The significance of metaexhalites, seafloor alteration and retrograde processes for metamorphosed mineral deposits: examples of distinct alteration styles from the Aileron Province

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Given that the majority of massive sulfide deposits form in basins that are subsequently deformed, metamorphosed and/or altered, most exploited massive sulfide deposits have been affected by these processes. In Australia, the granulite-facies *Broken Hill* deposit and the unmetamorphosed, weakly deformed *HYC* (*McArthur River)* deposit represent contrasting extreme effects of these post-depositional processes. The effects of alteration, deformation, and high-grade metamorphism on basin-hosted sulfide deposits commonly remove or obscure original deposit characteristics. As only ambiguous, or at best, circumstantial evidence for ore-forming processes are preserved in such settings, it is unsurprising that the genesis of many of these deposits remain unresolved with a number of conflicting ore deposit models proposed.

Identifying the relative effects of metamorphism, deformation and hydrothermal alteration on pre-existing orebodies is important for explorers. These processes can control the dissolution and re-precipitation of ore and associated alteration minerals, affect the economics of metal distribution and create structural and chemical traps for later epigenetic mineralisation. Understanding these processes can play an important role in predicting metal distribution and targeting favourable sites for both syn-sedimentary (syngenetic-diagenetic) and post-depositional (epigenetic) mineralisation.

This text describes several different alteration assemblages associated with basin-hosted sulfide mineralisation from Jervois Range and Strangways Range in the Palaeoproterozoic Aileron Province, central Australia (**Figure 1**). Most of these deposits share a similar ca 1.80–1.79 Ga age, and are formed in a contiguous northwest–southeast trending belt of basin successions along the tectonically active southern margin of the North Australian Craton (Scrimgeour 2013). The host rocks to the mineralisation at Jervois Range and Strangways Range were metamorphosed to amphibolite- and granulite-facies respectively. The distinct alteration assemblages and mineralogy found at these deposits can provide significant clues that can help determine ore-forming processes and depositional environments, leading to improved mineral deposit targeting for explorers.

The results presented herein demonstrate the potential for discovering outcropping alteration assemblages across the Aileron Province related to syn-sedimentary hydrothermal processes that may suggest nearby mineralisation. Some basin-hosted deposits contain syn-sedimentary alteration assemblages that were metamorphosed and then subsequently destroyed and/or overprinted by later hydrothermal alteration. This fluid-assisted retrograde alteration is commonly spatially or temporally associated with epigenetic copper mineralisation. These observations of multiple processes suggest that it is unrealistic for deposit models in metamorphic terranes to exclusively invoke either syngenetic or epigenetic ore-forming processes. Moreover, the composition of the host basin succession and syn-sedimentary alteration associated with early mineralisation can influence later mineralising episodes.

Metaexhalites and unusual mineralogy in the Jervois mineral field and their metallogenic implications

At the *Green Parrot, Marshall* and *Reward* deposits in the Jervois mineral field (**Figure 1**), there is a notable spatial association between metamorphosed syn-sedimentary mineralisation and unusual mineral assemblages (eg garnetites, tourmalinites, banded iron-rich rocks, apatite-rich rocks; **Figure 2**). These unusual rocks are found interlayered within the predominantly metasedimentary host succession, the Bonya Metamorphics. They are interpreted as metaexhalites that represent hydrothermal chemical sediments or 'exhalites' that were subsequently metamorphosed to produce the observed metaexhalites. For example, exhalites enriched in iron and manganese or boron would produce garnetites or tourmalinites respectively when metamorphosed. The specific processes involved in the formation of hydrothermal chemical sediments (ie exhalative, inhalative, replacement) remain subject to debate; however, it is understood that they are deposited by low to moderate temperature fluids that either replace aluminous clastic sediments or exhale into subaqueous basins, at or near the sediment–water interface during sedimentation or diagenesis (Spry *et al* 2000).

The identification of metaexhalites is important because these rocks are commonly spatially and temporally associated with metamorphosed stratabound massive sulfide deposits (eg Broken Hill-type and VMS deposits) formed in subaqueous settings within basin rift environments (Ridler 1971, Spry *et al* 2000). Identification of metaexhalites in the Aileron Province is particularly pertinent because such alteration has previously been considered absent in the Arunta Region (Shaw 1990). Understanding metaexhalites can be a helpful exploration tool; metaexhalites commonly form stratigraphically discrete layers above, below, within or along strike from exhalative ore deposits and indicate relic paleohydrothermal activity (Spry *et al* 2000). As such, the distribution and chemistry of metaexhalites can not only act as potential vectors to mineralisation, but can also indicate ore-forming processes and environments.

