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Formation of giant high-grade hypogene porphyry copper deposits during phyllic to advanced argillic alteration: textural evidence from automated SEM mapping at the Resolution and Hugo Dummett North deposits --Manuscript Draft--

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Abstract:	Detailed core logging, combined with TESCAN TIMA mineral quantification at two globally significant, high-grade porphyry deposits – Resolution, USA, and Hugo Dummett North, Mongolia – indicate that most chalcopyrite±bornite-pyrite is intergrown with muscovite that overprints earlier potassic alteration assemblages containing biotite and/or K-feldspar. Copper grades increase with the intensity of muscovite overprint on primary potassic assemblages supporting a link between high-grade Cu mineralization and phyllic alteration. Another zone of high-grade Cu mineralization occurs in the upper parts of the phyllic alteration zone and/or within later advanced argillic alteration, associated with high-sulfidation bornite±digenite±covellite±chalcocite-pyrite assemblages, that partly replace earlier chalcopyrite. These two high grade domains have comparable features in many other significant high-grade Cu porphyry deposits (Chuquicamata, Rosario, MMH, Onto, Butte) – all strongly telescoped systems that host significant amounts of high-grade Cu mineralization in phyllic and/or advanced argillic alteration that overprint potassic alteration. We suggest there are at least three reasons for the development of high-grade hypogene ore in telescoped porphyry systems: 1) rapid unroofing and exhumation can generate steep thermal gradients, promoting a rapid decrease in Cu solubility and efficient precipitation of sulfides; 2) rapid, syn-mineralization exhumation and magma doming when the rock mass behaves in an increasingly brittle fashion, create significant permeability in late stages of porphyry systems; 3) telescoping during syn-mineralization exhumation leads to overprinting of early sulfide assemblages by late-stage acidic and oxidized hydrothermal fluids that remobilize and concentrate early Cu,							

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Response to Reviewers:	Dear Prof. Lehmann, Thanks for your processing of our revision. I found AE Brian Tattitch made comments on the word file that you made comments last time, so the attached word file is a bit confusing with both your comments on it. Actually, we've made corrections based on your comments last time. So, this time, we just made the required corrections from Brian's comments. He sent us his comments in email, which are all followed here. We appreciate AE Dr. Brian Tattitch's detailed review and comments. He raised following questions and suggestions, which have already been taken actions during the modification and the Email exchange with him. 1, Table 1: Line 14 there is a "Porter Geo" in the references however this doesn't seem to be a reference (no year) and there is no Porter in the references list as a first author. Response: Porter Geo is an online source, which provides basic geology and resources information about some mineral deposits. It did not indicate a year when it was published, that's why a year is missing. But after reading it in detail, it said the information is updated in 2016. So, we changed the citing as: Porter Geo (2016) , and added it in the reference list as: Porter Geo (2016) Los Bronces-Disputada, Rio Blanco-Andina, Sur Sur, Chile. https://portergeo.com.au/database/mineinfo.asp?mineid=mn200 2, Table 2: reformatted out an extra "space after line" in the formatting so all core info boxes now line up. Check this looks ok to you. Response: That sounds great, we reformatted it now. 3, Figure 11: slight clarity on "remobilization"? The idea clearly seems to be that the "later stages" of HGHP mineralization from later fluids are stacked on top of HGHP I as the system contracts and telescopes and HGHP I sulfide is redissolved and remobilized? Often remobilization applies to downward supergene movement of Cu. I think the idea comes across pretty well in main text but it might be worth including "upgrading" or "overprinting" and a clarifier that it is the HGHP I from A that is locally remobilized/upgraded in the figure caption. I only note this as it is a figure caption and you want to capture the full model idea in this brief text... Response: I agree, it should be good to include "upgrading", so we can change the last bit to "...involving extensive Cu remobilization and upgrading of earlier mineralization". As in the text and figure, we believe that remobilization of Cu and Au very likely has happened, so we'd like to keep remobilization in the caption, although it may happen more in supergene processes. 4, Figure 5 caption still seems to have a % error based on the similar data in other captions. I've changed 15.7 % Cu to 15.7 wt% Cu. Response: Thanks for pointing out and correcting by adding wt. I overlooked that. 5, References: I added periods after pages and before the DOIs of several. Response: Thanks for your very detailed checking and correcting.

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Dear Editor of *Mineralium Deposita*

Understanding the controls of copper grade is scientifically and economically significant in studies of porphyry Cu deposits. In the current low-carbon transition era, the discovery of high-grade ores is increasingly important, particularly because of the lower energy cost and reduced waste associated with extraction. Supergene enrichment is well known as a control of high grades in such systems; however, how high-grade hypogene porphyry (HGHP) mineralization forms remain relatively poorly understood.

Hydrothermal alteration in porphyry Cu deposits provides important evidence for understanding Cu mineralization processes and their exploration. In this paper, we study the relationship between hydrothermal alteration and high-grade hypogene Cu mineralization by using state-of-art automated mineralogy and texture examination of samples from Resolution (USA), Hugo Dummett (Mongolia), and comparing them with 15 well-studied, giant HGHP systems (with >2 Mt HGHP resource). The goal is to develop a geological framework for understanding hydrothermal controls of HGHP deposits, and propose some key processes that may underpin HGHP development.

TESCAN TIMA mineral automated quantification demonstrates that in both cases, large amounts of Cu-sulfides are intergrowing with muscovite in the deep part, and Cu grade increases with the intensity of muscovite overprinting of primary potassic assemblages, indicating a link of high-grade Cu mineralization to lower temperature phyllic alteration. Another high-grade zone is in the upper part of phyllic alteration, or in advanced argillic alteration, associated with bornite $\pm$ digenite $\pm$ covellite $\pm$ chalcocite-pyrite sulfides. The two high-grade Cu orebodies are superimposed in both deposits, although in different degrees, evidenced by replacement of high-sulfidation state sulfides on chalcopyrite and overprinting of phyllic and advanced argillic alteration on potassic alteration. This is in accord with many other significant HGHP deposits (Chuquicamata, Rosario, MMH, Onto, Butte), which are strongly telescoped systems that host significant amounts of high-grade Cu mineralization in white mica-dominated phyllic alteration and/or advanced argillic alteration overprinting potassic alteration.

We proposed at least three reasons for the development of high-grade ore in telescoped systems: 1) steep thermal gradients in strongly telescoped systems promote a rapid decrease in Cu solubility and efficient precipitation of sulfides over a narrow interval; 2) the most significant permeability creation in porphyry systems often develops late – during rapid, syn-mineralization exhumation and magma doming stages – when the rock mass behaves in an increasingly brittle fashion; 3) telescoping during syn-mineralization exhumation leads to overprinting of early sulfide assemblages by late-stage acidic and oxidized hydrothermal fluids that remobilize and concentrate early Cu, lead to the precipitation of sulfides with high Cu/S ratios. We conclude that rapid exhumation coinciding with long-lived hydrothermal processes exert a significant control on the formation of high-grade hypogene porphyry Cu mineralization.

This framework will hopefully be of benefit in defining the exploration search space for HGHP systems and provide pointers for future research into HGHP deposit genesis. We believe that this study is suitable for *Mineralium Deposita*, and sincerely hope you would consider our work for publication in the journal.

Yours sincerely,

Chao Yang and Jamie Wilkinson

15th/Sep/2024

Formation of giant high-grade hypogene porphyry copper deposits during phyllic to advanced argillic alteration: textural evidence from automated SEM mapping at the Resolution and Hugo Dummett North deposits

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Abstract

Detailed core logging, combined with TESCAN TIMA mineral quantification at two globally significant, high-grade porphyry deposits – Resolution, USA, and Hugo Dummett North, Mongolia – indicate that most chalcopyrite ± bornite-pyrite is intergrown with muscovite that overprints earlier potassic alteration assemblages containing biotite and/or K-feldspar. Copper grades increase with the intensity of muscovite overprint on primary potassic assemblages supporting a link between high-grade Cu mineralization and phyllic alteration. Another zone of high-grade Cu mineralization occurs in the upper parts of the phyllic alteration zone and/or within later advanced argillic alteration, associated with high-sulfidation bornite ± digenite ± covellite ± chalcocite-pyrite assemblages, that partly replace earlier chalcopyrite. These two high grade domains have comparable features in many other significant high-grade Cu porphyry deposits (Chuquibambilla, Rosario, MMH, Onto, Butte) – all strongly telescoped systems that host significant amounts of high-grade Cu mineralization in phyllic and/or advanced argillic alteration that overprint potassic alteration.

We suggest there are at least three reasons for the development of high-grade hypogene ore in telescoped porphyry systems: 1) rapid unroofing and exhumation can generate steep thermal gradients, promoting a rapid decrease in Cu solubility and efficient precipitation of sulfides; 2) rapid, syn-mineralization exhumation and magma doming when the rock mass behaves in an increasingly brittle fashion, create significant permeability in late stages of porphyry systems; 3) telescoping during syn-mineralization exhumation leads to overprinting of early sulfide assemblages by late-stage acidic and oxidized hydrothermal fluids that remobilize and concentrate early Cu, leading to the precipitation of sulfides with high Cu/S ratios. We conclude that the coincidence of rapid exhumation and long-lived hydrothermal activity exerts a first order control on the formation of high-grade hypogene porphyry Cu mineralization.

Key words: High-grade hypogene porphyry copper, phyllic alteration, advanced argillic alteration; superimposition

Introduction

High-grade orebodies are of increasing significance to the mining industry in the low-carbon transition era because of the lower energy cost and reduced waste associated with extraction. However, such orebodies are infrequent: in the case of the most important Cu source, porphyry Cu deposits, our database for significant deposits (≥ 100 Mt ore resources, $n=446$, see ESM Table S1) shows that porphyry Cu deposits with a defined resource have a median Cu grade of 0.35 %, with only the top tenth percentile having a grade of over 0.62 % and just a handful with a grade over 1% (Fig. 1).

44 Some porphyry deposits contain supergene oxide and sulfide enrichment resources which
45 improve the overall Cu grade (e.g. Potrerillos, Chuquicamata and Escondida: Marsh et al.
46 1997; Ossandón et al. 2001; Padilla-Garza et al. 2001). However, here we focus only on high-
47 grade hypogene mineralization that is associated with magmatic-hydrothermal fluids exsolved
48 from porphyry intrusions. This is because, despite their economic significance, many
49 supergene ores have been mined out in recent decades so that future mining – especially of
50 deep deposits – will mostly involve exploitation of hypogene resources.

51 Sillitoe and Perelló (2023) proposed ≥ 1 % Cu as a definition for high-grade hypogene ore.
52 However, this definition does not refer to a deposit resource *per se*, so could apply for a tiny
53 amount of high grade ore in a large deposit, or a small deposit of entirely high grade. Sillitoe
54 (1998) classified large, high-grade hypogene porphyry deposits as having a grade of ≥ 1 % Cu
55 and over 1 billion tons (Gt) of ore (over 10 Mt fine copper). Few individual deposits meet this
56 criterion if referring to the grade of a whole deposit (Fig. 1A); probably only Resolution, USA
57 (1.8 Gt at 1.53 % Cu) and Hugo Dummett North, Mongolia (1.2 Gt at 1.06 % Cu; Rio Tinto
58 Annual report 2022). Some deposits contain high-grade ore zones exceeding 1 Gt, such as
59 Chuquicamata, Chile (2.0 Gt at 1.54 Cu; Ossandón et al. 2001), El Teniente, Chile (1.8 Gt at
60 1.17 % Cu; Sillitoe and Perelló 2023), Grasberg, Indonesia (2.3 Gt at 1.09 % Cu; Leys et al.
61 2012), Los Sulfatos, Chile (1.2 Gt at 1.46 % Cu; Irrazaval et al. 2010), and Rosario, Chile
62 (1.1 Gt at 1.03 % Cu; Masterman et al. 2005). Other deposits contain large amounts of high-
63 grade ore but less than the 1 Gt threshold, e.g. Golpu, Papua New Guinea (820 Mt at 1.0 %
64 Cu; Rinne et al. 2018) and Los Bronces (475 Mt at 1.03 % Cu; PorterGeo database). The
65 presence of by-product metals such as Au or Mo can improve deposit economics significantly,

66 however, for simplicity, we focus on Cu in this paper and refine the classification terminology
67 for giant high-grade hypogene porphyry (HGHP) deposits as those that contain >2 Mt of
68 hypogene Cu at a grade of ≥ 1 %, irrespective of the overall resource tonnage or grade – the
69 latter will in most cases be lower than 1 %. The threshold of >2 Mt of contained Cu at high
70 grade is somewhat arbitrary but corresponds to the largest 10% of individual deposits defined
71 as ‘giant’ by Singer (1995). This definition captures the major porphyry deposits worldwide
72 that contain substantive high-grade ore (Table 1).

73 Controls on the formation of high-grade hypogene porphyry Cu mineralization are
74 incompletely understood, yet such knowledge is valuable for successful exploration. Even the
75 relationship between Cu orebodies in general and hydrothermal alteration domains – key
76 geological evidence for deciphering hydrothermal mineralization processes (Dilles and
77 Einaudi 1992; Reed et al. 2013) and exploration footprints (Halley et al. 2015; Wilkinson et al.
78 2015) – remains contentious in many deposits. A major current debate is whether the bulk of
79 Cu mineralization in porphyry deposits develops in K-feldspar-biotite stable potassic or white
80 mica-quartz dominant phyllic alteration zones (Calder et al. 2022; Schirra et al. 2022;
81 Cernuschi et al. 2023). The host of high-grade hypogene Cu mineralization is similarly
82 contested: at Bingham Canyon, high grade mineralization has been linked to potassic
83 alteration (Redmond and Einaudi 2010), yet fluids associated with significant copper
84 deposition are constrained to temperatures below $\sim 400^{\circ}\text{C}$ (Landtwing et al. 2005). Significant
85 high-grade Cu mineralization occurs in phyllic and advanced argillic alteration at
86 Chuquicamata (Rivera et al., 2012) and in advanced argillic alteration at Onto (Burrows et al.
87 2020). However, Sillitoe and Perelló (2023) stated that A-type quartz veinlet stockworks

generated during potassic alteration in many deposits “clearly accompanies the high Cu $\pm$ Au values” and suggest that the association of high-grade Cu with chlorite-sericite “may result from overprinting of preexisting Cu-rich potassic zones”. In large systems with multiple porphyry emplacement events and/or telescoping, such as Resolution, Rosario, and Chuquicamata, the genetic relationships between high-grade Cu mineralization and each hydrothermal stage are not easily resolved. This becomes important when assessing the relative timing of Cu mineralization: Sillitoe and Perelló (2023) stated that potassic assemblages are “clearly the most common host of high-grade Cu, accounting for all or part of the >1% Cu ore” in two-thirds of the resources listed in their Table 1, yet most of these contain lower temperature, overprinting assemblages which may have greater significance than is currently attributed to them.

Here, we present the results of high-resolution automated mineralogical quantification and textural examination of samples from the “type” HGHP examples of Resolution (USA) and Hugo Dummett North (Mongolia) – the two highest Cu grade hypogene porphyry deposits worldwide (Fig. 1A). The objective was to determine the paragenetic relationships between Cu sulfides and alteration minerals using technology that provides more unequivocal evidence than more conventional approaches such as core logging or optical microscopy. These observations are complemented by comparison with data from a literature compilation of other giant high-grade hypogene porphyry deposits (with >2 Mt HGHP resource; Table 1). The goal is to identify commonalities and develop a geological framework for understanding the relative timing and hydrothermal processes that control HGHP development. This

framework will hopefully be of benefit in defining the exploration search space for HGHP systems and provide pointers for future research into HGHP deposit genesis.

Deposit geology

Resolution geology

Resolution is the highest grade hypogene porphyry Cu deposit in the world, containing 1859 Mt of ore at 1.52 % Cu, 3.12 g/t Ag, and 0.035 % Mo (Rio Tinto, Annual report 2022). It is located in the Superior district, Arizona, USA, which hosts several porphyry Cu-Mo deposits, epithermal Cu-Ag veins and mantos. The Resolution deposit is centered on a cluster of felsic porphyries that lie within the wider Laramide (80-50 Ma) orogenic belt of the southwestern USA (Dickinson 1989; Favorito and Seedorff 2020). These porphyries intruded a sequence comprising Proterozoic, Paleozoic and Cretaceous rocks, which are overlain by post-mineralization, middle to late Tertiary units.

Proterozoic units include the Paleoproterozoic (~1650 Ma) Pinal schist and Mesoproterozoic Apache Group volcanic and sedimentary rocks. The Pinal schist comprises quartz-muscovite and quartz-chlorite schists with minor intercalations of calcsilicate and metavolcanic rocks. It is intersected by few deep drill holes but is known to host small amounts of low-grade Cu mineralization (Fig. 2A). The Pinal schist is unconformably overlain by Mesoproterozoic sedimentary and mafic volcanic rocks of the Apache Group, which is composed of Pioneer shale, Drippings Springs quartzite, Mescal limestone, and Apache basalt. These rocks are overlain by the Mesoproterozoic Troy quartzite. The sequence was intruded by a series of diabase sills in the late Mesoproterozoic between 1140 and 1040 Ma (Bright et al. 2014). This

130 Proterozoic unit is widespread in southwestern USA, and is an important host of high-grade
131 mineralization in the Resolution deposit (Hehnke et al. 2012), as well as several other
132 deposits in this district, such as the Ray, Chilito and Christmas deposit (Phillips et al. 1974;
133 Force 1998).

134 Paleozoic carbonate rocks and quartzites unconformably overlie the Proterozoic rocks and the
135 carbonates host very high-grade skarn mineralization at Resolution (Hehnke et al. 2012). Late
136 Cretaceous andesitic to dacitic volcanoclastic and pyroclastic rocks (Kvs), dated at 75-66 Ma
137 (Manske and Paul 2002; Ballantyne et al. 2003; Zulliger 2007), host the upper part of the
138 Resolution mineralization (Fig. 2A).

139 Three types of felsic porphyry intrusions have been identified: rhyodacite (major phase),
140 quartz latite and latite porphyry, intruded between 69-64 Ma (Hehnke et al. 2012). Magmatic-
141 hydrothermal breccias were generated during porphyry emplacement, which contain clasts of
142 schist, diabase and Apache Group rocks. Middle to late Tertiary volcanic rocks
143 unconformably overlie the Proterozoic, Paleozoic and Cretaceous sequences and completely
144 cover Resolution (Fig. 2A).

145 Alteration and mineralization: Stockwork mineralization has an age of 64-65 Ma (Re-Os on
146 molybdenite) (Hehnke et al. 2012). The extent of high-grade mineralization at Resolution has
147 not been fully defined but a consistent zone of >1% Cu mineralization extends at least 2 km in
148 an east-northeast direction, 1.5 km in a north-northwest direction and is locally greater than
149 500 m thick (Fig. 2A). The high-grade mineralization preferentially occurs in suitable host
150 rocks, mainly diabase, carbonate rocks and permeable breccias. Deep hydrothermal alteration

151 is potassic, characterized by secondary biotite-rich diabase and K-felspar-rich felsic rocks
152 (Hehnke et al. 2012), although K-feldspar is likely to be much more abundant in diabase than
153 recognized from drillcore logging (Cooke et al. 2020). The potassic alteration is surrounded
154 by propylitic alteration, with abundant epidote and chlorite in mafic to felsic volcanic,
155 volcaniclastic and intrusive rocks (Phillips 2019; Cooke et al. 2020). The potassic and
156 propylitic rocks are extensively overprinted by white mica-dominant phyllic alteration and
157 occasionally kaolinite alteration for hundreds of meters upwards, transitioning into advanced
158 argillic assemblages (Fig. 2A). Advanced argillic alteration overprints phyllic alteration in the
159 central and upper parts of the deposit, mostly in the Cretaceous sedimentary, volcaniclastic
160 and volcanic rocks. Major alteration minerals in this zone are quartz, pyrite, kaolinite, dickite,
161 topaz, zunyite, alunite, APS (aluminium-phosphate-sulfate) minerals and minor pyrophyllite
162 (Harrison 2007; Winant 2010; Hehnke et al. 2012). Chalcopyrite is the dominant copper
163 sulfide in the potassic and deeper phyllic zones, accounting for ~65% of the total copper
164 sulfide (Hehnke et al. 2012). Overprinting of phyllic alteration is associated with replacement
165 of chalcopyrite by bornite with an attendant increase in the Cu grade (Schwartz 2010). A late-
166 stage, hypogene, high-sulfidation-state mineral assemblage of bornite-chalcocite-digenite-
167 covellite-pyrite associated with white mica and overprinting kaolinite caused further
168 upgrading of the Resolution ore zone, although the majority of high-grade Cu mineralization
169 is related to phyllic alteration (Manske and Paul 2002; Hehnke et al. 2012). Molybdenum has
170 a correlation with Cu in general, although their sulfides are not necessarily coexisting; most
171 molybdenite occurs in a distinct generation of quartz veins at depth, whereas Cu sulfides are

widely present in quartz veins, vein halos, disseminated in the ground mass or infilling pores within altered minerals.

Hugo Dummett North geology

The Hugo Dummett North deposit contains a total resource of 1,159 Mt of ore at 1.06 % Cu, 0.32 g/t Au, and 2.8 g/t Ag (Rio Tinto, Annual Report 2022). The deposit is located at the north end of the Oyu Tolgoi porphyry cluster, Mongolia, which hosts eight discrete porphyry deposits in Devonian and Carboniferous volcanic arc rocks (Wainwright et al. 2011; Crane and Kavalieris 2012). Porphyry mineralization at Hugo Dummett North is associated with Late Devonian quartz monzodiorite stocks and dikes (~372 Ma), that intruded the Oyu Tolgoi sequence (Bulagbayan Formation) which comprises augite basalt, volcanoclastic rocks and laminated siltstones (Fig. 2B). Volcanoclastic rocks are divided into a lower, strongly altered and mineralized sequence and an upper unaltered or weakly altered dacite sequence; the latter may be an allochthonous sheet that acted as post-mineral cover to preserve the porphyry mineralization (Wainwright et al. 2017). The Oyu Tolgoi sequence is overlain by the Heruga sequence, comprising basaltic rocks, breccia and siltstone (Fig. 2B). A suite of younger biotite granodiorite porphyry dikes (~370 Ma) intruded the quartz monzodiorite and volcanoclastic sequences (Fig. 2B) (Wainwright et al. 2017).

