Reconstruction of an early Permian, sub-lacustrine magmatic-hydrothermal system: Mt Carlton epithermal Au-Ag-Cu deposit, northeastern Australia

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Abstract

The Mt Carlton Au-Ag-Cu deposit, northern Bowen Basin, northeastern Australia, is an uncommon example of a sub-lacustrine hydrothermal system containing economic high-sulfidation epithermal mineralization. The deposit formed in the early Permian and comprises vein- and hydrothermal breccia-hosted Au-Cu mineralization within a massive rhyodacite porphyry (V2 open pit) and stratabound Ag – barite mineralization within volcano-lacustrine sedimentary rocks (A39 open pit). These ore bodies are all associated with extensive advanced argillic alteration of the volcanic host rocks. Stable isotope data for disseminated alunite ($\delta^{34}S$ = +6.3 to +29.2 ‰; $\delta^{18}O_{SO4}$ = -0.1 to +9.8 ‰; $\delta^{18}O_{OH}$ = -15.3 to -3.4 ‰; δD = -102 to -79 ‰) and pyrite ($\delta^{34}S$ = -8.8 to -2.7 ‰), and void-filling anhydrite ($\delta^{34}S$ = +17.2 to +19.2; $\delta^{18}O_{SO4}$ = +1.8 to +5.7 ‰), suggest that early advanced argillic alteration formed within a magmatic-hydrothermal system. The ascending magmatic vapor ($\delta^{34}S_{\Sigma S} \approx -1.3$ ‰) was absorbed by meteoric water (~50 to 60 % meteoric component), producing an acidic (pH ≈ 1) condensate that formed a silicic → quartz – alunite → quartz – dickite – kaolinite zoned alteration halo with increasing distance from feeder structures. The oxygen and hydrogen isotopic compositions of alunite-forming fluids at Mt Carlton are lighter than those documented at similar deposits elsewhere, probably due to the high paleo-latitude (~S60°) of northeastern Australia in the early Permian. Veins of coarse-grained, banded plumose alunite ($\delta^{34}S$ = +0.4 to +7.0 ‰; $\delta^{18}O_{SO4}$ = +2.3 to +6.0 ‰; $\delta^{18}O_{OH}$ = -10.3 to -2.9 ‰; δD = -106 to -93 ‰) formed within feeder structures during the final stages of advanced argillic alteration. Epithermal mineralization was deposited subsequently, initially as fracture- and fissure-filling, Au-Cu-rich assemblages within feeder structures at depth. As the mineralizing fluids discharged into lakes, they produced syngenetic Ag – barite ore. Isotope data for ore-related sulfides and sulfosalts ($\delta^{34}S$ = -15.0 to -3.0 ‰) and barite ($\delta^{34}S$ = +22.3 to +23.8 ‰; $\delta^{18}O_{SO4}$ = -0.2 to +1.3 ‰), and microthermometric data for primary fluid inclusions in barite (Th = 116 to 233°C; 0.0 to 1.7

wt.% NaCl), are consistent with metal deposition at temperatures of ~200 ± 40°C (for Au-Cu mineralization in V2 pit) and ~150 ± 30°C (Ag mineralization in A39 pit) from a low-salinity, sulfur- and metal-rich magmatic-hydrothermal liquid that mixed with vapor-heated meteoric water. The mineralizing fluids initially had a high-sulfidation state, producing enargite-dominated ore with associated silicification of the early-altered wall rock. With time, the fluids evolved to an intermediate-sulfidation state, depositing sphalerite- and tennantite-dominated ore mineral assemblages. Void-filling massive dickite ($\delta^{18}O$ = -1.1 to +2.1 ‰; δD = -121 to -103 ‰) with pyrite was deposited from an increasingly diluted magmatic-hydrothermal fluid (≥70 % meteoric component) exsolved from a progressively degassed magma. Gypsum ($\delta^{34}S$ = +11.4 to +19.2 ‰; $\delta^{18}O_{SO4}$ = +0.5 to +3.4 ‰) occurs in veins within post-mineralization faults and fracture networks, likely derived from early anhydrite that was dissolved by circulating meteoric water during extensional deformation. This process may explain the apparent scarcity of hypogene anhydrite in lithocaps elsewhere. While the Mt Carlton system is similar to those that form subaerial high-sulfidation epithermal deposits, it also shares several key characteristics with magmatic-hydrothermal systems that form base- and precious-metal mineralization in shallow-submarine volcanic arc and backarc settings. The lacustrine paleosurface features documented at Mt Carlton may be useful as exploration indicators for concealed epithermal mineralization in similar extensional terranes elsewhere.

Introduction

The Mt Carlton Au-Ag-Cu deposit is located within an extensively mineralized, lower Permian volcano-sedimentary succession in the northern Bowen Basin, northeastern Queensland, Australia (Fig. 1). The deposit was discovered in 2006 and contains a total resource of 11.9 Mt averaging 2.8 g/t Au, 28 g/t Ag and 0.44 % Cu (as of December 2017; M. Obiri-Yeboah, pers.

commun., 2018; Evolution Mining, 2019). The mining operation at Mt Carlton includes the larger V2 open pit in the NE – producing 112 koz Au with a processed grade of 5.6 g/t Au in 2018 (Evolution Mining, 2019) – and the smaller A39 open pit in the SW (Fig. 2).

Previous studies (Dugdale and Howard, 2017; Sahlström et al., 2017, 2018) indicated that Mt Carlton has many characteristics typical of high-sulfidation (HS) epithermal deposits (Arribas, 1995a; Hedenquist et al., 2000). Key among these are its tectonic setting within a volcanic arc (in this case, a backarc rift); intermediate-composition, calc-alkaline volcanic host rocks (rhyodacite porphyry and tuff) with an age similar to that of mineralization; laterally extensive, zoned advanced argillic alteration of magmatic-hydrothermal origin (Rye et al., 1992); and a HS ore mineral assemblage dominated by enargite (Einaudi et al., 2003). However, Mt Carlton differs from other HS epithermal deposits in that a lacustrine, shallow-water vent facies contains economic mineralization. Other notable features of Mt Carlton are well-defined mineral and metal zonation patterns in both time and space and its early Permian age (~280 Ma; Sahlström et al., 2018), which places Mt Carlton among the world's oldest non-metamorphosed HS epithermal deposits.

This study examines the genetic processes at Mt Carlton, building on the geological framework and mineral paragenesis studies presented by Sahlström et al. (2018). Emphasis is placed on the stable isotope and fluid inclusion systematics of the alteration and ore mineral assemblages, and the implications for processes within the magmatic-hydrothermal, magmatic-steam, and supergene environments (Rye et al., 1992; Rye, 2005). Our main objective is to reconstruct the Mt Carlton magmatic-hydrothermal system and to make comparisons to the generally much younger magmatic-hydrothermal systems that form comparable subaerial or shallow-water mineral deposits elsewhere. Some implications for mineral exploration are also discussed.

Regional Setting

The New England Orogen extends from eastern New South Wales to northeastern Queensland along the eastern coast of Australia (Fig. 1A), and may extend further offshore (Mortimer et al., 2008). It was a dynamic continental margin active mainly during the Carboniferous and Permian (Donchak et al., 2013). The Bowen Basin is an elongate, early Permian-Middle Triassic sedimentary basin that formed inland of the New England Orogen (Fig. 1). This basin is the northern continuation of a larger basin system that also includes the Sydney and Gunnedah basins (Korsch and Totterdell, 2009; Korsch et al., 2009; Donchak et al., 2013). The Bowen Basin opened in the early Permian, as a result of backarc extension within the lower Paleozoic metamorphic and sedimentary basement. Backarc rifting produced a series of isolated grabens and half-grabens that were filled with volcanic and sedimentary rocks (Esterle et al., 2002). The Lizzie Creek Volcanic Group and its associated hydrothermal mineral systems formed in the northern Bowen Basin during this stage. Hydrothermal activity mostly produced sub-economic porphyry and epithermal prospects (Fig. 1B), but the recent discovery of Mt Carlton has confirmed the potential for economic mineralization in the region.

Backarc rifting was followed in the middle Permian by thermal relaxation, widespread marine transgression, and deposition of shallow-water sediments (Malone et al., 1969; Allen and Fielding, 2007; Korsch and Totterdell, 2009; Korsch et al., 2009). In the late Permian, a series of westward-stepping orogenic fronts formed as a consequence of the ~265 – 235 Ma Hunter-Bowen Orogeny, causing tectonic inversion and development of a foreland basin sequence on top of the backarc basin (Donchak et al., 2013). Infilling by terrestrial sediments and thick coal measures in the foreland basin proceeded until the Bowen Basin closed in the Middle Triassic (Fielding et al., 1990; Fergusson, 1991; Holcombe et al., 1997; Esterle et al., 2002).