At the Marshall and Reward deposits, garnetites are the most common metaexhalite (**Figure 2a**). They form as ≤6 m thick intervals of massive garnet layers, commonly with quartz and magnetite. Garnet compositions are predominantly andradite (Ca-Fe-rich and Al-poor) although transitions to almandine (Fe-rich), spessartine (Mn-rich)

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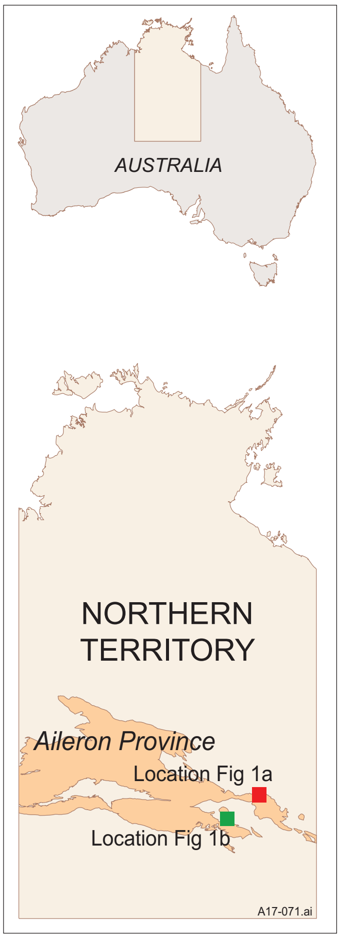