The Hugo Dummett North deposit has K-feldspar-dominated potassic alteration at depth, largely hosted by the quartz monzodiorite porphyry (Fig. 2B). This transitions upward into quartz-muscovite-dominant phyllic alteration in quartz monzodiorite and then to shallow

advanced argillic alteration (pyrophyllite-muscovite-kaolinite) that is generally hosted within the augite basalt (Fig. 2B). The phyllic alteration overprints deep K-feldspar alteration.

High-grade copper (>1 %) mineralization is largely associated with phyllic alteration and part of the upper potassic alteration zone (Fig. 2B). A very-high-grade copper (>2.5 % Cu) domain is mostly spatially associated with the upper part of the phyllic (quartz-muscovite) zone, close to the advanced argillic alteration above, mainly hosted in the quartz monzodiorite porphyry and partly in the augite basalt (Fig. 2B; Khashgerel et al. 2009; Crane and Kavalieris 2012). The phyllic-hosted mineralization is characterized by bornite-dominant sulfide associations, associated with intense quartz veins (over 90 % of quartz) in the highest-grade domains (Kirwin et al. 2005), termed QV90 (cf. Khashgerel et al. 2006; Crane and Kavalieris 2012).

Advanced argillic alteration at Hugo Dummett North is characterized by pyrophyllite and residual quartz, with minor muscovite, diaspore, zunyite, topaz, corundum, andalusite, APS minerals, alunite, kaolinite and dickite (Khashgerel et al. 2006, 2008). Although locally it contains high-grade bornite-dominant mineralization, it is primarily host to an enargite-pyrite assemblage with a low Cu grade (Crane and Kavalieris 2012). Other intermediate- to high-sulfidation sulfides such as chalcocite, covellite, tennantite and tetrahedrite have also been reported (Khashgerel et al. 2006, 2008, 2009; Crane and Kavalieris 2012). These sulfides have widely replaced chalcopyrite and bornite, suggesting that the Hugo Dummett North deposit is an extensively telescoped system, with lower-temperature alteration and mineralization superimposed on earlier higher-temperature events.

Methods

To document key mineralogical features of high-grade Cu mineralization and its temporal relationship to hydrothermal alteration assemblages, we collected over ninety samples from several representative drillcores from Hugo Dummett North and Resolution (Fig. 2). These were prepared into 25 mm-diameter polished resin blocks and examined using reflected light optical microscopy and automated scanning electron microscopy. The Resolution samples were mostly selected from intervals of high-grade mineralization with a few distal and deep, low-grade samples for comparison (Fig. 2A). Samples from Hugo Dummett North were collected from high-grade, gold-rich, K-feldspar-altered monzodiorite porphyry from depth and the upper, high-grade copper zone related to phyllic-altered monzodiorite porphyry (Fig. 2B).

Automated mineralogy

The TESCAN Integrated Mineral Analyzer (TIMA) automated scanning electron microscope system from the Image and Analysis Center at the Natural History Museum in London, integrates quantitative energy-dispersive X-ray spectrometry (EDX) and an advanced statistical approach to enable mapping of mineral phases at high spatial resolution. Back-scattered electron (BSE) images and EDX data were collected simultaneously using the modal acquisition mode. BSE images were acquired with a 1 μm pixel size in dot mapping mode, with an EDX spacing of 7 μm . The data were collected using a 15 mm working distance, 25 keV beam energy, and 13-14 nA probe current. Based on their EDX spectra (information of geochemical composition) and prior knowledge of the mineral assemblage, a

custom classification scheme was developed by identifying unknown mineral phases (Hrstka et al. 2018). Polymorphs such as kaolinite and dickite in the samples cannot be discriminated by TIMA because of their similar geochemical compositions. Relatively small numbers of pixels remained unclassified, primarily due to mixed EDX signals of pixels at the boundary between two mineral phases and the presence of fine mineral phases smaller than the resolution of EDX acquisition. Area proportions of minerals were estimated using the total pixel area of each phase.

Results

Resolution

In the deepest parts of the Resolution deposit, high-grade Cu mineralized diabase exhibits a dark color attributed to secondary biotite (Figs. 3A, B and C). Abundant pale and white-colored minerals are present (Figs. 3A and C), which are mostly muscovite and minor illite and dickite/kaolinite (Fig. 3D). Locally, greenish muscovite occurs in halos of the quartz-sulfide veins in the diabase (Fig. 3B). Hydrothermal apatite is common within these veins (Fig. 3D). There is also abundant rutile formed with biotite from breakdown of precursor pyroxene or hornblende, evidenced by close spatial association between rutile and biotite (Fig. 3D). Chalcopyrite and minor bornite (with pyrite) are mainly hosted by quartz-sulfide veins, with halos of muscovite, that have overprinted potassic alteration (Fig. 3); these occur almost to the exclusion of typical A, B or C veins and do not fall into a typical porphyry veinlet category (Sillitoe 2010) but are clearly muscovite-stable and would therefore be most akin to D veins. To discriminate these from other types of D veins at Resolution, we name this chalcopyrite-rich vein type as D1. Quantitative mineralogy in the samples indicates that

255 muscovite is the dominant mineral with a mass proportion greater than biotite (averaging
256 28.1 % muscovite and 14.5 % biotite, n=4; Table 2). A broad spatial coincidence between
257 chalcopyrite and biotite (-K-feldspar) alteration is supported by our core logging, but the
258 detailed mineralogy shows that, although some chalcopyrite grains are disseminated within
259 biotite (Fig. 3D; compare Hehnke et al., 2012, Fig. 8), chalcopyrite is most commonly
260 surrounded by and intergrown with muscovite (Fig. 3D), or occurs within veins that have
261 muscovite halos that have themselves been replaced locally by kaolinite. These observations
262 indicate a close genetic relationship between high-grade Cu mineralization and muscovite
263 alteration of previously potassic-altered rocks.

264 In areas where particularly strong phyllic overprinting of potassic alteration is observed, Cu
265 grades are even higher (>2 %; Fig. 2A), lending further support for a link between high
266 grades and muscovite alteration. Transitions in individual sections of drillcore provide
267 valuable insights into the overprinting processes. The images shown in Figure 4 exemplify the
268 mineralogical changes during phyllic overprinting of strongly potassic-altered diabase (Figs.
269 4A-C) and strongly potassic- altered volcanoclastic rock (Figs. 4D-F). Biotite predominates in
270 the diabase (Fig. 4A) and K-feldspar in the volcanoclastic sample (Fig. 4C) but both minerals
271 are replaced by muscovite in the more altered equivalents. The extent of muscovite alteration
272 parallels the increase in abundance of chalcopyrite and Cu grade (Fig. 4). In the diabase
273 sample (Fig. 4A), the upper section with more muscovite (30.1 %) is associated with more
274 chalcopyrite (1.3 %; Fig. 4B) compared to the lower section with 19.9 % muscovite and
275 0.5 % chalcopyrite (Fig. 4C). The volcanoclastic sample (Fig. 4D) shows a similar trend with
276 the upper section containing 23.6 % muscovite associated with 17.0 % chalcopyrite, with both

277 forming as a replacement of K-feldspar (Fig. 4E), but the lower, less phyllic-altered sample
278 containing only 4.1 % muscovite and 0.3 % chalcopyrite, again after K-feldspar. Kaolinite is
279 present in diabase at all depths in Resolution and chalcopyrite occurs spatially with kaolinite
280 in many cases (Figs. 4B, C).

281 In the upper parts of the Resolution deposit (Fig. 2A), and locally at greater depths, rocks are
282 more strongly altered by muscovite that has largely replaced biotite, with muscovite
283 increasing to 34.2 % but biotite decreasing to 0.1 % (Fig. 5B), and biotite itself also partly
284 overprinted by kaolinite/dickite; in this process, nearly all biotite has been destroyed (Fig. 5B;
285 Table 2). Although not obvious in drillcore, muscovite is predominant in the altered diabase
286 (Fig. 5B), whereas more dickite/kaolinite occurs in the quartz-sulfide veins (compare Fig. 5C
287 with Fig. 5B). Pyrite and bornite comprise the major sulfide assemblage (Figs. 5B, C), distinct
288 from the chalcopyrite(-pyrite) assemblage that predominates at depth, suggesting a higher
289 sulfidation state. Covellite, digenite and chalcocite are also commonly seen in the shallow
290 part of the very high-grade Cu mineralization zone, that have replaced earlier chalcopyrite
291 (Figs. 6B, C and D). A replacement sequence of chalcopyrite → bornite →
292 chalcocite/covellite/digenite can be observed locally (Figs. 6A-D), indicating a progressive
293 increase in sulfidation state. These high-sulfidation state, sulfide-enriched quartz veins in this
294 part of the deposit are classified as D2 veins. A large amount of rutile, formed during biotite
295 breakdown, is preserved during later dickite/kaolinite alteration (Fig. 5B). Microbrecciation in
296 quartz-sulfide veins at this level is commonly observed (Figs. 5C and D). Locally, alunite and
297 high-sulfidation Cu-sulfide veins are present with minor pyrophyllite (Fig. 3D). Notable

amounts of hydrothermal apatite (Fig. 5D) are intergrown with bornite and advanced argillic minerals (APS minerals, fluorite, alunite, kaolinite and quartz).

Although much of the pervasive muscovite alteration is associated with high-grade D1 and D2 veins, there are plenty of more typical, barren D veins occurring in distal positions, where Cu grade is generally below 0.5 % (Fig. 2A). These quartz veins mainly contain pyrite and occasionally chalcopyrite or bornite, and have muscovite halos but exhibit limited overprinting by kaolinite/dickite (Fig. 3E). These are classified as D3 veins in this study.

Hugo Dummett North

Deep, high Cu-Au grade mineralized monzodiorite at Hugo Dummett North has a red color (Fig. 7A), generally attributed to strong K-feldspar alteration. Representative quantification results indicate that K-feldspar accounts for ~33 % of the monzodiorite. Although muscovite is not obvious in drillcore (Fig. 7A), significant amounts (~19 %) are present (Table 2) indicative of phyllic overprinting even at depth. The spatial association between high-grade Cu and core intervals logged as potassic has been typically interpreted to represent a genetic association (Khashgerel et al. 2006; Crane and Kavalieris 2012). However, TIMA maps show that bornite and chalcopyrite (with minor digenite and tennantite, Figs. 6E and F), the major host of Cu, is in fact associated with muscovite that has partly replaced K-feldspar and occurs as late mineral infill in cracks that crosscut earlier quartz veins (Fig. 7B). Virtually no Cu-sulfide grains are found within secondary K-feldspar (Fig. 7B). In these very deep locations, bornite is replaced by a minor, later stage of digenite (Fig. 6E) and tennantite (Fig. 6F), which

are probably products from late, high-sulfidation mineralization. Abundant hydrothermal apatite (0.3 %) is also associated with muscovite (Fig. 7B), as noted at Resolution.

In the upper part of the deposit, there is a lower Cu grade (<1 %) interval below the very high-grade (>2.5 % Cu) mineralization, associated with intense quartz-muscovite alteration and disseminated chalcopyrite (Figs. 7C and D). Chalcopyrite in this zone can also be found to be replaced by tennantite locally, occurring as replacement of bornite and chalcopyrite (Fig. 6F). The upper part of very-high-grade Cu mineralization in quartz-muscovite assemblage is also associated with intense phyllic alteration, which is not easy to discriminate from the lower Cu grade zone from hydrothermal alteration minerals, that are both characterized by an intense quartz-muscovite assemblage (Figs. 7E and F). In this material, abundant disseminated sulfide is clearly texturally associated with muscovite, both within the rock mass and within cracks cutting quartz veins (Figs. 7E, F). Bornite is the dominant Cu sulfide, with some chalcopyrite and a minor amount of molybdenite (Fig. 7F). The two main Cu sulfides are often intergrown and pyrite is scarce. In the QV90 zone, slightly above this upper phyllic domain (Fig. 2B), copper grades can be extremely high, normally over 5 %. The sulfide assemblage here is dominated by bornite with minor chalcopyrite that occurs in cracks and vugs within the quartz veins (Fig. 7H). Some muscovite and kaolinite can be seen in addition to sulfides (Fig. 7H).

Discussion

Wider evidence for the relationship between HGHP mineralization and alteration

Most of the high-grade hypogene porphyry deposits in our classification share key features with the two HGHP deposits described, that have high-grade Cu mineralization in the deep part of phyllic alteration that overprints potassic alteration, across to upper, lower temperature phyllic and/or advanced argillic alteration. For example, Cu grades at Rosario in the Collahuasi district, Chile, gradually increase from K-feldspar-rich potassic, through phyllic to advanced argillic alteration zones with a quartz-alunite-pyrite-dickite(-pyrophyllite) assemblage (Fig. 8A; Masterman et al. 2005). Onto, in Indonesia, has nearly all the high-grade mineralization in advanced argillic alteration, although the >1 % high-grade Cu zone has not been outlined (Burrows et al. 2020). Chuquicamata, northern Chile, hosts higher Cu grades (>1.5 % Cu) in the phyllic alteration zone (associated with quartz-muscovite and minor alunite, pyrophyllite and dickite) than in the quartz-K-feldspar potassic alteration zone (Fig. 8C; Ossandón et al. 2001). The features are also found in MMH (Ministo Hales, Chile), and Čukaru Peki (Serbia), as well as several others (Table 1). White mica in these systems has a pale gray color compared to that in the deeper gray-green phyllic domain that has a closer spatial and temporal relationship with potassic alteration, and has a composition closer to muscovite or illite (rather than phengite). Superimposition of both phyllic-associated and advanced argillic-associated high-grade mineralization is commonplace in these deposits.

High-grade Cu mineralization link to potassic or phyllic alteration?

Disagreements remain concerning the association of the principal ore stage to potassic or phyllic alteration in several HGHP deposits. Because phyllic alteration is usually closely superimposed on the potassic zone, it can be difficult to ascertain at which stage the high-grade mineralization was generated, particularly from drillcore logging and composite

360 drillcore assays. For example, large volumes of potassic alteration are linked to high-grade Cu
361 mineralization at Bingham Canyon (Gruen et al. 2010; Redmond and Einaudi 2010), although
362 there remains a contradiction regarding the textural siting of sulfides in relation to low-
363 temperature quartz and inferred, relatively low-temperature Cu precipitation conditions
364 (Redmond et al. 2004; Landtwing et al. 2005). Although the majority of very-high-grade (2 %)
365 Cu mineralization at Grasberg is proposed to occur within the K-feldspar alteration zone (Fig.
366 8D) by Leys et al. (2012), other studies suggested that white mica-chlorite alteration may be
367 associated with the primary mineralization stage (Sapiie and Cloos 2013). At El Teniente,
368 although potassic assemblages are reported to be broadly spatially associated with high Cu
369 and Mo grades (Camus 1975; Skewes et al. 2002; Cannell et al. 2005), both Cannell et al.
370 (2005) and Vry et al. (2010) found that potassic-stage quartz(-magnetite-biotite-Kspar) veins
371 have commonly been reopened and infilled with later-stage sulfides and concluded that the
372 most important Cu-introduction event was during the formation of quartz-free C-veins during
373 the transition to phyllic alteration. Skewes et al. (2002) also noted that phyllic-stage veins are
374 associated with high-grade Cu, with the association between bulk Cu grade in 6 m drillcore
375 assays and such veins confirmed by detailed logging of vein type abundances by Spencer et al.
376 (2015). There is a similar issue in the supergiant Río Blanco-Los Bronces district (including
377 the Río Blanco and Los Sulfatos deposits): although recent studies revealed biotite-cemented,
378 chalcopyrite-bornite-pyrite breccias at depth (Toro et al. 2012), the relationship of these zones
379 to the wider distribution of Cu grades is not described. An earlier study (Warnaars et al. 1985)
380 reported that early mining of >4.5 % Cu ores, which would have been from the upper, phyllic

381 or advanced argillic alteration zones, although they may contain supergene enrichment ores,
382 but volume is uncertain.

383 Interpretations of the location and timing of high-grade mineralization in deep parts of
384 porphyry systems vary between deposits and this remains a controversial topic. Fluid
385 inclusion data, (controversial) textural evidence and numerical modelling studies suggest that
386 most Cu-sulfide precipitation in porphyry systems occurs during silica dissolution and
387 reactivation of permeability at relatively modest temperatures (perhaps mostly between 425
388 °C and 375 °C; Monecke et al. 2018), rather than during the A- and B-type vein stages
389 associated with potassic alteration (Hedenquist et al. 1998; Driesner and Heinrich 2019;
390 Schirra et al. 2022). This type of model was proposed for Butte by Cathles and Shannon
391 (2007) in which the potassic stage was interpreted as a large-scale, rapid, near explosive,
392 unmineralizing fluid release event. It created much fracture permeability which was followed
393 by distinctly later episodes of mineralizing fluid expulsion as the system cooled under
394 muscovite-stable and later advanced-argillic conditions.

395 Conversely, Cernuschi et al. (2023) proposed that sulfides are introduced initially during
396 high-temperature potassic alteration, but that they may be remobilized locally into later veins
397 during phyllic alteration. The very frequently observed association between sulfides and late,
398 dull-luminescent, low-temperature quartz in A- and B-type veins (e.g., Rusk and Reed 2002;
399 Redmond et al. 2004; Riveros et al. 2022) was explained by preferential reopening of veins
400 during low-temperature reactivation alongside pre-existing sulfides. However, the detailed
401 textural relationships can alternatively be explained by later sulfide introduction (and/or
402 remobilization), similar to what we document here (e.g., Figs. 7B, D, F). Furthermore, some

reported examples of late, dully luminescent, relatively low-temperature quartz cannot be interpreted in terms of formation during later reopening alongside earlier sulfides, and there are clear cases of early, higher-temperature quartz that has been partially dissolved and postdated by the precipitation of the bulk of the copper sulfides (e.g., Vry et al. 2010: Fig. 8; Riveros et al. 2022: Figs. 4 and 5). We think that, in part, the contradictory explanations stem from the perspective by which the classic series of quartz vein generations are viewed: either as a series of discrete cross-cutting events as they tend to appear, or as the macro-scale manifestation of a much more complex fracture and microfracture permeability network in the rock mass that allows multiple stages of reactivation and reopening of prior discontinuities, making it difficult to resolve the exact stage of sulfide precipitation, whether in veins or disseminated within the rock. Here, we place more emphasis on the textural association of sulfides with alteration minerals, whether they are contained within veins in crosscutting cracks, in microfracture networks or disseminated patches in the wallrock. This evidence at Resolution and Hugo Dummett North clearly points to the bulk of early, high-grade copper mineralization being introduced during white-mica stable alteration.

Therefore, in the major HGHP deposits worldwide (Table 1), we conclude that potassic alteration-related HGHP mineralization is generally subordinate in Cu grade to that associated with lower-temperature transitional phyllic and phyllic to advanced argillic overprints. In cases where HGHP ore is attributed to the potassic alteration stage, evidence is ambiguous and commonly disputed. Based on evidence from Chuquicamata (Rivera et al. 2012), Butte (Brimhall 1979) and other HGHP systems, plus the typical grades observed in potassic zones in non-HGHP systems such as Haquira East and Encuentro (Cernuschi et al. 2023), we

suggest that potassic-stage mineralization rarely introduces mineralization with Cu grades above ~1 % Cu.

High-grade Cu mineralization in upper-zone phyllic alteration and advanced argillic alteration

High-grade mineralization in the upper phyllic and/or advanced argillic zones mainly comprises bornite, digenite, chalcocite and covellite, coexisting with pyrite (see Table 1 for references). These minerals are typically associated with sulfosalts (enargite and tennantite) and other minor sulfides (nukundamite, mawsonite, colusite, idaite etc); most of them are high-sulfidation state sulfides (Einaudi et al. 2003; Pollard et al. 2005; Hedenquist and Arribas 2022). In some deposits, high-grade ore comprises veins that may be meters in width, such as at Rosario (Masterman et al. 2004) and Butte (Houston and Dilles 2013). Various, these veins are categorized as Butte-type, Cordilleran or massive sulfide veins or lodes (Bendezú and Fontboté 2009; Fontboté and Bendezú 2009; Catchpole et al. 2011). The upper parts of the high-grade mineralization at Resolution are also recognized to be of this type (Manske and Paul 2002), although very thick high-sulfidation veins are not very common. Where telescoping has occurred, it is clear that such veins formed later than deeper, higher-temperature alteration zones as evidenced by crosscutting relationships and sulfide replacement textures (e.g., Figs. 6A-D). Geochronology suggests that this high-sulfidation mineralization can be several million years younger than spatially-associated plutons exposed at the same crustal level and their related porphyry-style mineralization (Houston and Dilles 2013; Catchpole et al. 2015), implicating younger porphyry centers at depth (Padilla-Garza et al. 2004; Hedenquist et al. 2020).

In addition to these hydrothermal processes, there are certain host rocks that can be favorable to promote efficient Cu precipitation and hosting high-grade ores. For example, mafic and carbonate rocks at Resolution shape the outline of large parts of high-grade Cu mineralization (Fig. 2A). Mafic and carbonate rocks are thought to be efficient traps for Cu sulfides because of their capacity to act as an impermeable, ductile seal, reduce oxidized magmatic fluids via the oxidation of ferrous iron, or buffering fluid pH to cause rapid Cu precipitation (Sillitoe 1997, 2010). However, this relationship between Proterozoic diabase and high-grade Cu mineralization at Resolution does not necessarily extend to all other deposits nearby in Arizona (Manske and Paul 2002). Some of the high-grade mineralization at Hugo Dummett North is hosted by olivine basalt; however, the quartz monzodiorite porphyry is the major host (Khashgerel et al. 2009). Thus, although mafic rocks may well be a contributor, it is clearly not the primary control of Cu grade. Also, it is rare for any single deposit forming high-grade Cu mineralization only aligning with a specific unit of host rock.

Physicochemical conditions driving high-grade Cu deposition in the moderate-temperature window

Thermodynamic models of Cu solubility (Liu and McPhail 2005; Rubtsova et al. 2023), as well as fluid inclusion data from natural systems (Hezarkhani et al. 1999; Ulrich et al. 2001; Redmond et al. 2004; Landtwing et al. 2005; Klemm et al. 2007; Schirra et al. 2022), suggest that the sort of steep decrease of Cu solubility in salt solutions from thousands to a few ppm that favors precipitation of high-grade mineralization occurs in the temperature interval that includes the late potassic (K-feldspar stable) but is largely within the phyllic (muscovite stable) alteration window, at temperatures of ~425 to 375 °C (Fig. 9).

