Metal sources for the Katanga Copperbelt deposits (DRC): insights from Sr and Nd isotope ratios.

Jorik VAN WILDERODE¹, Hamdy A. EL DESOUKY², Marlina A. ELBURG³, Frank VANHAECKE⁴ & Philippe MUCHEZ¹

¹ Department of Earth and Environmental Sciences, KU Leuven, Celestijnenlaan 200E, 3001 Leuven, Belgium
² Geology Department, Menoufyia University, Shebin El-Kom, Egypt
³ Discipline of Geological Sciences, SAEES, University of KwaZulu-Natal, Westville Campus Private Bag X54001, 4000 Durban, South-Africa
⁴ Department of Analytical Chemistry, Ghent University, Krijgslaan 281-S12, 9000 Ghent, Belgium

ABSTRACT. The ore deposits of the Central African Copperbelt formed during a multiphase mineralisation process. The basement underlying the Neoproterozoic Katanga Supergroup that hosts the ore, demonstrates the largest potential as metal source. Various ore deposits that formed during different mineralisation phases are taken as case studies, i.e. Kamoto, Luiswishi, Kambove West, Dikulushi and Kipushi (Democratic Republic of Congo, DRC). The Sr and Nd isotopic compositions of gangue carbonates associated with these deposits is determined and compared with those of rocks from several basement units, bordering or underlying the Copperbelt, to infer the metal sources. The mineralising fluid of diagenetic stratiform Cu-Co mineralisation interacted with felsic basement rocks underlying the region. The Co from these deposits is most likely derived from mafic rocks, but this is not observed in the isotopic signatures. Syn-orogenic, stratabound Cu-Co mineralisation resulted mainly from remobilisation of diagenetic sulphides. A limited, renewed contribution of metals from felsic basement rocks might be indicated by the isotope ratios in the western part of the Copperbelt, where the metamorphic grade is the lowest. The mineralising fluid of syn- and post-orogenic, vein-type mineralisations interacted with local mafic rocks, and with felsic basement or siliciclastic host rocks.

KEYWORDS: Sediment-hosted deposits, Vein-type deposits, Central Africa, Copper, Cobalt, Zinc

1. Introduction

The Central African Copperbelt represents a world class metallogenic province at the border between the Democratic Republic of Congo (DRC) and Zambia (Fig. 1). The orebodies are hosted by rocks of the Neoproterozoic Katanga Supergroup, which were deformed during the Luflilian orogeny (~590-530 Ma). Numerous metallogenic studies have investigated the formation of the Copperbelt ore deposits, resulting in syn-sedimentary (e.g. Garlick, 1989), early to late diagenetic (e.g. Bartholomé et al., 1972) and syn-orogenic (e.g. McGowan et al., 2003) models. An historical overview of these models has been presented by Sweeney et al. (1991) and Cailteux et al. (2005). Recently, consensus has been growing towards a multiphase mineralisation process (Selley et al., 2005; Dewaele et al., 2006; El Desouky et al., 2010; Haest & Muchez, 2011). Ore formation started with an early to intermediate diagenetic stratiform Cu-Co phase, followed by metamorphic and syn-orogenic stratabound Cu-Co mineralisation (El Desouky et al., 2010). Late to post-orogenic ore formation resulted in vein-type Cu-Zn deposits (Haest et al., 2007; Heijlen et al., 2008). Supergene remobilisation constitutes a last mineralisation phase (Decrée et al., 2010; De Putter et al., 2010). Selley et al. (2005), Kampunzu et al. (2009) and Haest & Muchez (2011) summarize the current knowledge for some of the most important ore deposits. This study addresses the possible interaction of mineralising fluids with basement units and rocks of the Katanga Supergroup to infer the most likely metal source. This is done by comparing the Sr and Nd isotopic composition of various host and basement rocks with those of gangue carbonates associated with the ore deposits (e.g. Walshaw et al., 2006).

2. Geological setting

2.1 General

The Neoproterozoic Katanga Supergroup is subdivided into the Roan, Nguba and Kundelungu Groups, and was deposited after emplacement, exhumation and erosion of the Nchanga granite...
Table 1. Lithostratigraphy of the Katanga Supergroup in the DRC. S.D.B.: Shales Dolomitiques de Base; R.S.C.: Roches Siliceuse Cellulaire; R.S.F.: Roche Siliceuse Feuilletée; D. Strat.: Dolomie Stratifée (after François, 1974; Calleux et al., 1994, 2005; Batumike et al., 2007; Kampunzu et al., 2009).

