

Characterization of Rock Samples from Yale Area of the Upper East Region of Ghana

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ABSTRACT

Quantitative analysis of the mineral and elemental components of rock samples in Yale locality of Ghana, Africa has been done by using the Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectroscopy (AAS). Both the INAA and AAS tests independently showed that the samples were dominated by Mn. INAA showed that across all samples the average composition of Mn was 3322.90 +/-169.60 ppm. Ti (6625.299 +/- 344.68 ppm), Cr (291.27 +/-48.13 ppm) and Cu (16.50 +/- 1.43 ppm) were also revealed by the INAA test on the samples. The results from the AAS test confirmed that Mn was dominant, with an average composition of 6052.22 +/- 2219.03 ppm. The presence of Cr (67.32 +/-72.73 ppm) and Cu (91.61 +/- 69.53 ppm) was also confirmed in the samples from AAS tests. Additionally, Au (1.5 +/- 0.66 ppm) and Co (49.14 +/-15.18ppm) were found, but an AAS test could not be used to confirm the presence of these elements. Gold was detected and estimated for the first time in the rock sample in that area of Ghana. These preliminary results indicate that the Yale area in the Upper East region of Ghana has substantial amounts of Mn, Ti and gold, and signify that the area is a potential mining zone for Mn and Au. The results of the present study add to information on the minerology of the Yale area.

Keywords: INAA, AAS, X-ray Diffraction, Mineral content, Yale Ghana

Introduction

Surface mining is widespread across Ghana today. In some communities, the mining potential has somehow been convincing enough to attract foreign miners, especially from South East Asia. Information on the host rock of any locality is important for mining there. The Minerals Commission, Ghana, does share mining data to inform mining. Other references such as the work of Kesse (Kesse, 1985), also provide important information on the distribution of minerals across the country. Data on mineralogy applicable to the Yale area in the Upper East region was however from sources as old as five decades. For example, Junner *et al.* were among the earliest documented to have sampled and studied the mineralogy of the Yale area (Junner, 1954). Murray's studies (Murray, 1960), which covered a wider

area between latitude 10 30' to 11 00' and longitude 0 30' – 1 00', also included Yale. There are very few available recent reports on work on the area. Yet, whilst collecting data for this study in the Upper East region, artisanal prospecting for gold or gold mining by both native and Asian groups was very active in many communities and this was said to be on the increase. It is fair to state, given the basic manner in which mining was carried out, that such activities are based on no scientific reference data on the mining potential of the area. Availability of data on the composition of the rock in any locality does not only provide information on the mineral prospects of the area, but also gives vital evidence on some minerals which may be deleterious (Petruk, 2000; Chryssoulis, Cabri, & Salter, 1987). Thus, from the environmental or

agricultural perspective, information on characterized ores is important for safety management. This work is partly an attempt to add material to the documentation of the mineralogy of the Yale area.

In conducting this study, the Yale area in the Upper East region of Ghana was thought to be an interesting sampling site for three reasons. 1. There is active prospecting for gold in the region recently, especially in and around the locality, making Yale a good representative sample site for the region. 2. A lot of artisanal miners already had very deep pits in the locality, which suggested that there could

be mineral ore in them, and this made sampling from them attractive. 3. The area has a relatively old history of rock sampling but little reference literature. The current study is also an effort to explore the mineralogy of that section of the country by projecting data from a representative sample site.

In this study, the rock samples obtained from selected parts of Yale community were examined to identify their mineral components. Figure 1 is a map of the Yale area indicating spots from which samples were taken. (Spots closer the 2 km apart were marked as one).