469 This temperature range corresponds to the onset of significant SO₂ disproportionation that
470 provides H₂S for the precipitation of Cu sulfides (Fig. 9); reaction of sulfate with ferrous iron-
471 bearing silicates can lead to further H₂S production and sulfide precipitation. Consumption of
472 aqueous sulfide can then drive further disproportionation of SO₂. At the same time,
473 dissociation of H₂SO₄ and HCl will decrease pH to stabilize muscovite as an alteration
474 mineral (Fig. 9A) and increase sulfate activity that can lead to precipitation of anhydrite at
475 higher temperatures and alunite-APS minerals at lower temperatures in acid alteration
476 assemblages (Simonson and Palmer 1993; Seedorff et al. 2005), such as at Resolution (Fig. 3).
477 Prior to phyllic alteration, porphyry systems typically pass through the retrograde silica
478 solubility window at temperatures of ~500-400 °C during their evolution (Fig. 9C; Fournier
479 1985), although this may also happen at even higher temperatures of 550-450 °C at higher
480 pressure (~70 MPa; Rusk and Reed 2002). This dissolution process can generate conduits in
481 pre-existing veins for input of later hydrothermal fluids. Cracking of pre-existing quartz veins
482 during thermal contraction at 575-400 °C (e.g., Cernuschi et al., 2023) will also serve to create
483 additional permeability as conditions transition into the muscovite-stable window. In systems
484 undergoing telescoping, the lower temperature of fluids as they reach the prior potassic vein
485 level will lead to precipitation of Cu sulfides, eventually coincident with a return to prograde
486 silica solubility; this can account for the occurrence of sulfides within late, dully luminescent
487 quartz in such veins that formed below ~370 °C (Monecke et al. 2018).
488 In this window of cooling to below 400 °C and transition to phyllic alteration, host rocks will
489 also pass through the ductile-brittle transition (Fournier 1999). In tectonically active settings,
490 this will favor extensive rock fracturing, involving both reopening of existing veins and the

development of new, large veins, explaining the high density of veins and breccias that are typically formed at the phyllic or even lower-temperature advanced argillic stage, as well as the common structural control of phyllic alteration domains such as at Rosario (Masterman et al. 2005) and Chuquicamata (Ossandón et al. 2001).

Hypogene enrichment

At moderate temperature and under oxidizing hydrothermal conditions, hypogene enrichment may take place, as observed at Resolution and locally at Hugo Dummett North (Fig. 6), via the replacement of early-formed sulfides by higher sulfidation state sulfides and/or by dissolution of early sulfides and reprecipitation at shallower levels. This process has been recognized to significantly improve the Cu grade in a number of systems (cf. Gustafson and Hunt 1975; Brimhall 1979; Ossandón et al. 2001). Additionally, this evolution of the sulfide assemblage is associated with increasing Cu but decreasing Fe and S contents of the sulfides, which significantly improves the quality of the ore in terms of metallurgy and environmental impacts. Iron and S may go into pyrite, which is a common mineral in high-sulfidation state mineral assemblages (Einaudi et al. 2003).

Hypogene enrichment of this kind is considered a critical process in the development of HGHP ores and can potentially rationalize the observation of secondary, potentially higher-grade mineralization, superimposed on earlier, lower-grade potassic veins, but with enrichment not occurring where prior potassic-stage mineralization did not exist (Cernuschi et al. 2023). Enrichment could also occur by overprinting of sulfides initially precipitated in the phyllic alteration zone. The process is driven by telescoping of the porphyry-hydrothermal

system, with downward penetration of relatively cold meteoric water during exhumation (Brimhall 1979), which causes downward migration of isotherms and hence oxidation and acidification of fluids at progressively lower levels in the system (Heinrich 2005; Reed et al. 2013). This has been documented in a number of major porphyry systems, such as Chuquicamata (Ossandón et al. 2001; Rivera et al. 2012). The high-sulfidation assemblages overprint and likely remobilize earlier sulfide assemblages at depth (thereby obscuring primary mineral zoning and textures) because of increasing fO_2 and decreasing pH and fH_2S (Fig. 10). Dissolution of pre-existing chalcopyrite(-bornite) solubilizes copper (Fig. 10), most likely in the form of aqueous $CuCl_2^-$ (Crerar and Barnes 1976; Hezarkhani et al. 1999), or possibly as Cu-S complexes (Brimhall 1979, 1980). This corresponds to a spatial-temporal stage of porphyry-Cu evolution when copper leaching rather than deposition predominates, leading to the production of zones of barren or low-grade quartz-sericite-pyrite alteration (Fig. 10; Brimhall 1980), which potentially can be observed even down to the individual vein scale (Cernuschi et al. 2023).

The dissolved Cu from earlier sulfides is thought to be mixed with additional Cu from a deeper magmatic source at this stage, making the later acidic and oxidized fluid enriched with Cu. (Brimhall 1979; Hezarkhani et al. 1999). A delay in buffering of fluid acidity and oxidation state by the rock mass could lead to significant over-step in fO_2 and pH, with fluids essentially following the ‘gas buffer’ (Giggenbach 1980, 1987), thereby attaining extremely high sulfidation states. Irrespective, once sulfide supersaturation is eventually attained, such as via cooling or fluid mixing, deposition of high Cu:Fe and Cu:S ratio sulfides in bornite-pyrite-dominant mineralization associated with phyllic to advanced argillic alteration, or

eventually digenite-covellite-chalcocite-dominant mineralization with advanced argillic assemblages can result in anomalously high-grade Cu ores (Brimhall 1979, 1980; Hezarkhani 2002).

A geological model for HGHP genesis

The relationships between alteration and high-grade Cu at both Resolution and Hugo Dummett North show that HGHP mineralization is largely associated with white-mica-stable phyllic alteration that in part overprints pre-existing potassic alteration. The phyllic alteration is itself overprinted by advanced argillic alteration, with further Cu grade upgrading. Even when elevated grades are observed within ostensibly potassic-dominated domains, the sulfides are always mostly associated with an incipient muscovite overprint. Based on these observations, and our literature review, we define two different domains that can host HGHP Cu mineralization (Fig. 11A). One occurs at depth (HGHP-I), associated with moderate to intense overprinting of biotite or K-feldspar by muscovite in potassic alteration, and is characterized by ~1.0 % Cu mineralization (e.g. deep zones of both Resolution and Hugo Dummett North). This typically comprises chalcopyrite with some bornite; minor digenite occurring in a low-sulfidation state assemblage is also reported in the deep parts of several other HGHP systems such as Chuquicamata, Grasberg and Bingham Canyon (see Table 1 for references).

The second HGHP zone (HGHP-II) is located in the upper phyllic and advanced argillic domain, which can host higher-grade ores of 1.0-2.5 % Cu, as exemplified by the upper ore zones at both Resolution and Hugo Dummett North. In both cases, the systems are telescoped,

555 with advanced argillic alteration superimposed on phyllic alteration, which in turn has
556 overprinted potassic alteration, leading to close proximity, or even overlap of HGHP-I and
557 HGHP-II mineralization. Resolution is an example of an extremely telescoped system in
558 which kaolinite/dickite-rich advanced argillic alteration has extensively overprinted biotite-
559 rich potassic alteration.

560 Most of the HGHP deposits defined and reviewed in this study have protracted (but episodic)
561 magmatic-hydrothermal lifespans mostly between 1 and 5 Myrs (Table 1). For example, the
562 earliest hydrothermal event at Resolution is recorded by molybdenite that formed at $63.53 \pm$
563 0.38 Ma, and late muscovite formed at 61.93 ± 0.34 Ma, with late pyrite-alunite dated at ~ 51
564 Ma (Hehnke et al. 2012). Due to this, these systems can, over time, release the large amounts
565 of water essential for the formation of large porphyry deposits (Richards 2011; Chiaradia and
566 Caricchi 2017; Virmond et al. 2024) by tapping extensive and/or repeatedly replenished
567 magma reservoirs that can exist for long periods in the crust in crystal-rich “cold storage”
568 (e.g., Nathwani et al. 2023). This allows multiple stages of Cu transport into the same shallow
569 crustal system with such multi-stage addition helping to develop high grades (e.g. El Teniente;
570 Vry et al. 2010).

571 During long magmatic-hydrothermal lifespans, syn-mineralization exhumation and
572 telescoping can take place as a result of shallow crust collapse, magma intrusion doming or
573 erosion (Sillitoe 1994; Dahlström et al. 2022; Evenstar et al. 2025). The rates and degree of
574 exhumation control the superimposition and telescoping of multiple hydrothermal events
575 which will influence grade development in individual deposits. We would expect to see two

separate domains of high-grade mineralization (Fig. 11A) only in untelescoped systems, with a “barren sericitic zone” in between (e.g., Brimhall 1980).

However, many high-grade porphyry deposits appear to have experienced rapid exhumation and strong telescoping, leading to superposition of HGHP-II on HGHP-I (Fig. 11B). This process is thought to account for several extremely high-grade systems (e.g. Chuquicamata, Resolution, Hugo Dummett North, Rosario, Butte, Onto and Golpu) and results in enriched hypogene ore hosted mostly by phyllic and/or advanced argillic alteration. The effect of telescoping on grade is also evidenced in the Río Blanco-Los Bronces district, where average Cu grades increase from 0.63 to 0.90 % from north to south with increasing degree of telescoping (Toro et al. 2012). During this exhumation and superposition process, a transition to extensional stress during the formation of phyllic and advanced argillic alteration at shallow levels (Sillitoe and Hedenquist 2003; Piquer et al. 2021; Skarmeta 2021), would further favor development of open fractures and breccia zones, helping to focus mineralizing fluids at the very late stage of evolution (Sibson 1996; Sanderson and Zhang 1999). The development of such extensive permeability networks can allow downward ingress of cold meteoric water (Fig. 11B), which would compress thermal gradients and be another key driver of rapid Cu solubility decrease in ascending fluids (Fournier 1999; Weis et al. 2012).

It is thought likely that there is a critical range of exhumation rates that are conducive to the formation of HGHP deposits where the degree of telescoping has optimized remobilization and concentration of Cu, in a manner somewhat analogous to supergene enrichment associated with a descending water table (Sillitoe 2005; Dahlström et al. 2022). At Butte, the main-stage mineralization formed at a rapid estimated exhumation rate of 1-3 mm/yr

(Houston and Dilles 2013), faster than any stages of the precursor porphyry system. In the northern Andes, the main hypogene mineralization in the late Eocene porphyry deposits formed at relatively high exhumation rates averaging ~0.3 mm/yr (Dahlström et al. 2022). The supergiant, high-grade Miocene-Pliocene porphyry deposits (e.g. El Teniente and Río Blanco-Los Bronces) in Central Chile are also associated with rapid exhumation at around 1 mm/yr (Farías et al. 2008; Maksaev et al. 2009; Skarmeta et al. 2024). However, precise exhumation rates are challenging to constrain, and more work is required to better understand this aspect of porphyry system evolution and its impact on system longevity and the size and grade of deposits.

Although rapid exhumation is thought to be important for generating the highest hypogene grades by telescoping, this process can also lead to exposure and destruction of such mineralization. Thus, a timely cessation of uplift and, potentially, subsequent burial under volcanic or sedimentary cover is necessary to preserve high-level HGHP ores. Examples of HGHP systems that have post-mineral cover or where exhumation ceased or was extremely slow prior to exposure include Hugo Dummett North, Chuquicamata, Čukaru Peki and deposits in the Río Blanco-Los Bronces district (Hervé et al. 2012; Rivera et al. 2012; Toro et al. 2012; Jelenković et al. 2016; Wainwright et al. 2017). The time interval between mineralization and inferred cessation of exhumation is normally ≤ 5 My, although, in a few cases (e.g. Resolution), the interval can be longer (Hehnke et al. 2012).

Conclusions

We conclude that long-lived magmatic-hydrothermal activity, accompanied by strong uplift, exhumation and telescoping, are the first-order controls on the generation of the highest-grade

hypogene porphyry Cu deposits. These conditions lead to steep thermal gradients and high permeability development in increasingly cool, brittle rocks which favor efficient sulfide precipitation from focused fluids. At the same time, superposition of lower-temperature, acidic and oxidative alteration on primary potassic stage mineralization can cause remobilization and concentration of Cu in higher-sulfidation state minerals with lower S content, increasing grade and improving ore quality. This model links high-grade ore development to two, relatively low-temperature stages, associated either directly with phyllic to advanced argillic alteration, or to the onset of phyllic overprinting of potassic-altered rocks. On the broader scale, recognition of the right geodynamic settings, the more local tectonic controls of enhanced exhumation and the existence of long-lived magmatic-hydrothermal centers are key to the identification of areas with high HGHP potential.

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653

654 **Author Contributions**

655 Both authors contributed to the study conception and design. Samples collection and selection
656 were performed by both authors. Data analysis and collection were conducted by Chao Yang.
657 The first draft of the manuscript was written by Chao Yang under the supervision of Jamie
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Figure caption

Fig. 1. Statistics of copper grade for economic porphyry Cu deposits (filtered by ≥ 100 Mt mineralized rock, n=446). Data in ESM Table S1.

Fig. 2. Geology, alteration and grade distribution of the two highest-grade hypogene porphyry Cu deposits. A. Resolution, Arizona, USA (modified from Hehnke et al. 2012); B. Hugo Dummett North, Oyu Tolgoi, Mongolia (modified from Khashgerel et al. 2009).

Fig. 3. Examples of typical high-grade drillcore samples (A, Res-17Q, 1821.6m, 5.6 wt% Cu; B, Res-5M, 1970.1m, 0.73 wt% Cu; C, Res-35N, 1819.7 m, 2.7 wt% Cu) from the potassic-phyllic transition zone at Resolution, and matching TESCAN TIMA image (D) of Sample C. Deep, high-grade mineralization is related to quartz-chalcopyrite veins primarily associated with muscovite and minor kaolinite/dickite alteration. It is noteworthy how much muscovite alteration is present in the sample even though much appears to be biotite in the drillcore sample. E. Res-35N, 1789.2m, alunite-bornite-pyrite veins in diabase. F. Res-31B, 1706.8m, high-grade quartz-pyrite-chalcocite-digenite veins with muscovite alteration. Abbreviations: Alu-alunite, Ap-apatite, Bn-bornite, Bt-biotite, Ccp-chalcopyrite, Kln-kaolinite, Ms-muscovite, Py- pyrite, Rt-rutile.

Fig. 4. Quantitative mineralogy of samples illustrating representative potassic to phyllic transitions within individual lengths of drillcore from Resolution. A. Diabase sample (R-17Q-1822.1 m) with variable extents of phyllic alteration after predominantly biotitic potassic alteration. The upper section (B) has stronger phyllic alteration with more muscovite (30.1 %) and associated chalcopyrite (1.3 %) and less biotite (21.9 %) than the lower section (19.9 %

992 muscovite, 40.1 % biotite, 0.5 % chalcopyrite, C). D. Volcaniclastic sample (R-1B-2323.4 m)
 993 with weak and intense phyllic alteration after predominantly K-feldspathic potassic alteration.
 994 The upper section (E) has muscovite-anhydrite as the dominant alteration minerals after K-
 995 feldspar, with significant chalcopyrite (17.0 %); the lower section (F) is dominated by K-
 996 feldspar containing small amounts of chalcopyrite (0.3 %) and with a weak muscovite-pyrite(-
 997 chalcopyrite) overprint. The numbers in the parentheses are area percentage of minerals. Anh-
 998 anhydrite, Ill-illite, Mol-molybdenite, K-feld-K-feldspar, Qz-quartz. Other mineral
 999 abbreviations as Fig. 3. Numbers in the bracket are area percentage of minerals, same in other
 1000 figures.

1001 Fig. 5. Example of strongly Cu-mineralized diabase from Resolution (A) with intense
 1002 muscovite and kaolinite alteration (Res-35N, 1799.1 m, 15.7 wt% Cu). B. TIMA image of
 1003 strongly silicified wallrock exhibiting development of advanced argillic assemblages after
 1004 phyllic alteration. C. TIMA image of an area within the quartz-sulfide vein showing very
 1005 high-grade mineralization of bornite-pyrite(-chalcopyrite) associated with kaolinite/dickite,
 1006 quartz, apatite, APS minerals and fluorite. Microbrecciation textures are evident.

1007 Fig. 6. Replacement textures observed in very-high-grade mineralization at Resolution (A-D)
 1008 and Hugo Dummett North (E-F). A. Chalcopyrite largely replaced by bornite and minor
 1009 chalcocite (Res-35N-1799). B. Bornite partly replaced by covellite and chalcocite (Res-35N-
 1010 1666.6). C. Chalcopyrite replaced by bornite and digenite (Res-17Q-1779.7). D. Chalcopyrite
 1011 replaced by covellite (Res-5M-1890.7). E. Deep muscovite overprinting K-feldspar-rich
 1012 potassic zone, chalcopyrite mineralization replaced by bornite and digenite (HD-UGD103-
 1013 150.9). F. Deep potassic zone, bornite replaced by tennantite (HD-OTD976A-1528.6). Cc-
 1014 chalcocite, Cv-covellite, Dg-digenite, Tnt-tennantite, other mineral abbreviations as Fig. 3
 1015 and 4.

1016 Fig. 7. Typical high-grade core samples and matching TESCAN TIMA images from Hugo
 1017 Dummett North. A, B: deep, K-feldspar-dominant potassic alteration (HD-OTD976A-1528.6,
 1018 1.2 wt% Cu). Although the drillcore specimen shows abundant, red K-feldspar, which would
 1019 likely be linked genetically to coincident high-grade copper assays without further

information, detailed TIMA images show that Cu-sulfides (predominantly bornite) are texturally associated with a significant, but relatively diffuse, muscovite overprint, with no sulfide grains that can be confidently interpreted to be coeval with K-feldspar. C, D: Middle phyllic alteration zone with intermediate Cu grade (HD-OTD976A-1504.2, 0.97 wt% Cu). Quartz and muscovite are the major mineral phase with disseminated chalcopyrite mineralization. E, F: Upper phyllic alteration zone (HD-UGD103-481.9, 4.35 wt% Cu). In this zone, muscovite and quartz are the predominant alteration minerals, with abundant disseminated bornite-chalcopyrite mineralization. G, H: Very high grade “QV90” core sample (HD-UGD103-693.7, 6.34 wt% Cu). Very abundant bornite occurs in dissolution cavities and infilling narrow fractures in quartz, with a small amount of muscovite. Ank-ankerite, other abbreviations as Fig. 3, 4, 5 and 6.

Fig. 8. Alteration and hypogene Cu grade distributions in several high-grade hypogene porphyry Cu deposits. A. Rosario, Collahuasi District, Chile (modified from Masterman et al. (2005); B. Onto, Indonesia (modified from Burrows et al. (2020); C. Chuquicamata, Chile (modified from Ossandón et al. (2001); D. Grasberg, Indonesia (modified from Leys et al. (2012).

Fig. 9. High-grade Cu mineralization associated with transitional K-silicate-sericite alteration and phyllic to advanced argillic alteration coincides with key hydrothermal reactions and decreasing Cu-sulfide solubility between 425 and 375 °C, across the brittle-ductile transition and within or just below the window of retrograde silica solubility. A. In this temperature range, muscovite becomes stable and is subsequently replaced by pyrophyllite at slightly lower temperatures (modified from Hedenquist and Arribas 2022). B. Extensive Cu-sulfide precipitation will occur as the solubility of chalcopyrite (dissolved in the form of CuCl_2) decreases rapidly over four orders of magnitude (after Hezarkhani et al. 1999 and Liu and McPhail 2005). The onset of significant SO_2 disproportionation at ~400 °C facilitates Cu precipitation as sulfides (Holland 1965), by generating H_2S directly; further H_2S can be produced by reduction of aqueous sulfate via oxidation of minerals containing ferrous iron. C. At ~400 °C, rocks transform from ductile to brittle behavior, close to the region where retrograde silica solubility occurs in low-salinity, intermediate-density magmatic fluids

(Fournier 1999); both processes act to help generate permeability for focusing fluid flow. The region highlighted in pink is the inferred window for high-grade Cu-sulfide precipitation.

Fig. 10. Modelled fluid properties and phase stability during progressive fluid interaction with monzonitic hostrock, explaining hypogene enrichment processes. Modified from Brimhall (1980).

Fig. 11. Geological model for high-grade hypogene porphyry Cu mineralization. Alteration model modified from Sillitoe (2010). During telescoping processes, isotherms are increasingly steep (from A to B) and the two high-grade mineralization domains are superimposed and result in a large and very-high-grade HGHP system involving extensive Cu remobilization and Cu-upgrading of earlier mineralization.

1060

Table 1. Key features of high-grade hypogene mineralization in selected significant porphyry copper deposits.