Mt Carlton HS Epithermal Deposit

Tectono-stratigraphic evolution

The crystalline basement in the Mt Carlton area is formed of fine- to medium-grained monzogranites of the Urannah Batholith (Unit 1, ~302-296 Ma; Sahlström et al., 2018; I. Corral, unpub. data, 2018). The basement is overlain by a sequence of volcanic and sedimentary rocks belonging to the lower Permian Lizzie Creek Volcanic Group (~288-275 Ma; Sahlström et al., 2018; I. Corral, unpub. data, 2018). From bottom to top, the Lizzie Creek sequence exposed near the open pits at Mt Carlton consists of (Fig. 3): fine-grained andesite lava and minor volcaniclastic rocks (Unit 2); massive, locally flow-banded, porphyritic rhyodacite and minor rhyolite lava (Unit 3); well-bedded, fragmental, rhyodacitic lapilli tuff with interbedded carbonaceous lacustrine sediments (Unit 4A); massive, bedded dacitic tuffs (Unit 4B); volcaniclastic dacitic rocks including ignimbrites (Units 5A-C); fragmental andesite with local rounded boulders (Unit 6); coal-bearing volcano-sedimentary rocks of andesitic to dacitic composition (Unit 7); and strongly flow-banded porphyritic rhyolite (Unit 8). Whereas Units 2 and 8 are regionally continuous, Units 3-7 are laterally discontinuous due to deposition during active rifting and exhibit facies variability typical of volcanic-dome complex environments, the most common setting for HS epithermal deposits (Sillitoe, 1999; Hedenquist et al., 2000). Mineralization is hosted partly in massive and flow-banded rhyodacite porphyry (Unit 3), and partly in overlying volcano-lacustrine sedimentary rocks (Unit 4A; Fig. 3; Sahlström et al., 2018).

Hydrothermal alteration and mineralization at Mt Carlton occurred at ~280 Ma, during high-angle normal faulting in response to both E-W and N-S extension, partly contemporaneously with deposition of volcanic sediments into localized half-graben and graben basins (D_1; Sahlström et al., 2018). Continued E-W extension in the northern Bowen

Basin caused Mt Carlton to be buried beneath volcano-sedimentary cover, which contributed to the preservation of the deposit. Extension also produced a series of low-angle, locally layer-parallel normal faults that cut across the mineralized rock pile (D_2). In the northern wall of the V2 pit, D_2 faults are crosscut by a younger, rhyodacitic volcanic vent that was emplaced at ~266 Ma (Sahlström et al., 2018; I. Corral, unpub. data, 2018). High-angle normal faulting in response to N-S extension with an overall S-down movement (D_3) was followed by block rotation of kilometer-scale lithological domains across steep NNW-trending normal faults and ENE-trending cross faults (D_4). A NNW-trending D_4 normal fault separates the V2 and A39 pits, and has caused segmentation of the stratigraphy, the ore zones and the alteration halo of Mt Carlton. Primary sedimentary layering and mineralization have been reoriented locally. Due to D_4 block rotation, mineralization in the A39 pit now plunges ~32° to the WSW, whereas mineralization in the V2 pit retains its originally steep orientation (Figs. 2, 3). Emplacement of plagioclase – pyroxene ± hornblende phyric basaltic dikes into pre-existing high-angle faults (D_5) was followed by dextral-dominant strike-slip faulting along the dike margins (D_6). The final deformation stage at Mt Carlton involved emplacement of WNW-trending, feldspar phyric basaltic dikes containing quartz amygdules (D_7), which may be linked to basaltic flows that occur west of the pit area (Sahlstrom et al., 2018).

As a result of post-mineralization deformation, the deeper parts of the mineralized feeder system and the causative intrusion (including any potentially associated porphyry mineralization) are expected to be displaced from the current location of the Mt Carlton HS epithermal deposit (Sahlström et al., 2018). The rhyodacite package that hosts Mt Carlton is divided into two tectonic blocks that are internally intact (V2 and A39 blocks; Fig. 3A), such that the magmatic-hydrothermal system is undisturbed over several hundred meters.

Paragenetic sequence

A paragenetic sequence of alteration and ore minerals at Mt Carlton was established by Sahlström et al. (2018) based on overprinting and crosscutting relationships (Fig. 4). Stage 1A is represented within the host volcanic units by alteration assemblages that are zoned outward, away from the paleo-fluid conduits as follows: silicic (locally with vuggy texture) → quartz – alunite → quartz – dickite – kaolinite (Figs. 3, 4). This alteration halo envelops mineralization in Units 3 and 4A and has a lateral extent of several hundred square meters. The silicic zones have a gradational contact with the surrounding quartz – alunite zones. Stage 1A alunite is typified by up to ~300 μm long, pink to red, euhedral and platy crystals that are either disseminated in microcrystalline quartz, or aggregated, replacing feldspar phenocrysts or filling vugs (Figs. 5A-B). Alunite has compositions within the alunite – natroalunite solid solution series [trigonal $KAl_3(SO_4)_2(OH)_6$ – $NaAl_3(SO_4)_2(OH)_6$]. The crystals are commonly zoned with respect to Na and K contents, locally with cores of aluminium-phosphate-sulphate (APS) minerals of the woodhouseite – svanbergite solid solution series [trigonal $CaAl_3(SO_4)(PO_4)(OH)_6$ – $SrAl_3(SO_4)(PO_4)(OH)_6$], typical of magmatic-hydrothermal alunite (c.f., Rye et al., 1992; Rye, 2005). Finely disseminated pyrite generally co-exists with alunite (Fig. 5A). Anhydrite, which is rarely reported in HS epithermal deposits and lithocaps, is present locally within the silicic cores (Fig. 4). It occurs as euhedral, tabular crystals, locally in massive aggregates, that fill open spaces (Fig. 5E). However, most of the Stage 1A anhydrite was dissolved, leaving behind distinctive casts (Fig. 5F).

Alunite also occurs in monomineralic veins within the silicic alteration zones (Stage 1B; Figs. 4, 5A, 5C-D, 6C; Sahlström et al., 2018). The Stage 1B veins generally post-date silicic alteration and exhibit a banded arrangement of coarse, plumose alunite crystals. They are texturally similar to the type occurrence of magmatic-steam alunite at Marysvale, Utah (Cunningham et al., 1984; Rye et al., 1992; Rye, 2005).

Epithermal mineralization at Mt Carlton evolved temporally with respect to metal contents and mineral assemblages. Stage 2 of the paragenetic sequence comprises three sub-stages (Stages 2A-C; Fig. 4; Sahlström et al., 2018), all hosted mainly within the silicic cores. The initial stage of Cu-Au-Ag mineralization is dominated by enargite, a HS state sulfosalt, and is associated with barite gangue as well as silicification of the early-altered wall rocks (Stage 2A; Figs. 4, 5G, 6A-D). The Stage 2A assemblage is crosscut by a younger, well-developed stage of Zn-Pb-Au-Ag mineralization dominated by Fe-poor (<350 ppm Fe) sphalerite, with tetrahedrite-group minerals and chalcopyrite present, indicating an intermediate-sulfidation (IS) state (Stage 2B; Figs. 4, 6C-D; Sahlström et al., 2017). Stage 2B mineralization is overprinted by another IS stage that is rich in Cu, Au and Ag (Stage 2C; Fig. 4). The Stage 2C mineral assemblage is dominated by tennantite, visible at a microscopic scale. Late-stage, voluminous hydrothermal void fill of massive, microcrystalline dickite with pyrite overprinted Stage 2 mineralization throughout Mt Carlton (Stage 3; Figs. 4, 5G, 6D-E).

Pervasive illite – montmorillonite ± red hematite alteration developed during the D_2 deformation event, affecting Units 2, 4, 5 and 6 in the area near the open pits (Stage 4; Figs. 3, 4). Veins of fibrous gypsum with a well-developed shear fabric occur near the major D_2 and D_3 faults (Fig. 5H). Finally, a suite of secondary Cu-bearing ore minerals, including covellite, chalcocite and malachite, have locally overprinted the Stage 2 ore assemblages, caused by recent supergene oxidation in the upper ~50 meters of the present-day deposit (Stage 5; Fig. 4; Sahlström et al., 2018).

Alteration and mineralization zonation

The alteration and mineralization at Mt Carlton produced distinct spatial zonation patterns across the deposit. In the V2 pit, Au-Cu mineralization occurred in paleo-fluid conduits in the rhyodacite porphyry (Unit 3), producing steeply dipping veins and hydrothermal breccia (Fig.