<table>
<thead>
<tr>
<th>Group</th>
<th>Subgroup</th>
<th>Formation</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bianco - R 1</td>
<td></td>
<td>calcareous dolomite</td>
<td></td>
</tr>
<tr>
<td>Ngulu (formerly Lower Tekenge) - Ng 1</td>
<td></td>
<td>dolomite with dolomitic siltstones and shales</td>
<td></td>
</tr>
<tr>
<td>Kansuki - R 2.2</td>
<td></td>
<td>dolomite at the base and dolomitic siltstones</td>
<td></td>
</tr>
<tr>
<td>Kanianga - R 2.2.1 &amp; 2.2.2</td>
<td></td>
<td>dolomitic siltstones (&quot;Roches Gréso-Schisteuses&quot;)</td>
<td></td>
</tr>
<tr>
<td>Kaponda - R 2.2.3</td>
<td></td>
<td>dolomite at the top and dolomitic siltstones</td>
<td></td>
</tr>
<tr>
<td>Kamoya dolomie Tigrée at the base</td>
<td></td>
<td>dolomite</td>
<td></td>
</tr>
<tr>
<td>Mofya - R 3.3</td>
<td></td>
<td>massive siltstones</td>
<td></td>
</tr>
<tr>
<td>Lusele</td>
<td></td>
<td>massive, laminated, shaly or talcose dolomites;</td>
<td></td>
</tr>
<tr>
<td>Mwashya; Cailteux et al., 2007)</td>
<td></td>
<td>dolomite (R.S.C.), silicified/arene dolomite</td>
<td></td>
</tr>
<tr>
<td>Hapetwe - R 3</td>
<td></td>
<td>chloritized dolomites</td>
<td></td>
</tr>
<tr>
<td>Katete</td>
<td></td>
<td>massive siltstones</td>
<td></td>
</tr>
<tr>
<td>Mwale and Kyandamu Formations, mark the</td>
<td></td>
<td>massive, laminated, shaly or talcose dolomites;</td>
<td></td>
</tr>
<tr>
<td>base of the Nguba and Kundelungu Groups, respectively (Table</td>
<td></td>
<td>chloritized dolomites</td>
<td></td>
</tr>
<tr>
<td>1). They have been correlated with the Sturtian and Marinoan</td>
<td></td>
<td>chloritized dolomites</td>
<td></td>
</tr>
<tr>
<td>glacial events (Batumike et al., 2006, 2007). Volcaniclastic</td>
<td></td>
<td>chloritized dolomites</td>
<td></td>
</tr>
<tr>
<td>rocks of the Kansuki Formation (previously known as Lower</td>
<td></td>
<td>chloritized dolomites</td>
<td></td>
</tr>
<tr>
<td>Mwashya; Cailteux et al., 1994, 2005; Batumike et al.,</td>
<td></td>
<td>chloritized dolomites</td>
<td></td>
</tr>
<tr>
<td>Kampunzu et al., 2009).</td>
<td></td>
<td>chloritized dolomites</td>
<td></td>
</tr>
</tbody>
</table>

(883 ± 10 Ma; Armstrong et al., 2005). Two regional conglomerate occurrences, the Mwale and Kyandamu Formations, mark the base of the Nguba and Kundelungu Groups, respectively (Table 1). They have been correlated with the Sturtian and Marinoan glacial events (Batumike et al., 2006, 2007). Volcaniclastic rocks of the Kansuki Formation (previously known as Lower Mwashya; Calleux et al., 2007) occur in the upper part of the underlying Roan Group. The classical stratigraphy adopted here was challenged by Wendorf (2000, 2005), however, this discussion falls outside the scope of the current study.