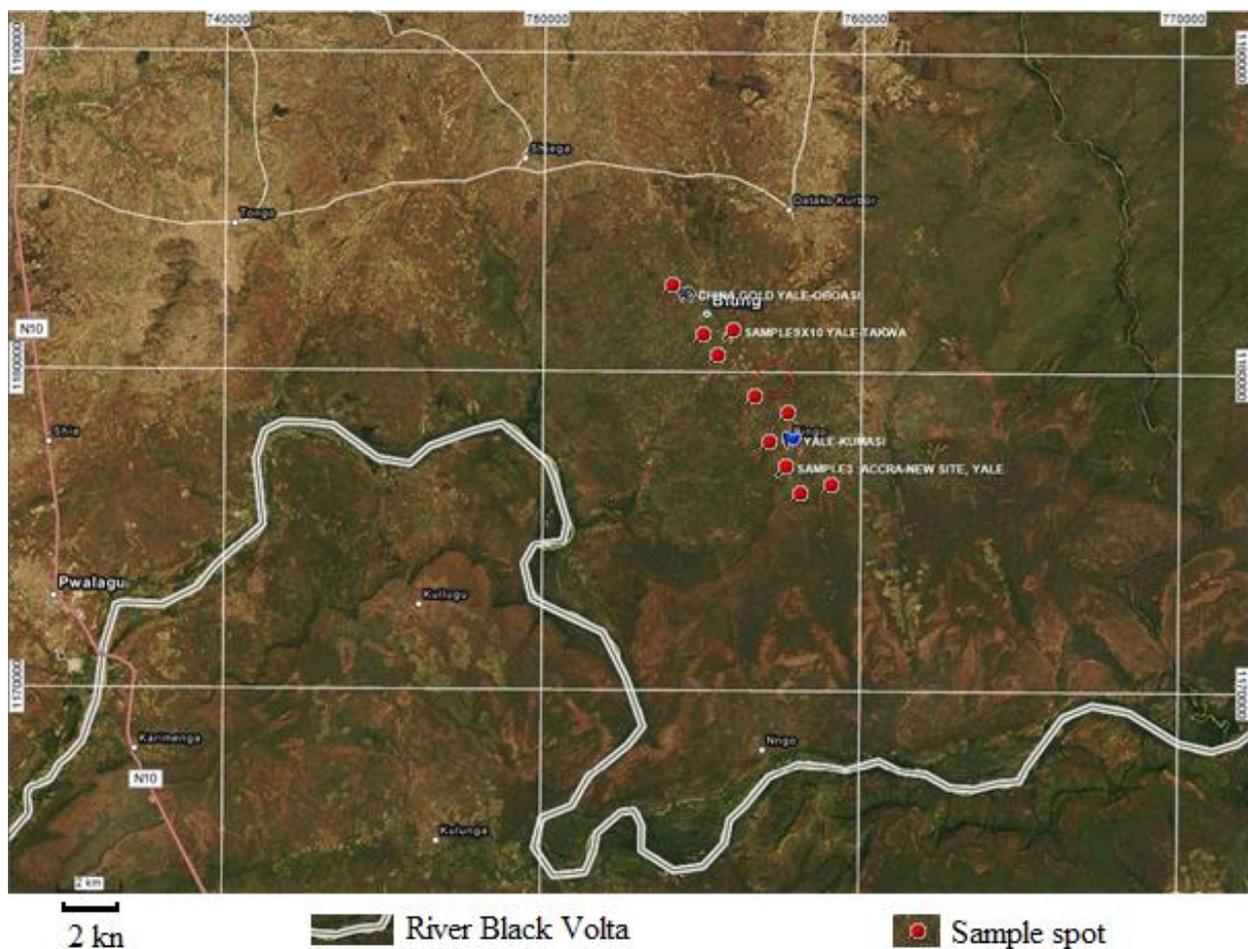


Fig. 1: Map of Yale area showing the sampling sites (Source: www.googlemaps.com)

The work focused on the main components of the rock samples. Identified elements were quantified to enable a discussion of the mining potential of the Yale locality.

A variety of lab methods are available for characterizing suspected ore samples. The methods suggested by the Minerals Commission, Ghana, include gravimetry, fire assay, neutron activation, cyanidation or aqua regia followed by Atomic Absorption and Atomic Emission Spectroscopy (Griffis *et al.*, 2002). Elsewhere (Champion & Huston, 2016), radiogenic techniques have been applied to study the origin of minerals. The focus of this study however is more on establishing the constitution of the sample than on revealing their genesis. Recently, a technique for processing laterite ores using hydrochloric acid and atmospheric pressure leaching has been reported to yield high concentrates of minerals (Guo *et al.*, 2015). However, this technique was not pursued in the current work, as no particular mineral was targeted for purification. It is worth noting that the use of an analysis technique depends on the objective of the analysis (i.e. qualitative, semi-quantitative or quantitative).

In the present work, Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectroscopy (AAS) were applied for characterizing the rock samples collected. The purpose was to determine the chemical composition of the rock samples as well as any relevant compounds. INAA is not often used in mineralogy (Oerter *et al.*, 2007), but it was applied in this work because of its accuracy. AAS is a common and reliable method (Kryazhov, 2014; Shokrollahi, 2017) often applied in mineral characterization or quantification. It was used in this work for qualitative comparison with the INAA results. Results from both high resolution lab methods corroborated each other fairly well.

