

Figure 2. Plan view map of the location of the historical main Number One orebodies (purple) and the South Reef (orange), and drill hole collars from which samples were collected.

Although standard analytical methods are effective at accurately measuring the abundance of numerous elements including Cu, Co, and Zn, Ge concentrations are commonly under-represented because of volatilisation during sample digestion. However, limited multi-element data (Grannito et al. 2019, Trilogy Metals, Written Communication, 2018) demonstrate that elevated Ge concentrations occur locally in the Bornite deposit.

Reconnaissance, high-quality data indicate that Ge-rich intervals correlate with bornite-rich copper zones. Cobalt mainly occurs as cobaltiferous pyrite within and around the copper mineralised zones and as carrollite and cobaltite directly associated with copper bearing minerals. Therefore, areas with visibly high chalcocite, bornite and chalcopyrite were chosen for sampling.

The aim of this study was to improve our understanding of the occurrence and sequestration of Ge in the South Reef of the Bornite deposit and to develop a workflow using co-registered datasets to better understand the critical mineral endowment. Optical microscopy, μ -X-ray fluorescence (μ -XRF) mapping, field emission scanning electron microscopy (FE-SEM) backscattered electron (BSE) imaging coupled with energy dispersive spectroscopy (EDS) for semi-quantitative chemical analysis, and SEM-based automated mineralogy were employed on samples taken from the South Reef orebody.

2 Samples and Methods

2.1 Samples

Quarter-core samples were collected from variably mineralised Cu intercepts from 6 drill holes in the South Reef (shown in Fig. 2). Drill hole RC11-0187 was the most extensively sampled (48 of the 98 total samples) because of its extremely thick Cu-mineralised intercept. Samples from the Number

One ore body were provided by the U.S. Geological Survey (USGS) prior to sample collection for the purpose of initial reconnaissance. The South Reef samples were chosen based on the availability of modern drill core, modern reconnaissance Ge assay data, and the opportunity to sample different intensities of mineralisation.

2.2 Methods

Forty-one of the 98 drill core samples collected were selected for analysis in the Mineral and Materials Characterization Facility at the Colorado School of Mines because they reflect different intensities of mineralisation. Our workflow was multi-step. First, a mapping μ -XRF (M4 Tornado, Bruker) was used as a reconnaissance tool to determine elemental distributions in these 41 samples so that a sub-sampling strategy could be determined. Next, billets from selected areas on 25 samples were cut for thin section preparation for more detailed study. These billets were mapped using the μ -XRF at a higher resolution prior to thin section preparation. Third, the finished thin sections were inspected under transmitted and reflected light, FE-SEM BSE (MIRA, Tescan) and EDS (XFlash® 6/30 silicon drift detector, Bruker) and SEM-based automated mineralogy (TIMA, Tescan) to understand mineral paragenesis and related occurrence and distribution of cobalt and germanium in the South Reef.

3 Results and Discussion

Mineral paragenesis of the South Reef was determined based on a combination of petrography and co-registered micro-analytical methods such as mapping μ -XRF, SEM-based automated mineralogy, and traditional FE-SEM BSE and EDS analyses. The South Reef consists of localised high grade Cu intercepts, including massive bornite and chalcocite that extend laterally into more abundant chalcopyrite-rich zones.

Micro-XRF mapping (Fig. 3) showed that Co is hosted in cobaltiferous **Capitalized** illite, and cobaltite and revealed a strong correlation between Cu and Fe, and that high Co values almost always correspond to high Ni values. Barium and K as well as Ge and K show a significant spatial correlation. A notable correlation was seen between Co, Bi, As, and Pb in some samples. Within areas showing high Cu (Cu sulphides), bright areas of Ge could be found.