6A). The mineralized fracture systems have predominantly NE to NNE trends, and three distinct ore zones (Eastern, Western and Link; Fig. 2) are aligned in an en echelon fashion along a broadly E-trending corridor. The Western ore zone extends ~600 m to the SW, into the A39 pit, and it exhibits a well-defined metal zonation along strike from NE to SW of: Au-Cu → Cu-Zn-Pb-Ag → Ag-Pb-(Cu) → Ag (Figs. 2, 3). Along the same spatial trend, the Na-content of Stage 1A disseminated alunite in the alteration halo decreases (Sahlström et al., 2018). Furthermore, the abundance of both APS minerals and pyrite associated with disseminated alunite decreases to the SW, and both minerals are largely absent in the SW parts of the deposit. Stage 1B plumose alunite veins are predominantly concentrated in the high-grade feeder structures in the V2 pit. However, they have also been observed locally in small veins occurring distal to the main feeders, including in the A39 pit.

Silver mineralization is concentrated in the A39 pit within the volcano-lacustrine sedimentary rocks (Unit 4A) that overlie the rhyodacite porphyry (Fig. 3). In A39 pit, mineralization is stratabound and oriented parallel to primary sedimentary bedding. Hydrothermal features observed in rocks from A39 pit include: 1) voluminous deposits of finely laminated quartz sediment (interpreted as recrystallized from amorphous silica; Sillitoe, 2015); 2) massive layers of spherulitic pyrite and dickite; 3) skeletal aggregates of enargite and luzonite; and 4) a variety of synsedimentary deformation textures, such as growth faults and soft-sediment slumping and fluidization structures (Figs. 6B, 6D-E; Sahlström et al., 2018, their Figure 13). Barite is present in minor amounts in the V2 pit, occurring as up to ~0.5 cm diameter crystals intergrown with massive enargite or sphalerite. Barite is primarily concentrated in the A39 pit, where it occurs as disseminated to massive accumulations closely associated with, and capping, the Ag mineralization. In A39 pit, barite locally also occurs as coarse-grained halos to enargite veinlets (Fig. 7B). Barite at Mt Carlton is highly enriched in Pb (average 1.3 wt.%), and to a lesser degree, in Sr (solid solution toward hokutolite:

[Ba,Pb,Sr]SO_4; Sahlström et al., 2017). Because galena and other Pb-rich minerals are volumetrically minor in the A39 pit, the distal geochemical anomaly of Pb observed there (Figs. 2, 3) essentially outlines the spatial distribution of barite.

Overall, these observations consistently indicate that, at the time of ore formation, the position of the stratigraphic sequence in the V2 pit was deep and intrusion-proximal relative to the sequence in the A39 pit. Mineralization in A39 pit has been interpreted to have formed essentially at the paleosurface in a sub-lacustrine environment (Sahlström et al., 2018).

Fluid Inclusions

Petrography

Suitable host minerals for fluid inclusion study are typically uncommon in HS epithermal deposits (Arribas, 1995a), which also limited this study. Aqueous fluid inclusions occur in igneous quartz phenocrysts within the silicic and quartz – alunite alteration zones at Mt Carlton. Although lacking temporal information, such inclusions can provide insights into the fluid regime in HS epithermal deposits (e.g., Bruha and Noble, 1993; Arribas et al., 1995, Ruggieri et al., 1997; Corral et al., 2017). There is evidence for hydrothermal fluids being trapped along fractures in quartz phenocrysts during alteration (e.g., replacement of primary melt inclusions by hydrothermal illite in quartz phenocrysts at the Rodalquilar HS epithermal deposit, Spain; Arribas et al., 1995, their Figure 8G). In the studied sections from Mt Carlton, quartz phenocrysts exhibit fractures and corrosion textures, which are infilled with Stage 1A hydrothermal quartz and alunite (Fig. 7A). Fluid inclusions locally occur in trails that propagate from such fractures or from the quartz crystal boundaries (Fig. 7C), and are interpreted to be secondary in nature (Roedder, 1984). The inclusion trails cannot be observed to crosscut quartz crystal boundaries, due to the microcrystalline texture of the surrounding minerals (Fig. 7A). The inclusions range from <1 to ~35 μm in diameter, and have irregular to sub-rounded shapes.

They are two-phase and liquid-rich, with a dark vapor bubble typically occupying up to ~30 vol.% of the inclusion (Fig. 7C).

Aqueous fluid inclusions are also present in barite associated with Stage 2A mineralization, as isolated, two-phase liquid-vapor inclusions with up to ~30 vol.% vapor (Fig. 7D). The inclusions are irregular to sub-rounded, up to ~15 µm in diameter, and are interpreted as primary based on the criteria of Roedder (1984). The primary inclusion fields are crosscut by trails of small (<2 µm) monophase liquid inclusions that also crosscut cleavage planes and barite crystal boundaries. These secondary fluid inclusions (Roedder, 1984) were not studied as they represent late-stage fluids not related to mineralization.

Methods

Microthermometric measurements of fluid inclusions were conducted at the Department of Geosciences, James Cook University, Australia, on doubly polished sections (~200 µm thick) using a Linkam MDS600 heating-freezing stage. The instrument was calibrated by measuring the melting temperature of CO_2 (−56.6°C) in synthetic H_2O-CO_2 fluid inclusions, and the melting point of pure H_2O (0°C) in synthetic H_2O fluid inclusions. The two-phase fluid inclusions in quartz and barite were observed for final melting of ice (Tm; $\text{ice} + \text{liq}_{aq} + \text{vap} \rightarrow \text{liq}_{aq} + \text{vap}$) and homogenization into the liquid phase (Th; $\text{liq}_{aq} + \text{vap} \rightarrow \text{liq}_{aq}$). The instrument reproducibility is generally ±0.5°C during Tm measurements and ±5°C during Th measurements. Salinities and densities were calculated from final ice melting and homogenization temperatures using the HOKIEFLINCS_H2O-NACL spreadsheet (Steele-MacInnis et al., 2012).

Results

Secondary fluid inclusions in quartz phenocrysts – Microthermometric measurements of secondary fluid inclusions in quartz phenocrysts were done on two samples collected from the proximal (V2 pit) and distal (A39 pit) parts of Mt Carlton, respectively (Fig. 8; Table 1). Measurements of 57 inclusions in the proximal sample (MCR024D-177) yielded a Th range of 163 to 264°C (Figs. 8, 9; Table 1). The fluid inclusions appeared to melt instantaneously at their final melting point and no initial melting could be observed, indicating that NaCl is the dominant solute. The Tm values range between -0.9 and 0.0°C, corresponding to salinities between 0.0 and 1.6 wt.% NaCl. The fluid inclusion densities range between 0.77 and 0.91 g/cm^3. Measurements of 72 inclusions in the distal sample (HC14DD1133-178) yielded partly overlapping, but generally lower Th values, between 137 and 231°C, and Tm values between -0.7 and 0.0°C (0.0 and 1.2 wt.% NaCl; Figs. 8, 9; Table 1). The fluid inclusion densities range between 0.82 and 0.93 g/cm^3.

Primary fluid inclusions in barite – Primary fluid inclusions in Stage 2A barite were measured from two samples – one from the V2 pit (proximal) and another from the A39 pit (distal; Fig. 8; Table 1). The sample from V2 pit (V2-ORE-2) is a high-grade vein that contains barite crystals intergrown with massive enargite ore, whereas the sample from A39 pit (HC10RCD935-168) is an enargite veinlet that has coarse-grained barite in its halo (Fig. 7B). Barite-hosted fluid inclusions are particularly susceptible to stretching during freezing and heating (Ulrich and Bodnar, 1988). However, after measurements in this study, no petrographic evidence for stretching (i.e., visible change in the size of the vapor bubble, or fracturing after the heating-freezing experiments) was observed, and repeat measurements were within error.

Measurements of 38 inclusions in the proximal sample (V2-ORE-2) yielded a Th range of 157 to 233°C (Figs. 8, 9; Table 1). Similar to the quartz phenocryst-hosted fluid inclusions, these inclusions melted instantaneously at their final melting point and no initial melting could be observed. Final melting of ice ranges between -1.0 to -0.2°C, corresponding to salinities between 0.4 and 1.7 wt.% NaCl. The densities of the fluid inclusions range between 0.82 and 0.92 g/cm^3. Measurements of 32 inclusions in the distal sample (HC10RCD935-168) yielded

Th values varying between 116 and 183°C and a Tm range of -0.2 to 0.0°C (Figs. 8, 9; Table 1). These measurements indicate salinities and densities ranging between 0.0 and 0.4 wt.% NaCl and between 0.89 and 0.95 g/cm^3, respectively.

