

# The influence of spreading rate, basement composition, fluid chemistry and chimney morphology on the formation of gold-rich SMS deposits at slow and ultraslow mid-ocean ridges

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**Abstract** Seafloor massive sulphide (SMS) deposits are variably enriched in precious metals including gold. However, the processes invoked to explain the formation of auriferous deposits do not typically apply to mid-ocean ridge settings. Here, we show a statistically significant, negative correlation between the average gold concentration of SMS deposits with spreading rate, at non-sedimented mid-ocean ridges. Deposits located at slow spreading ridges (20–40 mm/a) have average gold concentrations of between 850 and 1600 ppb; however, with increasing spreading rate (up to 140 mm/a), gold concentrations gradually decrease to between ~ 50 and 150 ppb. This correlation of gold content with spreading rate may be controlled by the degree and duration of fluid-rock interaction, which is a function of the heat flux, crustal structure (faulting) and the permeability of the source rocks. Deposits at ultraslow ridges, including ultramafic-hosted deposits, are particularly enriched in gold. This is attributed to the higher permeability of the ultramafic source rocks achieved by serpentinisation and the inherent porosity of serpentine minerals, combined with relatively high gold concentrations in peridotite compared with mid-ocean ridge basalt. Variations in fluid chemistry, such as reducing conditions and the

potential for increased sulphur availability at ultramafic-hosted sites, may also contribute to the high concentrations observed. Beehive chimneys, which offer more favourable conditions for gold precipitation, may be more prevalent at ultramafic-hosted sites due to diffuse low-velocity venting compared with more focussed venting at basalt-hosted sites.

**Keywords** Gold mineralisation · Massive sulphide · Mid-ocean ridge · Hydrothermal · Ultramafic

## Introduction

Gold-rich volcanogenic massive sulphide (VMS) deposits and their modern-day equivalents, seafloor massive sulphide (SMS) deposits, are usually associated with arc, immature back-arc and rifted environments where felsic lithologies comprise a significant component of the host rocks (Hannington et al. 1997; Dubé et al. 2007). In these tectonic environments, gold is enriched by the oxidation of sulphides in the mantle wedge (Mungall 2002) which promotes the formation of gold-rich magmas (Botcharnikov et al. 2010), and ultimately the addition of a gold-bearing magmatic fluid to seafloor hydrothermal systems (Yang and Scott 1996, 2006). In comparison, massive sulphide deposits forming at mid-ocean ridge and mature back-arc spreading centres are typically gold-poor. In these settings, contributions of metal-rich magmatic fluids are volumetrically insignificant due to the lack of water- and volatile-rich magmas that are prevalent at convergent margins (Hannington et al. 2005). Gold concentrations in mid-ocean ridge basalt (MORB)-hosted SMS deposits are typically ten times lower than defined auriferous VMS deposits (Mercier-Langevin et al. 2011; Patten et al. 2015). However, some SMS deposits along slow spreading mid-ocean ridges as well as ultramafic-hosted deposits which

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typically form along ultraslow spreading ridges can host significant gold concentrations of between 850–1600 and 4700–7900 ppb, respectively (Murphy and Meyer 1998; Mozgova et al. 1999; Munch et al. 2001; Bogdanov et al. 2002; Nayak et al. 2014; Fouquet et al. 2010; Webber et al. 2015). These data suggest that the measured gold concentrations might be related to spreading rate, although this relationship has not been rigorously tested.

Here, we show that the average gold concentration of samples collected from SMS deposits has a statistically significant negative relationship with spreading rate. Furthermore, ultramafic-hosted deposits, which predominantly form along ultraslow spreading ridges, are particularly gold-rich. We speculate that this relationship may be due to a range of factors including the degree and duration of fluid-rock interaction, basement composition, fluid chemistry and precipitation processes.

## Methods

We have updated and manipulated a pre-existing global geochemical database of SMS deposits produced by Hannington et al. (2004) with the addition of recently published data for mid-ocean ridge-hosted SMS deposits (Stepanova et al. 1996; German et al. 1999; Marques et al. 2006, 2007; Bogdanov et al. 2008; Kristall et al. 2011; Szamalek et al. 2011; Nayak et al. 2014). Further information was also added from the InterRidge 3.2 database, e.g. deposit/site name alias(es), ocean basin, region and tectonic setting, latitude and longitude, host rock(s), whether the site is active or inactive, current maximum temperature, maximum depth or depth range and spreading rate where applicable.

The data were processed to calculate mean, minimum and maximum values for a suite of elements for individual deposits. With a focus on gold and cobalt, weighted averages were calculated, which compensated data that have already been processed to mean values. Values that fell below the limit of detection were corrected to a value equal to half of the detection limit for their inclusion in these calculations.

In the majority of cases, samples in the database are taken from the surfaces of SMS mounds, which may be enriched in metals due to zone refining, with an increase in the concentration of gold with zinc towards the surface of the mounds (e.g. Hannington et al. 1986, 1995; Petersen et al. 2003). Similarly, massive sulphide chimneys which are naturally metal-rich are also over-represented. These enriched surface samples are unlikely to be representative of the deposits in their entirety. However, since there is a great range of gold concentrations across all deposits that have been sampled in this manner, we assume that the gold concentration in these surface samples is generally indicative of how gold-rich a deposit is.