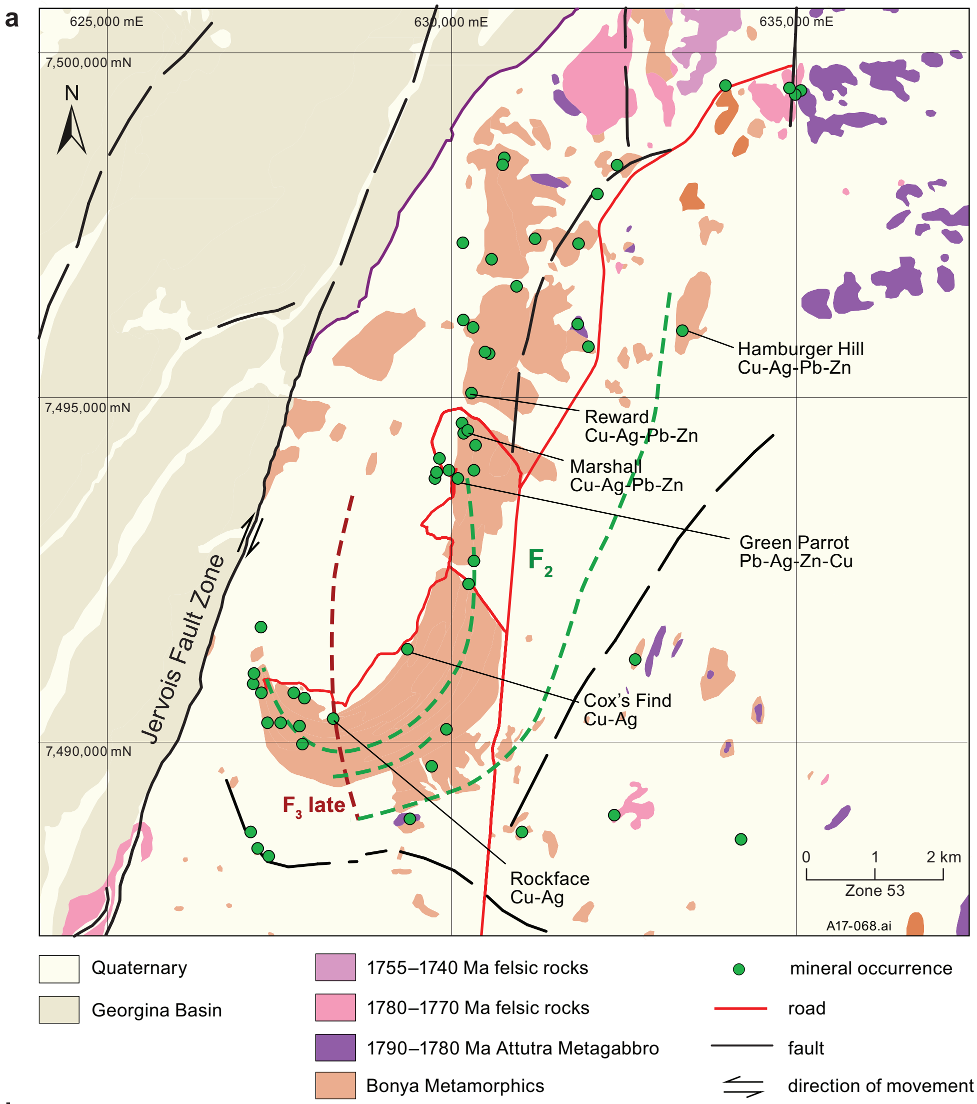

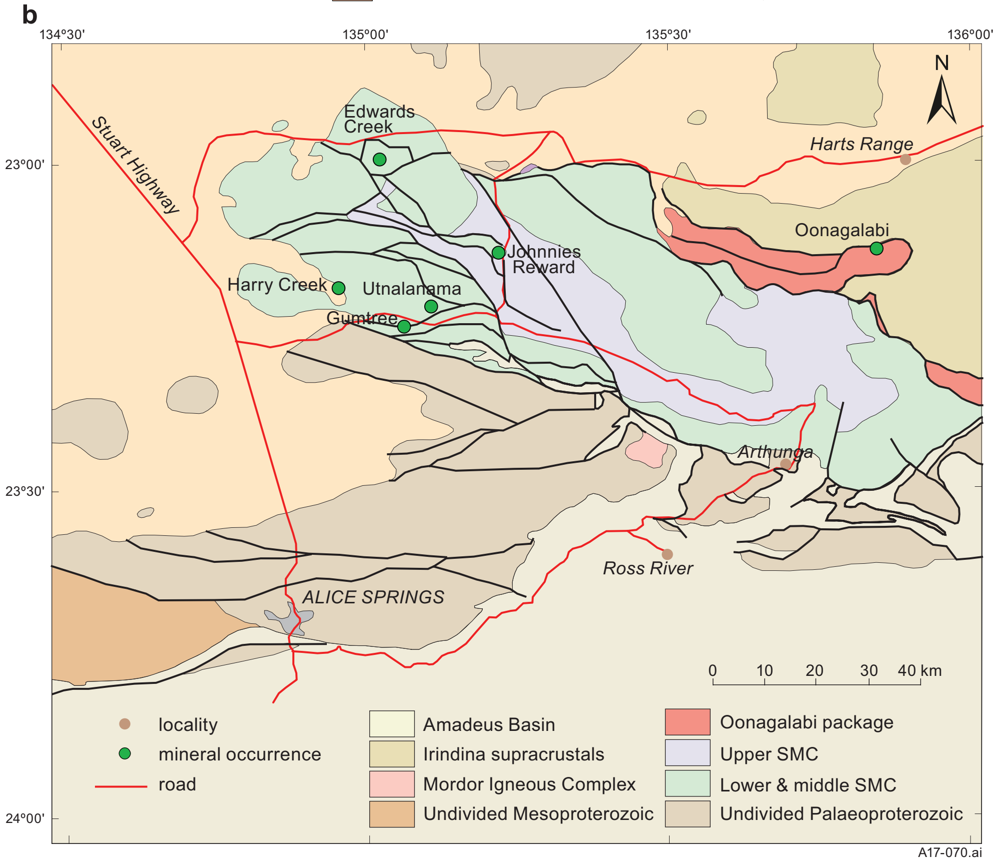

Figure 1. Map of the Aileron Province and locations and deposits discussed in this paper. **(a)** Jervois mineral field. **(b)** Strangways Range. SMC = Strangways Metamorphic Complex.

and grossular (Ca-rich) varieties do occur (Smith *et al* 2016). Discrete but massive layers of these different garnet compositions are found above, within or below zones of sulfide mineralisation. The garnet compositions and textures vary spatially, supporting the genetic interpretation that these discrete bands of metaexhalite relate to a syn-sedimentary mineralising process. For example, the common Fe- and Mn-rich garnets from the garnetites at *Marshall* and *Reward* have distinct major element chemistry compared with garnets found away from mineralisation in the Bonya Metamorphics (McGloin *et al* 2016). This difference suggests that analyzing the major and trace element chemistry of metamorphic minerals, particularly those associated with metaexhalites, may be a useful tool in identifying vectors towards syn-sedimentary mineralisation regionally.

