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Element mobility in the weathering environment and surface vectors to mineralisation—A case study from the Mashitu South Cu-Co deposit, Katanga, Democratic Republic of Congo



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ABSTRACT

The Cu-Co deposits of the Katangan Copperbelt are affected by a deep chemical weathering regime. Meteoric fluids leached mobile elements from the near-surface environment and have redistributed them further down, forming remobilised supergene Cu deposits at a depth of \sim 30–50 m which are highly economic. The same process has caused residual enrichment of less mobile elements such as Co, forming 'cobalt caps' in the near-surface above such supergene Cu deposits. Elements which are associated with hypogene Cu-Co mineralisation, but which are relatively immobile during supergene alteration, can make effective surface vectors to buried supergene Cu deposits; especially where these deposits have experienced a high degree of leaching and where high regional background Cu concentrations obscure surface Cu anomalies.

This study uses an average-normalisation technique, applied to a large whole-rock-geochemistry database, to assess the variation in geochemistry between different depth intervals at the Mashitu South Cu-Co deposit. Geochemical variation by depth acts as an empirical proxy for element mobility during weathering, with the average concentrations of more mobile elements being depleted in the near surface profile.

Of the major and trace elements which are known to be associated with hypogene mineralisation at Mashitu South, Cu, Ni, S and Zn are depleted in the near-surface environment, whereas Co, Bi, V, Mo, As and Fe experienced residual enrichment due to supergene alteration. Indeed, Bi and V exhibit an even greater degree of residual enrichment than Co, which is known as a surface pathfinder to Cu deposits in Katanga. It is suggested that Bi, V and Co would make effective surface vectors to Katangan Cu-Co deposits that have experienced a high degree of leaching; deposits which may evade detection by exploration solely for Cu surface anomalies. The average-normalisation technique utilised by this study can be used to identify immobile surface vectors to any polymetallic deposit which has been significantly affected by chemical weathering.

1. Introduction

The Mashitu South Cu-Co deposit (referred to as Mashitu Sud in Belgian literature), part of the 'Mashitu Complex' of deposits, lies approximately 25 km east of the city of Kolwezi in the Katanga Province of south-eastern Democratic Republic of Congo (DRC). It is situated within the Katangan Copperbelt, part of the Central African Copperbelt (CAC) (Fig. 1), a metallogenic province that contains ~6% of the world's known Cu reserves and ~48% of the world's known Co reserves (USGS, 2016), with remarkably high average Cu-Co grades relative to other global sources.

The exploitation of Cu-Co deposits in Katanga has, to date, mostly focussed on oxidised, supergene ores (Hitzman et al., 2012) which are economically attractive due to their high average grades, ease of mineral processing and proximity to the surface. Mining of these oxidised ores dates to at least the 4th Century CE (de Maret, 1982, 1986) and artisanal diggings, abundant in the area, have offered an easy guide for colonial and post-colonial era exploration. More recently, regional and local soil geochemical surveys have also met with success in locating Cu-Co deposits, through the targeting of Cu surface anomalies (Chimvinga, pers. comm., 2014). However, many Cu-Co deposits do not exhibit a discernible Cu anomaly at surface when compared to the regionally high background soil Cu concentrations, largely due to intense weathering in the region and high mobility of Cu in the near-surface environment. Soil samples taken from over Mashitu South, for example, have an average Cu concentration of ~ 192 ppm. While this is above the average Cu-in-soil concentration for a regional study carried out by Eurasian Resources Group (ERG) comprising a ~ 300 km² licence area

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Fig. 1. Location map of the Mashitu Complex showing its position within the Katangan Copperbelt and outcrops of Roan Group metasedimentary rocks. After François (1974).

(~94 ppm Cu), it is not significantly above the average for a smaller, ~25 km² portion of this region (~163 ppm Cu) which comprises prospective stratigraphy in which Mashitu South is situated. Indeed, only values of > 720 ppm Cu for the larger, ~300 km² licence area and > 360 ppm Cu for the smaller, ~25 km² prospective stratigraphy portion are statistically indicated to be 'anomalously high', making the ~192 ppm Cu-in-soil-average of Mashitu South easy to overlook as a target for further exploration (Gigler, 2016).

The targeting of Co anomalies is well known as an alternative to targeting Cu as a means of exploration for Cu-Co deposits. In Katanga, Co is frequently associated with Cu mineralisation in stratiform, hypogene deposits, however the two metals are known to decouple during supergene alteration (Gauthier and Deliens, 1999; Decrée et al., 2010; Fay and Barton, 2012). Cobalt is less mobile than Cu in the oxidising environment and remains near the surface residually, or travels a short distance downwards to form remobilised Co-oxide deposits, usually as heterogenite - CoOOH (Decrée et al., 2015). By contrast, Cu tends to leach more efficiently from the oxidised zone, travelling downwards to the water table where it precipitates primarily as malachite $(Cu_2CO_3(OH)_2)$ in voids (De Putter et al., 2010). This results in 'cobalt caps' of 'black earth' which overlie supergene copper deposits (Decrée et al., 2010). Over such deposits, one would expect the Co surface anomaly to be stronger and more easily discernible than the Cu anomaly.

