MINERALOGICAL AND CHEMICAL CHARACTERIZATION OF ZARARA HILL COPPER DEPOSIT, KANO STATE, NORTHWESTERN NIGERIA

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ABSTRACT
A new copper deposit associated with the marginal granite porphyry of Banke Younger Granite Complex was discovered at Zarara hill, Kano State Nigeria. Preliminary study was undertaken with the main objectives of mineralogical and chemical characterization of the deposit. Twelve samples were obtained polished thin sections were prepared and studied using backscattered images and electron microprobe techniques. The results indicate that the ore mineralogical assemblage comprises of primary chalcopyrite, galena, sphalerite, arsenopyrite and pyrite, while secondary minerals formed from the alteration of the primary ore minerals are malachite, azurite, chalcocite and goethite. The gangue mineral assemblage include quartz, feldspar and hematite. Hence, chemical characterization of the deposit revealed that the economic metals include Cu, Pb, Zn, and S with trace concentrations of Cd, Co, Se, Ni, Mo etc. Therefore, adequate mineralogical and chemical characterization of mineral deposits is essential as a prerequisite for deposit's evaluation because other elements with possible economic and environmental significance might be present within the ore minerals as solid solutions.

Keywords: *EMPA; Zarara Hill; Chalcopyrite; Galena; Sphalerite; Elemental compositions*

1. INTRODUCTION

Mineralogical and trace element composition data on mineral deposits is essential because it determines the economic value of the deposit and could also be useful in scientific prospection and genetic interpretation of the geological environment (Deore, and Navrotsky, 2006) These data could also give useful clues to the possible environmental implications of mining and exploitation of the mineral deposit (Jambor, 1994).

The Zarara hill deposit is part of Banke Younger Granite Complex which belongs to the economically important geological province known as the Nigerian Younger Granite province. Many economically important mineral deposits were reported from this geological province (Pastor and Turaki 1983, Kinnaird and Bowden, 1985)
In this study, representative samples were obtained from the Zarara hill Copper deposit and analyzed using the technique of Electron Microprobe Analysis (EMPA). Preliminary geological studies of the deposit was undertaken by Ekwerre (1981) but the mineralogical and chemical compositions of the constituent minerals was not undertaken hence the need for this study. This paper is therefore, the first reference work on the microchemical characterization of the Zarara hill Copper deposit.

2 LOCATION OF STUDY

The location of the Zarara hill deposit on the geological map of the Banke complex is shown in Fig. 1. The area lies between Latitudes 10° 50' 00" and 10° 51'00"N and Longitudes 8° 33'00" to 8°35'00"E. Zarara hill is generally accessible by means of tarred-roads and footpaths, and through Unguwan Bawa-Tudun Wada-Kano tarmac road which runs along the eastern margin of the Banke Complex.

2.0 MATERIALS AND METHODS

2.1 Analytical methods

Twelve samples were obtained from the deposit and polished thin-sections were produced and carbon-coated. These used for mineralogical and microchemical studies using JOEL 733 Super-probe electron microprobe at the Earth and Planetary Sciences Department, McGill University, Montreal Canada. The instrument was equipped with 5 WD detectors and with a CL detector using an extended wavelength range from 200 to 900 nm. The instrument was operated at an acceleration voltage of 20Kv and 2-4 uA beam width. A counting time of 100 seconds was used for the elements except Au and Ag, which a counting time of 50 seconds was used. ZAF correction was applied to signals for all elements prior the calculation of elemental concentrations (Blackburn and Schwendeman, 1977).

Backscattered electron images (Fig.2) were acquired using slow beam scan rates of 20s at processing resolution of 1024 × 860 pixels and 256 grey levels. The electron beam voltage and current was 30 kV and 200 nA, respectively. The backscattered electron images assist in mineral identification and location of points for microchemical characterization. Instrumental signals were converted into concentrations, after making appropriate matrix corrections using the phi-rho-z method of Steger and Desjardins, (1980). Counting times for lower and upper background were 150 and 250 sec respectively for the elements analysed. Limits of detection (LOD) were 15 ppm for Fe, 11 ppm for As, 15 ppm for Zn, 51 ppm for Cu, 10 ppm for S, Se, Ni, Pb, Au, Co, Sn and Mo. Limit of Detection(LOD)'s were calculated from 5 background measurements with 95% confidence using the Student's t-distribution (Steger, and Desjardins, (1980).

