material; Table 1). Open squares denote a first leaching step with 7 M nitric acid that dissolves all sulfides (A) and thus all Fe present in pyrite and arsenopyrite (B) as well as Ca+Mg present as minor carbonates (C). A second step of leaching by aqua regia is shown by full squares if enough Ag was obtained for isotope analysis (C11-2), and full squares also denote results of direct dissolution of essentially pure hand-picked gold flakes. Residues of whole-rock samples were dissolved in a third step with a hydrofluoric-nitric acid mixture, with concentrations denoted by open diamond symbols, liberating silicates as monitored by Al (D). Half-symbols denote estimated upper limits of analytical detection.

Discussion: Silver isotope fractionation during hydrothermal transport and precious-metal deposition

Significant Ag isotope variations are evident for the investigated metal samples (Fig. 5). Three single gold flakes (S0-1, 2, 3) from one gold rich sample of Sheba display identical Ag isotope compositions with an average $\epsilon^{109}\text{Ag}$ of 3.49 ± 0.28 . Analytically significant variations between different silver deposits of similar epithermal origin had raised our initial expectation of possible variations among different mineral provinces, as implied by Desauty and colleagues based on systematic variations of $\epsilon^{109}\text{Ag}$ among historic silver coins (Desauty et al., 2011; Desauty and Albarede, 2013). However, the data from the Barberton gold system argue against a simple source control on $\epsilon^{109}\text{Ag}$ variations.

The multiply analysed sample S0 from Sheba mine yields the heaviest $\epsilon^{109}\text{Ag}$ value of the investigated native gold samples from Barberton. A separate gold sample (S6) from the same mine displays a notably lighter but still negative $\epsilon^{109}\text{Ag}$ value of -1.32 ± 0.44 . Two mineralogically different samples (C21-2, C11-1) from New Consort almost overlap in their Ag isotope composition, but show consistently positive $\epsilon^{109}\text{Ag}$ value, differing from those of Sheba by 6-8 ‰, i.e., by as much as the total Ag isotope variation among all precious metal samples that were studied worldwide so far. Given the similar timing and tectonic setting in the Barberton Greenstone Belt, two mineralization events with two distinct metal sources of vastly different Ag isotope composition seem very unlikely. More probable is an explanation relating Ag isotope variations to mass-dependent fractionation during the process of hydrothermal ore formation. The deposits formed at different temperatures, therefore a strong T-dependence of isotope fractionation could be responsible for the apparently systematic variation. However, similar positive and negative $\epsilon^{109}\text{Ag}$ values were found in silver ore samples from various epithermal vein deposits (Fig. 5), arguing against a simple temperature correlation.

At equilibrium, solid precipitates are commonly enriched in heavy isotopes compared to gaseous and dissolved species (e.g., Hoefs, 2009). Silver is transported as Ag^+_{aq} , complexed with chloride or bisulfide in hydrothermal solution (Seward, 1976; Stefansson and Seward, 2003) and its precipitation to metallic Ag^0 in gold solid solution therefore involves reduction. The only available experimental data on Ag isotope fractionation refer to Ag nanoparticles precipitated from acidic solutions, yielding conflicting results (Kelly and Wasserburg, 1978; Yang et al., 2009; Lu et al., 2016). Presently, not even the sign of isotope fractionation between aqueous silver and metallic silver is experimentally confirmed. In the experimentally and theoretically better-studied S, Fe and Cu isotope systems, isotope fractionation dominantly occurs between oxidized (aqueous or mineral) species like sulfate, Fe(III) and Cu(II) that are enriched in the heavier isotopes, and reduced species including sulfide, Fe(II), Cu(I) enriched in the lighter isotope (Ehrlich et al., 2004; Anbar et al., 2005; Markl et al., 2006a; Markl et al., 2006b; Hoefs, 2009). Fractionation factors for the transition metals are in the range of several ‰ at hydrothermal conditions, or even a few permil at surface temperatures (Moynier et al., 2017). In the case of Fe, reduced Fe^{2+} is the more soluble form, which is commonly precipitated upon oxidation to isotopically heavy Fe(III) oxides and hydroxide minerals (Ehrlich et al., 2004; Anbar et al., 2005; Markl et al., 2006a). In the Cu system, the same redox dominance is observed (Markl et al., 2006b), but there are also example systems including tenorite (CuO ; (Moynier et al., 2017) and covellite (CuS ; (Sherman, 2013), where the solid minerals are depleted in the heavy isotopes compared to the aqueous species of the same nominal valency. It is therefore plausible to assume, in analogy with Cu and Fe, that the redox effect also dominates Ag isotope fractionation during precipitation. Therefore, we tentatively predict that Ag^+_{aq} is enriched in ^{109}Ag compared to $\text{Ag}^0_{\text{metal}}$ in solid solution with gold. Silver isotope fractionation during precipitation of gold may not reflect fractionation at equilibrium. However, kinetic effects generally also produce precipitates that are isotopically light (e.g. Eiler et al. 2014) and therefore shift the Ag isotopes composition in the same direction as in our tentative prediction.

