In-situ Cu-isotope systematics of the Copperbelt (DRC, Zambia): variations at different scales

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Abstract. The internal zone of the Central African Copperbelt (CAC) is characterized by several mineralization stages. Cu isotope signatures from the Lumwana deposit were analyzed by secondary ion microprobe (SIMS). Chalcopyrite and bornite from the two main mineralization stages display both δ^{65}Cu values between -1.37±0.23‰ and +2.95±0.19‰. These results do not allow to determine a specific metal source.

These δ^{65}Cu signatures are compared to Cu-Co deposits of the external zone of the CAC that are characterized by several mineralization stages. The latter stages involve remobilization of an earlier mineralization during the Pan-African orogeny. Copper-sulfides of the CAC present a wide range of more than 6‰ in δ^{65}Cu values. Deposits from the external zone of the CAC have mostly negative δ^{65}Cu values, whereas the internal zone shows ^{65}Cu enrichment. The fractionation at the grain scale can reach up to 3‰. This is significant when compared to the regional scale fractionation. This in-situ method also reveals equilibrium fractionation between the different Cu-phases. Mechanisms for such fractionations remain to be constrained.

1 Introduction

The Lufilian Pan-African orogenic belt hosts the world's largest sediment-hosted stratiform Cu-Co province, namely the Central African Copperbelt (CAC, Fig. 1; Selley et al. 2005), which is divided in two distinct metallogenic zones: the external and internal zone.

The external zone encompasses the Congolese and the Eastern Zambian Copperbelt, where metamorphism reached *P-T* conditions up to greenschists facies (Fig.2; Selley et al. 2005). Deposits of this zone are interpreted as the result of a multiphase mineralization ranging from diagenetic to syn- and post-orogenic (El Desouky et al. 2010; Muchez et al. 2015).

The internal zone is located in the Domes region, and corresponds to the Western Zambian Copperbelt (WZC). It records metamorphic *P-T* conditions up to upper-amphibolite facies (Fig. 2; Eglinger et al. 2014; Turlin et al., 2016). Several mineralization stages have been documented in this internal zone and including pre-, syn- and post-orogenic phases (Bernau et al. 2013; Turlin et al. 2016). However, whether the syn-orogenic Cu was derived from remobilization of a first pre-orogenic phase remains unclear due to the high-grade metamorphic overprint (Turlin et al. 2016). In order to constrain the origin of the Cu, a Cu-isotope study could provide some useful insights. However, the size of the pre-orogenic Cu-sulfide crystals and the common bornite-chalcopyrite intergrowths (e.g. Turlin et al. 2016) do not allow bulk Cu-isotope analyses, but require an *in-situ* method.

The aim of this study is to determine the relationship between the different Cu mineralization stages by analyzing the Cu-isotope signatures of chalcopyrite-bornite assemblages by secondary ion microprobe (SIMS) of both the internal and external zones of the CAC. Copper-Cobalt assemblages are hosted in (i) kyanite-micaschists from the Lower Roan Group or from its pre-Katanga basement (Lumwana deposit, Turlin et al. 2016); (ii) in the siliciclastic Lower Roan Group of the Katanga series (Kambove, Luiswishi, Konkola and

Nkana-Mindola) (Cailteux et al. 2005); and (iii) in the dolomites and sandstones of the Kundelungu Group (Dikulushi) (Haest et al. 2007). These data allow to discuss small and regional scale Cu isotope variation and fractionation, processes that could be due to differences in the source of the metal, temperatures, Eh or pH conditions of the mineralizing fluid.