Prograde metamorphic silicate minerals (eg garnet, cordierite, staurolite) found near to mineralised zones commonly have Mn-, Fe- or Zn-rich chemistries (Dobos 1978, McGloin and Weisheit 2015) suggesting the existence

Figure 2. Example images of unusual mineral assemblages in the Aileron Province. From the Jervois mineral field: (**a**) garnetite from the Reward deposit; (**b**) mineralised garnet-biotite rock from the Hamburger Hill prospect; (**c**) tourmalinite from the J-Fold near to the Cox's Find prospect; (**d**) banded iron layers showing magnetite part oxidized to hematite, folded by F_2 that probably represent an S_0-S_1 composite; (**e**) Banded zones of apatite from drill core at the Reward deposit (NTGS database reference ID 8446368 derived from NTGS HyLogger™ TSG dataset). From the Strangways Range: (**f**) garnet-biotite rock from the Johnnies Reward deposit; (**g**) garnet-biotite rock from the Oonagalabi deposit.

of base metals mineralisation before peak-pressure D_2 metamorphism. The localised presence of staurolite and gahnite in the lode sequence (Dobos 1978, Teale 1982, Peters *et al* 1985) is also noteworthy as these minerals are absent in the regional metamorphic assemblage (Reno *et al* 2016). The application of element composition studies of these minerals and assessing their distribution should also provide vectors towards mineralisation.

The *Hamburger Hill* Cu-Ag-Pb-Zn prospect, 3 km east of the main lode sequence, shares the same host succession and a similar base metals assemblage as the other syn-sedimentary deposits of the Jervois mineral field. **Figure 2b** shows unusual stratabound zones comprising porphyroblastic garnet–biotite schist enriched in Cu-Ag-Pb-Zn and interlayered within the metasedimentary succession. The garnet-biotite schist has an unusual mineral assemblage lacking quartz or feldspar (70–80% of the host rock comprises garnet and biotite). The significance of these zones has not previously been recognised. They are interpreted here to represent metamorphosed hydrothermal chemical sediments or alteration related to such processes similar to alteration assemblages identified locally at Green Parrot, Marshall and Reward.

Tourmalinites (layered tourmaline–quartz rocks) are found as 1 to 10 m-thick stratabound beds in the Jervois mineral field and commonly contain anomalous concentrations of magnetite and apatite (**Figure 2c**; Peters *et al* 1985). The chemistry and isotopic signature of these tourmalinites provides insight into ore-forming processes and depositional environments locally. Tourmaline has schorl-dravite compositions (Fe-Mg chemistry) and is characterised by extremely light $\delta^{11}B$ isotope values (-19 to -23 ‰; McGloin *et al* 2016). The $\delta^{11}B$ data from the tourmalinites in the Jervois mineral field yield some of the lightest $\delta^{11}B$ values ever recorded. Only the Broken Hill deposit has comparably light $\delta^{11}B$ tourmaline values (Slack *et al* 1989) for any ore-related tourmaline assessed globally to date. The extremely light $\delta^{11}B$ values recorded in the Jervois mineral field indicate that only two boron sources can be proposed: borate from terrestrial evaporites, or boron from highly-fractionated S-type granite magmas (Marschall and Jiang 2011, McGloin *et al* 2016). Regional mapping on HUCKITTA has failed to demonstrate any evidence for S-type granitoids older than peak-pressure metamorphism at ca 1.76 Ga (Beyer *et al* 2016; Reno *et al* 2017). As the tourmalinites pre-date this metamorphism, any primary link to S-type magmatism is precluded; thus, terrestrial evaporites are the more likely source for boron in the tourmalinites. It is inferred that boron was leached from a terrestrial evaporite source containing borate, and then transported and expelled from hydrothermal fluids to form tourmaline or a precursor B-rich mineral in sediments at or near the sediment–water interface. The extremely light $\delta^{11}B$ signature detected also implies little or no marine influence on the infiltrating hydrothermal fluids that formed the tourmalinite precursor sediments since marine borate has heavier $\delta^{11}B$ values (modern day oceans have $\delta^{11}B$ values of ~40 ‰; Swihart *et al* 1986). Oceanic $\delta^{11}B$ values are not well constrained for the Palaeoproterozoic however examples from Precambrian ore deposits with marine-influenced geological processes yield similarly heavy marine-like tourmaline $\delta^{11}B$ values >20 ‰ (Xavier *et al* 2008, Mercadier *et al* 2012).

The interpretation of evaporites in the host succession in the Jervois mineral field enhances prospectivity of the region for a wide range of hydrothermal ore deposits, including sediment-hosted, Broken-Hill type, iron oxide copper-gold and skarn deposits. Evaporites provide a locally accessible source for generating highly saline hydrothermal fluids with increased capacity for metal transport. Given their higher salinity, the chloride-rich nature of the brines generated allows base metals to be scavenged and mobilized more effectively at lower temperatures (~100–350°C) than comparably saline higher temperatures (~450–600°C) magmatic-hydrothermal or metamorphic fluids.