With this prediction, the observed difference in $\epsilon^{109}\text{Ag}$ between Sheba and New Consort (Fig. 5) could be explained by a fractionation process resulting from progressive reduction of the precious metals, as they precipitate from oxidized aqueous metal species in the hydrothermal fluid. Let us consider a gold and silver rich fluid with an assumed initial Ag isotope composition near 0, injected from a deep crustal or mantle source outside the greenstone sequence, e.g., from the potassic magmas represented by the pegmatites at New Consort. For the simplest illustration, let us assume a fractionation factor $10^4 \ln \alpha^{109}\text{Ag} = \epsilon^{109}\text{Ag}(\text{Ag}^+_{\text{aq}}) - \epsilon^{109}\text{Ag}(\text{Ag}^0_{\text{metal}})$ of 6 ‰ at equilibrium (i.e., $\Delta^{109}\text{Ag}_{\text{Ag}^+_{\text{aq}}-\text{Ag}^0_{\text{metal}}} = 0.6$ permil) and any starting concentration of Ag^+_{aq} with an initial bulk $\epsilon^{109}\text{Ag} = 0$. If 50% of the initially dissolved quantity of silver was precipitated together with gold during a first step, the precipitated metal will have a light $\epsilon^{109}\text{Ag}(\text{Ag}^0_{\text{metal}}) = -3$, whereas the remaining Ag^+_{aq} in the re-equilibrated solution will have a correspondingly elevated $\epsilon^{109}\text{Ag}(\text{Ag}^+_{\text{aq}}) = +3$. Precipitation of this remaining silver in a second step along the flow path of the same fluid will deposit precious metal with this heavier composition, $\epsilon^{109}\text{Ag}(\text{Ag}^0_{\text{metal}}) = +3$. This prediction of negative $\epsilon^{109}\text{Ag}$ values for the early-precipitated fraction of Ag is in agreement with the consistently light Ag isotope data obtained from the New Consort mine, which is indeed more proximal to the inferred metal source located outside the greenstone belt. Sheba can accordingly be explained as the product of a more fractionated, isotopically ^{109}Ag enriched fluid that had already lost some of its silver and gold closer to the fluid source.

Fractional precipitation in the real geological system will not occur in two discrete steps, but in a more continuous distillation process in an open system, as modelled and illustrated with hypothetical assumptions in Figure 8. The solid curves show the Ag isotope composition of instantaneously precipitated $\text{Ag}^0_{\text{metal}}$, as a function of progressive extraction of isotopically lighter silver from a fluid containing Ag^+_{aq} of initially intermediate isotopic composition of $\epsilon^{109}\text{Ag}_{\text{aq}} = 0$. The dashed lines depict the isotopic evolution of the coexisting fluid or dissolved Ag^+_{aq} , calculated from the Rayleigh distillation equation $\epsilon^{109}\text{Ag}(f) = \epsilon^{109}\text{Ag} + E^{109}\text{Ag} \cdot \ln f$, where E is the fractionation factor, f is the fraction of reactant remaining, and $1-f$ is the fraction of the initial Ag precipitated, as shown on the horizontal axis of Figure 8 (Rayleigh, 1902). This model calculation ignores the likely temperature dependence of isotope fractionation, which will increase with falling temperature but cannot be quantified at this stage. The model curves in Figure 8 were assumed to start from a fluid composition close to 0, as expected from a crustal source of the silver (marine shale; Fig. 5). However, provided that the fractionation factor is at least 0.6, the same explanation also works for a starting composition closer to the inferred Bulk Silicate Earth estimated from modern basalts, with an average $\epsilon^{109}\text{Ag}$ of $+2.2 \pm 0.7$ (Schönbächler et al., 2010; Fig. 5).

Figure 8. Distillation model comparing the observed $\epsilon^{109}\text{Ag}$ values in the Barberton gold mines with calculated Rayleigh fractionation curves assuming stepwise precipitation of Ag^0 in solid solution with metallic gold from dissolved and complexed Ag^+ in hydrothermal solution. Curves are for three assumed fractionation factors $10^4 \ln \alpha^{109}\text{Ag} = \epsilon^{109}\text{Ag}(\text{Ag}^+_{\text{aq}}) - \epsilon^{109}\text{Ag}(\text{Ag}^0_{\text{metal}})$ of 3, 6 and 10, ignoring the likely additional effects of temperature variation. Results show that the variation from low $\epsilon^{109}\text{Ag}$ in the New Consort deposit (close to the inferred source of

fluids outside the greenstone contact) to higher $\epsilon^{109}\text{Ag}$ in the Sheba mine (hosted by the interior of the greenstone belt) may be explained by a distillation process of progressive enrichment of ^{109}Ag from an initial fluid with an intermediate $\epsilon^{109}\text{Ag} \sim 0$.

