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VHMS mineralization at Erayinia in the Eastern Goldfields Superterrane: Geology and geochemistry of the metamorphosed King Zn deposit

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- 21

22 Abstract

23 Despite having been a target for volcanic-hosted massive sulfide (VHMS) deposits since the 1960s, few resources have been defined in the Archean Yilgarn Craton of Western 24 25 Australia. Exploration challenges associated with regolith and deep cover exacerbate the already difficult task of exploring for small, deformed deposits in stratigraphically complex, 26 27 metamorphosed volcanic terranes. We present results of drillcore logging, petrography, whole rock geochemistry and pXRF data from the King Zn deposit, to help refine mineralogical and 28 29 geochemical halos associated with VHMS mineralization in amphibolite facies greenstone 30 sequences of the Yilgarn Craton.

The King Zn deposit (2.15 Mt at 3.47% Zn) occurs as a 2-5m thick stratiform lens 31 dominated by iron sulfides, in an overturned, metamorphosed volcanic rock-dominated 32 sequence located ~140km east of Kalgoorlie. The local stratigraphy is characterized by garnet 33 amphibolite and strongly banded intermediate to felsic schists, with rare horizons of graphitic 34 schist. Massive sulfide mineralization is characterized by stratiform pyrite-pyrrhotite-35 sphalerite at the contact between quartz-muscovite schists ('the footwall dacite') and banded 36 quartz-biotite/amphibole±garnet schists of the stratigraphic hanging-wall. A zone of pyrite-37 38 (sphalerite) and pyrrhotite-pyrite-(chalcopyrite) veining extends throughout the stratigraphic footwall. Footwall garnet-amphibolites are of sub-alkaline basaltic affinity, with a central zone 39 dominated by chlorite±magnetite interpreted to represent the Cu-bearing feeder zone. SiO₂, 40 CaO, Fe₂O_{3T}, MgO and Cu concentrations are highly variable, reflecting quartz-41 42 epidote±chlorite±magnetite±sulfide alteration. Hydrothermal alteration in stratigraphically overlying intermediate to felsic rocks is characterized by a mineral assemblage of quartz-43

muscovite±chlorite±albite±carbonate. Cordierite and anthophyllite are locally significant and
indicative of zones of Mg-metasomatism prior to metamorphism. Increases of SiO₂, Fe₂O_{3T},
pathfinder elements (e.g. As, Sb, Tl), and depletions of Na₂O, CaO, Sr, and MgO occur in
footwall quartz-muscovite schists approaching massive sulfide mineralization.

Within all strata (including the immediate hanging-wall), the following pathfinder 48 49 elements are strongly correlated with Zn: Ag, As, Au, Bi, Cd, Eu/Eu*, Hg, In, Ni, Pb, Sb, Se, Tl. These geochemical halos resemble less metamorphosed VHMS deposits across the Yilgarn 50 Craton and suggest that although metamorphism leads to element mobility and mineral 51 segregation at the thin section scale, assay samples of ~20cm length are sufficient to vector to 52 mineralization in amphibolite facies greenstone belts. Recognition of minerals such as Mg-53 chlorite, muscovite, cordierite, anthophyllite, biotite/phlogopite, and abundant garnet are 54 significant, in addition to Al-rich phases (i.e. kyanite, sillimanite, and alusite and/or staurolite) 55 not identified at King. Chemographic diagrams may be used to identify and distinguish 56 57 different alteration trends, along with several alteration indices (e.g. AI, CCPI, SI) and the abundance of normative corundum and quartz. 58

59

60 **1. Introduction**

For the last four decades, exploration for volcanic-hosted massive sulfide (VHMS) 61 mineralization in the Archean Yilgarn Craton of Western Australia (Fig. 1) has been hampered 62 by a perceived lack of prospectivity and difficult exploration conditions. The latter include 63 64 deep and transported overburden, a paucity of outcrop, high strain, and saline groundwaters (McConachy et al. 2004; Yeats, 2007; Vearncombe, 2010; Hollis et al. 2015). In many 65 greenstone belts, the proximity of supracrustal rocks to late stage granites, which comprise 66 67 much of the craton, adds further complications. Metamorphic grade varies across the craton from greenschist to granulite facies, generally being higher closer to greenstone margins, and 68 within narrower greenstone belts (e.g. Witt, 1991; Swager, 1997; Witt & Hagemann, 2012). 69

Few VHMS deposits have been identified in greenstone sequences metamorphosed to 70 relatively high grade in the Yilgarn Craton (reviewed in Hollis et al. 2017a), as relatively simple 71 primary alteration assemblages are often overprinted and obscured, with host rocks now 72 comprising mineralogically complex banded schist or gneiss. For example, at Kingsley (the 73 Wheatley prospect, South West Terrane: Fig. 1), massive sulfide mineralization is hosted at a 74 75 transition between quartz-feldspar-biotite gneiss and hornblende-plagioclase-biotite-76 quartz±garnet amphibolite, marking a shift from felsic to mafic volcanism (Yeats, 2007; Hassan, 2017a). Sodium depletion in felsic gneisses underneath mineralization and the Al-rich 77 minerals sillimanite, staurolite, kyanite and garnet provide evidence for a metamorphosed 78 hydrothermal system (Yeats, 2007; Hassan, 2017a). In the eastern half of the Quinns district 79 80 (Murchison Domain, Youanmi Terrane: Fig. 1), schistose rhyolite contains locally abundant and coarse-grained andalusite±kyanite±garnet where associated with VHMS mineralization 81 (Duuring et al. 2016; Hassan, 2017b). The recognition of garnet and staurolite porphyroblasts 82 for 30m above and below the Hollandaire deposit (Murchison Domain, Younami Terrane: Fig. 83 84 1) was also significant for VHMS exploration in the area (Hayman et al. 2015a).

Despite the increased difficulty of discovery, the metamorphism and deformation of
 VHMS deposits may bring economic benefits. These can include the significant upgrading and

redistribution of gold during metamorphism (e.g. Boliden deposit, Sweden; Wagner, et al.
2007), and the thickening of massive sulfide ores in hinge zones of folds (Dusel-Bacon, 2012).

We present results of drillcore logging, petrography, whole rock geochemistry and pXRF data

90 from the King Zn VHMS deposit in the Erayinia region of the southern Kurnalpi Terrane

90 If on the King 2n VHWS deposit in the Erayina region of the southern Kurnalpi Terrane 91 (Edjudina Domain, **Fig. 1**). We show that the mineralogical and geochemical signatures of the

magmatic, hydrothermal and metamorphic events can be resolved. From these inferences we
 discuss features that may be used to identify VHMS deposits that have been metamorphosed

- 94 at amphibolite facies in the Yilgarn Craton.
- 95

96 **2. Geological setting**

The Yilgarn Craton has historically been divided into a series of terranes based on distinct 97 lithological associations, geochemistry and ages of volcanism (Gee et al. 1981; Myers, 1990; 98 99 Cassidy et al. 2006). The western half of the Yilgarn Craton comprises the Narryer, South West and Youanmi terranes (Fig. 1). East of the Ida Fault, the Eastern Goldfields Superterrane (EGS) 100 can be divided into the Kalgoorlie, Kurnalpi, Burtville and Yamarna terranes (Pawley et al. 101 2012; Fig. 1). The geology of the Yilgarn Craton with respect to VHMS mineralization has 102 103 recently been discussed by Hollis et al. (2015; 2017a). Here we summarise the regional geology of the Kalgoorlie and Kurnalpi terranes (Figs. 1 & 2). 104

105 The geology of the Kalgoorlie Terrane is broadly divisible into the lower 2720-2690 Ma mafic-ultramafic Kambalda Sequence (Beresford et al. 2005) and the overlying 2690-2660 106 Ma Kalgoorlie Sequence (Krapež & Hand, 2008) (Fig. 2). At least two magmatic cycles, 107 interpreted as plume related, are recognized in the lower sequence (Hayman et al. 2015b). The 108 overlying 2690-2660 Ma Kalgoorlie Sequence comprises a >3km thick package of 109 volcaniclastic rocks, felsic volcanic rocks, and mafic intrusive complexes with minor mafic 110 volcanic rocks (Squire et al. 2010; Fig. 2). Late doming and extension associated with the 111 emplacement of a widespread tonalite-trondjhemite-granodiorite (TTG) suite produced the late 112 clastic basins of the Eastern Goldfields (Wyche et al. 2013; Fig. 2). 113

114 Broadly coeval with the Kambalda Sequence of the Kalgoorlie Terrane, the Kurnalpi and Minerie sequences of the Kurnalpi Terrane are represented by a more intermediate package 115 of rocks (Fig. 2). Although some workers have attributed the Kurnalpi andesites to an Archaean 116 arc (and thus the Kalgoorlie Terrane to a back-arc; e.g. Czarnota et al. 2010), they are also 117 geochemically consistent with the fractionation of plume-related tholeiitic basalts, coupled 118 with their contamination by contemporaneous partial melts of pre-existing continental crust 119 (Barnes & Van Kranendonk, 2014). Between 2692 and 2680 Ma, volcanic centres in the 120 Kurnalpi Terrane (Gindalbie Domain and further south; Fig. 1) are associated with largely 121 bimodal (basalt-rhyolite) volcanic and associated sedimentary rocks, although some contain 122 123 significant volumes of andesites (Fig. 2). These felsic rocks are significantly enriched in the high field strength elements (HFSE) and heavy rare earth elements (HREE) (Brown et al. 2002; 124 Barley et al. 2008; Hollis et al. 2015), and are diagnostic of shallow crustal melting (Lesher et 125 al. 1986; Piercey et al. 2001; Hart et al. 2004). This region of HFSE-enriched felsic volcanic 126 rocks and broadly coeval HFSE-enriched granitic intrusions (Hollis et al. 2015) coincides with 127 an area of juvenile crust revealed through regional Sm-Nd (granite; Fig. 3) and Pb isotope 128

129 (galena) variations (Huston et al. 2005, 2014). Interpreted as a paleo-rift zone, where juvenile material was added to the crust, similar isotopic features have also been recognized in the 130 Youanmi Terrane (i.e. Cue Zone) and Abitibi-Wawa subprovince of Canada where they are 131 associated with VHMS mineralization (Huston et al. 2014). To date only three VHMS deposits 132 have been mined in the Eastern Goldfields Superterrane - all from the c. 2690 Ma Teutonic 133 Bore volcanic complex (Hallberg & Thompson, 1985; Belford et al. 2015; Fig. 3). A significant 134 resource of Ag-rich VHMS mineralization has also been recognized in the Kalgoorlie Terrane 135 at Nimbus (Fig. 3), interpreted to represent a shallow water and low temperature deposit 136 formed on the margin of the Kurnalpi rift zone at c. 2705 Ma (Hollis et al. 2017b). 137

138 **3. Regional Geology of Erayinia**

The regional geology of the Erayinia area in the southern Kurnalpi Terrane is detailed in the 1:100,000 GSWA explanatory notes (Jones, 2007). Two major faults (Claypan and Roe Hills) divide the area into three domains - Edjudina, Murrin and Menangina (**Fig. 4**). As the Edjudina Domain at King is the focus of this paper, the other two domains will not be discussed. An account of VHMS mineralization in the Murrin Domain ~4km NW of King will be presented elsewhere (Hollis et al. in prep).

The Edjudina Domain across its ~300km length (Fig. 1) is dominated by several 145 basaltic to rhyolitic volcanic complexes, and laterally extensive belts of intermediate schist 146 predominantly derived from andesitic precursors (Swager, 1995, 1997). Prominent, though 147 volumetrically minor, marker beds of banded iron formations (BIF), chert and fine grained 148 metasedimentary rocks cap the aforementioned sequence, which are intruded by extensive 149 dolerite sills (Swager, 1995, 1997). A narrow eastern belt of thin basalt which contains 150 komatiite layers was also recognized. Existing U-Pb zircon ages from the southern half of the 151 Edjudina Domain are limited to: i) 2708 ± 6 Ma from a fragmental metadacite porphyry in a 152 felsic sequence associated with calc-alkaline rocks ~100km N of King (Nelson, 1995); ii) 2698 153 \pm 10 Ma from a metatonalite intrusion also ~100km N of King (Nelson, 1996); and iii) 2680 \pm 154 4 Ma from a granite gneiss at Coonana Hill ~30km NE of King (Wingate et al. 2016). The 155 distribution of komatiite and BIF with in the southern Eastern Goldfields, along with all current 156 157 U-Pb zircon ages from the region, is shown in Figure 5.