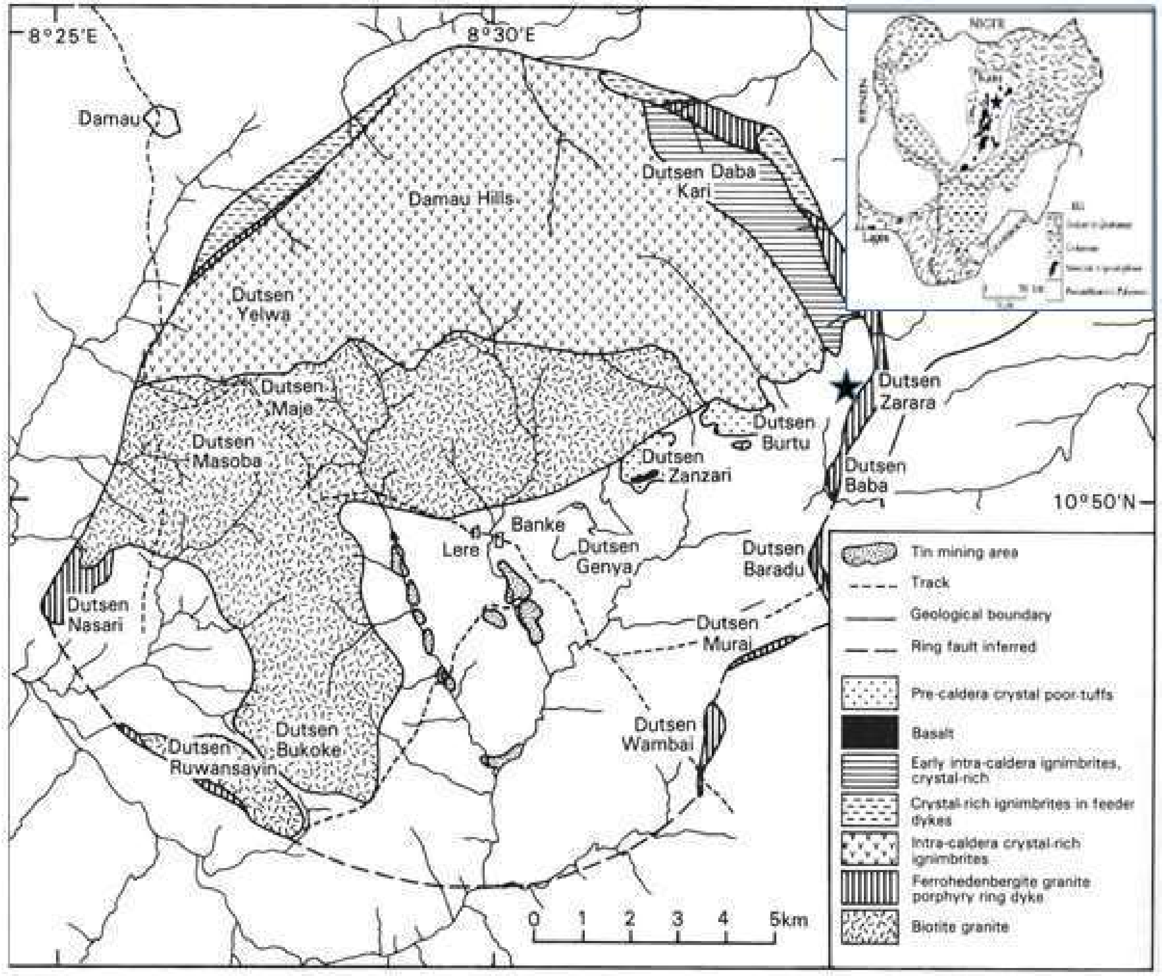

Fig. 1. Geological map of Banke Complex with the location of Zarara Hill Deposit indicated with a star (Modified after Bennett et al 1984).

3 RESULTS AND DISCUSSION

3.1 Mineralogical Composition

These minerals were identified on the based on their backscattered and optical characteristics. The photomicrographs and backscattered images obtained are shown in Fig.2. The sulphides identified include chalcopyrite, galena, sphalerite, and pyrite are the most dominant minerals in the Zarara hill deposits. These were accompanied by gangue mineral assemblage that comprises of quartz, feldspar and hematite. The secondary mineral assemblage formed from the alteration of the sulphide minerals are malachite, azurite, chalcocite and goethite.

Chalcopyrite ($CuFeS_2$)

Chalcopyrite is the most common sulphide in the samples and it exhibit features of physical deformation and shapes that are more rounded than euhedral. Chalcopyrite occurs mainly as exsolution inclusion, lamellae or oriented patches that fill micro fractures within sphalerite (Plate). It occurs as individual xenomorphic grains, which are clearly younger than sphalerite as they are commonly found along gran boundaries or in the intergranular spaces of the sphalerite. Chalcopyrite has been observed as coarse crystals intergrown with galena. Alteration products observed include malachite, azurite, and goethite. This could be due to the effect primary and secondary destruction of the sulphide as described by Jambor (1994).

