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RESEARCH ARTICLE

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Pre-Klondikean oxidation prepared the ground for Broken Hill-type mineralization in South Africa

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Abstract
New Cu isotope data obtained on chalcopyrite from the Black Mountain and the Broken Hill deposits in the medium- to high-grade metamorphic Aggeneys-Gamsberg ore district (South Africa) require a revision of our understanding of the genesis of metamorphic Broken Hill-type massive sulphide deposits. Chalcopyrite from both deposits revealed unusually wide ranges in δ^{65}Cu (−2.41 to 2.84‰ NIST 976 standard) in combination with distinctly positive mean values (0.27 and 0.94‰, respectively). This is interpreted to reflect derivation from various silicate and oxide precursor minerals in which Cu occurred in higher oxidation states. Together with the observation of a typical supergene base metal distribution within the deposits and their spatial association with an unconformity only meters above the ore horizon, our new data are best explained by supergene oxidation of originally possibly SEDEX deposits prior to metamorphic sulphide formation, between the Okiepian (1,210–1,180 Ma) and Klondikean (1,040–1,020 Ma) orogenic events.

1 | INTRODUCTION

The Aggeneys-Gamsberg ore district, located c. 700 km north of Cape Town (South Africa), represents one of the world's largest base metal anomalies. It comprises four deposits, including the world-class Gamsberg deposit (Figure 1). All of those were classified as deposits of the Broken Hill-type, traditionally interpreted as representing original sedimentary exhalative (SEDEX) deposits that became metamorphosed at amphibolite- to granulite-facies conditions. Peculiar mineral assemblages, a pronounced metal zonation across the ore district, and the appearance of various geochemical anomalies in the vicinity of the ore district (e.g. Willner et al., 1990) have, however, never been properly explained by such a genetic model.

Recently, the Cu isotope system has become a useful tool in ore deposit research, especially because of its high sensitivity to low-temperature supergene processes (Mathur & Fantle, 2015; Mathur et al., 2014). High-temperature hydrothermal processes as well as metamorphic overprint allegedly have only limited impact on the Cu isotopic characteristics of a deposit (Höhn et al., 2017; Ikehata et al., 2011). Consequently, Cu isotopes should provide a perfect tool to detect pre-metamorphic oxidation in the metallogenesis of sulphidic deposits. The mineralogical variability in the vicinity and substantial previous investigations revealing inconsistencies with regard to redox state make this ore district a perfect ground for testing the possible role of supergene redistribution of metals prior to final constitution of the ore in the course of metamorphism.

2 | GEOLOGICAL SETTING

The Aggeneys-Gamsberg ore district is located in the Bushmanland Subprovince of the Namaqua Province, which constitutes the western part of the Mesoproterozoic Namaqua-Natal metamorphic belt (e.g., Cornell et al., 2006). Stratigraphically, the ore-bearing units are within a metavolcano-sedimentary succession (Bushmanland Group), comprising biotite-sillimanite schist, paragneiss, quartzite, in places graphite-rich sillimanite-mica schist, and in the vicinity of the stratiform ore bodies at the top of the group meta-exhalites like iron formation (Figure 2). The Bushmanland Group is unconformably overlain by a volcano-sedimentary succession (Koeris Formation), starting with a basal metaconglomerate and containing quartzite, para- and orthogneisses as well as amphibolite.

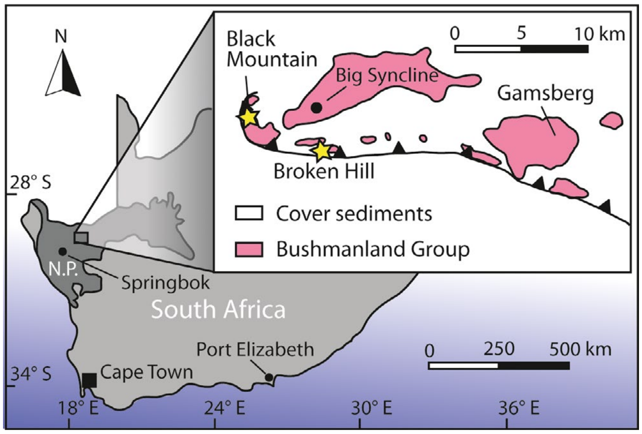

FIGURE 1 Location of the Aggeneys-Gamsberg ore district; magnified area shows the position of the main deposits within the local Bushmanland Group outcrops; N.P. – Namaqualand Province (after McClung et al., 2007; Stalder & Rozendaal, 2004)