	Deposit	Age (Ma)	Cu resource (Mt)	Grade (%)	HGHP ore-related alteration minerals	HGHP ore-related sulfide assemblage	Occurrence	References
1	Chuquicamata northern Chile	35-31	31.3 62.7*	1.54 0.43*	Early: K-feldspar bands with green-white mica (no pyrite) superposition; Main: quartz, white mica	Early: chalcopyrite-bornite-digenite; main: enargite, covellite, digenite, pyrite	Stockwork veins, disseminated sulfide in white mica and K-feldspar halos; main sulfide stage mostly in white mica Veins and disseminated	Ossandón et al. (2001); Rivera et al. (2012); CODELCO annual report (2021)
2	Resolution, Arizona, USA	64-60	27.3	1.53	Phengitic white mica, quartz, kaolinite, with minor fluorite, anhydrite, rutile	Chalcopyrite, pyrite, bornite in potassic overprinting zone; sericite-kaolinite zone with bornite, chalcocite, digenite, pyrite Chalcopyrite, minor bornite		Manske and Paul (2002);Hehnke et al. (2012); Rio Tinto annual report (2021)
3	El Teniente central Chile	6.3-4.4	23.2 ¹ 92.1*	1.27 ¹ 0.56*	Biotite, K-feldspar, albite, anhydrite, tourmaline breccia; paragonitic and phengitic muscovite, quartz, chlorite		Chalcopyrite in breccia, chalcopyrite-bornite-bearing thick quartz-sulfide veins (up to 4 cm), late quartz-tourmaline-chlorite-muscovite veins with chalcopyrite-bornite-pyrite-tennantite Veins and cavities	Skewes et al. (2002); Cannell et al. (2005); Vry et al. (2010); Spencer et al. (2015); CODELCO annual report (2021)
4	Grasberg, Papua, Indonesia	3.33-3.01	18.3 ¹ 31.6*	1.56 ¹ 0.75*	K-feldspar-magnetite-anhydrite with major Cu-Au; muscovite, pyrophyllite, illite, kaolinite altered rocks with mixed copper sulfide.	Grasberg Cu-Au stage: chalcopyrite–bornite ± pyrite ± gold ± hematite; mixed copper sulfide: chalcopyrite, bornite, covellite-nukundamite, digenite, chalcocite Chalcopyrite, pyrite and minor bornite		Pollard and Taylor (2002); Pollard et al. (2005); Leys et al. (2012); Leys et al. (2020)
5	Río Blanco, central Chile	8.2-4.3	17.9 ¹ 135.2*	1.19 ¹ 0.62*	K-feldspar, biotite, albite, magnetite, anhydrite, tourmaline, specularite, gray-green white mica and chlorite		Stockwork quartz veins, hydrothermal breccias, late-stage polymetallic veins	Warnaars et al. (1985);Ricardo et al. (1999);Deckart et al. (2005); Toro et al. (2012); CODELCO annual report (2021)
6	Los Sulfatos, central Chile	7.3-6.3	17.5 40.5*	1.46 0.90*	Biotite, K-feldspar, tourmaline, specularite, anhydrite	Chalcopyrite, bornite ± digenite	Hydrothermal breccia, quartz-sulfide veins, late-stage polymetallic veins Veins and disseminated	Irarrazaval et al. (2010); Toro et al. (2012)
7	Hugo North, Mongolia	Dummett 374-371	12.3	1.06	Muscovite, pyrophyllite, alunite	Bornite ± chalcocite; bornite-chalcopyrite		Khashgerel et al. (2006); Khashgerel et al. (2009); Crane and Kavalieris (2012)
8	Rosario, northern Chile	34.5-32.6	11.3	1.03	Early: K-feldspar, biotite, albite, illite, chlorite. Late: muscovite, pyrophyllite, dickite, alunite, quartz	Early bornite, chalcopyrite; late pyrite, chalcopyrite, bornite, chalcocite, tennantite and enargite	Massive high-sulfidation sulfide veins	Dick et al. (1994); Masterman et al. (2004); Masterman et al. (2005)
9	Onto, Indonesia	0.04-0.54	8.4	0.87	Quartz, pyrophyllite, dickite, alunite	Covellite-pyrite, minor bornite-chalcocite-chalcopyrite, nukundamite	Leached open-space filling and replacements	Burrows et al. (2020)
10	Butte, Montana, USA	66-62	8.2 ¹ 35.1*	4.26 ¹ 0.67*	Deep: biotite-Kspar±musc±andalusite. Main stage: gray-green muscovite, chlorite, quartz, pyrophyllite, dickite/kaolinite, topaz	Bornite, covellite, digenite, chalcocite, enargite, pyrite	Lode veins	Brimhall (1979; 1980); Rusk et al. (2008); Reed et al. (2013); Houston and Dilles (2013); Reed and Dilles (2020)

11	Golpu, Guinea	Papua New Guinea	8.7	8.2	1.00	Early: biotite, K-feldspar, magnetite, actinolite. Late: alunite, kaolinite, quartz	Chalcopyrite-bornite; pyrite-covellite-bornite-tennantite	Vein and disseminated	Rinne et al. (2018)
12	Čukaru Peki, Serbia		87-84.5	7.8 ¹ 18.6*	1.12 ¹ 0.76*	Quartz, magnetite, anhydrite	Mainly chalcopyrite, with covellite and minor enargite replacement	Vein and disseminated	Jelenković et al. (2016); Klimentyeva et al. (2022); Zijin Annual report. (2023)
13	Bingham Utah, USA	Canyon, USA	37.6-37.1	6.6 ¹ 28.5*	1.03 ¹ 0.88*	Intense K-feldspar and biotite, muscovite overprint	Chalcopyrite-bornite-digenite-gold; nukundamite	Veins and disseminated	Parry et al. (2001); Inan and Einaudi (2002); Redmond and Einaudi (2010)
14	Los central Chile	Bronces, Chile	8.2-4.3	4.9 12.5*	1.03 0.39*	Quartz, tourmaline, specularite, anhydrite, white mica, chlorite	Chalcopyrite with minor bornite	Late magmatic-hydrothermal breccia	Warnaars et al. (1985); Toro et al. (2012); Porter Geo. (2016)
15	MMH Hales), Chile	(Ministro northern	35-31	2.4 21.9*	1.06 0.72*	Deep: K-feldspar-biotite. Shallow: quartz, alunite, pyrophyllite, white mica, dickite	Deep: bornite, chalcopyrite; shallow: chalcocite, bornite, covellite, enargite, tennantite, pyrite	Hydrothermal breccia	Boric et al. (2009); Rivera et al. (2012); Zentilli et al. (2015); Zentilli et al. (2018); CODELCO annual report (2021)

*Total copper resource in the deposit; ¹ Data on high-grade portion from Sillitoe and Perelló (2023).

The actual white mica mineral phase is given where known, otherwise “white mica” is used.

The global distribution of these deposits is shown in ESM Fig. S1

Table 2. TESCAN TIMA mineralogical quantification of representative samples (modal percentage by area)

	Resolution, USA										Hugo Dummett North, Mongolia				
Mineral phase	Deep potassic with muscovite overprints				Deep potassic with intense muscovite overprints				Upper phyllic alteration		Deep potassic with muscovite overprints		Middle intense muscovite alteration	Upper intense quartz-muscovite and QV90 alteration	
	R-17Q-1822.1 (Fig. 4B)	R-17Q-1822.1 (Fig. 4C)	R-1B-2323.4 (Fig. 4E)	R-1B-2323.4 (Fig. 4F)	R-5M-1970.1 (Fig. 3B)	R-35N-1819.7 (Fig. 3C)	R-35N-1819.3	R-17Q-1821.6 (Fig. 3A)	R-35N-1799.1 vein (Fig. 5D)	R-35N-1799.1 (Fig. 5B)	OTD976A-1528.6 (Fig. 7B)	UGD103-150.9	OTD976A-1504.2 (Fig. 7D)	UGD103-481.9 (Fig. 7F)	UGD103-693.7 (Fig. 7H)
Quartz	12.0	8.7	31.4	12.3	22.3	17	11.9	47.2	18.6	29.1	34.9	50.6	56.3	48.4	83.3
K-feldspar	-	0.3	19.0	72.4	-	0.7	0.4	-	0.1	0.1	32.8	17.7	0.3	0.2	-
Biotite	21.9	40.1	0.7	4.9	12.3	15.5	29.5	0.8	-	0.1	0.1	0.1	-	-	-
Muscovite	30.1	19.9	23.6	4.1	26.8	32.0	41.0	12.7	0.9	34.2	18.9	16.0	30.1	37.3	0.4
Kaolinite*	9.7	8.1	-	-	3.6	5.3	7.1	2.9	5.1	3.7	-	-	-	-	0.3
Pyrite	0.1	-	-	0.2	17.3	0.1	-	-	32.6	6.4	-	-	-	-	-
Bornite	-	-	-	-	1.6	0.1	-	0.3	30	1.4	2.1	1.2	-	4.0	13.2
Chalcopyrite	1.3	0.5	17.0	0.3	0.2	10.1	0.9	23.5	2.4	0.1	0.1	1.4	0.8	1.1	-
Molybdenite	-	-	-	-	-	-	-	0.44	-	-	-	-	-	-	-
Illite	4.0	4.0	-	-	1.7	3.2	3.9	1.1	0.1	7.2	1.5	0.9	5.7	3.7	-
Rutile	1.0	0.6	-	0.3	0.5	2.2	0.3	0.3	0.1	3.4	0.1	-	0.1	-	-
Apatite	0.2	0.1	-	-	0.1	0.2	-	0.8	0.4	-	0.3	0.1	0.2	0.1	-
APS	-	-	-	-	0.1	0.4	0.1	0.1	3	0.6	-	-	-	-	-
Ankerite	-	-	-	-	-	-	-	-	-	-	1.9	4.6	-	-	-
Covellite	-	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-
Tennantite	-	-	-	-	-	-	-	-	-	-	0.2	-	-	-	-
Fluorite	-	-	-	-	-	0.5	0.1	0.78	1.3	0.3	-	-	-	-	-
Chlorite	-	-	-	-	-	-	0.2	-	-	-	-	-	-	-	-
Zircon	-	-	-	-	-	-	-	0.15	-	-	-	-	-	-	-
Anhydrite	-	-	2.5	1.0	-	-	-	-	-	-	-	-	-	-	-
Total	81.7	83.7	96.3	96.7	86.4	87.2	95.4	90.9	94.9	86.5	92.9	92.8	93.8	94.9	97.3

- Data less than 0.1%; APS - aluminum-phosphate-sulfate mineral; * “Kaolinite” refers to the mineral group, it can be either kaolinite or dickite. Totals <100% indicate the proportion of pixels unclassified by the TIMA, mainly due to mixed EDS spectra along grain boundaries and associated with fine-grained intergrowths of minerals

Formatted Table

1 Formation of giant high-grade hypogene porphyry copper deposits during phyllic to
2 advanced argillic alteration: textural evidence from automated SEM mapping at the
3 Resolution and Hugo Dummett North deposits

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9 **Abstract**

10 Detailed core logging, combined with TESCAN TIMA mineral quantification at two globally
11 significant, high-grade porphyry deposits – Resolution, USA, and Hugo Dummett North,
12 Mongolia – indicate that most chalcopyrite $\pm$ bornite-pyrite is intergrown with muscovite that
13 overprints earlier potassic alteration assemblages containing biotite and/or K-feldspar. Copper
14 grades increase with the intensity of muscovite overprint on primary potassic assemblages
15 supporting a link between high-grade Cu mineralization and phyllic alteration. Another zone
16 of high-grade Cu mineralization occurs in the upper parts of the phyllic alteration zone and/or
17 within later advanced argillic alteration, associated with high-sulfidation bornite $\pm$ digenite $\pm$
18 covellite $\pm$ chalcocite-pyrite assemblages, that partly replace earlier chalcopyrite. These two
19 high grade domains have comparable features in many other significant high-grade Cu
20 porphyry deposits (Chuquicamata, Rosario, MMH, Onto, Butte) – all strongly telescoped
21 systems that host significant amounts of high-grade Cu mineralization in phyllic and/or
22 advanced argillic alteration that overprint potassic alteration.

We suggest there are at least three reasons for the development of high-grade hypogene ore in telescoped porphyry systems: 1) rapid unroofing and exhumation can generate steep thermal gradients, promoting a rapid decrease in Cu solubility and efficient precipitation of sulfides; 2) rapid, syn-mineralization exhumation and magma doming when the rock mass behaves in an increasingly brittle fashion, create significant permeability in late stages of porphyry systems; 3) telescoping during syn-mineralization exhumation leads to overprinting of early sulfide assemblages by late-stage acidic and oxidized hydrothermal fluids that remobilize and concentrate early Cu, leading to the precipitation of sulfides with high Cu/S ratios. We conclude that the coincidence of rapid exhumation and long-lived hydrothermal activity exerts a first order control on the formation of high-grade hypogene porphyry Cu mineralization.

Key words: High-grade hypogene porphyry copper, phyllic alteration, advanced argillic alteration; superimposition

Introduction

High-grade orebodies are of increasing significance to the mining industry in the low-carbon transition era because of the lower energy cost and reduced waste associated with extraction. However, such orebodies are infrequent: in the case of the most important Cu source, porphyry Cu deposits, our database for significant deposits (≥ 100 Mt ore resources, $n=446$, see ESM Table S1) shows that porphyry Cu deposits with a defined resource have a median Cu grade of 0.35 %, with only the top tenth percentile having a grade of over 0.62 % and just a handful with a grade over 1% (Fig. 1).

Some porphyry deposits contain supergene oxide and sulfide enrichment resources which improve the overall Cu grade (e.g. Potrerillos, Chuquicamata and Escondida: Marsh et al. 1997; Ossandón et al. 2001; Padilla-Garza et al. 2001). However, here we focus only on high-grade hypogene mineralization that is associated with magmatic-hydrothermal fluids exsolved from porphyry intrusions. This is because, despite their economic significance, many supergene ores have been mined out in recent decades so that future mining – especially of deep deposits – will mostly involve exploitation of hypogene resources.

Sillitoe and Perelló (2023) proposed ≥ 1 % Cu as a definition for high-grade hypogene ore. However, this definition does not refer to a deposit resource *per se*, so could apply for a tiny amount of high grade ore in a large deposit, or a small deposit of entirely high grade. Sillitoe (1998) classified large, high-grade hypogene porphyry deposits as having a grade of ≥ 1 % Cu and over 1 billion tons (Gt) of ore (over 10 Mt fine copper). Few individual deposits meet this criterion if referring to the grade of a whole deposit (Fig. 1A); probably only Resolution, USA (1.8 Gt at 1.53 % Cu) and Hugo Dummett North, Mongolia (1.2 Gt at 1.06 % Cu; Rio Tinto Annual report 2022). Some deposits contain high-grade ore zones exceeding 1 Gt, such as Chuquicamata, Chile (2.0 Gt at 1.54 Cu; Ossandón et al. 2001), El Teniente, Chile (1.8 Gt at 1.17 % Cu; Sillitoe and Perelló 2023), Grasberg, Indonesia (2.3 Gt at 1.09 % Cu; Leys et al. 2012), Los Sulfatos, Chile (1.2 Gt at 1.46 % Cu; Irrarazaval et al. 2010), and Rosario, Chile (1.1 Gt at 1.03 % Cu; Masterman et al. 2005). Other deposits contain large amounts of high-grade ore but less than the 1 Gt threshold, e.g. Golpu, Papua New Guinea (820 Mt at 1.0 % Cu; Rinne et al. 2018) and Los Bronces (475 Mt at 1.03 % Cu; PorterGeo database). The presence of by-product metals such as Au or Mo can improve deposit economics significantly,

however, for simplicity, we focus on Cu in this paper and refine the classification terminology for giant high-grade hypogene porphyry (HGHP) deposits as those that contain >2 Mt of hypogene Cu at a grade of ≥ 1 %, irrespective of the overall resource tonnage or grade – the latter will in most cases be lower than 1 %. The threshold of >2 Mt of contained Cu at high grade is somewhat arbitrary but corresponds to the largest 10% of individual deposits defined as ‘giant’ by Singer (1995). This definition captures the major porphyry deposits worldwide that contain substantive high-grade ore (Table 1).

Controls on the formation of high-grade hypogene porphyry Cu mineralization are incompletely understood, yet such knowledge is valuable for successful exploration. Even the relationship between Cu orebodies in general and hydrothermal alteration domains – key geological evidence for deciphering hydrothermal mineralization processes (Dilles and Einaudi 1992; Reed et al. 2013) and exploration footprints (Halley et al. 2015; Wilkinson et al. 2015) – remains contentious in many deposits. A major current debate is whether the bulk of Cu mineralization in porphyry deposits develops in K-feldspar-biotite stable potassic or white mica-quartz dominant phyllic alteration zones (Calder et al. 2022; Schirra et al. 2022; Cernuschi et al. 2023). The host of high-grade hypogene Cu mineralization is similarly contested: at Bingham Canyon, high grade mineralization has been linked to potassic alteration (Redmond and Einaudi 2010), yet fluids associated with significant copper deposition are constrained to temperatures below $\sim 400^{\circ}\text{C}$ (Landtwing et al. 2005). Significant high-grade Cu mineralization occurs in phyllic and advanced argillic alteration at Chuquicamata (Rivera et al., 2012) and in advanced argillic alteration at Onto (Burrows et al. 2020). However, Sillitoe and Perelló (2023) stated that A-type quartz veinlet stockworks

generated during potassic alteration in many deposits “clearly accompanies the high Cu $\pm$ Au values” and suggest that the association of high-grade Cu with chlorite-sericite “may result from overprinting of preexisting Cu-rich potassic zones”. In large systems with multiple porphyry emplacement events and/or telescoping, such as Resolution, Rosario, and Chuquicamata, the genetic relationships between high-grade Cu mineralization and each hydrothermal stage are not easily resolved. This becomes important when assessing the relative timing of Cu mineralization: Sillitoe and Perelló (2023) stated that potassic assemblages are “clearly the most common host of high-grade Cu, accounting for all or part of the >1% Cu ore” in two-thirds of the resources listed in their Table 1, yet most of these contain lower temperature, overprinting assemblages which may have greater significance than is currently attributed to them.

Here, we present the results of high-resolution automated mineralogical quantification and textural examination of samples from the “type” HGHP examples of Resolution (USA) and Hugo Dummett North (Mongolia) – the two highest Cu grade hypogene porphyry deposits worldwide (Fig. 1A). The objective was to determine the paragenetic relationships between Cu sulfides and alteration minerals using technology that provides more unequivocal evidence than more conventional approaches such as core logging or optical microscopy. These observations are complemented by comparison with data from a literature compilation of other giant high-grade hypogene porphyry deposits (with >2 Mt HGHP resource; Table 1). The goal is to identify commonalities and develop a geological framework for understanding the relative timing and hydrothermal processes that control HGHP development. This

framework will hopefully be of benefit in defining the exploration search space for HGHP systems and provide pointers for future research into HGHP deposit genesis.

Deposit geology

Resolution geology

Resolution is the highest grade hypogene porphyry Cu deposit in the world, containing 1859 Mt of ore at 1.52 % Cu, 3.12 g/t Ag, and 0.035 % Mo (Rio Tinto, Annual report 2022). It is located in the Superior district, Arizona, USA, which hosts several porphyry Cu-Mo deposits, epithermal Cu-Ag veins and mantos. The Resolution deposit is centered on a cluster of felsic porphyries that lie within the wider Laramide (80-50 Ma) orogenic belt of the southwestern USA (Dickinson 1989; Favorito and Seedorff 2020). These porphyries intruded a sequence comprising Proterozoic, Paleozoic and Cretaceous rocks, which are overlain by post-mineralization, middle to late Tertiary units.

Proterozoic units include the Paleoproterozoic (~1650 Ma) Pinal schist and Mesoproterozoic Apache Group volcanic and sedimentary rocks. The Pinal schist comprises quartz-muscovite and quartz-chlorite schists with minor intercalations of calcsilicate and metavolcanic rocks. It is intersected by few deep drill holes but is known to host small amounts of low-grade Cu mineralization (Fig. 2A). The Pinal schist is unconformably overlain by Mesoproterozoic sedimentary and mafic volcanic rocks of the Apache Group, which is composed of Pioneer shale, Drippings Springs quartzite, Mescal limestone, and Apache basalt. These rocks are overlain by the Mesoproterozoic Troy quartzite. The sequence was intruded by a series of diabase sills in the late Mesoproterozoic between 1140 and 1040 Ma (Bright et al. 2014). This

130 Proterozoic unit is widespread in southwestern USA, and is an important host of high-grade
131 mineralization in the Resolution deposit (Hehnke et al. 2012), as well as several other
132 deposits in this district, such as the Ray, Chilito and Christmas deposit (Phillips et al. 1974;
133 Force 1998).

134 Paleozoic carbonate rocks and quartzites unconformably overlie the Proterozoic rocks and the
135 carbonates host very high-grade skarn mineralization at Resolution (Hehnke et al. 2012). Late
136 Cretaceous andesitic to dacitic volcanoclastic and pyroclastic rocks (Kvs), dated at 75-66 Ma
137 (Manske and Paul 2002; Ballantyne et al. 2003; Zulliger 2007), host the upper part of the
138 Resolution mineralization (Fig. 2A).

139 Three types of felsic porphyry intrusions have been identified: rhyodacite (major phase),
140 quartz latite and latite porphyry, intruded between 69-64 Ma (Hehnke et al. 2012). Magmatic-
141 hydrothermal breccias were generated during porphyry emplacement, which contain clasts of
142 schist, diabase and Apache Group rocks. Middle to late Tertiary volcanic rocks
143 unconformably overlie the Proterozoic, Paleozoic and Cretaceous sequences and completely
144 cover Resolution (Fig. 2A).

145 Alteration and mineralization: Stockwork mineralization has an age of 64-65 Ma (Re-Os on
146 molybdenite) (Hehnke et al. 2012). The extent of high-grade mineralization at Resolution has
147 not been fully defined but a consistent zone of >1% Cu mineralization extends at least 2 km in
148 an east-northeast direction, 1.5 km in a north-northwest direction and is locally greater than
149 500 m thick (Fig. 2A). The high-grade mineralization preferentially occurs in suitable host
150 rocks, mainly diabase, carbonate rocks and permeable breccias. Deep hydrothermal alteration

is potassic, characterized by secondary biotite-rich diabase and K-felspar-rich felsic rocks (Hehnke et al. 2012), although K-feldspar is likely to be much more abundant in diabase than recognized from drillcore logging (Cooke et al. 2020). The potassic alteration is surrounded by propylitic alteration, with abundant epidote and chlorite in mafic to felsic volcanic, volcaniclastic and intrusive rocks (Phillips 2019; Cooke et al. 2020). The potassic and propylitic rocks are extensively overprinted by white mica-dominant phyllic alteration and occasionally kaolinite alteration for hundreds of meters upwards, transitioning into advanced argillic assemblages (Fig. 2A). Advanced argillic alteration overprints phyllic alteration in the central and upper parts of the deposit, mostly in the Cretaceous sedimentary, volcaniclastic and volcanic rocks. Major alteration minerals in this zone are quartz, pyrite, kaolinite, dickite, topaz, zunyite, alunite, APS (aluminium-phosphate-sulfate) minerals and minor pyrophyllite (Harrison 2007; Winant 2010; Hehnke et al. 2012). Chalcopyrite is the dominant copper sulfide in the potassic and deeper phyllic zones, accounting for ~65% of the total copper sulfide (Hehnke et al. 2012). Overprinting of phyllic alteration is associated with replacement of chalcopyrite by bornite with an attendant increase in the Cu grade (Schwartz 2010). A late-stage, hypogene, high-sulfidation-state mineral assemblage of bornite-chalcocite-digenite-covellite-pyrite associated with white mica and overprinting kaolinite caused further upgrading of the Resolution ore zone, although the majority of high-grade Cu mineralization is related to phyllic alteration (Manske and Paul 2002; Hehnke et al. 2012). Molybdenum has a correlation with Cu in general, although their sulfides are not necessarily coexisting: most molybdenite occurs in a distinct generation of quartz veins at depth, whereas Cu sulfides are

widely present in quartz veins, vein halos, disseminated in the ground mass or infilling pores within altered minerals.

