Stable C, O and S Isotope Record of Magmatic-Hydrothermal Interactions Between the Falémé Fe Skarn and the Loulo Au Systems in Western Mali

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Abstract

The Gara, Yalea and Gounkoto Au deposits of the 17+ Moz Loulo Mining District, largely hosted by the Kofi Series metasediments, are located several kms to the east of the 650 Mt Fe skarn deposits in the adjacent Falémé Batholith. The Au deposits are interpreted to have formed through phase separation of an aqueous-carbonic fluid, which locally mixed with a hypersaline brine of meta-evaporite origin. Recognition of an intrusive relationship between the Falémé Batholith and Kofi Series opens the possibility that the Fe skarns and Au deposits are part of the same mineral system. In this paper, we combine new δ13C, δ18O and δ34S data from the Karakaene Ndi skarn, minor Au occurrences along the western margin of the Kofi Series, and zircons within plutonic rocks of the Falémé Batholith with existing data from the Loulo Au deposits, to model the contribution of magmatic volatiles to Au mineralization.

C- and O-isotope compositions of auriferous carbonate-quartz-sulfide veins from the Loulo Au deposits have wide ranges (δ13C: –21.7 to –4.5 ‰ and δ18O: 11.8 to 23.2 ‰), whereas values from carbonate veins in Kofi Series Au prospects close to the Falémé Batholith, and the Karakaene Ndi Fe skarn deposit, have more restricted ranges (δ13C: –16.8 to –3.7 ‰, δ18O: 11.4 to 17.2 ‰ and δ13C –3.0 ± 1 ‰, δ18O 12.6 ± 1 ‰, respectively). Kofi Series dolostones have generally higher isotopic values (δ13C: -3.1 to 1.3 ‰ and δ18O: 19.1 to 23.3 ‰). Pyrite from Kofi Series Au prospects adjacent to the Falémé
Batholith, have a wide range of $\delta^{34}$S values (~4.6 to 14.2 ‰), similar to pyrite from the Karakaene Ndi skarn (2.8 to 11.9 ‰), whereas $\delta^{34}$S values of pyrite and arsenopyrite from the Loulo deposits are consistently > 6 ‰.

Comparison of the C- and O-isotopic data with water-rock reaction models indicates the Loulo Au deposits formed primarily through unmixing of an aqueous carbonic fluid derived from the devolatilisation of sedimentary rocks with an organic carbon component. Isotopic data are permissive of the hypersaline brine which enhanced this phase separation including components derived from both Kofi Series evaporite horizons interlayered with the dolostones and a magmatic-hydrothermal brine. This magmatic-hydrothermal component is particularly apparent in O-, C-, and S-isotopic data from the Gara deposit and Au prospects immediately adjacent to the Falémé Batholith.
Introduction

Orogenic deposits account for ~30% of total Au production, reserves, and resources (Frimmel and Hennigh, 2015), making them one of the most important sources of Au globally. Most of these deposits formed from near neutral low salinity aqueous-carbonic fluids at temperatures between 250-400°C in greenschist facies metamorphic terranes (e.g. Groves et al., 1998; Goldfarb et al., 2005; Phillips and Powell, 2010; Goldfarb and Groves, 2015). There is widespread consensus that metasedimentary and/or metabasaltic rocks undergoing metamorphic devolatilization reactions are the ultimate source of the ore fluids in orogenic gold deposits, with the metals scavenged from the same rocks (Henley et al., 1976; Norris and Henley, 1976; Kerrich and Wyman, 1990; Goldfarb et al., 1991; Phillips and Powell, 1993; McCuaig and Kerrich, 1998; Pitcairn et al., 2006; Gaboury, 2013; Tomkins, 2013; Pitcairn et al., 2014; Yardley and Cleverley, 2015; Goldfarb and Groves, 2015; Wyman et al., 2016; Groves et al., 2019). However, speculation remains that some deposits include hydrothermal fluids exsolved from crystallizing magmas (Lawrence et al., 2013a, 2013b; Xue et al., 2013; Treloar et al., 2015; Spence-Jones et al., 2018). Resolving this question is an important part of the development of a holistic mineral system model for orogenic Au deposits (Wyman et al., 2016; Groves et al., 2019).

The 17+ Moz Loulo Au Mining District in the Kédougou-Kéniéba inlier in western Mali and eastern Senegal is one of the most richly endowed orogenic Au districts in the West Africa craton (Fig. 1). It includes three major multi-million ounce deposits, including Gara, Yalea, and Gounkoto and numerous satellite deposits that typically contain <1 Moz Au (e.g., Baboto, Faraba, Loulo 3, Loulo 2, P64, and P129). Small-displacement, discontinuous shear-zones, some of which may have nucleated along earlier fold axial planes. Quartz-tourmaline-altered quartz gritstone units within the Kofi Series siliciclastic, carbonate, and evaporitic rocks host the Au deposits. The western margin of the Kofi Series is intruded and unconformably overlain by high-K plutonic rocks of the Falémé Batholith and related Bambadji Formation volcanic rocks, respectively. Magnetite and hematite-rich endoskarns, which contain > 650 Mt Fe, are present within the Falémé Batholith. Related exoskarns locally extend into the Bambadji Formation and the western-most parts of the Kofi Series, further demonstrating the intrusive relationship between the Falémé Batholith and Kofi Series at the time skarn mineralization occurred.

Despite several detailed studies of the Au deposits (Fouillac et al., 1993; Lawrence et al., 2013a; Lawrence et al., 2013b; Lambert-Smith et al., 2016b; Lambert-Smith et al., 2016c), the ultimate source of fluids and Au in the Loulo mineral system remains uncertain. Lawrence et al. (2013b) proposed a magmatic contribution to auriferous fluids due to the presence of a high-temperature (~400 ºC) hypersaline brine in several deposits. However, Lambert-Smith et al. (2016b) argued against a magmatic source for the brines on the basis of B, S, C, and O isotopic data. In particular, B-isotope data indicate derivation of brines from evaporite units in the Kofi Series (Lambert-Smith et al., 2016c). Nevertheless, the Falémé Batholith and associated skarns intrude and extend into the Kofi Series,
instead of being separated by a terrane boundary (Senegal-Mali Shear Zone), reopens the possibility that the Falémé Fe magmatic-hydrothermal system contributed to Au mineralization at Loulo. Furthermore, Masurel et al. (2017c) report direct overprinting of calc-silicate skarn mineralization by biotite-calcite-quartz ± K-feldspar-tourmaline-actinolite alteration associated with Au mineralisation at the Sadiola Hill Au deposit. The deposit is carbonate-hosted and located in the northern part of the Kédougou-Kéniéba inlier in the vicinity of an intrusive centre correlative with the Falémé Batholith.

The Baqata, Kolya, Kabe West and Gefa (Fig. 2) prospects are hosted in the Kofi Series, less than 2 km from the intrusive contact with the Falémé Batholith. Minor Au-bearing veins are also present within the Falémé Batholith, at the Boboti target. These Au occurrences, within the batholith and midway between the batholith margin and major Au deposits of the Loulo Mining District, provide an opportunity to examine the genetic links between the Falémé Fe skarns (Schwartz and Melcher, 2004) and the Loulo Au deposits. Furthermore, samples from the Karakaene Ndi Fe skarn deposits provide data on the isotopic character of the Fe skarns and any local magmatic-hydrothermal contribution to the Au deposits. Here we use new C, O and S isotope data from these Au occurrences and from the Karakaene Ndi skarn, together with existing isotopic data from Gara, Yalea and Gounkoto (Fouillac et al., 1993; Lawrence et al., 2013b; Lambert-Smith et al., 2016b), as tracers for the source to ore pathways of auriferous fluids. The magmatic contribution, if any, to Au mineralization in the Kofi Series is based on new Sensitive High-Resolution Ion Microprobe (SHRIMP) $\delta^{18}$O analyses of magmatic zircons recovered from the Falémé Batholith.

Geological Setting

The 2.27 to 2.05 Ga Paleoproterozoic terranes of the southern West African Craton constitute one of the world’s leading Au–provinces, with an overall endowment in excess of 350 Moz (Goldfarb et al., 2017; Thebaud et al., in press). Paleoproterozoic rocks are exposed in the Baoulé-Mossi domain, the Kédougou-Kéniéba and Kayes inliers (Fig. 1), and in the eastern Reguibat Rise in North Africa. They include shear-bounded, linear and arcuate belts of volcano-sedimentary rocks ca. 2270-2150 Ma old (e.g. Baratoux et al., 2011), younger sedimentary basins ca. 2135-2095 Ma old (e.g. Taylor et al., 1992; Lebrun et al., 2015), and granitoid-dominated terranes ca. 2190-2060 Ma old (e.g. Hirdes et al., 1992; Parra-Avila et al., 2017). The volcano-sedimentary belts largely comprise lavas of tholeiitic and calcalkaline affinity, volcaniclastic rocks, and epiclastic sedimentary rocks. The basins are filled with siliciclastic rocks, including arkoses, greywackes, argillites, arenites, and rare limestones and chemical sediments. Multiple suites of granitoid rocks intrude both the belts and the basins.