Statement of significance

Our manuscript presents state-of-the-art Cu isotope analyses for the Aggeneys-Gamsberg ore-district, one of the world's biggest base metal anomalies. From a theoretical point of view, the high sensitivity of the Cu isotope system to low-temperature supergene processes and its high inalterability in high-temperature hydrothermal processes should make it a perfect tool to detect pre-metamorphic redox processes. Here, we present the first empirical study on this issue, using the Aggeneys-Gamsberg ore-district in South Africa as example. Our data do not only prove the very limited impact of metamorphic overprint on the δ^{65}Cu characteristics of the ore bodies but it also challenges our traditional understanding of the genesis of Broken Hill-type deposits by providing strong indications for a pre-metamorphic oxidation/weathering process that dictated the distribution of the ore.

The protoliths of the Bushmanland Group predate the Namaquan collision at ~1,200 Ma (Clifford et al., 2004). The depositional age of the base metal-rich strata is constrained between 1,285 ± 14 and 1,198 ± 18 Ma (Cornell et al., 2009). The hiatus between the Bushmanland Group and the post-Okiepian Koeris Formation, located only a few meters above the ore-bearing stratigraphic level (e.g. Lipson, 1990; Rozendaal et al., 2017; Ryan et al., 1986), is considered to range between <1 and 130 million years (Colliston et al., 2012).

The protracted thermal history of the Bushmanland Group (Bial et al., 2015) can be subdivided into an early Okiepian (1,210–1,180 Ma) and a late Klondikean (1,040–1,020 Ma) orogenic event

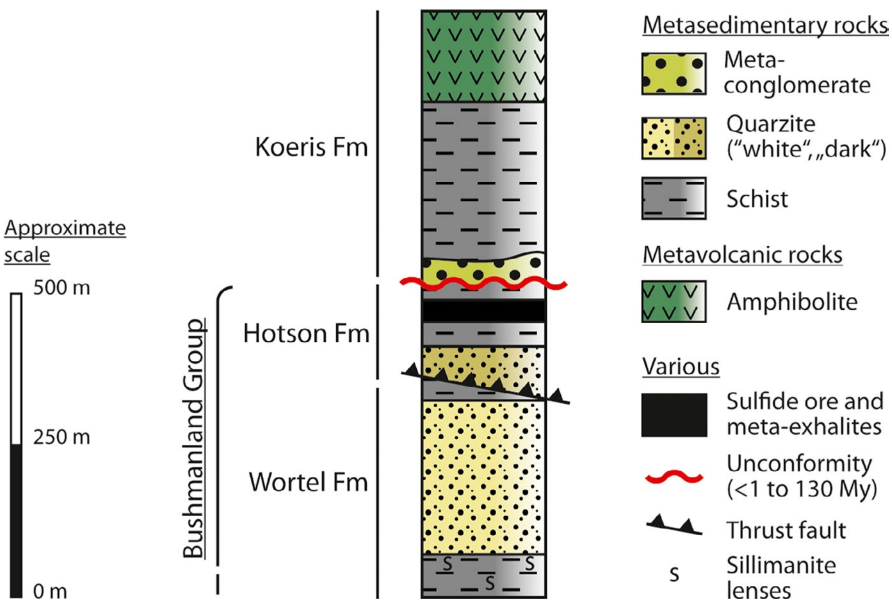

FIGURE 2 Stratigraphic column of the meta-volcanosedimentary sequence at Aggeneys (after Colliston et al., 2012; Cornell et al., 2006; Stalder & Rozendaal, 2005)

(Clifford et al., 2004; Cornell et al., 2009), reaching upper amphibolite facies in the ore district (Willner et al., 1990).