Jones (2007) provides a more local summary of the geology at Erayinia east of the 158 Claypan Fault (Fig. 4). According to Jones (2007), greenstone sequences contain interlayered 159 mafic and felsic schists, ferruginous chert bands and silicified black shales that define tight 160 folds on aeromagnetic images. Further east, along the eastern margin of Erayinia, thin units of 161 meta-ultramafic rocks (komatiite?) and metabasalt are interlayered with metasedimentary 162 rocks (Fig. 4). The mapped meta-ultramafic rocks are preserved as deeply weathered talc-163 chlorite-(carbonate) schists ~17 SE of King (Fig. 4) (Jones, 2007). Together with the presence 164 of a large rubbly outcrop of Fe-rich chert ~10km N of King, that is similar in appearance to 165 BIF (Jones, 2007), this may suggest the local stratigraphy is >2.7 Ga in age and belongs to the 166 Minerie or Kurnalpi sequence (Fig. 2). The Gindalbie age $(2680 \pm 4 \text{ Ma})$ from a 'granite gneiss' 167 at Coonana Hill ~30km NE of King (Wingate et al. 2006; Fig. 5) may belong to a similar 168 sequence to the 'schist derived from granite rock' mapped by Jones (2007) in Figure 4. 169

Unfortunately, our attempted U-Pb dating of the King stratigraphy was unsuccessful due to apaucity of zircons recovered from footwall quartz-muscovite schists.

172 Regional deformation of the Erayinia region is complex and typically involved an early 173 extensional event (D_E), followed by: D_1 compression involving thrusting and recumbent 174 folding (F_1); D_2 ENE-WSW crustal shortening, producing major upright folding (F_2 : 2675-175 2657 Ma); D_3 sinistral movement and associated folding on NNW-trending regional strike slip 176 faults; and D_4 overprinting with oblique reverse movements on the same structures (Jones, 177 2007).

Peak metamorphism across the Eastern Goldfields is most intense (upper amphibolite 178 facies) surrounding large granitoid bodies that were emplaced at 2660-2640 Ma, broadly 179 contemporaneous with D₂ deformation (Witt, 1991; Nelson, 1997; Swager et al. 1997). Away 180 from these granitoids, porphyroblasts of biotite and andalusite grew over and across the vertical 181 regional foliation indicating the relatively late timing of peak regional metamorphic conditions 182 (Swager, 1997). Lower grade zones of greenschist facies metamorphism are found in the 183 central parts of greenstone belts (Jones, 2007). A marked increase in metamorphic grade was 184 noted by Jones (2007) across the Claypan Fault (Fig. 4), from relatively undeformed 185 greenschist facies felsic volcaniclastic rocks and basalt in the west, to muscovite schist, 186 chlorite-muscovite schist, and biotite-garnet schist east of the fault. 187

188 4. King deposit stratigraphy

The King Zn deposit (~2.146 Mt at 3.47% Zn, non-compliant at 1% cut off) occurs in an 189 overturned and east-dipping volcanic-dominated sequence (Fig. 6) located approximately 190 140km east of Kalgoorlie (Fig. 1) and 36km south of the Trans Australian Railway. Although 191 the area had previously been explored for uranium and gold, base-metal mineralization was 192 first targeted during the 1990s by Sons of Gwalia. Following geological mapping, ground 193 magnetometry and surface TEM geophysics, a conductor was recognized as coincident with a 194 magnetic anomaly. Further soil sampling and Reverse Circulation (RC) drilling led to the 195 interception of narrow massive sulfide layers at King (formerly called Calliope). The most 196 extensive exploration activity was undertaken by ABM Resources from 2005 to 2012 as the 197 manager of a joint venture with Hawthorn Resources Ltd (detailed in Podmore & James, 2016). 198 Subsequent diamond, RC and Rotary Air Blast (RAB) drilling by ABM defined the current 199 size of the King deposit (Figs. 6a, b). More recently, a soil and rock chip sampling programme, 200 and VTEM (Versatile Time Domain EM) geophysical survey, was undertaken by Black Raven 201 Mining (2012-2017) over the extended licence areas. 202

Our current interpretation is that the volcanic stratigraphy at King is overturned and dipping to the east (**Fig. 6c**). This is based on metal zonation in the deposit, and the distribution and intensity of logged hydrothermal alteration assemblages (see Discussion). An intensely chloritized zone of discordant alteration with abundant chalcopyrite and Fe-sulfides lies above a sheet-like body of massive Fe-Zn sulfide (**Fig. 6d**), the opposite to most VHMS systems (Hannington et al. 2005; Galley et al. 2007). Graded were beds also noted by ABM geologists from drilholes EC120D and EC116D (ABM Resources NL, 2008) consistent with our interpretation, although these have not been verified since. Possible graded bedding from hole
EC056D is shown in Figure 7l. An overturned stratigraphy is also consistent with Swager's
(1995, 1997) description of rocks from the Edjudina domain - namely basaltic to felsic volcanic
complexes, overlain by fine grained sedimentary rocks, chert and BIF intruded by mafic sills
– and also a recent study from King North (Kelly, 2018, unpublished thesis; Fig. 4).

Photographs of the main lithologies and styles of mineralization present in diamond drillcore are shown in **Figures 7 and 8**. The stratigraphy at the King deposit from interpreted stratigraphic footwall to hanging-wall, assuming an overturned stratigraphy (**Fig. 6c**), is characterised by:

Footwall garnet-amphibolite: A thick (>300m) sequence of foliated garnet-amphibolite or 219 hornblende-garnet-quartz schist (Figs. 7ab, 9a) occurs in the deep stratigraphic footwall of the 220 King deposit, with the top contact now ~100-150m above mineralization (Fig. 6c). The 221 groundmass is dominated by fine granulose green hornblende with interstitial fine anhedral 222 quartz, minor epidote, and carbonate (Fig. 9a). Garnet porphyroblasts contain quartz and 223 hornblende inclusions. A general anastomosing schistosity (Fig. 7b) is paralleled by the 224 granulose hornblende texture. Local zones with abundant ragged and acicular actinolite (to 225 ~3mm in drillcore) also occur. Towards the centre of the King deposit a zone characterized by 226 abundant chlorite is present (Figs. 6d, 9d). This is best observed in drillhole EC116D where 227 fine magnetite crystals are disseminated throughout the core in close association with 228 chalcopyrite±pyrite blebs and stringers (Figs. 8a-b, 9b-c). Contacts are gradational with 229 230 surrounding garnet-amphibolites, with the change in rock type reflecting an increased abundance of chlorite±magnetite to hornblende-garnet-quartz. 231

The thick sequence garnet-amphibolite is interpreted to represent a sheared and 232 metamorphosed sequence of mafic rocks. It is unclear due to the strong banding and 233 recrystallization whether these represent metamorphosed coherent mafic flows, volcaniclastic 234 rocks or thick basaltic sills. Primary volcanic textures such as pillows, varioles, chilled margins 235 and peperite are not preserved. Similar mafic lithologies have been mapped by Jones (2007) 236 along strike to the north of the King deposit (weakly foliated amphibolite; Fig. 4). Quartz and 237 epidote altered mafic volcanic rocks (greenschist facies) have also been recently drilled at King 238 North along strike (Fig. 4), which are geochemically similar to those described here (Kelly, 239 2018, unpublished thesis). The zone of intense chlorite with Cu-Fe sulfides is interpreted to 240 represent the feeder zone to massive sulfide mineralization that was enriched in Mg prior to 241 242 metamorphism (see Discussion).

Mixed footwall sequence: Stratigraphically overlying the garnet amphibolite is a ~30 to 130m 243 thick mixed sequence of intensely altered, intermediate to felsic schist. Rare units (<15m thick) 244 resembling the aforementioned footwall garnet-amphibolite also occur. Rocks of the mixed 245 footwall sequence are highly variable in their mineralogy and are strongly banded and folded 246 (Figs. 7d-g). More leucocratic (intermediate to felsic) lithologies are dominated by a 247 combination of quartz, chlorite and carbonate with lesser hornblende, biotite and epidote (Figs. 248 9e-h). Where present, biotite parallels the schistosity and is often retrogressed to chlorite. 249 250 Leucoxene, zircon and titanite are present as accessory phases. Zones rich in albite and/or

muscovite also occur. In the rare mafic lithologies, the metamorphic matrix is dominated by
hornblende with minor epidote in darker bands, and quartz-epidote-chlorite in paler bands.

253

Throughout each of the drillholes logged at the King deposit (**Fig. 6a**) a distinct zone of intense brown and green banding is common (**Fig. 7d**). This occurs at depths anywhere from ~50 to 150m in the footwall to massive sulfide mineralization and varies in thickness from a few metres to tens of metres. This lithology is characterized by quartz, anthophyllite, clinozoisite and biotite (intergrown with anthophyllite and replaced by chlorite) (**Fig. 9f-h**).

259

The mixed footwall sequence is interpreted to represent a package of metamorphosed intermediate to felsic volcaniclastic rocks, with rare mafic sills/lava flows (now garnetamphibolite) and thin beds of deep marine argillaceous sediments (typically <2m thick; preserved as graphitic schist; see section below). Rare examples of lapilli tuff have been described from this sequence, with relict quartz clasts apparent in thin section. The zone rich in anthophyllite is interpreted to reflect Mg-metasomatism prior to metamorphism in the intermediate to felsic lithologies.

267

268 Quartz-muscovite schist (footwall dacite): A ~50 to 90m thick sequence of leucocratic and variably banded quartz-muscovite schist of dacitic composition comprises the immediate 269 stratigraphic footwall to massive sulfide mineralization at King (Figs. 6c, 7h). In some 270 instances, coherent and weakly altered units occur in close proximity to mineralization, 271 surrounded by intensely altered and sheared lithologies. Quartz-muscovite schists are 272 dominated by fine granoblastic quartz with interstitial platy muscovite defining the schistosity 273 (Figs. 9i-j), and minor epidote. Locally, Mg-rich cordierite can be significant ($\leq 5\%$) as 274 aggregates and crystals throughout the matrix. This is often replaced by sericite and associated 275 276 Mg-chlorite. Bands of sericitised plagioclase occur in the matrix of some samples. Sulfides, 277 tourmaline, hornblende, leucoxene and zircon are present as accessory phases (Fig. 9k). Garnets are rare, but small (<2mm) pink to red porphyroblasts are disseminated throughout 278 most units logged. Directly under massive sulfides (Fig. 9l, described in Section 5), the quartz-279 muscovite schists are intensely silicified in hand specimen. With depth, an increase in 280 muscovite, chlorite and albite is clear in drillcore (Fig. 6c). Contacts between different styles 281 of alteration are gradational. Where present, pyrite and sphalerite occur as stringers and 282 disseminated throughout the host stratigraphy (Figs. 8c, 9k; see Section 5). 283

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The thick sequence of quartz-muscovite schist is interpreted to represent a mixed, hydrothermally altered and metamorphosed sequence of dacitic volcaniclastic rocks and more coherent volcanic lithologies (either representing flows or high-level intrusions). No quartz or feldspar phenocrysts were observed; all rocks examined in thin section are strongly recrystallized and show evidence of shearing.