The Paleoproterozoic terranes formed, accreted, and were deformed over ~200 Myr (e.g. Perrouty et al., 2012; White et al., 2014; Parra-Avila et al., 2016; Grenholm et al., 2019; Thebaud in press) during the 2266-2140 Ma Eoeburnean, and 2135-2050 Ma Eburnean periods (e.g. Taylor et al., 1992; Dia et al., 1997; Loh et al., 2000; Allibone et al., 2002; Gueye et al., 2007; Hein, 2010; De Kock et al., 2011;
Baratoux et al., 2011; Tshibubudze et al., 2015). Initial volcanism, granitoid emplacement, fold and thrust tectonics, and metamorphism took place during Eoeburnean crustal growth and accretion. The ages of the youngest detrital zircon populations indicate that the sedimentary basins developed from 2135 to 2095 Ma (Davis et al., 1994; Oberthür et al., 1998; Hirdes and Davis, 2002; Vidal et al., 2009; Lebrun et al., 2016). Emplacement of younger granitoid plutons (Parra-Avila et al., 2018; Masurel et al., 2017a), further contractional deformation and metamorphism, late strike-slip deformation, and widespread Au mineralization occurred during the subsequent Eburnean orogeny (Oberthür et al., 1998; McFarlane et al., 2011; Parra-Avila et al., 2015; Fontaine et al., 2017; Fougerouse et al., 2017; Masurel et al., 2017b). Greenschist facies mineral assemblages dominate in most Paleoproterozoic rocks across West Africa, but amphibolite and granulite facies assemblages are present locally within both the Eoeburnean belts and Eburnean sedimentary basins (John et al., 1999; White et al., 2014; MacFarlane et al., 2019). Particularly low geothermal gradients of 10-12° C km\(^{-1}\) are consistent with modern subduction processes during Eburnean time in some parts of the craton (Ganne et al., 2011; Block et al., 2015).

**Geology of the Loulo Mining District**

The Kofi Series comprises metamorphosed immature detrital sedimentary and carbonate rocks deposited after 2120-2100 Ma. The former are dominantly sandstones, wackes, and argillites that include both quartz- and feldspar-rich siliciclastic components. Carbonate lithologies are more abundant in the west, close to the contact with the Falémé Batholith (Fig. 2). These are dominantly dolomitic, with mm to cm-scale marl horizons that contain clasts of fine-grained, sub-angular quartz and feldspar and very fine-grained muscovite. Carbonate lithologies also contain a minor graphitic-argillaceous component, present as mm to sub-mm scale lamellae, or as fine rounded and strained clasts. The Kofi Series sedimentary rocks were tilted upright, tightly folded, cut by reverse faults, and metamorphosed under upper greenschist facies biotite zone conditions during D\(_1\) contractional deformation between ca. 2100-2090 Ma. Later small-scale (< 1 km) folding and development of an associated steeply dipping axial planar cleavage, and Au mineralization occurred during D\(_2\) sinistral transcurrent deformation between ca. 2085 and 2060 Ma (Hirdes and Davis, 2002; Schwartz and Melcher, 2004; Lawrence et al., 2013a; Masurel et al., 2017a; Masurel et al., 2017b). The Falémé Batholith, and associated outlying plutons and dikes, intruded the Kofi Series between 2084 ± 8 Ma and 2075 ± 6 Ma, after inversion of the Kofi Series during D\(_1\) contraction. Outlying dikes of the Falémé batholith at Gounkoto and Gara have been affected by the later stages of hydrothermal activity and syn-Au deformation indicating magmatism occurred during the earlier stage(s) of D\(_2\), prior to mineralisation, but nevertheless part of the same overall D\(_2\) event. While the exact timing of mineralization is yet to be determined, these relationships suggest magmatic activity and Au mineralization were broadly synchronous.
Lawrence et al. (2013a, b) describe two end-member styles of Au mineralization at Loulo, termed Gara- and Yalea-style, respectively. Gara-style deposits are characterized by pyrite dominated ores with metal signatures enriched in Fe-Rare Earth Element (REE)-W and rare base metals. Intense tourmaline alteration, which is atypical of orogenic Au deposits (e.g. Groves et al., 1998), and hypersaline fluid inclusions further characterise this style of mineralization (Lawrence et al., 2013b). Conversely, Yalea-style deposits are As-rich and lack REE and base metal enrichment. Alteration assemblages consist of early quartz-carbonate-albite, overprinted by sericite-chlorite-sulfide-Au (Lawrence et al., 2013a). Fluids are dilute and aqueous-carbonic in character (Lawrence et al., 2013b). The Gounkoto deposit exhibits characteristics in common with both styles, including hypersaline fluid inclusions and As-rich sulfide assemblages (Lambert-Smith et al., 2016b). Satellite deposits and exploration targets in the region display characteristics of either style (Lawrence et al., 2013a; Lambert-Smith, 2014a). All Au and Fe mineralization in the district is associated with moderate to intense albitization, which affects most rock types.

Lawrence et al. (2013b) interpreted fluid inclusion assemblages as representing two distinct end-member fluids: 1) a high T, high-salinity, CO$_2$-poor, aqueous fluid (~400°C; ~45-55 wt. % NaCl equiv.); and 2) a moderate T, dilute, aqueous-carbonic fluid (270-350°C; <10 wt. % NaCl equiv.). Partial mixing between these fluids at Gara-style ore bodies resulted in retrograde boiling and changes in the physicochemical state of both fluids leading to sulfide mineralization and Au precipitation (Lawrence et al., 2013a, b). At Yalea, the hypersaline fluid is absent and fluid inclusion assemblages feature two immiscible phases derived from phase separation of a dilute aqueous-carbonic fluid (Lawrence et al., 2013b). This likely occurred in response to a combination of fluid-rock interaction, particularly sulfidation, and pressure fluctuations along the brittle-ductile host structures. Stable isotope data from Au-related quartz (δ$^{18}$O from 12.9 to 17.4 ‰), dolomite (δ$^{13}$C from -21.7 to -4.5 ‰), and pyrite (δ$^{34}$S from 5.8 to 15.5 ‰) (Lawrence et al., 2013b) at Gara, Yalea and Gounkoto are generally consistent with fluids being sourced from the devolatilization of Kofi Series metasedimentary rocks (Lambert-Smith et al., 2016b), though δ$^{18}$O and δ$^{13}$C values partially overlap magmatic fields. Furthermore, B-isotope data from hydrothermal tourmaline indicates a meta-evaporite source for B, implying evaporite devolatilization in the genesis of the hypersaline brine (Lambert-Smith et al., 2016c).

**Au and Fe mineralization in the western Kofi series and Falémé Batholith**

The minor Au occurrences along the western margin of the Kofi Series at Baqata, Kolya, Kabe West, Boboti and Gefa (Fig. 2) have been described in detail by (Lambert-Smith, 2014a). The key geological characteristics of these occurrences and the larger deposits are summarized in Table 1.

Baqata is located ~6.2 km SE of Gounkoto (Fig. 2). Mineralization is hosted in a package of altered Kofi Series quartz wacke, dolostone, and argillite interbedded with siltstones and sandstones, which dips 60° W and strikes 185°. Bedding is cut by a sub-vertical NNE-striking cleavage which is axial.
planar to 100 m-scale SSW plunging asymmetric F2 folds. The sequence is intruded by 1-10 m thick, variably albitized diorite and monzodiorite dikes, and cut by steeply dipping NNW-striking (80E/350) shear zones. Mineralized rocks include both Gara-style ankerite-quartz-pyrite stockworks in tourmalinized quartz wacke and disseminated pyrite and chlorite-pyrite stringers in albitized dolostone and quartz wacke. Au grades locally reach 13.4 g/t but are discontinuous along strike and down-dip. Like at Gara, accessory Ni-sulfides (e.g. millerite), xenotime, and monazite are present. Gold, tellurobismuthite (Bi2Te3), calaverite and bismuth are occluded in pyrite and the gangue.

At Kolya, ~13 km south of Gara, discontinuous zones of mineralized rock that contain up to ~5.8 g/t Au are hosted in a package of argillites, greywackes, tourmalinized quartz wackes, and dolostones, which dips 70° W and strikes 350°. These rocks are folded, cleaved, and cut by shear zones in the same manner as those at Baqata. Dolerite dikes intrude the sedimentary rock package. Mineralized rocks at Kolya comprise chlorite-pyrite veins primarily within the dolerite dikes, and minor hydrothermal breccias and ankerite-quartz-pyrite vein stockworks in tourmalinized quartz wacke. Gold occurs as occluded grains and fracture-fill in pyrite and arsenian pyrite, where it is associated with minor altaite (PbTe), melonite (NiTe2) and tellurobismuthite. Kolya lacks Ni-sulfide phases.

Kabe West is located ~2.5 km south west of Kolya. Gold is hosted in intensely albitized igneous rocks which intrude albitized dolostone, siliciclastic rocks and hydrothermal breccias. Gold grades are typically 2-4 g/t (locally up to 11.3 g/t) and spatially discontinuous. Structural controls on mineralization are not known due to poor exposure, lack of oriented drill core, and overprinting of pre-mineralization fabrics by intense albitization. Pyrite is the dominant ore phase and contains up to 1.9 wt. % Co and 0.5 wt. % Ni. Gold, altaite and melonite occur as inclusions within, or annealed to, pyrite grains, which are disseminated in albitized wall rock and in hydrothermal breccias with tourmaline or dolomite cement.

Mineralized rocks at Gefa, ~7 km south of Baqata, are hosted in a package of albitized argillite, dolostone, and greywacke. The host sedimentary rocks strike N-S and dip 80° W and are intruded by unmineralized diorite and quartz feldspar porphyry dikes. These rocks are cut by sheared polymict hydrothermal breccias. Mineralized rocks are generally characterized by Au grades < 0.5 g/t, localized within zones of brittle quartz-carbonate-pyrite veining that cross cut intensely albitized rock.