Hugo Dummett North geology

The Hugo Dummett North deposit contains a total resource of 1,159 Mt of ore at 1.06 % Cu, 0.32 g/t Au, and 2.8 g/t Ag (Rio Tinto, Annual Report 2022). The deposit is located at the north end of the Oyu Tolgoi porphyry cluster, Mongolia, which hosts eight discrete porphyry deposits in Devonian and Carboniferous volcanic arc rocks (Wainwright et al. 2011; Crane and Kavalieris 2012). Porphyry mineralization at Hugo Dummett North is associated with Late Devonian quartz monzodiorite stocks and dikes (~372 Ma), that intruded the Oyu Tolgoi sequence (Bulagbayan Formation) which comprises augite basalt, volcanoclastic rocks and laminated siltstones (Fig. 2B). Volcanoclastic rocks are divided into a lower, strongly altered and mineralized sequence and an upper unaltered or weakly altered dacite sequence; the latter may be an allochthonous sheet that acted as post-mineral cover to preserve the porphyry mineralization (Wainwright et al. 2017). The Oyu Tolgoi sequence is overlain by the Heruga sequence, comprising basaltic rocks, breccia and siltstone (Fig. 2B). A suite of younger biotite granodiorite porphyry dikes (~370 Ma) intruded the quartz monzodiorite and volcanoclastic sequences (Fig. 2B) (Wainwright et al. 2017).

The Hugo Dummett North deposit has K-feldspar-dominated potassic alteration at depth, largely hosted by the quartz monzodiorite porphyry (Fig. 2B). This transitions upward into quartz-muscovite-dominant phyllic alteration in quartz monzodiorite and then to shallow

advanced argillic alteration (pyrophyllite-muscovite-kaolinite) that is generally hosted within the augite basalt (Fig. 2B). The phyllic alteration overprints deep K-feldspar alteration.

High-grade copper (>1 %) mineralization is largely associated with phyllic alteration and part of the upper potassic alteration zone (Fig. 2B). A very-high-grade copper (>2.5 % Cu) domain is mostly spatially associated with the upper part of the phyllic (quartz-muscovite) zone, close to the advanced argillic alteration above, mainly hosted in the quartz monzodiorite porphyry and partly in the augite basalt (Fig. 2B; Khashgerel et al. 2009; Crane and Kavalieris 2012). The phyllic-hosted mineralization is characterized by bornite-dominant sulfide associations, associated with intense quartz veins (over 90 % of quartz) in the highest-grade domains (Kirwin et al. 2005), termed QV90 (cf. Khashgerel et al. 2006; Crane and Kavalieris 2012).

Advanced argillic alteration at Hugo Dummett North is characterized by pyrophyllite and residual quartz, with minor muscovite, diaspore, zunyite, topaz, corundum, andalusite, APS minerals, alunite, kaolinite and dickite (Khashgerel et al. 2006, 2008). Although locally it contains high-grade bornite-dominant mineralization, it is primarily host to an enargite-pyrite assemblage with a low Cu grade (Crane and Kavalieris 2012). Other intermediate- to high-sulfidation sulfides such as chalcocite, covellite, tennantite and tetrahedrite have also been reported (Khashgerel et al. 2006, 2008, 2009; Crane and Kavalieris 2012). These sulfides have widely replaced chalcopyrite and bornite, suggesting that the Hugo Dummett North deposit is an extensively telescoped system, with lower-temperature alteration and mineralization superimposed on earlier higher-temperature events.

Methods

To document key mineralogical features of high-grade Cu mineralization and its temporal relationship to hydrothermal alteration assemblages, we collected over ninety samples from several representative drillcores from Hugo Dummett North and Resolution (Fig. 2). These were prepared into 25 mm-diameter polished resin blocks and examined using reflected light optical microscopy and automated scanning electron microscopy. The Resolution samples were mostly selected from intervals of high-grade mineralization with a few distal and deep, low-grade samples for comparison (Fig. 2A). Samples from Hugo Dummett North were collected from high-grade, gold-rich, K-feldspar-altered monzodiorite porphyry from depth and the upper, high-grade copper zone related to phyllic-altered monzodiorite porphyry (Fig. 2B).

Automated mineralogy

The TESCAN Integrated Mineral Analyzer (TIMA) automated scanning electron microscope system from the Image and Analysis Center at the Natural History Museum in London, integrates quantitative energy-dispersive X-ray spectrometry (EDX) and an advanced statistical approach to enable mapping of mineral phases at high spatial resolution. Back-scattered electron (BSE) images and EDX data were collected simultaneously using the modal acquisition mode. BSE images were acquired with a 1 μm pixel size in dot mapping mode, with an EDX spacing of 7 μm . The data were collected using a 15 mm working distance, 25 keV beam energy, and 13-14 nA probe current. Based on their EDX spectra (information of geochemical composition) and prior knowledge of the mineral assemblage, a

custom classification scheme was developed by identifying unknown mineral phases (Hrstka et al. 2018). Polymorphs such as kaolinite and dickite in the samples cannot be discriminated by TIMA because of their similar geochemical compositions. Relatively small numbers of pixels remained unclassified, primarily due to mixed EDX signals of pixels at the boundary between two mineral phases and the presence of fine mineral phases smaller than the resolution of EDX acquisition. Area proportions of minerals were estimated using the total pixel area of each phase.

Results

Resolution

In the deepest parts of the Resolution deposit, high-grade Cu mineralized diabase exhibits a dark color attributed to secondary biotite (Figs. 3A, B and C). Abundant pale and white-colored minerals are present (Figs. 3A and C), which are mostly muscovite and minor illite and dickite/kaolinite (Fig. 3D). Locally, greenish muscovite occurs in halos of the quartz-sulfide veins in the diabase (Fig. 3B). Hydrothermal apatite is common within these veins (Fig. 3D). There is also abundant rutile formed with biotite from breakdown of precursor pyroxene or hornblende, evidenced by close spatial association between rutile and biotite (Fig. 3D). Chalcopyrite and minor bornite (with pyrite) are mainly hosted by quartz-sulfide veins, with halos of muscovite, that have overprinted potassic alteration (Fig. 3); these occur almost to the exclusion of typical A, B or C veins and do not fall into a typical porphyry veinlet category (Sillitoe 2010) but are clearly muscovite-stable and would therefore be most akin to D veins. To discriminate these from other types of D veins at Resolution, we name this chalcopyrite-rich vein type as D1. Quantitative mineralogy in the samples indicates that

255 muscovite is the dominant mineral with a mass proportion greater than biotite (averaging
256 28.1 % muscovite and 14.5 % biotite, n=4; Table 2). A broad spatial coincidence between
257 chalcopyrite and biotite (-K-feldspar) alteration is supported by our core logging, but the
258 detailed mineralogy shows that, although some chalcopyrite grains are disseminated within
259 biotite (Fig. 3D; compare Hehnke et al., 2012, Fig. 8), chalcopyrite is most commonly
260 surrounded by and intergrown with muscovite (Fig. 3D), or occurs within veins that have
261 muscovite halos that have themselves been replaced locally by kaolinite. These observations
262 indicate a close genetic relationship between high-grade Cu mineralization and muscovite
263 alteration of previously potassic-altered rocks.

264 In areas where particularly strong phyllic overprinting of potassic alteration is observed, Cu
265 grades are even higher (>2 %; Fig. 2A), lending further support for a link between high
266 grades and muscovite alteration. Transitions in individual sections of drillcore provide
267 valuable insights into the overprinting processes. The images shown in Figure 4 exemplify the
268 mineralogical changes during phyllic overprinting of strongly potassic-altered diabase (Figs.
269 4A-C) and strongly potassic- altered volcanoclastic rock (Figs. 4D-F). Biotite predominates in
270 the diabase (Fig. 4A) and K-feldspar in the volcanoclastic sample (Fig. 4C) but both minerals
271 are replaced by muscovite in the more altered equivalents. The extent of muscovite alteration
272 parallels the increase in abundance of chalcopyrite and Cu grade (Fig. 4). In the diabase
273 sample (Fig. 4A), the upper section with more muscovite (30.1 %) is associated with more
274 chalcopyrite (1.3 %; Fig. 4B) compared to the lower section with 19.9 % muscovite and
275 0.5 % chalcopyrite (Fig. 4C). The volcanoclastic sample (Fig. 4D) shows a similar trend with
276 the upper section containing 23.6 % muscovite associated with 17.0 % chalcopyrite, with both

forming as a replacement of K-feldspar (Fig. 4E), but the lower, less phyllic-altered sample containing only 4.1 % muscovite and 0.3 % chalcopryrite, again after K-feldspar. Kaolinite is present in diabase at all depths in Resolution and chalcopryrite occurs spatially with kaolinite in many cases (Figs. 4B, C).

In the upper parts of the Resolution deposit (Fig. 2A), and locally at greater depths, rocks are more strongly altered by muscovite that has largely replaced biotite, with muscovite increasing to 34.2 % but biotite decreasing to 0.1 % (Fig. 5B), and biotite itself also partly overprinted by kaolinite/dickite; in this process, nearly all biotite has been destroyed (Fig. 5B; Table 2). Although not obvious in drillcore, muscovite is predominant in the altered diabase (Fig. 5B), whereas more dickite/kaolinite occurs in the quartz-sulfide veins (compare Fig. 5C with Fig. 5B). Pyrite and bornite comprise the major sulfide assemblage (Figs. 5B, C), distinct from the chalcopryrite(-pyrite) assemblage that predominates at depth, suggesting a higher sulfidation state. Covellite, digenite and chalcocite are also commonly seen in the shallow part of the very high-grade Cu mineralization zone, that have replaced earlier chalcopryrite (Figs. 6B, C and D). A replacement sequence of chalcopryrite → bornite → chalcocite/covellite/digenite can be observed locally (Figs. 6A-D), indicating a progressive increase in sulfidation state. These high-sulfidation state, sulfide-enriched quartz veins in this part of the deposit are classified as D2 veins. A large amount of rutile, formed during biotite breakdown, is preserved during later dickite/kaolinite alteration (Fig. 5B). Microbrecciation in quartz-sulfide veins at this level is commonly observed (Figs. 5C and D). Locally, alunite and high-sulfidation Cu-sulfide veins are present with minor pyrophyllite (Fig. 3D). Notable

amounts of hydrothermal apatite (Fig. 5D) are intergrown with bornite and advanced argillic minerals (APS minerals, fluorite, alunite, kaolinite and quartz).

Although much of the pervasive muscovite alteration is associated with high-grade D1 and D2 veins, there are plenty of more typical, barren D veins occurring in distal positions, where Cu grade is generally below 0.5 % (Fig. 2A). These quartz veins mainly contain pyrite and occasionally chalcopyrite or bornite, and have muscovite halos but exhibit limited overprinting by kaolinite/dickite (Fig. 3E). These are classified as D3 veins in this study.

Hugo Dummett North

Deep, high Cu-Au grade mineralized monzodiorite at Hugo Dummett North has a red color (Fig. 7A), generally attributed to strong K-feldspar alteration. Representative quantification results indicate that K-feldspar accounts for ~33 % of the monzodiorite. Although muscovite is not obvious in drillcore (Fig. 7A), significant amounts (~19 %) are present (Table 2) indicative of phyllic overprinting even at depth. The spatial association between high-grade Cu and core intervals logged as potassic has been typically interpreted to represent a genetic association (Khashgerel et al. 2006; Crane and Kavalieris 2012). However, TIMA maps show that bornite and chalcopyrite (with minor digenite and tennantite, Figs. 6E and F), the major host of Cu, is in fact associated with muscovite that has partly replaced K-feldspar and occurs as late mineral infill in cracks that crosscut earlier quartz veins (Fig. 7B). Virtually no Cu-sulfide grains are found within secondary K-feldspar (Fig. 7B). In these very deep locations, bornite is replaced by a minor, later stage of digenite (Fig. 6E) and tennantite (Fig. 6F), which

are probably products from late, high-sulfidation mineralization. Abundant hydrothermal apatite (0.3 %) is also associated with muscovite (Fig. 7B), as noted at Resolution.

In the upper part of the deposit, there is a lower Cu grade (<1 %) interval below the very high-grade (>2.5 % Cu) mineralization, associated with intense quartz-muscovite alteration and disseminated chalcopyrite (Figs. 7C and D). Chalcopyrite in this zone can also be found to be replaced by tennantite locally, occurring as replacement of bornite and chalcopyrite (Fig. 6F). The upper part of very-high-grade Cu mineralization in quartz-muscovite assemblage is also associated with intense phyllic alteration, which is not easy to discriminate from the lower Cu grade zone from hydrothermal alteration minerals, that are both characterized by an intense quartz-muscovite assemblage (Figs. 7E and F). In this material, abundant disseminated sulfide is clearly texturally associated with muscovite, both within the rock mass and within cracks cutting quartz veins (Figs. 7E, F). Bornite is the dominant Cu sulfide, with some chalcopyrite and a minor amount of molybdenite (Fig. 7F). The two main Cu sulfides are often intergrown and pyrite is scarce. In the QV90 zone, slightly above this upper phyllic domain (Fig. 2B), copper grades can be extremely high, normally over 5 %. The sulfide assemblage here is dominated by bornite with minor chalcopyrite that occurs in cracks and vugs within the quartz veins (Fig. 7H). Some muscovite and kaolinite can be seen in addition to sulfides (Fig. 7H).

Discussion

Wider evidence for the relationship between HGHP mineralization and alteration

Most of the high-grade hypogene porphyry deposits in our classification share key features with the two HGHP deposits described, that have high-grade Cu mineralization in the deep part of phyllic alteration that overprints potassic alteration, across to upper, lower temperature phyllic and/or advanced argillic alteration. For example, Cu grades at Rosario in the Collahuasi district, Chile, gradually increase from K-feldspar-rich potassic, through phyllic to advanced argillic alteration zones with a quartz-alunite-pyrite-dickite(-pyrophyllite) assemblage (Fig. 8A; Masterman et al. 2005). Onto, in Indonesia, has nearly all the high-grade mineralization in advanced argillic alteration, although the >1 % high-grade Cu zone has not been outlined (Burrows et al. 2020). Chuquicamata, northern Chile, hosts higher Cu grades (>1.5 % Cu) in the phyllic alteration zone (associated with quartz-muscovite and minor alunite, pyrophyllite and dickite) than in the quartz-K-feldspar potassic alteration zone (Fig. 8C; Ossandón et al. 2001). The features are also found in MMH (Ministo Hales, Chile), and Čukaru Peki (Serbia), as well as several others (Table 1). White mica in these systems has a pale gray color compared to that in the deeper gray-green phyllic domain that has a closer spatial and temporal relationship with potassic alteration, and has a composition closer to muscovite or illite (rather than phengite). Superimposition of both phyllic-associated and advanced argillic-associated high-grade mineralization is commonplace in these deposits.

High-grade Cu mineralization link to potassic or phyllic alteration?

Disagreements remain concerning the association of the principal ore stage to potassic or phyllic alteration in several HGHP deposits. Because phyllic alteration is usually closely superimposed on the potassic zone, it can be difficult to ascertain at which stage the high-grade mineralization was generated, particularly from drillcore logging and composite

360 drillcore assays. For example, large volumes of potassic alteration are linked to high-grade Cu
 361 mineralization at Bingham Canyon (Gruen et al. 2010; Redmond and Einaudi 2010), although
 362 there remains a contradiction regarding the textural siting of sulfides in relation to low-
 363 temperature quartz and inferred, relatively low-temperature Cu precipitation conditions
 364 (Redmond et al. 2004; Landtwing et al. 2005). Although the majority of very-high-grade (2 %) Cu
 365 mineralization at Grasberg is proposed to occur within the K-feldspar alteration zone (Fig.
 366 8D) by Leys et al. (2012), other studies suggested that white mica-chlorite alteration may be
 367 associated with the primary mineralization stage (Sapiie and Cloos 2013). At El Teniente,
 368 although potassic assemblages are reported to be broadly spatially associated with high Cu
 369 and Mo grades (Camus 1975; Skewes et al. 2002; Cannell et al. 2005), both Cannell et al.
 370 (2005) and Vry et al. (2010) found that potassic-stage quartz(-magnetite-biotite-Kspar) veins
 371 have commonly been reopened and infilled with later-stage sulfides and concluded that the
 372 most important Cu-introduction event was during the formation of quartz-free C-veins during
 373 the transition to phyllic alteration. Skewes et al. (2002) also noted that phyllic-stage veins are
 374 associated with high-grade Cu, with the association between bulk Cu grade in 6 m drillcore
 375 assays and such veins confirmed by detailed logging of vein type abundances by Spencer et al.
 376 (2015). There is a similar issue in the supergiant Río Blanco-Los Bronces district (including
 377 the Río Blanco and Los Sulfatos deposits): although recent studies revealed biotite-cemented,
 378 chalcopyrite-bornite-pyrite breccias at depth (Toro et al. 2012), the relationship of these zones
 379 to the wider distribution of Cu grades is not described. An earlier study (Warnaars et al. 1985)
 380 reported that early mining of >4.5 % Cu ores, which would have been from the upper, phyllic

or advanced argillic alteration zones, although they may contain supergene enrichment ores, but volume is uncertain.

Interpretations of the location and timing of high-grade mineralization in deep parts of porphyry systems vary between deposits and this remains a controversial topic. Fluid inclusion data, (controversial) textural evidence and numerical modelling studies suggest that most Cu-sulfide precipitation in porphyry systems occurs during silica dissolution and reactivation of permeability at relatively modest temperatures (perhaps mostly between 425 °C and 375 °C; Monecke et al. 2018), rather than during the A- and B-type vein stages associated with potassic alteration (Hedenquist et al. 1998; Driesner and Heinrich 2019; Schirra et al. 2022). This type of model was proposed for Butte by Cathles and Shannon (2007) in which the potassic stage was interpreted as a large-scale, rapid, near explosive, unmineralizing fluid release event. It created much fracture permeability which was followed by distinctly later episodes of mineralizing fluid expulsion as the system cooled under muscovite-stable and later advanced-argillic conditions.

Conversely, Cernuschi et al. (2023) proposed that sulfides are introduced initially during high-temperature potassic alteration, but that they may be remobilized locally into later veins during phyllic alteration. The very frequently observed association between sulfides and late, dull-luminescent, low-temperature quartz in A- and B-type veins (e.g., Rusk and Reed 2002; Redmond et al. 2004; Riveros et al. 2022) was explained by preferential reopening of veins during low-temperature reactivation alongside pre-existing sulfides. However, the detailed textural relationships can alternatively be explained by later sulfide introduction (and/or remobilization), similar to what we document here (e.g., Figs. 7B, D, F). Furthermore, some

reported examples of late, dull luminescent, relatively low-temperature quartz cannot be interpreted in terms of formation during later reopening alongside earlier sulfides, and there are clear cases of early, higher-temperature quartz that has been partially dissolved and postdated by the precipitation of the bulk of the copper sulfides (e.g., Vry et al. 2010: Fig. 8; Riveros et al. 2022: Figs. 4 and 5). We think that, in part, the contradictory explanations stem from the perspective by which the classic series of quartz vein generations are viewed: either as a series of discrete cross-cutting events as they tend to appear, or as the macro-scale manifestation of a much more complex fracture and microfracture permeability network in the rock mass that allows multiple stages of reactivation and reopening of prior discontinuities, making it difficult to resolve the exact stage of sulfide precipitation, whether in veins or disseminated within the rock. Here, we place more emphasis on the textural association of sulfides with alteration minerals, whether they are contained within veins in crosscutting cracks, in microfracture networks or disseminated patches in the wallrock. This evidence at Resolution and Hugo Dummett North clearly points to the bulk of early, high-grade copper mineralization being introduced during white-mica stable alteration.

Therefore, in the major HGHP deposits worldwide (Table 1), we conclude that potassic alteration-related HGHP mineralization is generally subordinate in Cu grade to that associated with lower-temperature transitional phyllic and phyllic to advanced argillic overprints. In cases where HGHP ore is attributed to the potassic alteration stage, evidence is ambiguous and commonly disputed. Based on evidence from Chuquicamata (Rivera et al. 2012), Butte (Brimhall 1979) and other HGHP systems, plus the typical grades observed in potassic zones in non-HGHP systems such as Haquira East and Encuentro (Cernuschi et al. 2023), we

suggest that potassic-stage mineralization rarely introduces mineralization with Cu grades above ~1 % Cu.

High-grade Cu mineralization in upper-zone phyllic alteration and advanced argillic alteration

High-grade mineralization in the upper phyllic and/or advanced argillic zones mainly comprises bornite, digenite, chalcocite and covellite, coexisting with pyrite (see Table 1 for references). These minerals are typically associated with sulfosalts (enargite and tennantite) and other minor sulfides (nukundamite, mawsonite, colusite, idaite etc); most of them are high-sulfidation state sulfides (Einaudi et al. 2003; Pollard et al. 2005; Hedenquist and Arribas 2022). In some deposits, high-grade ore comprises veins that may be meters in width, such as at Rosario (Masterman et al. 2004) and Butte (Houston and Dilles 2013). Various, these veins are categorized as Butte-type, Cordilleran or massive sulfide veins or lodes (Bendezú and Fontboté 2009; Fontboté and Bendezú 2009; Catchpole et al. 2011). The upper parts of the high-grade mineralization at Resolution are also recognized to be of this type (Manske and Paul 2002), although very thick high-sulfidation veins are not very common. Where telescoping has occurred, it is clear that such veins formed later than deeper, higher-temperature alteration zones as evidenced by crosscutting relationships and sulfide replacement textures (e.g., Figs. 6A-D). Geochronology suggests that this high-sulfidation mineralization can be several million years younger than spatially-associated plutons exposed at the same crustal level and their related porphyry-style mineralization (Houston and Dilles 2013; Catchpole et al. 2015), implicating younger porphyry centers at depth (Padilla-Garza et al. 2004; Hedenquist et al. 2020).