The ore-district comprises four major deposits (Figure 1) with estimated resources of 385 Mt ore @ up to 6.73% Zn, 2.88% Pb, 0.5% Cu and 34 ppm Ag (Rozendaal et al., 2017). A metal zonation is noted across the whole district with Cu-Pb-rich ores in the west and Zn-rich ores in the east. In places, "meta-exhalites" like iron formation, coticules, apatite-rich rocks and quartz-gahnite rocks are spatially associated with the ore (McClung et al., 2007; Rozendaal et al., 2017).

The Black Mountain and the Broken Hill deposits each consist of two separate ore-bodies, an upper and a lower one. The upper ore-bodies share the same stratigraphic position with close spatial association with a folded quartz-magnetite rock (Rozendaal et al., 2017). The sulphide assemblages of both are similar with pyrite, pyrrhotite, galena, sphalerite and chalcopyrite but the modal proportions differ and make Black Mountain a Pb-Cu-Zn-Ag deposit, whereas Broken Hill is described as Pb-Zn-Cu-Ag-deposit (McClung et al., 2007). In low-strain areas of the ore-bodies, sedimentary structures such as bedding-planes are still preserved. Therein, the sulphides, including chalcopyrite are fine-grained and disseminated (Ccp-1), whereas elsewhere, such as in fold hinges, the sulphides, including chalcopyrite (Ccp-2), are distinctly coarser grained (Ryan et al., 1986), as can be expected for recrystallization under higher fluid/rock ratios (e.g. Marshall et al., 2000).

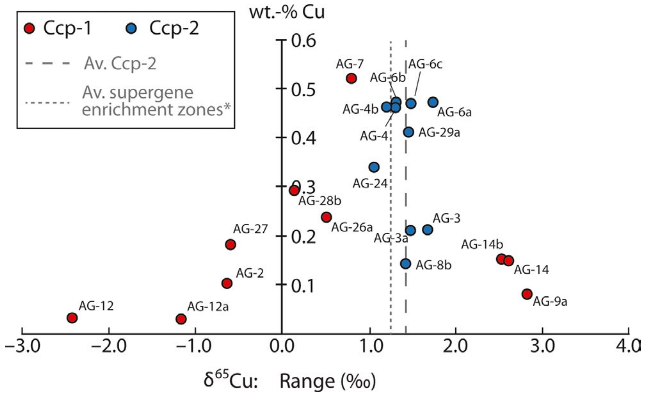

FIGURE 3 Cu isotope ratios for chalcopyrite from the Broken Hill deposit in combination with the Cu content of their host rock; * = global average for supergene Cu minerals from Mathur and Fantle (2015)

3 | SAMPLE MATERIAL AND ANALYTICAL PROCEDURE

Exploration drill core was sampled from Black Mountain supplemented by specimens from the upper ore body of the Broken Hill deposit (Table S1) collected previously in the early 1990s. On these, a total of 34 Cu isotope analyses of were performed. Fourteen of these on the upper ore-body of the Black Mountain and 20 on the upper ore-body of the Broken Hill deposit. To exclude isotopic fractionation effects between different minerals, only samples were used in which chalcopyrite is the only detectable Cu-mineral. Because of the very fine grain-size of the sulphides, selected bulk samples composed of sulphides and silicates (Figure S1) were analysed. Furthermore, we discarded all sample material that showed signs of sulphide alteration on a macroscopic and microscopic scale.

The purification of Cu was conducted at the Laboratoire G-Time at the Université libre de Bruxelles (ULB), Belgium, using anionic resin and HCl. Measurements of the Cu isotopic composition were performed using a Nu Plasma HR-MCICP-MS, also at ULB, following the procedure described by Höhn et al. (2017). All isotope ratios are reported in standard per mil notation relative to the NIST 976 standard with $2\sigma \le 0.10$.

For both ore-bodies, half of the analyses were performed on the fine-grained (ø ≤ 1 mm), disseminated chalcopyrite (Ccp-1), from low-strain areas with well-preserved sedimentary structures like bedding planes and the other half on coarser grained (ø ≥ 1 mm) samples that evidently are syn-metamorphic remobilization products (Ccp-2).