290

Mixed hanging-wall sequence: The immediate hanging-wall of the King deposit is dominated
 by finely banded (mm to cm scale) schists of mafic to felsic composition (Fig. 7i), grouped
 together here as quartz-biotite/amphibole±garnet schists. Banding reflects the varying

294 abundance of fine to medium granoblastic quartz (with lesser biotite) to tremolite/actinolite±garnet (Figs. 90-p). Garnet can be retrogressed to fibrous chlorite 295 aggregates with quartz. Calcite is present throughout the matrix, as well as in veinlets and vugs 296 (Figs. 9q-r). Magnetite is disseminated (3-5%) throughout the matrix of the banded schists 297 directly overlying massive sulfides (Fig. 6). In the deeper sections of the deposit where 298 299 magnetite has not been replaced by secondary Fe-oxides, a very strong magnetic signature persists for ~1 to 4m into the stratigraphic hanging-wall. This zone is typically more magnetic 300 than the pyrrhotite-magnetite-bearing chloritic feeder zone, but the intensity of both varies 301 significantly from hole to hole. Pyrite stringers are abundant close to massive sulfides and are 302 strongly recrystallized. These pyrite parallel and cut metamorphic banding at high angles (Fig. 303 8f). The most convincing example of grading, shown in Fig. 7l, is consistent with an 304 overturned stratigraphy. 305

Thin horizons of graphitic schist (described below), pyrite-bearing polymict volcanic 306 breccias (Fig. 7k), and rare, coherent carbonate-altered rocks of mafic composition (herein 307 308 termed the hanging-wall amphibolites) are also present in the stratigraphic hanging-wall to mineralization. The hanging-wall amphibolites (~3m thick) are dominated by amphibole and 309 quartz, with carbonate alteration and relict clinopyroxene. Garnets can be present, but not in 310 every drillhole. Finely banded chert-like rocks were noted at ~385m depth in drillhole EC056D 311 (Fig. 7j). The polymict volcanic breccias (~382m in EC056D) are intensely brecciated, quartz 312 313 veined, contain clasts up to 4cm of surrounding lithologies (e.g. layered chert, banded schist, amphibolite), and thin stringers of magnetite. 314

The mixed hanging-wall sequence is interpreted to represent a sequence of metamorphosed interbedded volcanic/volcaniclastic rocks of varying composition, with interbedded fine grained, deep marine sedimentary rocks. The hanging-wall amphibolites may represent very thin lava flows or coeval basaltic sills (e.g. Swager, 1997).

Horizons of graphitic schist: Thin (0.4-2m) horizons of graphitic schist have been identified 319 320 throughout the King stratigraphy in both the interpreted footwall (ED086 303m) and hangingwall (ED143 ~505m) to massive sulfide mineralization. Similar lithologies were also noted as 321 deformed fragments within the massive sulfide zone of drillhole EC116D, where they are 322 intensely chloritized and in some sections appear to have been replaced by sulfides. The 323 horizons of graphitic schist are always intensely fractured, strongly sheared, and can be 324 intermittently banded with surrounding lithologies (e.g. garnet amphibolite, quartz-muscovite 325 schists). In most instances fault gouges are closely associated with the graphitic schists, 326 indicative of thrusting in the stratigraphy. The graphitic schists most likely represent 327 328 metamorphosed deep marine argillaceous sediments precipitated under anoxic conditions.

329

330 Quartz-feldspar phyric intrusive rocks: The King stratigraphy has been intruded by at least 331 two generations of quartz-feldspar porphyry sills that broadly parallel bedding (Fig. 6). The 332 earlier set appears to be broadly coeval with the volcanic stratigraphy and are ~0.7 to 1.5m 333 thick with sharp margins (e.g. at 309m EC056D; 387m EC116D). They exhibit a similar 334 mineralogy (quartz-muscovite) to the footwall felsic rocks they intrude, contain disseminated sulfides, and have a strong foliation which parallels surrounding strata (Fig. 6c, labelled 1; Fig.
7m).

A presumably younger set of thinner (5-30cm) quartz-feldspar phyric sills intrude the hanging-wall to massive sulfide mineralization in hole EC056D (~363m; **Fig. 6c**, labelled 2). This suite is less foliated (**Fig. 7n**) and resemble those of the Erayinia NW area closely associated with late high-Ca granitoid intrusions of the eastern Murrin Domain (Hollis et al. in prep). Sharp unchilled margins are orientated parallel to banding in surrounding schists.

Late basaltic dykes: Late basaltic dykes crosscut the stratigraphy and are undeformed. These
rocks are typically ~0.5 to 2.5m thick, coarsen to doleritic centres, and display chilled margins
and varioles (Fig. 70). They most likely belong to the Palaeoproterozoic Widgiemooltha Dyke
Suite (Fig. 6). The suite is clearly visible in regional magnetics and intrudes the area in
predominantly E-W and NNE-SSW orientations (Fig. 4).

347 5. Sulfide mineralization at King

Sulfide mineralization at King occurs predominantly as a stratiform, ~1 to 7m thick, 348 sheet-like body of massive pyrite-pyrrhotite with subordinate sphalerite, at the contact between 349 intensely silicified dacite (footwall quartz-muscovite schist) and banded quartz-350 biotite/amphibole±garnet schist (Fig. 6c). This zone of stratiform massive sulfide 351 mineralization dips at 45-70° eastwards, has a confirmed depth of at least 400m, and has been 352 drilled across a strike length of ~600m (Fig. 6a). Diamond drilling is restricted to the central 353 450m (Fig. 6a). Two small, high-grade lenses of Zn mineralization have been recognised 354 separated by a central zone (150-200m long) with lower Zn grades (Fig. 6b). The best intercept 355 is 5m at 10.6% Zn in drillhole EC116D. There has been sporadic analysis for gold in both 356 massive sulfides and the feeder zone. Significant intercepts include 5m at 0.6 g/t Au (hole 357 EC046D) and 5.9m at 0.3g/t Au (EC031D) (Fig. 6b). Stratigraphically underlying the 358 stratiform massive sulfides a zone of discordant vein and disseminated sulfides (from pyrite-359 sphalerite to pyrrhotite-chalcopyrite-pyrite; Fig. 8a-b) extends throughout the underlying strata 360 (Fig. 6d). It is important to note that all sulfide assemblages show evidence for 361 recrystallization. 362

Within the massive sulfides two broad styles of mineralization can be defined: a lower 363 zone characterized by fine to coarse grained subhedral pyrite with replacive interstitial 364 red/brown sphalerite (Fig. 8d), and a stratigraphically overlying zone dominated by iron 365 sulfides (pyrite and/or pyrrhotite) with large milled clasts of surrounding lithologies (Figs. 8e, 366 91-n). In the stratigraphically lower Zn-rich zone, abundant fine to coarse grained subhedral 367 pyrite is replaced by sphalerite (Figs. 8d, 9l). Anhedral quartz and Fe-chlorite are interstitial 368 369 to sulfide phases. Pyrrhotite is concentrated locally in the matrix. Galena is rare, and is present both as rims to, and inclusions in, pyrite. Tetrahedrite locally replaces galena and exhibits 370 simple intergrowths with sphalerite. 371

In the overlying Fe-rich zone, pyrite and/or pyrrhotite are typically the dominant sulfide phase with subordinate sphalerite and rare galena. Chalcopyrite inclusions occur in pyrrhotite. Siliceous clasts of varying size are present in the sulfide matrix. These are well rounded and 375 represented by quartz-muscovite schist derived from the underlying footwall, or schist from
376 the stratigraphic hanging-wall (Figs. 9m-n). Garnet in the hanging-wall schist fragments is
377 retrogressed to chlorite (Fig. 9n). In drillhole EC116D, abundant fragments of chloritized and
378 deformed graphitic schist are within the massive sulfides.

Silicified felsic footwall rocks immediately underlying massive sulfides contain veinlets of pyrite-sphalerite, which become more sphalerite poor with depth. These are often strongly sheared, with trails of coarse euhedral pyrite orientated parallel to metamorphic banding (**Fig. 8c**), and the contact with overlying massive sulfides (**Fig. 8d**). When present, sphalerite occurs interstitially to euhedral pyrite (**Fig. 9k**), with both phases cut by veinlets of galena.

In the chlorite-rich zone of garnet-amphibolite (Fig. 6d) chalcopyrite is most common 385 as blebs and stringers, along with veinlets and individual crystals of pyrrhotite and pyrite (e.g. 386 EC116D; Figs. 8a-b). Sphalerite crystals are often strongly deformed and may be intergrown 387 with both chalcopyrite and pyrrhotite. Ilmenite (FeTiO₃) occurs as exsolution lamellae in the 388 coarse magnetite grains, and as individual crystals in pyrrhotite (Fig. 9b-c). Pentlandite 389 ([Fe,Ni]₉S₈) is rare and is intergrown with pyrrhotite. Chalcopyrite is also intergrown with 390 pyrrhotite and fills fractures in magnetite grains (Fig. 9c). Drillcore logging also revealed that 391 secondary Cu minerals (predominantly malachite) are present in the uppermost sections of the 392 King deposit, most likely remobilised from the underlying Cu-bearing chloritic stockwork. 393

The immediate hanging-wall above massive sulfides can contain abundant stringers of coarse euhedral pyrite (**Fig. 8g**) orientated both along the main foliation and crosscutting brecciated hanging-wall lithologies.

397 6. Geochemistry

- 398 **6.1. Methods**
- 399 Whole rock lithogeochemistry

A total of twenty-three samples of diamond drillcore from the King stratigraphy (holes 400 401 EC116D, EC031D, EC056D; Fig. 6c) were analysed for whole rock geochemistry at ALS Laboratories, Perth, Australia. Major element concentrations were determined by four acid 402 digestion and ICP-OES finish on fused glass beads. Trace element, HFSE and REE 403 concentrations were determined by lithium borate fusion and ICP-MS finish. Base metals (e.g. 404 Cu, Pb, Zn, Ni) and trace metals (e.g. As, Sb, Tl, Bi) were analysed by multi-acid digestion, 405 followed by ICP-OES and ICP-AES, respectively. Carbon and S concentrations were 406 determined by total combustion using a Carbon-Sulfur Analyser, and LOI using a robotic 407 thermo-gravimetric system. Gold, Pt and Pd concentrations were analysed by fire assay and 408 409 ICP-OES.

Accuracy (%RD) was monitored using laboratory blind, mineralized and unmineralized
 international standards (e.g. OREAS-24b – granodiorite, OREAS-620 – Golden Grove ore).
 Precision (%RSD) was monitored by repeat analysis of submitted standard OREAS-24b

413 (granodiorite). Both precision and accuracy are considered excellent to good after Jenner 414 (1996; i.e. within $\pm 10\%$ RSD and <10% RD) for the majority of elements from both datasets. 415 W, Li, Sn and Mo data was discarded due to poorer accuracy and/or precision than the other 416 elements (consistently >10% RD to international standards). Thallium data was retained due to 417 excellent precision (<1% RSD), but absolute values here should be treated with caution as 418 accuracy was poor (>30% RD). Whole rock geochemistry results are presented in 419 **Supplementary Table 1** and plotted in **Figures 10 to 13**.