Five paragenetic stages were delineated: (I) dolomitisation, (II) ferroan alteration, (IIIa) veining, (IIIb) brecciation, (IV) main ore forming event (Fig. 4), and (V) a post ore forming event. Stage I predominantly consists of diagenetic low-temperature dolomite and pyrite, followed by ferroan stage II dolomite and pyrite as reported by Hitzman (1986). Stage III includes different carbonates, pyrite, cobaltiferous pyrite, and the Ba-minerals cymrite and alstonite. During the main ore forming

stage IV, cobaltiferous pyrite was replaced by mainly chalcocite and subordinately bornite. Trace elements in stage III cobaltiferous pyrite (Co, As, Pb) were liberated and precipitated as cobaltite, carrolite, galena, tennantite (Mahaffey 2021; this study). Petrographic observations reveal a distinct precipitation succession of the different Cu-sulphide minerals in stage IV. Chalcocite, bornite, and chalcopyrite did not precipitate in equilibrium but are staggered in space and time, with chalcocite precipitating first in the centre of the deposit,

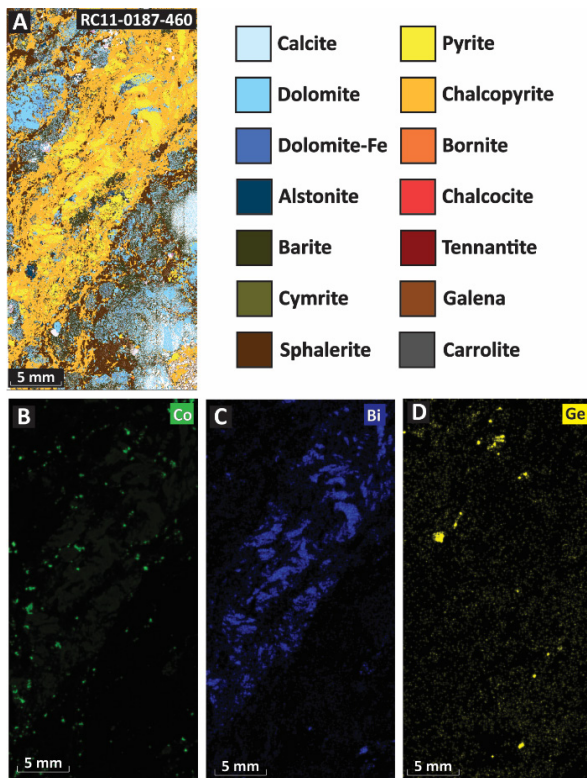


Figure 3. Sample RC11-0187-460. A) SEM-based automated mineralogy images, and μ -XRF element maps of B) Co, C) Bi, and D) Ge.

followed by bornite and then chalcopyrite (Hitzman 1986, Conner 2015, this study). The mineral renierite is the Ge bearing sulphide in the South Reef orebody. Renierite predominantly occurs as inclusions in chalcocite and bornite and is significantly less abundant in chalcopyrite. Renierite grains in chalcopyrite are commonly in contact with residual bornite and are always much smaller than renierite inclusions in chalcocite and bornite. These textures suggest that renierite, like bornite and chalcocite, is no longer in equilibrium in the presence of chalcopyrite. Discrete cobalt minerals occur in high-grade Cu zones and are represented by carrolite and cobaltite.

Hitzman (1986) suggested that the mineralizing fluid was a warm (100 to 215°C) basinal brine, rich in hydrocarbons, suggesting that the fluid responsible for ore formation was highly reduced. A reduced and acidic basinal brine at 200°C is able to transport significant amounts of Cu, Ba, and Zn (Cooke et al. 2000; Pfaff and Graham 2013).