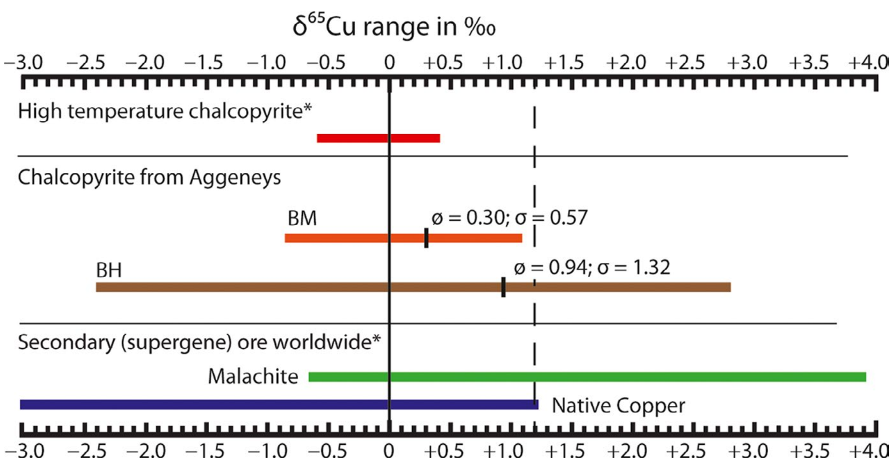

FIGURE 4 δ^{65}Cu values of chalcopyrite from the Broken Hill and Black Mountain deposit at Aggeneys compared to terrestrial high-temperature chalcopyrite and supergene ores worldwide. * = Ikehata et al. (2011). Broken line = Supergene average (Mathur & Fantle, 2015)

4 | RESULTS

With δ^{65}Cu ratios between −2.41‰ and 2.84‰ (*n* = 20) the Cu isotope values of chalcopyrite from Broken Hill (Figure 3) distinctly exceed the range known for terrestrial high-temperature chalcopyrite (δ^{65}Cu = −0.6 to 0.4‰) as defined by Ikehata et al. (2011). The reason for this wide range is the fine-grained disseminated chalcopyrite (Ccp-1), covering the full range between −2.41‰ and 2.84‰ (mean = 0.47‰, σ = 1.77; *n* = 10). In contrast, the coarser grained remobilized chalcopyrite (Ccp-2) yielded a much narrower range between 1.06 and 1.74‰ (mean = 1.42‰, σ = 0.21; *n* = 10).

Chalcopyrite from the Black Mountain deposit has a narrow range in between −0.84‰ and 1.08‰ (mean = 0.30‰, σ = 0.57; *n* = 14), which is, however, distinctly higher than δ^{65}Cu typical of high-temperature chalcopyrite reported from other localities (Figure 4). No significant difference exists between the two chalcopyrite types Ccp-1 (mean δ^{65}Cu = 0.17‰; σ = 0.57; *n* = 8) and Ccp-2 (mean δ^{65}Cu = 0.48‰; σ = 0.56; *n* = 6).

5 | INTERPRETATION AND DISCUSSION

Preservation of sedimentary structures, such as fine syn-sedimentary lamination, sharp contacts between different rock types and steep chemical gradients on a centimeter-scale, points to very limited element mobility during high-grade metamorphism. Mobilization of sulphides was restricted to high-strain domains affected by higher fluid/rock ratios. Consequently, the sulphides from those low-strain domains should carry a primitive isotope signal. The wide δ^{65}Cu range obtained for Ccp-1 from the Broken Hill deposit (−2.41‰ to 2.84‰) is much larger than previously reported for chalcopyrite from other areas, that is, 0.0 ± 0.5‰ (Ikehata et al., 2011; Markl et al., 2006). Comparable wide ranges in δ^{65}Cu have been reported, so far, only from secondary Cu minerals in supergene base metal-enrichment zones. In such zones, the high diversity in Cu minerals generally causes a wide δ^{65}Cu range between −6 and +8‰ (Mathur & Fantle, 2015). Furthermore, the elevated mean δ^{65}Cu ratio of Ccp-1 from Broken Hill (0.47‰) is in good agreement with supergene enrichment in heavy isotopes of those minerals in which Cu occurs in a high oxidation state (Haest et al., 2009; Polyakov & Mineev, 2000).

