1 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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## 9 Abstract

10 Seafloor massive sulphide (SMS) deposits are variably enriched in precious metals including 11 gold. However, the processes invoked to explain the formation of auriferous deposits do not 12 typically apply to mid-ocean ridge settings. Here we show a statistically significant, negative 13 correlation between the average gold concentration of SMS deposits with spreading rate, at 14 non-sedimented mid-ocean ridges. Deposits located at slow spreading ridges (20-40 mm/a) have average gold concentrations of between 850-1600 ppb, however, with increasing 15 16 spreading rate (up to 140 mm/a), gold concentrations gradually decrease to between ~50-150 17 ppb. This correlation of gold content with spreading rate may be controlled by the degree and 18 duration of fluid-rock interaction, which is a function of the heat flux, crustal structure 19 (faulting) and the permeability of the source rocks. Deposits at ultraslow ridges, including 20 ultramafic-hosted deposits, are particularly enriched in gold. This is attributed to the higher 21 permeability of the ultramafic source rocks achieved by serpentinisation and the inherent 22 porosity of serpentine minerals, combined with relatively high gold concentrations in 23 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 24 25 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-26

hosted sites due to diffuse low-velocity venting compared with more focussed venting atbasalt-hosted sites.

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30 *Keywords:* Gold Mineralisation; Massive Sulphide; Mid-Ocean Ridge; Hydrothermal;
31 Ultramafic

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#### 33 Introduction

34 Gold-rich volcanogenic massive sulphide (VMS) deposits and their modern-day equivalents, 35 seafloor massive sulphide (SMS) deposits, are usually associated with arc, immature back-arc 36 and rifted environments where felsic lithologies comprise a significant component of the host 37 rocks (Hannington et al. 1997; Dubé et al. 2007). In these tectonic environments, gold is 38 enriched by the oxidation of sulphides in the mantle wedge (Mungall 2002) which promotes 39 the formation of gold-rich magmas (Botcharnikov et al. 2010), and ultimately the addition of 40 a gold-bearing magmatic fluid to seafloor hydrothermal systems (Yang and Scott 1996, 41 2006). In comparison, massive sulphide deposits forming at mid-ocean ridge and mature 42 back-arc spreading centres are typically gold-poor. In these settings, contributions of metal-43 rich magmatic fluids are volumetrically insignificant due to the lack of water- and volatile-44 rich magmas that are prevalent at convergent margins (Hannington et al. 2005). Gold 45 concentrations in mid-ocean ridge basalt (MORB) -hosted SMS deposits are typically ten 46 times lower than defined auriferous VMS deposits (Mercier-Langevin et al. 2011; Patten et 47 al. 2015). However, some SMS deposits along slow spreading mid-ocean ridges as well as 48 ultramafic-hosted deposits which typically form along ultraslow spreading ridges, can host 49 significant gold concentrations of between 850-1600 ppb and 4700-7900 ppb, respectively 50 (Murphy and Meyer 1998; Mozgova et al. 1999; Munch et al 2001; Bogdanov et al. 2002;

51 Nayak et al. 2014; Fouquet et al. 2010; Webber et al. 2015). These data suggest that the 52 measured gold concentrations might be related to spreading rate, although this relationship 53 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.

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#### 61 Methods

62 We have updated and manipulated a pre-existing global geochemical database of SMS 63 deposits produced by Hannington et al. (2004) with the addition of recently published data 64 for mid-ocean ridge-hosted SMS deposits (Stepanova et al. 1996; German et al. 1999; 65 Margues et al. 2006; 2007; Bogdanov et al. 2008; Kristall et al. 2011; Szamałek et al. 2011; Nayak et al. 2014). Further information was also added from the InterRidge 3.2 database; 66 67 e.g., deposit/site name alias(es), ocean basin, region and tectonic setting, latitude and 68 longitude, host rock(s), whether the site is active or inactive, current maximum temperature, 69 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. 75 In the majority of cases, samples in the database are taken from the surfaces of SMS mounds, 76 which may be enriched in metals due to zone refining, with an increase in the concentration 77 of gold with zinc towards the surface of the mounds (e.g., Hannington et al. 1986, 1995; 78 Petersen et al. 2003). Similarly, massive sulphide chimneys which are naturally metal-rich 79 are also over-represented. These enriched surface samples are unlikely to be representative of 80 the deposits in their entirety. However, since there is a great range of gold concentrations 81 across all deposits that have been sampled in this manner, we assume that the gold 82 concentration in these surface samples are generally indicative of how gold-rich a deposit is.