Boboti is located ~8.3 km to the south west of Baqata. Mineralization is hosted in albitized subvolcanic andesites and medium to coarse-grained diorites of the Boboti Pluton. Gold is hosted by pyrite grains within carbonate-pyrite veinlets and minor disseminated pyrite in the immediate wall rock to veins. Grades reach a maximum of 2.6 g/t Au, but mineralized zones are rarely continuous over more than 1 meter downhole.
The Falémé Iron District (Schwartz and Melcher 2004) endo- and exoskarn deposits are located within the Falémé Batholith, associated altered Bambadji Formation volcanic rocks, and western-most parts of the Kofi Series (Fig. 2). In the skarns, proximal halos of calc-silicate alteration (actinolite-epidote-allanite-titanite ± clinopyroxene-garnet) overprint regional albitization (Fig.3 a-e). This is further overprinted by massive magnetite ±apatite ore (Fig. 3f). Late sulfide mineralization which typically includes coarse disseminated pyrite and chalcopyrite, or pyrite-chalcopyrite-calcite veins cuts the iron ore (Fig. 3f, g). These sulfides are locally auriferous, typically containing < 0.5 g/t Au and rarely up to 3 g/t Au associated with trace amounts of Co-Ni-U-bearing phases. Preliminary fluid inclusion studies by Schwartz and Melcher (2004) and Lambert-Smith (2014a) tentatively indicate a H$_2$O-NaCl-CO$_2$ magmatic fluid, with low salinity (approx. 3.3 wt. % NaCl equiv.) and XCO$_2$ = 0.11. The alteration and ore mineralogy of the skarns share commonalities with Fe-oxide apatite deposits, and their close spatial association with a large orogenic Au camp hints at IOCG affinities (Schwartz and Melcher 2004, Lawrence et al. 2013a).

Sample characteristics and Methods

δ$^{13}$C and δ$^{18}$O was measured in 28 samples from the Kolya, Baqata, Boboti, Gefa and Kabe West exploration targets and 7 samples from the Karakaene Ndi skarn (Fig. 2). These data include ankerite, calcite and dolomite from auriferous, skarn-related, and barren hydrothermal veins and wall rock alteration, and dolomite from host dolostone units (Fig. 4a). A further 49 δ$^{13}$C and δ$^{18}$O analyses are included from published data for Gounkoto (Lambert-Smith et al., 2016b); Gara (Fouillac et al., 1993; Lawrence et al., 2013b), and Yalea (Lawrence et al., 2013b). δ$^{34}$S was measured in 23 pyrite samples from Kolya, Baqata, Boboti and Kabe West exploration targets and in 11 pyrite samples from the Karakaene Ndi skarn. Zircon δ$^{18}$O values were measured by SHRIMP on 3 samples of quartz monzodiorite and quartz monzonite from the Falémé Batholith (RG10036, RG10039, RG10050) and one sample of Bambadji Formation andesitic volcaniclastic rock (RG10030).

Mineralized vein characteristics

Tourmalinized quartz wacke units are important ore hosts at Gara and the P-64 satellite, subordinate ore hosts at Gounkoto, and host sub-economic mineralization at the Baqata and Kolya targets. Tourmalinization involves the replacement of the matrices of wackes with cryptocrystalline tourmaline, making the unit more brittle and therefore susceptible to the development of ankerite-quartz-pyrite-Au ± dolomite ± tourmaline hydro fracture vein stockworks (Fig. 4b). These stockworks contain several vein morphologies characteristic of the brittle-ductile environment, including planar centimeter- to millimeter-scale veins and veinlets, brecciated and boudinaged veins, and sigmoidal vein arrays. Veining is typically multi-generational, occurring in multiple orientations and at multiple scales (~100 μm to ~2-3 cm vein width). This stockwork style of mineralization typically affects ~1 to 20 m thick
units and is associated with Au grades up to ~100 g/t. High grades are generally associated with strongly altered host rocks, high carbonate and sulfide content in the veins, and the most intense vein networks with several generations of veins. Veins at Gara commonly include late, gray, quartz-pyrite-Au cores (Lawrence et al., 2013b).

In contrast, veining is a minor part of the mineralized rocks at Yalea and Gounkoto, which include a larger proportion of sulfide stringers, disseminations in the matrix of hydrothermal breccias, and chloritic ductile shear zones. Mineralized veinlets at Yalea cross-cut ductile shear fabrics, and contain arsenopyrite-pyrite-arsenian pyrite-Au ± quartz ± ankerite (Fig. 4c). At Gounkoto quartz-carbonate-pyrite-chlorite veins commonly occur several 10s of meters outside the main ore zone and are associated with grades up to ~5 g/t Au. Veins are typically undeformed and may cross-cut earlier Au mineralization. Mineralogically similar veins have been observed in high grade ore shoots but are typically highly deformed and overprinted by later Au mineralization. Sulfides occupy up to 50 vol. % of the vein assemblage (more typically ~20 %), and carbonate mineralogy is commonly dolomitic and rarely ankeritic. Vein width varies from <100 μm up to 6-7 cm. Many veins have been reactivated and brecciated by later hydrothermal events. Undeformed hydrofracture veins and veinlets are also common at the Baqata, Boboti, Gefa and Kabe West exploration targets.

At the Karakaene Ndi skarn, veining generally postdates the oxide ore. Veins are <1 mm to 6 cm thick and composed of <100 μm to >5 mm calcite-pyrite ± quartz ± chlorite ± Au, with pyrite ≈ calcite (Fig. 3g). Sulfide-rich veins do not show the zoned calc-silicate alteration halos characteristic of primary oxide mineralization.

A small number of veins sampled from the Kofi Series were classified as mineralized based on the presence of sulfide minerals, despite returning fire assay results below detection limit (<0.01 ppm). These veins contain fine pyrite and chalcopyrite in variable abundance. Several of these veins contain only one or two sub-mm-scale grains of pyrite or chalcopyrite (Fig. 4d), while others contain several modal percent of coarse pyrite (some with multiple generations) (Fig. 4g).

**Barren vein characteristics**

Barren hydrothermal veining occurs throughout the Loulo Mining District (Fig. 4e-f). Pre-mineralization barren quartz-carbonate veins are deformed and display asymmetric fold patterns (Fig. 4f). Late-stage barren quartz-carbonate veins, including at Gara, Yalea, and Gounkoto, cross cut mineralization and alteration (Lawrence et al., 2013a). Elsewhere in the district, similar veining cross cuts barren country rock (Fig. 4e). These late veins are typically undeformed. The timing of veins occurring outside the footprint of the large deposits is somewhat uncertain; it is possible that some of these veins are barren equivalents to mineralized veins. The mineralogy in barren veins comprises
variable proportions of quartz-dolomite ± chlorite, with no sulfide minerals present. Vein width ranges
from <1 mm to approximately 8 cm (typically <1 cm).

Analytical procedures

Energy-dispersive X-ray spectroscopy - Mineral compositions were determined using an Oxford
Instruments X-ACT Energy Dispersive System detector mounted on a Zeiss EVO 50 Scanning Electron
Microscope at Kingston University London. The EDS employed an accelerating voltage of 20 kV, a
beam current of 1.5 nA, and a detector process time of 4 seconds. The detection limit for all elements
was ~0.2 wt. %.

Stable isotopes in carbonates and pyrite- Carbon and oxygen isotopic analyses of carbonate minerals
were carried out at the Scottish Universities Environmental Research Centre (SUERC) in East Kilbride,
Scotland. CO$_2$ was liberated via in vacuo reaction with 100 % phosphoric acid at 100 °C for dolomite
and ankerite, and at 25 °C for calcite. The CO$_2$ was analysed on a VG SIRA 10 mass spectrometer. Data
were corrected using oxygen fractionation factors for acid-extracted CO$_2$ at 100 °C of 1.00913 and
1.00901 for dolomite and ankerite, respectively (Rosenbaum and Sheppard, 1986). CO$_2$ liberated at 25
°C from calcite was corrected using α of 1.0014 (Craig, 1957). Carbon and oxygen isotope data are
reported as per mill (‰) deviations relative to Vienna PeeDee belemnite (V-PDB) and Vienna Standard
Mean Ocean Water (V-SMOW), respectively. Lab reproducibility based on complete analysis of
internal standard MAB 2 (Carrara marble) and replicate analyses of calcite unknowns (including acid
digestion at 25°C) was ± 0.10 ‰ for δ$^{13}$C and ± 0.12 ‰ for δ$^{18}$O (1σ). Reproducibility based on repeat
analysis of dolomite unknowns (including acid digestion at 100°C) was ± 0.09 ‰ for δ$^{13}$C and ± 0.10
‰ for δ$^{18}$O (1σ).

Pyrite separates were analysed by standard techniques (Robinson and Kusakabe, 1975). SO$_2$ gas was
liberated by combusting sulfides with excess Cu$_2$O at 1075 °C, in vacuo. Liberated SO$_2$ was analysed
on a VG Isotech SIRA II mass spectrometer, and standard corrections applied to raw δ$^{34}$S values to
produce δ$^{34}$S. The data were calibrated using international standards NBS-123 (Sharp, 2017) and IAEA-
S-3 (Mann et al., 2009), and the SUERC standard CP-1. Lab reproducibility was ± 0.3 ‰ (1σ). Data
are reported in δ$^{34}$S notation as per mil (‰) deviations from the Vienna Cañon Diablo Troilite (V-CDT)
standard.

Oxygen isotopes in magmatic zircons- Zircon δ$^{18}$O values were measured by SHRIMP on 3 samples of
quartz monzodiorite and quartz monzonite from the Falémé Batholith (RG10036, RG10039, RG10050)
and one sample of Bambadji Formation andesitic volcaniclastic rock (RG10030) (Fig. 2). Descriptions
of these rocks and the associated U-Pb zircon geochronology are provided by Allibone et al. (in press).
Oxygen (δ$^{18}$O/δ$^{16}$O) isotope ratios were measured for a selection of magmatic areas within zircon grains
in order to characterize the isotopic composition of the magma from which they crystallized and thereby
investigate the nature of the source(s) of these magmas. Following the U-Pb analyses, the SHRIMP U-
Pb pits, 1-2 µm deep, were lightly polished away and oxygen isotope analyses were made in exactly the
same location using SHRIMP II fitted with a Cs ion source and an electron gun for charge compensation
as described by Ickert et al. (2008). Oxygen isotope ratios were determined in multiple-collector mode
using an axial continuous electron multiplier (CEM) triplet collector, and two floating heads with
interchangeable CEM - Faraday Cups. The FC1 (Duluth Gabbro) reference zircons were analyzed to
monitor and correct for isotope fractionation. The measured $^{18}\text{O}/^{16}\text{O}$ ratios and calculated $\delta^{18}\text{O}$ values
have been normalized relative to a FC1 weighted mean $\delta^{18}\text{O}$ value of 5.61 ‰ (Fu et al., 2015).
Reproducibility in the FC1 reference zircon $\delta^{18}\text{O}$ value was ± 0.40 ‰ (2σ uncertainty) for the analytical
session. Temora 2 reference zircons were analysed in the same session as a secondary reference and
gave a $\delta^{18}\text{O}$ value of 8.04 ± 0.37 ‰, in agreement with that reported by Ickert et al. (2008).