The Cu isotope ratios of the coarse-grained, remobilized Ccp-2 from the Broken Hill deposit shows a comparatively narrow standard deviation (σ = 0.21), which is in line with the textural interpretation of this generation being syn-metamorphic (Höhn et al., 2017; Ikehata et al., 2011). Its mean value of δ^{65}Cu (1.42‰) is, again, far outside the range defined for high-temperature hydrothermal chalcopyrite but close to the ratio of 1.2‰, which is the typical mean value in the enrichment zone of supergene systems (Mathur & Fantle, 2015). As evident from Figure 3, mobilization and concentration in the presence of metamorphic fluids in high-strain zones is suggested to have led to a progressive homogenization of δ^{65}Cu, which approached a "supergene-like" average of 1.2‰.

A direct comparison with non-altered, unmetamorphosed SEDEX deposits, the likely starting material for the ore bodies in the study area (Sangster, 2020; Stalder & Rozendaal, 2004), is not possible because of the lack of data. Other sediment-hosted stratiform Cu-deposits, however, like the Kupferschiefer (Poland) or the Timna deposit (Israel) have a distinctly different isotopic composition with lower, negative mean δ^{65}Cu values of −0.39 and −2.04‰ and lower standard deviation of 0.36 and 0.44, respectively (Asael et al., 2009).

The Cu isotope range in chalcopyrite from the Black Mountain deposit also revealed a wider range (δ^{65}Cu = −0.84‰ and 1.08‰) and higher average (0.30‰) than typical terrestrial chalcopyrite, but the difference is not as pronounced as in the Broken Hill deposit. No significant differences in metamorphic grade have been noted across the ore district (Willner et al., 1990). This precludes metamorphism as a reason for the differences in the Cu isotope range of the investigated deposits and calls for an alternative explanation.

The peculiar Cu isotopic characteristics are best explained by supergene oxidation in the complex multistage mineralization history of the ore district. The supergene Skorpion Zn deposit in the eastern Gariep Belt, southern Namibia, may serve as useful reference. There, within the supergene oxidation zone, very similar isotopic characteristics have been reported for secondary Cu-Pb-Zn-rich sulphides and oxides (Borg et al., 2009).

Independent support for supergene mobilization of base metals at a deposit scale can be derived from the base metal distribution at Black Mountain. There, both limbs of an Okiepian (1,210–1,180 Ma) F1 fold (Ryan et al., 1986) display a metal zonation from Cu-rich (NNW) to Zn-rich (SSE) (Cawood & Rozendaal, 2020). Stedman (1980) explained this by a hypothetical hydrothermal feeder zone that would have been fortuitously placed exactly in the position of the later fold hinge. Alternatively, this could be the product of progressive supergene alteration of an Okiepian fold structure from a fault in the north-northwest, along which meteoric waters had infiltrated downwards.

Further evidence of supergene oxidation is indirectly given by the spatial association of the Aggeneys-Gamsberg ore deposits with an unconformity only meters above the ore horizon (Figure 2). The unconformity represents a hiatus of poorly constrained duration but long enough for deep chemical weathering having taken place and reached the underlying ore bodies. A very early pre-metamorphic oxidation of the deposited sulphides, comparable to processes in active seafloor vents (Ikehata et al., 2011), could theoretically cause similar Cu isotopic characteristics but is not in good agreement with the previously mentioned structural and stratigraphic observations.