Experimental methods

Sampling of rocks

Rock samples were taken from eleven random locations within the chosen locality. The locations from which samples were taken are indicated in Fig. 1. To ensure

that rock samples were not oxidized or weathered by exposure to air or to water, they were taken from depths of no less than 9 m, and to avoid the possibility of sampling from the same rock, sample spots were more than 1 km apart. Each sample was then sealed in a separate sample bag before being transported to the laboratories for conditioning and experiments. The labels on the samples were kept throughout the analysis, as they appear in the tables below. The procedure adopted for handling the rock samples was necessary in order to avoid cross contamination between samples and was also in accordance with the recommendation of the Minerals Commission (Griffis *et al.*, 2002).

Conditioning of sample for experiments

The samples were then crushed, pulverized and further sieved to at most 50 μm at the National Centre for Nuclear Research Laboratory of the Ghana Atomic Energy Commission (GAEC-NCNR). To avoid sample contamination during grinding, the grinder was used on quartz and cleaned in between samples. A portion of each of the so conditioned samples was taken for separate INAA and AAS analyses.

Atomic Absorption analyses were carried out at the ECOLAB of the Institute for Environment and Sanitation Studies, University of Ghana, using a Perkin Elmer Spectrophotometer. Distilled water was used as blank. Thus distilled water and standard solutions of the element to be tested were used to calibrate the system. To avoid cross contamination, different pipettes were used for solutions of different samples and only glassware was used as containing vessels. The calibration procedure was applied to each of the samples for the test of elements within the test list of the ECOLAB: Mn, Cu, Zn, Pb, Cr, Ni, and Cd. (Although some of these elements could not be tested using INAA, the full result is presented as tested). About 0.5 - 1.0 g of each sample was first digested in nitric acid solution and topped with distilled water to a volume of 100 mL for 36-48 hrs and then irradiated with a lamp consisting of different elements to be tested.

Neutron Activation Analyses for elemental composition and concentration of the samples were done at the Ghana Atomic Energy Commission - National Nuclear Research Centre (GAEC-NCNR) laboratory following the procedure detailed in Atarah (2015) and summarized here. About 100 mg of each sample was weighed (3 replicates each) into irradiation capsules and heat sealed for neutron activation (irradiation). NIST Standard Reference Material 1646a Estuarine Sediment and IAEA Reference Materials SL-3 were similarly weighed as the control samples for calibration. The samples were irradiated in the Ghana Research Reactor-1 (GHARR-1) operated at 15 kW. Thermal neutron flux of $5.0 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ was used for radiation. The radio activated samples were delayed for a period of 2-5 minutes before counting for identification of short lived radionuclides. For medium lived radionuclides the delay was for a maximum of 24 hours. In either case, counting was done for 10 minutes. Radioactivity measurements of induced radionuclides were performed by a PC-based γ -ray spectrometry set-up, which consisted of an N-type HyperpureGe detector coupled to a computerized multi-channel analyzer via electronic modules.

Results

AAS Data

Fig. 2 shows a calibration graph for Cu. During measurements the spectrometer returns readings in mg/L, representing the amount of test sample in 100 mL. The concentration of the samples was determined in mg/kg (i.e. parts per million, ppm) from:

$$\frac{Q_r(\mu\text{g/mL}) \times V_{\text{sol}}(\text{mL})}{M_{\text{sample}}(\text{g})} \quad (1)$$

Where Q_r is the returned reading, V_{sol} is the volume of solution and M_{sample} is the mass of the sample digested.

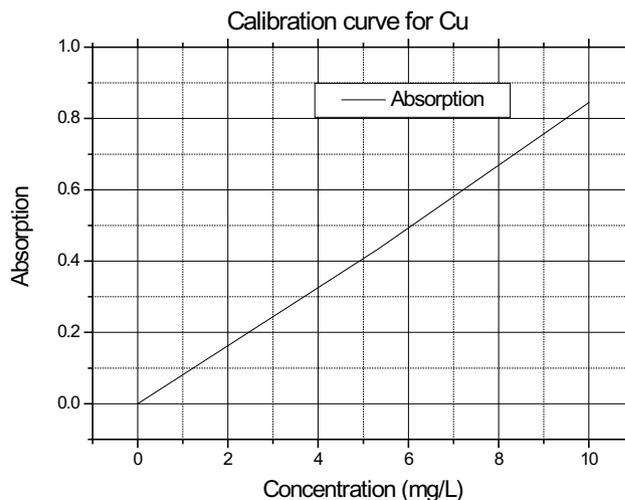


Fig. 2: Calibration graph for measuring Cu concentration in a sample

Fig. 3 shows the composition of the ore samples as obtained from the AAS analysis. The figure shows the percentage composition by weight of the element in the samples. For clear contrast, the data is presented in relative form (percentages) which enables visualization of the dominant components of the rock samples.