Although Cu and Co are the primary products of mining in the Central African Copperbelt, many deposits are polymetallic, with economic concentrations of Ni, Zn, Pb, Ag, Au, Ge and U as well as subeconomic concentrations of As, V, Mo, Bi, Ga, Pt and Pd closely associated with hypogene copper mineralisation (Torrealday et al., 2000; Broughton et al., 2002; McGoldrick et al., 2003; Dewaele et al., 2006a; Kampunzu et al., 2009; McGoldrick et al., 2010; Selley et al., 2010; Halley et al., 2016). At Mashitu South, hypogene mineralisation has been shown to have a geochemical association of Cu + Co + Bi + Ni + V + S \pm Mo \pm As \pm Fe \pm Zn, while supergene Cu-oxide mineralisation has a geochemical association of Cu-Be-P \pm Zn (Gigler, 2016).

In this study, analysis of massed drill-core assay data from Mashitu South is used to characterise the geochemical variation of major and trace elements through the depth profile of the deposit. This variation in geochemistry empirically reflects the mobility of these different elements under oxidising, leaching conditions. Identifying elements which are associated with hypogene Cu mineralisation, but which are less mobile than Cu in the supergene environment, can lead to the development of surface pathfinder elements to buried supergene Cu deposits. The approach developed in this paper can be applied to identify surface pathfinder elements to any polymetallic mineral deposit which has been heavily leached through chemical weathering.

2. Geological setting

The Cu-Co deposits of the Katangan Copperbelt are hosted in rocks of the Katangan Supergroup, which were deposited between ~880 Ma (Armstrong et al., 2005) and ~573 Ma (Master et al., 2005). The rocks of the lowermost Roan Group host the majority of regional mineralisation and are made up of a sequence of siliciclastic argillites and arenites (the Roches Argilo-Talqueuse - 'RAT' Subgroup) which transition upwards into a sequence of dolostones and dolomitic shales (the Mines Series Subgroup). The Mines Series comprises (from bottom to top): The Dolomies Stratifiées (DStrat), Roches Siliceuses Feuilletées (RSF) and Roches Siliceuse et Cellulaire (RSC) units (the Kamoto Formation), the Shales Dolomitique (SD) unit (the Dolomitic Shales Formation) and the Calcaire à Minéraux Noire (CMN) unit (the Kambove Formation). The primary regional mineralisation event occurred between ~875 and ~750 Ma (Key et al., 2001; Selley et al., 2006; Muchez et al., 2010; Decrée et al., 2014), forming syn-diagenetic, stratiform Cu-Co sulphides (Dewaele et al., 2006b) hosted mainly in the Mines Series Subgroup. Subsequent to the deposition and stratiform mineralisation of the Mines Series, the Roan Group experienced an episode of tectonic disruption wherein the strata were deformed and fragmented into 'megabreccias'. This disruption created 'megaclasts' or 'rafts' of intact stratigraphy, often several cubic km in volume, which lie in a 'matrix' of heterogeneous breccias and smaller megaclasts. The most widely-accepted explanation for this disruption is that it was caused by halokinetic diapirism of thick evaporite units previously located in the RAT and Dipeta Subgroups of the Roan Group (Bell, 1989; Jackson et al., 2003; Hitzman et al., 2012). The sedimentary rocks of the Katangan Supergroup were also deformed by the Lufilian Orogeny, from which peak metamorphism is dated to ~540-535 Ma (Kröner and Stern, 2005), reaching maximum P/T conditions of lower greenschist facies in Katanga (Ramsay and Ridgway, 1977). A second, 'vein-type' hypogene mineralisation event is distinguished in the region by Dewaele et al. (2006b), which formed vein-hosted Cu-Co sulphides and

is dated to a wide range of ages in different locations around the Copperbelt, spanning from ~615–470 Ma (Richards et al., 1988a, 1988b; Dawson, 2002; Selley et al., 2006; Torrealday et al., 2000). Pre, syn and post-folding structural relationships are identified in the host veins, indicating that multiple post-lithification hydrothermal events contributed to the formation of this stage of mineralisation. It should be noted that compared to stratiform Cu-Co mineralisation, vein-hosted Cu-Co mineralisation in the Katangan Copperbelt tends to be volume-trically and economically minor (Sweeney et al., 1991; Sweeney and Binda, 1994; Dewaele et al., 2006b).

The post-Lufilian geological history of Katanga is dominated by uplift, erosion, weathering and supergene mineralisation. Decrée et al. (2010) discerned two periods of supergene mineralisation in the region. dated to the Late Miocene, at or before ~ 10.3 Ma, and the Pliocene (~5.3-2.3 Ma), respectively. The Miocene period coincided with epeirogenic uplift initiated by the reactivation of the West African tectonic margin (Lavier et al., 2001), which excavated Roan Group stratigraphy and exposed rocks that hosted hypogene mineralisation to the action of meteoric fluids. The Pliocene supergene ore-formation event coincided with a regional transition to a more humid climate (Alexandre, 2002; Giresse, 2005; Miller et al., 2010) during which weathering processes were accelerated by warmer, wetter, more tropical conditions than those that prevailed in the Miocene or today (Gasse, 2006; Peel et al., 2007; Miller et al., 2010). It is possible, however, that earlier supergene events may have occurred which have since been overprinted; Hitzman (pers. comm., 2016) relates an incidence of supergene enrichment at the nearby Kolwezi deposit which is covered by Karoo Supergroup rocks, indicating a possible Mesozoic or even Palaeozoic age for enrichment. Today, there is a deep saprolite over much of the Katangan substratum, with around 10 m of clay, often kaolinite (Al₂Si₂O₅(OH)₄), developed at the surface (Giresse, 2005; Timmermans, 2015). This attests to a deep weathering regime which influenced the considerable supergene alteration to the Cu-Co deposits in the region (Dewaele et al., 2006b). Supergene Cu-Co deposits in Congo typically occur at a depth of < 100 m (Ngongo, 1975) however supergene alteration may occur at depths of > 1 km (Hitzman et al., 2012), particularly where there is a fluid pathway such as a breccia or a permeable stratigraphic unit to facilitate downwards migration of meteoric fluids (Fay and Barton, 2012). Elements which are more mobile under weathering conditions are depleted from the near surface environment, and enriched at depth due to re-precipitation under favourable Eh-pH conditions.