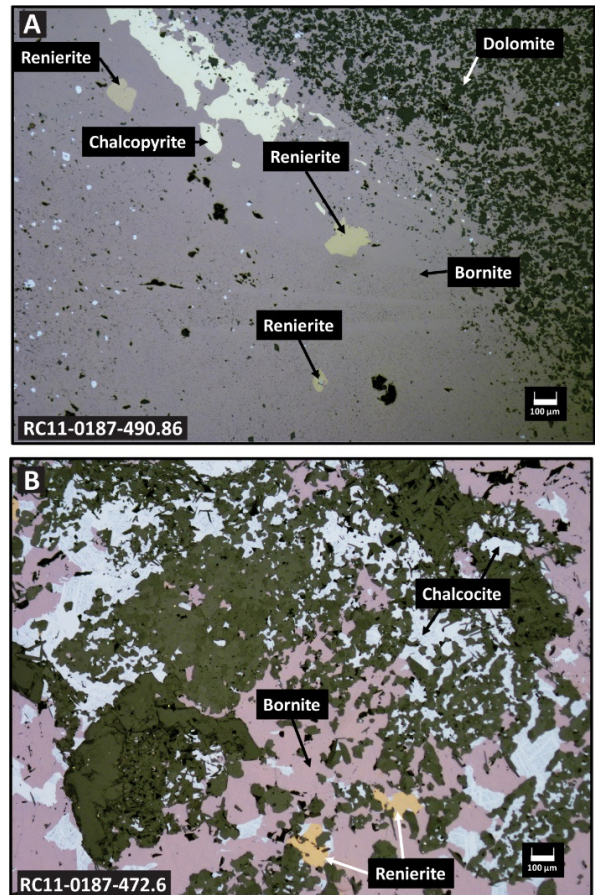


Figure 4. Stage IV ore mineralogy. Renierite hosted in bornite and in association with chalcocite and minor chalcopyrite.

This is consistent with observations from other carbonate hosted Cu-sulphide deposits such as the Black Butte deposit in Montana (Pfaff and Graham 2013) or the lead-zinc clastic sediment hosted Sullivan Deposit (Cooke et al. 2000). It is suggested here that reduced acidic basinal brines ascended along basal faults and precipitated at the site of the deposit. A shift in pH towards more alkaline conditions during the precipitation of ore minerals. The succession of Cu-sulphide minerals is interpreted to reflect the evolving fluid during fluid-rock interaction leading to more alkaline conditions and to a concomitant decrease in sulphide activity in the mineralizing fluid over space and time. When the sulfur activity in the fluid decreases, chalcopyrite is formed at the expense of bornite and pyrite and renierite is destabilised (Einaudi et al. 2005). Similar textural evidence can also be observed at Kipushi where renierite preferentially occurs in chalcocite and bornite (De Vos et al. 1974, Schneider et al. 2007).

5 Conclusions

The South Reef of the Bornite Cu-Co-(Ge) deposit is host to substantial amounts of high-grade Cu, Co, and Zn, but also hosts elevated concentrations of

Ge. With an increasing demand for Co and Ge and the lack of literature on their occurrence and sequestration within primary ore deposits, understanding known Co- and Ge-bearing ore deposits is critical for future exploration efforts. Five paragenetic stages have been delineated at the South Reef of the Bornite Cu-Co-(Ge) deposit: (I) dolomitisation, (II) ferroan alteration, (IIIa) veining, (IIIb) brecciation, (IV) ore forming event, and (V) post ore forming event. Cobalt occurs in cobaltiferous pyrite, carrollite, and cobaltite. Germanium occurs in renierite as well as enrichments in white mica, illite, galena and feldspars within the South Reef. Highest Ge-mineral (renierite) as well as Co-minerals (carrollite and cobaltite) abundances appear to correlate with highest bornite and chalcocite concentrations.

We propose that reduced acidic basinal brines capable of transporting significant amounts of Cu entered the organic matter rich carbonates and phyllites, leading to fluid-rock interaction at the site of deposition. The ore-forming basinal brine was subsequently buffered to an intermediate oxidation state and a near-neutral pH. Petrographic observations and SEM-based automated mineralogy reveal a distinct spatial and temporal precipitation succession from chalcocite, bornite, followed by chalcopyrite. This succession in Cu-minerals is interpreted to reflect the evolving ore forming fluid at the site of deposition, characterised by a decrease in temperature and a concomitant decrease in sulphide activity of the mineralizing fluid. This shift in pH towards more alkaline conditions, and subordinately a decrease in temperature and concomitant decrease in sulphide activity, are thought to have been the predominant precipitation mechanism leading to the distinct mineral zonation in space and time. Cobalt, which predominantly occurs in pre-main ore stage cobaltiferous pyrite, was replaced and Co was liberated during the ore forming process, leading to the formation of discrete Co-minerals (carrollite and cobaltite). Germanium is interpreted to have precipitated contemporaneously with chalcocite and bornite when the sulphur activity in the fluid was still high, forming discrete renierite minerals.

The Bornite deposit shares many similarities with other Ge-bearing carbonate hosted base metal deposits in Africa such as the Tsumeb, Kipushi, Khusib Springs, Kombot, and Kabwe deposits, however it seems to be of lower germanium grade than these deposits.

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