Interpretations

Previous studies of primary fluid inclusions hosted in enargite from other HS epithermal deposits have reported a wide range of salinities, from 0.2 to 20.4 wt.% NaCl (Deen et al., 1994; Mancano and Campbell, 1995; Arribas, 1995a; Kouzmanov, 2001; Bailly et al., 2002; Sillitoe and Hedenquist, 2003; Moritz et al., 2004). However, a study by Moritz (2006) found that salinities obtained for fluid inclusions in enargite were commonly overestimated due to heating of the sample by the infrared light source used during measurements (e.g., salinities of ~20 wt.% NaCl were actually <2 wt.% NaCl). At the El Indio HS epithermal deposit, Chile, quartz associated with enargite contains fluid inclusions with salinities of 2.9 to 4.6 wt.% NaCl, whereas the salinity of the later, Au-rich stage is <1.7 wt.% NaCl (Jannas et al., 1990). The primary fluid inclusions in barite measured here show relatively low salinities (<1.7 wt.% NaCl), similar to those identified from the study of enargite- and quartz-hosted fluid inclusions from other HS epithermal deposits. It remains unclear whether the secondary fluid inclusions in quartz phenocrysts at Mt Carlton formed during early advanced argillic alteration (as suggested by their intimate association with Stage 1A quartz and alunite; Fig. 7A) or from later mineralizing fluids. However, the overlap in density and salinity between the quartz-hosted and barite-hosted fluid inclusions, and identical Tm *vs.* Th trends (Fig. 9C-D), indicate that the two fluid inclusion assemblages formed from similar fluids at similar temperatures. Geologic evidence indicates that Mt Carlton formed at shallow depth (Sahlström et al., 2018), such that the temperature of homogenization was close to the trapping temperature of the fluid inclusions (Wilkinson, 2001).

The two principal ore-forming physical processes occurring in the epithermal environment are fluid mixing and fluid boiling (Giggenbach and Stewart, 1982; Hedenquist et al., 1992). Microthermometric data for both secondary fluid inclusions in quartz phenocrysts (Fig. 9C) and primary fluid inclusions in Stage 2A barite (Fig. 9D) at Mt Carlton show a dominant mixing trend, where higher Th values and salinities are shifted to Th values of ~150 ± 40°C at nil salinity. This trend is interpreted to reflect dilution and the resultant cooling of a hydrothermal fluid during outflow from the deep area of the causative intrusion (c.f., Arribas, 1995, and references therein; Mancano and Campbell, 1995; Hedenquist et al., 1998). The diluent is most likely magmatic vapor-heated meteoric groundwater, typical of that on the deep margins of geothermal systems (Hedenquist, 1990, 1991). Additionally, the well-developed hydrothermal breccias observed in the feeder zones at Mt Carlton (Fig. 6A) would have been associated with sharp decreases in pressure that likely would have led to local flashing and boiling (e.g., Hedenquist and Henley, 1985; Sillitoe, 1985). A shift to lower Tm and Th values due to boiling could potentially explain some of the scatter in the fluid inclusion data (Fig. 9C-D; e.g., Shepherd et al., 1985; Wilkinson, 2001). Alternatively, the scatter could simply be related to variability in the trapping of the fluid inclusions.

Stable Isotopes

Methods

Mineral samples for stable isotope study were collected from drill cores and exposures in the Mt Carlton open pits. Rocks were crushed, sieved into size fractions of 300-500 μm and 110-300 μm, and cleaned in an ultrasonic bath; mineral separates were then obtained by hand picking under a stereo microscope. The paragenetic stages studied include: Stage 1A, early advanced argillic alteration (alunite, pyrite and anhydrite separates); Stage 1B, plumose alunite veins; Stage 2A, Cu-Au-Ag mineralization (pyrite, enargite and barite); Stage 2B, Zn-Pb-Au-

Ag mineralization (pyrite, sphalerite and galena); Stage 2C, Cu-Au-Ag mineralization (tennantite); Stage 3, late-hydrothermal void fill (dickite); and Stage 4, post-hydrothermal gypsum veins. Backscatter electron (BSE) imaging revealed no more than trace to minor amounts (<10 vol.%) of contaminating quartz, clays or sulfides in the separates.

Sulfur isotope analyses of sulfates, sulfides and sulfosalts – Sulfur isotope analyses were conducted in laboratories of the Geology, Geophysics and Geochemistry Science Center, U.S. Geological Survey, Denver, Colorado, USA. Mineral separates were analyzed for δ^{34}S using a CE Elantech Inc. Flash 2000 elemental analyzer coupled to a ThermoFinnigan Delta Plus XP mass spectrometer (Johnson et al., 2018). The system was calibrated with NBS-127 and IAEA-SO-6 standards (for sulfate analysis) or NBS-123 and IAEA-S-3 standards [for sulfide and sulfosalt analysis, the accepted compositions for which were taken from Brand et al. (2014)]. The δ^{34}S values are reported in per mil relative to Vienna Cañon Diablo Troilite (VCDT) with a precision of 0.2 ‰ based on replicate analyses.

Oxygen and hydrogen isotope analyses of sulfates – In order to isolate the SO_4 molecule in alunite, anhydrite and gypsum, mineral separates were dissolved in a sodium hydroxide solution and reprecipitated as $BaSO_4$, using methods described by Carmody et al. (1998). Mineral samples and $BaSO_4$ precipitates were weighed into silver capsules and analysed for δ^{18}O (alunite, barite, anhydrite and gypsum) and δD (alunite) at the U.S. Geological Survey in Denver, using a ThermoFinnigan high-temperature conversion elemental analyzer coupled to a ThermoFinnigan Delta Plus XL mass spectrometer. The complete set of isotope data for alunite was obtained following the methodology of Wasserman et al. (1992). The mass spectrometer system was calibrated by using the IAEA-SO-5 and IAEA-SO-6 standards (for δ^{18}O measurements) or a series of reference materials that included IAEA-CH-7 and NBS-22 standards (Brand et al., 2014) as well as kaolinite and benzoic acid internal standards (for δD measurements). Isotopic compositions are reported in per mil relative to Vienna Standard Mean

Ocean Water (VSMOW) with a reproducibility of ± 1 ‰ for $\delta^{18}O$ and ± 4 ‰ or better for δD, based on replicate analyses.

Oxygen and hydrogen isotope analyses of dickite – Samples of dickite were analyzed for oxygen and hydrogen isotopes at the GNS Stable Isotope Laboratories in Wellington, New Zealand. Oxygen was extracted from sample powders using a CO_2 laser and BrF_5, and subsequently analyzed for $\delta^{18}O$ in a Geo20-20 mass spectrometer (Sharp, 1990). Samples were analyzed alongside, and normalized to, international standards NBS-28 and UWG-2 (Brand et al., 2014). The δD analyses were done using a HEKAtech high-temperature elemental analyzer coupled to a GV Instruments IsoPrime mass spectrometer, following reduction of the samples in silver capsules at 1450°C. The system was calibrated with IAEA-CH-7, NBS-30 and NBS-22 standards (Brand et al., 2014). The data are reported in per mil relative to VSMOW with a reproducibility of ± 0.2 ‰ for $\delta^{18}O$ and ± 2 ‰ or better for δD.

Results

Alunite, pyrite and anhydrite (Stage 1A) – Disseminated alunite of Stage 1A alteration (Figs. 5A-B, 7A) has variable $\delta^{34}S$ (+6.3 to +29.2 ‰), $\delta^{18}O_{SO4}$ (-0.1 to +9.8 ‰), $\delta^{18}O_{OH}$ (-15.3 to -3.4 ‰) and δD (-102 to -79 ‰) values (Figs. 10, 11; Table 2). Pyrite that co-precipitated with this alunite has $\delta^{34}S$ values between -8.8 and -2.7 ‰, whereas void-filling Stage 1A anhydrite (Fig. 5E) has narrow ranges of $\delta^{34}S$ (+17.2 to +19.2 ‰) and $\delta^{18}O_{SO4}$ (+1.8 to +5.7 ‰) values (Fig. 10; Table 2). The sulfur isotope compositions of Stage 1A alunite, pyrite and anhydrite from Mt Carlton are similar to those reported for magmatic-hydrothermal sulfates and sulfides from HS epithermal deposits elsewhere (e.g., Hedenquist and Garcia, 1990; Rye et al., 1992; Vennemann et al., 1993; Arribas, 1995a; Hedenquist et al., 1998; Rye, 2005; Bethke et al., 2005).

Plumose alunite veins (Stage 1B) – Alunite forms from acidic hydrothermal fluids generated through the condensation of magmatic vapor into groundwater (magmatic-hydrothermal alunite; Rye et al., 1992; Rye, 2005). In addition, alunite is argued to also form from expanding SO_2-rich magmatic vapor that rises rapidly from a degassing magma. Such magmatic-steam alunite (Rye et al., 1992; Rye, 2005) typically occurs as monomineralic, banded and plumose alunite in open tension fractures and breccias. It is predicted to have $\delta^{34}S$ values near that of the total sulfur value (due to sulfur isotopic disequilibrium among the parental aqueous sulfur species); the δD and $\delta^{18}O_{SO4}$ values are near magmatic values, with $\delta^{18}O_{OH}$ values in equilibrium with the fluid unless OH underwent retrograde exchange (Rye et al., 1992; Rye, 2005; Fifarek and Rye, 2005).

