Environmental chemistry and mineralogy of particulate air matter around Selebi Phikwe nickel-copper plant, Botswana

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Abstract

This study aimed at chemically and mineralogically characterizing whole particulate air matter (PM) occurring at the Selebi Phikwe nickel-copper (Ni-Cu) area in Botswana, and quantifying its potential environmental implications. Heavy metals concentrations in PM samples around the Selebi Phikwe Ni-Cu plant were determined by atomic absorption spectrometry and the mineral phases identified by X-ray powder diffraction technique. The particles consisted of quartz, pyrrhotite, chalcopyrite, biotite and calcite. Concentration levels of heavy metals contained in PM samples could be related to mineral phases present. Quite significantly is the occurrence of quartz, which has not been found in both the orebody and surrounding soil. Dureide polymorphs formed from secondary mineralization of chalcopyrite and the gases H2S and SO2 released from concentration/oxidation processes. Possible environmental chemistry of the whole PM based on its mineralogy at Selebi Phikwe area is discussed.

Keywords: Environmental; Mining; Pollution; Sulphide ore; Oxidation

1. Introduction

Recent growth in mining activities in Botswana may have generated corresponding increase in particulate air matter (PAM) considered as environmental contaminant. The Selebi Phikwe Ni-Cu mine area, where mining and smelting activities may pose as sources of environmental contamination, is of particular concern to the country. Selebi Phikwe is one of the main urbanised townships of Botswana, rated after Gaborone, Francistown, Maun and Lobatse (Grant and Grant, 1995). The study area is located in the north-eastern part of the country (Fig. 1) between longitudes 26° 43'E and 27° 57'E, and latitudes 22° 55'S and 22° 06'S (Department of Town and Regional Planning, 1996).

Previous studies conducted at Selebi Phikwe were directed at understanding the petrogenesis (brown, 1987), structural geology (Galton, 1988), and mineralogy (Nkoma and Ekosse, 1993, 1999, 2000) of the orebodies. The X-ray powder diffraction (XRD) studies of Ni-Cu orebodies from Selebi Phikwe identified transition sulphide minerals, which included chalcopyrite, pentlandite, pyrrhotite, bornite, chalcocite, enargite and magnetite. Nkoma and Ekosse, 1993, 1999, 2000). Studies on soil mineralogy identified actinolite, biotite, quartz, microcline, anorthite, pyrrhotite, apatite, ilite, kaolinite and smectite as well as cobalt oxide and silicon oxide (Ekosse et al., 2003). However, no research on the PAM around Selebi Phikwe has been documented.

Over the past years, there has been growing concern on some possible environmental implications of PAM resulting from the mining and extraction activities at Selebi Phikwe. Previous air pollution studies conducted (USA EPA, 1990) show that PAM with an est. of ≤10 μm could be inhaled into the human respiratory system and could be deposited on the lungs. Acute exposure may lead to loss of lung function, aggravation of existing respiratory and cardiovascular diseases, loss of capacity to resist infection, carcinogenesis, and premature death (NIOSH, 1995). In this work, chemical
analysis and XRPD study were carried out to establish the concentration levels of heavy metals and identify the mineral constituents in PAM around Selebi Phikwe.

2. Materials and methods

Sampling for PAM from source and non-source emission points according to US NIOSH Method 0500 (NIOSH, 1995), was conducted from January to July 2000 (Table 1). However, it was not possible to obtain PAM samples on a monthly basis due to unusually heavy rains during the wet season of the year. Six Gillian Gilair—3 personal air sampling system (South African version) for low flow and two Airecon 2 constant medium flow samplers were used for sampling of PAM. The medium flow samplers were used to obtain samples over a period of three days at each of the sampling points. The samples for low flow were placed at the various sampling points and allowed to run for 12 h at a flow rate of 1–3 l/min, as specified by the NIOSH Manual of Analytical Methods (NIOSH, 1995).

Elements analyzed were those considered to be those associated with Ni–Cu mining and smelting. The elements included Cd, Cr, Co, Cu, Fe, Ni, Sc and Zn, which were likely to be found in Ni–Cu orebodies and released into the atmosphere through mining and smelting activities. Ionic concentrations of Cd, Cr, Co, Ni and Sc present in extracts of PAM samples were determined using a Varian Spectra AA 400 plus atomic absorption spectrometer (AAS) with a Zeeman graphite tube atomizer (GTA) 96. Ionic concentrations of Cu, Fe and Zn were measured with a Varian Spectra AA 10 Flame Atomic Absorption Spectrometer (FAAS).