The Gamsberg deposit was not included in this study because of a lack of Cu minerals there (except for voluminously insignificant chalcopyrite inclusions in sphalerite). Nevertheless, independent evidence of supergene oxidation can be found there as well: The strong enrichment in Zn without corresponding Pb in the Gamsberg deposit is not typical of SEDEX deposits where both base metals normally are in close spatial proximity. It is, however, in perfect agreement with Pb-depleted and Zn-enriched zones of supergene non-sulphide deposits. Interestingly, Zn isotope ratios from Gamsberg are hardly fractionated (Foulkes, 2014), which can only be explained by a redox-driven process because Zn is non redox-sensitive. Comparable isotopic characteristics have been described from Indian laterites that have been affected by intense supergene alteration (Little et al., 2019). Moreover, strata-bound peraluminous rocks, which underly the mineralization in places, can be explained by intense chemical weathering (Willner et al., 1990).

Further evidence of oxidation of a SEDEX-like precursor prior to metamorphism comes from magnetite-rich iron formation, which has been often described as one of the most characteristic features of Broken Hill-type (BHT) deposits in general. Sangster (2020) argued that simple high-grade metamorphic overprint of a SEDEX deposit cannot explain the prevalence of iron formation in BHT deposits and explained them by originally high proportions of siderite in the precursor, which dissociates under amphibolite-facies metamorphic conditions into magnetite and graphite. However, most SEDEX deposits are not rimmed by laterally extensive siderite but pyrite beds. A direct transition from the latter to magnetite under normal metamorphic conditions is not possible. If the pyrite beds had been oxidized, however, prior to metamorphism, the resulting Fe-oxides, hydroxides and carbonates can be converted to magnetite in the course of metamorphism (Pilchin, 2010; Tao et al., 2013).

Incomplete re-sulphidation during metamorphism, which is evident throughout the ore district by its various base metal-rich silicates (Frimmel et al., 1995; O'Brien et al., 2015) and oxides (Spry, 2000), is most probably the product of the interaction between non-sulphidic base metal minerals and S-rich fluids under varying metamorphic conditions. The most likely source for such fluids are shallow marine carbonate-dominated deposits within the Koeris Formation, which are interpreted as former evaporites. This is indicated by a trend towards increasing $\delta^{34}S$ from west to east within ore district. The Gamsberg deposit, for which nearly complete oxidation can be inferred from its Zn-dominated base metal content, has $\delta^{34}S$ of 29.9 ± 1.0‰ (McClung et al., 2007) in line with typical Mesoproterozoic sulphate values ($\delta^{34}S$ = c. 24‰; Fike et al., 2015). Taking today's area of the overturned Gamsberg fold as minimum aerial extent of the inferred evaporite beds, the amount of sulphur necessary for the complete resulphidation of the oxidized ore would correspond to not more than 0.95 m of anhydrite. The higher Cu-Pb content of the Black Mountain deposit indicates a lesser extent of pre-Klondikean oxidation, which is supported by its lower $\delta^{34}S$ of 16.0 ± 1.6‰; McClung et al., 2007).

6 | CONCLUSIONS

New Cu isotope data, together with previously described mineral assemblages, distinct metal zonations and the spatial association of the sulphidic ore with magnetite-rich iron formation, overlain by a regional unconformity all point at a multi-stage mineralization history in the Aggeneys-Gamsberg ore district: (a) initial SEDEX-type stratiform sulphide mineralization was followed by intense deformation (regional D1) during the Okiepian (1,210–1,180 Ma) orogeny; (b) during subsequent erosion and peneplanation, the ore horizon was subjected to deep chemical weathering, which lead to supergene oxidation of the primary sulphides and to the development of a distinct metal zonation. This was followed by renewed deformation and metamorphism during the Klondikean (1,040–1,020 Ma) orogeny, resulting in re-sulphidation of the ore and formation of the current sulphide ore bodies. Our finding of an intermediary supergene oxidation stage between initial SEDEX-type mineralization and metamorphic recrystallization might be applied also to other Broken Hill-type deposits and should assist in future exploration strategies for such deposits.

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CONFLICTS OF INTEREST

The authors of this manuscript certify that they do not have financial or non-financial interest in any subject discussed in this manuscript.

DATA AVAILABILITY STATEMENT

All data used in this manuscript are available in the Supplementary Material.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

Fig S1. Samples locations within the Aggeneys-Gamsberg ore district

Table S1. Cu isotopic composition of chalcopyrite types from the Broken Hill and the Black Mountain deposit.

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