The interpretation of a terrestrial (non-marine) evaporitic borate source for the tourmalinites at Jervois implies a very specific depositional environment for a portion of the former palaeobasin with potential metallogenic implications. Present day terrestrial evaporites are typified by the Salar evaporite deposits of Chile, Argentina and Bolivia (Warren 2016). The formation of terrestrial borate evaporites requires explicit climatic and geographical constraints (Evans 2006, Warren 2016, Steinmetz 2017). These are arid climates in areas of high topographic relief in active or formerly active volcanic terrains where terrestrial waters evaporate in a hydrologically-closed basin setting. This interpretation is consistent with the continental back-arc setting currently proposed for the study area (Reno *et al* 2017). Such volcanogenic-influenced terrestrial environments are likely to be more prospective for VMS and Broken Hill-type mineralisation than McArthur- or Mount Isa-type mineralisation (eg Huston *et al* 2006). The latter deposits generally form in more passive extensional settings that lack active volcanism and magmatism during sedimentation; they also have a greater degree of marine influence, commonly hosting organic-rich matter and abundant carbonate sequences.

Alteration and mineralogy associated with stratabound sulfide deposits in the Strangways Range

The Strangways Range hosts a number of Cu-Pb-Zn (Au-Ag) deposits and associated alteration that, in most cases, were metamorphosed to granulite-facies conditions during the Palaeoproterozoic (**Figure 1**). These deposits are generally considered to represent a spectrum of volcanic-associated massive sulfide (VAMS), carbonate-replacement and iron oxide copper-gold-type deposits (Warren and Shaw 1985, Hussey *et al* 2005).

The mineralogy and geometries of the alteration assemblages associated with these deposits vary but many suggest the influence of syngenetic seafloor or sub-seafloor alteration processes. This seafloor setting also appears to be different to the depositional setting suggested for the Jervois paleobasin, with more pronounced Mg- rather than Fe-rich alteration in many locations. In several locations in the Strangways Range, rocks abundant in Mg-rich aluminosilicate minerals (**Figure 3a-e**) such as sapphirine, cordierite and anthophyllite (eg Goscombe 1992, Hussey *et al* 2005) have been identified. For example, some Utnalanama VAMS deposits (eg *Edwards Creek*, *Utnalanama*, *and Harry Creek*) host asymmetric stratiform amphibole, spinel or orthopyroxene-rich assemblages (**Figure 3a**) associated with cordierite and garnet-quartzite proximal to sulfide mineralisation (Hussey *et al* 2005). Where abundant, such minerals are considered to represent high grade, Mg- and Al-rich, and K-, Na- and Si-depleted assemblages resulting from metamorphism of host rocks that were previously altered by hydrothermal fluids. One interpretation for this alteration is that prior to granulite-facies metamorphism, the precursor basin succession underwent chlorite alteration via hydrothermal fluids that entrained seawater into the footwall removing Si and adding Mg to the bulk composition of these rocks.

At the *Oonagalabi* Cu-Zn deposit hosted in the Bungitina Metamorphics (**Figure 1**), ore-forming processes remain uncertain, but are likely to represent either a carbonate-replacement or VAMS style mineralisation (Hussey *et al* 2005). The succession is interpreted to have been deposited and metamorphosed during the Palaeoproterozoic (Hussey *et al* 2005), then overprinted by Palaeozoic shearing (Skidmore 1996). In light of this, the timing of mineralisation at Oonagalabi remains unconstrained, with Palaeoproterozoic versus mid-Palaeozoic ages proposed by these authors. Furthermore, ore forming processes and associated alteration are difficult to resolve.

The Oonagalabi deposit shares some similar alteration assemblages to the Utnalanama deposits, but appears to show some evidence for symmetric or gradational alteration of marble and calc-silicate rocks to amphibole-rich rocks (Hussey *et al* 2005) rather than the asymmetric alteration typical of the latter deposit type. Mineralisation at Oonagalabi is found almost exclusively in carbonate-rich lithologies; both veined and disseminated types are present. The intimate association of mineralisation with massive anthophyllite (**Figure 3b**) is noteworthy and indicates pervasive Mg alteration of carbonate protoliths. Mineralisation is also associated with other unusual stratabound alteration assemblages including garnet- and gahnite-rich metasandstone, cordierite-quartz gneiss, and