## Results

### Spreading rate and gold concentration

Minimum, maximum and average gold concentrations for each mid-ocean ridge-hosted SMS deposit are presented in Table 1. Ultramafic-hosted deposits at slow and ultraslow spreading ridges record high average gold values of between ~ 4700 and 7900 ppb. The highest average gold concentrations are recorded from the Beebe Vent Field, which is a MORB-hosted deposit forming along the ultraslow Cayman Rise and will be discussed later in detail. Average gold concentrations of other MORB-hosted deposits at slow spreading ridges (20–40 mm/a) vary between ~ 850 and 1600 ppb, excluding the MIR zone which is comparable to that of ultramafic-hosted deposits (3733 ppb). In deposits at intermediate spreading ridges (40–90 mm/a), average gold concentrations range from ~ 90 to 1000 ppb. The majority of deposits have concentrations of less than ~ 280 ppb with the Galapagos Rift, Magic Mountain, Source and the MESO Zone exhibiting higher concentrations of 427, 723, 975 and 1024 ppb, respectively. At fast spreading ridges (90–140 mm/a), deposits have low average gold concentrations ranging from ~ 50 to 150 ppb. However, at ultrafast spreading sites (> 140 mm/a), average gold concentrations of between ~ 320 and 580 ppb are observed. All three ultrafast-hosted deposits are located along the southern East Pacific Rise; EPR 16°43'S, EPR 18°26'S, and EPR 21°25'S with concentrations of 322, 575 and 413 ppb, respectively.

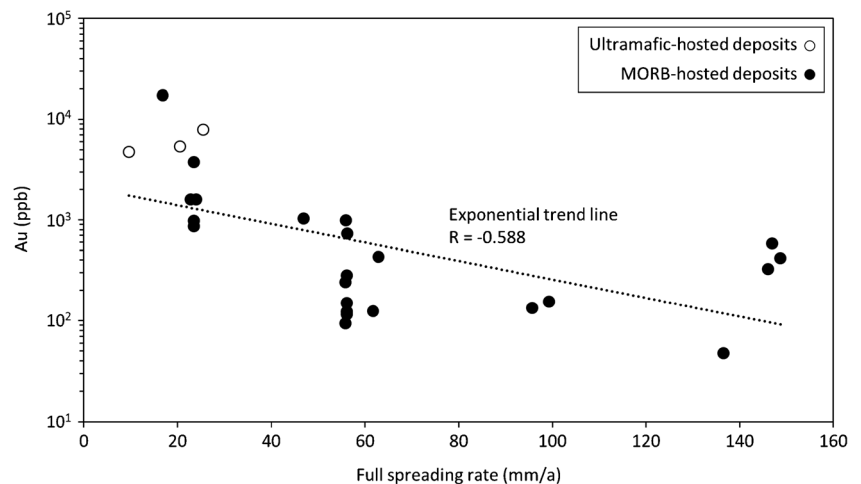
There is a statistically significant relationship, at the 99% confidence interval, between full spreading rate and average gold concentrations ( $n = 26$ ,  $r = -0.588$ , Fig. 1). As full spreading rate increases from 20 to 140 mm/a, the gold content of the associated sulphide deposits decreases by up to two orders of magnitude. This relationship is exponential in nature. Grouping the data for each site into their respective categories (i.e. grouping all gold data for ultramafic- and MORB-hosted SMS deposits into ultramafic, slow, intermediate, fast, and ultrafast categories as a function of spreading rate) confirms the relationship of gold variation with spreading rate (Fig. 2). Kruskal-Wallis tests were performed on these grouped data and show that there are statistically significant variations between the medians of these groups at a confidence level of 95%, except between the slow and ultrafast spreading groups where there is no significant difference (Table 2). Ultramafic-hosted deposits associated with ultraslow spreading rates (< 20 mm/a) are significantly more enriched in gold than other MORB-hosted sites, even along slow spreading ridges (Figs. 1, 2 and 3). Whilst ultrafast southern EPR sites are not auriferous, they do appear more gold-rich than predicted by the overall trend (Fig. 2).