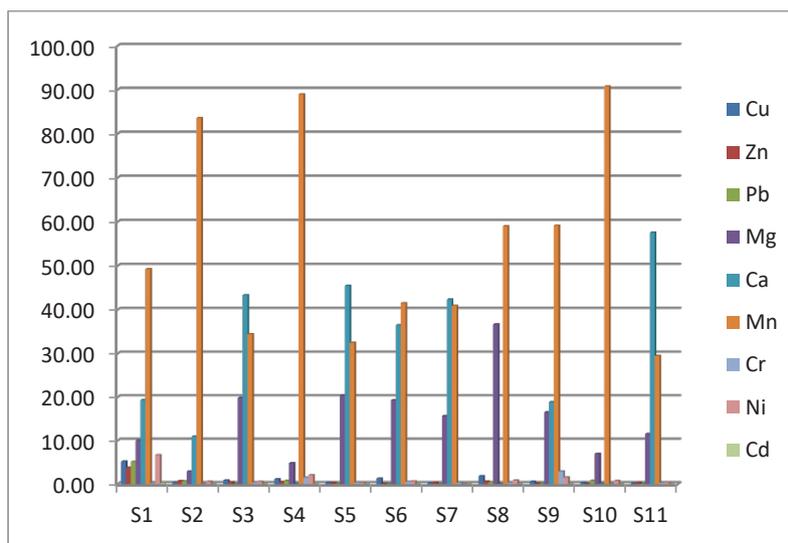


Fig. 3: AAS analysis of elemental composition of the sample, in wt %

Table 1: AAS data showing the elemental composition and concentration (wt %) of the samples

| Sample Code | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 |
|-------------|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Element | Proportions of the elements contained in each sample, as revealed by AAS, are shown below in wt%. | | | | | | | | | | |
| Cu | 5.21 | 0.43 | 0.89 | 1.14 | 0.40 | 1.29 | 0.27 | 1.84 | 0.61 | 0.34 | 0.22 |
| Zn | 3.80 | 0.73 | 0.49 | 0.52 | 0.34 | 0.07 | 0.38 | 0.62 | 0.20 | 0.11 | 0.34 |
| Pb | 5.14 | 0.68 | 0.02 | 0.79 | 0.13 | 0.05 | 0.05 | 0.46 | 0.17 | 0.82 | 0.10 |
| Mn | 49.26 | 83.60 | 34.47 | 88.97 | 32.50 | 41.51 | 40.92 | 59.01 | 59.14 | 90.79 | 29.51 |
| Cr | 0.23 | 0.04 | 0.36 | 1.50 | 0.37 | 0.57 | 0.30 | 0.36 | 2.94 | 0.05 | 0.28 |
| Ni | 6.69 | 0.58 | 0.55 | 2.09 | 0.32 | 0.65 | 0.02 | 0.87 | 1.53 | 0.77 | 0.41 |
| Cd | 0.22 | 0.01 | 0.00 | 0.05 | 0.02 | 0.00 | 0.02 | 0.03 | 0.01 | 0.01 | 0.00 |

The data shows that at least 40% of each sample is composed of Mn. The results also show that 10 - 15% of all but three samples (S2, S4 and S10) were composed of Mg. There was no INAA data on Mg to verify these. The rest of the elements that were tested for existed in the samples only in trace from (< 1%). The proportions of the elements (wt %) are also shown in Table 1.

INAA Data

Radionuclides were identified by their specific γ -ray energy using the relative comparator method and ORTEC

MAESTRO-32. Fig. 4 shows the energy distribution curve recorded by the detector during counting for sample S9. The main constituent elements are indicated.

The components were identified by the characteristic γ -ray energy distribution of their activated nuclides. A multipurpose γ -ray spectrum analysis software winSPAN-2010 ver. 2.10 (Preece *et al.*, 1999) was used for their concentration analysis. Fig. 5 shows the percentage elemental composition of the samples as obtained by INAA. The composition and proportions of all the samples are presented in Table 2.