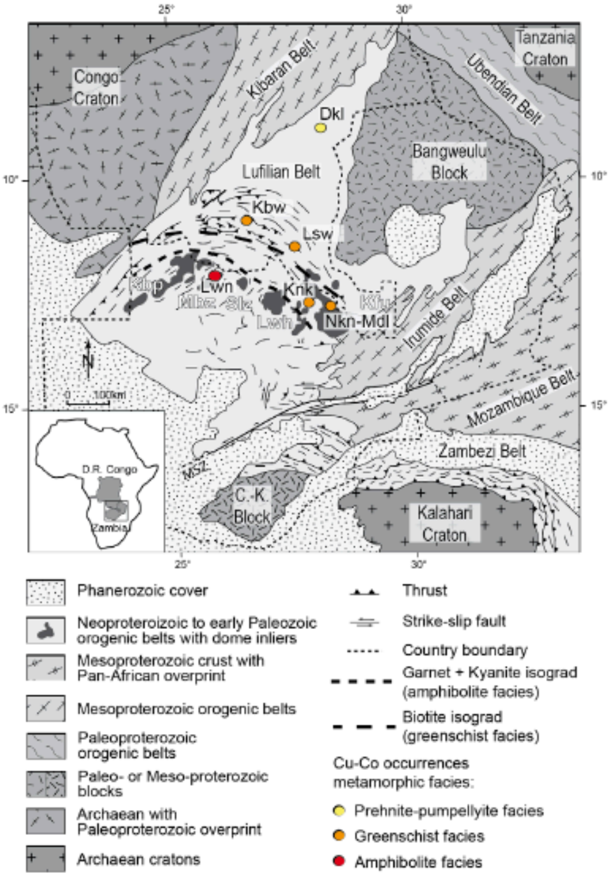

Figure 1. Geological map of the Central African Copperbelt hosting the investigated deposits. *Dkl: Dikulushi, Kbw: Kambowe, Knk: Konkola, Lsw: Luiswishi, Lwn:Lumwana, Mdl: Mindola, Nkn: Nkana*

2 Geological context

The Pan-African orogenic cycle started after intrusion, uplift and erosion of granites, which have been dated at ca. 880 Ma. It forms part of the break-up of the Rodinia supercontinent that initiated the deposition of the Katanga Supergroup in a continental rift (Hanson et al. 1994). A second rifting stage took place between ca. 750 and 720 Ma which led to the formation of an oceanic basin in the Zambezi Belt (Key et al. 2001). An inversion of the tectonic regime is recorded by eclogitic boudins between ca. 660 and 610 Ma (John et al. 2003). Subduction of the Congo craton underneath the Kalahari craton was initiated at ca. 595 Ma (John et al. 2003, 2004). A continental collision that led to the formation of the Lufilian Belt followed this subduction and is characterized by a peak of metamorphism dated at ca. 550 Ma in the internal zone (John et al. 2004; Eglinger et al. 2014b; Turlin et al. 2016). Finally, a post-orogenic exhumation between ca. 510 and 470 Ma led to the exhumation of high-grade metamorphosed rocks (Cosi et al. 1992; John et al. 2004; Eglinger et al. 2014; Turlin et al. 2016).

3 Cu-isotopes analyzed with SIMS

SIMS Cu-isotope analyses were performed for the first time, with a Cameca IMS 1270 E7 and 1280 HR2 at CRPG, Nancy. SIMS analyses were performed by standard bracketing measurements. Chalcopyrite and bornite grains from the Copperbelt were measured by MC-ICP-MS to determine their δ^{65}Cu values relative to NIST 976 The measured values are $\delta^{65}Cu_{ccp}$=-0.721±0.03‰ and $\delta^{65}Cu_{bn}$=-0.376±0.03‰ respectively. These reference materials were analyzed with SIMS each day prior to any sample analysis.