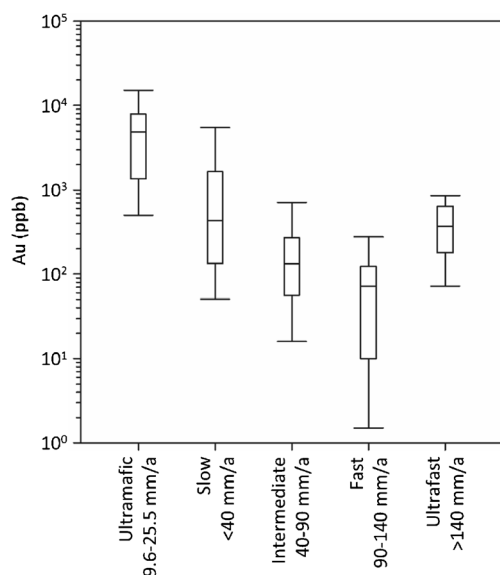
**Table 1** Table showing mean, minimum and maximum gold concentrations for SMS deposits at ultraslow-slow, intermediate, fast and ultrafast spreading mid-ocean ridges

Full spreading rate (mm/a)	Deposit name	Gold concentrations (ppb)			No. of analyses
		Mean	Min	Max	
<b>Ultraslow-slow spreading ridges</b>					
<i>Ultramafic-hosted</i>					
9.6	Mount Jourdanne	4705	0	12,500	21
20.6	Rainbow Field	5342	1530	12,100	6
25.5	Logatchev	7893	100	56,000	55
<i>MORB-hosted</i>					
16.9	Beebe Vent Field	17,096	458	93,600	29
22.9	Broken Spur	1577	8	5580	15
23.6	Mir Zone	3733	42	22,600	52
23.6	Alvin Zone	854	680	1020	7
23.6	TAG Mound	971	< 5	42,960	439
24.1	Snake Pit	1575	< 20	10,739	100
<b>Intermediate spreading ridges</b>					
47.0	MESO Zone	1024	200	6000	24
55.9	North Cleft	241	30	510	20
55.9	South Cleft	93	< 100	130	3
56.0	Source	975	13	2060	6
56.2	High-Rise Field	279	< 5	1130	46
56.2	Mothra Field	115	< 2	570	202
56.2	Clam Bed	122	20	336	5
56.2	Main Endeavour Field	148	< 2	1620	85
56.3	Magic Mountain	723	21	3757	51
61.8	EPR, 21 N	123	< 200	480	24
63.0	Galapagos Rift, 85°50'W	427	0	7240	122
<b>Fast spreading ridges</b>					
95.8	EPR, 11°30'N	133	1	649	10
99.4	Feather Duster	153	5	287	11
136.6	EPR, 7°25'S	47	1	88	13
<b>Ultrafast spreading ridges</b>					
146.1	EPR, 16°43'S	322	1	1020	19
147.0	EPR, 18°26'S	575	160	1200	14
148.7	EPR, 21°25'S	413	100	680	12

Those at ultraslow-slow spreading ridges are subdivided into ultramafic- and MORB-hosted deposits

**Fig. 1** Mean gold concentrations of SMS deposits at non-sedimented mid-ocean ridges (including MORB- and ultramafic-hosted sites) plotted as a function of spreading rate. An exponential trendline shows a significant correlation with an *R* value of  $-0.588$





**Fig. 2** Box and whisker plot showing gold concentrations of ultramafic and MORB-hosted SMS deposits grouped into ultramafic, slow, intermediate, fast and ultrafast categories as a function of spreading rate. Boxes show 25th–75th percentile including median line, whiskers show 10th–90th percentile and outliers have been omitted for clarity

## Discussion

There is a negative correlation between the average gold concentration of SMS deposits at non-sedimented mid-ocean ridges and spreading rate, with ultramafic-hosted deposits at slow and ultraslow spreading ridges particularly enriched in gold. The processes responsible for this correlation that require discussion are the degree and duration of fluid-rock interaction, gold content of the source rocks, variation in fluid chemistry and surface precipitation mechanisms.

### Gold enrichment as a function of the degree and duration of fluid-rock interaction

The degree and duration of fluid-rock interaction is critical in determining the quantity of metals leached from a given lithology

(Reed 1997). Provided there is enough time for hydrothermal fluids to interact with a sufficient source of unaltered rock, greater quantities of gold may be leached from the crust if gold remains undersaturated in the fluid. Consideration of the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{18}\text{O}$  signatures of hydrothermal fluids from vent sites along mid-ocean ridges indicate that hydrothermal fluids from slower spreading ridges are more rock-dominated compared to those measured at faster spreading ridges (Fig. 4; Bach and Humphris 1999). These rock-dominated signatures in hydrothermal fluids at slow spreading ridges are the result of greater Sr and O exchange with the oceanic crust which reflects increased residence time and deeper hydrothermal fluid-flow pathways (Bach and Humphris 1999). These findings are supported by numerical modelling studies which demonstrate that the thermal regime at slow spreading ridges is generally cooler (Brown and White 1994) and hydrothermal fluids require deeper penetration into, and longer residence time within the oceanic crust to achieve the temperatures typically measured for fluids emanating at hydrothermal vent sites of 350–400 °C (Pelayo et al. 1994). Furthermore, at slow and ultraslow spreading ridges, tectonic extension often gives rise to low-angle detachment faults which form oceanic core complexes (e.g. Escartín et al. 2008). These detachment faults maintain long-lived fluid-flow pathways and support continued convection (Wilcock and Delaney 1996) as evidenced by the extreme alteration of oceanic rocks along a detachment fault at 15°45'N near the Mid-Atlantic Ridge (McCaig et al. 2007). Conversely, at fast spreading ridges, episodes of vigorous venting are linked to dyke intrusion events which act as significant heat sources into the upper crust and increase permeability near the ridge axis (Wilcock and Delaney 1996). These conditions give rise to shallow, short-lived fluid circulation and limit the abundance of source rocks available, particularly those that are unaltered.

