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Distribution of Arsenic, Copper, Lead, Zinc elements in water and soils of sulfur deposits in the North West of Hanoi

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Abstract. The quantitative distribution of As, Cu, Pb, Zn elements in water and soils around Giáp Lai and Minh Quang sulfur deposits is presented in this work. The preliminary results delineate the following: i) The content of As in water is quite low and is below the polluted limit. The soils was symptomatic of pollution by As at low level. ii) The contents of Cu and Zn are higher than that of Pb, especially in some localities, Cu and Zn contents are over the permissible threshold of the surface water quality and form high anomalies. iii) The content of As, Cu, Zn, Pb in the Red River's water is higher than that in the exploitation area. This reveals that the arsenic and other heavy metals presented in the Red River's water may come from other sources located in the upper course of the river .

Keywords: Arsenic, Copper, Zinc, Lead; Soils; Sulfur Deposits; Pollution; Hanoi area.

1. Introduction

Currently, its exists different opinions on the causes of heavy metallic pollution (especially arsenic) in the water of the Bac Bo delta plain. Some authors tentatively conclude that the arsenic, mangan and ammonium pollution of the underground water is caused by household, industrial and agricultural waste and water overexploitation [3,7]. Some others emphasized the natural causes of the pollution. According to Nguyễn Văn Đản and Nguyễn Thị Dung, components of the Quaternary sediments in the study area may be the source produced contaminated elements [5]. Phạm Hùng Việt et al. argue that the existence of high content of Arsenic in underground water of the Bac Bo delta plain may be related to the "erosion and weathering processes leading to the enrichment of arsenic in iron ores such as iron oxy-hydroxide. These ores would become the sedimentary materials for the formations bearing As" [6].

In the present work, one hypothesis has been formulated as following: the heavy metallic pollution in the water of the Bac Bo delta plain may be caused from sulfur ores deposits from the Red River upper course. This hypothesis is rational if it considers the emission of As and other heavy metallic elements to the soil and water environment due to sulfur disintegration [1,2]. In order to accept

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or reject this hypothesis, Giáp Lai and Minh Quang pyrite ores deposits were investigated to characterize the geochemical distributions of As, Cu, Zn, Pb in soils and water environment surrounding these deposits.

2. Methods

To study the distribution of those elements in soil and water environments in relation to the pyrite exploitation and processing at the Giáp Lai and Minh Quang deposits, the surveys start from the center of deposits to bigger rivers in the area through out the small streams. In the Minh Quang deposits, the survey was taken from Minh Quang stream to Da river. In the Giap Lai area, the survey was taken from the Bứa river to Tứ Kỳ Bridge, where it confluence with the Red River, and then expanded upward and downward along the Red River to the Phong Châu Bridge (Fig. 1). The investigated targets compose of stream and river water, household well, soils and ores. These samples were analyzed by Atomic Absorption method at Sub-Institute of Technology and Environment Protection. The polished samples are examined under the reflected light microscope Axioscope 40 in the Mineral-Petrological Lab at Hanoi University of Science.