At Mt Carlton, plumose alunite in veins (Stage 1B; Figs. 4, 5C-D, 6C) has $\delta^{34}S$ values of +0.4 to +7.0 ‰, noticeably lower than the values of Stage 1A disseminated alunite yet distinctly higher than the value for total sulfur (Fig. 10; Table 2). The highest $\delta^{34}S$ values correspond to samples collected outside the main feeder zones, including one sample from the A39 pit (Table 2). The $\delta^{18}O_{SO4}$ (+2.3 to +6.0 ‰) and $\delta^{18}O_{OH}$ (-10.3 to -2.9 ‰) values overlap those of Stage 1A alunite, whereas the δD values (-106 to -93 ‰) overlap or are slightly lower than Stage 1A values (Fig. 11; Table 2).

Ore minerals and barite (*Stage 2)* – Sulfides and sulfosalts formed during Stage 2 have negative $\delta^{34}S$ values: -8.0 to -5.0 ‰ for Stage 2A pyrite, -9.9 to -3.0 ‰ for Stage 2A enargite, -6.6 to -4.4 ‰ for Stage 2B pyrite, -15.0 to -6.8 ‰ for Stage 2B galena, -6.8 to -4.5 ‰ for Stage 2B sphalerite, and -9.1 ‰ for Stage 2C tennantite (Fig. 10; Table 2). Barite that formed with Stage 2A enargite has $\delta^{34}S$ values of +22.3 to +23.8 ‰ and $\delta^{18}O_{SO4}$ values of -0.2 to +1.3 ‰ (Fig. 10; Table 2).

Void-filling dickite (Stage 3) – Stage 3 massive dickite (Fig. 5G) has $\delta^{18}O$ values of -1.1 to +2.1 ‰ and δD values of -121 to -103 ‰ (Fig. 11; Table 2).

Gypsum veins (Stage 4) **–** Gypsum in Stage 4 veins (Figs. 4, 5H) has $\delta^{34}S$ values between +11.4 and +19.2 ‰ and $\delta^{18}O_{SO4}$ values between +0.5 and +3.4 ‰ (Fig. 10; Table 2). These isotopic compositions overlap those of Stage 1A and Stage 2A sulfates (Fig. 10; Table 2).

Interpretation

Total sulfur composition and redox state of the magmatic-hydrothermal system – Co-precipitated, magmatic-hydrothermal alunite and pyrite in HS epithermal deposits typically retain sulfur isotope equilibrium (Rye et al., 1992; Rye, 2005). Assuming sulfate-sulfide equilibrium, the approximate redox state (H_2S/SO_4) of the fluid and the $\delta^{34}S$ value of total sulfur ($\delta^{34}S_{\Sigma S}$) were estimated using a $\delta^{34}S_{alunite}$ and $\delta^{34}S_{pyrite}$ *vs.* $\Delta\delta^{34}S_{alunite\text{-}pyrite}$ plot (Field and Gustafson, 1976; Kusakabe et al., 1984; Field et al., 2005). The resulting $\delta^{34}S_{\Sigma S}$ value during early Stage 1A advanced argillic alteration at Mt Carlton is approximately -1.3 ‰ (Fig. 10). This value is similar to total sulfur values reported from HS epithermal and porphyry Cu systems related to I-type granites, and is consistent with a magmatic source for the sulfur (Ohmoto and Rye, 1979; Hedenquist and Lowenstern, 1994; Arribas, 1995a). The approximate values of X_{H2S} and X_{SO4} are 0.85 and 0.15, respectively, which correspond to a H_2S/SO_4 of 5.7. This value is within the range of H_2S/SO_4 values reported for other HS epithermal deposits (4 ± 2; Rye et al., 1992; Hedenquist et al., 1994; Arribas, 1995a).

Geothermometry – Sulfur isotope fractionation between alunite and pyrite in the magmatic-hydrothermal environment is argued to be a robust geothermometer (Rye et al., 1992; Rye, 2005). Temperatures were calculated for 10 Stage 1A alunite – pyrite pairs from Mt Carlton, using the fractionation factor of Ohmoto and Rye (1979), yielding an average of 207°C. Alunite – pyrite pairs from the V2 pit show a temperature range of 152 to 251°C (n = 8; Fig. 8; Table

2), which compares well with homogenization temperatures measured in secondary fluid inclusions in quartz phenocrysts (163-264°C, average 222°C; Figs. 8, 9; Table 1).

Geothermometry based on oxygen isotope fractionation between SO_4 and OH in alunite was calculated using the fractionation factor of Stoffregen et al. (1994), yielding unrealistically low equilibrium temperatures of -91 to 81°C (average 22°C) for Stage 1A disseminated alunite and -31 to 95°C (average 18°C) for Stage 1B plumose alunite (not shown in Table 2). We interpret this to be caused by retrograde isotopic exchange between water and OH in alunite, as previously suggested by Rye et al. (1992) and Rye (2005).

Enargite and sphalerite are expected to show similar isotopic partitioning behavior due to their structural similarities (Hedenquist et al., 2017). To estimate the equilibrium temperatures of Stage 2A enargite – barite pairs at Mt Carlton, an equation for sulfur isotope fractionation between sphalerite and barite was used (Ohmoto and Rye, 1979), because of the lack of such parameters for enargite. One enargite – barite pair from V2 pit yielded a temperature of 211°C, while four pairs from A39 pit yielded temperatures between 150 and 178°C (Fig. 8; Table 2). These temperatures compare well with homogenization temperatures obtained from primary fluid inclusions in barite (157-233°C in V2 pit, 116-183°C in A39 pit; Figs. 8, 9; Table 1), which adds confidence to the results.

Fluid modelling – The oxygen and hydrogen isotope composition of fluids involved in the formation of Stage 1A alunite were calculated using the fractionation factor of Stoffregen et al. (1994), using temperatures of 200 to 250°C based on $\Delta\delta^{34}S_{\text{alunite-pyrite}}$ geothermometry, fluid inclusion microthermometry, and published temperature constraints on alunite-bearing mineral assemblages (Reyes, 1990; Hedenquist et al., 1998; Watanabe and Hedenquist, 2001; Hedenquist and Taran, 2013). The calculated fluid compositions are intermediate between magmatic vapor discharged from high-temperature volcanic fumaroles (Giggenbach, 1992) and early Permian meteoric water at Mt Carlton ($\delta^{18}O$ = -17 ± 3 ‰ and δD = -130 ± 30 ‰; Fig. 11). The composition of meteoric water was estimated from current $\delta^{18}O$ and δD values of global precipitation at a latitude of 60°, the latter based on tectonic paleo-reconstructions (Scotese, 2001) indicating that northeastern Australia had a latitude of approximately S60° in the early Permian. This estimate does not take into account $\delta^{18}O$ and δD variations due to the paleo-climate or paleo-elevation (e.g., Bradley, 1999; Ravelo and Hillaire-Marcel, 2007). Based on mixing between a typical magmatic vapor and early Permian meteoric water, Stage 1A alunite-forming fluids at Mt Carlton had a 50 to 60 % meteoric component (Fig. 11). The magmatic vapor contribution to the hydrothermal condensate resulted in sufficient reactivity to cause strong alteration and acid leaching of the host rocks. In general, the Stage 1A alunite-forming fluids at Mt Carlton ($\delta^{18}O$ = -11 to -2 ‰; δD = -96 to -73 ‰; Fig. 11) are isotopically light compared to similar acidic fluids associated with hypogene advanced argillic alteration elsewhere ($\delta^{18}O$ = -3 to +11 ‰; δD = -80 to -10 ‰; Arribas, 1995a, and references therein). This is consistent with Mt Carlton having formed at a high paleo-latitude (~S60°; Scotese, 2001), whereas most young porphyry-epithermal systems studied around the world have formed at lower latitudes (Arribas, 1995a; Sillitoe, 2010).

Hydrothermal fluids in equilibrium with Stage 1B plumose alunite were modelled using the same methodology and parameters as for Stage 1A disseminated alunite. Stage 1B alunite-forming fluids show $\delta^{18}O$-δD systematics similar to those of the Stage 1A fluids, albeit slightly lower δD values, the latter likely explained by progressive degassing of the causative intrusion (Fig. 11; Taylor, 1988; Hedenquist and Richards, 1998). These data indicate that there was also a significant involvement of meteoric water during the formation of the Stage 1B plumose alunite veins. Combined with the higher-than-predicted $\delta^{34}S$ values, this suggests that plumose alunite at Mt Carlton did not form in a pure magmatic-steam environment, in contrast to the arguments of Rye et al. (1992).

The $\delta^{18}O$ compositions of hydrothermal fluids in equilibrium with Stage 2A barite were calculated using the fractionation factor of Zheng (1999), using temperatures of 150 to 200°C based on thermometric data from fluid inclusions and enargite – barite sulfur isotope pairs. The calculated barite-forming fluids have $\delta^{18}O$ values that generally overlap those of the most dilute Stage 1A alunite-forming fluids, indicating a 60 to 70 % meteoric component (Fig. 11).