420 Portable X-ray Fluorescence geochemistry

The above whole rock geochemical data from the King deposit is complemented by 421 ~620 portable X-ray Fluorescence (pXRF) measurements on diamond drillcore (5 holes). 422 Portable XRF measurements were made every 0.5 to 2m of core (dependent on hole length) 423 using an Olympus InnoveX Systems Delta 2012 series model between March and May 2015. 424 425 The counting time was 60 seconds per analysis in soil mode. Several studies using international reference materials have shown pXRF data to be precise for a number of major and trace 426 elements (e.g. Piercey & Devine, 2014). Although the accuracy of pXRF data ranges widely 427 from excellent (<7% RD) to poor ($\pm 20\%$ RD), and often needs correcting (e.g. Fisher et al. 428 2014; Le Valliant et al. 2014), downhole profiles replicate the geometry of those obtained from 429 conventional analyses (Piercey & Devine, 2014). Such data is fit-for-purpose and useful for 430 enhancing downhole geochemical trends obtained by conventional methods but should not be 431 used as a substitute for high-quality lithogeochemistry (Piercey & Devine, 2014). 432

pXRF data was corrected using eleven standards from OREAS (OREAS-22d, 24b, 24c, 433 434 36, 38, 70b, 76b, 291, 931, 935, 991) for the following elements: As, Cr, Cu, Fe, Mn, Ni, Pb, Rb, Sr, Ti, V, Y, Zn, Zr. These standards cover a wide range of concentrations for each element 435 (e.g. 38 ppm to 12.4% Cu, 4.45-23.6 wt% Fe). Calibration equations were obtained by plotting 436 certified concentrations against obtained pXRF values for each element. Only standards that 437 returned pXRF values above the limit of determination (LOD: 3x detection) were used in each 438 439 equation. This process was done separately for each drillhole. As an increase in pXRF machine internal temperature (and consequently air pressure) is known to cause instrument drift over 440 time (due to peak positions migrating; Fisher & Gazley, 2014), standard OREAS-24b was 441 analysed every 15-20 spot analyses (total n=71 for 5 holes). Apart from single point anomalies, 442 instrument drift was found to be negligible and non-systematic. 443

Calibration equations used to correct pXRF data are provided in Supplementary Table 444 2 along with R^2 values, which were generally excellent (most >0.98) apart from for Cr and V 445 (which were rarely above LOD). Slight offsets between corrected pXRF and lithogeochemical 446 datasets are to be expected due to the effect of spot analysis (~10mm diameter) on 447 heterogeneous drillcore (Fisher & Gazley, 2014), and attenuations of elements by the plastic 448 bags in which standards were analysed (see Fisher et al. 2014). That said, these combined 449 effects appear to be minimal here for the elements of interest. Our corrected pXRF data closely 450 follow data obtained by conventional lithogeochemical methods. Calculated precision and 451 accuracy data for standard OREAS-24b is presented in Supplementary Table 3 following the 452 453 correction of each element. Note the excellent data quality for Sr and Rb regardless of date,

454 poorer data quality for As regardless of date, and reduced precision for all elements on the 14th 455 of May, 2015 (drillhole EC056D; most likely due to the pXRF overheating). The following 456 elements reported by the pXRF were discarded: Ag, Au, Bi, Hf, Sb, Sn, Mo, Th, U, W. These 457 were rarely above LOD and were associated with large errors (e.g. Ag \pm 9 ppm, Sb \pm 20 ppm). 458 Corrected pXRF data is presented in **Supplementary Table 4**.

459 *Magnetic susceptibility*

Magnetic susceptibility measurements were taken systematically every 1m of diamond
 drillcore logged on metre marks using a Fugro RT-1 Magnetic Susceptibility Meter (~2000
 measurements from 10 holes).

463 6.2. Immobile element geochemistry

The mobility of most of the major and trace elements during hydrothermal alteration is well 464 established in the literature (e.g. MacLean, 1990; Jenner, 1996). Only the following elements, 465 that are demonstrably immobile during both hydrothermal alteration and amphibolite-facies 466 metamorphism, are used here to elucidate petrogenesis: Al₂O₃, TiO₂, Th, Co, V, the HFSE (e.g. 467 Nb, Y, Sc) and REE (minus Eu) (Pearce & Cann, 1973; MacLean, 1990; Jenner, 1996). While 468 these elements may move on the millimetre scale during hydrothermal alteration and 469 subsequent metamorphism (as they are transferred into new minerals), they can be considered 470 immobile at the hand-specimen scale and particularly in sections of drillcore analysed here 471 (~20cm length). 472

The immobile element geochemistry of samples analysed from the King deposit is 473 illustrated in Figures 10 and 11. All samples of garnet-amphibolite from the footwall of the 474 deposit (and thin amphibolite units from the hanging-wall) are of calc-alkaline basaltic affinity 475 according to both the Zr/TiO₂ vs Nb/Y classification diagram of Pearce (1996; Fig. 10a), and 476 the Co vs Th diagram of Hastie et al. (2007; Fig. 10d). One exception is sample GK021, which 477 displays more intermediate geochemical characteristics (Fig. 10a). This is consistent with its 478 position near the overlying mixed footwall sequence (Fig. 6c) that is dominated by more 479 480 siliceous rocks. Footwall garnet-amphibolites are generally characterised by consistently high Sc (17-46 ppm) and Co (84-119 ppm) concentrations, and variable Cr (<10-150 ppm) and 481 immobile element ratios (e.g. Zr/Y 2.2-12.8). Chondrite normalized REE profiles show little 482 variation between units in terms of the HREE (Dy/Yb 1.4-1.9), but there is significant LREE 483 484 variation in the samples analysed (La/Yb 1.7-16.5; Fig. 11d). This may be a consequence of LREE mobility in the intensely chloritized feeder zone underlying massive sulfides (e.g. 485 Barrett & MacLean, 1994). Two samples of amphibolite analysed from the hanging-wall of the 486 King deposit (Fig. 6c) contain lower Co concentrations (Fig. 10d), higher Zr/TiO₂ ratios (Fig. 487 10a) and similar chondrite normalized HREE profiles to those from the footwall (Fig. 11d). 488

Rocks of intermediate composition from the mixed footwall sequence display gently dipping REE profiles (La/Yb 5.8-9.1; **Fig. 11e**). Zr/TiO₂ ratios, and concentrations of Th, Sc and Co are similar to overlying quartz-muscovite schists at King (**Fig. 10b**). Niobium, Y, Hf and Zr concentrations are generally higher in the intermediate volcaniclastic rocks than 493 overlying felsic rocks; however, this may be a function of higher mass gain in the quartz-494 muscovite schists, as ratio combinations of these elements yield similar values.

495 Quartz-muscovite schists from the immediate footwall of the King deposit are 496 characterised by andesitic to dacitic Zr/TiO_2 ratios (223-284; **Fig. 10b**), and calc-alkaline Zr/Y497 (4.6-15.0) and La/Yb ratios (>9.0). Cr concentrations are below detection (<10 ppm), and Co 498 concentrations are generally low (**Fig. 10d**), both of which are consistent with a dacitic 499 protolith. Low HFSE concentrations (<5.7 ppm Hf, 5.3-15.7 ppm Y, <0.4 ppm Ta) indicate 495 these rocks are of FI (to FII) affinity (**Fig. 10e-f**). Chondrite normalized REE profiles have 496 intermediate characteristics between felsic rocks from Nimbus and Teutonic Bore (**Fig. 11f**).

Hanging-wall banded schists range in composition from mafic to felsic according to 502 their Zr/TiO₂ ratios and Co concentrations (Fig. 10c, d), consistent with their variations in 503 mineralogy (quartz-biotite dominated to amphibole±garnet) (Fig. 7f). Quartz-porphyry sills 504 505 that intrude and are interpreted as coeval with the King stratigraphy (Fig. 6c; labelled 1) are intermediate to dacitic in composition (Fig. 10c, d), with high calc-alkaline Zr/Y (16.7-18.5) 506 and Th/Yb ratios, and low HFSE concentrations (Fig. 10e-f). Chondrite normalized REE 507 profiles are steep, both with respect to the LREE and HREE (Fig. 11a). The younger quartz-508 porphyry sills (Fig. 6c, labelled 2) and late basaltic dykes were not analysed. 509

510 **6.3. Mobile element geochemistry**

511 The mobile element geochemistry of the King deposit is illustrated in Figures 12 and 13. 512 Regional metamorphism at King can be considered isochemical at the hand-specimen scale. Although dewatering reactions during regional metamorphism may lead to the mobility of 513 volatile species (e.g. H₂S, F, CO₂; Spry, 2000; Corriveau & Spry, 2014), mobile element 514 characteristics will primarily reflect hydrothermal alteration prior to metamorphism (detailed 515 in Bonnet & Corriveau, 2007; Corriveau & Spry, 2014). Mass change values were not 516 calculated for samples from King as a suitable least altered precursor was not identified. 517 Weakly altered rocks analysed from Erayinia NW (eastern Murrin Domain) have distinct 518 immobile element characteristics (Hollis et al. in prep.) and are therefore not suitable for mass 519 change calculations at King, whereas those from King North are similarly altered to the rocks 520 described here (Kelly, 2018, unpublished thesis). 521

Garnet-amphibolites from the deep footwall of the King deposit are characterised by 522 high Fe₂O_{3T} (18-28 wt.%), and variable Cu (75-1315 ppm) and MgO (3-13 wt.%) 523 concentrations (Figs. 12, 13). This is consistent with varying degrees of Mg-metasomatism and 524 pyrrhotite-magnetite±chalcopyrite±pyrite mineralization in the feeder zone, stratigraphically 525 526 underlying massive sulfide mineralization (Fig. 6d; see Discussion). Calcium and SiO₂ concentrations are variable (39-51 wt.% SiO2, 1-18 wt.% CaO) reflecting the abundance of 527 hornblende, epidote and quartz (Fig. 12). Sodium and K concentrations are low (<0.8 wt% for 528 each), consistent with a mafic protolith. Most pathfinder element concentrations are anomalous 529 (e.g. 2.8-15.1 ppm As, 0.3-4.2 ppm Sb) compared to unmineralized mafic rocks from the 530 Yilgarn Craton (Hollis et al., 2015), except for Tl, Bi and Au which are generally low (Fig. 531 532 12). Very high Mo (534 ppm) was noted in sample GK004 which is being targeted for Re-Os

geochronology. On the Box Plot of Large et al. (2001a) samples plot in both the 'least altered
mafic' field and between the ankerite/dolomite and chlorite/pyrite mineral nodes reflecting
variable enrichments in Ca, Fe and Mg.

Intermediate banded schists from the mixed footwall sequence show increased SiO₂ 536 (58-76 wt.%) concentrations when compared to the stratigraphically underlying footwall 537 garnet-amphibolites and have highly variable K₂O (0.3-1.4 wt.%) and Na₂O (0.7-2.7 wt.%) 538 539 concentrations. This is consistent with the intense silicification in the mixed footwall sequence (Fig. 6d), together with a more evolved precursor composition (reflected by lower TiO₂ 540 concentrations; Fig. 13 - EC056D), and varying albitic alteration. Significantly lower Fe₂O_{3T} 541 (2.2-7.3 wt.%), MgO (2.8-7.4 wt.%), and Cu (3-58 ppm) reflect the decreased abundance of 542 chlorite, sulfide and magnetite present in the drillcore (e.g. EC116D: Fig. 13). Lower Ag, As, 543 Bi, Hg, Sb, and Alteration Index (A.I.) values in the intermediate rocks correlate with a 544 decreased abundance of Zn (Figs. 12, 13). All samples analysed plot with the 'least altered 545 andesite' field of the Box Plot (Fig. 12). 546

Quartz-muscovite schists in the immediate footwall to massive sulfides at King are 547 characterized by the highest SiO₂ (72.5-93.4 wt.%) values measured, and variable Fe₂O_{3T} (0.5-548 6.7 wt.%) (Fig. 12). This reflects the intense silicification of host rocks and variable sulfide 549 mineralization (pyrite±sphalerite). Low Na₂O (typically ~0.3 wt), MgO (0.2-1.0 wt.%) and 550 CaO, correspond to lesser chloritic and albitic alteration, and Na-depletion though the 551 sericitization of feldspar (subsequently recrystallized to coarse muscovite during prograde 552 553 metamorphism). Element concentrations may have also been reduced through large mass gains of SiO₂. Sample GK044 (Fig. 6c) shows significantly higher concentrations of Na₂O, CaO (4.3 554 wt.%), MgO (2.5 wt.%), and lower SiO₂ (59.8 wt.%). This sample is a coherent, weakly altered 555 556 dacite surrounded by sheared and intensely silica-sericite altered dacite. It most likely 557 represents a coherent lava flow or a high-level intrusion that is interbedded with volcaniclastic rocks of similar composition. Hydrothermal fluids would have been preferentially focused 558 through the latter. Only sample GK044 plots within the 'least altered dacite' field of the Box 559 Plot with other samples trending towards the chlorite/pyrite and sericite mineral nodes (Fig. 560 12). Pathfinder elements vary in abundance in the quartz-muscovite schists, but are often high 561 (to 72ppm Cd, 465 ppm Pb, 35 ppm Sb, >25 ppm Hg) compared to all other lithologies except 562 massive sulfides (Figs. 12, 13; see following). Downhole concentrations of Ni and MnO 563 correlate well with increased amounts of Fe and base metals (Zn+Pb) in the core (EC031D: 564 Fig. 13). Arsenic concentrations increase systematically towards massive sulfides in the top 565 ~10m of quartz-muscovite schist in hole EC031D, with corresponding increases in Ag, Au, Sb, 566 567 Tl and positive Eu anomalies (Eu/Eu*; Fig. 13).