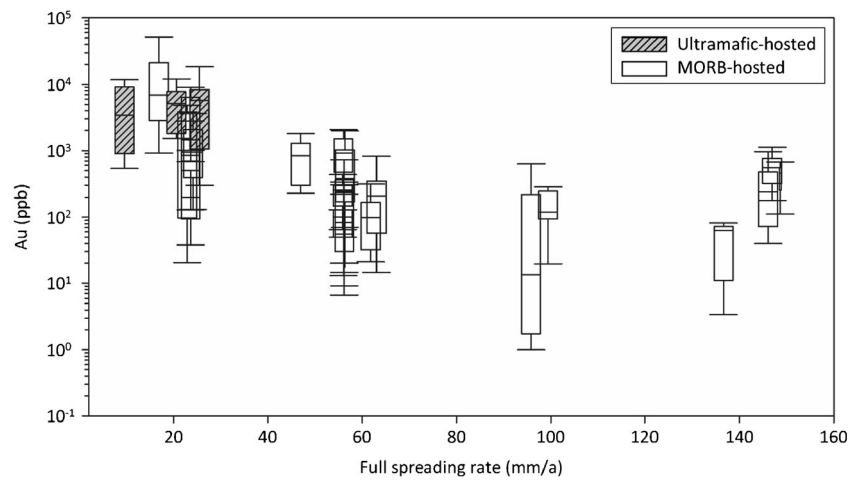
The degree of fluid-rock interaction may be further enhanced for ultramafic-hosted deposits. The serpentinisation of ultramafic rocks is accompanied by a volume increase of 25–50% resulting in episodic fracturing (Schwarzenbach 2016). However, this process should be self-limiting as the fractures

**Table 2** Table showing gold data from mid-ocean ridge-hosted deposits grouped into categories based on spreading rate (slow, intermediate, fast and ultrafast) with ultramafic-hosted sites grouped separately

	Ultramafic	Slow	Intermediate	Fast	Ultrafast
No. of analyses	76	525	588	34	45
Mean Au ppb	6708	2380	301	107	425
Median Au ppb	4860	430	133	72	370
Kruskal-Wallis test <i>P</i> values					
Ultramafic	N/A	1.655E-17	1.809E-36	1.675E-15	3.795E-14
Slow		N/A	1.154E-34	5.799E-11	0.1541
Intermediate			N/A	4.776E-04	8.562E-07
Fast				N/A	5.243E-08
Ultrafast					N/A

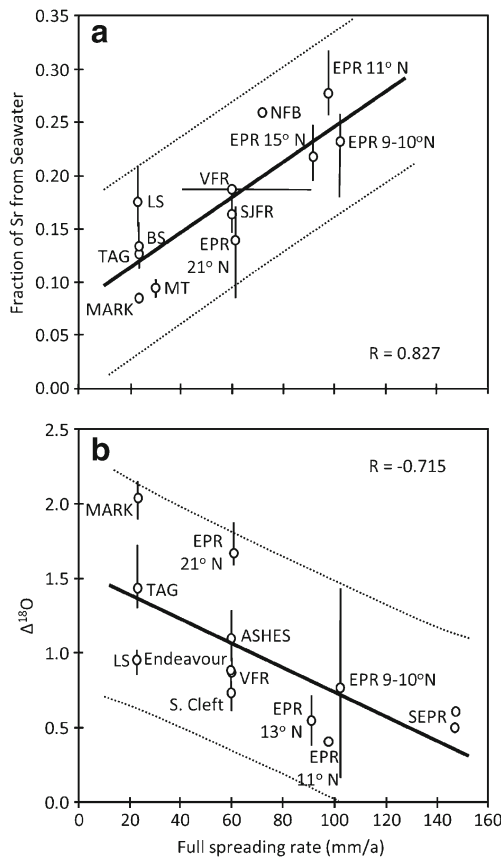
*P* values derived from Kruskal-Wallis tests between the different groups are also provided. With values < 0.05, these data show that the difference between the group medians is significant with a confidence level of 95%

**Fig. 3** Box and whisker plot showing gold concentrations of ultramafic- and MORB-hosted SMS deposits as a function of spreading rate. Boxes show 25th–75th percentile including median line, whiskers show 10th–90th percentile and outliers have been omitted for clarity



are subsequently filled with serpentine minerals closing fluid-flow pathways and preventing further serpentinisation and fluid-rock interaction (Macdonald and Fyfe 1985; O’Hanley

1992; Schwarzenbach 2016). Recent work shows that serpentine and associated accessory phases form with their own inherent nano-scale porosity, which allows continued diffusive fluid-flow and pervasive serpentinisation of ultramafic rocks (Tutolo et al. 2016), possibly resulting in increased leaching of gold from base metal sulphides. Furthermore, the heat of exothermic serpentinisation reactions may contribute to long-lived hydrothermal activity at ultramafic-hosted SMS sites (Lowell and Rona 2002; German and Lin 2004). Therefore, hydrothermal fluids at slow and ultraslow spreading ridges experience long-lived, deep hydrothermal circulation resulting in greater degrees of fluid-rock interaction with a greater potential to leach gold from the oceanic crust, particularly where ultramafic rocks are present.