The Mashitu South deposit is situated roughly 25 km east of the city of Kolwezi, within a roughly triangular structure of heterogenous, brecciated Roan Group stratigraphy, informally termed the 'Kalukundi Diapir' by Hitzman (pers. comm., 2015). The deposit is a domal fragment of Mines Series Subgroup rocks which is bounded by RAT Subgroup rocks, heterogenous breccias and another underlying fragment of Mines Series along the eastern margin. It lies amongst a cluster of several other fragments of Mines Series and Cu-Co deposits termed the 'Mashitu Complex' (Fig. 2). The regolith at Mashitu South is deep and almost exclusively residual, and there is almost no surface expression to the Mines Series Subgroup fragment on which the deposit is centred. There is typically a ~ 10 m thick ferruginous pedolith at the top of the profile which retains none of the fabric of the original rock from which it formed. Below this is a ferruginous-pallid mottled zone of variable thickness and a kaolinitic saprolite which extends to $\sim 50 \text{ m}$ depth. Saprock may be found to a depth of between $\sim 100-200$ m before striking unweathered bedrock. The thicknesses of the zones of the regolith profile are highly variable and dependent upon the primary lithologies which have been weathered; saprock and unweathered bedrock are generally found at shallower depths in the siliciclastic RAT Subgroup rocks, whereas the primarily calcareous Mines Series Subgroup rocks tend to have a thicker and more well-developed saprolitic zone. In addition, weathering was enhanced in the vicinity of permeable breccias and stratigraphic units such as the RSC, and by the presence of sulphides in the weathering rocks (Gigler, 2016).

The Mashitu South fragment has been extensively delineated by drilling between 2005 and 2012. There are three main types of orebody at Mashitu South (Gigler, 2016). The first is a stratiform-disseminated chalcocite (Cu₂S) – carrollite (CuCo₂S₄) orebody hosted in the silicified, dolomitic Kamoto Formation, equivalent to the 'Lower Orebody' of regional literature (Hitzman et al., 2012). The second is a stratiform-disseminated chalcopyrite (CuFeS₂) – bornite (Cu₅FeS₄) dominated orebody developed in the \sim 5 m thick SD2d stratigraphic unit, a carbonaceous shale within the Dolomitic Shales Formation. The third type of orebody is supergene in origin, hosted in the RAT Subgroup and is dominated by void-filling malachite. This type of orebody generally occurs within 30-50 m of the surface and within the lower saprolite or upper saprock, beneath the former position of leached and eroded Mines Series stratigraphy.

Gigler (2016) distinguished four discrete mineralising events at Mashitu South. The stratiform orebodies in the SD2d and the Kamoto Formation were created *syn*-diagenetically in a protracted event equated with the main stratiform mineralisation stage in the region. A 'vein-type' second mineralisation stage is also evident; however, this did not significantly remobilise or re-concentrate ore at Mashitu South and is not responsible for the present-day distribution of any of the orebodies. The third and fourth mineralisation stages are both supergene and are equated to the Miocene-Pliocene events described by Decrée et al. (2010). The most recent of these supergene events is interpreted to have controlled the distribution of the RAT-hosted malachite orebodies, which are of significant economic importance.

3. Methods

3.1. Data capture

A geochemical assay database provided by Comide S.P.R.L. was the source of data for this study. This database was compiled from assays on half-core, < 1 m long samples from diamond drill core of varying thicknesses drilled at the Mashitu South deposit. These samples were selected by Comide employees from areas containing visible Cu-Co mineralisation, stratigraphic intervals which were expected to host mineralisation, and the broad environs of each (Chimvinga, pers. comm., 2014). Once selected, the samples were split, crushed and sent to ALS Global Laboratories. Copper and cobalt were assayed using the 'ME-OG62' technique: 'Ore-grade elements by four acid digestion using conventional inductively coupled plasma - atomic emission spectroscopy (ICP-AES) analysis', and Ag, Al, As, Ba, Be, Bi, Ca, Cd, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sc, Sr, Ti, U, V, W and Zn were assayed using the 'ME-ICP61' technique: 'Trace level methods using conventional ICP-AES analysis'. Both methods involve four-acid-digestion of the samples followed by ICP-AES analysis of the resultant solutions. More information on these techniques can be found on the ALS Global website (ALS Global, 2009a, 2009b).

These two assay techniques for the 28 elements were used respectively in the amended final database because they had the lowest associated margins of error and Lower Limit of Detection (LLOD), out of the variety of assay techniques conducted on the samples in the original database provided by Comide. Only samples which had a full suite of ICP-AES results for the 28 elements mentioned above and which were coded as belonging to the MSS deposit were included in the final amended database. The database was then 'cleaned' by removing values below the LLOD and replacing them with half the LLOD, to remove spuriously low values and to give non-zero values for statistical analysis. The detection limits for each elemental analysis are given below in Table 1.