Three samples of massive sulfide were analysed from the King deposit (holes EC116D and EC113D). These rocks are characterized by high Fe_2O_{3T} (24-27 wt.%) and variable Zn (0.4-15.9 wt.%), reflecting the abundance of pyrrhotite, pyrite and sphalerite (**Figs. 12, 13**). Pathfinder concentrations of the following elements are anomalous to moderately high: Ag (28-50 ppm), As (40->250 ppm), Bi (2-52 ppm), Cd (95-452 ppm), Hg (>23 ppm), In (3-20 ppm), Te (4-10 ppm), Sb (6->250 ppm), and Se (5-25 ppm). Lead, Cu and Au concentrations are low (0.46-0.93 wt.% Pb, <125 ppm Cu, <0.1 g/t Au) compared to other VHMS deposits in the Eastern Goldfields (Hollis et al. 2015). All samples display prominent positive Eu anomalies
(Fig. 11c). Although Sn data is considered unreliable here due to poor accuracy and precision,
massive sulfides have concentrations (27-112 ppm) well in excess of all other rocks analysed
from the King deposit (typically ~2 ppm).

Hanging-wall strata (both banded schists and coherent amphibolites) are characterized 579 by low SiO₂ (<57.2 wt.%). Concentrations of K₂O (0.7-1.7 wt.%), Na₂O (0.03-2.74 wt.%), 580 581 MgO (1.5-7.8 wt.%) and CaO (0.8-7.9 wt.%) are variable (Fig. 12). Iron concentrations are high (11-24 wt.% Fe₂O_{3T}) reflecting the presence of abundant disseminated magnetite (with 582 corresponding high magnetic susceptibility) and stringer pyrite (Fig. 13). Thallium and Sb 583 concentrations are moderately high and similar to the quartz-muscovite schists adjacent to 584 massive sulfides. All samples analysed plot near the ankerite/dolomite mineral node of the Box 585 Plot due to very high CCPI, but moderate A.I. (~50%; Fig. 12). High CCPI is predominantly 586 due to the abundance of Fe, with local carbonate-alteration (Fig. 9p-r). Pathfinder 587 concentrations are typically low, except sample GK027 (with abundant stringer pyrite) that 588 589 contains high As (167 ppm) and Se (7.6 ppm). This sample displays the most prominent positive Eu anomaly from those analysed in the hanging-wall of the King deposit (Fig. 11b). 590

591 **7. Discussion**

All the available evidence obtained to date is consistent with the King Zn deposit and its stratigraphy representing a metamorphosed and overturned VHMS system. This model is in agreement with the nature of the host rocks, grade and tonnage of the deposit, styles of mineralization, the observed mineralogy of the host sequence, and its geochemical characteristics. Each are discussed in turn. Finally, we discuss potential halos that may be used to find VHMS deposits in amphibolite facies greenstone belts of the Yilgarn Craton.

598 7.1. Volcanic environment

Although the host stratigraphy of the King deposit has been metamorphosed to 599 amphibolite facies and is strongly deformed (e.g. Fig. 7e-f), its geological features are 600 consistent with an evolving volcanic sequence deposited in a deep-marine, rifted-arc or more 601 likely cratonic-rift setting. Immobile element geochemistry highlights an evolution of the 602 footwall sequence from calc-alkaline basaltic magmatism with high Co and Ti concentrations, 603 to andesitic and dacitic rocks (Figs. 10, 13) capped by massive sulfides. The return of thin 604 605 mafic lithologies in the hanging-wall of similar composition to the footwall (Figs. 10, 11) is consistent with a shift in the geodynamic environment, possibly related to further extension 606 (Piercey, 2011). This cyclicity has been noted from many VHMS camps worldwide, with 607 mineralization occurring towards the end of a mafic to felsic eruptive cycle (Galley et al. 2007). 608 609 It is difficult to determine if the volcanic sequence is dominated by flow or volcaniclastic units. However, recrystallised quartz clasts in the some of the mixed footwall sequence, along with 610 the broad and diffuse alteration halo associated with VHMS mineralization at King favour the 611 latter interpretation (after Gibson & Galley, 2007). 612

The presence of sulfide bearing graphitic schists at several stratigraphic horizons, including the ore horizon (drillhole EC116D), are indicative of a deep marine euxinic 615 environment, below storm wave base, for the entire stratigraphy. This setting would have provided a favourable chemical environment for the preservation of massive sulfides if formed 616 on the paleoseafloor. By contrast, if mineralization formed through subseafloor replacive 617 processes, fine-grained sediments may have acted to seal the hydrothermal system (Franklin et 618 al. 2005). Due to the extensive recrystallization of primary textures, it is unclear whether the 619 King deposit formed on the seafloor, or through replacive processes. The thin, sheet-like 620 morphology of massive sulfide mineralization may suggest mineralization preferentially 621 replaced a thin stratigraphic horizon, possibly of fine-grained graphitic sediments near the top 622 of the quartz-muscovite schists (as appears to be the case in EC116D; Fig. 91). The presence 623 of minor sulfide mineralization (Fig. 8g) and the enrichment of pathfinder elements (e.g. Tl, 624 Sb) in the immediate hanging-wall (Fig.12) could be consistent with either a replacive model, 625 or seafloor exhalation if hydrothermal activity continued after the deposition of hanging-wall 626 strata. Further evidence for a replacive model is the presence of milled rock fragments within 627 628 massive sulfides (Figs. 8e,i). If massive sulfide mineralization formed predominantly through replacive processes, these clasts may represent remnants of the unreplaced host stratigraphy 629 that were subsequently deformed during metamorphism and shearing. 630

The tectonic setting of the King stratigraphy, must be considered with regards to the 631 wider 'arc vs plume' debate for the origin of the Eastern Goldfields (Czarnota et al. 2010; 632 Barnes et al. 2012; Barnes & Van Kranendonk, 2014; Hollis et al. 2015, 2017a). The arc 633 scenario, used to interpret the geochemistry of rock types present in the Eastern Goldfields 634 Terrane (EGS), does not explain evidence for a common history between the Youanmi Terrane 635 and EGS, which includes: (i) contemporaneous magmatism across the EGS and Youanmi 636 Terrane from at least c. 2.82 Ga (Ivanic et al. 2010; Barnes et al. 2012); (ii) simultaneous 637 inferred 'subduction-related' magmatism across the whole of the craton, which is inconsistent 638 with the geometry of modern arc systems (Van Kranendonk et al. 2013); and (iii) stratigraphic 639 640 similarities between the Kalgoorlie and Yamarna terranes, and Youanmi and Burtville terranes (Pawley et al. 2012). Furthermore, recent work has also demonstrated that mafic to felsic rocks 641 642 of the EGS are geochemically consistent with the fractionation of plume-related tholeiitic basalts, coupled with their contamination by contemporaneous partial melts of pre-existing 643 continental crust (Barnes et al. 2012; Barnes & Van Kranendonk, 2014; Hayman et al. 2015b). 644 An arc is therefore not required. 645

Whole rock geochemical data from King are shown on the Th/Yb vs Nb/Yb plot of 646 647 Pearce (2008) in Figure 10g. The geochemical trend away from the mantle array to higher Th/Yb ratios at King, favours the fractionation and crustal contamination of plume-derived 648 basaltic magmas, rather than subduction related magmatism (which would parallel the mantle 649 array; see Bédard et al. 2013). This trend is also apparent in samples analysed from Erayinia 650 NW (~4km NW of King in the Murrin Domain; Hollis et al. in prep.) and at King North (Kelly, 651 2018, unpublished thesis). Magmatic activity inferred to be plume-related precedes all episodes 652 of VHMS mineralization in the Younami Terrane (at c. 2.9 Ga, 2815 Ma, 2750 Ma and 2720 653 Ma; see Hollis et al. 2015). This plume-related activity is reflected by the repeated occurrence 654 of komatiitic or high-Mg basaltic magmatism in the Youanmi Terrane, followed by the eruption 655 and emplacement of major extrusive/intrusive mafic suites, terminated by felsic volcanism (van 656

Kranendonk et al. 2013; Ivanic et al. 2010) that hosts VHMS deposits (reviewed in Hollis et al. 2015, 2017b). Although the age of the King deposit is not clear, the presence of komatiite and BIF in the local area (see Regional Geology of Erayinia) may suggest it is of similar age to the Nimbus and Anaconda deposits of the Eastern Goldfields (~2705 Ma; Hollis et al., 2015, 2017b).

662 **7.2. Deposit type, style, grade and tonnage**

There are over 800 significant (>0.2 Mt) VHMS deposits worldwide, mostly of small 663 tonnage (Galley et al. 2007; Piercey et al. 2015). Metal ratios reflect the tectonic setting at the 664 time of mineralization, as metals are derived through the leaching of underlying strata with 665 magmatic inputs in arc/backarc environments (Franklin et al. 2005; Galley et al. 2007; Piercey, 666 2011). Deposits may be classified as Cyprus-, Besshi-, Noranda-, Kuroko- and Bathurst-types, 667 corresponding to the nature of their host rock sequences and dominant metals (i.e. mafic Cu-668 Zn, mafic-siliciclastic Cu-(Co-Zn-Ni), bimodal mafic Cu-Zn-Pb-(Ag-Au), bimodal-felsic Zn-669 Pb-Cu-(Au-Ag), and felsic-siliciclastic Zn-Pb-Cu-(Au-Ag) groups respectively; Franklin et al. 670 2005; Piercey, 2011). A sixth VHMS type (i.e. Eskay Creek-type), rich in precious metals, 671 reflects hybrid deposits with both VHMS and shallow water epithermal characteristics 672 (Piercey, 2011). 673

674 Equivalents to most of these VHMS types are present in the Yilgarn Craton. The Teutonic Bore, Jaguar and Bentley deposits of the Kambalda Terrane (Fig. 1) occur in mafic 675 dominated volcanic sequences, with felsic volcanic complexes and deep-marine argillaceous 676 sedimentary rocks near the ore horizon (Hallberg & Thompson, 1985; Belford et al. 2015). 677 678 Although these deposits are relatively small (1.6 to 3.05 Mt), Zn grades are high (9.8 to 11.3%) and significant amounts of Cu are present (2 to 3.5%) with minor Pb (~0.6%). The Teutonic 679 Bore deposits therefore closely resemble bimodal-mafic or Noranda-type deposits worldwide 680 (median 3.0 Mt at 5.2% Zn, 1.7% Cu, 0.9% Pb: Piercey et al. 2015). Bimodal-felsic or Kuroko-681 type deposits are typically characterised by significantly higher Pb (~1.9%) and lower Cu 682 (~1.4%) concentrations (Piercey et al. 2015; Yeats et al. 2017), but are more common in 683 Palaeozoic volcanic sequences than the Archean (Huston et al. 2010). Examples of felsic-684 siliciclastic and hybrid-epithermal deposits in the Yilgarn Craton include the Hollandaire 685 (Hayman et al. 2015a) and Nimbus deposits (Hollis et al. 2017a). 686

687 The current King deposit resource (2.15 Mt at 3.47% Zn), while significantly smaller than VHMS deposits in the Golden Grove camp of the Youanmi Terrane (e.g. Scuddles 10.5 688 Mt; Fig. 1), is of comparable size to most other resources in the Yilgarn Craton (e.g. Teutonic 689 Bore 1.68 Mt, Just Desserts 1.07 Mt, Hollandaire 2.8 Mt; Austin 1.48 Mt, Manindi 1.35 Mt; 690 see Hollis et al. 2015). The largest deposits in the Yilgarn often comprise multiple stacked 691 lenses of massive sulfides (e.g. Gossan Hill: Sharpe & Gemmell, 2001; Nimbus: Hollis et al. 692 2017a). The King deposit is classified as a metamorphosed bimodal-mafic or Noranda-type 693 VHMS deposit, due to the abundance of mafic to felsic volcanic rocks, low volume of 694 siliciclastic rocks, low Pb concentrations in massive sulfides (0.47-0.93%), and presence of 695 significant chalcopyrite in the feeder zone. 696