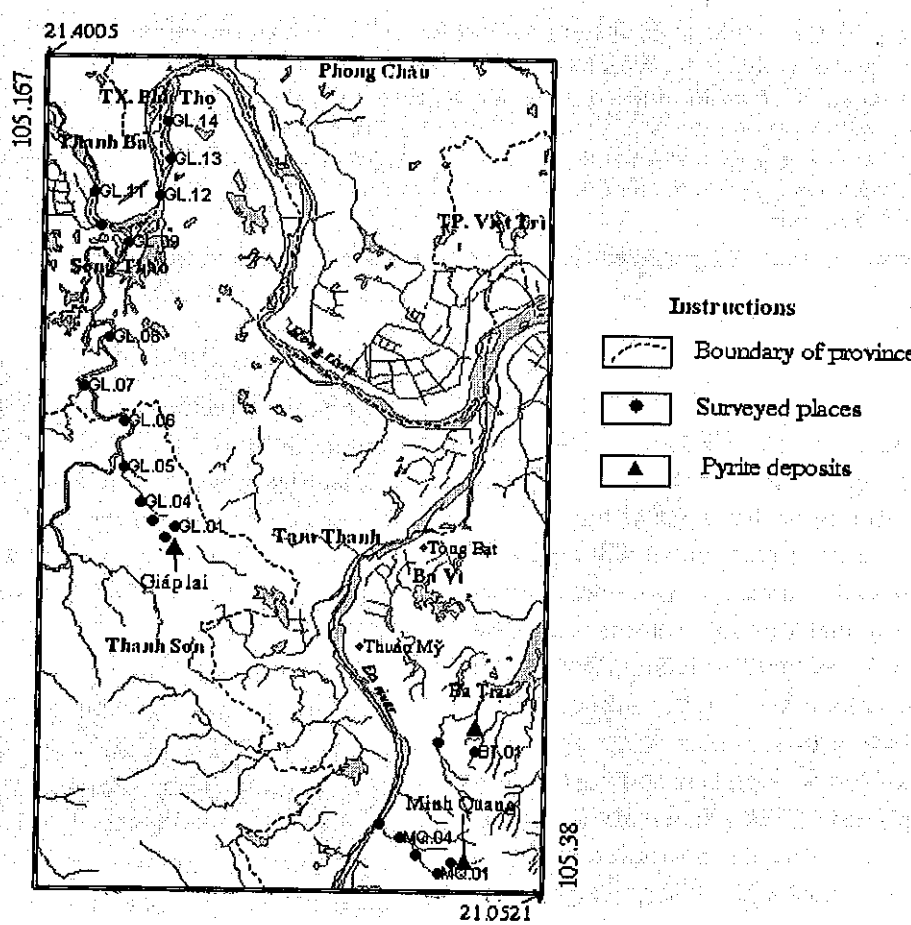

Fig. 1. The map showing the surveyed data.

3. General geochemical-mineralogical characteristics of pyrite mines

3.1. The Giáp Lai pyrite mine

It locates at Giáp Lai commune, Thanh Sơn district, Phú Thọ province.

Co-ordinate:

21°11'45" N;

105°15'30" E.

The mine originates from hydrothermal metasomatosed type. The country rocks include dolomite marble, mica schist of the Thach Khoan formation, among which the marble contains ore minerals. There are approximately 40 ore bodies making parallel array and coinciding with the azimuth of country rocks. They have different shapes including lode, fasciculate and lenticle types [9]. Some ore bodies are exposed to the surface and the others still locate under the surface. The mine cover an area with 1100m in length and 180m in width. The size of the ore bodies and sulfur content decrease downward. Main mineral of these bodies is pyrite and pyrotine.

By minerallographical analysis, most of pyrite crystals possess semi-euhedral, 0,2-2,5mm in size, 53% in coefficient of reflection. They occur in form of chains which are dispersed and clearly distinguished from host rock. Some pyrites suffer from limonitzation (Fig. 2,3). Ore characterized disseminated structure; These ore consists of 30% pyrite the rest are non-ore minerals.

There are 2 types of pyrite, fresh and weathered ore. The majority belongs to the first one. Fresh pyrite locates below the water table and possesses high content of sulphur (>30%). Due to the present of water table, at the top of ore bodies, pyrite exists in form of very fine grain and unconsolidated state mixed with 30-40% of clay minerals. Downward, the pyrites are more rigid. They occur mainly in marbles in form of dissemination with sulphur content less than 30%.

Weathered pyrite ores formed a 5-45 m thick layer consisting of limonite with the content of Fe over 40%.

Average content of sulphur in ore deposits is about 24.45%.

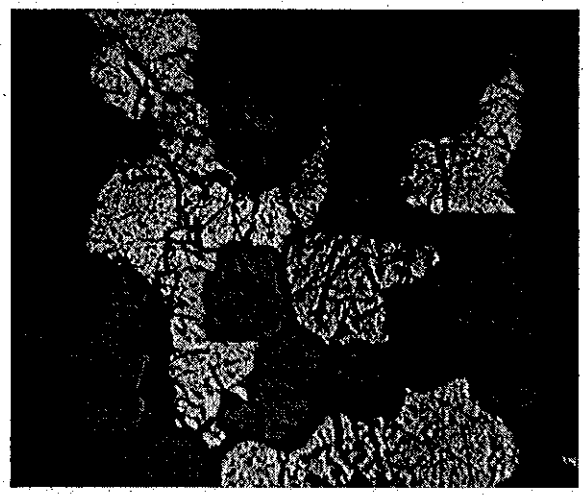

Fig. 2. Beaded assemblage of pyrite (sample GL.01).

3.2. The Minh Quang pyrite mine

It situates in Minh Quang commune, Ba Vì district, Hà Nội

Co-ordinate:

21°03'30" N;

105°20'36" E.

Fig. 3. Semi-euhedral pyrite (sample GL.02).