**Fig. 4** **a** The fraction of Sr in vent fluids that is derived from seawater and **b**  $\Delta^{18}\text{O}$  (the difference between  $\delta^{18}\text{O}$  values of hydrothermal vent fluids and  $\delta^{18}\text{O}$  of local seawater) plotted against full spreading rate (redrawn from Bach and Humphris 1999). Open circles represent average values for individual spreading segments; bars show range of values. Bold lines are regression lines through average values. Thin stippled lines mark error bounds (95% significance level) of the regression lines. See Bach and Humphris (1999) for full explanation and abbreviations

**Gold content of the source rocks**

Differences in source rock composition, particularly between MORB and ultramafic lithologies, have been shown to exert a control on the composition of the sulphides precipitated at SMS deposits (e.g. Wang et al. 2014; German et al. 2016). The geochemical characteristics of the host rocks of SMS deposits at mid-ocean ridges are a function of crustal thickness which varies with spreading and magma supply rates (Bown and White 1994; Niu and Hékinian 1997). At ridges where the temperature is sufficient to sustain magmatism capable of developing a full thickness of oceanic crust (> 20 mm/a), the host rocks are typically MORB (InterRidge 3.2 database). However, at ultraslow spreading ridges (< 20 mm/a), there is a greater component of tectonic extension and amagmatic spreading via detachment faulting which exhumes mantle material (e.g. Escartín et al. 2008), in some cases giving rise to ultramafic-hosted SMS deposits. Furthermore, low magma supply rates also occur at the termination of ridge sections which may also result in the exhumation of ultramafic rocks (Fouquet et al. 2010). Ultramafic rocks are partially exhumed in this manner at the termination of intermediate spreading

ridge sections (40–90 mm/a); however, they are not exposed at the seafloor surface, rather their existence in the sub-seafloor is evidenced by vent fluids with high H<sub>2</sub> and CH<sub>4</sub> gas contents and sulphide compositions (e.g. at the Kairei hydrothermal field, Central Indian Ridge; Wang et al. 2014), or by geothermobarometry indicating that fluid circulation occurs at depths greater than the thickness of the basaltic crust (Webber et al. 2015).

The average concentration of gold in MORB is 0.34 ppb (Webber et al. 2013) whereas the concentration of gold in peridotites is typically > 1 ppb (e.g. Lorand et al. 1999; Luguet et al. 2002; Maier et al. 2012). This is a result of the high partition coefficient for gold between sulphide and silicate melts of ~ 10,000 (Peach et al. 1990), which causes gold to be retained in mantle sulphides until relatively high degrees of partial melting (Peach et al. 1990; Naldrett 2011). Therefore, while the degree of fluid-rock interaction may account for the systematic increase in gold concentrations in SMS deposits with decreasing spreading rate, variations in the gold content of different source rocks may also contribute to the formation of gold-rich ultramafic-hosted deposits.

Further evidence for the leaching of gold from peridotite-hosted sulphides is recognised by the association of gold with bismuth- and tellurium-bearing minerals in the ultramafic-hosted Rainbow deposit (Fouquet et al. 2010). These semi-metals are likely sourced from mantle sulphides with gold and the platinum-group elements (PGE). This is supported by PGE enrichment in ultramafic-hosted SMS deposits, with up to 190 ppb Pt at Rainbow (Bogdanov et al. 2002) and up to 183 ppb Pt at Logatchev (Mozgova et al. 1999).

### Fluid chemistry

It has been argued that variation in the gold content of the source rocks does not necessarily explain the differences in gold concentration observed between MORB- and ultramafic-hosted SMS deposits (Fouquet et al. 2010), with the oxidation state of the hydrothermal fluids and inputs from metal-rich magmatic fluids the dominant processes in producing gold-rich SMS deposits (Herzig et al. 1993; Herzig and Hannington 1995; Hannington et al. 2005). However, these arguments are only relevant for arc- and immature back-arc-hosted deposits as metal-rich magmatic fluids are volumetrically insignificant at mid-ocean ridges (Hannington et al. 2005) and the oxidation of hydrothermal fluids may only occur as a result of the dehydration or partial melting of a subducting slab. Alternative variations in fluid chemistry must be considered in the formation of gold-rich SMS deposits at mid-ocean ridges.

The transport of gold in high-temperature systems is favoured by acid oxidised fluids and/or the presence of high-salinity brines (Huston and Large 1989; Hannington et al.