The Lufilian orogeny gave rise to the "Lufilian Arc" and a northern foreland known as the Kundelungu Plateau. The former is a convex belt with a total width of ~150 km and stretches for ~450 km from NW to SE. Within the arc, ore deposits are found in the external fold-and-thrust belt (DRC and Zambia), and in the adjacent Domes region (Zambia). Despite many studies (e.g. Porada, 1989; Costi et al., 1992; Kampunzu & Calleux, 1999; Jackson et al., 2003), the timing and mode of deformation remains an important discussion. Nevertheless, early and peak metamorphism can be set at ~590 Ma (Rainaud et al., 2005) and ~530 Ma (John et al., 2004; Rainaud et al., 2005), respectively. The main deformation period likely started around 560 Ma, which is the age of syn-orogenic granites (Hanson et al., 1993; Porada & Berhorst, 2000). However, Lufilian deformation probably did not affect the Kundelungu plateau before 525 Ma (Hæst et al., 2009). The Lufilian orogen is surrounded by the Kibara Belt in the NW, the Bangweulu Block in the NE and the Irumide Belt in the East (Fig. 2). The Kibara orogen was active between ~1.4-1.38 Ga (accretionary stage) and ~1.0-0.95 Ga (continental collision; Kokonyangi et al., 2006). The oldest of four meta-sedimentary groups comprising the Kibara Supergroup was affected by arc-related cale-alkaline and peraluminous magmatism at 1.38 Ga (Kokonyangi et al., 2006; Tack et al., 2010). Late to post-orogenic granites and pegmatites, formed after 1.0 Ga, host Sn and W deposits (Kokonyangi et al., 2006; Tack et al., 2010; Dewaele et al., 2011). The apparent northern continuation of the Kibara Belt was previously known as the North-Eastern Kibara Belt, but was redefined by Tack et al. (2010) as the Karagwe-Ankole Belt. The Palaeoproterozoic Bangweulu Block contains a granitoid basement and a cover of mainly fluvial, aeolian and lacustrine sediments (Anderson & Unrug, 1984). De Waele et al. (2006) recognised four main igneous phases in the Irumide Belt and interpreted this belt as the repeatedly destabilised southern boundary of the Bangweulu Block. The destabilisation occurred at 2.0, 1.85, 1.6 and 1.0 Ga. The meta-sedimentary cover consists of alternating quartzites and pelites (De Waele & Mapani, 2002; De Waele & Fitzsimons, 2007). Within the Lufilian Arc, basement is cropping out in the Domes Region and was dated at 1.88 Ga (Ngoyi et al., 1991). Taking into account regional age data, Ngoyi et al. (1991), Ngoyi & Degonghe (1995) and De Waele et al. (2006) consider the doming basement to be part of a Bangweulu Metacraton. This Bangweulu Metacraton acted as a basement to the Lufilian Belt and underlies the largest part of the Copperbelt (De Waele et al., 2006). 2.2 The Kamoto, Luvisiwi and Kambove deposits The Kamoto Cu-Co deposit is part of the Kolwezi megabreccia klippe, located in the north-western part of the Copperbelt (Fig. 1). It presumably represents a remnant of a thrust sheet and contains faulted blocks forming isoclinal folds (François, 1974). The Kambove West Cu-Co mineralisation occurs in the central part of the Copperbelt (Fig. 1) within a north-verging syncline (Cailleux, 1983). The Luvisiwi Cu-Co deposit is situated in the eastern part of the Congolese Copperbelt (Fig. 1) and occurs in a fractured, north-verging isoclinal synform (Cailleux et al., 2003). The main mineralisation at these deposits is hosted by the lower parts of the Kamoto and Dolomite Shales Formations (Table 1; Cailleux et al., 2005). The Lower and Upper Orebodies are separated by the
generally barren R.S.C. Member (Roche Siliceuses Cellulaires), a massive silicified stromatolitic dolomite.

The first stratiform hydrothermal Cu-Co mineralisation phase at Kamoto, Luwiswishi and Kambove West produced fine- to medium-grained sulphides that occur disseminated, within small nodules and in thin, discontinuous layers (Muczeh et al., 2008; Van Langendonck et al., 2013). Mineralisation took place during diagenesis of the host rocks from a moderate saline fluid (20-25 wt.% NaCl equiv.) at a temperature between 115 and 220°C (El Desouky et al., 2009). The R.S.C. member might have acted as a conduit for this mineralising fluid (Fay & Barton, 2012; Muczeh & Corbella, 2012). Sulphides display δ34S values between -10.3 and +3.1 ‰ V-CDT, corresponding to a fractionation of 14.4 to 27.8 ‰ from Neoproterozoic seawater sulphate (Muczeh et al., 2008). Such large fractionation suggests bacterial mediated sulphate reduction (BSR).

The second Cu-Co mineralisation phase at Kamoto, Luwiswishi and Kambove West took place during the Lufilian Orogeny. It formed coarse-grained sulphide minerals in veins, breccia cements and nodules with varying shapes (El Desouky et al., 2010; Van Langendonck et al., 2013). The mineralising fluid was highly saline (35-45.5 wt.% NaCl equiv.) and hot (270-385°C; El Desouky et al., 2009). Most δ34S values range from -13.1 to +5.2 ‰ V-CDT, comparable to the δ34S signature of the first mineralisation phase. A few sulphides display higher δ34S values between +18.6 and +21.0 ‰ V-CDT (El Desouky et al., 2010). As BSR is not possible at the high temperature of the second mineralisation phase, the former range indicates remobilisation of sulphur from first phase sulphides. The latter range resembles the marine seawater δ34S signature between 840 Ma and the Sturtian Glaciation around ~700 Ma (+17.5 to +19.0 ‰ V-CDT; Veizer et al., 2009). Such large fractionation suggests bacterial mediated sulphate reduction (BSR).

2.3 The Dikulushi and Kipushi deposits

The Dikulushi Cu-Ag mineralisation is a vein-type deposit found about 200 km north of the Copperbelt in the foreland of the Luflilian orogen (Fig. 2). The host rocks belong to the Lubudi and Mongwe Formations (Table 1; Cailete et al., 2005). A syn-orogenic, moderately saline (20-25 wt.% NaCl equiv.) and warm (90-140°C) fluid precipitated Cu-Pb-Zn-Fe ore in a zone of crosscutting east and north-east oriented faults (Haest et al., 2009b). A post-orogenic, saline (>20 wt.% NaCl equiv.) and low temperature (<90°C) fluid subsequently remobilised ore metals and NaCl from north-eastern oriented faults and caused Cu-Ag mineralisation after mixing with a low saline (<3 wt.% NaCl equiv.) fluid. This event may have occurred only ca. 100 Ma ago (Haest et al., 2009b). δ34S values for sulphides of the first and second mineralisation phase are similar, i.e. +11.3 to +14.1 ‰ and +10.0 to +13.5 ‰ V-CDT, respectively (Haest et al., 2009b). This indicates TSR for the former and remobilisation of first phase sulphides at a low temperature during the second mineralisation phase.