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#### 84 **Results**

#### 85 Spreading rate and gold concentration

86 Minimum, maximum and average gold concentrations for each mid-ocean ridge-hosted SMS 87 deposit are presented in Table 1. Ultramafic-hosted deposits at slow and ultraslow spreading 88 ridges record high average gold values of between ~4700-7900 ppb. The highest average gold 89 concentrations are recorded from the Beebe Vent Field, which is a MORB-hosted deposit 90 forming along the ultraslow Cayman Rise and will be discussed later in detail. Average gold 91 concentrations of other MORB-hosted deposits at slow spreading ridges (20-40 mm/a) vary 92 between ~850-1600 ppb; excluding the MIR zone which is comparable to that of ultramafic-93 hosted deposits (3733 ppb). In deposits at intermediate spreading ridges (40-90 mm/a), 94 average gold concentrations range from ~90-1000 ppb. The majority of deposits have 95 concentrations of less than ~280 ppb with the Galapagos Rift, Magic Mountain, Source and 96 the MESO Zone exhibiting higher concentrations of 427, 723, 975 and 1024 ppb, 97 respectively. At fast spreading ridges (90-140 mm/a), deposits have low average gold 98 concentrations ranging from ~50-150 ppb. However, at ultrafast spreading sites (>140 mm/a),

average gold concentrations of between ~320-580 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.

102 There is a statistically significant relationship, at the 99% confidence interval, between full 103 spreading rate and average gold concentrations (n = 26, r = -0.588, Fig. 1). As full spreading 104 rate increases from 20 mm/a to 140 mm/a, the gold content of the associated sulphide 105 deposits decreases by up to two orders of magnitude. This relationship is exponential in 106 nature. Grouping the data for each site into their respective categories (i.e., grouping all gold 107 data for ultramafic, slow, intermediate, fast and ultrafast spreading MORB sites) confirms the 108 relationship of gold variation with spreading rate (Fig. 2). Kruskal-Wallis tests were 109 performed on these grouped data and show that there are statistically significant variations 110 between the medians of these groups at a confidence level of 95 %, except between the slow 111 and ultrafast spreading groups where there is no significant difference (Table 2). Ultramafic-112 hosted deposits associated with ultraslow spreading rates (<20 mm/a) are significantly more 113 enriched in gold than other MORB-hosted sites, even along slow spreading ridges (Figs. 1-3). 114 Whilst ultrafast southern EPR sites are not auriferous, they do appear more gold-rich than 115 predicted by the overall trend (Fig. 2).

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#### 117 **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 precipitationmechanisms.

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

126 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 127 128 hydrothermal fluids to interact with a sufficient source of unaltered rock, greater quantities of 129 gold may be leached from the crust if gold remains undersaturated in the fluid. Consideration of the  ${}^{87}$ Sr/ ${}^{86}$ Sr and  $\delta^{18}$ O signatures of hydrothermal fluids from vent sites along mid-ocean 130 131 ridges indicate that hydrothermal fluids from slower spreading ridges are more rock-132 dominated compared to those measured at faster spreading ridges (Fig. 4; Bach and Humphris 133 1999). These rock-dominated signatures in hydrothermal fluids at slow spreading ridges are 134 the result of greater Sr and O exchange with the oceanic crust which reflects increased 135 residence time and deeper hydrothermal fluid-flow pathways (Bach and Humphris 1999). These findings are supported by numerical modelling studies which demonstrate that the 136 thermal regime at slow spreading ridges is generally cooler (Brown and White 1994) and 137 hydrothermal fluids require deeper penetration into, and longer residence time within the 138 139 oceanic crust to achieve the temperatures typically measured for fluids emanating at 140 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 141 142 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 143 144 Delaney 1996) as evidenced by the extreme alteration of oceanic rocks along a detachment 145 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.