A temperature range of 120-150°C was used to calculate the $\delta^{18}O$ and δD compositions of fluids in equilibrium with Stage 3 dickite, based on the late paragenesis of dickite, mineral stability data (Reyes, 1990), and previously published isotopic modelling of similar dickite-forming fluids at the Lepanto HS epithermal deposit, Philippines (Hedenquist et al., 1998). Calculations were done using the fractionation factors of Sheppard and Gilg (1996), and Gilg and Sheppard (1996). The results indicate that fluid $\delta^{18}O$ values overlap, or are slightly lower than, those of the earlier alunite-forming and barite-forming fluids, which was likely caused by the involvement of ≥70 % meteoric water (Fig. 11). However, the δD values of the Stage 3 dickite-forming fluids are distinctly lower than those of the Stage 1 alunite-forming fluids (Fig. 11). In addition to a greater meteoric water component, we interpret this to potentially reflect a combination of 1) the magmatic component during Stages 2 and 3 being a liquid, isotopically distinct (lower δD) from magmatic vapor during Stage 1; and 2) continuous degassing of the causative intrusion over the life of the magmatic-hydrothermal system, depleting both melt and exsolved fluids in δD with time (Fig. 11; Taylor, 1988; Hedenquist and Richards, 1998).

Discussion

Evolution of the magmatic-hydrothermal system at Mt Carlton

Early advanced argillic alteration – Stage 1A alteration assemblages at Mt Carlton exhibit stable isotope systematics similar to those of advanced argillic alteration documented at other HS epithermal deposits, consistent with a magmatic-hydrothermal origin (Rye et al., 1992;

Rye, 2005). As is the case with porphyry-epithermal systems in volcanic arcs worldwide, the causative intrusion at Mt Carlton most likely crystallized from an I-type, magnetite-series magma (Ishihara, 1981) saturated with sulfur- and metal-rich aqueous fluids (Sillitoe, 2010). Saline supercritical fluid exsolved from the intrusion and initially accumulated at deeper levels (e.g., below the brittle-ductile transition; Fournier, 1999). This fluid subsequently separated into a hypersaline liquid and a low-salinity vapor (Henley and McNabb, 1978). The dense hypersaline liquid likely produced potassic alteration and associated mineralization in and around magmatic apophyses from the intrusion (Hedenquist et al., 1998; Sillitoe, 2010), whereas the buoyant low-salinity vapor ascended along steep normal faults and fracture networks that formed in the Mt Carlton area during early Permian rifting (Fig. 12). Lakes developed at the surface within localized rift basins, into which volcanic as well as organic sediments were deposited (Sahlström et al., 2018). During extensional episodes, meteoric water penetrated to depth via open veins and absorbed rising magmatic vapor plumes (Fig. 12). The resulting vapor condensate became increasingly acidic upon cooling, first by disproportionation of SO_2 to form H_2S and H_2SO_4 below ~400°C (Sakai and Matsubaya, 1977; Arribas, 1995a), then by progressive dissociation of H_2SO_4 and HCl at lower temperatures (<300°C; Hedenquist and Taran, 2013). Alunite would have started to form at temperatures ~300°C (Arribas, 1995a). Upon cooling to temperatures below 200°C at a high condensate/rock ratio (>10:1), alunite started to dissolve, with intense leaching at $pH \approx 1$ forming cores of silicic alteration in and around the fluid channels (Hedenquist and Taran, 2013). Away from the feeder structures, fluid flow was less focused and increasingly diluted, causing alunite and then dickite – kaolinite to form (Stoffregen, 1987; Hedenquist and Taran, 2013). These reactions produced the observed silicic → quartz – alunite → quartz – dickite – kaolinite zoned alteration halo around Mt Carlton, which is typical of HS epithermal deposits globally (Steven and Ratté, 1960; Arribas, 1995a). Progressively greater dilution of the magmatic condensate by meteoric water led to lower temperatures and more oxidizing conditions toward the shallow and distal parts of the Mt Carlton lithocap, as indicated by the fluid inclusion and stable isotope data (Figs. 8, 9), plus the decreasing Na-content in alunite (Stoffregen and Cygan, 1990; Chang et al., 2011; Sahlström et al., 2018) and the disappearance of APS minerals and pyrite in the alunite assemblage (Hedenquist et al., 1998; Watanabe and Hedenquist, 2001).

Within the volcano-lacustrine setting in which Mt Carlton formed, the paleo-water table was essentially at the paleo-surface at the time of magmatic-hydrothermal activity (Fig. 12). As such, the absence of a vadose zone would have inhibited atmospheric oxidation of ascending, magmatic H_2S and formation of steam-heated acidic waters. This may explain why steam-heated advanced argillic alteration (Rye et al., 1992; Hedenquist et al., 2000) is absent from the top of the Mt Carlton deposit, at least on the basis of the evidence within the rock units in the A39 pit, which represents the shallowest part of the Mt Carlton system.

Deposition of plumose alunite veins – Coarse-grained, banded, plumose alunite was deposited into open space along tension fractures during the final stages of advanced argillic alteration at Mt Carlton. The genetic environment that produces such alunite is poorly understood, particularly with respect to the oxidation process and the transport and precipitation mechanisms of alunite (Rye et al., 1992). Although the Stage 1B plumose alunite at Mt Carlton has different characteristics than Stage 1A disseminated alunite, the isotopic compositions of this mineral are not consistent with a magmatic-steam origin (c.f., Marysvale, Utah; Cunningham et al., 1984; Rye et al., 1992; Rye, 2005; Landis and Rye, 2005).

Similar atypical isotopic signatures in plumose alunite in the Pierina HS epithermal deposit, Peru, were interpreted to reflect unusually slow ascent of magmatic vapor from the intrusive source to the site of alunite deposition (Fifarek and Rye, 2005). Longer residence times during fluid transport would allow for 1) sulfur isotope exchange between H_2S and SO_4, producing higher-than-predicted δ^{34}S values in alunite, and 2) uptake of groundwater, producing lower-than-predicted $\delta^{18}O_{SO4}$, $\delta^{18}O_{OH}$ and δD values in alunite (Fifarek and Rye, 2005). Slow magmatic vapor transport may reflect lithological and hydrodynamic barriers (e.g., Pierina; Fifarek and Rye, 2005), or simply distance between the degassing intrusion and the lithocap (Rye, 2005). The latter scenario would be consistent with the observed zonation in the δ^{34}S values of plumose alunite at Mt Carlton, where the highest values are seen distal to the main feeder structures (Table 2). Because the Mt Carlton deposit formed in an extensional tectonic setting during subsidence and burial, it is unlikely that the magmatic-hydrothermal system underwent telescoping during its lifetime (c.f., Sillitoe, 1994). Therefore, the causative intrusion was likely separated from the near-surface Mt Carlton HS epithermal deposit by a significant distance at the time of mineralization (>1-2 km; Sillitoe, 1999).

An alternative, and perhaps simpler interpretation of the observed isotopic compositions of plumose alunite at Mt Carlton is that they reflect a formation environment unrelated to a purely magmatic-steam origin. This might have involved alunite formation within a magmatic-hydrothermal environment similar to that of Stage 1A, but under more oxidized conditions ($\delta^{34}S_{alunite}$ closer to $\delta^{34}S_{\Sigma S}$, no sulfide). In this case, the difference between the two alunite types at Mt Carlton would largely be textural, reflecting alunite formed as wall rock replacement (Stage 1A disseminated alunite) or as infill in open fractures (Stage 1B plumose alunite). The greater abundance of plumose alunite veins at Mt Carlton than at most other HS epithermal deposits may be attributed to the extensional tectonic setting. Overall, the evidence from alunite at Mt Carlton further highlights the potential for transitions between the magmatic-hydrothermal (slow vapor ascent, sulfur isotope equilibrium, extensive vapor condensation) and magmatic-steam (rapid vapor ascent, sulfur isotope disequilibrium, no condensation) environments in these often very dynamic volcanic settings.

Epithermal mineralization – The fluids that form HS Au ± Ag ± Cu mineralization at epithermal deposits are argued to be low- to moderate-salinity aqueous liquids, sulfur- and metal-rich, which are generated during the waning stages of magmatism and cause white mica (sericitic) alteration below the lithocap environment (e.g., Shinohara and Hedenquist, 1997; Hedenquist et al., 1998; Sillitoe and Hedenquist, 2003; Heinrich et al., 2004; Heinrich, 2005; Pudack et al., 2009; Sillitoe, 2010). Such a mineralizing fluid, which originally would have had an IS state at deeper levels and higher temperature, entered the lithocap at Mt Carlton, where the limited buffering capacity of the leached volcanic host rocks allowed the fluid to evolve to a HS state upon cooling (Einaudi et al., 2003). This fluid evolution is evident in the paragenetic transition from IS state minerals (tennantite – tetrahedrite – goldfieldite) to enargite in the early Stage 2A ores (Fig. 4; Sahlström et al., 2018).