Sphalerite (ZnS)

This is the second most abundant sulphide mineral in the Zarara hill mineralized quartz veins and forms about 10% of the vein volume. The sphalerite occurs as irregularly distributed massive ore usually separated by large patches of barren quartz. Clusters of sphalerite crystals may lie across instead of parallel to vein walls while some occur as projections into cavities formed because of incomplete vein fillings. It is extremely coarse grained with grey to dark lustre.

Sphalerite ranges in color from yellow-brown to dark chocolate brown, depending mainly on its iron content. In single crystal, the colour of the sphalerite appeared to be uniform. The grain size ranges from a few tenths of a millimeter up to several centimeters, averaging about a 0.5 millimeter.

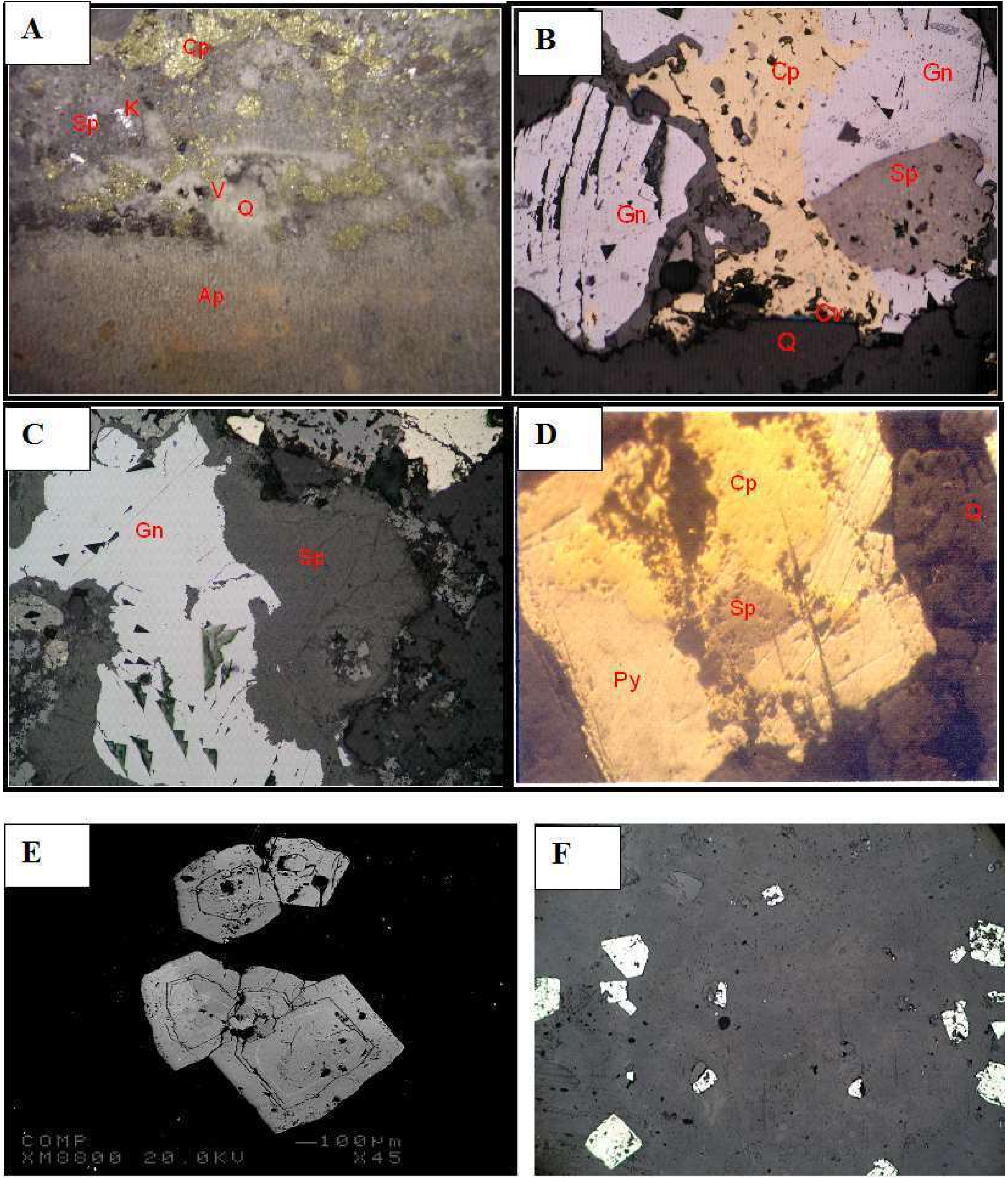

Fig 2 .Photomicrographs and backscattered images of the Zarara hill deposit (Gn, galena's, sphalerite, K-feldspar, Vugs, quartz: and Ap, apatite).