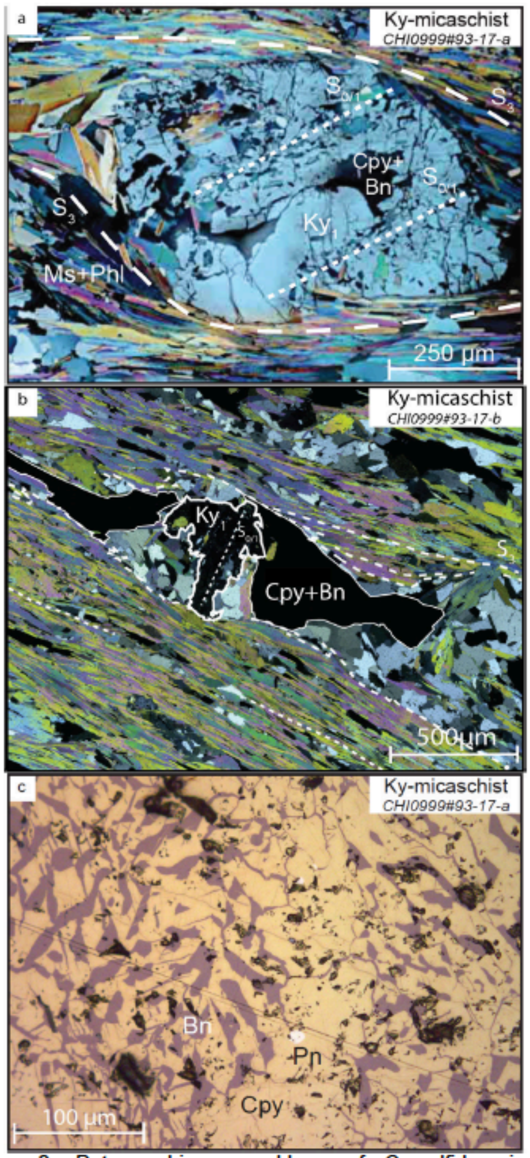

Figure 2. Petrographic assemblage of Cu-sulfides in Ky-micaschists of the Lumwana deposit (WZC). *a.* inclusions of Cu-sulfides in Ky_1=Cu_1. *b.* Cu-sulfides in a pressure shadow around Ky_1=Cu_2. *c.* intergrown bn-cpy characteristic of Cu_2 (after Turlin et al. 2016). Bn: bornite, Cpy: chalcopyrite, Pn: pentlandite.

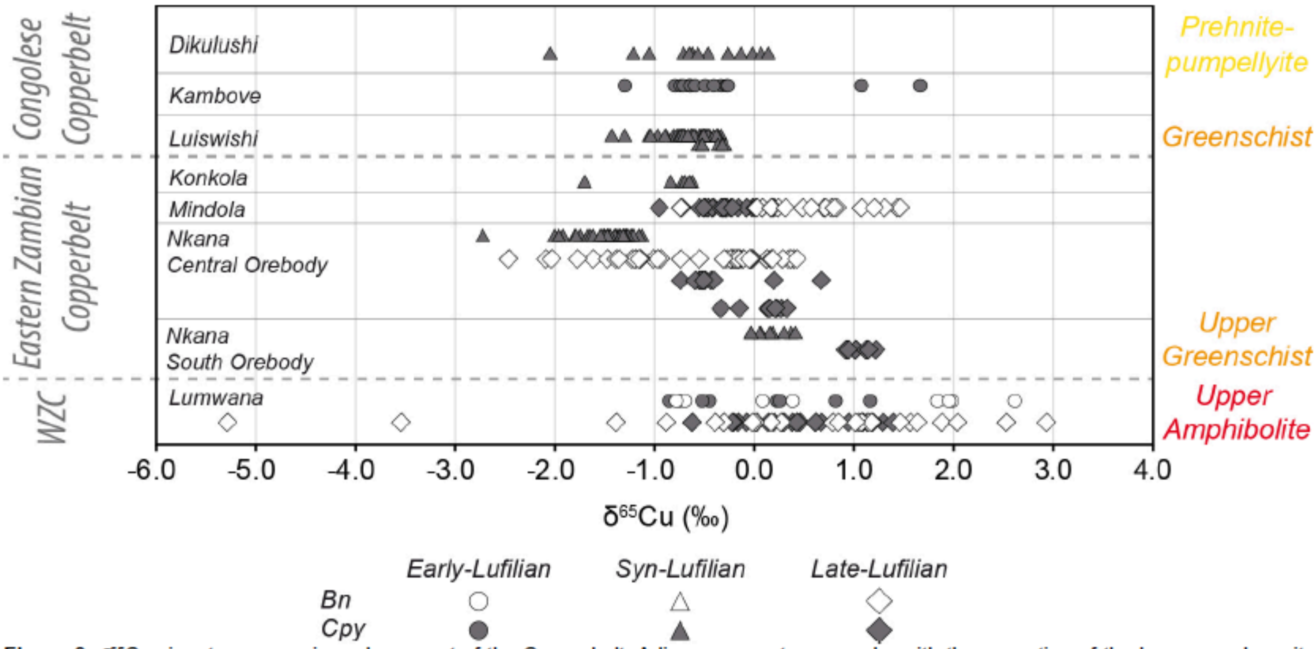

Figure 3. δ^{65}Cu signatures covering a large part of the Copperbelt. A line represents a sample, with the exception of the Lumwana deposit where several samples are combined. Early-Lufilian = late-diagenetic mineralizing stage (ca. 590 Ma); Syn-Lufilian = syn-orogenic mineralizing stage coeval with the regional peak of metamorphism (ca. 580-520 Ma), Late-Lufilian= a late- to post-orogenic stage (ca. 520–490 Ma). See references in the text for details on the sample age.