The procedure for the determination of the concentrations of heavy metals used in this study was adapted from both Beach (1989) for the Zeeman GFAAS and NIOSH (1995) manual of analytical methods for FAAS depending on the analyte being analyzed. Analytical grade reagents were used in all the chemical analyses. Samples were homogenized and 0.5 g of sample was weighed into a 30 ml Teflon beaker. The sample solution was heated slowly at low temperature to dry. Aching of analyte occurred at a high temperature. Subsequently, followed by atomization, samples were treated with HNO₃ digestion at a temperature not exceeding 50 °C. Zero point one gram of sample was weighed into a Pt crucible wetted with water, each sample was digested with 0.2 ml of 72 vol.% perchloric acid and 5 ml of 48% hydrofluoric acid on a sand bath at 200–225 °C in a partially closed Pt crucible with lid. The residue was collected by boiling the sample with 5 ml of 60 vol.% HCl and 10–15 ml of water. The contents of the crucible together with its lid were washed into a 100 ml volumetric flask filled to mark with ultra pure water from which very small aliquots were aspirated into the graphite furnace for atomization and analysis of the heavy metal concentrations in the samples.

The mineral phases contained in the PAM, were identified using XRPD techniques. In XRPD, diffraction peaks occur when the path of the diffracted X-rays is equal to an integer multiple of the path difference expressed by Bragg’s equation which is given by

\[ n \lambda = 2d \sin \theta \]  

where \( n \) is an integer, \( \lambda \) is the wavelength, \( d \) is the interatomic spacing, and \( \theta \) is the diffraction angle (Bailey,

Table 1

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1960). The samples were scanned using a Philips PW 3710 XRPD system, from 2° to 70° 2θ, and the diffractograms were recorded for scanned samples. The analytical system operated at 40 kV and 45 mA, with a CuKα cathode radiation source. The samples were measured in steps made with steps of 0.02° 2θ and a counting time of 2 s.

The data was obtained with the aid of a graphite monochromator PW 1877 Automated Powder Diffraction, and an XPERT Data Collector software package. The collected data was processed for qualitative identification of the minerals from both the data and patterns obtained by scanning using a 1999 Philips XPERT Cu-Bragg and I.D. software package. The interpreted results were compared with data and patterns available in the Mineral Powder Diffraction File, data book and the search manual issued by the International Centre for Diffraction Data (2001) for confirmation.

3. Results

Average concentration values of the heavy metals in PAM are given in Table 2. Concentration values for Fe, Cu and Ni in PAM were significantly higher than those for Cd, Co, Cr, Se and Zn. The results of the XRPD analyses of the PAM samples were indicative of very fine quartz, pyrrhotite, chalcopyrite, albite and dijulite mineral phases as shown in Fig. 2.

<table>
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<tr>
<th>Element</th>
<th>Concentration in ppm</th>
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<td>Cd</td>
<td>0.05</td>
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<td>Co</td>
<td>12</td>
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<td>Cr</td>
<td>19</td>
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<td>Cu</td>
<td>17</td>
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<td>Fe</td>
<td>91</td>
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<td>Ni</td>
<td>41</td>
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<td>Se</td>
<td>0.01</td>
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<td>Zn</td>
<td>4</td>
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4. Discussion

4.1. Meteorological aspects

In the mornings, during sampling days, the temperatures were low between 14 and 28 °C during the day. The wind speed was also appropriate in the mornings and during the day ranging between 2 and 6 m s⁻¹. Annual Report from the Department of Mines (1998) indicates that winds prevail from the North East 40% of the time. Prevailing winds carry PAM. The velocity of the prevailing winds during sampling periods was low consequently reflected in very low quantities of PAM which was sampled.

4.2. Chemical and mineralogical aspects

Quartz, SiO₂; penlandite, (Fe₃Ni₃S₄); chalcopyrite (CuS); pyrrhotite, (Ni₃Cu₃S₈); pyrite (Fe₃S₈) chalcopyrite, CuFeS₂; manganite, (FeO₂); barite (BaSO₄) and albite NaAlSi₃O₈ have been identified in the Ni-Cu orebodies (Nkoma and Ekose, 1998, 1999 2000). In this study, different concentration levels of heavy metals which included Cd, Cr, Co, Cu, Fe, Ni, Se and Zn were identified in the PAM. Except for Zn, the seven other heavy metals were contained in the minerals which have been identified in PAM, possibly due to mining and smelting activities. Very high concentration levels of Cu and Fe could be explained from the dominance of chalcopyrite and dijulite which are Cu-bearing minerals, and pyrrhotite and chalcopyrite which are Fe-bearing minerals, all contained in the PAM. Low concentration levels of Ni and Co could be associated with effective extraction metallurgical processes at the mine, and lower concentration levels of Cd, Cr and Se could be attributed to their generally low level occurrences in Ni-Cu orebodies.