Results

Sulfur isotopes

Sulfur isotope data are listed in full in Table 2. Auriferous sulfides from the Loulo Au deposits and their
satellites have $\delta^{34}\text{S}$ values between 5.8 and 15.5 ‰, with a mean of 9.6 ‰ (n=74) (Fouillac et
al., 1993; Lambert-Smith et al., 2016b; Lawrence et al., 2013b). Diagenetic pyrite from the Kofi series
shows a broad range from 6.4 to 25.1 ‰. New $\delta^{34}\text{S}$ data (Fig. 5b) from Kabe West ranges from -4.6 to
3.4 ‰ (n=9; mean of -0.4 ‰). Sulfides at Baqata range from 5.5 to 11.8 ‰ (n=4; mean of 8.1 ‰).
Kolya exhibits $\delta^{34}\text{S}$ values from 4.2 to 14.2 ‰ (n=5; mean of 9 ‰). Mineralization at Boboti ranges
from 1.7 to 3.9 ‰ (n=5; mean of 2.5 ‰). Sulfides at the Karakaene Ndi skarn range from 2.8 to 11.9
‰ (n=11; mean of 5.3 ‰) (Fig. 5c). Early sulfides disseminated within the massive Fe ore and hosted
in Fe oxide veins range from 2.8 to 4.4 ‰, whereas late sulfide-rich veins range from 4.9 to 11.9 ‰.

Carbon isotopes

Carbon isotope data are listed in full in Table 3. The $\delta^{13}\text{C}$ values for carbonate country rocks, and barren
and mineralized veins in the Loulo Mining District range from -21.7 to 3.8 ‰ (mean of -7.3 ‰; n=79).
The dataset for Au-bearing veins exhibits peaks in $\delta^{13}\text{C}$ at -10 ‰, -6 ‰ and at 0 ‰ (Fig. 6a). Data from
Kofi Series dolostones provide a local $\delta^{13}\text{C}$ values for carbonate country rocks. These range from -3.1
to 1.3 ‰ (mean of -0.5 ‰; n=10).
Sulfidized carbonate-bearing veins in the Kofi Series show a broad range in $\delta^{13}\text{C}$ values from -21.7 to
344 -3.7 ‰ (n=55) (Fig. 6a). This population is largely unimodal, with a minor negative skew toward lower
$\delta^{13}\text{C}$ values (mode at approximately -8 ‰). The Bambadji exploration targets (Fig. 6b) show a range in
$\delta^{13}\text{C}$ from -16.8 to -3.7 ‰ (mean of -8.4 ‰; n=13). Baqata veins range from -15.0 to -3.7 ‰ (mean of
-8.6 ‰; n=6). Kolya veins range from -8.8 to -5.1 ‰ (mean of -7.7 ‰; n=5). Kabe West ranges from -
Gefa ranges from -16.8 to -7.0 ‰ (mean of -10.2 ‰; n=4). Gara, Yalea, and Gounkoto show the greatest range of values, from -21.7 to -4.5 ‰ (mean of -11.6 ‰; n=32). Gara shows a range from -14.4 to -4.5 ‰ (mean of -9.6 ‰; n=16), Yalea from -21.7 to -10.6 ‰ (mean of -16.7 ‰; n=8), and Gounkoto from -13.6 to -6.3 ‰ (mean of -9.1 ‰; n=8). In contrast, barren (sulfide absent) carbonate-bearing hydrothermal veins show a similar population distribution to carbonate country rocks. This ranges from -2.4 to 3.8 ‰ (mean of -0.7 ‰; n=9) (Fig. 6a). Calcite from sulfide veins at the Karakaene Ndi skarn deposit range from -4.1 to -1.8 ‰ (n=7; mean of -3.0 ‰) (Fig. 6c).

Oxygen isotopes in carbonates

Oxygen isotope data for carbonate minerals are listed in full in Table 3. The O isotope ratios of carbonates in the Loulo district exhibit a wide range from 11.4 to 23.3 ‰ (n=79). The data are not normally distributed and have a positive skew toward higher δ18O values (Fig. 6d). Kofi series limestones tend to exhibit heavier δ18O values than hydrothermal veining, ranging between 19.1 and 23.3 ‰, with one outlying value at 15.1 ‰ (mean of 20.3 ‰; n=10). Barren hydrothermal veins are indistinguishable from mineralized hydrothermal veins based on their O-isotopic composition (Fig. 6e). Barren veins range from 11.7 to 21.1 ‰ (mean of 15.8 ‰; n=14). Mineralized veins range from 11.4 to 23.2 ‰ (mean of 15.6 ‰; n=55). Calcite from sulfide veins at the Karakaene Ndi skarn deposit range from -12.0 to -13.5 ‰ (n=7; mean of -12.6 ‰) (Fig. 6f).

Oxygen isotopes in magmatic zircons

Oxygen isotope data in magmatic zircons is listed in full in Appendix Table A1. The zircon δ18O values obtained from Bambadji Formation andesitic volcaniclastic rock sample RG10030 range between 6.4 and 8.4 ± 0.5 ‰ with a weighted mean value of 7.2 ± 0.7 ‰ (MSWD of 13). However, a probability density plot shows a minor mode at around 6.5 ‰, with scatter among higher values. All grains analysed have U-Pb isotopic ratios < 10% discordant implying their oxygen isotope ratios are unlikely to have been markedly affected by post crystallisation Pb-loss ref. Zircons from two samples of the Highway Pluton (RG10036, RG10039) were analysed. The 5 most concordant zircon analyses in RG10036 have δ18O ratios of between 7.0 and 8.4 ± 0.5 ‰. The two most concordant analyses from RG10039 have associated δ18O ratios of 7.0 and 8.1 ± 0.5 ‰, respectively. Remaining discordant zircons from these two samples have δ18O ratios (6.5 to 8.4 ‰), which are in broad agreement with the range of values in concordant zircons in all the samples (6.4 to 8.4 ‰) and may therefore be considered with the other data. The weighted mean for RG10036 is 7.9 ± 0.4 ‰ (MSWD of 8.4). RG10039 has too few analyses to be significant, though the weighted mean of 7.7 ‰ is in broad agreement with data from the other samples. A sample from the Balangouma Pluton, west of Gara (RG10050), contains relatively abundant concordant zircon whose δ18O ratios range between 6.5 and 8.1 ± 0.5 ‰ with a mean of 7.6 ± 0.3 ‰ (MSWD of 3.8).
A weighted mean of all the zircon data yields a $\delta^{18}$O value of 7.6 ± 0.2 with an MSWD of 8.2. However, a probability density plot of the entire dataset suggests that there are two general values recorded, with a major mode at : a more prominent value around 7.9 ± 0.1 ‰ and a less prominent lower value minor mode around 6.7 ± 0.2‰.

**Discussion**

*S-isotope Compositions and Sulfur Sources*

New $\delta^{34}$S data from the Au occurrences at Kabe West, Baqata, Boboti, and Kolya (-4.6 to 14.2 ‰) partially overlap the range of values for the Loulo Au deposits (5.8 to 15.5 ‰) and those of diagenetic pyrite from the Kofi series (6.4 to 25.1 ‰), though they also extend to lower ratios (Fig. 5 a and b). Lambert-Smith et al. (2016b) interpret these data to indicate that sulfur in the main Loulo Au deposits is derived from a metasedimentary source. Sulfides at the Karakaene Ndi Fe skarn change from lower isotopic values in early disseminated sulfides (2.8 to 4.4 ‰), to higher values in late sulfide-rich veins (4.9 to 11.9 ‰), which overlap with the range of $\delta^{34}$S in Kofi series diagenetic pyrite (Fig. 5c). This suggests that paragenetically early sulfur in the skarn was dominantly sourced from magmatic fluids ($\delta^{34}$S = 0±2 ‰) (Ohmoto, 1972), but as the hydrothermal system developed, sulfur with high $\delta^{34}$S (> 4 ‰) was incorporated from the Kofi series metasedimentary rocks or the Bambadji Formation volcanic rocks. Persistently low $\delta^{34}$S values at the Boboti and Kabe West Au prospects (-4.6 to 3.9 ‰) imply a magmatic sulfur source.

*C-isotope Compositions and Carbon Sources*

Carbonate minerals from barren hydrothermal veins and dolostone country rocks throughout the southern Kofi Series have $\delta^{13}$C values between -3.1 ‰ and 3.8 ‰ (Fig. 6a, b), with means of -0.7 and -0.5 ‰, respectively. These values are typical for Paleoproterozoic marine carbonate (Strauss and Moore, 1992). This indicates that barren veins likely formed through dissolution of carbonate minerals in the host sedimentary rocks (Dietrich et al., 1983; Elmer et al., 2006; Lawrence et al., 2013b).