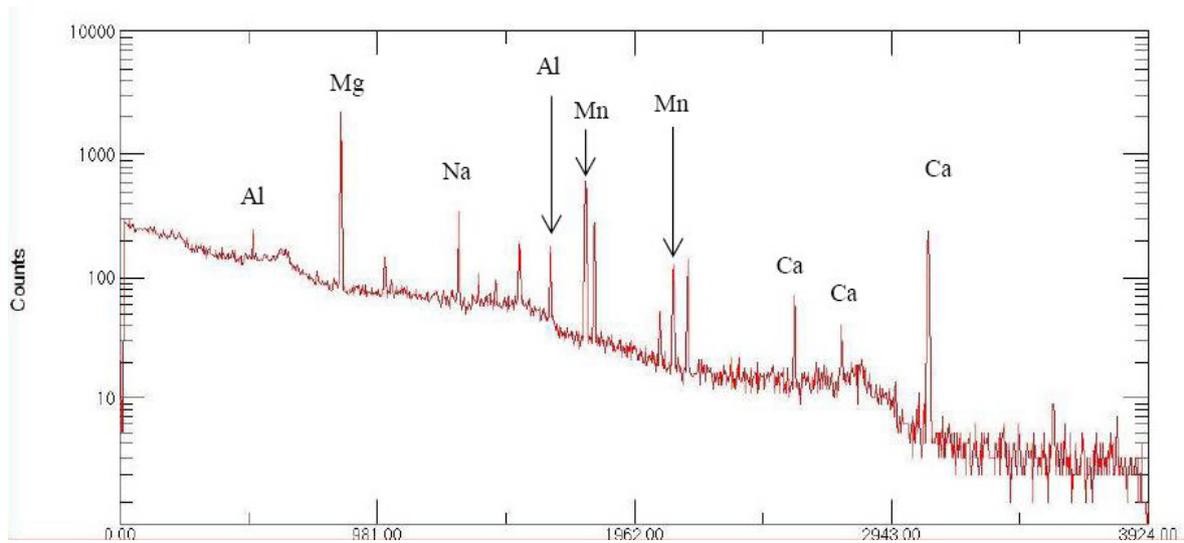


Fig. 4: Energy distribution curve for sample S9

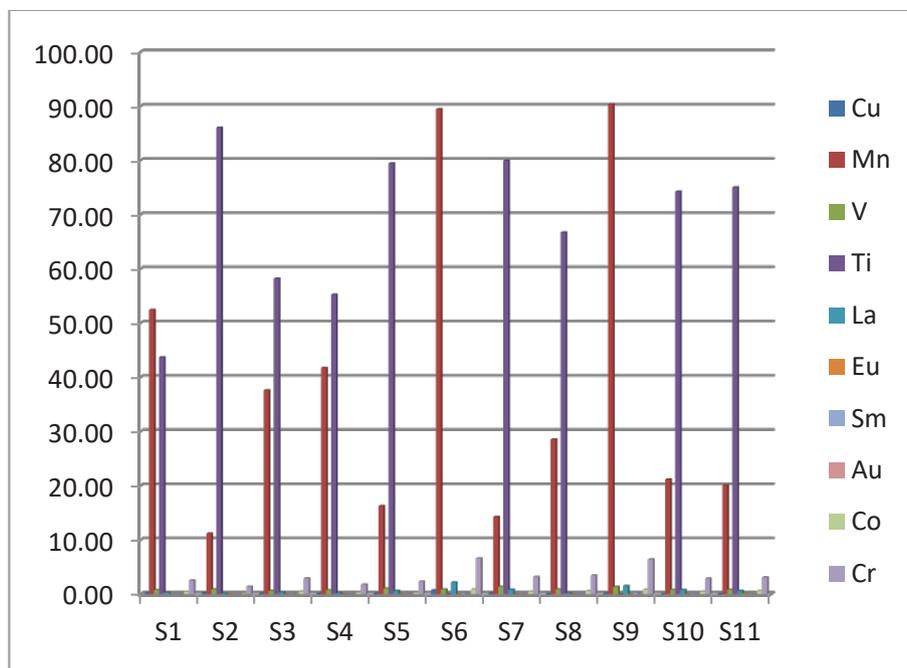


Fig. 5: Elemental composition by wt% of samples as obtained by INAA

Table 2: INAA data showing the elemental composition and their wt% in the samples