697 Within VHMS deposits worldwide a common metal zonation is often observed. In bimodal-mafic deposits, feeder systems are typically dominated by Cu and Fe sulfides, 698 primarily chalcopyrite, pyrite and/or pyrrhotite (Galley et al. 2007). Overlying lenses of 699 massive sulfides become increasingly pyrite-sphalerite±(galena) rich and pyrrhotite-700 chalcopyrite poor towards the paleo-seafloor (Galley et al. 2007). Gold and Ag may be 701 702 associated with Cu-rich, Zn-rich mineralization, or both (Gibson & Galley, 2007), as appears to be the case at King (Fig. 13). Despite the extensive recrystallization of sulfide assemblages 703 at King, the zonation from a pyrite-sphalerite rich lens of massive sulfide, stratigraphically 704 underlain by a chloritic stockwork with abundant chalcopyrite, pyrrhotite and magnetite (Fig. 705 6c), is consistent with Noranda-type deposits if the local stratigraphy has been overturned. No 706 resource is available for Cu and Au, due to the limited assaying for Au in massive sulfides, and 707 both metals in the chloritic feeder zone. Samples analysed in this study reached 0.2 g/t Au in 708 footwall rocks and 0.1 g/t Au in massive sulfides (Sup. Table 1). Historic intercepts include 709 710 5m at 0.6 g/t Au (drillhole EC046D) and 5.9m at 0.3g/t Au (EC031D). Copper concentrations reached 0.13% in lithogeochemistry samples (in the garnet-amphibolite), with corrected pXRF 711 spot analyses reaching a maximum of 0.7%. 712

713 7.3. A metamorphosed hydrothermal system

Primary alteration minerals surrounding VHMS deposits include chlorite, sericite, carbonate, 714 quartz and pyrite, with talc, epidote, albite and kaolinite (or sometimes other clay minerals) 715 often present (Barrett et al. 2005; Galley et al. 2007; Yeats et al. 2017). In upper greenschist-716 717 to amphibolite-facies metamorphic terranes, distinctive coarse grained mineral suites commonly define VHMS alteration zones (Galley et al. 2007; Dusel-Bacon, 2012). These 718 minerals can include, but are not limited to: chloritoid, garnet, staurolite, kyanite, andalusite, 719 720 phlogopite, and gahnite (zincian spinel). The presence or absence of each of these minerals not only reflect VHMS style hydrothermal alteration and P-T conditions during metamorphism, 721 but also the thermal gradient during metamorphism (Dusel-Bacon, 2012). A comprehensive 722 list of metamorphosed VHMS deposits under different conditions (e.g. greenschist, granulite, 723 blueschist), and common minerals associated with each, was given by Corriveau and Spry 724 (2014). 725

Hydrothermal dominated by 726 alteration at King is quartzmuscovite±chlorite±albite±carbonate in felsic to intermediate banded schists, and quartz-727 epidote±chlorite±magnetite in garnet-amphibolite. Cordierite and anthophyllite also occur in 728 relatively minor amounts ($\leq 5\%$) in felsic to intermediate footwall rocks. According to 729 Corriveau and Spry (2014), the "best documented alteration types associated with 730 metamorphosed VHMS deposits are the cordierite-anthophyllite schists, commonly the 731 amphibolite facies analogues of chloritic alteration pipes" (p.181). Their distinct 732 lithogeochemical signature (+Mg, +Fe, -Ca, -Na, -K) results in mineral assemblages that may 733 include cordierite, orthoamphibole/orthopyroxene, Al₂SiO₅ polymorphs, garnet, or staurolite, 734 735 quartz, biotite, and plagioclase, depending on P-T conditions. The aluminous minerals garnet, chloritoid, staurolite and the Al₂SiO₅ polymorphs (=andalusite, kyanite, sillimanite) commonly 736 occur close to high-T alteration pipes. This reflects the enrichment of Al by leaching of alkalis 737

under high fluid/rock ratios (Dusel-Bacon, 2012). Metamorphosed phyllic, sericitic, and
argillic alteration zones (+K, +Mg, ±Fe, -Ca, -Na) will result in the formation of diagnostic
peraluminous and/or mica-rich metamorphic rocks (e.g. those unusually rich in Al₂SiO₅
polymorphs, cordierite, garnet, K-feldspars, and/or micas) (Corriveau & Spry, 2014).

At King, the abundance of silica-epidote in the footwall garnet-amphibolites is 742 consistent with typical seafloor alteration of basaltic rocks prior to metamorphism (Galley et 743 744 al. 2007). Prograde metamorphism of an Al-rich assemblage of basaltic rocks is also recorded by the presence of abundant garnet, with hornblende and biotite. Garnet can locally form up to 745 50% of the rock (Fig. 7a – upper core), which has often retrogressed to chlorite and quartz. 746 The Cu-Fe sulfide bearing zone rich in chlorite and magnetite within the footwall garnet-747 amphibolites is consistent with a stockwork zone that often underlie lenses of massive sulfides 748 that has been metamorphosed (Galley et al. 2007). The LREE variation in these footwall rocks 749 has also been observed in intensely chlorite-altered stockwork zones elsewhere (e.g. Barrett & 750 MacLean, 1994). 751

In overlying intermediate and felsic rocks the presence of significant Mg-rich cordierite 752 and anthophyllite may also be taken as evidence for Mg-metasomatism prior to metamorphism 753 (Barrett et al. 2005; Corriveau & Spry, 2014). Anthophyllite and cordierite are present within 754 other metamorphosed VHMS footwall rocks of the Yilgarn Craton. Anthophyllite has been 755 identified from the Just Desserts deposit (1.07 Mt at 1.82% Cu; Hassan, 2014), and in the 756 Quinns district associated with the Austin deposit (1.48 Mt at 1.39% Zn, 1.02% Cu; Duuring 757 758 et al. 2016). Cordierite-rich rocks have been identified associated with VHMS mineralization at Ravensthorpe (Witt, 1999), and Mount Gibson (Yeats & Groves, 1998). 759

The transition from chloritic and albitic alteration in intermediate lithologies to quartz-760 muscovite alteration in the overlying dacitic rocks (with lower $TiO_2 - Fig. 13$) reflects 761 increased sericitization (+K, -Na, -Ca, -Mg) towards mineralization in footwall rocks prior to 762 metamorphism. The intermediate rocks analysed here are generally only weakly altered (Fig. 763 764 12 - see Box Plot). In the footwall quartz-muscovite schists, prograde metamorphism led to the recrystallization of an assemblage most likely dominated by quartz-sericite±pyrite 765 ±(chlorite). These rocks are now dominated by fine granoblastic quartz with interstitial platy 766 muscovite. Minor epidote, garnet and hornblende became sinks for Ca, Al, Fe, Mg and Na. 767 Subsequent retrograde metamorphism is recorded by the replacement of the coarse muscovite 768 by sericite and Mg-chlorite, sericitisation of cordierite, and breakdown of garnet to chlorite and 769 770 quartz.

Most VHMS deposits worldwide metamorphosed to amphibolite facies are 771 characterized by at least one Al-rich phase (Araujo et al. 1995). As stated previously, alteration 772 assemblages containing Al-rich mineral phases are interpreted to represent the removal of SiO₂ 773 774 and alkali elements by acidic fluids, and the residual concentration of Al₂O₃ in footwall rocks prior to metamorphism (Galley et al. 2007; Duuring et al. 2016). Staurolite porphyroblasts have 775 been recognized surrounding the Hollandaire deposit with garnet (Hayman et al. 2015a), and 776 777 at Wheatley with garnet, sillimanite and kyanite (Yeats, 2007; Hassan, 2017a) (Fig. 1). 778 Andalusite has been identified in metamorphosed sedimentary and felsic rocks from the 779 Dalgaranga greenstone belt (Superior Zn prospect; Butt & Sergeev, 2003), in altered footwall rocks at Teutonic Bore (albeit in minor amounts; Hallberg & Thompson, 1985), at Hollandaire 780 (with kyanite; Hayman et al. 2015a), and the Quinns district (with kyanite; Tasman and 781 Franklin prospects: Duuring et al. 2017; Hassan, 2017b) (Fig. 1). Minor andalusite was also 782 reported by Sharpe & Gemmell (2001) from the stratabound chlorite-(carbonate) alteration 783 enveloping massive magnetite and sulfide mineralization at Gossan Hill. More globally, the 784 Archean Geco deposit of the Superior Province, Canada, is a well-studied example of a 785 bimodal-mafic VHMS deposit metamorphosed to upper amphibolite facies. Ore hosting 786 lithologies now comprise muscovite-quartz±sillimanite schist, interpreted as a metamorphosed 787 sericitic alteration zone (Dusel-Bacon, 2012). 788

789 Research on the Kristineberg VHMS deposit of lower amphibolite facies from the Skellefte district, Sweden, has shown that very different secondary assemblages such as 790 andalusite-quartz-muscovite and cordierite-chlorite-talc can both be produced from the same 791 precursor (e.g. rhyolite); and conversely the same mineral assemblages can also be produced 792 793 from different precursor rocks, such as a weakly altered andesite and strongly altered rhyolite 794 (Barrett et al. 2005). The authors proposed a series of reactions to explain the observed (namely quartz, cordierite, 795 mineralogy at Kristineberg Mg-chlorite, muscovite, phlogopite/biotite, and alusite and pyrite). The most significant reactions here are: 796

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798 799

- 1. 280 chlorite + 131 quartz \rightarrow 231 cordierite + 180 anthophyllite + water
- 2. 40 chlorite + 28 sericite + 9 quartz \rightarrow 33 cordierite + 32 phlogopite + 12 and alusite + 16 water
- 3. 140 chlorite + 49 sericite + 51 quartz \rightarrow 141 cordierite + 56 phlogopite + 30 anthophyllite + water

The numbers before mineral names give the Niggli cation amounts of each mineral involved in the reactions. Note that the major difference between the second and third equations is the proportion of chlorite. When this is higher (eq. 3), cordierite, phlogopite/biotite, and anthophyllite may be produced without andalusite (Barrett et al. 2005). This may explain the prevalence of cordierite and anthophyllite (plus biotite) at King. Although we cannot rule out the presence of an Al₂SiO₅ phase, none were observed in thin section or under SEM.

806 7.4. Prospectivity of felsic rocks

The immobile element geochemistry of felsic volcanic rocks has long been used to 807 distinguish VHMS fertile from unprospective camps (Lesher et al. 1986; Hart et al. 2004; 808 Piercey, 2011). Quartz-muscovite schists of dacitic composition from King display similar 809 geochemical characteristics to felsic rocks associated with VHMS deposits throughout the 810 Yilgarn Craton (Hollis et al. 2015, 2017a), but with subtle differences. VHMS associated felsic 811 rocks throughout the Yilgarn are characterized by: i) high SiO₂ in unaltered rocks; ii) tholeiitic 812 to transitional Zr/Y and La/Yb values (i.e. FII to FIII affinity: Fig. 14b); iii) flattish REE 813 profiles (La/Sm_{CN} <3, Dy/Yb_{CN} ~1); iv) high HFSE concentrations; v) high Sc/TiO₂ and Sc/V 814 ratios; and low Th/Yb ratios (<2) (Hollis et al. 2015, 2017a). These felsic rocks are also 815 equivalent to those which host VHMS deposits of the Pilbara Craton of Australia (Vearncombe 816 & Kerrich, 1999) and the Abitibi greenstone belt of Canada (Barrie et al. 1993; Fig. 14a). One 817 exception is the Nimbus Ag-Zn-(Au) deposit, near Kalgoorlie, which is hosted by FI affinity 818 calc-alkaline dacite (Figs. 11f, 14b; Hollis et al. 2017b). Precious metal rich VHMS deposits 819

(i.e. Eskay Creek-type deposits) typically form at shallower water depths to classic Zn-Cu
deposits and are often hosted by 'less prospective' FI- to FII-affinity, calc-alkaline rocks
(Mercier-Langevin et al. 2011; Fig. 14a).