151 The degree of fluid-rock interaction may be further enhanced for ultramafic-hosted deposits. 152 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-153 154 limiting as the fractures are subsequently filled with serpentine minerals closing fluid-flow 155 pathways and preventing further serpentinisation and fluid-rock interaction (Macdonald and 156 Fyfe 1985; O'Hanley 1992; Schwarzenbach 2016). Recent work shows that serpentine and 157 associated accessory phases form with their own inherent nano-scale porosity, which allows 158 continued diffusive fluid-flow and pervasive serpentinisation of ultramafic rocks (Tutolo et 159 al. 2016); possibly resulting in increased leaching of gold from base metal sulphides. 160 Furthermore, the heat of exothermic serpentinisation reactions may contribute to long-lived 161 hydrothermal activity at ultramafic-hosted SMS sites (Lowell and Rona 2002; German and 162 Lin 2004). Therefore, hydrothermal fluids at slow and ultraslow spreading ridges experience 163 long-lived, deep hydrothermal circulation resulting in greater degrees of fluid-rock 164 interaction with a greater potential to leach gold from the oceanic crust, particularly where 165 ultramafic rocks are present.

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#### 167 Gold content of the source rocks

168 Differences in source rock composition, particularly between MORB and ultramafic 169 lithologies, have been shown to exert a control on the composition of the sulphides 170 precipitated at SMS deposits (e.g., Wang et al. 2014; German et al. 2016). The geochemical 171 characteristics of the host rocks of SMS deposits at mid-ocean ridges are a function of crustal 172 thickness which varies with spreading and magma supply rates (Bown and White 1994; Niu 173 and Hékinian 1997). At ridges where the temperature is sufficient to sustain magmatism 174 capable of developing a full thickness of oceanic crust (>20 mm/a), the host rocks are 175 typically MORB (InterRidge 3.2 database). However, at ultraslow spreading ridges (<20 176 mm/a), there is a greater component of tectonic extension and amagmatic spreading via 177 detachment faulting which exhumes mantle material (e.g., Escartín et al. 2008), in some cases 178 giving rise to ultramafic-hosted SMS deposits. Furthermore, low magma supply rates also 179 occur at the termination of ridge sections which may also result in the exhumation of 180 ultramafic rocks (Fouquet et al. 2010). Ultramafic rocks are partially exhumed in this manner 181 at the termination of intermediate spreading ridge sections (40-90 mm/a), however, they are 182 not exposed at the seafloor surface, rather their existence in the sub-seafloor is evidenced by 183 vent fluids with high H<sub>2</sub> and CH<sub>4</sub> gas contents and sulphide compositions (e.g., at the Kairei 184 hydrothermal field, Central Indian Ridge; Wang et al. 2014), or by geothermobarometry 185 indicating that fluid circulation occurs at depths greater than the thickness of the basaltic crust 186 (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-richultramafic-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 semimetals 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).

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#### 203 Fluid chemistry

204 It has been argued that variation in the gold content of the source rocks does not necessarily 205 explain the differences in gold concentration observed between MORB- and ultramafic-206 hosted SMS deposits (Fouquet et al. 2010), with the oxidation state of the hydrothermal fluids 207 and inputs from metal-rich magmatic fluids the dominant processes in producing gold-rich 208 SMS deposits (Herzig et al. 1993; Herzig and Hannington 1995; Hannington et al. 2005). 209 However, these arguments are only relevant for arc- and immature back-arc-hosted deposits 210 as metal-rich magmatic fluids are volumetrically insignificant at mid-ocean ridges 211 (Hannington et al. 2005) and the oxidation of hydrothermal fluids may only occur as a result 212 of the dehydration or partial melting of a subducting slab. Alternative variations in fluid 213 chemistry must be considered in the formation of gold-rich SMS deposits at mid-ocean 214 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

218 precipitated with Cu-Fe-rich sulphides before being subsequently remobilised by late low-219 temperature (<250°C) fluids as aqueous sulphur complexes, and concentrated in zinc-rich 220 polymetallic sulphides along with other elements such as Ag, As, Sb, Hg, and Pb 221 (Hannington et al. 1986; Herzig et al. 1993).

At ultramafic sites, the transport of gold as  $Au(HS)_2^-$  and  $Au(HS)^0$  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.