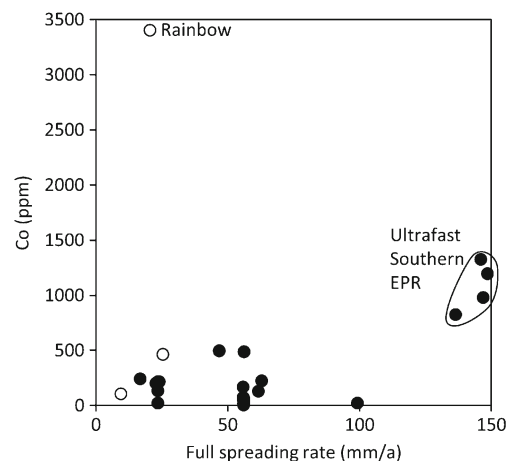
1997). Gold is transported and concentrated as chloride complexes at high temperatures (> 300 °C) and precipitated with Cu-Fe-rich sulphides before being subsequently remobilised by late low-temperature (< 250 °C) fluids as aqueous sulphur complexes and concentrated in zinc-rich polymetallic sulphides along with other elements such as Ag, As, Sb, Hg and Pb (Hannington et al. 1986; Herzig et al. 1993).

At ultramafic sites, the transport of gold as Au(HS)<sub>2</sub><sup>-</sup> and Au(HS)<sup>0</sup> complexes could be enhanced by reducing conditions and the fact that sulphur may be more readily available. Alternatively, it has been suggested that abiotic organic complexes (hydrocarbons) may be important in the transport of gold in ultramafic rocks (Fouquet et al. 2010); however, this has not been investigated in detail to date.

Three SMS deposits along the ultrafast spreading southern East Pacific Rise with relatively elevated gold concentrations reverse the trend of gold with spreading rates above 140 mm/a. Notably, these sites, as well as one other southern EPR site (EPR 7°25'S), also have significantly higher average cobalt concentrations (~ 978–1321 ppm) than all the other MORB-hosted deposits (2–494 ppm), as well as most ultramafic-hosted sites (103–465 ppm) except for Rainbow (3402 ppm; Fig. 5). Phase separation, known to occur along the southern EPR (Charlou et al. 1996), may be responsible for the elevated concentrations of cobalt and gold observed. This results in the formation of brines with the capacity to leach gold and cobalt from the crust as chloride complexes with the latter transported as CoCl<sub>4</sub><sup>2-</sup>, particularly at temperatures > 250 °C (Liu et al. 2011; Migdisov et al. 2011).

### Precipitation mechanisms

At mid-ocean ridge vent sites, base and precious metals are precipitated from hot acidic hydrothermal fluids during mixing with cold circumneutral seawater. However, the nature



**Fig. 5** Average cobalt concentrations of ultramafic- and MORB-hosted SMS deposits as a function of spreading rate

of this mixing has implications for the ratio of metals precipitated into the sulphides or lost into the black smoker plume. A study of chimney types at the northern Cleft segment on the Juan de Fuca Ridge found that chimney type is one of the main controls on fluid mixing and metal precipitation; zoned tubular Cu-rich chimneys result from focussed high-temperature fluids (up to 328 °C), beehive or diffuser chimneys result from diffuse high-temperature fluids (up to 315 °C), and columnar Zn-sulphide-rich chimneys, with narrow channels, result from focussed low-temperature (261 °C) fluid-flow (Koski et al. 1994).

Focussed-flow organ-style chimneys which promote the mixing and rapid dilution of metals in a large volume of seawater is not considered favourable for gold saturation, with > 90% of the fluid metal budget potentially dispersed in the black smoker plume (Fouquet et al. 1993). In contrast, within beehive chimneys, cooling occurs within the chimney structure and gold is probably precipitated from  $\text{Au}(\text{HS})_2^-$  complexes at low temperatures (< 160 °C) along with sphalerite and pyrite as a result of restricted mixing with seawater at the outer part of the structure (Fouquet et al. 1993). The increased efficiency of gold precipitation through enhanced cooling and oxidation of hydrothermal fluids through diffuse venting was also noted at the TAG deposit, although in this case associated with white smoker venting (Hannington et al. 1995). However, subsequent zone refining has also concentrated gold and zinc at the surface of the TAG deposit so the effect of diffuse venting on gold precipitation cannot be quantified.

The formation of beehive chimneys has been linked to lower effusive velocities of the hydrothermal fluid (e.g. Fouquet et al. 1993; Tivey 1995; Webber et al. 2015). As opposed to the conical sulphide mounds typically observed at MORB-hosted sites, ultramafic-hosted SMS deposits are flat and disorganised, which is attributed to poorly focussed diffuse venting (Fouquet et al. 2010). We speculate that this diffuse, low-velocity venting may give rise to the formation of more beehive-type chimneys compared with basalt-hosted sites, therefore providing more opportunities for gold to precipitate from the hydrothermal fluid into the sulphide mound.