Pyrite (FeS₂)

Pyrite is present in almost every sample and it was detected in every polished section prepared. Some pyrite crystals occur as tiny veins cutting sphalerite (Fig. 2). These pyrite veinlets formed later than chalcopyrite and galena because the latter show no tendency for localization by the fractures controlling the pyrite deposition. In few cases (Fig 2d), the pyrite crystals were veined by chalcopyrite. Cubes of early pyrite were documented, replaced along surfaces and cracks by sphalerite, chalcopyrite and galena (Fig.2d).

Chemical Compositions of Sulphide Minerals

The major and trace elements compositions data of primary sulphide minerals in Zarara hill Copper deposit are listed in Table 1 to 4. The tables represent the averages of 25 spot analyses. The elements listed against corresponding minerals were found to be below the detection limits of the analytical instrument: Chalcopyrite; Mo, Cd; Sphalerite; Ni; Galena; Au and Co Pyrite; Mo, Cd and Pb.

Table 1. Chemical composition data on chalcopyrite (wt. %)

No.	1	2	3	4	5	6	7	8	9	10	11	12
Fe	29.93	29.83	29.92	29.73	30.06	29.96	29.83	29.89	29.93	29.92	30.17	30.10
As	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.03
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ag	0.02	0.04	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.03
S	35.26	35.06	35.19	35.25	35.26	35.24	35.23	35.36	35.32	35.19	35.22	35.27
Cu	34.56	34.29	34.65	34.54	34.62	34.61	34.52	34.47	34.66	34.48	34.52	34.63
Se	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.01	0.02	0.03
Ni	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.03	0.01	0.01	0.00	0.00
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au	0.01	0.00	0.02	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00
Co	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Sn	0.00	0.02	0.02	0.01	0.00	0.02	0.03	0.02	0.01	0.00	0.00	0.00
Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.78	99.29	99.83	99.54	99.96	99.83	99.61	99.79	99.93	99.64	100.03	100.09

Table 2. Chemical composition data on galena (wt. %)

No.	Fe	As	Zn	Ag	S	Cu	Se	Ni	Pb	Au	Co	Sn	Mo	Cd	Total
1	0.00	0.05	0.02	0.00	13.54	0.00	0.05	0.01	87.05	0.02	0.00	0.00	0.00	0.00	100.74
2	0.00	0.05	0.01	0.00	13.48	0.00	0.02	0.01	86.59	0.03	0.00	0.01	0.05	0.00	100.24
3	0.99	0.02	0.04	0.00	13.33	0.00	0.04	0.01	86.09	0.00	0.00	0.05	0.06	0.00	100.62
4	0.03	0.01	0.00	0.00	12.96	0.00	0.14	0.00	86.08	0.00	0.00	0.01	0.07	0.00	99.30
5	0.02	0.04	0.01	0.00	13.17	0.00	0.10	0.01	86.40	0.00	0.01	0.00	0.10	0.00	99.85
6	0.04	0.02	0.00	0.00	13.12	0.02	0.11	0.00	86.43	0.00	0.00	0.02	0.06	0.00	99.82
7	0.04	0.04	0.00	0.00	13.15	0.03	0.11	0.00	86.17	0.00	0.04	0.02	0.16	0.00	99.76
8	0.02	0.02	0.00	0.00	12.99	0.00	0.11	0.03	86.00	0.00	0.00	0.02	0.06	0.00	99.23
9	0.01	0.06	0.00	0.00	13.10	0.02	0.06	0.00	85.88	0.00	0.00	0.00	0.12	0.00	99.25
10	0.02	0.07	0.01	0.00	13.09	0.00	0.13	0.01	86.03	0.00	0.01	0.00	0.04	0.00	99.40
11	0.00	0.05	0.00	0.00	12.95	0.02	0.25	0.01	86.32	0.00	0.00	0.00	0.01	0.00	99.61

Table 3. Chemical composition data on sphalerite (wt. %)