A primary negative oxygen beam (duoplasmatron) accelerated to 13 keV with an intensty of 10 nA was used for measurments. Secondary ions were measured with a mass resolution (M/ΔM) of 5000 in FC multicollection mode. The measured isotope ratio was converted in delta notation by using the equation:

$$\delta^{65}Cu_{IMF}= [(R_{SIMS}/R_{NIST})- 1]x1000$$

where R_{SIMS} is the $^{65}Cu/^{63}Cu$ ratio measured by SIMS and R_{NIST} is the $^{65}Cu/^{63}Cu$ ratio of NIST976.

The $\delta^{65}Cu_{IMF}$ is then corrected from the instrumental mass fractionation using the equation:

$$\delta^{65}Cu_{sample}= \Delta^{65}Cu_{sample}+(X- \Delta^{65}Cu_{std})$$

where Δ^{65}Cu is equivalent to the $\delta^{65}Cu_{IMF}$ and X is the true δ^{65}Cu of the standard obtain by MC-ICP-MS.

4 Sampling

Samples analyzed with the SIMS come from deposits from the Congolese Copperbelt (Dikulushi, Kambove, and Luiswishi), the Eastern Zambian Copperbelt (Konkola, Mindola and Nkana) and the Western Zambian Copperbelt (Lumwana) (Fig.3). All these samples were taken from previous scientific studies whose ages and mineralization stages were determined based on detailed petrographic and microstructural observations coupled with geochronological analysis. (Haest et al. 2007, 2009a; Brems et al. 2009; El Desouky et al. 2010; Van Langendock et al. 2013; Torremans et al. 2013; Turlin et al., 2016 and references therein) No detailed petrography was carried out in this study.

Statistically, only a few samples from the late diagenetic stage have been analyzed compared to the syn-, late- and post-orogenic stages. The reason why the earliest phases are underrepresented in the samples is due to their lower preservation potential during the Lufilian orogeny.

5 Cu-isotope signatures of the Copperbelt

The pre- and syn-orogenic mineralization stages of the Lumwana deposit present a similar range of Cu isotope values between -1.37±0.23‰ and +2.95±0.19‰, with the exception of a few outliers (Fig. 3).

Deposits from the Congolese and Zambian Copperbelt display δ^{65}Cu values between -2.72±0.10‰ and +2.95±0.19‰ (Fig. 3).

6 Fractionation processes

Based on the similarities in the range of signatures, no distinct metal source could be identified for the multiple mineralization stages of the internal zone of the Copperbelt. The following sections deal with Cu-isotope fractionation processes recorded from grain-scale to regional-scale, as evidenced by the *in-situ* analyses.

6.1 Equilibrium fractionation

In the external zone of the CAC, bornite shows δ^{65}Cu values 1‰ higher than chalcopyrite (e.g. Mindola deposit, Fig. 3). Sample measurements have been standardized to their equivalent standards in order to avoid matrix effects. Accordingly, these differences cannot be attributed to this latter effect.

Such differences are not observed in the Lumwana deposit where analysis of both sulfides yielded similar values (Fig. 3) and where chalcopyrite and bornite show intergrowth textures (Fig. 2c; Turlin et al. 2016). Such textures are not present in deposits from the external zone where both sulfides coexist. Internal processes associated with these textures need to be investigated to understand how they influence fractionation.

6.2 Grain-scale fractionation

The grain-scale fractionation can be as important as the deposit-scale variation, as shown by a Dikulushi sample where Cu isotopes fractionate up to 2‰, i.e. as much as the deposit-scale variation measured by MC-ICP-MS (cf. Haest et al. 2009). Fractionation up to 3‰ has been recorded by a single mm-sized grain from the Nkana Central Orebody amounting to a significant fraction of the observed regional-scale variation of 6‰ (Fig. 3).

These observations demonstrate that processes that affect fractionation at a large scale could also play a significant role at the grain scale.

7 Conclusion

No specific metal source can be attributed to the different mineralization stages recognized at the Lumwana deposit in the Western Zambian Copperbelt.

The *in-situ* Cu-isotope analyses enable to investigate Cu-isotope fractionation between different phases and at different scales showing that there is as much variation in Cu isotopes within a grain as in a deposit.

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