The Kipushi vein-type Cu-Zn deposit is positioned in the south-eastern part of the Katanga Copperbelt (Fig. 1) within the northern flank of a NW-SE trending anticline. The anticlinal core consists of a megabrecia of Roan Group rocks known as the Axial Breccia (De Magnée & François, 1988). The pipe-like ore-body crosscuts rocks of the Kakontwe, Kipushi and Katete Formations (Table 1; Batumike et al., 2007), and was dated at 455.0 ± 3.4 Ma (Schneider et al., 2007). The main mineralisation phase formed from a highly saline (30-43 wt.% NaCl equiv.) and hot (287-331°C) fluid (Chabu, 1995; Heijlen et al., 2008). A fluid of lower salinity (~23-31 wt% NaCl equiv.) and temperature (~170°C) caused a minor secondary mineralisation phase (Heijlen et al., 2008). δ34S signatures of the ore-body demonstrate that the major part of the sulphides was derived from seawater sulphate through TSR (up to +19.2 ‰ V-CDT), while a small part was inherited from BSR (down to -2.6 ‰ V-CDT; Dechow & Jensen, 1965).

3. Possible metal sources

A magmatic-hydrothermal metal source for the Copperbelt deposits was favoured by early workers (e.g. Bateman, 1930), but refuted by the presence of unconformable sediment-granite contacts (Garlick & Brummer, 1951) and granite dating (e.g. Armstrong et al., 2005). Oxidised silicilastic sediments or red beds of the R.A.T. Subgroup (Roan Group) formed in an early rift basin and underlie the mineralised strata (Table 1; Kampunzu et al., 2000). This configuration mimics other important sediment-hosted stratiform Cu provinces, like the Permian basin of Central Europe (e.g. Hitzman et al., 2000). Red beds contain feldspars, micas absorbed on an adjacent and other detrital mafic minerals, providing an excellent source for ore metals (e.g. Brown, 1984; Schuh et al., 2012). However, Hitzman (2000) assessed the volume of red beds underlying or lateral to the Zambian Copperbelt, and found a deficiency in red bed volume to account for the known mineralisations. Similarly, Cailteux et al. (2005) calculated that at least 100 times the volume of footwall sedimentary rocks in the Lufilian arc is required to provide sufficient amounts of copper. Several authors mentioned the possibility of a metal contribution from a larger part of the local stratigraphy (e.g. De Magnée & Francois, 1988; Lefebvre, 1989), although Selley et al. (2005) considered it rather unlikely due to an insufficient sediment rock volume. Hitzman (2000) argued in favour of significant tectonic displacement of the ore-bearing strata from a south-western source basin. However, structurally conformable contacts both within the Katanga Supergroup and between basement and basin strata do not concur with such displacement (Koziy et al., 2009).

Unlike other possibilities, the basement provides great potential as a metal source (e.g. Sweeney et al., 1991; Sweeney & Binda, 1994; Roberts et al., 2009). Metal sulphide occurrences are reported within the basement at Samba, Lumwana, Mkushi and elsewhere (e.g. Schneiderhöhn, 1937; Pienaar, 1961; Omenetto, 1973; Whyte and Green, 1971; Wakefield, 1978; Sweeney et al., 1991; Bernau et al., 2013). For the cases where they underlie sediment-hosted orebodies, Whyte and Green (1971) suggested that these occurrences might be the result of downward migration of metals into the basement. The basement-hosted mineralisations are mostly found close to the basin unconformity of the Katanga Supergroup and contain similar gangue assemblages as found in sediment-hosted deposits. Therefore, Selley et al. (2005) considered them a correlative rather than a possible source to the sediment-hosted deposits. Even so, a high Cu and Co content is found in basement granitoids even when no sulphides are present. Sweeney et al. (1991) listed recorded metal concentrations of several hundred ppm of Cu and Co in basement rocks, reviewing data from amongst others Pienaar (1961), Mendelsohn (1961) and Garlick (1973). These rocks might be source rocks, since numerical modelling for the Zambian Copperbelt shows that buoyancy-driven fluid flow across the basin-basement contact is very well possible, even with a low-permeable basement and without the presence of major vertical fault systems (Koziy et al., 2009).

