

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

G. Ekosse ^{a,*}, D.J. van den Heever ^b, L. de Jager ^c, O. Totolo ^d

^a Department of Geology, University of Botswana, P/Bag 0022 Gaborone, Botswana

^b VDH Industrial Hygiene C.C., P.O. Box 26792 Langenhoven Park, 9330 Free State, South Africa

^c Department of Environmental Health, Technikon Free State, P/Bag 320539 Bloemfontein, 9301 Free State, South Africa

^d Department of Environmental Science, University of Botswana, P/Bag 0022 Gaborone, Botswana

Abstract

This study aimed at chemically and mineralogically characterizing whole particulate air matter (PAM) occurring at the Selebi Phikwe nickel–copper (Ni–Cu) area in Botswana, and postulating its possible environmental implications. Heavy metals concentrations in PAM 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, chalcocopyrite, albite and djurleite. Concentration levels of heavy metals contained in PAM samples could be related to mineral phases present. Quite significantly is the occurrence of djurleite, which has not been found in both the orebody and surrounding soils. Djurleite polymorphs formed from secondary mineralization of chalcocite and the gases H₂S and SO₂ released from concentration/smelting processes. Possible environmental chemistry of the whole PAM 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 contaminants. 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 27° 47'E and 27° 53'E, and latitudes 22° 55'S and 22° 00'S (Department of Town and Regional Planning, 1996).

Previous studies conducted at Selebi Phikwe were directed at understanding the petrogenesis (Brown,

1987), structural geology (Galon, 1986), and mineralogy (Nkoma and Ekosse, 1998, 1999, 2000) of the orebodies. The X-ray powder diffraction (XRPD) studies of Ni–Cu orebodies from Selebi Phikwe identified transition sulphide minerals, which included chalcocopyrite, pentlandite, pyrrhotite, bunsenite, chalcocite, penroseite and magnetite (Nkoma and Ekosse, 1999, 2000). Studies on soil mineralogy identified actinolite, albite, quartz, microcline, anorthite, pyrrhotite, cuprite, illite, 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, 1995) show that PAM with an esd of $\leq 10 \mu\text{m}$ 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

*Corresponding author. Tel: +267-355-2369 (OH)/+267-716-09489 (Cell); fax: +267-585-097.

E-mail addresses: gkossae@esuite.com, ekossae@mopipi.ub.bw (G. Ekosse).



Fig. 1. Map of Botswana showing the study area.

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 Gilian Gilair—3 personal air sampling system (South African version) for low flow and two Aircon 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 samplers 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, Se 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 Se 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. Ashing of analyte occurred at a high temperature, subsequently followed by atomization. Samples were treated with HNO₃ digestion at a temperature not exceeding 500 °C. Zero point one gram of sample was weighed into a Pt crucible wetted with water. Each sample was digested with 0.5 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 atomisation 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

$$n\lambda = 2d \sin \theta \quad (1)$$

where n is an integer, λ is the wavelength, d is the interatomic spacing, and θ is the diffraction angle (Bailey,

Table 1
Dates which particulate air matter samples were obtained at the study site

Month	January 2000	February 2000	March 2000	April 2000	May 2000	June 2000	July 2000
Date	15 29	12 26	11 25	15 29	13 27	10 24	15 29

1980). The samples were scanned using a Philips PW 3710 XRPD system, from $2^{\circ} 2\theta$ to $70^{\circ} 2\theta$, and the diffractograms were recorded for scanned samples. The analytical system operated at 40 kV and 45 mA, with a $\text{CuK}\alpha$ cathode radiation source. The samples were measured in stepscan mode with steps of $0.02^{\circ} 2\theta$ 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 Graphics and Identify 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 djurleite mineral phases as shown in Fig. 2.

Table 2
Concentrations of heavy metals contained in particulate air matter

Element	Concentration in ppm
Cd	0.05
Co	12
Cr	19
Cu	87
Fe	91
Ni	41
Se	0.01
Zn	4

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 ranged between 2 and 6 ms^{-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, SiO_2 ; pentlandite, $(\text{Fe},\text{Ni})_9\text{S}_8$; chalcocite, (Cu_2S) ; penroseite, $(\text{Ni},\text{Cu})\text{S}_2$; pyrrhotite, $(\text{Fe}_{1-x}\text{S})$; chalcopyrite, CuFeS_2 ; magnetite, (Fe_3O_4) ; bunsenite, (NiO) and albite, $\text{NaAlSi}_3\text{O}_8$ have been identified in the Ni–Cu orebodies (Nkoma and Ekosse, 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 djurleite 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.

Djurleite which has so far not been identified from previous mineralogical studies of the orebody (Nkoma and Ekosse, 1998, 1999, 2000; Gallon, 1986), and the surrounding soils (Ekosse et al., 2003) was found to be

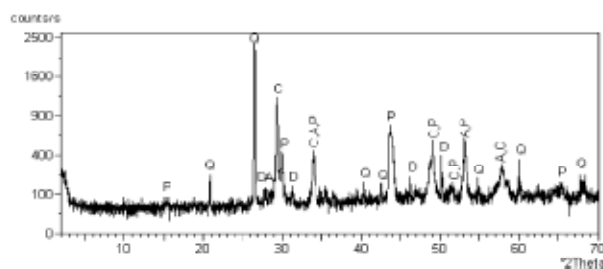
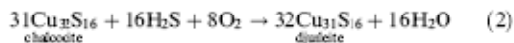
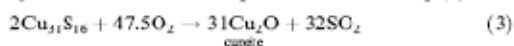


Fig. 2. X-ray powder diffractogram of the representative PAM sample (Q is quartz, F is pyrrhotite, C is chalcopyrite, A is albite and D is djurleite).

present in the PAM. Consequently, its polymorphs ($\text{Cu}_{31}\text{S}_{16}$ and $\text{Cu}_{1.93}\text{S}$) could have been formed from secondary mineralization of chalcocite and H_2S released from concentration/smelting processes, as expressed in Eq. (2) below.



Djurleite 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_2S and SO_2 hovered in the atmosphere. In the soils, cuprite was identified (Ekosse et al., 2003). It is suggested that djurleite is oxidized to cuprite as shown in Eq. (3).



Djurleite has a monoclinic crystal system, with a hardness of 2.5 to 3 on the Mohr's scale of hardness. It is grayish blue to black with a metallic to opaque luster (Roseboom, 1962). Naturally, it occurs in enrichment zones of copper deposits, and is mainly associated with chalcocite, chalcopyrite and pyrite. Djurleite polymorphs are closely related to the chalcocite polymorphs, Cu_2S , $\text{Cu}_{32}\text{S}_{16}$ and $\text{Cu}_{1.96}\text{S}$.

4.3. Environmental implications

Minerals make up 14.6–69.9 wt.% of the major constituent 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. Regional climatic and geomorphic factors such as draught and desertification encroachment tended to increase the quantity of PAM entering into both the atmosphere and troposphere (Ringrose 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, regionally 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 cycles of N, S, and oxidants in the air. When mineral particles 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 phenomenon 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 contents identified in the PAM at Selebi Phikwe is reflective of acidic nature. These minerals could easily combine with H_2S and SO_2 and atmospheric moisture to release H_2SO_4 , which is the primary chemical constituent of acid rain. Acidic PAM deteriorates 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 photosynthesis to take place. The plants become distorted and eventually die through suffocation.

5. Conclusions

This work has chemically and mineralogically analyzed PAM occurring at Selebi Phikwe by XRPD. Results obtained from chemical analyses relate well with minerals identified by XRPD for PAM samples. Djurleite has been identified as a neomineralized phase occurring 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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