Additionally, in order to create discrete depth values for each sample, a mid-point depth was calculated for each, by averaging the 'depth from' and 'depth to' attributes as logged by Comide employees. Stratigraphy, lithology and Hole I.D. attributes were then added to each



Fig. 2. Local geology map showing the four deposits of the Mashitu Complex, Mashitu North, Mashitu Principal, Mashitu South and Safwe North. CMN: Calcaire à Minéraux Noire Unit, SD: Shales Dolomitique Unit, RSC: Roches Siliceuse et Cellulaire Unit, RSF: Roches Siliceuses Feuilletées Unit, DStrat: Dolomies Stratifiées Unit, RAT: Roches Argilo-Talqueuse, i.e. RAT Gris and RAT Rouge units. Data provided by Eurasian Resources Group (ERG).

Table 1

LLOD (Lower Limit Of Detection) values for the ME-ICP61 and ME-OG62 assay techniques on the 28 different elements considered in this study, supplied by Comide S.P.R.L. and ALS Global.

Element	Assay technique	LLOD (ppm)
Ag	ME-ICP61	0.5
Al	ME-ICP61	100
As	ME-ICP61	5
Ba	ME-ICP61	10
Be	ME-ICP61	0.5
Bi	ME-ICP61	2
Ca	ME-ICP61	100
Cd	ME-ICP61	0.5
Со	ME-OG62	10
Cu	ME-OG62	10
Fe	ME-ICP61	100
K	ME-ICP61	100
La	ME-ICP61	10
Mg	ME-ICP61	100
Mn	ME-ICP61	5
Мо	ME-ICP61	1
Na	ME-ICP61	100
Ni	ME-ICP61	1
Р	ME-ICP61	100
Pb	ME-ICP61	2
S	ME-ICP61	100
Sc	ME-ICP61	1
Sr	ME-ICP61	1
Ti	ME-ICP61	100
U	ME-ICP61	10
V	ME-ICP61	2
W	ME-ICP61	10
Zn	ME-ICP61	2

sample by comparison of the geochemical assay and geological databases provided by Comide. The final product was a Microsoft Excel database of 12,058 samples from almost 200 drill holes at Mashitu South, each with 32 attributes: Hole ID, depth, stratigraphy, lithology, and assay values for each of the 28 elements considered in this study.

3.2. Normalisation techniques

In order to assess the relative concentration of different elements at different depth intervals, a self-normalisation method was conceived. This involved first calculating the average concentration of each element within the amended final database, by calculating the mean concentration out of the 12,058 samples for each element. This gave values dubbed the 'Average Concentration of Elements at Mashitu South', or ACEMS values. The ACEMS values were then used to normalise split datasets by dividing concentration values from a particular sample, or average concentration values from a split dataset, by the ACEMS values for each element. The ACEMS values are given in Table 2.

By normalising to ACEMS, an immediate picture is obtained of whether any element is concentrated or depleted within a particular sample or dataset, relative to the average concentration of that element for the 12,058 samples in the amended final Mashitu South database.

To assess the variation in element geochemistry by depth caused by weathering, samples were split into different sub-databases using the 'DEPTH' attribute in the amended final database: for example, 0–10 m, 10–50 m and 50–100 m sub-databases were created. Mean concentration values for each of these depth intervals were then calculated and normalised to ACEMS, to give an idea of the relative depletion or enrichment of these elements at each given depth interval.

The amended final database was primarily split simply by depth intervals, with a view to providing a general idea of element variation by depth irrespective of lithology or stratigraphy. However, the database was also split into sub-databases for each stratigraphy, which were themselves split into sub-databases by depth, to assess the weathering mobility of elements in different types of mineralised stratigraphic units.

4. Results

The ACEMS-normalised element plot for the < 10 m, 10-50 m,

Table 2

Table of ACEMS (average concentration of elements at Mashitu South) values, calculated by taking the mean concentration of all 12,058 samples in the amended final database and used as normalising factors.

Element	ACEMS value (ppm)	
Mg	70,189.53	
Al	39,312.94	
Ca	36,095.20	
Fe	19,676.71	
Cu	6388.14	
К	5204.34	
Co	1623.43	
Ti	1498.93	
S	1429.81	
Mn	651.96	
Р	401.62	
Na	238.29	
Ba	139.64	
V	103.64	
Ni	42.80	
Sr	34.08	
Zn	24.31	
La	18.35	
Pb	10.59	
U	9.25	
W	8.61	
Sc	8.31	
As	7.09	
Bi	3.63	
Мо	2.31	
Be	2.25	
Ag	1.09	
Cd	0.31	

50–100 m, 100–200 m and > 200 m depth intervals at Mashitu South (Fig. 3) shows that the concentrations of most of the 28 elements analysed vary significantly between each depth interval. These depth intervals were chosen to give a near surface, maximally weathered portion roughly equivalent to the ferruginous pedolith (< 10 m), an interval which corresponds to the saprolite, in which most of the remobilised supergene mineralisation is observed in core logs at the deposit (10-50 m), an interval generally comprised of saprock (50-100 m), a depth interval in which the weathering zone classification varies considerably between saprock and 'fresh' bedrock in different drillcores (100-200 m) and a minimally weathered portion comprised almost exclusively of unweathered bedrock (> 200 m). It should be noted that the correspondence of these depth intervals with weathering zone classifications is highly approximate and the accuracy varies considerably between the > 200 drill-cores from Mashitu South analysed as part of this study, for reasons discussed in Section 2: Geological setting.