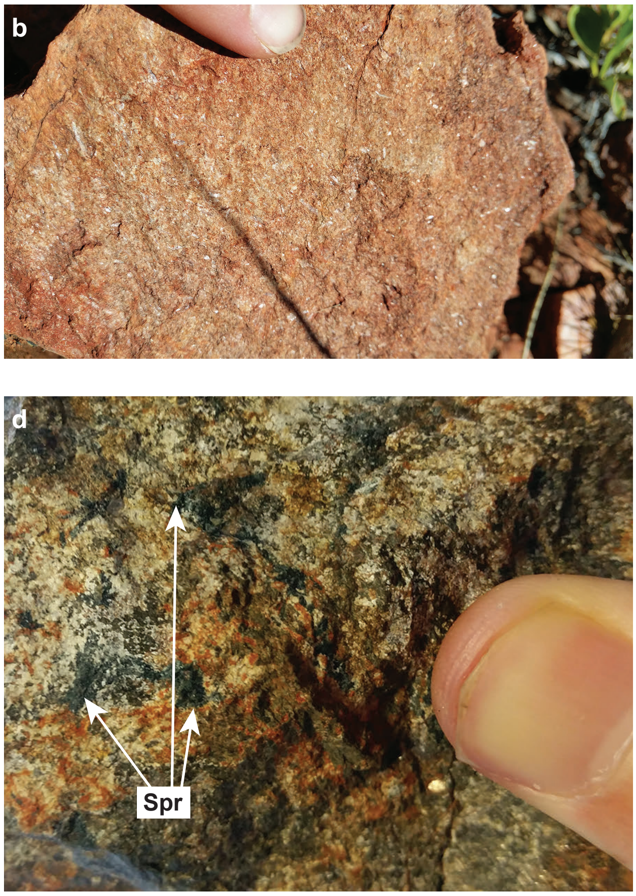

Figure 3. Example images of common alteration assemblages in the Strangways Range. (**a**) Cordierite-orthopyroxene-bearing rock from the Edwards Creek deposit. (**b**) Massive anthophyllite from the Oonagalabi deposit. (**c**) Massive magnetite-amphibole-spinel rock from the Oonagalabi deposit. (**d**) Unspecified metapelitic gneiss containing sapphirine (Spr). (**e**) Diopside-tremolite-magnetite-quartz rock from the Johnnies Reward deposit.

a variety of magnetite ± amphibole ± spinel ± pyroxenite rocks (**Figure 3c**; Skidmore 1996, Hussey *et al* 2005).

The presence of veined mineralisation intruding carbonate-rich lithology at Oonagalabi allows for an epigenetic component to the ore-forming and associated alteration story. However, the observed evidence cannot preclude contributions from earlier syngenetic or diagenetic processes on the alteration and mineralisation observed. Consequently, an alternative interpretation whereby the stratabound nature of the unusual mineral assemblages at Oonagalabi may represent syngenetic seafloor-style alteration processes may be valid. Metamorphism of Mg-rich, Si-depleted alteration zones can explain the formation of anthophyllite–cordierite-bearing assemblages. Some of the garnet-biotite rich assemblages and other unusual mineral assemblages identified may represent hydrothermal chemical sediments metamorphosed to granulite-facies. Nonetheless, the timing of the introduction of base metals at Oonagalabi remains uncertain and may not necessarily parallel this stratabound alteration. The observed epigenetic mineralised veins may represent remobilization of pre-existing mineralisation rather than newly introduced mineralisation. Hydrothermal fluid flow associated with such veining could also produce the symmetric alteration that obscures or obliterates evidence for pre-existing alteration.

At the *Johnnies Reward* Cu-Pb-Zn-Ag-Au deposit hosted in the Cadney Metamorphics, drill core and petrographic observations show evidence for a prograde metamorphic assemblage of banded garnet-biotite rock (**Figure 2f**). As with the examples given from the Jervois mineral field and Oonagalabi, this alteration assemblage is interpreted as representing metamorphosed hydrothermal chemical sediments, or alteration related to such a process. This implies syn-sedimentary hydrothermal fluids were active in the paleobasin. The deposit has a lode sequence (a diopside–tremolite–magnetite-quartz rock; **Figure 3e**) with an apparent stratiform nature that shows evidence for subsequent magnetite-chlorite alteration, coupled with Mn-rich anthophyllite and manganocummingtonite as identified in the mineralised sequence (Hussey *et al* 2005). These observations are re-interpreted here to support a syn-sedimentary component to the mineralising process at Johnnies Reward. However, definitive evidence for either a syngenetic or later timing for mineralisation is precluded by a lack of temporal constraints on mineralisation as well as constraints on ages for sedimentation, magmatism and metamorphism in the host succession.