227 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. 228 229 Notably, these sites, as well as one other southern EPR site (EPR 7°25'S), also have 230 significantly higher average cobalt concentrations (~978-1321 ppm) than all the other 231 MORB-hosted deposits (2-494 ppm), as well as most ultramafic-hosted sites (103-465 ppm) 232 except for Rainbow (3402 ppm; Fig. 5). Phase separation, known to occur along the southern 233 EPR (Charlou et al. 1996) may be responsible for the elevated concentrations of cobalt and 234 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  $CoCl_4^{2-}$ , particularly 235 at temperatures >250°C (Liu et al. 2011; Migdisov et al. 2011). 236

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#### 238 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 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 248 249 in a large volume of seawater is not considered favourable for gold saturation, with >90% of 250 the fluid metal budget potentially dispersed in the black smoker plume (Fouquet et al. 1993). 251 In contrast, within beehive chimneys, cooling occurs within the chimney structure and gold is probably precipitated from Au(HS)<sub>2</sub> complexes at low temperatures (<160°C) along with 252 sphalerite and pyrite as a result of restricted mixing with seawater at the outer part of the 253 254 structure (Fouquet et al. 1993). The increased efficiency of gold precipitation through 255 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 256 257 (Hannington et al. 1995). However, subsequent zone refining has also concentrated gold and 258 zinc at the surface of the TAG deposit so the effect of diffuse venting on gold precipitation 259 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 266 providing more opportunities for gold to precipitate from the hydrothermal fluid into the 267 sulphide mound.

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269 Case study: The Beebe Vent Field

270 The Beebe Vent Field (BVF) is a high-temperature black smoker vent site in the Cavman 271 Trough (Connelly et al. 2012). It is situated 3 km from the spreading centre on a volcanic 272 mound composed of basaltic pillow lavas, which is part of a spur off the main spreading axis. 273 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 274 275 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 276 277 comprises several mounds of sulphide, with current high-temperature venting from two areas; 278 Beebe-125 and Beebe Woods. Both of these sites vent fluid with the same end-member 279 salinity, indicating that the fluids experience similar sub-surface processes. The primary 280 difference between the two areas is that Beebe-125 is comprised of tall, slender Cu-rich 281 chimneys, and Beebe Woods hosts a large cluster of zinc-rich beehive chimneys. Both sites 282 are gold-rich, but Beebe Woods is significantly richer, containing 19-93 ppm gold (mean = 283 48.8, n = 8) compared to 0.5-8 ppm (mean = 2.6, n = 5) at Beebe-125. The striking difference 284 between the gold concentration of the vent sites, and the similarity of the vent fluid 285 compositions, suggest a strong control on gold content by chimney morphology. The beehive 286 chimneys of Beebe Woods are highly porous and comprised primarily of laths of pyrrhotite 287 with pyrite, sphalerite and minor chalcopyrite. This highly reduced mineralogy, together with 288 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 289

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.

293 Although surface processes have controlled the abundance of gold at Beebe Woods compared 294 to Beebe-125, both sites are relatively auriferous, suggesting an underlying cause for high 295 gold at the BVF. Given an extremely low spreading rate and low melt supply, the fluids 296 circulating beneath the spreading centre at Beebe may be interacting with ultramafic 297 lithologies at depth. This is supported by surveys of the canyon walls that describe basalt, 298 gabbro and peridotite with no clear crustal structure (Stroup and Fox 1981), whilst 299 geophysics suggests a thin veneer of basalt over gabbro and ultramafic lithologies (ten Brink 300 et al. 2002). Trace element geochemistry of the BVF sulphides suggests a basement 301 composition part way between basaltic and ultramafic (Webber et al. 2015). Following this 302 pervasive interaction with and leaching of gold from ultramafic rocks at depth, the 303 hydrothermal fluids are then refocussed in the overlying basalt, producing steep, cone-like 304 sulphide mounds as opposed to flat mounds formed in ultramafic-hosted deposits which 305 result from diffuse venting over wide areas (Fouquet et al. 2010). The BVF demonstrates that 306 a combination of sub-surface and precipitation processes have combined to produce a gold-307 rich SMS deposit.

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#### 309 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 ultraslow 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.

320 At slower spreading ridges, hydrothermal fluids have deep, long-lived fluid-flow pathways which is evidenced by the  ${}^{87}$ Sr/ ${}^{86}$ Sr and  $\delta^{18}$ O signatures of the vent fluids (Bach and 321 322 Humphris 1999) and a consequence of low heat flux. At slow spreading ridges (Fig. 6C), 323 hydrothermal fluids are restricted to interacting with gold-poor source rocks consisting 324 predominantly of MORB (0.34 ppb Au; Webber et al 2013). However, the longevity of these 325 hydrothermal cells which remain largely undisturbed by infrequent magmatic activity, and an 326 abundance of unaltered source rocks leads to the formation of large SMS deposits moderately 327 enriched in gold.