Four trends in element concentration vs. depth are observable at Mashitu South. Calcium, sulphur, strontium, magnesium, barium and uranium all display a pattern of progressively higher concentrations with increasing depth intervals, suggesting that they are depleted by surficial processes. Conversely, the elements La, W, Bi, Mo, Co, V and Ag are progressively more concentrated towards the surface. The concentrations of Al, Ti, Sc, Na, Pb, Cd and Mn show very little variation throughout the profile. Copper, beryllium, phosphorous, nickel, potassium, zinc, arsenic and iron have inconsistent patterns of increases or decreases in concentration by depth interval.

The variation in geochemistry by depth is reflected at multiple scales. Fig. 4 shows the ACEMS-normalised concentration of three groups of elements at 10 m intervals to a depth of 100 m, a portion encompassing the pedolith, saprolite and saprock weathering zones at Mashitu South and containing most of the leached, oxide and mixed

Fig. 3. ACEMS-normalised average concentration of elements within the < 10 m (Pedolith), 10–50 m (Saprolite), 50–100 m (Saprock), 100–200 m (Saprock/Bedrock) and > 200 m (Bedrock) depth intervals at Mashitu South.





oxide-sulphide mineralisation zones at the deposit. Fig. 4a presents elements from the hypogene mineralisation association: $Cu + Co + Bi + Ni + V + S \pm Mo \pm As \pm Fe \pm Zn$, Fig. 4b presents elements from the supergene mineralisation association: Cu-Be-P \pm Zn and Fig. 4c presents the 'immobile' elements Al and Ti for comparison.

Fig. 5 shows the geochemical variation between elements of the hypogene mineralisation association at 1 m intervals in the < 10 m, near surface portion of the deposit, to give a picture of the transition to

Fig. 4. a: ACEMS-normalised average concentration of the hypogene-mineralisation-associated elements within the top 100 m of the profile at Mashitu South, presented in 10 m increments. The < 10 m interval corresponds to the pedolith weathering zone, the 10-50 m interval corresponds to the saprolite weathering zone and the 50-100 m interval corresponds to the saprock weathering zone.

b: ACEMS-normalised average concentration of elements associated with supergene Cuoxide mineralisation, within the top 100 m of the profile at Mashitu South, presented in 10 m increments. The < 10 m interval corresponds to the pedolith weathering zone, the 10–50 m interval corresponds to the saprolite weathering zone and the 50–100 m interval corresponds to the saprock weathering zone.

c: ACEMS-normalised average concentration of 'immobile' elements within the top 100 m of the profile at Mashitu South, presented in 10 m increments. The < 10 m interval corresponds to the pedolith weathering zone, the 10–50 m interval corresponds to the saprolite weathering zone and the 50–100 m interval corresponds to the saprock weathering zone.

surface geochemistry.

5. Discussion

The variation of average element concentration at different depth intervals is primarily due to depth-dependant geological processes. Querying such a large database smooths out variation in element geochemistry caused by varying stratigraphy, lithology, or mineralisation. All stratigraphic units of the Mines Series at the deposit are represented in the final amended MSS dataset (Table 3). Additionally, the domal structure of Mashitu South, together with the stratiform manner of primary mineralisation means that most stratigraphic units, including the mineralised ones, are found both near the surface and at great depth. It should be noted that, as discussed in the methods section, drillcore sampling was not systematic and targeted only areas of visible mineralisation. Therefore, interpretations drawn from this study contain a degree of bias towards well mineralised areas.

At Mashitu South, elements which would be expected to be relatively immobile during weathering, such as Al and Ti, show very little variation in ACEMS-normalised concentration between different depth intervals when compared to elements which would be expected to be mobile during weathering such as Ca and S (Figs. 3, 4a and c). These patterns of element distribution support the hypothesis that variation in average element geochemistry by depth at Mashitu South is primarily influenced by weathering.

5.1. Redistribution of elements in the profile

The varying average concentrations of the elements associated with hypogene mineralisation at different depth intervals (Figs. 3, 4a) indicate that these elements dissociate spatially in the supergene environment and are redistributed according to their mobility in meteoric fluids.

5.1.1. Copper distribution

Copper displays the highest average concentrations between 30 and 50 m depth. The other elements which make up the supergene mineralisation association, Be, P and Zn, also show high average concentrations relative to ACEMS at this depth (Fig. 4b). The reason for this is the presence of large supergene orebodies in the RAT unit beneath leached and eroded fragments of Mines Series at Mashitu South, which have significant economic potential (Chimvinga, pers. comm., 2014). These oxide-zone orebodies consist of malachite chrvsocolla $((Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O)$ – pseudomalachite $(Cu_5(PO_4)_2(OH)_4)$ dominated, void-filling mineral assemblages (Gigler, 2016), and are 'exotic' in the sense that they formed from copper-bearing solutions leached from the Mines Series. These solutions then migrated downwards and precipitated copper oxides below the original position of hypogene ore where Eh-pH conditions were more reducing. At Mashitu this occurred at around 30-50 m depth, roughly coincident with the position of the present-day water table (Robertson, pers. comm., 2014), 3.5

3.0

Fig. 5. ACEMS-normalised average concentration of hypogenemineralisation-associated elements within the top 10 m of the profile (roughly equivalent to the pedolith) at Mashitu South, presented in 1 m increments.