Regional retrograde magnetite-chlorite alteration associated with epigenetic copper mineralisation

A distinct magnetite-chlorite-copper association is evident at several deposits and prospects across the Aileron Province (eg Johnnies Reward, *Gumtree*, Rockface, some parts of Green Parrot and Reward). This mineralisation has previously been suggested to be metamorphosed iron oxide copper-gold style with some affinities to deposits in Mount Isa and Tennant Creek (eg Hussey *et al* 2005, Corriveau and Spry 2014). Unlike the other deposit styles discussed already, these deposits and prospects can be distinguished because of their widespread magnetite-chlorite alteration and their greater copper endowment.

The recent discovery of high grade Cu-Ag-only mineralisation at Rockface in the Jervois mineral field (Mayes and Bennet 2017) is significant for two reasons. It represents another example of this distinct magnetite-chlorite-associated copper mineralisation style. More importantly, the mineralisation and alteration style at Rockface is distinct from the polymetallic sulfide mineralisation and alteration found at other nearby deposits and prospects (eg Green Parrot, Marshall, Reward, Hamburger Hill). Although the evidence for syn-sedimentary sulfide mineralisation in these other deposits is well established, the timing and origin of certain aspects of the mineralisation process remains unresolved, with ample evidence for both syn- and post-metamorphic alteration and remobilization.

Excepting Hamburger Hill, all these deposits also show strong evidence for epigenetic copper mineralisation commonly associated with magnetite and chlorite that overprints older syn-sedimentary mineralisation and alteration (McGloin and Weisheit 2015; **Figure 4a-b**). Although syn-sedimentary mineralisation and alteration zones in the Jervois mineral field can be carefully discerned using a combination of structural, textural and paragenetic mineral observations, precursor prograde metamorphic assemblages are commonly obscured or obliterated near to epigenetic mineralisation. The close proximity of the two mineralisation styles is fortuitous because it allows a direct comparison. Observing differences and similarities therefore allows the relative contributions of syngenetic and epigenetic mineralisation and alteration processes in the Jervois mineral field to be better understood.

Petrographic observations from drill core at Rockface demonstrate that copper was introduced after peak-pressure metamorphism, overprinting massive magnetite zones that formed post-D_2 (**Figures 4b-f**). This mineralisation also lacks lead and zinc enrichment characteristic of the nearby syn-sedimentary mineralisation. In drill core and photomicrographs, an earlier garnet-biotite assemblage can be seen breaking down to form magnetite and chlorite (**Figure 4b-d**).

A comparison of the Hamburger Hill prospect with the other syn-sedimentary mineralised deposits in the Jervois mineral field is also warranted. The Hamburger Hill prospect differs in that it is relatively unaltered, does not contain magnetite, and lacks evidence for pervasive retrograde magnetite-chlorite alteration (**Figure 2b**). Most importantly, there are stratabound zones of massive garnet–biotite enriched in Cu-Ag-Pb-Zn and no epigenetic copper mineralisation. These observations imply that the magnetite–chlorite alteration forms through the destruction of silicate minerals found in metaexhalites or associated alteration zones, and that this process is somehow related to later copper mineralisation.

Similarly, the retrograde alteration of silicate minerals is evident at the Johnnies Reward deposit. In **Figure 4g**, the mineralogy observed in drill core from Johnnies Reward changes over short distances. Chlorite can be seen as