Our calculation is hypothetical so far, and more extensive studies with larger numbers of samples and better spatial control (e.g., over the extended depth interval accessible within each of the mines, including the observed temperature-gradient of mineralization within New Consort mine may refine the redox distillation model proposed in Figure 8, provided that experimentally determined fractionation factors including their temperature dependence become available. Similar interpretations of fractional precipitation have been proposed to explain indications of deposit-scale zonation of $\delta^{65}\text{Cu}$ in porphyry copper deposits (e.g., Li et al., 2010).

In summary — and perhaps disappointingly — this study indicates that Ag isotopes are unlikely to be the proverbial ‘silver bullet’ for tracing the original source of precious metals in hydrothermal lode-gold deposits. We cannot assess at this point whether the two near-zero values of the two carbon-leader gold samples of the Witwatersrand basin reflect a mixture of lode gold ore, or a distinct mantle source such as Archaean flood basalts and their volatiles. In any case, our study indicates the need for rigorous laboratory determination of Ag isotope fractionation between metal and aqueous species, as a prerequisite to understand hydrothermal fractionation processes in precious-metal ore systems in a more quantitative way.

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Location	Sample description and processing	Weight (1) g or µg	ϵ^{100}_{Ag} (2)	$\pm 2\sigma$	Ag	Au (3) wt% or ppb	Mg (4) ppm	Al ppm	Ca ppm	Fe ppm	Cu ppm	As ppm	S ppm	Pt ppm	Hg ppm	Pb ppm
Sheba mine:	<i>Massive black quartz with bonanza-grade gold (10wt %) in fractures and in white qtz - Au - py - veins (unlocated test sample, courtesy Marc Grünenfelder, ETH Zurich)</i>															
S0-1a	Hand picked Au grain with <1% qz impurity, full analysis	387 µg	3.30		4.69	95.29	<30	621	67	906	227	8	957	3.2	88	27
S0-1b	Same solution, Ag isotopes remeasured later day	387 µg	3.47		4.69	95.29	<30	621	67	906	227	8	957	3.2	88	27
S0-1c	Same solution, Ag isotopes remeasured another day	387 µg	3.32		4.69	95.29	<30	621	67	906	227	8	957	3.2	88	27
S0-1d	Same solution, Ag isotopes remeasured another day	387 µg	3.78		4.69	95.29	<30	621	67	906	227	8	957	3.2	88	27
	Average of four independent analyses and their 2σ		3.47	0.44												
S0-2	Second Au grain with <1% qz impurity, full analysis	290 µg	3.37		4.76	95.18	<30	30	318	1,344	575	5	2,753	3.2	111	418
S0-3	Third Au grain with <1% qz impurity, full analysis	3725 µg	3.64		4.55	95.41	<30		111	134	350	5	112	3.3	166	11
	<i>Black quartz vein with ank + py + 1% free Au, cutting quartz - fuchsite schist of uppermost Onverwacht Group (ZK orebody, 36 level; Fig. 3A)</i>															
S6	Hand picked Au grain with <1% qz impurity, full analysis	637 µg	1.32		6.76	93.19	156	306	256	4,241	446	262	4,247	2.9	147	1.2
Fairview mine:	<i>Asp - py halo along cb-qz vein cutting schistose meta-greywacke of Fig Tree Group (Core sample MRC orebody, hole BH-5894-62-RAMP-86.5m; Fig. 3C)</i>															
FC-nitric	Bulk rock, leached by 7 M HNO ₃	0.977 g			0.000002	<3 ppb	9,790	2,010	4840	103,400	41	55,300	29,900	<0.1	<0.1	12
FC-regia	Residue leached with aqua regia, relative to bulk rock	0.977 g			0.000065	16.0 ppb	558	7,460	153	1,527	1	805	566	<0.1	<0.1	1.4
FC-fluoric	Residue dissolved with conc. HNO ₃ - HF, relative to bulk rock	0.977 g			0.000025	1.8 ppb	147	36,500	<3	1,591	1	72	<20	<0.1	<0.1	<0.1
	<i>Bio - chl - qz metasiltstone of Fig Tree Group with disseminated asp needles and py (total 4 % sulfide); low-grade (few g/t Au) bulk ore (Commitment Reef, UG Level 42)</i>															