In addition to these hydrothermal processes, there are certain host rocks that can be favorable to promote efficient Cu precipitation and hosting high-grade ores. For example, mafic and carbonate rocks at Resolution shape the outline of large parts of high-grade Cu mineralization (Fig. 2A). Mafic and carbonate rocks are thought to be efficient traps for Cu sulfides because of their capacity to act as an impermeable, ductile seal, reduce oxidized magmatic fluids via the oxidation of ferrous iron, or buffering fluid pH to cause rapid Cu precipitation (Sillitoe 1997, 2010). However, this relationship between Proterozoic diabase and high-grade Cu mineralization at Resolution does not necessarily extend to all other deposits nearby in Arizona (Manske and Paul 2002). Some of the high-grade mineralization at Hugo Dummett North is hosted by olivine basalt; however, the quartz monzodiorite porphyry is the major host (Khashgerel et al. 2009). Thus, although mafic rocks may well be a contributor, it is clearly not the primary control of Cu grade. Also, it is rare for any single deposit forming high-grade Cu mineralization only aligning with a specific unit of host rock.

Physicochemical conditions driving high-grade Cu deposition in the moderate-temperature window

Thermodynamic models of Cu solubility (Liu and McPhail 2005; Rubtsova et al. 2023), as well as fluid inclusion data from natural systems (Hezarkhani et al. 1999; Ulrich et al. 2001; Redmond et al. 2004; Landtwing et al. 2005; Klemm et al. 2007; Schirra et al. 2022), suggest that the sort of steep decrease of Cu solubility in salt solutions from thousands to a few ppm that favors precipitation of high-grade mineralization occurs in the temperature interval that includes the late potassic (K-feldspar stable) but is largely within the phyllic (muscovite stable) alteration window, at temperatures of ~425 to 375 °C (Fig. 9).

469 This temperature range corresponds to the onset of significant SO₂ disproportionation that
470 provides H₂S for the precipitation of Cu sulfides (Fig. 9); reaction of sulfate with ferrous iron-
471 bearing silicates can lead to further H₂S production and sulfide precipitation. Consumption of
472 aqueous sulfide can then drive further disproportionation of SO₂. At the same time,
473 dissociation of H₂SO₄ and HCl will decrease pH to stabilize muscovite as an alteration
474 mineral (Fig. 9A) and increase sulfate activity that can lead to precipitation of anhydrite at
475 higher temperatures and alunite-APS minerals at lower temperatures in acid alteration
476 assemblages (Simonson and Palmer 1993; Seedorff et al. 2005), such as at Resolution (Fig. 3).

477 Prior to phyllic alteration, porphyry systems typically pass through the retrograde silica
478 solubility window at temperatures of ~500-400 °C during their evolution (Fig. 9C; Fournier
479 1985), although this may also happen at even higher temperatures of 550-450 °C at higher
480 pressure (~70 MPa; Rusk and Reed 2002). This dissolution process can generate conduits in
481 pre-existing veins for input of later hydrothermal fluids. Cracking of pre-existing quartz veins
482 during thermal contraction at 575-400 °C (e.g., Cernuschi et al., 2023) will also serve to create
483 additional permeability as conditions transition into the muscovite-stable window. In systems
484 undergoing telescoping, the lower temperature of fluids as they reach the prior potassic vein
485 level will lead to precipitation of Cu sulfides, eventually coincident with a return to prograde
486 silica solubility; this can account for the occurrence of sulfides within late, dully luminescent
487 quartz in such veins that formed below ~370 °C (Monecke et al. 2018).

488 In this window of cooling to below 400 °C and transition to phyllic alteration, host rocks will
489 also pass through the ductile-brittle transition (Fournier 1999). In tectonically active settings,
490 this will favor extensive rock fracturing, involving both reopening of existing veins and the

development of new, large veins, explaining the high density of veins and breccias that are typically formed at the phyllic or even lower-temperature advanced argillic stage, as well as the common structural control of phyllic alteration domains such as at Rosario (Masterman et al. 2005) and Chuquicamata (Ossandón et al. 2001).

Hypogene enrichment

At moderate temperature and under oxidizing hydrothermal conditions, hypogene enrichment may take place, as observed at Resolution and locally at Hugo Dummett North (Fig. 6), via the replacement of early-formed sulfides by higher sulfidation state sulfides and/or by dissolution of early sulfides and reprecipitation at shallower levels. This process has been recognized to significantly improve the Cu grade in a number of systems (cf. Gustafson and Hunt 1975; Brimhall 1979; Ossandón et al. 2001). Additionally, this evolution of the sulfide assemblage is associated with increasing Cu but decreasing Fe and S contents of the sulfides, which significantly improves the quality of the ore in terms of metallurgy and environmental impacts. Iron and S may go into pyrite, which is a common mineral in high-sulfidation state mineral assemblages (Einaudi et al. 2003).

Hypogene enrichment of this kind is considered a critical process in the development of HGHP ores and can potentially rationalize the observation of secondary, potentially higher-grade mineralization, superimposed on earlier, lower-grade potassic veins, but with enrichment not occurring where prior potassic-stage mineralization did not exist (Cernuschi et al. 2023). Enrichment could also occur by overprinting of sulfides initially precipitated in the phyllic alteration zone. The process is driven by telescoping of the porphyry-hydrothermal

system, with downward penetration of relatively cold meteoric water during exhumation (Brimhall 1979), which causes downward migration of isotherms and hence oxidation and acidification of fluids at progressively lower levels in the system (Heinrich 2005; Reed et al. 2013). This has been documented in a number of major porphyry systems, such as Chuquicamata (Ossandón et al. 2001; Rivera et al. 2012). The high-sulfidation assemblages overprint and likely remobilize earlier sulfide assemblages at depth (thereby obscuring primary mineral zoning and textures) because of increasing fO_2 and decreasing pH and fH_2S (Fig. 10). Dissolution of pre-existing chalcopyrite(-bornite) solubilizes copper (Fig. 10), most likely in the form of aqueous $CuCl_2^-$ (Crerar and Barnes 1976; Hezarkhani et al. 1999), or possibly as Cu-S complexes (Brimhall 1979, 1980). This corresponds to a spatial-temporal stage of porphyry-Cu evolution when copper leaching rather than deposition predominates, leading to the production of zones of barren or low-grade quartz-sericite-pyrite alteration (Fig. 10; Brimhall 1980), which potentially can be observed even down to the individual vein scale (Cernuschi et al. 2023).

The dissolved Cu from earlier sulfides is thought to be mixed with additional Cu from a deeper magmatic source at this stage, making the later acidic and oxidized fluid enriched with Cu. (Brimhall 1979; Hezarkhani et al. 1999). A delay in buffering of fluid acidity and oxidation state by the rock mass could lead to significant over-step in fO_2 and pH, with fluids essentially following the ‘gas buffer’ (Giggenbach 1980, 1987), thereby attaining extremely high sulfidation states. Irrespective, once sulfide supersaturation is eventually attained, such as via cooling or fluid mixing, deposition of high Cu:Fe and Cu:S ratio sulfides in bornite-pyrite-dominant mineralization associated with phyllic to advanced argillic alteration, or

eventually digenite-covellite-chalcocite-dominant mineralization with advanced argillic assemblages can result in anomalously high-grade Cu ores (Brimhall 1979, 1980; Hezarkhani 2002).

A geological model for HGHP genesis

The relationships between alteration and high-grade Cu at both Resolution and Hugo Dummett North show that HGHP mineralization is largely associated with white-mica-stable phyllic alteration that in part overprints pre-existing potassic alteration. The phyllic alteration is itself overprinted by advanced argillic alteration, with further Cu grade upgrading. Even when elevated grades are observed within ostensibly potassic-dominated domains, the sulfides are always mostly associated with an incipient muscovite overprint. Based on these observations, and our literature review, we define two different domains that can host HGHP Cu mineralization (Fig. 11A). One occurs at depth (HGHP-I), associated with moderate to intense overprinting of biotite or K-feldspar by muscovite in potassic alteration, and is characterized by ~1.0 % Cu mineralization (e.g. deep zones of both Resolution and Hugo Dummett North). This typically comprises chalcopyrite with some bornite; minor digenite occurring in a low-sulfidation state assemblage is also reported in the deep parts of several other HGHP systems such as Chuquicamata, Grasberg and Bingham Canyon (see Table 1 for references).

The second HGHP zone (HGHP-II) is located in the upper phyllic and advanced argillic domain, which can host higher-grade ores of 1.0-2.5 % Cu, as exemplified by the upper ore zones at both Resolution and Hugo Dummett North. In both cases, the systems are telescoped,

with advanced argillic alteration superimposed on phyllic alteration, which in turn has overprinted potassic alteration, leading to close proximity, or even overlap of HGHP-I and HGHP-II mineralization. Resolution is an example of an extremely telescoped system in which kaolinite/dickite-rich advanced argillic alteration has extensively overprinted biotite-rich potassic alteration.

Most of the HGHP deposits defined and reviewed in this study have protracted (but episodic) magmatic-hydrothermal lifespans mostly between 1 and 5 Myrs (Table 1). For example, the earliest hydrothermal event at Resolution is recorded by molybdenite that formed at 63.53 ± 0.38 Ma, and late muscovite formed at 61.93 ± 0.34 Ma, with late pyrite-alunite dated at ~ 51 Ma (Hehnke et al. 2012). Due to this, these systems can, over time, release the large amounts of water essential for the formation of large porphyry deposits (Richards 2011; Chiaradia and Caricchi 2017; Virmond et al. 2024) by tapping extensive and/or repeatedly replenished magma reservoirs that can exist for long periods in the crust in crystal-rich “cold storage” (e.g., Nathwani et al. 2023). This allows multiple stages of Cu transport into the same shallow crustal system with such multi-stage addition helping to develop high grades (e.g. El Teniente; Vry et al. 2010).

During long magmatic-hydrothermal lifespans, syn-mineralization exhumation and telescoping can take place as a result of shallow crust collapse, magma intrusion doming or erosion (Sillitoe 1994; Dahlström et al. 2022; Evenstar et al. 2025). The rates and degree of exhumation control the superimposition and telescoping of multiple hydrothermal events which will influence grade development in individual deposits. We would expect to see two

separate domains of high-grade mineralization (Fig. 11A) only in untelescoped systems, with a “barren sericitic zone” in between (e.g., Brimhall 1980).

However, many high-grade porphyry deposits appear to have experienced rapid exhumation and strong telescoping, leading to superposition of HGHP-II on HGHP-I (Fig. 11B). This process is thought to account for several extremely high-grade systems (e.g. Chuquicamata, Resolution, Hugo Dummett North, Rosario, Butte, Onto and Golpu) and results in enriched hypogene ore hosted mostly by phyllic and/or advanced argillic alteration. The effect of telescoping on grade is also evidenced in the Río Blanco-Los Bronces district, where average Cu grades increase from 0.63 to 0.90 % from north to south with increasing degree of telescoping (Toro et al. 2012). During this exhumation and superposition process, a transition to extensional stress during the formation of phyllic and advanced argillic alteration at shallow levels (Sillitoe and Hedenquist 2003; Piquer et al. 2021; Skarmeta 2021), would further favor development of open fractures and breccia zones, helping to focus mineralizing fluids at the very late stage of evolution (Sibson 1996; Sanderson and Zhang 1999). The development of such extensive permeability networks can allow downward ingress of cold meteoric water (Fig. 11B), which would compress thermal gradients and be another key driver of rapid Cu solubility decrease in ascending fluids (Fournier 1999; Weis et al. 2012).

It is thought likely that there is a critical range of exhumation rates that are conducive to the formation of HGHP deposits where the degree of telescoping has optimized remobilization and concentration of Cu, in a manner somewhat analogous to supergene enrichment associated with a descending water table (Sillitoe 2005; Dahlström et al. 2022). At Butte, the main-stage mineralization formed at a rapid estimated exhumation rate of 1-3 mm/yr

(Houston and Dilles 2013), faster than any stages of the precursor porphyry system. In the northern Andes, the main hypogene mineralization in the late Eocene porphyry deposits formed at relatively high exhumation rates averaging ~ 0.3 mm/yr (Dahlström et al. 2022). The supergiant, high-grade Miocene-Pliocene porphyry deposits (e.g. El Teniente and Río Blanco-Los Bronces) in Central Chile are also associated with rapid exhumation at around 1 mm/yr (Farías et al. 2008; Makshev et al. 2009; Skarmeta et al. 2024). However, precise exhumation rates are challenging to constrain, and more work is required to better understand this aspect of porphyry system evolution and its impact on system longevity and the size and grade of deposits.

Although rapid exhumation is thought to be important for generating the highest hypogene grades by telescoping, this process can also lead to exposure and destruction of such mineralization. Thus, a timely cessation of uplift and, potentially, subsequent burial under volcanic or sedimentary cover is necessary to preserve high-level HGHP ores. Examples of HGHP systems that have post-mineral cover or where exhumation ceased or was extremely slow prior to exposure include Hugo Dummett North, Chuquicamata, Čukaru Peki and deposits in the Río Blanco-Los Bronces district (Hervé et al. 2012; Rivera et al. 2012; Toro et al. 2012; Jelenković et al. 2016; Wainwright et al. 2017). The time interval between mineralization and inferred cessation of exhumation is normally ≤ 5 My, although, in a few cases (e.g. Resolution), the interval can be longer (Hehnke et al. 2012).

Conclusions

We conclude that long-lived magmatic-hydrothermal activity, accompanied by strong uplift, exhumation and telescoping, are the first-order controls on the generation of the highest-grade

hypogene porphyry Cu deposits. These conditions lead to steep thermal gradients and high permeability development in increasingly cool, brittle rocks which favor efficient sulfide precipitation from focused fluids. At the same time, superposition of lower-temperature, acidic and oxidative alteration on primary potassic stage mineralization can cause remobilization and concentration of Cu in higher-sulfidation state minerals with lower S content, increasing grade and improving ore quality. This model links high-grade ore development to two, relatively low-temperature stages, associated either directly with phyllic to advanced argillic alteration, or to the onset of phyllic overprinting of potassic-altered rocks. On the broader scale, recognition of the right geodynamic settings, the more local tectonic controls of enhanced exhumation and the existence of long-lived magmatic-hydrothermal centers are key to the identification of areas with high HGHP potential.

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Author Contributions

Both authors contributed to the study conception and design. Samples collection and selection were performed by both authors. Data analysis and collection were conducted by Chao Yang. The first draft of the manuscript was written by Chao Yang under the supervision of Jamie Wilkinson. Both authors made corrections and approved the final manuscript.

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971 **Figure caption**

972 Fig. 1. Statistics of copper grade for economic porphyry Cu deposits (filtered by ≥ 100 Mt
 973 mineralized rock, n=446). Data in ESM Table S1.

974 Fig. 2. Geology, alteration and grade distribution of the two highest-grade hypogene porphyry
 975 Cu deposits. A. Resolution, Arizona, USA (modified from Hehnke et al. 2012); B. Hugo
 976 Dummett North, Oyu Tolgoi, Mongolia (modified from Khashgerel et al. 2009).

977 Fig. 3. Examples of typical high-grade drillcore samples (A, Res-17Q, 1821.6m, 5.6 wt% Cu;
 978 B, Res-5M, 1970.1m, 0.73 wt% Cu; C, Res-35N, 1819.7 m, 2.7 wt% Cu) from the potassic-
 979 phyllic transition zone at Resolution, and matching TESCAN TIMA image (D) of Sample C.
 980 Deep, high-grade mineralization is related to quartz-chalcopyrite veins primarily associated
 981 with muscovite and minor kaolinite/dickite alteration. It is noteworthy how much muscovite
 982 alteration is present in the sample even though much appears to be biotite in the drillcore
 983 sample. E. Res-35N, 1789.2m, alunite-bornite-pyrite veins in diabase. F. Res-31B, 1706.8m,
 984 high-grade quartz-pyrite-chalcocite-digenite veins with muscovite alteration. Abbreviations:
 985 Alu-alunite, Ap-apatite, Bn-bornite, Bt-biotite, Ccp-chalcopyrite, Kln-kaolinite, Ms-
 986 muscovite, Py- pyrite, Rt-rutile.

987 Fig. 4. Quantitative mineralogy of samples illustrating representative potassic to phyllic
 988 transitions within individual lengths of drillcore from Resolution. A. Diabase sample (R-17Q-
 989 1822.1 m) with variable extents of phyllic alteration after predominantly biotitic potassic
 990 alteration. The upper section (B) has stronger phyllic alteration with more muscovite (30.1 %)
 991 and associated chalcopyrite (1.3 %) and less biotite (21.9 %) than the lower section (19.9 %

992 muscovite, 40.1 % biotite, 0.5 % chalcopryite, C). D. Volcaniclastic sample (R-1B-2323.4 m)
 993 with weak and intense phyllic alteration after predominantly K-feldspathic potassic alteration.
 994 The upper section (E) has muscovite-anhydrite as the dominant alteration minerals after K-
 995 feldspar, with significant chalcopryite (17.0 %); the lower section (F) is dominated by K-
 996 feldspar containing small amounts of chalcopryite (0.3 %) and with a weak muscovite-pyrite(-
 997 chalcopryite) overprint. The numbers in the parentheses are area percentage of minerals. Anh-
 998 anhydrite, Ilt-illite, Mol-molybdenite, K-feld-K-feldspar, Qz-quartz. Other mineral
 999 abbreviations as Fig. 3. Numbers in the bracket are area percentage of minerals, same in other
 1000 figures.

1001 Fig. 5. Example of strongly Cu-mineralized diabase from Resolution (A) with intense
 1002 muscovite and kaolinite alteration (Res-35N, 1799.1 m, 15.7 wt% Cu). B. TIMA image of
 1003 strongly silicified wallrock exhibiting development of advanced argillic assemblages after
 1004 phyllic alteration. C. TIMA image of an area within the quartz-sulfide vein showing very
 1005 high-grade mineralization of bornite-pyrite(-chalcopryite) associated with kaolinite/dickite,
 1006 quartz, apatite, APS minerals and fluorite. Microbrecciation textures are evident.

1007 Fig. 6. Replacement textures observed in very-high-grade mineralization at Resolution (A-D)
 1008 and Hugo Dummet North (E-F). A. Chalcopryite largely replaced by bornite and minor
 1009 chalcocite (Res-35N-1799). B. Bornite partly replaced by covellite and chalcocite (Res-35N-
 1010 1666.6). C. Chalcopryite replaced by bornite and digenite (Res-17Q-1779.7). D. Chalcopryite
 1011 replaced by covellite (Res-5M-1890.7). E. Deep muscovite overprinting K-feldspar-rich
 1012 potassic zone, chalcopryite mineralization replaced by bornite and digenite (HD-UGD103-
 1013 150.9). F. Deep potassic zone, bornite replaced by tennantite (HD-OTD976A-1528.6). Cc-
 1014 chalcocite, Cv-covellite, Dg-digenite, Tnt-tennantite, other mineral abbreviations as Fig. 3
 1015 and 4.

1016 Fig. 7. Typical high-grade core samples and matching TESCAN TIMA images from Hugo
 1017 Dummet North. A, B: deep, K-feldspar-dominant potassic alteration (HD-OTD976A-1528.6,
 1018 1.2 wt% Cu). Although the drillcore specimen shows abundant, red K-feldspar, which would
 1019 likely be linked genetically to coincident high-grade copper assays without further

information, detailed TIMA images show that Cu-sulfides (predominantly bornite) are texturally associated with a significant, but relatively diffuse, muscovite overprint, with no sulfide grains that can be confidently interpreted to be coeval with K-feldspar. C, D: Middle phyllic alteration zone with intermediate Cu grade (HD-OTD976A-1504.2, 0.97 wt% Cu). Quartz and muscovite are the major mineral phase with disseminated chalcopyrite mineralization. E, F: Upper phyllic alteration zone (HD-UGD103-481.9, 4.35 wt% Cu). In this zone, muscovite and quartz are the predominant alteration minerals, with abundant disseminated bornite-chalcopyrite mineralization. G, H: Very high grade “QV90” core sample (HD-UGD103-693.7, 6.34 wt% Cu). Very abundant bornite occurs in dissolution cavities and infilling narrow fractures in quartz, with a small amount of muscovite. Ank-ankerite, other abbreviations as Fig. 3, 4, 5 and 6.

Fig. 8. Alteration and hypogene Cu grade distributions in several high-grade hypogene porphyry Cu deposits. A. Rosario, Collahuasi District, Chile (modified from Masterman et al. (2005); B. Onto, Indonesia (modified from Burrows et al. (2020); C. Chuquicamata, Chile (modified from Ossandón et al. (2001); D. Grasberg, Indonesia (modified from Leys et al. (2012).

Fig. 9. High-grade Cu mineralization associated with transitional K-silicate-sericite alteration and phyllic to advanced argillic alteration coincides with key hydrothermal reactions and decreasing Cu-sulfide solubility between 425 and 375 °C, across the brittle-ductile transition and within or just below the window of retrograde silica solubility. A. In this temperature range, muscovite becomes stable and is subsequently replaced by pyrophyllite at slightly lower temperatures (modified from Hedenquist and Arribas 2022). B. Extensive Cu-sulfide precipitation will occur as the solubility of chalcopyrite (dissolved in the form of CuCl_2^-) decreases rapidly over four orders of magnitude (after Hezarkhani et al. 1999 and Liu and McPhail 2005). The onset of significant SO_2 disproportionation at ~400 °C facilitates Cu precipitation as sulfides (Holland 1965), by generating H_2S directly; further H_2S can be produced by reduction of aqueous sulfate via oxidation of minerals containing ferrous iron. C. At ~400 °C, rocks transform from ductile to brittle behavior, close to the region where retrograde silica solubility occurs in low-salinity, intermediate-density magmatic fluids

(Fournier 1999); both processes act to help generate permeability for focusing fluid flow. The region highlighted in pink is the inferred window for high-grade Cu-sulfide precipitation.

Fig. 10. Modelled fluid properties and phase stability during progressive fluid interaction with monzonitic hostrock, explaining hypogene enrichment processes. Modified from Brimhall (1980).

Fig. 11. Geological model for high-grade hypogene porphyry Cu mineralization. Alteration model modified from Sillitoe (2010). During telescoping processes, isotherms are increasingly steep (from A to B) and the two high-grade mineralization domains are superimposed and result in a large and very-high-grade HGHP system involving extensive Cu remobilization and upgrading of earlier mineralization.