### Case study: the Beebe Vent Field

The Beebe Vent Field (BVF) is a high-temperature black smoker vent site in the Cayman Trough (Connelly et al. 2012). It is situated 3 km from the spreading centre on a volcanic mound composed of basaltic pillow lavas, which is part of a spur off the main spreading axis. The BVF could be considered an end-member vent site for several reasons; it is the world's deepest known vent site at ~ 4950 mbsl, venting some of the highest temperature hydrothermal vent fluids reported to date (up to 401 °C), and it is located on one of the world's slowest spreading

centres with a spreading rate of just 16.9 mm/a. The BVF comprises several mounds of sulphide, with current high-temperature venting from two areas: Beebe-125 and Beebe Woods. Both of these sites vent fluid with the same end-member salinity, indicating that the fluids experience similar sub-surface processes. The primary difference between the two areas is that Beebe-125 is composed of tall, slender Cu-rich chimneys, and Beebe Woods hosts a large cluster of zinc-rich beehive chimneys. Both sites are gold-rich, but Beebe Woods is significantly richer, containing 19–93 ppm gold (mean = 48.8,  $n = 8$ ) compared to 0.5–8 ppm (mean = 2.6,  $n = 5$ ) at Beebe-125. The striking difference between the gold concentration of the vent sites, and the similarity of the vent fluid compositions, suggest a strong control on gold content by chimney morphology. The beehive chimneys of Beebe Woods are highly porous and comprised primarily of laths of pyrrhotite with pyrite, sphalerite and minor chalcopyrite. This highly reduced mineralogy, together with high surface area, buffers the fluids close to the pyrite-pyrrhotite buffer, which allows gold precipitation at ~ 140 °C (Webber et al. 2017). This is supported by the abundance of sphalerite at Beebe Woods, which also precipitates at relatively low temperatures. In contrast, the slender chimneys of Beebe-125 vent the majority of the fluid at temperatures of ~ 400 °C, retaining gold in solution.

Although surface processes have controlled the abundance of gold at Beebe Woods compared to Beebe-125, both sites are relatively auriferous, suggesting an underlying cause for high gold at the BVF. Given an extremely low spreading rate and low melt supply, the fluids circulating beneath the spreading centre at Beebe may be interacting with ultramafic lithologies at depth. This is supported by surveys of the canyon walls that describe basalt, gabbro and peridotite with no clear crustal structure (Stroup and Fox 1981), whilst geophysics suggests a thin veneer of basalt over gabbro and ultramafic lithologies (ten Brink et al. 2002). Trace element geochemistry of the BVF sulphides suggests a basement composition part way between basaltic and ultramafic (Webber et al. 2015). Following this pervasive interaction with and leaching of gold from ultramafic rocks at depth, the hydrothermal fluids are then refocussed in the overlying basalt, producing steep, cone-like sulphide mounds as opposed to flat mounds formed in ultramafic-hosted deposits which result from diffuse venting over wide areas (Fouquet et al. 2010). The BVF demonstrates that a combination of sub-surface and precipitation processes have combined to produce a gold-rich SMS deposit.

### Summary and conclusions

Average gold concentrations in non-sedimented mid-ocean ridge-hosted SMS deposits show a negative correlation with spreading rate. Ultramafic-hosted deposits at slow and ultra-slow spreading ridges are particularly gold enriched, and

MORB-hosted deposits along slow spreading ridges may also host significant gold concentrations. Metal-rich magmatic fluids which are used to explain high gold concentrations in arc- and immature back-arc-hosted deposits (Hannington et al. 1997; Yang and Scott 2006) are volumetrically insignificant at mid-ocean ridges (Hannington et al. 2005). Instead, we suggest that the combined effects of the degree and duration of fluid-rock interaction, concentration of gold in the source rocks, fluid chemistry and precipitation mechanisms, all of which can be linked to spreading rate, control the gold content of SMS deposits.

At slower spreading ridges, hydrothermal fluids have deep, long-lived fluid-flow pathways which is evidenced by the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{18}\text{O}$  signatures of the vent fluids (Bach and Humphris 1999) and a consequence of low heat flux. At slow spreading ridges (Fig. 6c), hydrothermal fluids are restricted to interacting with gold-poor source rocks consisting predominantly of MORB (0.34 ppb Au; Webber et al. 2013). However, the longevity of these hydrothermal cells which remain largely undisturbed by infrequent magmatic activity, and an abundance of unaltered source rocks leads to the formation of large SMS deposits moderately enriched in gold.