The potential of the basement is supported by the co-variation of the Pb isotopic composition of Cu and Co-sulphides from various mineralisations and basement schists and granites underlying those various deposits (Carr et al., 1987). The same authors and Richards et al. (1988) used Pb isotopic compositions to demonstrate that mantle-derived basement rocks were no metal source to the stratiform deposits. Kamona et al. (1999) argues in favour of a mantle component for the Kipushi vein-type Cu-Zn deposit. However, this is refuted by Schneider et al. (2007), who confirm a crustal reservoir for the Kipushi Cu-Ag deposit, based upon Pb isotopic signatures and initial 87Sr/86Sr and 187Os/188Os ratios. Implicit in these studies is the assumption that both Pb and other ore metals originated from the same source. Furthermore, taking into account the high mobility of Pb and U, the Pb isotopic signatures should be interpreted with caution (e.g. Decrée et al., 2011).

Despite the apparent granitic association (Carr et al., 1987) and the paucity of mafic rocks in the area, the high Co grades in the stratiform ores are thought to originate from a mafic source rock (e.g. Annels et al., 1983; Annels & Simmonds, 1984; Unrug, 1988; Annels, 1989). Starting from a basement with 20 percent mafic and 80 percent felsic rocks, Koziy et al. (2009) model that only 40 percent of the Cu in the basement rocks affected by a high water-rock ratio needs to be leached to account for the Zambian ore deposits. Hence, the volume of source rocks
Table 2. Rb-Sr results with recalculation of the isotopic compositions at 816, 590, 525 and 451 Ma. 1: no age correction applied because of extreme Sr/Rb ratios of these pure carbonates; Dol: dolomite; Cal: calcite; Nod: nodules; Sbrg: Subgroup; Fm: Formation; Volc: volcanic; unk: unknown; na: not applicable (partly from Muchez et al., 2008; Haest et al., 2009b; Eliou, 2009; Van Wilderode et al., 2013).
4. Methodology

4.1 Strontium isotopic analysis

Carbonate powders (100 mg) from barren rocks and gangue minerals of the Kambove mineralisation were digested on a hot plate in 6 M HCl. Sr was isolated using Eichrom Sr Spec resin according to the procedure of De Muynck et al. (2009). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined using a Thermo Scientific NEPTUNE multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, UGent) and normalised to the invariant $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. Repeated analyses of the NIST SRM 987 isotopic reference material during the measurements yielded an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71030 ± 0.00008 (2s, n=41), in agreement with the accepted $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71025 ± 0.00001 (Thirlwall, 1991). Two procedural blanks showed insignificant intensities compared to standard and sample solutions (< 0.1 %). Errors on the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio are below 2%. Rb and Sr concentrations were determined using a Perkin-Elmer SCIEX ELAN 5000 quadrupole-based ICP-MS instrument. Rb-Sr data for the Kamoto and Luiswishi deposits were reported by Muchez et al. (2008) and El Desouky et al. (2010), for the Dikulushi deposit by Haest et al. (2009b), and for Kipushi by Van Wilderode et al. (2013).

Figure 3. εNd vs $^{87}\text{Sr}/^{86}\text{Sr}$ diagrams at relevant ages with reference to different basement units. Basement data are grouped according to rock type. Data of Duchesne et al. (n=12; 2004) for the Karagwe-Ankole Belt (K.-A.; formerly North-Eastern Kibara Belt) are shown in the same diagrams as data for the Kibara Belt (n=23) and data from De Waele et al. (n=19; 2006) are combined with own results for the Irumide Belt (n=10) and Bangweulu Block (n=14). For the Domes Region, n=19. 2s-errorbars, obtained via error propagation, are not drawn when smaller than sample symbols.
4.2 Neodymium isotopic analysis

About 100 mg of carbonate powder was dissolved in 6 M HCl on a hotplate at 120°C. The evaporated residue was taken up into 2 M HNO₃, Nd was isolated using two columns containing Eichrom TRU Spec and Ln Spec resins according to procedures developed by Pin et al. (1994) and Gano et al. (2012). The Nd isotopic composition was determined using a Thermo Scientific NEPTUNE MC-ICP-MS instrument (UGent) operated in static multi-collection mode. All Nd isotope ratios were normalised into 2 M HNO₃. Nd was isolated using two columns containing Eichrom TRU Spec and Ln Spec resins according to procedures developed by Pin et al. (1994) and Ganio et al. (2012). The Nd isotope ratio of 0.51211 ± 0.00001 (2s, n = 40), in agreement with the accepted ratio of 0.512115 ± 0.000007 (Tanaka et al., 2000). Two procedural blanks revealed insignificant intensities compared to standard and sample solutions (< 0.1 %). Errors on the $^{143}$Nd/$^{144}$Nd ratio of 0.51211 ± 0.00001 (2s, n = 40), in agreement with the accepted ratio of 0.512115 ± 0.000007 (Tanaka et al., 2000).