Table 1. Key features of high-grade hypogene mineralization in selected significant porphyry copper deposits.

	Deposit	Age (Ma)	Cu resource (Mt)	Grade (%)	HGHP ore-related alteration minerals	HGHP ore-related sulfide assemblage	Occurrence	References
1	Chuquicamata northern Chile	35-31	31.3 62.7*	1.54 0.43*	Early: K-feldspar bands with green-white mica (no pyrite) superposition; Main: quartz, white mica	Early: chalcopyrite-bornite-digenite; main: enargite, covellite, digenite, pyrite	Stockwork veins, disseminated sulfide in white mica and K-feldspar halos; main sulfide stage mostly in white mica	Ossandón et al. (2001); Rivera et al. (2012); CODELCO annual report (2021)
2	Resolution, Arizona, USA	64-60	27.3	1.53	Phengitic white mica, quartz, kaolinite, with minor fluorite, anhydrite, rutile	Chalcopyrite, pyrite, bornite in potassic overprinting zone; sericite-kaolinite zone with bornite, chalcocite, digenite, pyrite	Veins and disseminated	Manske and Paul (2002); Hehnke et al. (2012); Rio Tinto annual report (2021)
3	El Teniente central Chile	6.3-4.4	23.2 ¹ 92.1*	1.27 ¹ 0.56*	Biotite, K-feldspar, albite, anhydrite, tourmaline breccia; paragonitic and phengitic muscovite, quartz, chlorite	Chalcopyrite, minor bornite	Chalcopyrite in breccia, chalcopyrite-bornite-bearing thick quartz-sulfide veins (up to 4 cm), late quartz-tourmaline-chlorite-muscovite veins with chalcopyrite-bornite-pyrite-tennantite	Skewes et al. (2002); Cannell et al. (2005); Vry et al. (2010); Spencer et al. (2015); CODELCO annual report (2021)
4	Grasberg, Papua, Indonesia	3.33-3.01	18.3 ¹ 31.6*	1.56 ¹ 0.75*	K-feldspar-magnetite-anhydrite with major Cu-Au; muscovite, pyrophyllite, illite, kaolinite altered rocks with mixed copper sulfide.	Grasberg Cu-Au stage: chalcopyrite-bornite ± pyrite ± gold ± hematite; mixed copper sulfide: chalcopyrite, bornite, covellite-nukundamite, digenite, chalcocite	Veins and cavities	Pollard and Taylor (2002); Pollard et al. (2005); Leys et al. (2012); Leys et al. (2020)
5	Río Blanco, central Chile	8.2-4.3	17.9 ¹ 135.2*	1.19 ¹ 0.62*	K-feldspar, biotite, albite, magnetite, anhydrite, tourmaline, specularite, gray-green white mica and chlorite	Chalcopyrite, pyrite and minor bornite	Stockwork quartz veins, hydrothermal breccias, late-stage polymetallic veins	Warnaars et al. (1985); Ricardo et al. (1999); Deckart et al. (2005); Toro et al. (2012); CODELCO annual report (2021)
6	Los Sulfatos, central Chile	7.3-6.3	17.5 40.5*	1.46 0.90*	Biotite, K-feldspar, tourmaline, specularite, anhydrite	Chalcopyrite, bornite ± digenite	Hydrothermal breccia, quartz-sulfide veins, late-stage polymetallic veins	Irrazaval et al. (2010); Toro et al. (2012)
7	Hugo Dummett North, Mongolia	374-371	12.3	1.06	Muscovite, pyrophyllite, alunite	Bornite ± chalcocite; bornite-chalcopyrite	Veins and disseminated	Khashgerel et al. (2006); Khashgerel et al. (2009); Crane and Kavalieris (2012)
8	Rosario, northern Chile	34.5-32.6	11.3	1.03	Early: K-feldspar, biotite, albite, illite, chlorite. Late: muscovite, pyrophyllite, dickite, alunite, quartz	Early bornite, chalcopyrite; late pyrite, chalcopyrite, bornite, chalcocite, tennantite and enargite	Massive high-sulfidation sulfide veins	Dick et al. (1994); Masterman et al. (2004); Masterman et al. (2005)
9	Onto, Indonesia	0.04-0.54	8.4	0.87	Quartz, pyrophyllite, dickite, alunite	Covellite-pyrite, minor bornite-chalcocite-chalcopyrite, nukundamite	Leached open-space filling and replacements	Burrows et al. (2020)
10	Butte, Montana, USA	66-62	8.2 ¹ 35.1*	4.26 ¹ 0.67*	Deep: biotite-Kspar±musc±andalusite. Main stage: gray-green muscovite, chlorite, quartz, pyrophyllite, dickite/kaolinite, topaz	Bornite, covellite, digenite, chalcocite, enargite, pyrite	Lode veins	Brimhall (1979; 1980); Rusk et al. (2008); Reed et al. (2013); Houston and Dilles (2013); Reed and Dilles (2020)

11	Golpu, Papua New Guinea		8.7	8.2	1.00	Early: biotite, K-feldspar, magnetite, actinolite. Late: alunite, kaolinite, quartz	Chalcopyrite-bornite; pyrite-covellite-bornite-tennantite	Vein and disseminated	Rinne et al. (2018)
12	Čukaru Peki, Serbia		87-84.5	7.8 ¹ 18.6*	1.12 ¹ 0.76*	Quartz, magnetite, anhydrite	Mainly chalcopyrite, with covellite and minor enargite replacement	Vein and disseminated	Jelenković et al. (2016); Klimentyeva et al. (2022); Zijin Annual report. (2023)
13	Bingham Canyon, Utah, USA		37.6-37.1	6.6 ¹ 28.5*	1.03 ¹ 0.88*	Intense K-feldspar and biotite, muscovite overprint	Chalcopyrite-bornite-digenite-gold; nukundamite	Veins and disseminated	Parry et al. (2001); Inan and Einaudi (2002); Redmond and Einaudi (2010)
14	Los Bronces, central Chile		8.2-4.3	4.9 12.5*	1.03 0.39*	Quartz, tourmaline, specularite, anhydrite, white mica, chlorite	Chalcopyrite with minor bornite	Late magmatic-hydrothermal breccia	Warnaars et al. (1985); Toro et al. (2012); Porter Geo (2016)
15	MMH Hales), Chile	(Ministro northern	35-31	2.4 21.9*	1.06 0.72*	Deep: K-feldspar-biotite. Shallow: quartz, alunite, pyrophyllite, white mica, dickite	Deep: bornite, chalcopyrite; shallow: chalcocite, bornite, covellite, enargite, tennantite, pyrite	Hydrothermal breccia	Boric et al. (2009); Rivera et al. (2012); Zentilli et al. (2015); Zentilli et al. (2018); CODELCO annual report (2021)

*Total copper resource in the deposit; ¹ Data on high-grade portion from Sillitoe and Perelló (2023).

The actual white mica mineral phase is given where known, otherwise “white mica” is used.

The global distribution of these deposits is shown in ESM Fig. S1

Table 2. TESCAN TIMA mineralogical quantification of representative samples (modal percentage by area)

	Resolution, USA									Hugo Dummett North, Mongolia					
Mineral phase	Deep potassic with muscovite overprints				Deep potassic with intense muscovite overprints				Upper phyllic alteration		Deep potassic with muscovite overprints		Middle intense muscovite alteration	Upper intense quartz-muscovite and QV90 alteration	
	R-17Q-1822.1 (Fig. 4B)	R-17Q-1822.1 (Fig. 4C)	R-1B-2323.4 (Fig. 4E)	R-1B-2323.4 (Fig. 4F)	R-5M-1970.1 (Fig. 3B)	R-35N-1819.7 (Fig. 3C)	R-35N-1819.3	R-17Q-1821.6 (Fig. 3A)	R-35N-1799.1 vein (Fig. 5D)	R-35N-1799.1 (Fig. 5B)	OTD976A-1528.6 (Fig. 7B)	UGD103-150.9	OTD976A-1504.2 (Fig. 7D)	UGD103-481.9 (Fig. 7F)	UGD103-693.7 (Fig. 7H)
Quartz	12.0	8.7	31.4	12.3	22.3	17	11.9	47.2	18.6	29.1	34.9	50.6	56.3	48.4	83.3
K-feldspar	-	0.3	19.0	72.4	-	0.7	0.4	-	0.1	0.1	32.8	17.7	0.3	0.2	-
Biotite	21.9	40.1	0.7	4.9	12.3	15.5	29.5	0.8	-	0.1	0.1	0.1	-	-	-
Muscovite	30.1	19.9	23.6	4.1	26.8	32.0	41.0	12.7	0.9	34.2	18.9	16.0	30.1	37.3	0.4
Kaolinite*	9.7	8.1	-	-	3.6	5.3	7.1	2.9	5.1	3.7	-	-	-	-	0.3
Pyrite	0.1	-	-	0.2	17.3	0.1	-	-	32.6	6.4	-	-	-	-	-
Bornite	-	-	-	-	1.6	0.1	-	0.3	30	1.4	2.1	1.2	-	4.0	13.2
Chalcopyrite	1.3	0.5	17.0	0.3	0.2	10.1	0.9	23.5	2.4	0.1	0.1	1.4	0.8	1.1	-
Molybdenite	-	-	-	-	-	-	-	0.44	-	-	-	-	-	-	-
Illite	4.0	4.0	-	-	1.7	3.2	3.9	1.1	0.1	7.2	1.5	0.9	5.7	3.7	-
Rutile	1.0	0.6	-	0.3	0.5	2.2	0.3	0.3	0.1	3.4	0.1	-	0.1	-	-
Apatite	0.2	0.1	-	-	0.1	0.2	-	0.8	0.4	-	0.3	0.1	0.2	0.1	-
APS	-	-	-	-	0.1	0.4	0.1	0.1	3	0.6	-	-	-	-	-
Ankerite	-	-	-	-	-	-	-	-	-	-	1.9	4.6	-	-	-
Covellite	-	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-
Tennantite	-	-	-	-	-	-	-	-	-	-	0.2	-	-	-	-
Fluorite	-	-	-	-	-	0.5	0.1	0.78	1.3	0.3	-	-	-	-	-
Chlorite	-	-	-	-	-	-	0.2	-	-	-	-	-	-	-	-
Zircon	-	-	-	-	-	-	-	0.15	-	-	-	-	-	-	-
Anhydrite	-	-	2.5	1.0	-	-	-	-	-	-	-	-	-	-	-
Total	81.7	83.7	96.3	96.7	86.4	87.2	95.4	90.9	94.9	86.5	92.9	92.8	93.8	94.9	97.3

- Data less than 0.1%; APS - aluminum-phosphate-sulfate mineral; * “Kaolinite” refers to the mineral group, it can be either kaolinite or dickite. Totals <100% indicate the proportion of pixels unclassified by the TIMA, mainly due to mixed EDS spectra along grain boundaries and associated with fine-grained intergrowths of minerals

Figure1

[Click here to access/download;Figure;Fig. 1 Cu grade.jpg](#)

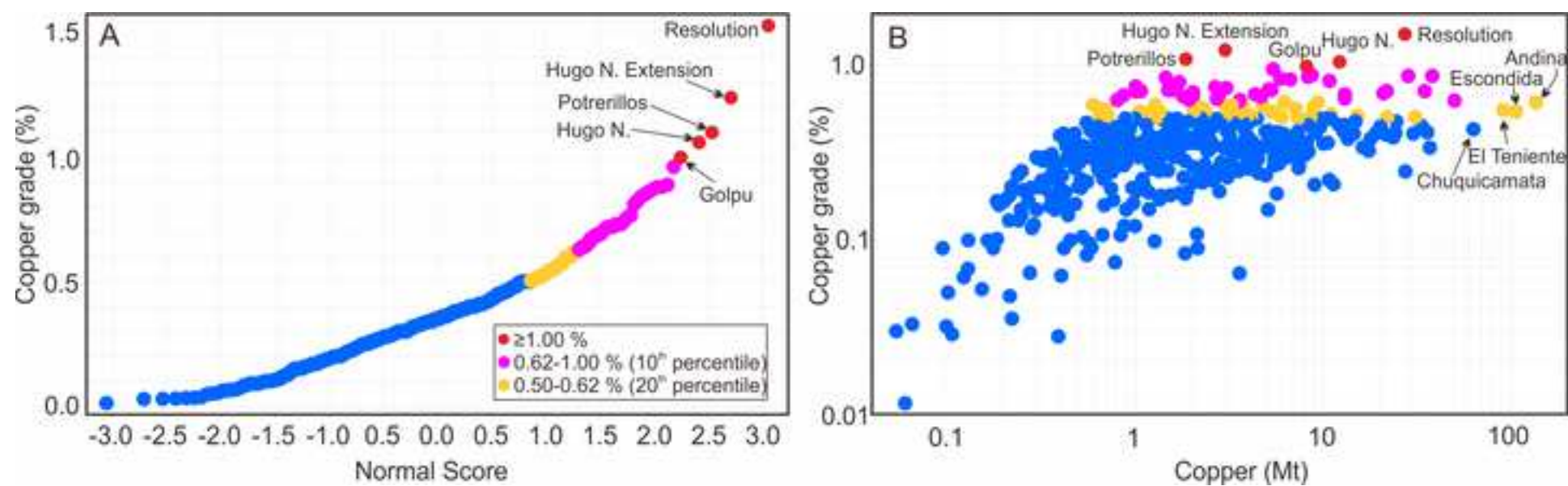
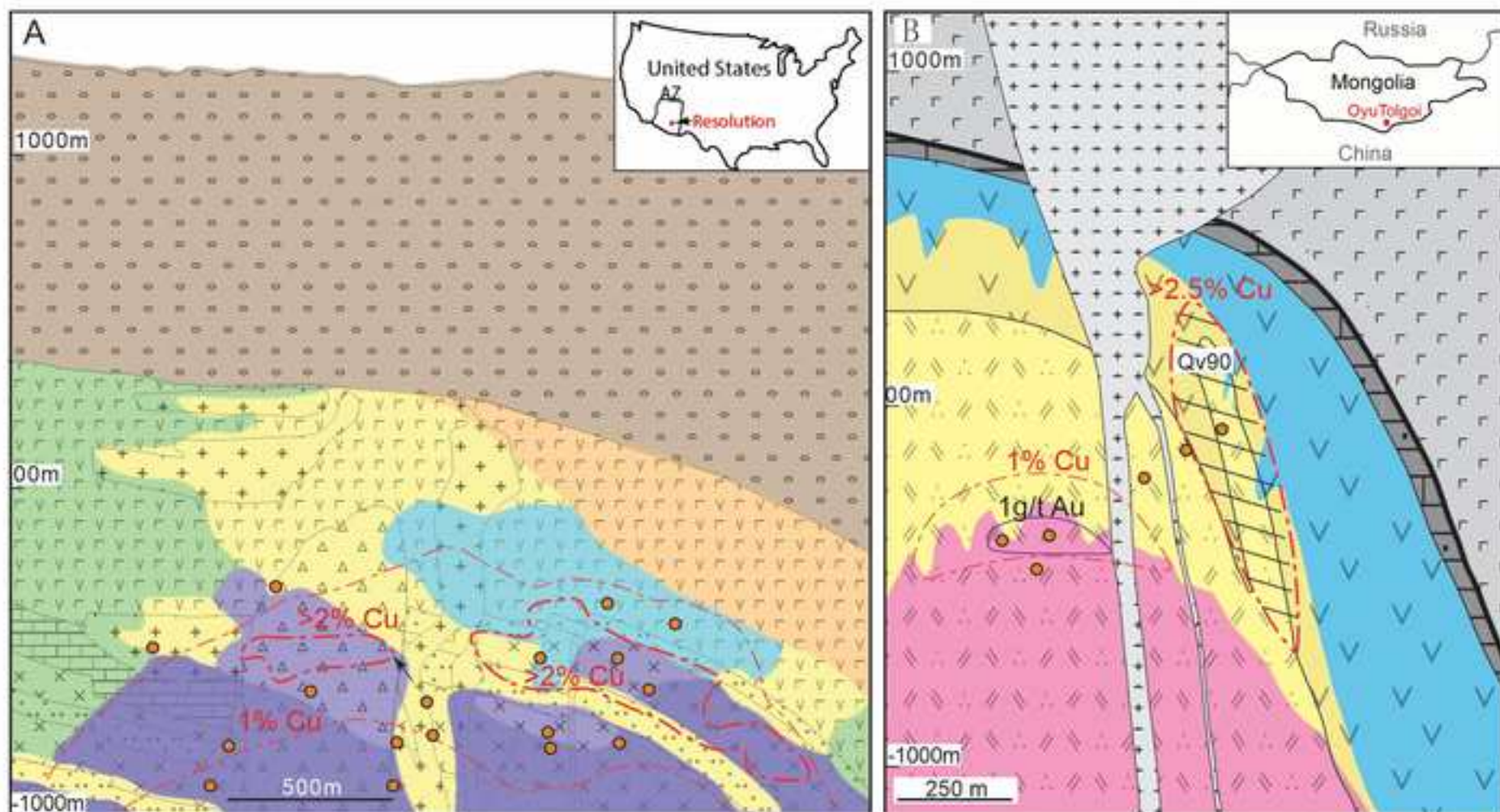


Figure2

[Click here to access/download;Figure;Fig. 2 Deposit Geology.jpg](#)


Resolution rock units

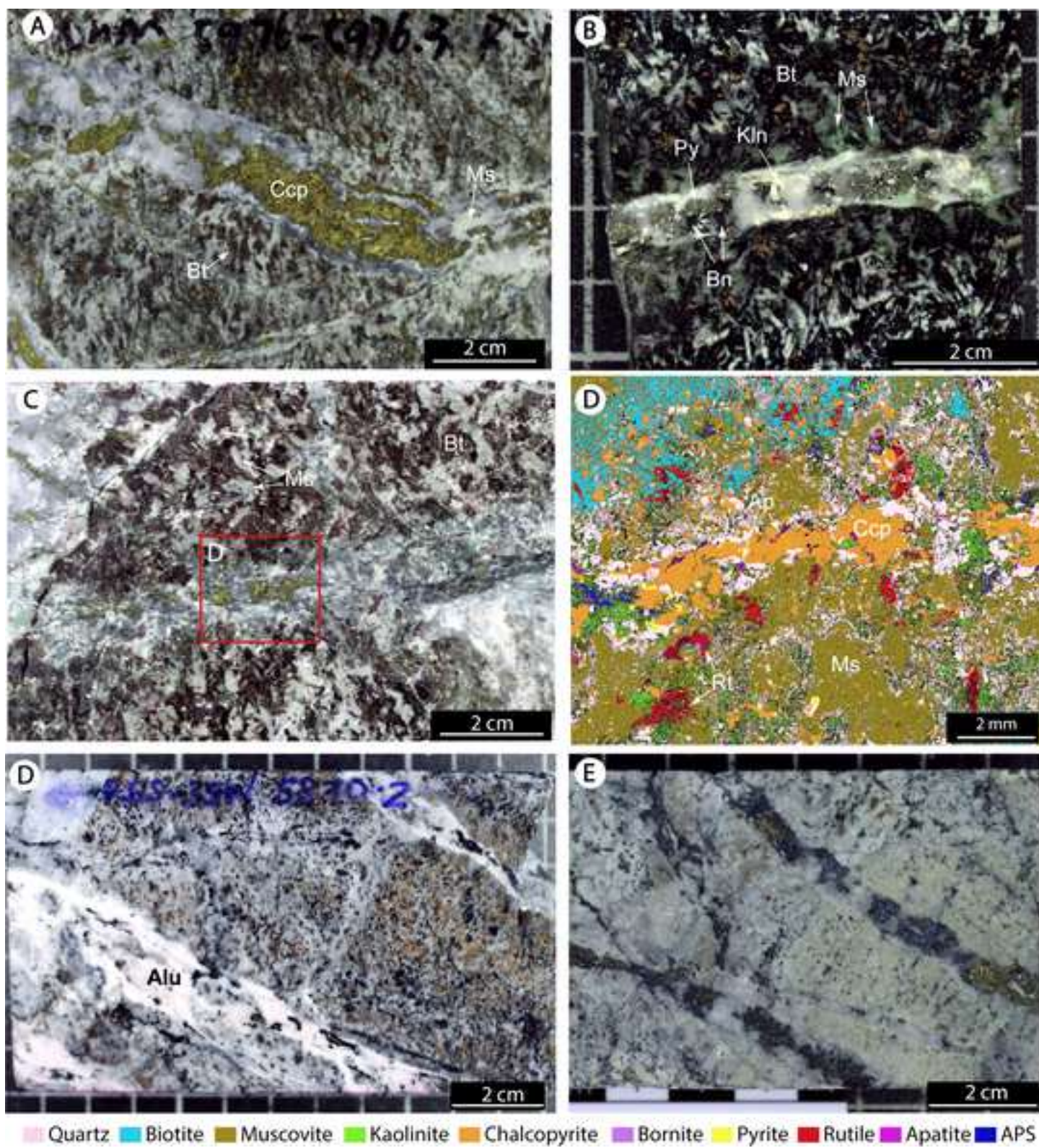
- Volcanic and sedimentary cover
- Magmatic-hydrothermal breccia
- Cretaceous granodiorite
- Cretaceous volcanoclastic rocks
- Paleozoic carbonates
- Mesoproterozoic diabase
- Mesoproterozoic Drippings Springs quartzite
- Paleoproterozoic Pinal schist