Table 3

Number of samples (N) in the Final Amended MSS (Mashitu South) database taken from each stratigraphic unit. CMN: Calcaire à Minéraux Noire Unit, SD: Shales Dolomitique Unit, RSC: Roches Siliceuse et Cellulaire Unit, RSF: Roches Siliceuses Feuilletées Unit, DStrat: Dolomies Stratifiées Unit, RAT: Roches Argilo-Talqueuse, i.e. RAT Gris and RAT Rouge units.

Stratigraphic Unit	Ν
CMN	1568
SD	2880
RSC	2085
RSF	977
DStrat	629
RAT Gris	781
RAT Rouge	2955
Undifferentiated Breccia	183
Total	12,058

which is a common site of deposition for remobilised malachite in Katanga (De Putter et al., 2010). The secondary ore at Mashitu is hosted in the mostly siliciclastic RAT unit and primarily occupies the pore spaces of arenaceous units, fills porous regions of breccias, and occurs in cavities where dolomite veins have dissolved. Within these orebodies, P is mineralogically accommodated by pseudomalachite and supergene apatite – $Ca_{10}(PO_4)_6(OH,F,Cl)_2$ (Gigler, 2016). The source of Be and Zn within the supergene association is unknown, but it is possible that they substitute for Cu within the structure of copper oxide minerals.

5.1.2. Cobalt distribution

Cobalt shows the highest average concentrations in the 20-30 m depth range, although it is also highly concentrated in the 10-20 m and < 10 m depth ranges. Copper and cobalt are closely associated in the hypogene environment and the spatial disparity in their concentrations in the near surface environment is an indicator of the dissociation of these two elements through supergene alteration. Such dissociation is well documented in Katanga, with Co-oxides frequently forming 'cobalt caps' in the near-surface environment above supergene copper deposits (Gauthier and Deliens, 1999; Decrée et al., 2010). At Mashitu South, near surface Co is accommodated primarily by

heterogenite, which is frequently residual and is hosted at or near the site of original hypogene mineralisation (Gigler, 2016). Cobalt has a high affinity for Mn and Fe oxides and may also be accommodated within such minerals, particularly within soil at the top of the profile (Pourret et al., 2015). Fig. 6, a downhole element profile for hole MSSD140, shows an example of high cobalt concentrations at a depth of \sim 7 m in the RSF and DStrat units, where Cu-Co hypogene ore is commonly present in rocks which have not experienced supergene alteration. This zone of residual Co enrichment overlies a large, remobilised, supergene Cu orebody hosted in the RAT unit at a depth of \sim 30–50 m.

5.1.3. Trace element and sulphur distribution

All of the other elements of the hypogene mineralisation association except for sulphur show higher ACEMS-normalised average concentrations than Cu in the top 20 m of the profile (Fig. 4a). In the <10 m interval, S, Cu, Ni and Zn are significantly depleted relative to ACEMS, levels of Fe and As are roughly equal to ACEMS levels, while Co, V, Mo and Bi are significantly enriched relative to ACEMS (Fig. 4a). The average concentration of Bi in particular is over twice that of A-CEMS in the < 10 m interval, and this concentration increases progressively in 1 m increments, such that Bi shows more than three times the average concentration in the < 1 m interval relative to ACEMS (Fig. 5). From this, it can be inferred that while S, Cu, Ni and Zn are depleted from the near-surface environment by chemical weathering, Co, V, Mo and particularly Bi experience residual, relative enrichment due to the same process. Spikes in the concentration of Co, V, Mo and Bi at the stratigraphic position of the RSF-DStrat 'lower orebody', within 10 m of the surface, are observable in hole MSSD140, shown in Fig. 6. Cu concentration at this depth is negligible by comparison.

After leaching and depletion from the surface, Cu and Zn migrated downwards and became enriched within oxide zone ores at around 30–50 m depth (Fig. 4b; Section 4.1.1). Sulphur leached from the surface may have contributed to the development of supergene Cu sulphides and sulphates deeper in the profile. However, S has not been reconcentrated at a particular depth level like Cu and there is no true 'chalcocite blanket' at Mashitu South (Gigler, 2016). Average sulphur concentrations increase progressively with depth (Fig. 3), indicating that there is net leaching of sulphur down to a depth of at least 200 m. The fate of Ni leached from the surface is unknown as no secondary Ni-



(2016), although it may have been fixed within supergene Cu sulphides. As discussed earlier, Co in the near surface environment is mostly present as residual heterogenite. The accommodation of V, Mo and Bi is less certain: these elements are present in concentrations of no more than tens to hundreds of ppm in any sample and no V, Mo or Bi-bearing minerals have been identified at Mashitu South. However, heterogenite is also a possible source as it commonly forms complex admixtures with Fe-Mn-Cu-Ni oxides, which are enriched in a number of trace elements and REE (Decrée et al., 2010; Decrée et al., 2015). High correlations between the concentrations of Co, and those of V, Mo and Bi in samples from the top 50 m of the profile also suggest that heterogenite may accommodate these trace elements.

bearing minerals were identified in the petrological study of Gigler

5.2. The effect of weathering on orebody geochemistry

To demonstrate how weathering changes the geochemistry of mineralised units at Mashitu South, the ACEMS-normalised geochemistry of the depth intervals from two units which commonly host contrasting styles of Cu-Co mineralisation are compared here: the RSF unit (Fig. 7a), which frequently hosts the majority of the stratiform, hypogene Cu + Co + Bi + Ni + V + S \pm Mo \pm As \pm Fe \pm Zn 'lower orebody', and the RAT Rouge unit, part of the RAT Subgroup, which only hosts remobilised, supergene, oxide zone Cu-Be-P \pm Zn type mineralisation (Fig. 7b). The contrasting variation in geochemistry by depth between the RSF and RAT Rouge units illustrates their predisposition to hosting hypogene and supergene mineralisation respectively.