Compositions of auriferous veins in the Kofi Series are more heterogeneous, ranging from -21.7 to -3.7 ‰ (mean of -9.9 ‰) (Fig. 6a, b). The lowest ratios at Yalea (-19.5 to -21.7 ‰) (Lawrence et al., 2013b), are within the $\delta^{13}$C range of Precambrian organic matter, at -24.7 ± 6 ‰ (Schidlowksi et al., 1975, Papineau et al., 2010). This is similar to carbonaceous material in of the Paleoproterozoic Kumasi Basin in Ghana, which yield mean $\delta^{13}$C$_{org}$ of -23 ± 5 ‰ (Mumin et al., 1996; Oberthuer et al., 1996). The $\delta^{13}$C of auriferous veins from elsewhere in the Loulo district, including most data from Baqata, Kolya, Kabe West and Gefa (Fig. 6b), fall between -16 and -4 ‰. These higher values could reflect contributions of carbon from either (1) the Kofi Series dolostones or (2) magmatic CO$_2$ ($\delta^{13}$C$_{CO2} \approx -5$ to -10 ‰; Ohmoto, 1972).
In either case, the range of compositions indicate a contribution of $^{13}$C-depleted organic carbon to the hydrothermal system (Fig. 6a). The two most probable mechanisms by which this might occur are: 1) oxidation of graphite derived from organic matter ($C + O_2 \rightarrow CO_2$), or 2) hydrolysis of graphite ($2C + 2H_2O \rightarrow CO_2 + CH_4$). Application of isotopic fractionation factors (using the equations of Ohmoto and Rye, 1979; Golyshhev, et al. 1981; Horita, 2001) for average ore forming temperatures in the Loulo district (ca. 320 °C; Lawrence et al., 2013b; Lambert-Smith et al., 2016b) suggests that in situ hydrolysis of graphite in Kofi dolostones would produce CO$_2$ with $\delta^{13}$C $\geq$ -17.5 ‰. Carbonate minerals precipitated from this fluid between 295 and 340 °C (after Lawrence et al 2013b) would have $\delta^{13}$C between of −18.1 and −19.2 ‰. This cannot therefore explain the lowest $\delta^{13}$C values at Yalea. Alternatively, C-isotope fractionation during hydrolysis could occur in the fluid source region. A fluid with $X$(CO$_2$) = 0.2-0.3 may be produced at temperatures of 500 to 520 °C at the greenschist-amphibolite transition (Elmer et al., 2006). This could produce $\delta^{13}$C$_{CO_2}$ values as low as -20.8 ‰ yielding $\delta^{13}$C$_{dolomite}$ as low as -21.7 ‰, depending on the initial $\delta^{13}$C$_{org}$ of the source material. In both cases we assume open system behaviour, whereby CO$_2$ has undergone significant fractionation from the source graphite composition. This $^{13}$C-depleted fluid may then have interacted with country rocks in the Kofi Series or a fluid (brine?) of differing composition, to produce the wide range of observed values.

The isotopic compositions of late carbonate-sulfide veining at the Karakaene Ndi Fe skarn deposit (-4.1 to -1.8 ‰) are ~1 ‰ above the expected range of values for a magmatic fluid (Fig. 6c). A cooling magmatic fluid should precipitate carbonate minerals with lower $\delta^{13}$C; therefore, it seems likely that fluid mixing or wall rock interaction have modified the fluid. The most likely scenario is incorporation of heavier $\delta^{13}$C from the Kofi dolostones during hydrothermal activity around the skarn (Fig. 6a, c). This is consistent with the interpretation of the $\delta^{34}$S data (Fig. 5a, c).

O-isotope Compositions and Oxygen Sources

The $\delta^{18}$O values in hydrothermal carbonate veins in the Kofi Series are more homogeneous compared with the $\delta^{13}$C values. Barren, sulfidized and auriferous veins have near identical mean $\delta^{18}$O values of 15.8, 15.0, and 15.6 ‰, respectively, and range from 11.4 to 23.2 ‰ (Fig. 6 d, e, f). Isotopic compositions above ~18 ‰ in auriferous veins are interpreted to represent disequilibrium as $\delta^{18}$O in paired quartz-dolomite samples at Gounkoto and Yalea display $\delta^{18}$O$_{quartz} < \delta^{18}$O$_{dolomite}$ (Lambert-Smith et al., 2016b; Lawrence et al., 2013b). This scenario suggests later modification of $\delta^{18}$O$_{dolomite}$ (Jenkin et al., 1991). Most samples with $\delta^{18}$O below ~14 ‰ are from the western Kofi Au prospects (Fig. 6d and e), which show relatively high $\delta^{13}$C values >10 ‰ (Fig. 6b). O-isotope compositions for Falémé batholith magmatic rocks are constrained by $\delta^{18}$O$_{zircon}$ data obtained via SHRIMP analysis, the dominant population of which yield a $\delta^{18}$O$_{zircon}$ value of 7.9 ± 0.1 ‰ (2 SD; n=28) (see App. Table A1). We estimated $\delta^{18}$O$_{magma}$ using melt-zircon fractionation values of Trail et
al. (2009) ($\Delta_{\text{melt-zircon}}$ at 800 °C = 1.7 ‰). We then applied the plagioclase-water fractionation values of Zheng (1993) ($\Delta_{\text{albite-H}_2\text{O}}$ at 700 °C = 0.2 ‰), to calculate a $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value of 9.4 ‰ for the Falémé batholith. Zircon crystallisation temperatures were estimated using data in Samperton et al. (2017). The maximum range of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values for a magmatic-hydrothermal fluid exsolved from the Falémé batholith is 7.9 to 10.0 ‰. The average $\delta^{18}\text{O}_{\text{fluid}}$ value calculated from carbonates in the Loulo district overlaps this range at 10.2 ± 2.3 ‰ (calculated at 320 °C using the equations of Zheng, 1999). However, these data alone cannot constrain the fluid source as $\delta^{18}\text{O}_{\text{fluid}}$ values for local magmatic and metamorphic water (~4 to 25 ‰) overlap (Sheppard, 1986). At best these data are permissive of either, or both, fluid sources, and so must be interpreted in their geological context, together with $\delta^{13}\text{C}$ data. The western Kofi Au prospects have lower average $\delta^{18}\text{O}_{\text{fluid}}$ values of 9.1 ‰ (Baqata), 8.6 ‰ (Kolya), 8.3 ‰ (Kabe West), and 8.5 ‰ (Gefa), whereas the intrusive-hosted Boboti target has a significantly lower value of 6.6 ‰. These lower values suggest the involvement of fluids sourced from the Falémé batholith in Au mineralization at these locations. Similarly, $\delta^{18}\text{O}_{\text{calcite}}$ at Karakaene Ndi, at temperatures of 550 °C, yield a $\delta^{18}\text{O}_{\text{fluid}}$ range from 9.6 to 11.1 ‰, overlapping the upper end of local magmatic water values.

Carbon-Oxygen Isotope Modelling

To test whether magmatic fluids may have contributed to the Au-bearing hydrothermal system of the Loulo district, we calculated the C-O isotope compositions of mixtures between a dilute metamorphic aqueous-carbonic fluid, and 1) a hypersaline brine derived from metaevaporites, and 2) a magmatic hydrothermal fluid sourced from the Falémé batholith. The equations of Schwinn et al. (2006) were used to calculate $\delta^{13}\text{C}$ values for carbonates precipitated from a mixed fluid ($\delta^{13}\text{C}_\text{M}$):

$$\delta^{13}\text{C}_\text{M} = \left(\frac{m^*_B f_B}{m^*_B f_B + m^*_A(1-f_B)}\right) \cdot \delta^{13}\text{C}_B + \left(\frac{m^*_A(1-f_B)}{m^*_B f_B + m^*_A(1-f_B)}\right) \cdot \delta^{13}\text{C}_A$$

Where $\delta^{13}\text{C}_B$, $\delta^{13}\text{C}_A$, and represent C-isotope compositions for the brine, the aqueous-carbonic fluid, respectively. The molalities of carbon in the brine $m^*_B$ and aqueous-carbonic fluid $m^*_A$, have been calculated using the following equation:

$$m^*_B = \frac{m_B}{n_w + \sum m_{i,B}}$$

where $n_w$ is the total number of moles H$_2$O in 1 kg water, $m_B$ is the uncorrected molality of carbon in the brine, and $\sum m_{i,B}$ is the sum of the molalities of all solutes in the brine. This approach considers the significant salinity differences between the two fluids by correcting for total solute concentrations (Schwinn et al., 2006). These equations were adapted to model $\delta^{18}\text{O}_{\text{fluid}}$.

End member fluid isotopic and chemical compositions are detailed in Table 4. The starting isotopic composition for the brine ($\delta^{13}\text{C}_{\text{fluid}} = 1.8 \%o$ and $\delta^{18}\text{O}_{\text{fluid}} = 17.3 \%o$) is based on devolatilization of a
dolostone with similar initial $\delta^{13}$C and $\delta^{18}$O to that of Kofi Series dolostones (Valley, 1986). Starting compositions of the magmatic fluid ($\delta^{13}$C$_{\text{fluid}} = -6.0$ ‰ and $\delta^{18}$O$_{\text{fluid}} = 9.4$ ‰) are based upon $\delta^{18}$O$_{\text{H}_2\text{O}}$ from the Falémé batholith (App. Table A1) and the accepted range of magmatic $\delta^{13}$C$_{\text{CO}_2}$ (Taylor, 1974). The aqueous-carbonic fluid is assumed to have the composition $\delta^{13}$C$_{\text{fluid}} = -27.0$ ‰ and $\delta^{18}$O$_{\text{fluid}} = 10.2$ ‰. This represents a fluid derived from metamorphic devolatilization of C$_{\text{org}}$ bearing sediments. $\delta^{13}$C and $\delta^{18}$O of dolomite were calculated at ore forming temperatures of 320 °C.