| Sample code | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 |
|-------------|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Element | Amounts of the elements contained in each sample, as revealed by INAA, are shown below in wt%. | | | | | | | | | | |
| Cu | 0.18 | 0.22 | 0.17 | 0.14 | 0.15 | 0.76 | 0.19 | 0.06 | 0.19 | 0.02 | 0.08 |
| Mn | 52.46 | 11.21 | 37.63 | 41.77 | 16.31 | 89.47 | 14.29 | 28.57 | 90.42 | 21.20 | 20.09 |
| V | 0.77 | 0.92 | 0.63 | 0.76 | 1.09 | 0.89 | 1.42 | 0.93 | 1.38 | 0.80 | 0.86 |
| Ti | 43.71 | 86.06 | 58.22 | 55.27 | 79.47 | 0.01 | 80.00 | 66.74 | 0.02 | 74.28 | 75.06 |
| La | 0.33 | 0.17 | 0.41 | 0.23 | 0.64 | 2.20 | 0.87 | 0.21 | 1.53 | 0.79 | 0.64 |
| Eu | 0.00 | 0.02 | 0.02 | 0.01 | 0.02 | 0.03 | 0.01 | 0.03 | 0.01 | 0.01 | 0.15 |
| Sm | 0.10 | 0.03 | 0.11 | 0.01 | 0.10 | 0.18 | 0.04 | 0.09 | 0.29 | 0.14 | 0.09 |
| Au | 0.02 | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.01 | 0.02 |
| Co | 0.49 | 0.18 | 0.55 | 0.36 | 0.30 | 0.90 | 0.51 | 0.58 | 0.87 | 0.52 | 0.65 |
| Cr | 2.54 | 1.41 | 2.92 | 1.82 | 2.32 | 6.63 | 3.21 | 3.46 | 6.45 | 2.89 | 3.12 |

Table 3: INAA data showing the compound composition and their wt% in the samples

| Oxides | MgO | Al ₂ O ₃ | Ca O | Na ₂ O | K ₂ O | Fe ₂ O ₃ |
|------------------------------|-------|--------------------------------|------|-------------------|------------------|--------------------------------|
| Concentration in percent (%) | | | | | | |
| S1 | 10.44 | 9.99 | 1.99 | 14.23 | 17.92 | 8.76 |
| S2 | 2.38 | 13.15 | 2.62 | 2.51 | 21.11 | 7.84 |
| S3 | 2.77 | 10.14 | 0.75 | 16.99 | 18.78 | 6.83 |
| S4 | 1.27 | 17.59 | 0.35 | 1.68 | 5.68 | 6.33 |
| S5 | 5.85 | 17.21 | 2.84 | 10.9 | 25.77 | 6.43 |
| S6 | 2.6 | 31.98 | 1.04 | 15.51 | 23.07 | 7.71 |
| S7 | 1.52 | 16.06 | 1.17 | 1.12 | 16.45 | 6.94 |
| S8 | 1.87 | 18.77 | 1.55 | 1.73 | 20.53 | 6.97 |
| S91 | 3.13 | 35.05 | 0.71 | 3.34 | 16.3 | 6.98 |
| S10 | 6.45 | 22.8 | 0.67 | 0.1 | 0.75 | 6.31 |
| S11 | 3.99 | 15.23 | 0.15 | 9.81 | 16.53 | 6.96 |

The INAA data also revealed the composition of oxides in the samples as shown in Table 3. As the samples were collected from great depth beneath the surface, these are likely to be stable oxides that were formed at the same

time as the rock. Indeed, except for Na, K and Al, the oxides in Table 3 are those of the elements revealed by the AAS study and contained in Fig. 3.

Discussion

AAS

The AAS data shows that Mn is the most dominant element across all the samples. Nearly half of the samples (according the AAS test) consisted of no less than 50 wt % of Mn. The result is in line with the fact that Mn is the most prevalent mineral in rock. The data also shows that Pb, along with Ni, Cd, Zn (as determined by AAS only), Cr, and Cu were all found to be in trace form only. (see also Table 1). Mn was also observed from the INAA data (in Fig. 4) to be in high concentrations in all the samples. The AAS data, showing the dominance of Mn in the samples, is in good agreement with that of the INAA. It must be stated however that as AAS equipment could only test for a limited list of elements, the comparison of data can be deemed incomplete as data on Ti, Au and the rare earth elements was not available from AAS tests. The absence of such data however is not enough to doubt the

data, as AAS has been applied for Au characterization in other works (Sighinolfi, 1976).

Instrumental Neutron Activation Analysis

The INAA experimental data is shown in Fig. 6. When examined in detail, it reveals two groups of minerals in terms of their concentrations. The data consisted of a few minerals each in high relative concentrations as shown in Fig. 6 (A). According to the figure, the components that dominated all samples were Ti and Mn, although the data also showed that there were moderate amounts of chromium. The dominance of Mn is totally in agreement with the observation from the AAS data (Fig. 3); however, Ti could not be tested by the latter method.