Although quartz-muscovite schists from King, display similar Zr/Y (4.6-15.0) and 823 La/Sm ratios to felsic rocks from Teutonic Bore, HFSE concentrations are significantly lower 824 (Fig. 10e-f; e.g. 68-236 ppm Zr) and HREE profiles are slightly steeper (Fig. 11f). While the 825 826 HFSE depletion in the King felsic rocks may be a function of element dilution through mass gain, this would not explain higher Dy/Yb ratios. The FI (to FII) characteristics at King (Fig. 827 **10e-f**) might suggest reduced base metal prospectivity for the immediate area, in keeping with 828 lower grades of Zn mineralization and abundant occurrences of massive Fe-sulfides. However, 829 the geochemistry of felsic rocks further into the hanging-wall or footwall of the stratigraphy 830 has not been tested. Furthermore, at King North (Fig. 4) recent geochemical work on rock chips 831 from RC drilling (Kelly, 2018, unpublished thesis) has highlighted both FII and FIII affinity 832 felsic rocks in close proximity to Cu-Zn-Au mineralization. 833

834 7.5. Vectors and halos to mineralization

Many vectors and halos have been proposed to help locate VHMS deposits in volcanic 835 terranes subject to greenschist facies metamorphism. These are most powerful when used in 836 combination, and include: i) changes in the mineralogy and chemistry of host sequence 837 associated with the formation of quartz, chlorite, carbonate and sericite and the breakdown of 838 839 feldspar and volcanic glass (e.g. Na₂O depletion); ii) elevated concentrations of pathfinder elements (e.g. Bi, Tl, Sb: Large et al. 2001b); iii) several alteration indices (e.g. Ishikawa, 840 Silicification, CCPI); and iv) changes in chlorite, carbonate and white mica chemistry (Duuring 841 et al. 2016). 842

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Regarding alteration mineralogy, we have already described common minerals 844 associated with metamorphosed VHMS systems. Recognition of mineral assemblages that 845 include cordierite, anthophyllite, biotite/phlogopite, and/or abundant garnet would be 846 847 significant in the Yilgarn Craton, in addition to Al-rich phases (i.e. kyanite, sillimanite, andalusite and/or staurolite) not present at King. In Ontario, Canada, mapping of the intensity 848 and distribution of anthophyllite, cordierite, sillimanite, garnet, quartz, muscovite and 849 staurolite led to the identification of footwall alteration and the discovery of the Archean 850 bimodal-mafic Winston Lake deposit (Dusel-Bacon, 2012). 851

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Zinc shows strong positive correlations with the following VHMS pathfinder elements 853 at King: Ag, As, Au, Bi, Cd, Eu/Eu* (Eu anomaly), Hg, In, Ni, Pb, Sb, Se, Tl. Similar VHMS 854 proximal metal enrichments of Ag, Au, Bi, Fe, In, MgO, Mo, S, Se and Te (with minor 855 enrichments in As, Cd, Mn, and V) were noted from the Quinns VHMS region by Duuring et 856 al. (2017). Thallium and Sb concentrations are moderately high and similar to quartz-muscovite 857 schists immediately underlying massive sulfides (Fig. 12) and are comparable to other 858 Australian VHMS systems which display well developed halos (Large et al. 2001b). Both 859 860 elements show a progressive increase in abundance from the deep footwall garnetamphibolites, through the mixed footwall sequence, quartz-muscovite schists, peaking in 861

massive sulfides and decreasing again in hanging-wall strata (**Fig. 12** – Box and Whisker diagrams). Although negative Eu anomalies may have been originally present as a primary feature of the felsic volcanic rocks due to plagioclase fractionation, Eu is readily liberated during hydrothermal alteration associated with the breakdown of feldspar at temperatures >250°C (Sverjensky, 1984). This leads to prominent positive Eu anomalies in hydrothermally altered and mineralized volcanic rocks, as observed at King (**Fig. 11**), Nimbus (Hollis et al. 2017), and other VHMS deposits in the Yilgarn (Hollis et al., 2015).

Chemographic ternary diagrams are useful for portraying common alteration trends in 869 metamorphosed terranes, as shown in Figure 15 (Bonnet & Corriveau, 2007; Corriveau & 870 Spry, 2014). Whereas samples of footwall garnet-amphibolite from the King deposit plot 871 towards the garnet, chlorite and hornblende mineral nodes, samples of quartz-muscovite schist 872 plot towards the cordierite node and A' corner (i.e. Al-rich end) of the diagram (Fig. 15a). The 873 prior is interpreted to reflect the intense Mg-Fe metamomatism of the feeder zone, and the latter 874 both quartz±sericite±pyrite alteration and Al-enrichment through alkali leaching of felsic 875 876 volcanic rocks prior to metamorphism. Weakly altered samples from the mixed footwall sequence and intrusive quartz-feldspar porphyries plot closer to the least altered volcanic field. 877 Data from the Teutonic Bore and Wheatley deposits are also shown for comparison (Figs. 878 15b,c). The intensity of Fe and Mg enrichment at Teutonic Bore is highlighted by the strong 879 880 clustering of both mafic and felsic footwall strata between cordierite and garnet. At Wheatley, 881 mineralized felsic gneisses plot towards the cordierite mineral nodes, whereas hanging-wall amphibolites are weakly altered. 882

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In metamorphosed terranes, the Mn contents of ferromagnesian minerals such as garnet, 884 biotite, staurolite, chlorite and amphibole have been observed to increase with proximity to 885 sulfide deposits, as well as the Zn content of staurolite and spinel (i.e. gahnite) (Spry, 2000; 886 887 Corriveau & Spry, 2014). The pink colour of garnets at King suggest they are Mn-rich (i.e. spessartine). MnO concentrations in the King footwall garnet-amphibolite reach 1.3wt% in 888 sample GK021. Large Mn peaks were also identified in garnet EDS spectra. Spessartine garnet 889 porphyroblasts have been observed in hanging-wall and footwall strata surrounding VHMS 890 mineralization in the Yilgarn Craton at Hollandaire and Wheatley (Hayman et al. 2015; Hassan, 891 2017a). Elevated contents of Mn in garnet from garnetites, and Zn in spinel from aluminous 892 gneisses were recently noted from granulite-facies rocks in the central Grenville Province, 893 894 Canada, highlighting its potential for VHMS mineralization (Hindemith et al. 2017). Corriveau and Spry (2014) have further suggested that staurolite becomes increasingly orange with Zn 895 content. This may prove useful to identify further resources at Hollandaire and other regions 896 where staurolite porphyroblasts surround mineralization (Hayman et al. 2015a). 897

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As regional metamorphism is largely an isochemical process at the core scale, combinations of indices such as Ishikawa Alteration Index (A.I.), Carbonate-chlorite-pyrite Index (CCPI; Large et al. 2001a), the Silicification Index ($100*SiO_2/SiO_2+Al_2O_3$) and the ACNK Index ($Al_2O_3/CaO+Na_2O+K_2O$; Grunsky, 2013) may be used to discriminate between different styles of footwall alteration and help locate mineralization. Alteration indices and pathfinder elements are plotted against vertical distance to mineralization at King in **Figure** 905 16. Zinc and Fe concentrations are erratic in footwall rocks using both lithogeochemical and pXRF datasets. Vanadium concentrations are highest in the feeder zone and may be useful to 906 identify such rocks elsewhere, particularly when combined with high A.I., ACNK Index values 907 and the abundance of normative corundum (see below). Antimony, Tl, In, and Eu/Eu* remain 908 low in both footwall and hanging-wall strata, only increasing significantly within short 909 distances (10s of metres) to mineralization. These are consequently only of use for exploration 910 when elevated. The ACNK Index and A.I. are high in both the chloritic zone and directly 911 underlying massive sulfides. The Silicification Index by contrast peaks in hanging-wall strata 912 directly overlying massive sulfides. 913

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The abundance of calculated normative corundum was used by Grunsky (2013) for 915 rocks from the Abitibi greenstone belt, Canada. When Al is in excess over (Ca+Na+K), the 916 presence of normative corundum may be interpreted as extensive alkali leaching, a 917 characteristic feature of footwall alteration associated with VHMS deposits. At King, 918 normative corundum abundance is highest in the chloritic feeder zone, but importantly is not 919 present (i.e. >0) in any hanging-wall strata regardless of composition. This reflects the lack of 920 921 alkali-leaching in the hanging-wall and may be a useful tool to identify hydrothermal upflow zones associated with VHMS deposits, and also hanging-wall from footwall sequences. 922 Normative quartz abundance generally parallels the Silicification Index trend, but drops in 923 weakly altered hanging-wall strata. 924

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926 8. Conclusions

The King Zn deposit (2.15 Mt at 3.47% Zn) occurs as a 2-5m thick stratiform lens dominated by Fe sulfides, in a structurally overturned volcanic dominated sequence located ~140km east of Kalgoorlie. The local stratigraphy is characterized by garnet amphibolite and strongly banded intermediate to felsic schists with rare horizons of graphitic schist. Sulfide mineralization is dominated by stratiform pyrite–pyrrhotite–sphalerite, with pyrite-(sphalerite) and pyrrhotite–pyrite–(chalcopyrite) stringers at depth. The King deposit is classified as a metamorphosed bimodal-mafic or Noranda-style VHMS deposit.

934 Footwall garnet-amphibolites are of sub-alkaline basaltic affinity, with high Co and Sc concentrations, and flat chondrite-normalized HREE profiles. SiO₂, CaO, Fe₂O_{3T}, MgO and 935 Cu concentrations are highly variable, reflecting quartz-epidote±chlorite±magnetite±sulfide 936 alteration. Chlorite±magnetite alteration is most intense in the discordant Cu-bearing chloritic 937 feeder zone. Intermediate rocks are predominantly of calc-alkaline affinity and are similar to 938 andesites from elsewhere in the Kurnalpi terrane (e.g. Teutonic Bore). Although footwall 939 quartz-muscovite schists display similar Zr/Y and La/Sm ratios to felsic rocks from other 940 Archean VHMS deposits, HFSE concentrations are significantly lower and HREE profiles are 941 steeper. Hydrothermal alteration in felsic to intermediate rocks is characterized by a mineral 942 943 assemblage of quartz-muscovite±chlorite±albite±carbonate. Cordierite and anthophyllite are locally significant and indicative of zones of Mg-metasomatism prior to metamorphism. 944 Increases of SiO₂, Fe₂O_{3T}, and depletions of Na₂O, CaO, and MgO occur in footwall quartz-945 muscovite schists approaching massive sulfide mineralization. 946

947 Within all strata (including the immediate hanging-wall), the following pathfinder elements are strongly correlated with Zn: Ag, As, Au, Bi, Cd, Eu/Eu*, Hg, In, Ni, Pb, Sb, Se, 948 Tl. These geochemical halos resemble less metamorphosed VHMS deposits across the Yilgarn 949 Craton, and suggest that although metamorphism leads to element mobility and mineral 950 segregation at the thin section scale, assay samples of ~20cm length are sufficient to vector to 951 952 mineralization in amphibolite facies greenstone belts of the Eastern Goldfields. Recognition of minerals such as Mg-chlorite, muscovite, cordierite, anthophyllite, biotite/phlogopite, and 953 abundant garnet are significant, in addition to Al-rich phases (kyanite, sillimanite, andalusite 954 and/or staurolite) not present at King. Chemographic diagrams (e.g. A'KF and AFM) may be 955 used to identify and distinguish different alteration trends, along with the following alteration 956 indices: Ishikawa Alteration Index, Sericite Index, Silicification Index, ACNK Alteration 957 Index, and the abundance of CIPW normative corundum and quartz. 958

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Figure 1. Major terrane and domain subdivisions of the Yilgarn Craton, Western Australia, showing
the distribution of greenstone belts and base metal occurrences (red stars) (after Hollis et al. 2015).
Significant VHMS deposits are labelled. *Domains:* B, Boorara; E, Edjudina; G, Gindalbie; L, Linden;
Me, Menangina; Mu, Murrin. *Other abbreviations:* GB, greenstone belt; MB, metamorphic belt. The
Teutonic Bore camp includes the Teutonic Bore, Jaguar and Bentley VHMS deposits.