Figure 7 shows that the isotopic character of auriferous hydrothermal veins at Loulo cannot be explained by binary mixing between end members of metamorphic aqueous-carbonic fluid and either a meta-evaporite derived brine, or a magmatic fluid from the Falémé batholith. We note above that the isotopic signature of the unequivocally magmatic Karakaene Ndi skarn does not correspond directly to Falémé magmatic fluid values. This suggests that any magmatic-hydrothermal fluid in even the most proximal parts of the hydrothermal system may be somewhat cryptic. We have therefore modelled the effects of water-rock reaction on the C-O isotope system (Fig. 7), with the objectives of (1) explaining the $\delta^{13}$C and $\delta^{18}$O signature of the Karakaene Ndi skarn and (2) investigating the magmatic contributions to the Loulo Au deposits, particularly the prospects in the western Kofi Series. This was accomplished using the following equation, assuming open system behaviour (modified after Shelton, 1983):

$$\delta^f_r = (\delta^i_r - \delta^i_w + \Delta)e^{-\frac{w_c}{Rc}} + \delta^i_w - \Delta$$

Where $r$ and $w$ denote rock and water (or mineral and fluid), respectively. $\delta^i$ and $\delta^f$ denote the initial and final isotopic composition, respectively. $\Delta$ is the fluid-mineral per mil fractionation as a function of temperature (in this case 320 °C for the metamorphic fluid and 550 °C for the magmatic-hydrothermal fluid). $C$ indicates concentration, $R$ mass of rock, and $W$ mass of water. The reaction curves were modelled for water-rock ratios between 100 and 0.01. The metamorphic fluid was modelled at XCO$_2$ = 0.2, and the magmatic-hydrothermal fluid at 0.11 (Lambert-Smith et al., 2016b, Lawrence et al., 2013b). End member fluid isotopic and chemical compositions are as detailed above (Table 4). Average Kofi dolostone compositions were used for the host rock.

**Interactions between the Loulo and Falémé Mineral Systems**

Carbonate veins from Karakaene Ndi fall along water-rock reaction pathways typical of magmatic-hydrothermal systems (Fig. 7) (e.g. Pass et al., 2014). These data represent a hot (~550 °C) magmatic fluid from the Falémé Batholith interacting with significantly cooler carbonate-rich wall rocks with high $\delta^{13}$C. This pattern is replicated in $\delta^{34}$S data (Fig. 5c), where a shift to higher $\delta^{34}$S in later veins suggests an influx of wall rock sulfur as the hydrothermal system began to cool and retrograde skarn mineralization began.
C-O isotope modelling indicates that water-rock reaction between a metamorphic fluid and carbonate-rich Kofi Series host rocks was an important process at Gara, Yalea and Gounkoto and can partly explain the C and O isotopic compositions of these deposits (Fig. 7). Critically, the three world class deposits at Loulo show limited isotopic evidence for direct contribution of magmatic volatiles, with the possible exception of Gara (Fig. 7). In contrast, the Au prospects in the western Kofi Series at Baqata, Kolya, Kabe West and Gefa (as well as limited data points from Gara) have higher δ¹³C and lower δ¹⁸O values than the main Loulo deposits, which fall between the aqueous carbonic fluid-dolostone and magmatic brine-dolostone reaction curves (Fig. 7).

On the basis of these data, we suggest that mineralization in the small Au prospects adjacent to the margin of the Falémé Batholith was deposited from a mixed aqueous-carbonic and magmatic fluid, both of which had been modified through reaction with Kofi Series dolostone and/or Bambadji Formation volcanic rocks prior to mixing. While isotopic values for the Kolya, Baqata and Gefa prospects are largely in agreement with those of the main Loulo Au deposits, including their low δ³⁴S values (Fig. 5a, b), those for Kabe West and Boboti plot at lower δ¹⁸O, implying a stronger magmatic-hydrothermal affinity (Fig. 6b and 7). Kabe West and Boboti are both hosted within intensely albitized igneous rocks on the margin of the Falémé batholith, which is intruded by multiple generations of small-scale dikes and stocks consistent with an elevated contribution of magmatic volatiles. Furthermore, low δ¹⁸O values at Baqata, Kolya, and Gefa are consistent with the presence of thin diorite dikes within 5 m of mineralization (Lambert-Smith, 2014a). These dikes may have exsolved small aliquots of magmatic-hydrothermal fluid similar to those responsible for skarn alteration, resulting in the heterogeneous isotopic signature of Au prospects in the western Kofi Series. It should also be noted that some of the isotopic values for hydrothermal minerals in the western Kofi Au prospects could be generated simply from a cooling end-member magmatic fluid.

**Metallogenic Model for the Loulo District**

Lambert-Smith et al. (2016c) reported that pre-ore hydrothermal tourmalines at Gara and Yalea North were deposited from an ¹¹B-rich fluid whose isotopic character was comparable with metaevaporite source rocks. While evaporite beds have not been identified in the Kofi series, the B-isotope data suggest the marly dolostones in the west of the Kofi basin may have contained evaporitic horizons (Fig. 8a). The Falémé batholith intruded these marly dolostones and evaporite horizons (Fig. 2) between 2084 ± 8 Ma and 2070 ± 5 Ma, during which time the Falémé skarns also formed (Fig. 8 b and c). Field relationships between albitization and magmatic rocks in the Kofi Series suggest NaCl, CO₂ and B were initially mobilized during syn-D₁ metamorphism of Kofi Series dolostones, before Falémé magmatism, giving rise to a paragenetically early brine and widespread associated albitic and tourmaline alteration. Falémé magmatism now seems likely to have contributed both heat and magmatic-hydrothermal fluid to this evolving system, synchronous with on-going D₂ metamorphism and minor transcurrent
deformation. These magmatic fluids may have evolved into high temperature saline brines through
reaction with the dolostones or mixing with a metamorphic brine derived from earlier devolatilization
of the dolostones and interbedded evaporites. This scenario would explain both the high fluid
temperatures (>400 °C) documented by Lawrence et al. (2013b) and the meta-evaporite B-isotope
signature described by Lambert-Smith et al. (2016c), as it seems likely that the dominant B reservoir in
such a scenario would be the evaporative wall rocks. High thermal gradients and permissive structural
architecture allowed widespread circulation of this hybrid magmatic-hydrothermal and meta-evaporitic
brine, resulting in on-going, multi-phase, district-scale Na and B metasomatism prior to and during Au
mineralization (Lawrence et al., 2013b; Lambert-Smith et al., 2016a; Lambert-Smith et al., 2016b;
Lambert-Smith et al., 2016c) (Fig. 8b). At the Karakaene Ndi skarn high δ^{34}S and δ^{13}C values suggest
a contribution to the hydrothermal system from wall rocks with isotopic characteristics similar to the
Kofi dolostones. Similarly, at Gara a shift from high δ^{11}B (~12.7 ‰) to lower values (~5 ‰) indicates
that in places, brines containing both evaporite and magmatic components (hybrid) mixed with more
dilute aqueous-carbonic fluids during Au mineralization (Lambert-Smith et al., 2016c). This implies
that the hybrid brine contributed to the formation of both the Falémé skarns and the Loulo Au deposits.

Given that the aqueous-carbonic fluid is present in all Au deposits in the Loulo region, whereas the
hypersaline brine is absent at Yalea, it seems likely that the former was more important in terms of
introducing Au to the system. Stable isotope data from Au-related pyrite and arsenopyrite (δ^{34}S 5.8 to
9.6 ‰), quartz (δ^{18}O 15.8 to 16.3 ‰) yielding a mean δ^{18}O_{fluid} of approx. 9.7 ‰ at 320 °C , dolomite
(δ^{13}C -15.8 to -21.7 ‰) (Lawrence et al., 2013b) and tourmaline (δ^{11}B -0.5 to 9.3 ‰) (Lambert-Smith
et al., 2016c) at Yalea are all compatible with the aqueous-carbonic fluid being sourced from Kofi Series
siliciclastic metasedimentary and carbonate rocks (Rye and Ohmoto, 1974; Sheppard, 1986; van
Hinsberg et al., 2011) with a significant organic C component (Schidlowski et al., 1975). Our new data
and modelling show that the brine with which the aqueous-carbonic fluid mixed is likely to have
evolved from interaction between magmatic-hydrothermal fluid(s) and the Kofi Series dolostones (±
meta-evaporites). Heat from the intrusion of the Falémé Batholith could conceivably have perturbed the
local geothermal gradient sufficiently to drive this district scale hydrothermal system.

Implications for Orogenic Au and other Hydrothermal Systems

Our data suggest that magmatic fluids can make a significant contribution to some orogenic Au
mineralization. In the Loulo example magmatism, combined with highly reactive dolostone and
evaporitic country rocks resulted in generation of a hybrid brine that appears to have acted as a chemical
trap for this and other aqueous carbonic Au-bearing fluids.

Comparisons between the Loulo District and some iron oxide Cu-Au (IOCG) provinces are also
instructive. Deposits of the Carajás Mineral Province of northern Brazil are somewhat analogous in that
they feature hypersaline brines (up to 58 wt. % equiv. NaCl) (da Costa Silva et al., 2015), which have
derived their salt content from meta-evaporitic rocks (Xavier et al., 2008; Riehl and Cabral, 2018). Intrusion of magma into evaporite bearing rocks has set up district-scale hydrothermal systems resulting in abundant sodic and calcic alteration. Schwartz and Melcher (2004) and Lawrence et al. (2013a) have both suggested that the Falémé skarns share characteristics with IOCG deposits. Notably, the skarns are rich in low-Ti iron oxides and are associated with widespread and paragenetically early alteration associated with both CO$_2$-rich and saline fluids. The Falémé skarns however, differ in that they contain no economic Cu, only relatively low-grade Au, and are more intimately associated with magmatic rocks than is typical for IOCG deposits (c.f. Williams et al., 2005).

The isotopic data largely supports a metamorphic devolatilization model for the system at Loulo (e.g. Groves et al., 2019). Though the term may not be wholly appropriate in describing the Loulo deposits, there is a clear metamorphic signature in the isotope data with deposits such as Yalea formed largely without the influence of the hybrid magmatic-hydrothermal/evaporite-derived brine.

**Conclusions**

Taken together, our data suggest a critical role for magmatism in the development of early alteration assemblages in the Loulo District, in the genesis of the Falémé iron skarns, and in those Au deposits that formed in response to fluid mixing. In these deposits, including Gara and the minor Au occurrences in close spatial association with dikes and sills on the margin of the Falémé Batholith, there is strong indications that evolved magmatic fluids were present during mineralization.