F4-nitric	Bulk rock, leached by 7 M HNO ₃	0.709 g			0.000003	<0.4 ppb	11,750	2,560	2752	31,200	14	8,890	14,200	<0.1	<0.1	3.9
F4-regia	Residue leached with aqua regia, relative to bulk rock	0.709 g			0.000008	4.5 ppb	1,168	8,435	63	1,410	1	229	271	<0.1	<0.1	0.4
F4-fluoric	Residue dissolved with conc. HNO ₃ - HF, relative to bulk rock	0.709 g			0.000012	<0.7 ppb	1,810	32,400	32	1,440	1	29	<20	<0.1	<0.1	0.4
New Consort mine:	<i>Qz vein with few 1mm-grains of free Au, cutting bio - amp - qz rich metachert of the Consort Bar (host rock see Fig. 3E; UG level 51)</i>															
C21-1	Hand picked Au grain with ~2% silicate	735 µg			3.90	95.99	562	560	289	503	1065	155	188	2.9	130	38
C21-2	Second hand picked Au grain with ~2% silicate	1457 µg	-3.27		3.57	96.32	305	677	48	394	1105	5	87	3.0	202	7.0
	<i>Massive euhedral asp (60%), po (20%, cpy, py (1% each) in matrix of bio, alb, qz, trm (each ~ 5%), free Au flakes in matrix and asp (Footwall Lens, Level 51, Fig. 3F)</i>															
C11-1	Hand picked tiny Au flake, probably from matrix	170 µg	-4.22		0.06580	1.28	752	174	673	443	31	0	1,590	0.1	193	2.0
C11-2-nitric	Asp-dominated rock fragment, leached by 7 M HNO ₃	0.055 g			0.00002	<9.8 ppb	239	1040	<88	270,900	198	217,100	99,500	<0.1	<0.1	3.4
C11-2-regia	Residue leached with aqua regia	0.055 g	-3.94		0.00587	0.072	5	295	16	90	1	16	824	<0.1	<0.1	0.1
C11-2-fluoric	Residue dissolved with conc. HNO ₃ - HF	0.055 g			<0.0002	< 8.8 ppb	249	3920	256	363	<3.8	5	<55	<0.1	<0.1	1.7
Witwatersrand:	<i>Two samples with free visible gold in carbon from 'carbon leader type' high-grade orebodies</i>															
W-CLR	Au in sheared carbon seam, Carbon Leader Reef, Krugersdorp	630 µg	-0.21		7.00	93.00	<30	93	22	25	16	6	37	0.28	7	57
W-VAAL	Au laminae coating vertical carbon fibres; Vaal Reef, Klerksdorp	255 µg	0.73		1.04	98.92		547	357	567	319	154	<100	0.35	76	848
Mont Charlotte vein stockwork,	<i>Yilgarn Craton: Quartz vein with free Au + pyrite along wall against py-ank-alb-altered dolerite (Heinrich and Candela, fig. 2d)</i>															
CHARL	mm-sized Au flake picked from qz -py vein, max 2% pyrite	2415 µg	4.20		7.79	92.18	<30	<8	48	1,010	328	5	886	3.07	465	34
Brusson orogenic gold district Western Alps:	<i>gold + calcite in late vug of large Feniliaz quartz vein, contact to py-altered ampl</i>															
BRUSS	mm-sized Auflake with max. 3% calcite	7470 µg	1.57		11.59	88.39	2123	4	3010	2,718	189	0	35	2.83	4334	1.0
Native silver ores from specimens of the National Museum of Natural History	<i>(Schönbächler and Hauri, unpublished reconnaissance data, Carnegie Institution Washington DC)</i>															
NMNHR8256	Zacualpan, Mexico: low-sulfidation epithermal vein		-3.71	0.17												
NMNHR164237	Cliff Mine, Michigan, USA		-0.42	0.19												
NMNHR6583	Miller Lake, O'Brien mine, Gowganda, Ontario Canada		-0.44	0.50												
NMNH140003	Maricunga, Chile: high-sulfidation epithermal district		0.80	0.50												
NMNH78478	Freiberg, Germany: metasediment-hosted epithermal vein		1.46	0.50												
NMNH13275	Aspen, CO, USA: supergene alteration of epithermal sulfide veins		2.01	0.41												
Comments																
(1) Mass of solid sample prior to first dissolution step; all concentrations are fractions relative to this solid weight																
(2) Repeat analyses of solution aliquots measured on different days: ± 0.44 ε = estimated uncertainty for Au samples																
(3) Au values of 88.39 to 98.92 % calculated by difference 100 - Ag wt % from precise Ag analyses of large metal flakes																
Smaller values by direct but lower-precision analyses of Au in the same solutions																
(4) In addition, Mn, Sr,Cd,Tl, Cr, Co, Ni, Zn, Zr, Mo, Ti, Rh, Pd, Sn, Te, Re, Ir were analysed – see Argapadmi (2015)																