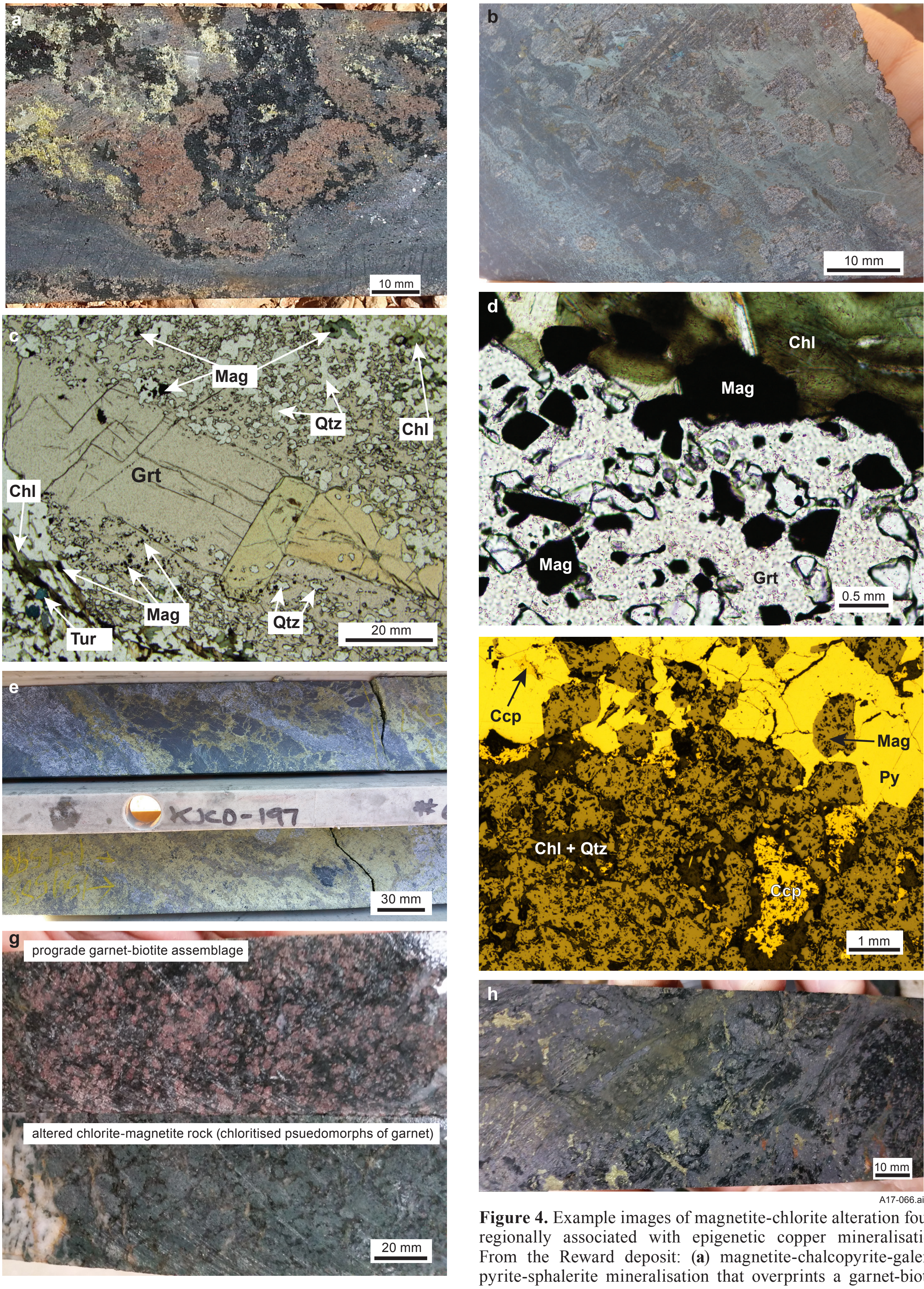

Figure 4. Example images of magnetite-chlorite alteration found regionally associated with epigenetic copper mineralisation. From the Reward deposit: (**a**) magnetite-chalcopyrite-galena-pyrite-sphalerite mineralisation that overprints a garnet-biotite assemblage. From the Rockface prospect: (**b**) magnetite-chlorite alteration that overprints an original garnet-biotite-rich assemblage; (**c**) photomicrograph showing the breakdown of garnet (Grt) to magnetite (Mag) and chlorite (Chl); Tur = tourmaline, Qtz = quartz; (**d**) photomicrograph showing a close-up of c; (**e**) typical chalcopyrite-pyrite mineralisation overprinting magnetite that also overprints the host rock assemblage; (**f**) photomicrograph showing the dominant mineral assemblage of magnetite, chalcopyrite (Ccp), pyrite (Py), chlorite and quartz. From the Johnnies Reward deposit: (**g**) comparison of garnet-biotite rock and altered chlorite-magnetite equivalent where chlorite can be seen as pseudomorphs after garnet porphyroblasts; (**h**) magnetite overprinted by chalcopyrite-pyrite with both overprinting an earlier garnet-biotite-rich assemblage.

pseudomorphs after garnet porphyroblasts, with the garnet–biotite assemblage breaking down progressively to form magnetite and chlorite that is overprinted by chalcopyrite-pyrite mineralisation (**Figure 4h**).

These regionally consistent observations suggest that some of the magnetite–chlorite alteration seen is generated by the retrograde, fluid-assisted breakdown of prograde garnet-biotite-rich alteration assemblages and associated iron-rich metaexhalites. If correct, this interpretation suggests that early syn-sedimentary hydrothermal processes may provide a fundamental control on the alteration associated with later epigenetic copper mineralisation regionally. However, it remains unclear whether copper that overprints the epigenetic magnetite-chlorite alteration is remobilized locally from pre-existing sulfide mineralisation, is introduced from more exotic sources such magmatic-hydrothermal fluids exsolved from felsic intrusions, or is leached from copper-rich country rocks during hydrothermal fluid circulation.

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