5. Results

5.1 Strontium isotopic analysis

Regarding the stratiform Cu-Co deposits of Kamoto and Luimushwi, the gangue carbonates of the diagenetic mineralisation phase show $^{87}$Sr/$^{86}$Sr ratios at 816 Ma between 0.70894 ± 0.00012 and 0.73467 ± 0.00004 (n=17; Table 2; Fig. 3, 4). The isotope ratios of all diagenetic gangue carbonates are more radiogenic than the Sr isotopic composition of Neoproterozoic marine carbonates (0.7150 < $^{87}$Sr/$^{86}$Sr < 0.73467 ± 0.00004 (n=17; Table 2; Fig. 3, 4). The distinctly high Sr isotopic composition of the Kamoto and Luimushwi deposits have varying Sr isotopic compositions (Fig. 3, at 816 Ma). The distinctly high Sr isotopic compositions (Fig. 3, at 816 Ma). The distinctly high Sr isotopic compositions (Fig. 3, at 816 Ma). The distinctly high Sr isotopic compositions (Fig. 3, at 816 Ma). The distinctly high Sr isotopic compositions (Fig. 3, at 816 Ma). The distinctly high Sr isotopic compositions (Fig. 3, at 816 Ma).

5.2 Neodymium isotopic analysis

For the stratiform Cu-Co deposits, $^{143}$Nd/$^{144}$Nd ratios of diagenetic dolomites lie between 0.51066 and 0.51133 at 816 Ma, corresponding to εNd values between -18.2 ± 2.3 and -8.9 ± 2.2 (n=6; Table 3; Fig. 3). Syn-orogenic dolomites show $^{143}$Nd/$^{144}$Nd signatures ranging from 0.51126 to 0.51163 at 525 Ma (n=16), or εNd values from -13.7 ± 2.4 to -6.4 ± 1.5. Syn-orogenic $^{143}$Nd/$^{144}$Nd ratios for gangue minerals of the vein-type mineralisation at Dikulushi are between 0.51149 and 0.51179 at 525 Ma (n=6), equivalent to εNd between -9.2 ± 1.2 and -3.4 ± 1.3. Post-orogenic gangue minerals at Kipushi have $^{143}$Nd/$^{144}$Nd ratios between 0.51176 and 0.51201 at 451 Ma (n=9), or εNd between -5.9 ± 1.1 and -0.9 ± 1.4. Table 3 also shows results for barren rocks of the Mines Subgroup (n=6), Dipeta Subgroup (n=1), Mwashya Subgroup (n=3) and Gombe Subgroup (n=4).

6. Discussion

6.1 Diagenetic mineralisation phase

Fig. 3 presents the isotope ratio data in εNd vs $^{87}$Sr/$^{86}$Sr diagrams, with the gangue carbonates plotted at relevant ages and in comparison with the host rocks and different basement units. The basement dataset (unpublished) is divided into fields of felsic igneous, mafic igneous and (meta)-sedimentary rocks. The diagenetic gangue minerals are plotted at 816 Ma (Fig. 3). 816 ± 62 Ma is a six-point Re–Os isochron age obtained from chalcopyrite of the Konkola deposit (Barra & Broughton, in Selley et al., 2005). This is the oldest published age for the Cu–Co ore deposits in the Copperbelt and in agreement with a diagenetic origin (Selley et al., 2005). In addition, unpublished detrital zircon studies suggest formation of the host rocks between 840 and 790 Ma (Selley, in Hitzman et al., 2010). The diagenetic gangue carbonates of the Kamoto and Luimushwi deposits have varying isotopic compositions (Fig. 3, at 816 Ma). The distinctly high radiogenic Sr values ($^{87}$Sr/$^{86}$Sr > 0.73) of two Kamoto samples are reliable, since they contain comparably low Rb concentrations like the less radiogenic samples (i.e. less than 1 ppm; Table 2). The gangue carbonates cannot simply be correlated with a single basement unit, although the Domal Region might represent a best average composition. They do show a typical felsic signature regarding their generally low εNd values. This supports the interpretation of Mucchuz et al. (2011) that the mineralising fluids interacted significantly with felsic basement rocks or sedimentary rocks derived from it. According to Haest & Muchez (2011), the compositional variation of such rocks and incomplete mixing of the fluids might have caused the variable Pb isotopic signatures measured in ore sulphides. Similar processes might be invoked for the variable Nd and Sr isotopic composition of the gangue carbonates. Such interaction with felsic rocks can account for the leaching and enrichment of Cu, however, it is not expected to give rise to the high Co content of the deposits. Co is most likely derived from mafic rocks (e.g. Annels & Simmonds, 1984). The isotopic signature might have been partly overprinted, although a single εNd value of -8.9 ± 2.2 for a sample from Kamoto might point to a metal contribution of mafic basement material.
Alternatively, anomalous Ho Co concentrations have been reported in some felsic basement rocks, e.g. 1000 ppm in Lufubu Schists in the Nchanga region (Mackenzie-Brown, in Sweeney et al., 1991). Host rocks of the Mines Subgroup have low radiogenic Sr isotopic compositions ([Sr] /[Sr] versus [Sr] versus [Sr] diagram). However, the isotopic signature of syn-orogenic gangue carbonates from Kambove West, both diagenetic and syn-metamorphism at ~590 Ma (U-Pb age; Rainaud et al., 2005), and therefore plotted at the onset of the orogeny during eclogite facies metamorphism (Fig. 3). This is impossible at the high temperatures of the syn-orogenic mineralisation phase and must be the result of remobilisation event throughout the Katanga Copperbelt. The good agreement of isotopic signatures from western Kamoto, both diagenetic and syn-orogenic gangue carbonates from Kambove West, which partly formed by bacterial sulphate reduction (El Desouky et al., 2009). This is impossible at the high temperatures of the syn-orogenic mineralisation phase and must be the result of remobilisation event throughout the Katanga Copperbelt. The good agreement of isotopic signatures from western Kamoto, both diagenetic and syn-orogenic gangue carbonates from Kambove West, which partly formed by bacterial sulphate reduction (El Desouky et al., 2009). This is impossible at the high temperatures of the syn-orogenic mineralisation phase and must be the result of remobilisation event throughout the Katanga Copperbelt.