Precipitation of Au and other metals in the epithermal environment occurs due to sharp decreases in metal solubility, commonly as a result of boiling and/or fluid mixing and cooling (e.g., Giggenbach and Stewart, 1982; Heinrich, 2005; Sillitoe, 2010). The fluid inclusion data for Stage 2 of Mt Carlton are consistent with mineralization having formed primarily due to the mixing of metalliferous, magmatic-hydrothermal liquid with vapor-heated (~150°C) meteoric water (Fig. 9). This initially produced fracture- and fissure-filling Au-Cu ore within the structural feeders of the deposit (Fig. 12). Subsequently, the mineralizing fluids dispersed laterally into the accumulating volcano-lacustrine sedimentary sequence and vented into the overlying lakes, producing syngenetic Ag – barite ore and associated amorphous silica sediment, spherulitic pyrite, skeletal enargite – luzonite, and various synsedimentary deformation textures (Figs. 6B, 6D-E, 12). Equivalent ore textures were produced within open fractures in the structural roots of the rift basins (Sahlström et al., 2018). The interaction between hydrothermal fluids and organic material within the shallow volcano-lacustrine sediments has been suggested as a cause of the enrichment of some elements (Ge, Ga and In) to economically significant concentrations in the ores (Fig. 12; Sahlström et al., 2017). The overprinting of younger, IS state mineral assemblages (Stages 2B and 2C; Figs. 4, 6C) on the initial enargite ores reflect an evolution of the mineralizing fluids, returning to lower sulfidation state, less oxidized and more neutral pH conditions over time, a commonly seen pattern (Arribas et al., 1995; Jannas et al., 1999), possibly due to interaction with the wall rock (Einaudi et al., 2003; Sillitoe and Hedenquist, 2003).

Late-stage hydrothermal void fill, and post-mineralization events – The widespread occurrence of late, massive dickite (Stage 3; Figs. 4, 5G) records the final stages of magmatic-hydrothermal activity at Mt Carlton. At this point, the causative intrusion was increasingly degassed, and there was a gradual transition from magmatic-dominant to meteoric-dominant conditions in the epithermal environment (Fig. 11).

Extensive illite – montmorillonite alteration and abundant gypsum veins formed during post-mineralization extensional deformation (Stage 4; Figs. 4, 5H). Gypsum sulfate likely came from dissolution of magmatic-hydrothermal anhydrite formed during Stage 1A advanced argillic alteration (Fig. 5E), as oxidation of pyrite to produce sulfate would tend to result in negative $\delta^{34}S_{sulfate}$ values (Rye, 2005). The common occurrence of cast textures in the altered rocks at Mt Carlton (Fig. 5F) indicates that original anhydrite was present and subsequently dissolved due to meteoric water circulation during deformation. The dissolved sulfate was then redeposited as gypsum within open space near the main fault zones, allowing the gypsum to maintain the heavy $\delta^{34}S$ signature of the anhydrite. Similar processes in which soluble sulfate minerals are dissolved and reprecipitated as gypsum veinlets are commonly observed in modern stratovolcano environments (Zimbelman et al., 2005). In addition, magmatic-hydrothermal anhydrite is predicted to be more abundant in lithocaps than what is observed in nature (Hedenquist and Taran, 2013), with this discrepancy explained by dissolution of anhydrite during late- to post-mineralization fluid flow (Cooke and Simmons, 2000;

Hedenquist and Taran, 2013). The textural and isotopic data from Mt Carlton support this explanation.

Conclusions

The mineralogy and zonation of alteration and mineralization observed at Mt Carlton, plus the stable isotope and fluid inclusion data, are generally consistent with that noted for younger, subaerial HS epithermal deposits (Arribas, 1995a; Hedenquist et al., 2000). There was a strong contribution of magmatic water and sulfur that generated a reactive hydrothermal system, manifested in the laterally extensive, zoned advanced argillic alteration halos to leached host rocks, and in monomineralic veins of banded, plumose alunite, followed by deposition of high-grade, HS epithermal mineralization. However, Mt Carlton represents a marked variation on this well-known ore-forming environment. Here, syn-hydrothermal extension resulted in a localized sub-lacustrine setting in which syngenetic mineralization and associated paleosurface features were formed and preserved since the Permian.

Due to the shallow-water vent component to the Mt Carlton system (Fig. 12), other obvious analogs are sulfide deposits that form in shallow-submarine volcanic arc and backarc settings and exhibit advanced argillic alteration, HS ore mineral assemblages, epithermal trace element suites, and evidence for a magmatic fluid component in the hydrothermal system (Sillitoe et al., 1996; Hannington et al., 1999; Hannington and Herzig, 2000). A particularly relevant example is the epithermal mineralization at the Pliocene Lerokis and Kali Kuning deposits, Wetar Island, Indonesia, where Au and Ag ore is associated with stratiform barite sand, which is underlain by polymetallic massive sulfide bodies (Sewell and Wheatley, 1994; Scotney et al., 2005). Other comparable examples include active submarine hydrothermal ore-forming systems such as the enargite – luzonite chimneys at North Su and Kaia Natai Volcanoes (Manus Backarc Basin; Dekov et al., 2016), and the barite – polymetallic sulfide mineralization at Palinuro Seamount (Aeolian Arc, Tyrrhenian Sea; Minniti and Bonnavia, 1984; Tufar, 1991), Brothers Volcano (Kermadec Arc; de Ronde et al., 2005, 2011) and the Hine Hina hydrothermal field (Lau Backarc Basin; Herzig et al., 1993, 1998; Fouquet et al., 1993).

The Mt Carlton deposit most likely formed at a water depth of no more than a few tens of meters (as supported by the presence of coal and fossilized wood fragments in the host sediments; Sahlström et al., 2018), much shallower than the depths at which seafloor massive sulfide deposits in submarine volcanic arc settings generally form (i.e., hundreds of meters to >1 km). Yet, Mt Carlton shares several key textural, mineralogical and geochemical features with such deposits. These include 1) a similar ore body morphology, with fracture- and fissure-filling mineralization within structural feeders at depth and syngenetic, stratiform mineralization at surface (e.g., Sato, 1977); 2) massive accumulations of Pb-Sr-enriched barite that cap the stratiform ore (Bonatti et al., 1972; Sewell and Wheatley, 1994; Sillitoe et al., 1996; Momoshima et al., 1997; Scotney et al., 2005); 3) laminations of amorphous silica, similar to those that accumulate in hyperacidic crater lake settings (Sillitoe, 2015), occurring either intimately associated with, or distal to, mineralization (e.g., Petersen et al., 2002; de Ronde et al., 2011); 4) spherulitic and skeletal ore textures, indicative of rapid mineral crystallization during venting (e.g., Tufar, 1991; Fouquet et al., 1993; Scotney et al., 2005; Xu and Scott; 2005; Dekov et al., 2016); 5) slumping textures and other synsedimentary deformation textures (Tufar, 1991; Scotney et al., 2005); 6) no development of steam-heated advanced argillic alteration due to the lack of a vadose zone (Sillitoe et al., 1996); and 7) evidence for a larger proportion of surface water (in this case, meteoric water) in the magmatic-hydrothermal system than in most subaerial HS epithermal deposits (Fig. 11), likely due to the sub-lacustrine setting of Mt Carlton.

The close relationship between paleosurface features and epithermal mineralization has been recognized for over a century (Sillitoe, 2015, and references therein), and has been successfully applied in mineral exploration (e.g., the discovery of the Fruta del Norte epithermal Au-Ag deposit, Ecuador, immediately beneath a silica sinter horizon; Leary et al., 2016). While paleosurface features associated with lakes have been documented near other HS epithermal deposits (e.g., Akaiwa, Japan, Arribas, 1995b; Yanacocha, Peru, Longo et al., 2010), the study of Mt Carlton highlights that they may occur in direct contact with economic mineralization. The lacustrine paleosurface features documented at Mt Carlton (e.g., laminated amorphous silica sediment, massive barite accumulations, and stratiform sulfides exhibiting venting textures and synsedimentary deformation textures), as well as the associated geochemical anomalies (e.g., Ba-Pb-Sr anomaly caused by barite), may therefore be indicators of potential concealed HS epithermal mineralization in volcano-sedimentary sequences elsewhere. The presence of such paleosurface features, and their application in mineral exploration, will be limited to regions with high preservation potential (Sillitoe, 2015). In particular, extensional settings conducive to HS epithermal formation and in which ore deposits would have been rapidly buried, such as backarc rifts, are especially deserving of attention.