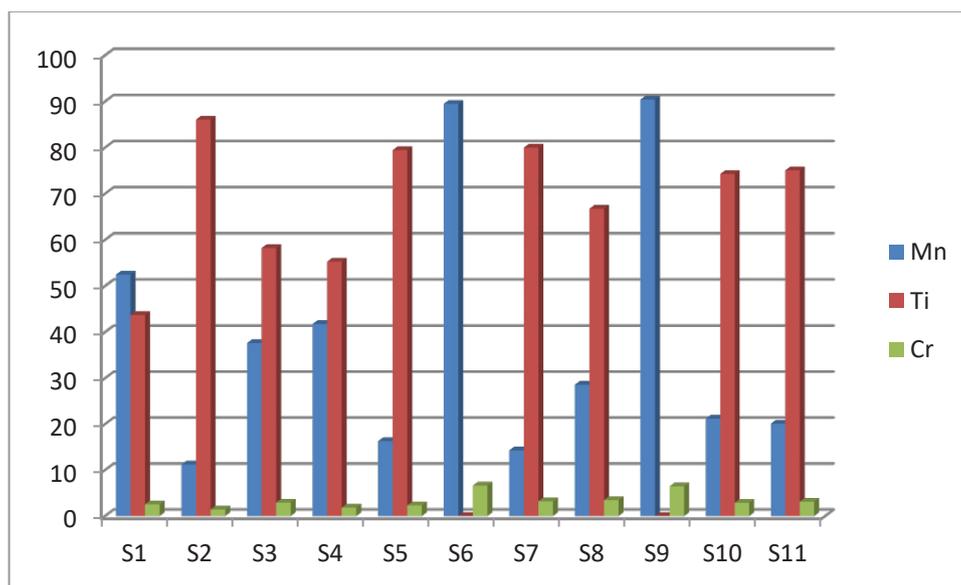


Fig. 6: A) INAA data showing minerals in relative high proportions (up to 90% wt)

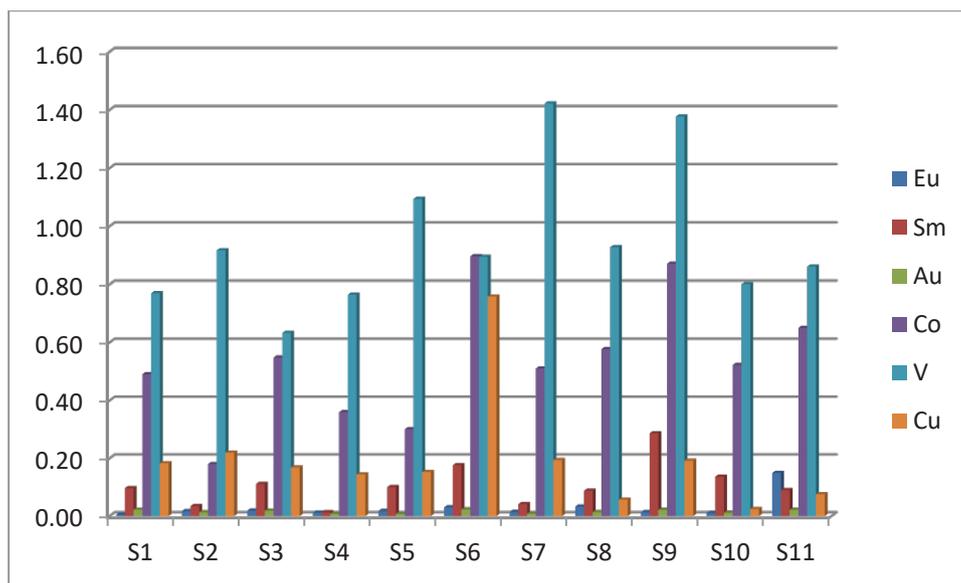


Fig. 6: B) INAA data showing smaller proportions (<1.5 % wt)

The other group of minerals from the INAA data consisted of those in smaller concentrations (< 1.55 wt %) as shown in Fig. 6 (B). These included 'economic' metals Au, Cu and Co as well as rare earth elements such as La, Eu and Sm. The proportions of the economic metals Cu and Au appear to be insignificant, but in absolute terms all samples contained up to 32.6 ppm of Cu. By the data, Au was present up to 2.67 ppm in all samples. Except for Au, the presence of Cu, Cr and Mn in the samples as established by AAS analysis was confirmed by the results from INAA experiments. Between the INAA and AAs tests, a difference in the relative proportions of the content of the samples is observable across the data sets. The trend appears to be a positive correlation, indicating that both qualitatively and quantitatively the components of the samples as characterized were cross confirmed.

In addition to Au and Mn, the data also showed substantial amounts of Co, which are of economic and commercial value. The study also established that Pb and Zn were in minor concentrations in the samples. Indeed, older reports indicate that no significant occurrences of Zn or Pb have been found in the country (Cooper,

1934). The data from the current study validates these earlier reports.