We envisage a scenario where the Falémé Batholith intrudes the marly evaporite-bearing carbonate rocks of the western Kofi Series. Fluids exsolved from the Falémé Batholith interacted with the marly dolostones generating a hypersaline brine which circulated through the Kofi and Falémé lithologies. This resulted in the widespread albitization and tourmalinization characteristic of the region, which hardens certain lithologies providing a favourable competency contrast for Au-bearing fluids to exploit. Early metasomatism is overprinted by orogenic-style Au and Fe skarn mineralization; the former related to the incursion of aqueous-carbonic fluids. These fluids largely precipitate minerals due to pressure fluctuations or water-rock reactions (Lambert-Smith et al., 2016b, Lawrence et al., 2013b), but in places partially mix with the magmatic-evaporitic brines which provide a chemical trap for Au mineralization. In this way, the intrusion of the Falémé Batholith played a direct role in the development of the Loulo Au mineral system. Skarn formation is likely to have been promoted by the presence of Cl-rich brines, which would have encouraged metal transport in FeCl$_2$ complexes.

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Table captions

Table 1 – Summary of key characteristics of Au and Fe mineralization in the Loulo District.

Table 2 - Table summarising stable sulfur isotope data from the Loulo Mining District. * - denotes data from Fouillac et al. (1993). † - denotes data from Lawrence et al. (2013b). ‡ - denotes data from Lambert-Smith et al. (2016b).

Table 3 – Table summarising stable carbon and oxygen isotope data from the Loulo Mining District. * - denotes data from Fouillac et al. (1993). † - denotes data from Lawrence et al. (2013b). ‡ - denotes data from Lambert-Smith et al. (2016b).

Table 4 – Chemical and isotopic fluid compositions used for end member components in fluid mixing and fluid-rock reaction models.

Figure captions

Fig. 1. Geological map of the southern West Africa Craton, highlighting the distribution of Au deposits (Modified after Baratoux et al., 2011; Fontaine et al., 2017; Thebaud et al. In Press). Location of major Au deposits are based on those reported in Markwitz et al. (2016), and Goldfarb et al. (2017).

Fig. 2. Geological map of the Loulo Mining District in the south eastern region of the Kédougou-Kéniéba inlier, with studied Au occurrences highlighted. Modified after Lawrence et al. (2013a), and Lambert-Smith et al. (2016c).

Fig. 3. Key alteration and ore mineral textures at Karakaene Ndi. (A) photograph of coarse epidote-albite-calcite vein cross cutting albitized igneous rock with envelopes of dark green actinolite replacement in the wall rock and Fe-rich halos encroaching on the albitized rock. Photomicrographs of (B) albitized wall rock with relict phenocrysts (replaced by albite) (XPL); (C) fine fibrous actinolite replacing wall rock with minor magnetite mineralization (PPL); (D) albitized wall rock overprinted by Fe-rich carbonate and disseminated actinolite with minor pyrite (PPL) and; (E) coarse intergrown epidote and albite in cross cutting vein (XPL). Photographs of ore textures in diamond drill core from Karakaene Ndi showing: (F) massive magnetite replacement with weak disseminated pyrite overprint and; (G) late calcite-pyrite-chlorite vein cross cutting magnetite mineralization.

Fig. 4. Field photographs showing (A) typical marly dolostones country rock with highly deformed calcite veining, argillaceous layers and graphitic material. (B) Ankerite-quartz-pyrite stockwork ore characteristic of the Gara and Gounkoto deposit (highly subordinate in the latter), the P64 satellite, and the Baqata and Kolya exploration targets. (C) Auriferous ankerite-quartz-pyrite veins cross cutting phyllic wall rock alteration at the Yalea deposit. (D) An example of sulfide-bearing carbonate veins with Au concentrations below the detection limit of fire assay in the meter of core sampled. (E) Barren
veining in unaltered and unmineralized Kofi Series metasedimentary country rock. (F) Folded, sulfide-
free veining in weakly altered, unmineralized metasedimentary host rock. (G) Sulfide-bearing veins
from the Kofi Series with fire assay results below detection limit (<0.01 ppm).

Fig. 5. Histograms showing δ^{34}S data from pyrite at (A) the Loulo Au deposits (Fouillac et al., 1993,
Lawrence et al., 2013b, Lambert-Smith et al., 2016b, Lambert-Smith, 2014b) and diagenetic pyrite from
the Kofi series dolostones, (B) the Kabe West, Kolya, Baqata and Bobotie exploration targets, (C) the
Karakaene Ndi skarn deposit, with paragenetic breakdown between sulfides disseminated in the iron ore
and those hosted in cross cutting veins (inset).

Fig. 6. Histograms showing δ^{13}C data from (A) ankerite and dolomite in auriferous hydrothermal veins,
barren hydrothermal veins, and carbonate country rocks from the Loulo-Gounkoto complex, including
the Gara, Yalea and Gounkoto mines (data from Fouillac et al., 1993, Lawrence et al., 2013b, Lambert-
Smith et al., 2016b); (B) ankerite and dolomite in auriferous and barren hydrothermal veins from the
Bambadji exploration targets, Gefa, Boboti, Kabe West, Kolya and Baqata; (C) calcite from late
hydrothermal veins at the Karakaene Ndi iron skarn deposit. Fields of typical C-isotope characteristics
of Precambrian marine carbonates and organic carbon are indicated (Schidlowski et al., 1975, Eichmann
and Schidlowski, 1975). Histograms showing δ^{18}O data from (D) ankerite and dolomite in auriferous
hydrothermal veins, barren hydrothermal veins, and carbonate country rocks from the Loulo-Gounkoto
complex; (E) ankerite and dolomite in auriferous and barren hydrothermal veins from the Bambadji
exploration targets, Gefa, Boboti, Kabe West, Kolya and Baqata; (F) calcite from late hydrothermal
veins at the Karakaene Ndi iron skarn deposit. Number of samples and key is equivalent to (A), (B) and
(C).

Fig. 7. δ^{18}O versus δ^{13}C plot showing isotopic compositions of ore related carbonate at Au deposits and
exploration targets in the Loulo District, in addition to compositional ranges of Kofi Series dolostones
and barren carbonate veining. Black curve with open circles represents C-O isotopic compositions
expected in carbonates precipitated from a mixture of aqueous-carbonic fluid with a starting
composition of δ^{18}O = 10.2 ‰ and δ^{13}C = -27 ‰ and a magmatic fluid with a starting composition of
δ^{18}O = 9.4 ‰ and δ^{13}C = -6 ‰ (red star). Black curve with grey circles represents C-O isotopic values
expected in carbonates precipitated from a mixture of the same aqueous-carbonic fluid with a brine of
meta-evaporite origin and starting isotopic composition of δ^{18}O = 16.2 ‰ and δ^{13}C = -2.6 ‰ (blue star).
Red curve represents C-O isotopic fluid values resulting from the magmatic fluid reacting with the Kofi
Series dolostones (light grey field; average composition of δ^{18}O = 21 ‰ and δ^{13}C = -0.5 ‰). The curve
was modelled at 550 °C XCO_2 of 0.11. Blue, violet, and purple curves represent isotopic compositions
resulting from reaction between the aqueous-carbonic fluid and the Kofi dolostones at 295, 325, and
400 °C, respectively and at XCO_2 of 0.2. Isotopic compositional ranges for magmatic fluids (red field)
(Ohmoto, 1972) and Precambrian marine carbonates (blue field) (Eichmann and Schidlowski, 1975) are given for reference.

Fig. 8. Cartoon cross section showing (A) Kofi Series metasedimentary rocks, including evaporite bearing dolostone horizons in the west of the Series, these are folded and metamorphosed prior to 2085 Ma, with minor albitisation indicating the presence of early saline brines. (B) Intrusion of the Falémé Batholith from approx. 2085 Ma increases the local geothermal gradient and exsolves magmatic-hydrothermal fluid. This event may both promote devolatilization of the dolostones in the Western Kofi Series and allow water-rock reaction between the magmatic fluids and the evaporite-bearing marly dolostones; this gives rise to a hybridized hypersaline magmatic-evaporitic brine, which circulates through the metasedimentary rocks leading to the development of albitized and tourmalinized rock packages. (C) Between 2085 and 2070 Ma hybrid brines continue to circulate, aqueous-carbonic fluids are introduced along significant structures in the Kofi Series and further magmatism in the Falémé batholith leads to emplacement of small stocks and dikes which extend into the Kofi Series. The aqueous-carbonic fluid unmixes in response to pressure fluctuations, contributing to Au mineralization; at Gara and several other deposits this process is enhanced by partial mixing with hybrid hypersaline brines. Minor amounts of magmatic-hydrothermal fluid derived from dikes cross cutting the Kofi Series may contribute volatiles directly to some of the minor mineralized rock packages in the west of the Loulo Au system. Magnetite skarn deposits simultaneously develop within and adjacent to small dioritic stocks in the Falémé batholith and western Kofi Series.
Paleoproterozoic (Rhyacian) rocks

- Undifferentiated granitoids, ca. 2195-2050 Ma
- Tarkwaian Group, late orogenic molasse sedimentary rocks, ca. 2110-2100 Ma
- Birimian sedimentary basins, ca. 2135-2100 Ma
- Volcanic, volcano-sedimentary and sedimentary rocks, ca. 2200-2160 Ma

Archean rocks, Kenema-Man Domain

Post-Paleoproterozoic rocks

Gold deposit styles
- Post-collision, orogenic
- Post-collision, Loulo/Falémé
- Granitoid-hosted
- Tarkwaian paleplacer
- Eburnean basin orogenic
- Eburnean orogenic, part or wholly hosted by Eoeburnian rocks
- Skarn
- Eoeburnean orogenic

Gold deposit size
- > 50 Moz
- 8 - 50 Moz
- 3 - 8 Moz
- < 3 Moz
Dolerite

Intense albition

Strong albition (protolith identifiable)