### 2.4 Syn-orogenic mineralisation phase

The age and duration of the Luflilian orogeny, as well as the structural style of deformation are highly debated. The data are therefore plotted at the onset of the orogeny during eclogite facies metamorphism at ~590 Ma (U-Pb age; Rainaud et al., 2005), and late in the orogenic evolution around 523 Ma, when deformation could have reached Dikulushi in the foreland (Haert et al., 2009b; Fig. 3). During this period, the isotopic signature of syn-orogenic gangue carbonates from Kambove West, both diagenetic and syn-orogenic gangue carbonates from Luflishi, and the host rocks of the Mines Subgroup cluster together. The diagenetic carbonates from Kamoto also plot in that cluster, except for two samples with very radiogenic Sr isotopic signatures. The fact that both samples have εNd values similar to the cluster and that comparable low Sr concentrations are observed in an εNd versus 1/Sr diagram (Fig. 4), probably indicates that they represent a remobilisation of diagenetic ore sulphides and strong interaction of the mineralising fluid with the host rocks during syn-orogenic mineralisation. Pitcairn et al. (2006) demonstrated the capacity of metamorphic fluids to mobilise metals. The importance of ore and/or iron sulphide remobilisation is supported by sulphur isotope ratios for Kamoto and Luflishi, which partly formed by bacterial sulphate reduction (El Desouky et al., 2009). This is impossible at the high temperatures of the syn-orogenic mineralisation phase and must be the result of remobilisation event throughout the Katanga Copperbelt. The good agreement of isotopic signatures from western Kamoto, both diagenetic and syn-orogenic gangue carbonates from Kambove West, which partly formed by bacterial sulphate reduction (El Desouky et al., 2009). This is impossible at the high temperatures of the syn-orogenic mineralisation phase and must be the result of remobilisation event throughout the Katanga Copperbelt. The good agreement of isotopic signatures from western Kamoto, both diagenetic and syn-orogenic gangue carbonates from Kambove West, which partly formed by bacterial sulphate reduction (El Desouky et al., 2009). This is impossible at the high temperatures of the syn-orogenic mineralisation phase and must be the result of remobilisation event throughout the Katanga Copperbelt.
Syn-orogenic vein-type Cu-Pb-Zn-Fe mineralisation occurred at Dikulushi around 525 Ma. The gangue minerals have a homogenous Sr isotopic composition (0.71270 ± 0.00001<sup>87</sup>Sr/86<sup>87</sup>Sr < 0.71533 ± 0.00002), while the εNd values vary between -9.2 ± 1.2 and -3.4 ± 1.3. Four samples from the Gombela Subgroup host rocks plot at the lower end of this Nd isotopic trend, whereas the higher end has a typical mafic composition like the basic rocks from the Karagwe-Ankole Belt. In addition, two samples from mafic Mwashya volcanic rocks plot at the extension of the trend. The isotopic signatures of the gangue carbonates therefore possibly lie on a mixing line resulting from interaction of the mineralising fluid with the local host rocks and mafic rocks from the Mwashya volcanic series or similar mafic suites. Within the Dikulushi mine, Haest et al. (2007) described basalt fragments in a breccia at a fault zone. These local basaltic and siliciclastic host rocks are a viable influence on the isotopic signature of the mineralising fluid, rather than a distant basement. Whether they were also able to provide the ore metal budget for the mineralisation is uncertain. However, Haest et al. (2010) inferred from Pb isotope ratio data that the Pb content of this mineralisation phase was mobilised from local and isotopically inhomogeneous clastic reservoirs.