Conclusions

AAS and INAA techniques were applied to quantitatively analyse the mineral and elemental components of rock samples in Yale locality in Ghana. In the limit of each technique the qualitative (content) results were well correlated. INAA and AAS tests independently showed the presence of Mn, Ti, Cr, Ca, Cu, Co and Au. According to the AAS data, Mn accounted for 29 - 59%. The AAS data showed that elements such as Cu, Zn, Pb, Cr, Ni and Cd are each less than 1% of the samples. The INAA data showed that Mn and Ti are the dominant components of all the samples, accounting for 11 - 90% and 43 - 86% of their content respectively (though two samples showed only 0.01 and 0.02% Ti). The data confirmed the presence of Cr (1.4 - 6.6%) and Cu in trace amounts. INAA data also showed that all samples contained 0.67 - 2.67 mg/kg of Au. These are minerals of economic and industrial value whose presence in this locality has never been analysed and documented.

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References

- Atarah, S. A., Atule, G. K., Egblewogbe, M. N. Y., Kuditcher, A. (2015). Instrumental analysis and characterization of mineral ores from Yale, Upper East Region, Ghana. *J. Appl. Sc. Tech*, 20(1 & 2), 62-68.
- Champion, D. C., & Huston, D. L. (2016). Radiogenic isotopes, ore deposits and metallogenic terranes: Novel approaches based on regional isotopic maps and the mineral systems concept. *Ore Geology Reviews*, 76, 229-256.
- Chryssoulis, S. L., Cabri, L. J., & Salter, R. S. (1987). Direct determination of "invisible" gold in refractory sulfide ores. In R. S. Salter, D. M. Wysouzil & G. M. McDonald (Eds.), *Proceedings of the International Symposium on Gold Metallurgy* (pp. 234-244). New York: Pergamon Press.
- Cooper, W. G. G. (1934). Zinc blende and galena in quartz reef at Chichiwere prospect, west of Kumasi. *Annual report of the Director of Geological Survey for the period 1933-34* (pp. 16).
- Griffis, R. J., Barning, K., Agezo, F. L., & Akosah, F. K. (2002). *Gold Deposits of Ghana*. Ontario, Canada: Gandalf Graphics Ltd.
- Guo, Q., Qu, J., Han, B., Zhang, P., Song, Y., & Qi, T. (2015). Innovative technology for processing saprolitic laterite ores by hydrochloric acid atmospheric pressure leaching. *Minerals Engineering*, 71, 1 - 6.
- Junner, N. R. (1954). *Notes on the classification of the Precambrian of West Africa*. Paper presented at the XIX Inter. Geol. Cong., Algiers. 20, 114-117
- Kesse, G. O. (1985). *The mineral and rock resources of Ghana*. Rotterdam: A.A Balkema.
- Kryazhov, A., Panova, S., Kolpakova, N., Pshenichkin, A. (2014). Determination of Au, Pb, Ni and Co in Mineral Raw Materials by Atomic Absorption Spectroscopy with Graphite Furnace. *Procedia Chemistry* 10, 437-440.
- Murray, R. J. (1960). The Geology of the "Zuarungu" 1/2° Field Sheet Latitude 10° 30' - 11° 00' Longitude 0° 30' - 1° 00' *Geological Survey Bulletin* (pp. 117). Accra: Ghana Geological Survey.
- Oerter, E. J., Brimhall Jr, G. H., Redmond, J., & Walker, B. (2007). A method for quantitative pyrite abundance in mine rock piles by powder X-ray diffraction and Rietveld refinement. *Applied Geochemistry*, 22(12), 2907-2925. doi: <http://dx.doi.org/10.1016/j.apgeochem.2007.08.002>.
- Petruk, W. (2000). *Applied Mineralogy in the Mining Industry*. Amsterdam: Elsevier, BV.
- Preece, R. D., Briggs, M. S., Mallozzi, R. S., & Brock, M. N. (1999). WINGSPAN: A WINDOWS Gamma-ray Spectral Analysis program. *Astrophysics Source Code Library, record ascl:9910.007*.
- Sighinolfi, G.P., Santos, A.M. (1976). Determination of gold in geological samples at part per milliard levels by flameless atomic-absorption spectroscopy. *Mikrochim. Acta*, 2, 33-40.
- Shokrollahi, A., Masoud Gohari (2017), Flame atomic absorption determination of zirconium in glass and refractory bricks after coprecipitation with aluminium hydroxide. *Journal of Taibah University for Science*, 11 (4), 540-547