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Figure captions

Fig. 1: **(A)** First-order geologic subdivisions of northeastern Queensland, Australia. Abbreviations: BB – Bowen Basin; GI – Georgetown Inlier; HF – Hodgkinson Formation; MO – Mossman Orogen; NEO – New England Orogen; PPC – Post-Permian Cover; TO – Thomson Orogen. Modified from McKibbin et al. (2017) and Cheng et al. (2018). **(B)** Geologic map of the northern Bowen Basin and New England Orogen, showing the locations of the known porphyry, epithermal and orogenic deposits and prospects (compiled from Geological Survey of Queensland databases). Grid – UTM zone 55; datum – GDA94. Modified from Sahlström et al. (2017, 2018).

Fig. 2: 3D model of the ore zones at Mt Carlton, showing the zonation of Au, Cu, Zn, Pb and Ag across the deposit. The stippled lines indicate the surface traces of the sections shown in Figure 3. Modified from Sahlström et al. (2018).

Fig. 3: Sections through Mt Carlton, showing the distribution of stratigraphic units, major structures, alteration assemblages and mineralization. **(A)** NE-SW long section oriented parallel to the Western ore zone. **(B)** NW-SE cross section through the SW V2 pit. Abbreviations: alu – alunite; anh – anhydrite; APS – aluminium-phosphate-sulphate minerals; brt – barite; chl – chlorite; dck – dickite; gyp – gypsum; hbx – hydrothermal breccia; hem – hematite; ill – illite; kln – kaolinite; mnt – montmorillonite; prl – pyrophyllite; py – pyrite; qtz – quartz; rt – rutile. Modified from Sahlström et al. (2017, 2018).

Fig. 4: Paragenetic sequence of alteration and ore minerals at Mt Carlton. Modified from Sahlström et al. (2018).

Fig. 5: Photographs and photomicrographs of selected alteration assemblages from Mt Carlton. **(A)** Stage 1A quartz – alunite – dickite – pyrite alteration developed in a quartz – feldspar phyric rhyodacite (Unit 3). The Stage 1A assemblage is crosscut by a younger Stage 1B plumose alunite vein. **(B)** Aggregate of Stage 1A alunite crystals that have replaced a pre-existing feldspar crystal (transmitted light, cross polarized). **(C)** Stage 1B banded, plumose alunite vein. The alunite vein has locally been overprinted by Stage 3 dickite – pyrite veinlets. **(D)** Plumose texture in a Stage 1B alunite vein (transmitted light, cross polarized). **(E)** Aggregate of tabular Stage 1A anhydrite crystals developed within open space in a silicic altered rhyodacite porphyry. **(F)** Similar alteration as in E), but with the anhydrite having been completely dissolved, leaving behind distinctive casts in the rock. **(G)** Stage 2A enargite – pyrite mineralization overprinted by void fill made up of Stage 3 massive dickite with pyrite. **(H)** Stage 4 illite – montmorillonite alteration developed in a massive dacite tuff (Unit 4B) in the northern wall of V2 pit. Veins made up of fibrous gypsum with a well-developed shear fabric occur near a D_2 fault zone. Abbreviations from Figure 3, and Eng – enargite.

Fig. 6: Photographs and photomicrographs of selected ore textures from Mt Carlton. **(A)** Silicic hydrothermal breccia cemented by Stage 2A enargite – pyrite mineralization (from V2 pit). **(B)** Skeletal aggregates of Stage 2A enargite and luzonite from A39 pit (transmitted light, plane polarized; c.f., Dekov et al., 2016, their Figure 3). **(C)** Composite vein from V2 pit, illustrating part of the temporal sequence of alteration and mineralization at Mt Carlton. A Stage 1A quartz – alunite – pyrite altered rhyodacite porphyry is crosscut by a Stage 1B plumose alunite vein.

The alunite vein served as a pathway for later mineralizing liquid, which deposited Stage 2A enargite ore and, subsequently, Stage 2B sphalerite – pyrite ore. **(D)** Sedimentary ore from A39 pit. The sediments are predominantly made up of finely laminated quartz. The siliceous sediments incorporated mineralized material from Stage 2A (fine-grained in photo), Stage 2B and Stage 3, as well as volcanic sediment in the form of quartz phenocrysts. **(E)** Layered massive sulfide mineralization consisting of spherulitic Stage 3 pyrite and dickite, within volcano-lacustrine sediment (Unit 4A; from SW corner of V2 pit). Abbreviations from Figure 3, and Eng – enargite; Luz – Luzonite; Sp – sphalerite.

Fig. 7: Photomicrographs of the studied fluid inclusion assemblages from Mt Carlton. **(A)** Igneous quartz phenocryst in a hydrothermally altered quartz – feldspar phyric rhyodacite. The quartz crystal exhibits fractures and corrosion textures, which have been infilled with Stage 1A quartz and alunite. Secondary fluid inclusions are locally developed in trails propagating from such fractures or from quartz crystal boundaries (transmitted light, cross polarized). **(B)** Coarse-grained, euhedral barite crystals occurring in the halo of a Stage 2A enargite veinlet. The barite crystals grew perpendicular to the enargite veinlet, and contain both primary and secondary fluid inclusions (transmitted light, plane polarized; see Sahlström et al., 2017, their Figure 4E). **(C)** Trail of secondary fluid inclusions developed within an igneous quartz phenocryst (transmitted light, plane polarized). **(D)** Primary fluid inclusion within a barite crystal associated with Stage 2A enargite mineralization (transmitted light, plane polarized). Abbreviations from Figure 3, and FI – fluid inclusion.

Fig. 8: Map of the Mt Carlton open pits (c.f., Fig. 2), showing the surface projections of samples used for geothermometry. Homogenization temperatures (Th) for fluid inclusions in quartz and

barite, and temperatures calculated from $\Delta\delta^{34}S_{sulfate\text{-}sulfide}$ values, are listed. All temperatures rounded to the nearest 5ºC. Sample HC09DD025-120 (alunite – pyrite; A39 pit) is shown, but not annotated, due to the unrealistically high calculated equilibrium temperature of this distal sample (330°C).

Fig. 9: Plots of fluid inclusion data. **(A)** Frequency histogram of homogenization temperatures (Th) of secondary fluid inclusions in quartz phenocrysts. **(B)** Frequency histogram of Th of primary fluid inclusions in barite associated with Stage 2A mineralization. **(C)** Homogenization temperature (Th) *vs.* final ice melting temperature (Tm) plot of secondary fluid inclusions in quartz phenocrysts. **(D)** Th *vs.* Tm plot of primary fluid inclusions in barite. The observed Th *vs.* Tm trends are interpreted to reflect mixing between magmatic-derived hydrothermal fluids and vapor-heated groundwater (~150°C, nil salinity). See text for detailed explanation.

Fig. 10: Summary plot of $\delta^{34}S$ values of sulfate, sulfide and sulfosalt minerals.

Fig. 11: Plot of $\delta^{18}O$ *vs.* δD values of Stage 1A and Stage 1B alunite ($\delta^{18}O_{SO4}$ plotted) and Stage 3 dickite from Mt Carlton. The calculated compositions of hydrothermal condensates in equilibrium with Stage 1A and Stage 1B alunite are plotted together with compositions of magmatic vapor discharged from high-temperature volcanic fumaroles (Giggenbach, 1992), water dissolved in felsic magma (Taylor, 1992), estimated early Permian meteoric water (latitude ~S60º; Scotese, 2001; this study), present-day Mt Carlton meteoric water (latitude ~S20º; $\delta^{18}O$ = -5.8 to -5.5 ‰, δD = -39 to -37 ‰; F. Sahlström, unpub. data), and acidic fluids related to advanced argillic alteration of worldwide HS epithermal deposits (Arribas, 1995, and

references therein). The trends defined by Stage 1A and Stage 1B alunite-forming fluids indicate condensation of magmatic vapor by local meteoric water (~50 to 60 % meteoric component). The Stage 2A barite ($\delta^{18}O$ values only) and Stage 3 dickite liquid compositions are also plotted, indicating an increasing meteoric water component with time (~60 to 70 % meteoric water during barite formation, ≥70 % during dickite formation). Magmatic liquid during Stages 2 and 3 was isotopically distinct (lower δD) from Stage 1 magmatic vapor. Additionally, progressive degassing of the causative intrusion depleted both melt and exsolved fluids in δD with time (Taylor, 1988; Hedenquist and Richards, 1998). See text for detailed explanation.

Fig. 12: Conceptual genetic model for Mt Carlton, integrating geological, structural, mineralogical and geochemical data and observations (Sahlström et al., 2017, 2018; this study). Mt Carlton formed in a shallow volcano-sedimentary rift environment, in a sub-lacustrine setting, where magmatic initially vapor condensed into meteoric water, followed by magmatic liquid diluted by meteoric water. See text for detailed explanation.

Table captions

Table 1: Summary of heating and freezing results for fluid inclusions from Mt Carlton. Coordinates: Grid – UTM zone 55; datum – GDA94.

Table 2: Stable isotope data (reported in per mil, ‰) and geothermometry for minerals from Mt Carlton. Coordinates: Grid – UTM zone 55; datum – GDA94.