### 6.3 Post-orogenic mineralisation phase

The gangue carbonates of the Kipushi Cu-Zn deposit have radiogenic 87Sr/86Sr ratios, which may be derived from local phyllosilicate-rich stratigraphic layers (Van Wilderode et al., 2013). They plot at high εNd values, resulting in isotopic signatures corresponding to the mafic Mwashya volcanics and to mafic rocks from the Karagwe-Ankole Belt (Fig. 3). The Sr concentration of the former is much lower than found in the gangue carbonates (outside the range of Fig. 4), however, this could also be due to post-depositional processes. The Sr concentration of the latter was high enough to supply the Sr in the mineralising fluid (Fig. 4). Given the large distance of the Karagwe-Ankole Belt to Kipushi, its mafic rocks most likely did not contribute metals to the deposit, but they serve as a good indication that a similar mafic source rock may have provided the ore metals. The slabs of gabbro found in the axial breccia (De Magnée & François et al., 1988) might be the required mafic source. However, Heijlen et al. (2008) measured high Ba, Fe, Zn and Pb to Na ratios in fluid inclusions and suggested a felsic basement as source rock. The mineralising fluid therefore must have interacted with both unidentified felsic basement rocks and mafic rocks occurring within the axial breccia (Van Wilderode et al., 2013). Whether the mafic rocks only altered the isotopic composition or also contributed metals to the fluid is uncertain.

Post-orogenic mineralisation at Dikulushi resulted in a Cu-Ag deposit. Pb isotope ratio systematics indicate that possibly around 100 Ma, both radiogenic Pb derived from local host rocks, and remobilised, less radiogenic Pb from the syn-orogenic ore went into the sulphides of the Cu-Ag deposit (Haest et al., 2010). Furthermore, the U-Th-Pb systems of the basalts occurring in the Dikulushi mine are disturbed at the same time, possibly meaning that they acted as additional sources of Cu and Ag (Haest et al., 2010). Two samples of gangue carbonates, predating but possibly associated with the Cu-Ag mineralisation (cal 3; Haest et al., 2009a), have very different εNd values at 100 Ma, i.e. -6.6 ± 1.2 and -15.3 ± 1.3 (not shown; Table 3). These signatures are similar to those of the syn-orogenic gangue minerals and the Gombela Subgroup host rocks at 100 Ma, respectively. This provides additional evidence for both remobilisation of precursor ore and interaction with the local host rock.

### 7. Conclusion

The basement beneath the Central African Copperbelt forms the most viable metal source for the numerous ore deposits in the region. Gangue carbonates of the diagenetic stratiform Cu-Co mineralisation phase show variable Sr and Nd isotopic compositions, but match best with felsic basement rocks, as exposed in the Domes Region. The origin of Co, which is typically derived from mafic rocks, remains uncertain. Homogeneous radiogenic isotope ratios, sulphur isotope ratios and the similar ore mineralogy indicate that the syn-orogenic mineralisation phase resulted from remobilisation of diagenetic sulphides. Few samples from the syn-orogenic phase at Kamoto have somewhat deviating isotopic signatures. This might point to additional, renewed input from felsic basement rocks. The higher metamorphic grade and resulting more pervasive remobilisation might mask this contribution in deposits lying in the central and eastern parts of the Katanga Copperbelt. The Sr and Nd isotopic composition of gangue minerals of the syn-orogenic, vein-type Cu-Pb-Zn-Fe mineralisation at Dikulushi lie on a mixing line between the isotopic signatures of the Gombela Subgroup host rocks and typical mafic rocks. The basaltic rocks occurring within the Dikulushi mine most likely represent the latter. Also Pb isotopic analyses indicated that these basalts acted as metal source (Haest et al., 2010). The mineralising fluid of the post-orogenic Cu-Zn deposit at Kipushi interacted with mafic rocks, most likely the gabbros occurring nearby. However, high Ba, Fe, Zn and Pb to Na ratios in fluid inclusions convincingly point towards a felsic metal source (Heijlen et al., 2008). Whether the gabbros contributed metals to the fluid or merely altered its isotopic signature is unclear.

### 8. Acknowledgements

The Royal Museum for Central Africa (RMCA, Tervuren) is thanked for permission to study the collections of P. Antun (Kipushi) and A. François and P. Antun (Katanga stratigraphy). Forrest International Group (F.I.G.) and Compagnie Minière du Sud Katanga (C.M.S.K.) allowed investigation of the Luisiwhishi samples and prof. dr. Eric Pirard (University of Liège, Belgium) provided samples of the Kamoto deposit. Sampling of the Kambove and Dikulushi deposits was permitted by the Société de Géocimines and Anvil Mining Congo, respectively. We are grateful to K. Latrue for technical assistance during MC-ICP-MS measurements. This research is financially supported by Agency for Innovation by Science and Technology (IWT), research grant ZKC2784-00-W01, and Research Foundation - Flanders (FWO), research grants G.0414.08 and G.0578.11N.

### 9. References


Kamoto, Katanga Copperbelt (Democratic Republic of Congo - DRC). Geologica Belgica, 16, 76-83.


Sweeney, M.A. & Binda, P.L., 1989. The role of diagenesis in the formation of the Konioka Cu-Au deposit, one of the oldest known Cu-Au deposits in the world and an indicator of a “snowball event” in Central Africa: Prominent emplacement of bimodal magmatism under extensional regime. Precambrian Research, 180, 63-84.