Iron skarn mineralisation

Faleme batholith plutonic rocks

Volcaniclastic and sedimentary rocks

Rhyolitic breccia

Marly and variably altered marble

Sandstones, siltstones, wackes and argillites with polymict conglomerate

Bedding

S cleavage

Magmatic and volcanic rock samples with $\delta^{18}O_{\text{zircon}}$ data

Exploration targets

Au mine

Faults, fractures and shear zones from drilling and outcrop and inferred from chargeability and VTEM data
albite altered
monzodiorite

actinolite replacement halo overprinting albitisation

Fe-rich alteration front with disseminated actinolite

epidote-albite-calcite vein

relict plagioclase phenocrysts

massive magnetite overprinting albitised host rocks

albitised igneous rock

weakly disseminated pyrite overprinting magnetite

Late pyrite-calcite vein cross cutting magnetite mineralisation

actinolite-magnetite mineralization
Fine-grained pyrite in carbonate vein

Marly dolostone

Phyllic wall rock alteration

Ankerite-quartz-pyrite veins

Barren ankerite-chlorite veins

Unaltered argillaceous quartz wacke country rock

Folded carbonate veining

Weakly albite-carbonate altered country rock

Unaltered quartz wacke sandstone

Dolomite-pyrite veins

Pyrite

Dolomite-chlorite-pyrite veins

Chlorite altered sandstone

Quartz-dolomite-pyrite vein

Pyrite

Dolomite-quartz-pyrite vein

Quartz-tourmaline altered sandstone

Pyrite
Boboti
Kolya
Kabe West
Baqata

Loulo satellite deposits
Gounkoto
Kofi diagenetic pyrite

Disseminated pyrite
Pyrite in Fe-oxide vein
Pyrite in sulphide vein
Kofi diagenetic pyrite

Magmatic sulfur (Ohmoto, 1972)

Karakaene Ndi
Gara
Yalea
Gounkoto
Loulo satellite deposits
Kofi diagenetic pyrite

Kofi diagenetic pyrite
Gara
Yalea
Gounkoto
Loulo satellite deposits
Kofi diagenetic pyrite

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Magmatic sulfur (Ohmoto, 1972)

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Yalea
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Loulo satellite deposits
Kofi diagenetic pyrite

Disseminated pyrite
Pyrite in Fe-oxide vein
Pyrite in sulphide vein
Kofi diagenetic pyrite

Magmatic sulfur (Ohmoto, 1972)
increasing contribution of organic carbon

increasing contribution of carbonate carbon

increasing contribution of magmatic oxygen

Paleoproterozoic
d°C, -24.7 ± 6‰
(Schidlowski et al., 1975)

Magmatic carbon
(Ohmoto, 1972)

Magmatic marine carbonates
(Bulman & Schidlowski, 1975)

Paleoproterozoic
δC, -24.7 ± 6‰
(Schidlowski et al., 1975)

δC (‰)
PDB

Boboti
Kolya
Kabe West
Baqata
Gefa
Barren Kofi Veins

Kofi diagenetic pyrite
Kofi Host Carbonate

Loulo satellite deposits
Gounkoto
Gar

Karakaene Ndi

increasing contribution of organic carbon
increasing contribution of carbonate carbon
increasing contribution of magmatic oxygen

Loulo satellite deposits
Gounkoto
Gar

Kofi diagenetic pyrite
Kofi Host Carbonate
Precambrian marine carbonates (Eichmann & Schidlowski, 1975)

Falémé batholith magmatic fluids (Taylor, 1974)

Barren hydrothermal veining in the Loulo district

C and O fractionation at 550 °C

C and O fractionation at 325 °C

Expected $\delta^13$C of carbonates precipitated from a cooling magmatic fluid

$400 °C$

$500 °C$

$295 °C$

$325 °C$

$Disequilibrium$

Isotopic composition of sedimentary brine

Carbonate precipitated from a mixture of magmatic brine and aqueous-carbonic fluid

Carbonate precipitated from a mixture of sedimentary brine and aqueous-carbonic fluid

Gara Deposits >3 Moz

Yalea Gounkoto Gefa

Exploration targets

Kofi dolostones

Karakaene Nd Fe skarn

Magmatic fluid range

Falémé dolostones

Kofo dolostones

$\delta^13$C$_{PDB}$‰

$\delta^18$O$_{V-SMOW}$‰

-22

-20

-18

-16

-14

-12

-10

-8

-6

-4

-2

0

2

4

6

8

10

12

14

16

18

20

22

24

Au mineralization

Legend

Isotopic composition of magmatic fluid

Falémé magmatic fluid

Magmatic fluid range

Kofo dolostones

Barren dolostones

Kofi dolostones

Dolostones

Kofo Series Dolostones
Dolostone with marl and siltstone horizons undergo minor devolatilisation during D1 and regional metamorphism.

Halite-bearing evaporitic horizons during D1 and regional metamorphism

D1 folds and reverse faults marking structural discontinuities in the Kofi series

Intrusion and early albitisation of the Falémé pluton

B-rich brines circulate promoting Na and B metasomatism

Tourmalinisation of grey wacke horizons

Albitisation of Kofi series

Magnetite skarns develop as brine is drawn into magmatic-hydrothermal system

Magmatic fluids mix with existing brines and/or react with evaporite-bearing wall rocks to form high-T, hypersaline brine.

FIAs indicative of immiscibility enhanced by fluid mixing at Gara and other deposits

Metamorphic fluid undergoes isotopic and chemical exchange with the carbonate-rich Kofi Series

Influx of ¹⁰C-depleted \( \text{H}_2\text{O}-\text{CO}_2-\text{NaCl-H}_2\text{S} \) fluid of metamorphic origin

Early albitisation of Kofi Series

Polyfolded Kofi siliciclastic metasediments

Late dioritic stocks and dykes

Magmatic fluids interact with wall rock in western-most Au deposits and occurrences in the Kofi Series.
<table>
<thead>
<tr>
<th>Ore Body</th>
<th>Key ore textures</th>
<th>Ore mineralogy</th>
<th>Alteration styles</th>
<th>P-T conditions</th>
<th>Constraint</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gara</td>
<td>carbonate-quartz-pyrite vein stockwork</td>
<td>pyrite (± Ni-Co)-monazite-xenotime-scheelite-gold-chalcopyrite-gersdorffite-pentlandite-Ni-pyrrhotite-arsenopyrite-molybdenite</td>
<td>Tourmalinisation and minor albitisation</td>
<td>&gt;340 °C at 1.75 kbar</td>
<td>Fluid inclusions, O-isotope equilibria, arsenopyrite geothermometry</td>
<td>Lawrence et al. (2013a, b)</td>
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<td>Yalea</td>
<td>Shear zone hosted sulphide stringers and hydrothermal breccia</td>
<td>arsenian pyrite-arsenopyrite-chalcopyrite-gold-pyrrhotite-jamesonite-galena-scheelite-tennantite</td>
<td>Early albitisation and syn-mineralisation chloritisation</td>
<td>320 °C at 1.45 Kbar (5.4 km)</td>
<td>Fluid inclusions, arsenopyrite and chlorite geothermometry, O-isotope equilibria</td>
<td>Lawrence et al. (2013a, b)</td>
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<tr>
<td>Gounkoto</td>
<td>Shear zone hosted sulphide stringers and hydrothermal breccia</td>
<td>pyrite (±As)-arsenopyrite-pyrrhotite-chalcopyrite-magnetite-haematite-gold-monazite-scheelite-gersdorffite-cobaltite-tennantite-altai-tellurium-callaverite-sylvanite-petitite</td>
<td>Early albitisation and syn-mineralisation chloritisation</td>
<td>340 °C at 1.4 Kbar (5.2 km)</td>
<td>Fluid inclusions, arsenopyrite and chlorite geothermometry, O-isotope equilibria</td>
<td>Lambert-Smith et al. (2016b)</td>
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<td>Quartz-dolomite veining, sulfide-chlorite-magnetite veining and disseminated</td>
<td>arsenian pyrite - arsenopyrite - magnetite-pyrrhotite-chalcopyrite - gold - tsumoite - altaite - hedleyite - bismuth</td>
<td>Early albitisation and syn-mineralisation chloritisation</td>
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<td>carbonate-quartz-pyrite vein stockwork and disseminated</td>
<td>pyrite (± Ni-As) - chalcopyrite-pyrrhotite-monazite-scheelite-xenotime-gold-millerite-polydymite-sterbergite-tellurium-bismuth</td>
<td>Tourmalinisation and albitisation</td>
<td>~315 °C at 1.3 Kbar (4.8 km)</td>
<td>Fluid inclusions, chlorite geothermometry</td>
<td>Lambert-Smith (2014)</td>
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<td>carbonate-quartz-pyrite vein stockwork</td>
<td>pyrite - chalcopyrite-arsenian pyrite-scheelite-xenotime-gold-tellurium-bismuth</td>
<td>Tourmalinisation and minor actinolite replacement</td>
<td>&gt;300 °C</td>
<td>Fluid inclusions (minimum trapping)</td>
<td>Lambert-Smith (2014)</td>
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<td>Kabe West</td>
<td>Hydrothermal breccia - carbonate vein stockwork</td>
<td>pyrite (± Ni-Co) - chalcopyrite-monazite-gold-xenotime-altaite-melinite</td>
<td>Albisation + weak tourmaline</td>
<td>~308 °C</td>
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<td>pyrite - chalcopyrite</td>
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<td>Karakaene Ndi</td>
<td>Massive magnetite with late disseminated and vein hosted sulphides</td>
<td>magnetite - haematite - pyrite (N ± As substitution)-apatite-chalcopyrite-monazite-gold-uraninite-bismuth-clausthalite</td>
<td>Early albitisation overprinted by calc-silicate and magnetite replacement</td>
<td>500 °C at 2.5 kbar</td>
<td>Fluid inclusions, O-isotope equilibria</td>
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<td>Sample</td>
<td>δ34S(‰ vs. CDT)</td>
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