In the RSF, Cu, S, and Ni are all greatly enriched relative to ACEMS in the > 200 m depth interval, being more concentrated here than at any depth. They also display significant depletion in the < 10 m depth interval, together with Zn. Cobalt also shows the highest ACEMS-relative enrichment at the greatest depth and the lowest at the shallowest depth interval. However, even in the < 10 m interval Co is still slightly enriched relative to ACEMS in the RSF, suggesting that it is slightly mobile within the RSF in the near-surface environment, but not to the same degree as Cu. Iron concentration is lower than ACEMS at all depth intervals but does not vary significantly between intervals. Arsenic, molybdenum and vanadium are slightly enriched in the RSF relative to **Fig. 6.** Near-surface downhole concentration plot for selected elements of the hypogene-mineralisation-association: Cu, Co, Bi, V and Mo, in hole MSSD140 at Mashitu South. Stratigraphic abbreviations: RSC: Roches Siliceuse et Cellulaire Unit, RSF: Roches Siliceuses Feuilletées Unit, DStrat Br: brecciated Dolomies Stratifiées Unit, RAT Gr: Roches Argilo-Talqueuse Grises Unit, RAT: Roches Argilo-Talqueuse Rouge Unit. Note that Cu no longer exists in appreciable concentrations at the expected stratigraphic position of the hypogene 'lower orebody': within the RSF and DStrat units. Instead it has been leached into a supergene orebody within the RAT Rouge unit, while the less mosbile elements associated with hypogene mineralisation have mostly remained behind (with the exception of Bi, which is also concentrated within the orebody).

ACEMS, but again with little variation between depth intervals. Bismuth displays high concentrations relative to ACEMS at all depth intervals, however the highest concentrations are to be found in the < 10 m interval (at $4 \times$ the ACEMS Bi value on average). This suggests surficial, residual enrichment of bismuth in the RSF unit.

The geochemistry of the RAT reflects the propensity of that unit to host supergene, rather than hypogene mineralisation. Most of the elements of the hypogene mineralisation association display average concentration values which are significantly below or roughly equal to the ACEMS values, except for in the < 10 m interval where Mo and V appear to display slight residual enrichment. Cobalt also displays slight enrichment in this interval, which may reflect limited downward migration of Co from the Mines Series to form remobilised near-surface heterogenite in alkaline pH conditions (Decrée et al., 2015). Copper is depleted relative to ACEMS in all intervals within the RAT Rouge except for the 10-50 m depth interval, where it displays relative enrichment, owing to the presence of the malachite-chrysocolla-pseudomalachite supergene orebodies discussed in Section 4.1.1. Beryllium is also slightly enriched at this interval compared to other intervals, but P and Zn do not appear to show preference for the 10-50 m compared to other intervals in the RAT Rouge, indicating that the RAT may be a source of these trace elements for supergene Cu-Be-P \pm Zn ores.

5.3. Implications for geochemical exploration

The hypogene ore association of $Cu + Co + Bi + Ni + V + S \pm Mo \pm As \pm Fe \pm Zn$ can be split into two groups of elements. Copper, nickel, sulphur and zinc are depleted from the surface by weathering, and Co, Bi, V, Mo, As and Fe experience residual enrichment in the near-surface. Fig. 5 shows that average concentrations of the latter group of elements remain high relative to ACEMS throughout the top 10 m of the depth profile, right to the < 1 m depth interval. It is therefore suggested that components from this group of elements would produce surface geochemical anomalies over leached, supergene Cu deposits which are greater in magnitude and more focussed than Cu itself, in cases where weathering has been severe, such as at Mashitu South. These anomalies would be expected in proximity to surface expressions of units which were originally host to hypogene ore, such as the RSF. Cobalt, bismuth and vanadium would be of





Fig. 7. a: ACEMS-normalised average concentration of elements within the < 10 m, 10–50 m, 50–100 m, 100–200 m and > 200 m depth intervals of the RSF (Roches Siliceuses Feuilletées) stratigraphic unit at Mashitu South.

b: ACEMS-normalised average concentration of elements within the <10 m, $10{-}50$ m, $50{-}100$ m, $100{-}200$ m and >200 m depth intervals of the RAT (Roches Argilo-Talqueuse) Rouge stratigraphic unit at Mashitu South.

particular use, as they are proven to be associated more exclusively with the hypogene mineralisation present at Mashitu South than Mo, As and Fe (Gigler, 2016), while still being more residually concentrated than the other elements of the association. It should be noted that, when using the average-normalisation technique presented in this paper to determine surface pathfinder elements to mineralisation, one must have a solid understanding of the major and trace elements which may be confidently associated with hypogene mineralisation of the type being explored for. This is important to exclude the erroneous use of elements as pathfinders which are simply enriched in the surface profile without being enriched in the rocks by hypogene mineralisation processes. At Mashitu South, the hypogene geochemical association of Cu + Co + Bi + Ni + V + S \pm Mo \pm As \pm Fe \pm Zn was determined by geostatistical and petrological studies of 'fresh' rock intervals known to be host to hypogene mineralisation, with minimal alteration by supergene processes (Gigler, 2016).