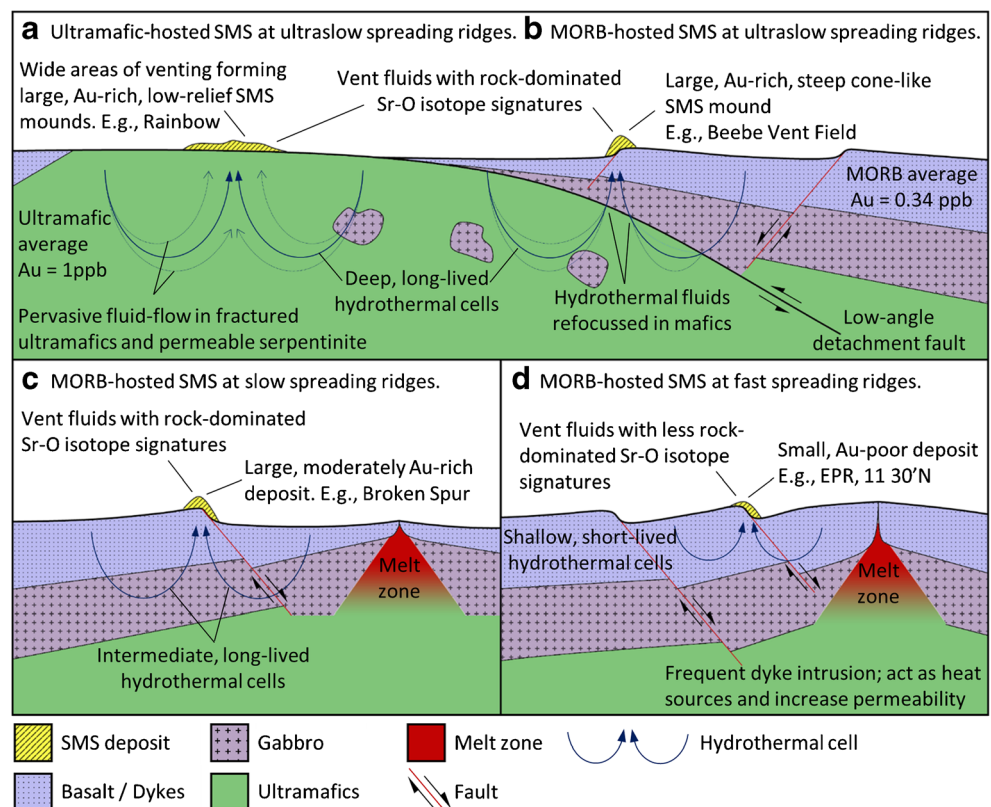
In addition to the above, at ultraslow spreading ridges, hydrothermal fluids forming both ultramafic-hosted (Fig. 6a) and MORB-hosted (Fig. 6b) SMS deposits, may interact with more gold-rich ultramafic source rocks (1 ppb; e.g. Lorand

et al. 1999; Luguet et al. 2002; Maier et al. 2012) which are susceptible to pervasive alteration given the volume increase of 25–50% associated with serpentinisation resulting in episodic fracturing (Schwarzenbach 2016) and the inherent nano-scale porosity that serpentine and associated accessory phases possess (Tutolo et al. 2016). The alteration of ultramafic rocks results in reducing conditions and greater concentrations of sulphur may be available, aiding the transport of gold as  $\text{Au}(\text{HS})_2^-$  and  $\text{Au}(\text{HS})^0$  complexes. At MORB-hosted ultraslow spreading ridges, hydrothermal fluids may interact with and leach gold from ultramafic lithologies at depth before being refocussed in the overlying basalt (Fig. 6b).

At fast spreading ridges (Fig. 6d), the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{18}\text{O}$  signatures of the vent fluids are less rock-dominated (Bach and Humphris 1999) suggesting that hydrothermal cells are shallow due to the emplacement of dykes which act as heat sources in the upper crust and increase permeability near the ridge axis (Wilcock and Delaney 1996). These shallow hydrothermal systems which react only with gold-poor MORB are also frequently disrupted by episodic eruptions leading to the formation of small, gold-poor SMS mounds.

Local controls on gold precipitation are evident in the form of sulphide chimney morphology. Organ-style chimneys focus high-temperature fluids ( $\sim 350\text{--}400\text{ }^\circ\text{C}$ ) which retain  $> 90\%$  of their contained metals which are then subsequently lost to the black smoker plume (Fouquet et al. 1993). Beehive chimneys allow for hydrothermal fluids to be oxygenated and

**Fig. 6** Schematic diagram summarising how the combined effects of the degree and duration of fluid-rock interaction, and the concentration of gold in the source rocks result in the formation of **a** large, Au-rich ultramafic-hosted deposits along ultraslow spreading ridges; **b** large, Au-rich MORB-hosted deposits along ultraslow spreading ridges; **c** large, moderately Au enriched MORB-hosted deposits along slow spreading ridges; and **d** small, Au-poor MORB-hosted deposits along fast spreading ridges





cooled within the structure of chimneys, resulting in the precipitation of gold at low temperatures with sphalerite and pyrite (Fouquet et al. 1993; Hannington et al. 1995). Alternatively, the mineralogy of these beehive chimneys combined with their high surface area may keep the fluid highly reduced and close to the pyrite-pyrrhotite buffer which raises the temperature at which gold can precipitate (Webber et al. 2017). We speculate that the diffusive low-velocity venting associated with slow and ultraslow ultramafic sites that results in the formation of flat sulphide mounds may also result in the formation of more beehive chimneys, and thus more sites to support gold precipitation compared to more focussed venting at basalt-hosted sites.

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