The Minh Quang pyrite mine is a effusive hydrothermal ones related to the Viên Nam formation (T_1vn) composing of komatite in the lower part and trachite, felsite in the upper part. The deposits consists of 4 ore bodies with 150-850 m in length, 20-150m in width and 2-46.4m in thickness. Main minerals in the ore deposits are pyrite, pyrotine, chalcopyrite and enargite. Host rock suffers from kaolinitization. Content of sulphur of ores ranges from 4.06 to 45.75% with 14.11% average.

Under the minerallographic microscope, 2 generations of pyrite were identified. The first one is characterized by aphanitic texture with unclear boundary. They forms the matrix or groundmass covering 60% of the polished samples under-investigation. The second generation is characterized by fine grains and clear boundary of bands setting up a net of pyrite crystals on the matrix (Fig. 4).

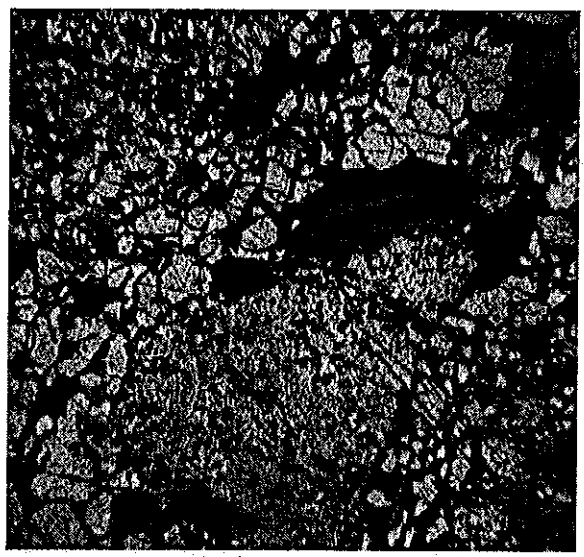

Fig. 4. 2 genesis Pyrite (sample MQ.01).

4. Analysis results and discussion

The content of As, Cu, Pb, Zn elements in soils and water are presented in the table 1. Their distribution will be discussed in the next paragraphs.

Table 1. Content of elements

Samples	As	Zn	Cu	Pb
Water samples (mg/l)				
MQ.01a	0.006	28.949	5.748	0.088
MQ.01b	0.002	26.983	4.535	0.007
MQ.04	0.007	0.225	0.046	0.015
GL.02	0.006	0.009	0.111	0.009
GL.04	0.004	0.112	0.005	0.005
GL.08	0.013	0.662	1.887	7.118
GL.09	0.036	0.258	0.080	0.057
GL.07	0.016	0.125	0.016	0.038
GL.12	0.048	0.590	0.545	0.877
Soil samples (ppm)				
GL-8Đ	8.559	No data	No data	No data
GL-12Đ	9.948	No data	No data	No data
GL-13Đ	9.201	No data	No data	No data

4.1. Arsenic

Arsenic content in the water samples ranges from 0.002 to 0.048 mg/l that is under the pollution threshold respect to surface water according to the surface water standard (TCVN 5942-1995). In comparison with the surface water standard TCVN 5502-2003, arsenic content in some analyzed samples in Giáp Lai deposit (GL.07, GL.08), in Bứa river (GL.09) and in the Red River (GL.12), are over standard.

Arsenic contents of the water samples from Giap Lai area and along the Red River are displayed in the Fig. 5. Note that the Bứa River, coming from the Giap Lai mine, flows to the Red River but the arsenic content along Bứa River is lower than that of samples taken from the Red River. This reveals that the high arsenic content in the Red River's water is not link directly to the Giap Lai mine.

Arsenic content in the soil samples taken from same area varies from 8.6 to 9.2 ppm. In comparison with the average arsenic content in

the world soil, these values are approximately double. However, it is symptomatic pollution in accordance with Canadian Standard with TEL co-efficient approximately equal 1.2. Similar to water samples, the arsenic content of the soil samples taken from the right bank of the Red River is also higher than those taken from the Giap Lai mine. The such variation of arsenic content in the water and soil environment reveals that the source of arsenic presented in the Red River is eventually link to the weathering in the upper course.

The arsenic content in samples collected from household wells in the Minh Quang and Giáp Lai areas is lower than that of standard. Paradoxically, the arsenic content in water samples at the Minh Quang exploitation site is very low ranging from 0.002-0.006 mg/l. Two typical samples have been selected to analyze. Sample MQ.01a taken from transparent and clear water has arsenic content smaller than that of MQ.01b taken from yellow water. The reason of this difference is unclear. However, the possible explanations link to the absorption of arsenic element by ferric (III) iron hydroxide.