328 In addition to the above, at ultraslow spreading ridges, hydrothermal fluids forming both 329 ultramafic-hosted (Fig. 6A) and MORB-hosted (Fig. 6B) SMS deposits, may interact with 330 more gold-rich ultramafic source rocks (1ppb; e.g., Lorand et al. 1999; Luguet et al. 2002; 331 Maier et al. 2012) which are susceptible to pervasive alteration given the volume increase of 332 25-50% associated with serpentinisation resulting in episodic fracturing (Schwarzenbach 333 2016) and the inherent nano-scale porosity that serpentine and associated accessory phases 334 possess (Tutolo et al. 2016). The alteration of ultramafic rocks results in reducing conditions 335 and greater concentrations of sulphur may be available, aiding the transport of gold as  $Au(HS)_2^-$  and  $Au(HS)^0$  complexes. At MORB-hosted ultraslow spreading ridges, 336 337 hydrothermal fluids may interact with and leach gold from ultramafic lithologies at depth 338 before being refocussed in the overlying basalt (Fig. 6B).

At fast spreading ridges (Fig. 6D), the  ${}^{87}$ Sr/ ${}^{86}$ Sr and  ${}^{18}$ 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.

345 Local controls on gold precipitation are evident in the form of sulphide chimney morphology. Organ-style chimneys focus high-temperature fluids (~350-400°C) which retain >90 % of 346 their contained metals which are then subsequently lost to the black smoker plume (Fouquet 347 348 et al. 1993). Beehive chimneys allow for hydrothermal fluids to be oxygenated and cooled 349 within the structure of chimneys, resulting in the precipitation of gold at low temperatures 350 with sphalerite and pyrite (Fouquet et al. 1993; Hannington et al. 1995). Alternatively, the 351 mineralogy of these beehive chimneys combined with their high surface area may keep the 352 fluid highly reduced and close to the pyrite-pyrrhotite buffer which raises the temperature at 353 which gold can precipitate (Webber et al. 2017). We speculate that the diffusive low-velocity 354 venting associated with slow and ultraslow ultramafic sites that results in the formation of flat 355 sulphide mounds may also result in the formation of more beehive chimneys, and thus more 356 sites to support gold precipitation compared to more focussed venting at basalt-hosted sites.

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552 Table Captions:

Table 1. Table showing mean, minimum, and maximum gold concentrations for SMS deposits at ultraslow-slow, intermediate, fast, and ultrafast spreading mid-ocean ridges. Those at ultraslow-slow spreading ridges are subdivided into ultramafic- and MORB-hosted deposits.

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 ultramafichosted sites grouped separately. 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%.

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563 Figure Captions:

Figure 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.

Figure 2. Box and whisker plot showing gold concentrations of ultramafic- and MORBhosted 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.

571 Figure 3. Box and whisker plot showing gold concentrations of ultramafic- and MORB-572 hosted SMS deposits as a function of spreading rate. Boxes show 25th-75th percentile 573 including median line, whiskers show 10th-90th percentile and outliers have been omitted for 574 clarity.

Figure 4. A) The fraction of Sr in vent fluids that is derived from seawater, and B)  $\Delta^{18}$ O (the difference between  $\delta^{18}$ O values of hydrothermal vent fluids and  $\delta^{18}$ 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 explanationand abbreviations.
- Figure 5. Average cobalt concentrations of ultramafic- and MORB-hosted SMS deposits as afunction of spreading rate.

Figure 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.

- 590
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- 592 Tables:
- 593 Table 1.

Full Spreading Rate	Deposit Name	Gold Concentrations (ppb)			No. of
(mm/a)		Mean	Min	Max	Analyses
Ultraslow-slow					
spreading ridges	Ultramafic-hosted				
9.6	Mount Jourdanne	4705	0	12500	21
20.6	Rainbow Field	5342	1530	12100	6
25.5	Logatchev	7893	100	56000	55
	MORB-hosted				
16.9	Beebe Vent Field	17096	458	93600	29
22.9	Broken Spur	1577	8	5580	15
23.6	Mir Zone	3733	42	22600	52
23.6	Alvin Zone	854	680	1020	7
23.6	TAG Mound	971	<5	42960	439
24.1	Snake Pit	1575	<20	10739	100
Intermediate					
spreading ridges					
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

Fast spreading ridges					
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
Ultrafast spreading					
ridges					
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

- 598 Table 2.

	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 tes	t p-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









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