Exploring for 'cobalt caps' is a well-known method of prospecting for supergene Cu in the region (Gauthier and Deliens, 1999; Decrée et al., 2010). However, near-surface element concentrations (Fig. 5) suggest that Bi and V make even better surface vectors than Co, as they are more residually enriched. Bismuth in particular should form the strongest, most localised anomalies directly over the position of former hypogene orebodies as it displays the most residual enrichment, at over $3 \times$ the ACEMS concentration in the top < 1 m of the profile. Indeed, a comparison of the near-surface element profile of the generally 'hypogene-mineralised' RSF and the 'hypogene-barren' RAT Rouge units highlights the usefulness of Bi as a surface vector. In the < 10 m depth interval of the RSF (Fig. 7a), Bi displays an average concentration of $3.8 \times$ ACEMS, compared to $0.1 \times$ ACEMS for Cu and $1.2 \times$ ACEMS for Co. By comparison, the typically 'hypogene-barren' RAT Rouge (Fig. 7b) has an average Bi concentration at < 10 m depth of $0.7 \times$ ACEMS, an average Cu concentration of $0.4 \times$ ACEMS and an average Co concentration of $1.4 \times$ ACEMS. The high average concentration of Bi in the near-surface profile of hypogene-mineralised units, such as the RSF, compared to its low average concentration in hypogene-barren units, such as the RAT-Rouge, recommends it as a surface vector to leached hypogene orebodies where Cu is not found in appreciable nearsurface quantities. The use of residually-concentrated trace elements associated with Cu-mineralisation as surface pathfinders, including Bi and Mo, has also been recommended at the supergene Cu deposits of the Mount Isa Inlier, NW Queensland, Australia by recent research (Salama et al., 2016a). Additionally, lateral migration of elements in the near-surface environment could encourage the formation of a 'bullseye' geochemical target, with more mobile elements such as Cu displaying broad, diffuse anomalies and less mobile elements such as Co and Bi displaying localised, intense anomalies directly above a supergene orebody beneath the centre of the 'bullseye'.

Soil concentrations of Cu have proven adequate for locating many Cu-Co deposits in the region (Chimvinga, pers. comm., 2014). However, the soil concentrations of Bi, Co and V, or multi-element concentrations of these three elements, could prove useful in locating hitherto undiscovered deposits which have been subjected to a high degree of chemical weathering, like Mashitu South. Pit sampling or shallow drilling of the pedolith, followed by high-precision 'wet-geochemistry' assay methods are recommended for use in this type of exploration. XRF analysis of soil samples may not be accurate enough to produce conclusive assay results for trace elements present in such low concentrations as Bi and V (Gigler, 2016). In their study of supergene Cu mineralisation at the Mount Isa Inlier, Salama et al. (2016a) find that Bi and V are effectively concentrated above Cu-sulphide deposits in ferruginous lag (> 7.6 mm size fraction) and in termitaria. Given a similar weathering regime between the two study areas, these materials are also recommended as sampling media in detecting highly residual surface pathfinders such as Bi and V while exploring for Cu-Co mineralisation in Katanga. Cobalt, which is slightly more mobile in the nearsurface than Bi and V (Fig. 5), is enriched in ferruginous duricrusts at the Mount Isa Inlier along with Cu and Ni (Salama et al., 2016a), so it is recommended that this medium be used as a sampling material when using these elements as pathfinders. When using Co and even Cu as surface pathfinders, it is recommended to normalise the concentration data against Mn in order to exclude false positives produced by scavenging of these metals by Mn oxides in the near-surface, which has been demonstrated to occur in Cu exploration over the buried Katangan Supergroup of NW Botswana (Salama et al., 2016b).

6. Conclusions

Splitting a large whole-rock-geochemistry dataset into sub-databases, then normalising average concentration values within those subdatabases to average values for the entire database, is an effective tool for assessing geochemical variation between datasets. This geochemical variation between different depth intervals at Mashitu South primarily reflects the effects of weathering. From the hypogene ore element association the deposit of Cu + Co + Bi + Ni + Vat + S \pm Mo \pm As \pm Fe \pm Zn, two groups of elements are distinguished: those which are depleted in the near-surface environment by weathering (Cu, Ni, S and Zn) and those which are residually enriched by weathering (Co, Bi, V, Mo, As and Fe). These residually enriched elements would be expected to be present in highly anomalous concentrations in the near-surface environment proximal to the original position of hypogene Cu-Co orebodies, even where Cu has been leached efficiently from the surface and no significant Cu anomaly exists. In such cases of extreme leaching, Cu is commonly re-concentrated at depth into supergene orebodies with high economic potential. It is therefore suggested that surface concentrations of Co, V and particularly Bi would be effective surface vectors to the position of similar supergene Cu orebodies in Katanga. The average-normalisation technique presented in this paper could be used to assess element variation by depth in large geochemistry databases from any polymetallic deposit which has undergone significant chemical weathering.

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