Dijulite which has so far not been identified from previous mineralogical studies of the orebody (Nkoma and Ekose, 1998, 1999, 2010; Gallon, 1886), and the surrounding soils (Ekose et al, 2003) was found to be

![Fig. 2. X-ray powder diffractogram of the representative PAM sample (Q is quartz, F is pyrrhotite, C is chalcopyrite, A is albite and D is dijulite)](image-url)
present in the PAM. Consequently, its polymorphs
(Cu$_2$S$_6$ and Cu$_3$S$_5$) could have been formed from
secondary mineralization of chalcocite and H$_2$S released
from concentration/smelting processes, as expressed in
Eq. (2) below.

$$3 \text{Cu}_2\text{S}_6 + 10\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{Cu}_3\text{S}_5 + 10\text{H}_2\text{O}$$

chalcocite
djulrite

Djulrite is secondary PAM, which possibly formed by
atmospheric chemistry, by reactions of primary PAM
with atmospheric gases and fluids. During sampling a
pungent odor of gases characteristic of H$_2$S and SO$_2$
hovered in the atmosphere. In the soils, cuprite was
identified (Rousse et al., 2003). It is suggested that
djulrite is oxidized to cuprite as shown in Eq. (3).

$$2\text{Cu}_{1.26}\text{O} + 47\text{SO}_2 \rightarrow 3\text{Cu}_2\text{O} + 22\text{SO}_3$$

cuprite
djulrite

Djulrite has a monoclinal crystal system, with a hard-
ness of 2.5 to 3 on the Mohs' scale of hardness. It is
grayish blue to black with a metallic to opaque luster
(Roseboom, 1967). Naturally, it occurs in enrichment
zones of copper deposits, and is mainly associated
with chalcocite, chalcopyrite and pyrite. Djulrite polymor-
phs are closely related to the chalcocite polymorphs,
Cu$_2$S, Cu$_{1.26}$O and Cu$_{1.06}$S.

4.3. Environmental implications

Minerals make up 14.6–99.9 wt.% of the major con-
stituent of atmospheric particles (USA-EPA, 1995). The
PAM at Selebi Phikwe consisted of particulate released
into the atmosphere from mining and smelting activities,
as well as spatially transported aeolian particulate. Re-
gional climatic and geomorphic factors such as draught
and desertification encroachment tend to increase the
quantity of PAM entering both the atmosphere and
troposphere (Ringer et al., 1995). This phenomenon
might dilute the proportions of heavy metals contained
in the Selebi Phikwe PAM.

Particulate air matter can force both cooling
and warming effects on its environment locally, region-
ally and globally depending on the quantity contained in
air as explained by Prospero (1999) and discussed by
Buseck and Posfai (1999). Mineral particles absorb light,
creating a heating effect as explained by Buseck and
Posfai (1999). The surfaces of PAM particles are used as
reactive milieus for a wide variety of chemical reactions
in the atmosphere, which significantly influence the cy-
cles of N, S, and oxidants in the air. When mineral par-
icles are associated with hygroscopic S compounds,
they act as cloud condensation nuclei (CCN) and
modify the cloud radiative properties as mentioned in
Buseck and Posfai (1999). In this regard, they promote
precipitation and concentration of ice. This pheno-
menon may explain why Selebi Phikwe has slightly more
rain than its neighboring areas even though they are
classified within the same climate type (Bhalotra, 1987).

The mineral content identified in the PAM at Selebi
Phikwe is reflective of acidic nature. These minerals
could easily combine with H$_2$S and SO$_2$ and atmo-
spheric moisture to release H$_2$SO$_4$, which is the primary
chemical constituent of acid rain. Acidic PAM deterior-
rates paint quality, marble buildings and bridges, and
vehicles within the vicinity of its influence. Particulate
air matter may damage crops, trees and shrubs. It may
congest the leaves and make it difficult for photosyn-
thesis to take place. The plants become distorted and
eventually die through suffocation.

5. Conclusions

This work has chemically and mineralogically ana-
alyzed PAM occurring at Selebi Phikwe by XRPD. Re-
results obtained from chemical analyses relate well with
minerals identified by XRPD for PAM samples. Djul-
rite has been identified as a nemoralized phase occur-
ring as a result of Ni-Cu mining/smelting activities.
We have further discussed the environmental
chemistry and mineralogy and examined some possible
environmental implications likely to be occurring as a
result of contaminated PAM at the Selebi Phikwe Ni-
Cu mine area.

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