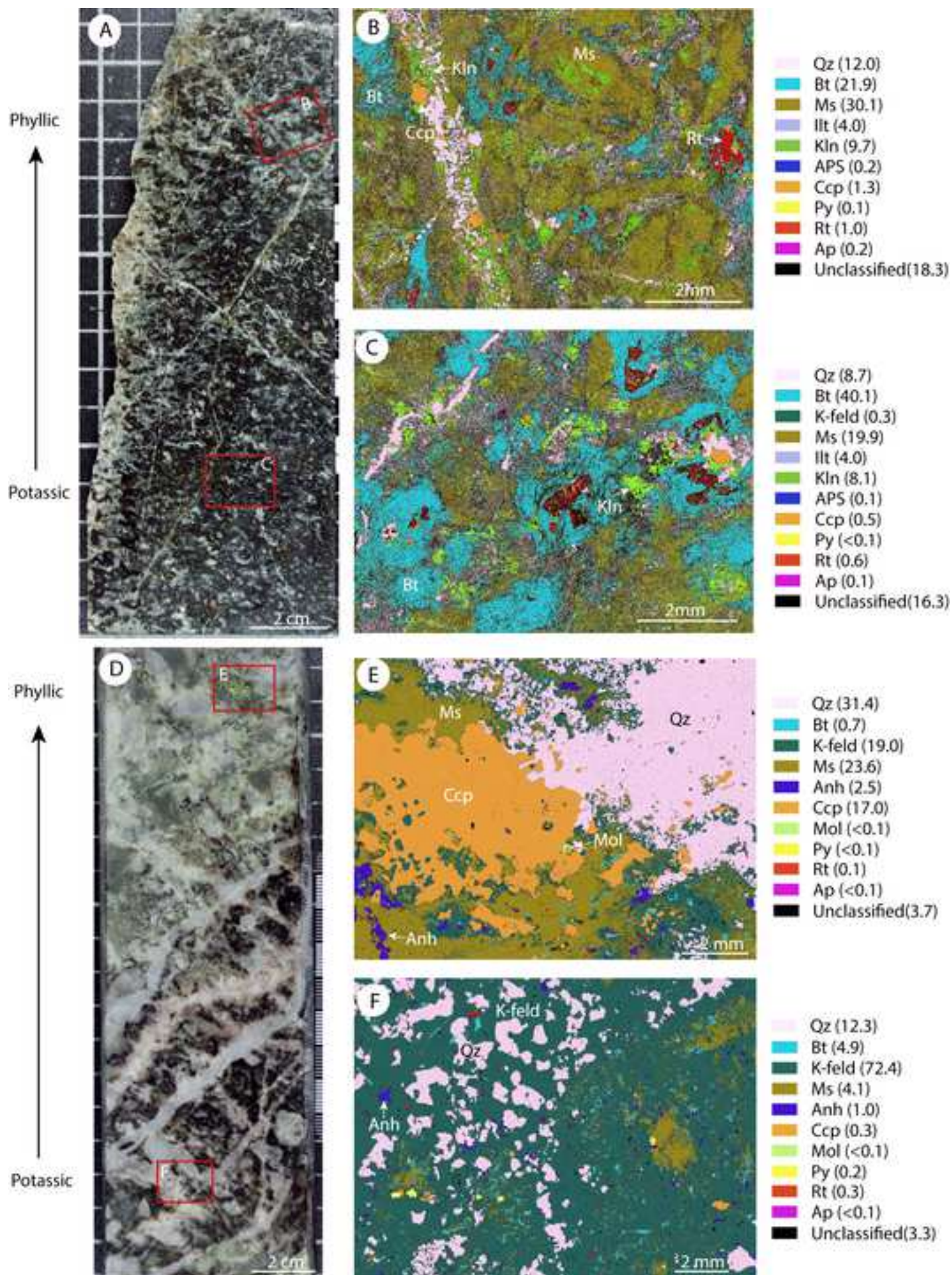
Hugo Dummett North rock units

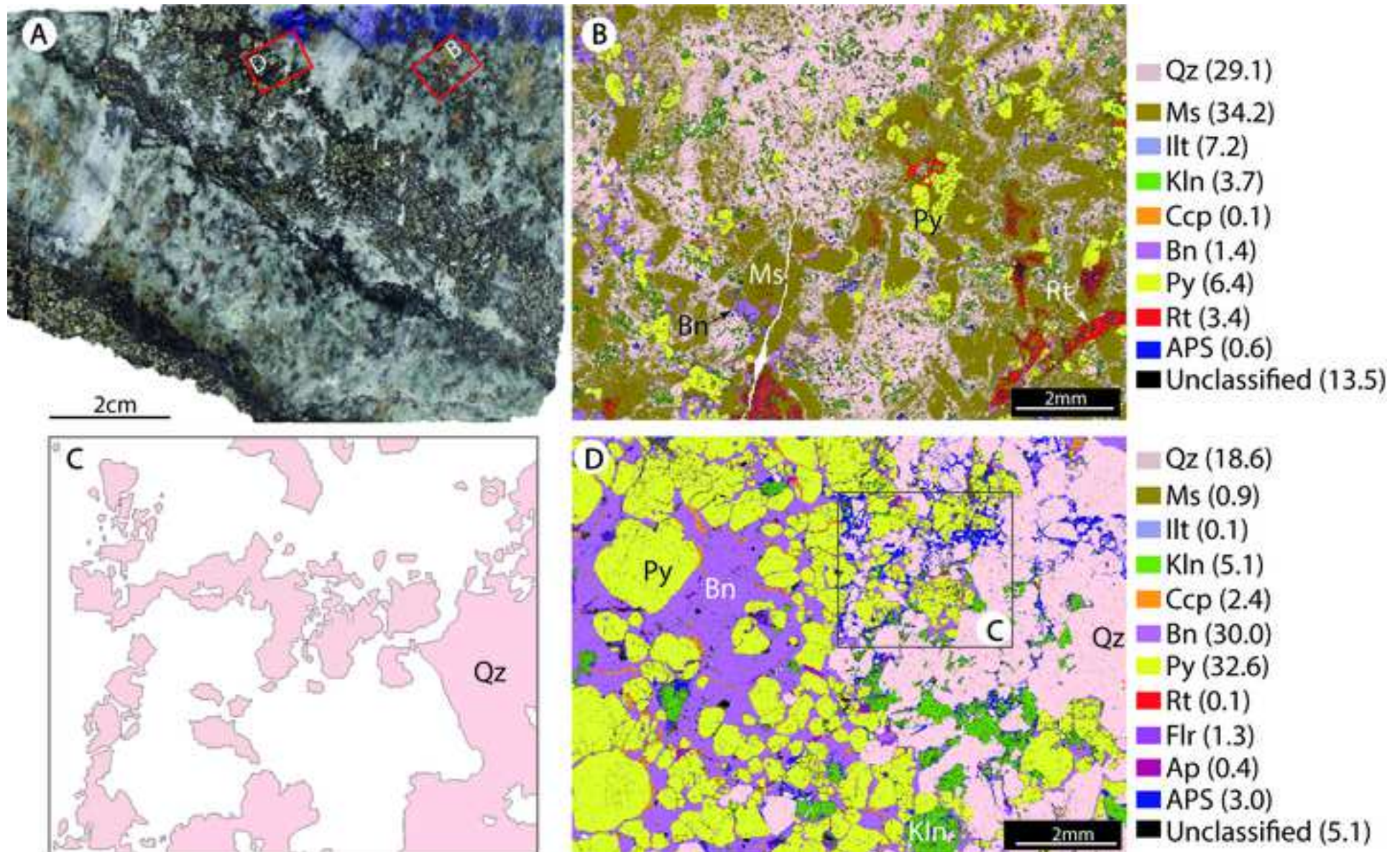
- Devonian or older carbonaceous siltstone
- Devonian or older augit basalt
- Devonian or older Heruga sequence
- Devonian quartz monzodiorite
- Biotite granodiorite
- Projected sample locations

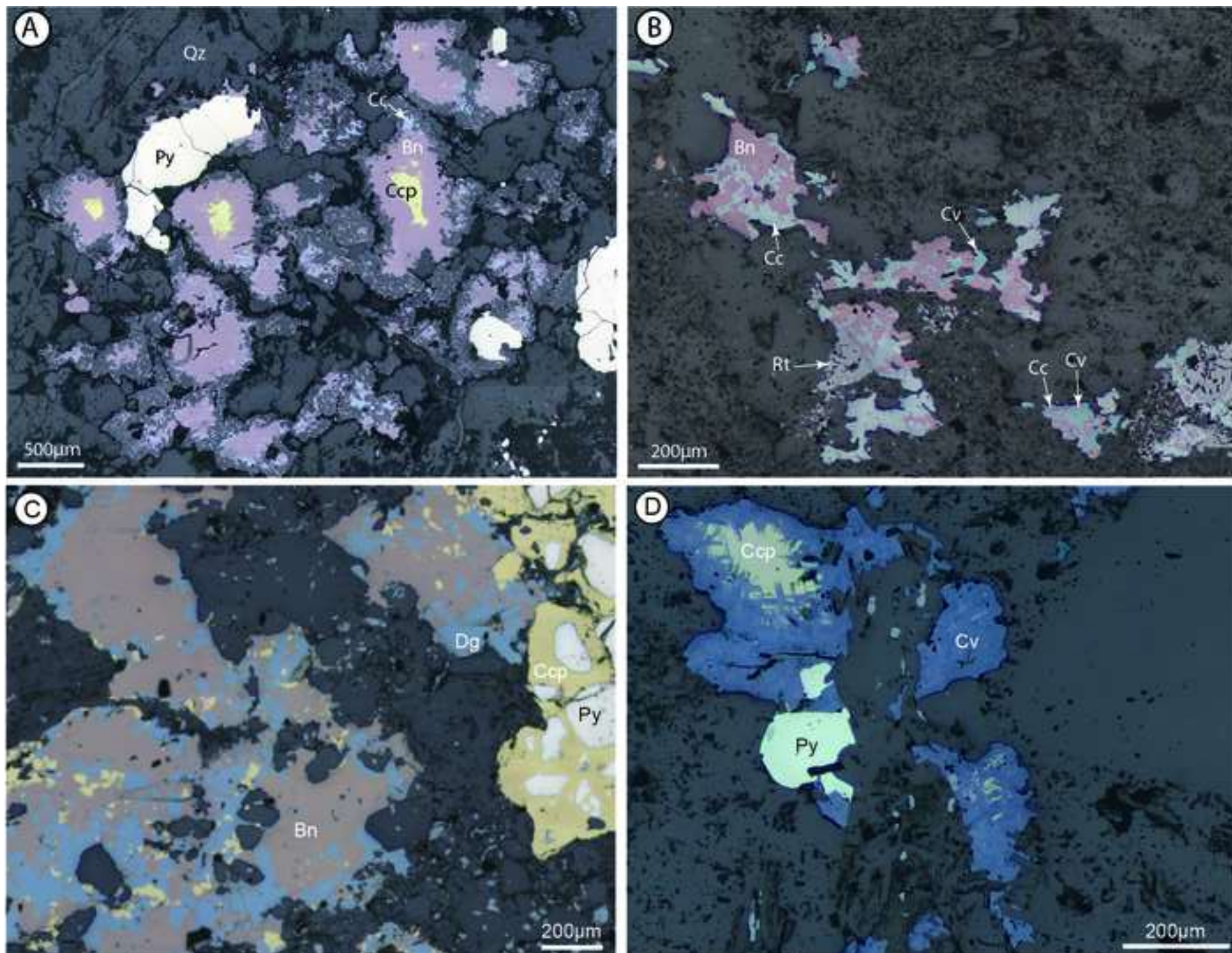
Alteration

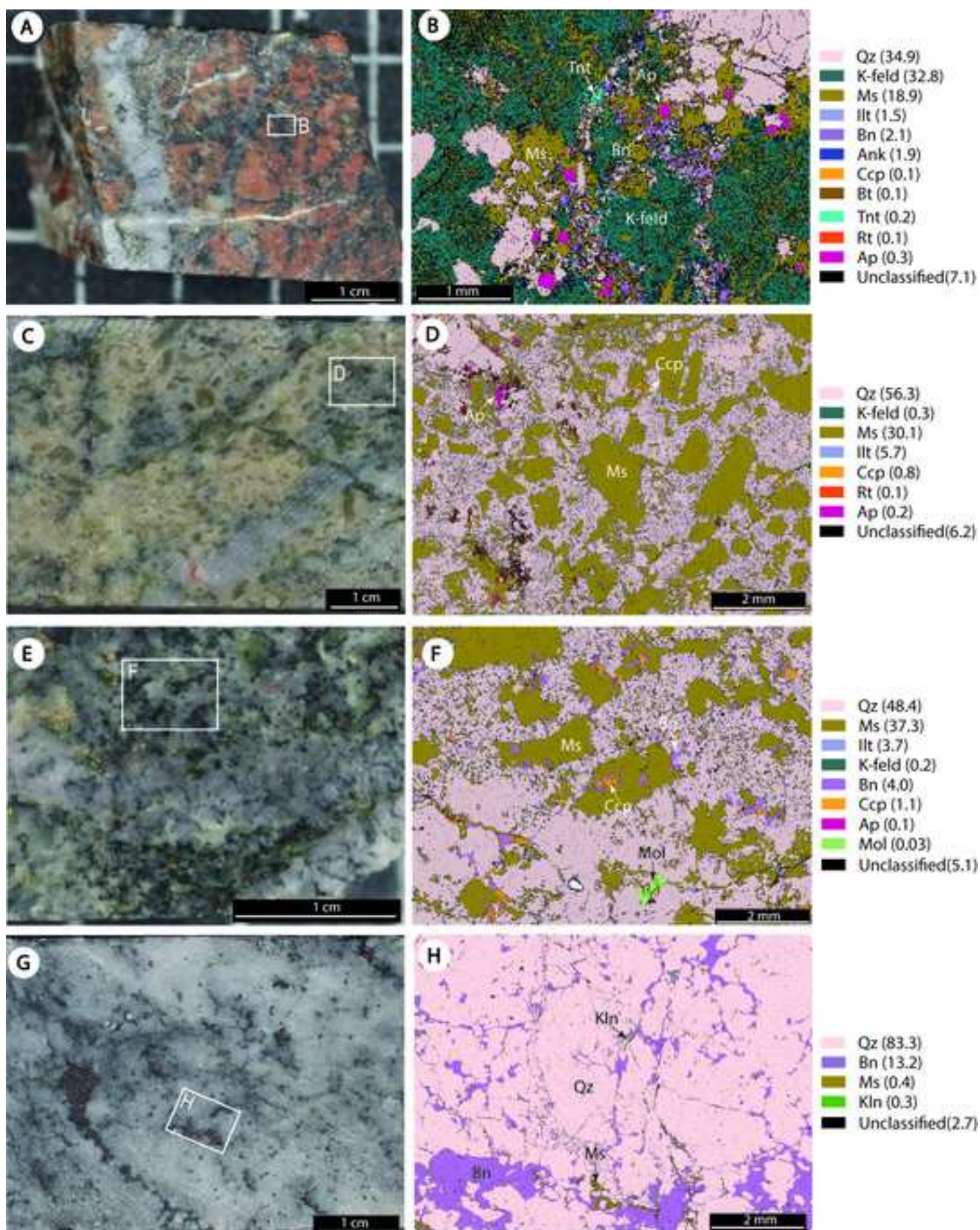
- Biotite-rich potassic
- K-feldspar-rich potassic
- Phyllic overprinting potassic
- Propylitic (chlorite-epidote)
- Quartz-muscovite
- Pyrophyllite-quartz-kaolinite ± alunite
- Supergene











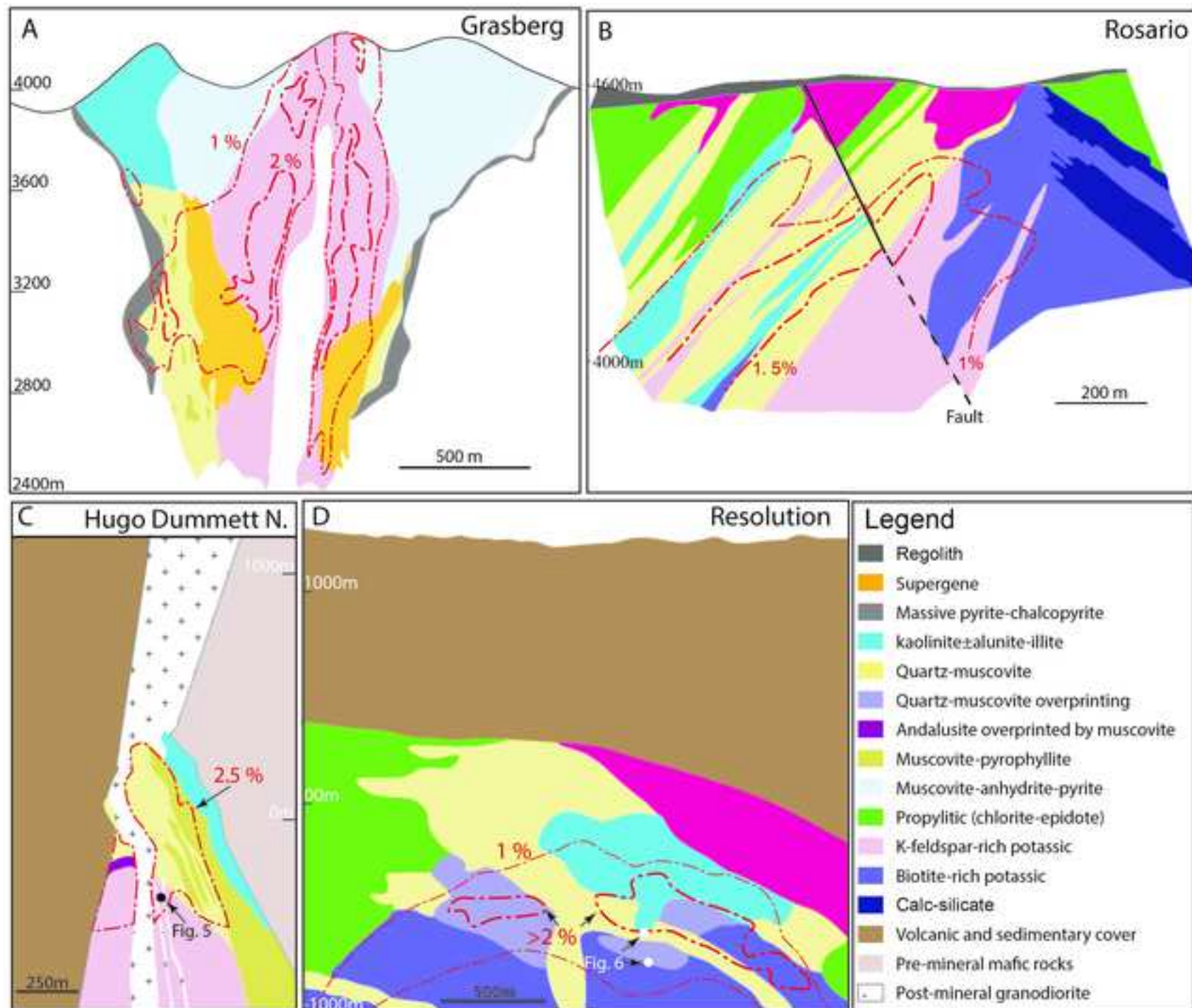


Figure9

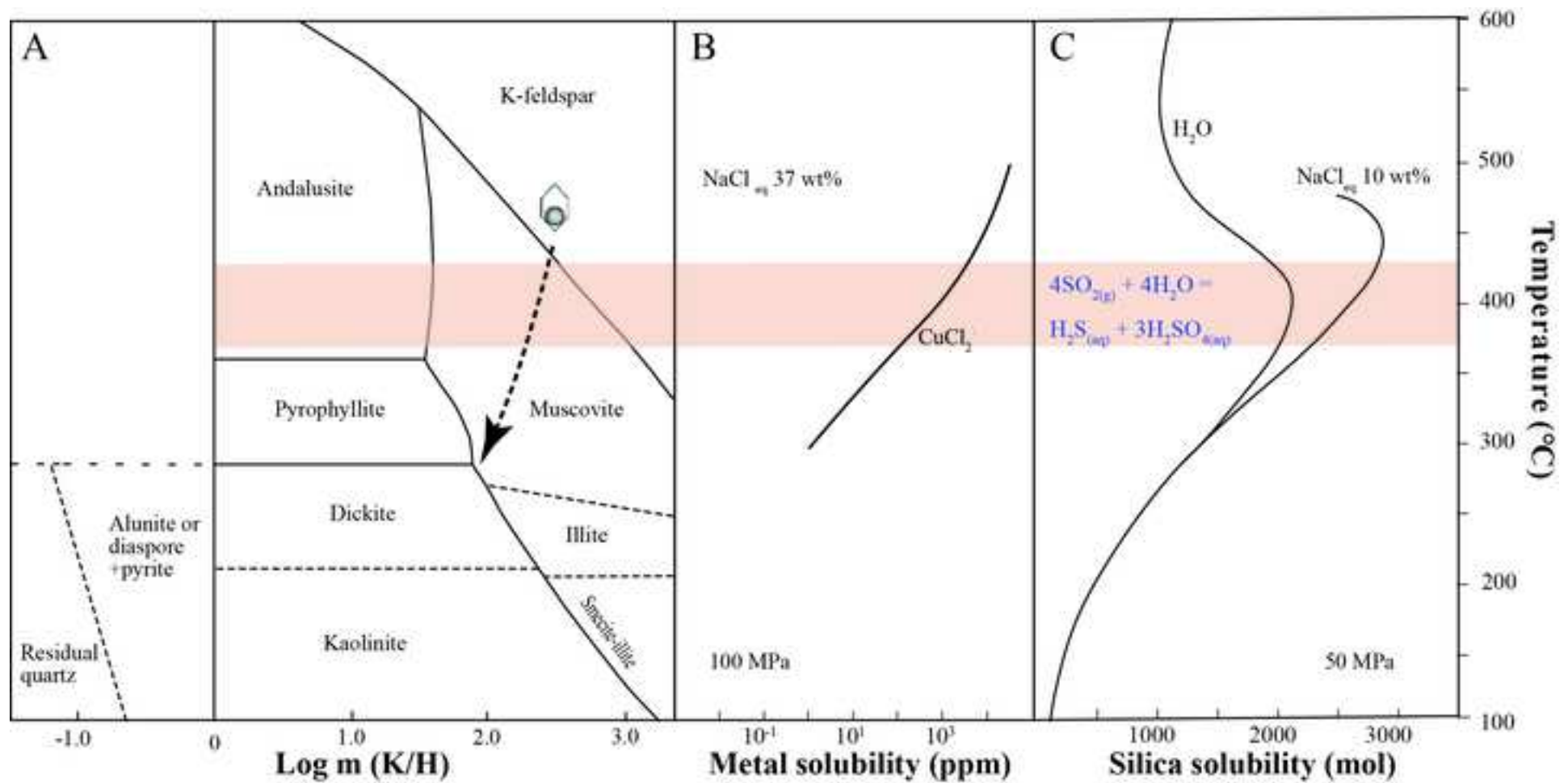


Figure10

[Click here to access/download;Figure;Fig.10 Hypogene enrichment.jpg](#)