No.	1	2	3	4	5	6	7	8	9	10	11
Fe	5.53	5.92	5.39	13.14	4.06	4.27	4.15	3.99	3.91	4.47	4.30
As	0.00	0.03	0.04	0.00	0.00	0.00	0.00	0.07	0.01	0.00	0.00
Zn	55.12	54.43	60.68	41.68	61.91	61.77	62.11	62.33	62.88	62.06	62.35
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.03	0.00
S	33.34	33.42	33.81	33.81	33.22	33.29	33.39	33.53	33.42	33.38	33.44
Cu	5.72	5.74	0.06	11.06	0.00	0.00	0.00	0.03	0.00	0.02	0.03
Se	0.00	0.05	0.01	0.03	0.02	0.00	0.01	0.01	0.00	0.01	0.00
Ni	0.01	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.00
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Co	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.00	0.03
Sn	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Mo	0.01	0.00	0.00	0.00	0.03	0.00	0.01	0.02	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Total	99.76	99.60	99.99	99.72	99.26	99.33	99.67	99.99	100.29	99.98	100.15

Table 4. Chemical composition data on pyrite (wt. %)

No.	Fe	As	Zn	Ag	S	Cu	Se	Ni	Pb	Au	Co	Sn	Mo	Cd	Total
1	45.79	0.02	0.32	0.00	53.18	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	99.33
2	45.22	0.00	0.75	0.00	52.88	0.27	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	99.14
3	46.23	0.01	0.00	0.00	53.50	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	99.76
4	45.89	0.00	0.00	0.01	53.19	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.00	0.00	99.13
5	46.21	0.26	0.00	0.01	53.26	0.00	0.02	0.02	0.00	0.01	0.00	0.00	0.00	0.00	99.79
6	45.77	0.37	0.00	0.00	53.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	99.18
7	45.91	0.72	0.04	0.03	52.95	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	99.66
8	45.64	0.69	0.02	0.02	53.11	0.00	0.01	0.00	0.00	0.00	0.03	0.01	0.00	0.00	99.53
9	45.96	0.09	0.00	0.00	53.53	0.02	0.01	0.02	0.00	0.00	0.02	0.00	0.00	0.00	99.64
10	46.00	0.58	0.00	0.05	53.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	99.65
11	46.01	0.00	0.02	0.00	53.36	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	99.41
12	45.93	0.10	0.00	0.00	53.41	0.01	0.01	0.00	0.00	0.01	0.02	0.00	0.00	0.00	99.49

3.2 DISCUSSION

Sphalerite (PbS)

Sphalerite can contain up to 10% CdS so it's not just a principal ore of zinc, but also of cadmium. In addition to the economic importance of sphalerite as a major ore mineral, both ZnS and CdS are important semiconductor materials, well known for their luminescence properties, with band gaps in the region that lend itself to technological applications.(e.g. Yu et al. 1986). These gaps can be fine-tuned by the addition of paramagnetic dopant ions (e.g., Twardoski 1990) for specific applications. More recently, a range of nanostructured materials such as nanowires (Zhang et al. 2005), nanosheets (Yue et al. 2006) and nanoparticles (Cao et al. 2004) has been produced, using both CdS and ZnS.

Galena (PbS)

Galena is the primary ore mineral of lead. Worked for its lead content as early as 3000 BC, it is found in ore veins with sphalerite, pyrite, chalcopyrite, tennantite-tetrahedrite, etc. and in skarns, as well as in sedimentary rocks where it may replace carbonate beds or be deposited in pore spaces. The crystals are bright when fresh but often tarnish after exposure to air. Galena has an important application as a semiconductor commonly as point contact diode in early radio wireless sets. It also has significant health risk because it contains lead, which can be poisonous when ingested.

Pyrite (FeS_2)

Pyrite is another important primary sulphide within Zarara hill deposits. An important uses of a natural pyrite is in the production of sulphiric acid (H_2SO_4) which is a primary feed stock for the manufacture of inorganic sulphur chemicals and a cardinal ingredient for the processing of aluminum and iron. Pyrite have also been known to influence the development of acid drainage in sulphide mineral deposit and hence has significance as natural source of groundwater contamination of groundwater.

4. CONCLUSIONS

Mineralogical and chemical characterization were used for the characterization of Zarara hill Copper deposit. The mineralogical composition of the Copper deposit comprises sulphide minerals, namely, chalcopyrite, sphalerite, galena and pyrite. These economically important sulphide minerals are mainly used as sources of economic metals and for scientific and technological applications. Microchemical characterization of elements were determined from these samples at different concentrations held as solid solutions. Trace element levels sulphides minerals affect their colour and purity and thus their economic values and potential environmental effects of their mining and exploitation. In particular, elements such as Ni, Cr and Fe in chalcopyrite and sphalerite are especially significant with regards to the quality of the purity of the sulphide. The trace elements contents of the sulphide have genetic implications because the trace element content of one geologic setting is different from that of others settings. Thus we can know sulphides formed from high temperature igneous processes and those from low temperature surficial processes.

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