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Figure 2. Simplified stratigraphy of the Kalgoorlie and Kurnalpi terranes of the Eastern Goldfields
(after Czarnota et al. 2010). Two main episodes of VHMS mineralization have been recognized (Hollis
et al. 2015, 2017a): 1. ca. 2705 Ma: Anaconda (A), Nimbus (N), King?; 2. ca. 2690-2680 Ma: Teutonic
Bore (TB), Jaguar, Bentley, Erayinia NW, Jungle Pool occurrence.

Figure 3. Regional Nd isotope variations of the Yilgarn Craton (modified after Wyche et al. 2013).
The position of significant VHMS occurrences associated with the Kurnalpi paleo-rift zone (highlighted by younger depleted mantle model ages) are indicated by red stars.

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- Figure 4. Geological map of the central Erayinia region (modified after Jones, 2007), highlightingthe position of the King deposit in the Edjudina Domain, east of the Claypan Fault.
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Figure 5. Distribution of banded iron formations (BIF) and komatiites in the southern Eastern
Goldfields Superterrane. The figure was derived from 2010 GSWA 1: 100 000 scale outcrop mapping,
overlain on the domains of Cassidy et al. (2006). Also shown are U-Pb zircon age constraints from
each domain, and the location of Ni-sulfide occurrences (from GeoVIEW; available at
www.dmp.wa.gov.au).

Figure 6. (a) Drillhole map of the King Zn-(Cu) deposit. (b) Composite longitudinal section through
the deposit highlighting the two Zn-rich ore lenses (after ABM Resources NL, Annual Report 2009).
Zinc (c) Cross section showing the interpreted main geological units discussed in the text. (d) Cross
section showing the main alteration minerals present and base-metal mineralization. Dashed lines
reflect the interpreted geology illustrated in Figure 5c.

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1314 Figure 7. Representative photographs of the main lithologies observed and styles of hydrothermal 1315 alteration present at King. (a-b) Variably banded and sheared footwall garnet-amphibolite. (c) 1316 Intensely chloritized zone of footwall amphibolite containing disseminated magnetite. (d) 1317 Anthophyllite-bearing schist from the mixed footwall sequence. (e-f) Folded and banded schist from the mixed footwall sequence with individual layers composed almost entirely of quartz, muscovite and 1318 epidote. (g) Albite-rich schists from the mixed footwall sequence. (h) Intensely silicified footwall 1319 1320 felsic rocks (quartz-muscovite schist). (i) Finely banded quartz-biotite/amphibole±garnet schists from the stratigraphic hanging-wall of the deposit. Note the variation in rock types and alteration. (j) Finely 1321 banded silicified hanging-wall schists. (k) Polymict volcanic breccia with clasts of surrounding 1322 1323 lithologies. (1) Possible grading in drillhole EC056D (hanging-wall strata), with coarse bases and

schists fining downhole. (m) Early quartz-feldspar porphyry sill intruding the King deposit
stratigraphy (sample GK024; Fig. 6c labelled 1). (n) Late unaltered quartz-feldspar porphyry sill
intruding the King deposit stratigraphy (Fig. 6c labelled 2). (o) Basaltic dyke most likely from the
Palaeoproterozoic Widgiemooltha Dyke Suite cutting the footwall garnet-amphibolite. Varioles are
often present near upper and lower contacts.

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1330 Figure 8. Representative drillcore photographs of the main styles of sulfide mineralization observed 1331 at the King deposit. (a) Stringer sulfide mineralization in the chloritic zone of the footwall garnet-1332 amphibolite, dominated by pyrrhotite with lesser chalcopyrite. (b) Blebby and stringer chalcopyritepyrite mineralization in footwall-garnet amphibolite. (c) Folded pyrite-sphalerite veins within the 1333 footwall quartz-muscovite schist. (d) Contact between the quartz-muscovite schist and 1334 stratigraphically overlying massive sulfides (dominated by pyrite with lesser replacive sphalerite). (e) 1335 1336 Cap of massive Fe-sulfides (dominated by pyrite and pyrrhotite) containing milled fragments of 1337 footwall and hanging-wall strata. (f) Recrystallized pyritic stringers in banded hanging-wall schists. (g) Stringers of coarse euhedral pyrite in hanging-wall schists directly overlying massive sulfides. 1338 Tightly folded and sheared, pyrite-rich hanging-wall schists. (i) Fault gouge within the thin (<30cm) 1339 1340 zone of massive sulfides in northernmost diamond drillhole EC063D.

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Figure 9. Photomicrographs, SEM images and chemical maps for representative samples from the 1342 King stratigraphy. (a) Footwall garnet-amphibolite with disseminated sulfides. (b) Reflected light 1343 1344 image of sulfide and oxide phases present within footwall garnet-amphibolites (c) Chemical map of the area in Figure 8b (denoted by a white box). (d) Intensely chloritized zone of garnet-amphibolites. 1345 1346 (e) Quartz-hornblende schist from the mixed footwall sequence (f-h) Anthophyllite bearing quartz-1347 biotite-chlorite-albite-epidote schist from the mixed footwall sequence. (i-j) Quartz-muscovite schist 1348 from the immediate footwall of the King deposit. (k) Coarse euhedral pyrite in quartz-muscovite schist, 1349 with interstitial sphalerite. (1) Massive sulfide with sphalerite replacing pyrite and large milled clasts of surrounding quartz-muscovite schist. (m-n) Massive sulfides containing garnet porphyroblasts 1350 retrograded to chlorite. (o-r) Petrographic and SEM images of hanging-wall mafic (o,r) and felsic (p-1351 1352 q) strata. Drillhole numbers and sample depths are indicated by the format 116/425m. Plane polarised light – Fig. 9a,f; Cross polarized light – Fig. 9d,e,i,j,o,p,q; SEM images – Fig. 9g,k,m,r. SEM 1353 1354 composite chemical maps - Fig. 9c,h,n. Chemical mapping was completed using a Hitachi 1355 TM3030Plus Tabletop Scanning Electron Microscope at University College Dublin, Ireland. Maps 1356 were completed over 2-3 hours each using a pixel dwell time of 800 µs, resolution of 1024 and process 1357 time of 4 seconds. Composite colour maps were produced by merging element concentration maps of 1358 interest using the Oxford Instruments Aztec One (v. 3.2) software.

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Figure 10. Immobile element geochemistry for samples analysed from the King deposit. (a-c) Zr/TiO₂ 1360 1361 vs Nb/Y discrimination diagrams for volcanic rocks (after Pearce, 1996). Probability ellipses for various rock types are shown after Pearce (1996). These represent 10% probability contours – that is 1362 1363 10% of samples from that group will plot outside the respective contour. (d) Th vs Co discrimination diagram of Hastie et al. (2007). (e-f) VHMS fertility diagrams of Lesher et al (1986; Fig. 9d) and Hart 1364 1365 et al (2004; Fig. 9f). Felsic volcanic rocks from Teutonic Bore are of FIII affinity characterised by 1366 high concentrations of the HFSE and low Zr/Y and La/Yb ratios. Footwall quartz-muscovite schist 1367 from King is of FI to FII affinity and less prospective for VHMS mineralization. (g) Th/Yb vs Nb/Yb 1368 diagram of Pearce (2008, 2014). Arc related volcanic rocks will parallel the mantle array, whereas samples trending obliquely to it are associated with crustal contamination (Pearce, 2008). 1. Yilgarn 1369 1370 Felsic Intrusion (Hayman et al. 2015b); 2. Felsic Archean Crust (Rudnick & Fountain, 1995); 3. Upper

1371 Continental Crust (Taylor & Mclennan, 1995).

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- Figure 11. Chondrite-normalized REE profiles (after McDonough & Sun, 1995) for samples analysed
 from the King deposit. Shaded fields for rocks from Nimbus and Teutonic Bore are from Hollis et al.
 (2017) and Hollis (unpublished) respectively.
- Figure 12. Mobile element geochemistry of samples analysed from King. The Box Plot (bottom left)
 uses both the Alteration Index (A.I.) of Ishikawa et al. (1976) and the Carbonate-chlorite-pyrite Index
 of Large et al. (2001a) to show common trends associated with hydrothermal alteration.
 A.I.=100*(K₂O+MgO)/(K₂O+MgO+Na₂O+CaO);
- $1381 \qquad \text{CCPI}=100*(\text{MgO}+\text{FeO})/(\text{MgO}+\text{FeO}+\text{Na}_2\text{O}+\text{K}_2\text{O}).$
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- Figure 13. Downhole geochemical profiles for drillholes EC116D, EC056D and EC031D using data
 obtained by both the pXRF and whole rock methods (see Figure 6 for drillhole locations). Eu/Eu*
 calculated after Boynton (1984).
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- Figure 14. Prospectivity of felsic rocks from (a) the Abitibi greenstone belt, Canada, and (b) Younami
 Terrane, and Eastern Goldfields, according to the Zr/Y vs Y felsic discrimination diagram of Lesher
 et al. (1986). All stacked plots are the same scale with Zr/Y ratios for each section of the stack indicated
 on y-axes. Adapted from Hollis et al. (2015), with additional data from Hollis et al. (2017a Nimbus
 deposit) and Hassan (2017a Wheatley deposit).
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1393 Figure 15. (a) Chemographic diagrams (A'CF, A'KF and AFM) used to portray common alteration 1394 trends and mineral nodes in metamorphosed terranes (diagrams modified after Bonnet & Corriveau, 1395 2007; Corriveau & Spry, 2014). Samples are plotted using molecular proportions (i.e. the chemical 1396 analysis of the rock is recalculated by dividing the molecular weight of each oxide constituent by the 1397 molecular weight of that oxide). (a) King deposit, (b-c) Mafic and felsic volcanic rocks analysed from the Teutonic Bore and Wheatley VHMS deposits (data from Hollis, unpublished; Hassan, 2017a). The 1398 point density contours in 14b reflect the field of least/weakly-altered felsic and intermediate 1399 1400 volcanic/volcaniclastic rocks from the Yilgarn Craton. This dataset, compiled by Hollis et al. (2015), was filtered to remove samples with anomalous Zn (>100 ppm) and high degrees of alteration 1401 1402 (Silicification Index >80%). A'CF: A'=Al₂O₃+Fe₂O₃-(K₂O+Na₂O), C=CaO, F=FeO+MnO+MgO. A'KF: A=Al₂O₃+Fe₂O₃-(K₂O+Na₂O+CaO), K=K2O, F=FeO+MnO+MgO. AFM: A=Al₂O₃-K₂O; 1403 1404 F=FeO, M=MgO. Abbreviations for mineral names (Whitney and Evans, 2010): Act - actinolite, Alm 1405 - almandine (garnet), An - anorthite, Ath - anthophyllite, Bt - biotite, Cal - calcite, Chl - chlorite, Crd 1406 - cordierite, Di - diopside, Ep - epidote, Grs - grossular (garnet), Grt - garnet, Hbl - hornblende, Hd -1407 hedenbergite, Kfs - K-feldspar, Ky - kyanite, Ms - muscovite, Opx - orthopyroxene, Prp - pyrope (garnet), Sil - sillimanite, Tr - tremolite. 1408

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Figure 16. Geochemical and mineralogical vectors to mineralization at King, plotted as distance to
massive sulfide mineralization (calculated perpendicular to ore in section 6538650mN; Fig. 6c).
Normative CIPW quartz and cordierite abundances (volume %) were determined using the Norm 4

1413 spreadsheet of Kurt Hollocher (Union College).





Basalt, dolerite/gabbro intrusions Komatiite, komatiitic basalt Intermediate volcanic/volcaniclastic rocks Felsic volcanic/volcaniclastic rocks Felsic intrusive rock Sedimentary rocks: fine-grained turbidites Sedimentary rocks: coarse (conglomerate) Black shale / Banded iron formation Fault contact





