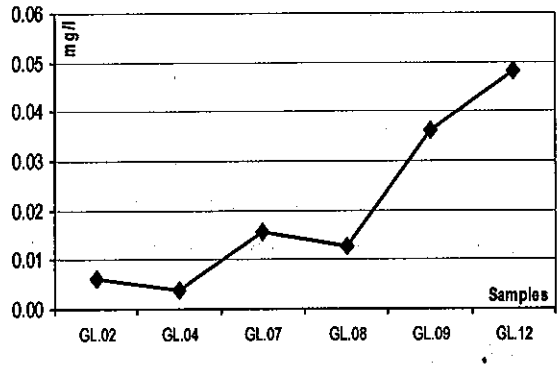

Fig. 5. Variation of arsenic content in water along the collected sample sections.

4.2. Copper

The content of Cu in the water samples collected in the study area ranges from 0.005 to 5.748 mg/l. The highest value measured in the samples collected in streams at the Minh Quang mine is 5 times higher than that of standard TCVN 5942-1995. Fortunately, the Cu content in samples collected in household wells is in safe range.

The Cu content in samples collected in streams and household wells in the Giáp Lai area is lower than 0.5 mg/l except one sample GL.08 (2mg/l) collected right at the dumping ground.

The Cu content of the samples (GL.02, GL.04, GL.07, GL.09, GL12) collected from Giap Lai mine to the Red River through the Bứa River tends to increase toward the Red River (Fig. 6).

4.3. Lead

In the area of the Minh Quang mine, the content of Pb in the water samples ranges from 0.007 to 0.088 mg/l. It is worthy that two samples MQ.04 taken from a household well and MQ.01a taken from Minh Quang stream have Pb content are 1.5 and 8 time respectively higher than that of the standard TCVN 5502-2003.

The content of Pb in almost of the water samples collected in the Giap Lai mine is lower than 0.01 mg/l and still safe condition. However, one sample collected at the dumping ground has lead content as high as 7.118mg/l. The Pb content tends to increase along the running course of the Bứa River to the Red River (Fig.6).

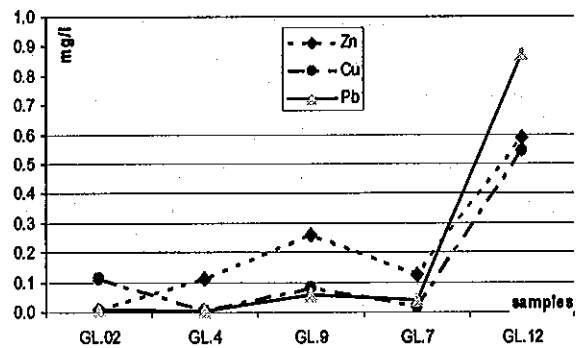

Fig. 6. Variation of Cu, Pb and Zn contents in water along the collected sample sections.

4.4. Zinc

The content of Zn in water samples collected in the Minh Quang streams is as high as 26-28mg/l while the standard TCVN 5942-1995 for drinking water is only 1mg/l. The sample collected in a household well has the Zn content 0.225mg/l and being still under the standard.

In the Giáp Lai area, the Zn content in the water samples is lower than 1mg/l and being still under the standard. The Zn content in the water sample collected from the Red River is 0.6 mg/l. Thus, the content of Zn tends to increase from the Bứa River to the Red River (Fig. 6).

Heavy metals such as As, Cu, Pb, Zn presented in water of the study areas may be linked to the oxidation of sulfides in the following manner:

$[M]S + O_2 \rightarrow [M]SO_4$

Where M denote to heavy metals

The solubility of sulfates is much higher than that of sulfides, especially $ZnSO_4$ and $CuSO_4$, for example the solubility of $ZnSO_4$ is 50.000 times higher than that of ZnS, the solubility of $CuSO_4$ is 400.000 times higher than that of CuS. However, the lead sulfate is quite difficult to dissolve (the solubility of anglezite is $1.3.10^{-4}$ mol/l). It is the scientific base to explain the existence of the Cu and Zn anomalies in the Minh Quang mine while the content of Pb is not very high. In the environment containing ferric (III) iron hydroxides, the form of existence of As ($FeAsO_4.2H_2O$) only dissolves in acid environment. This may be the reason for the low content of As in the water environment of the study area.

5. Conclusions

The results presented in this paper tend to following conclusions:

i. In the study area, the arsenic content in water environment is relatively low and still under the pollution threshold but symptomatic pollution in the soil.

ii. The contents of Cu and Zn are higher than that of Pb in water samples. In some places they form high anomalies with contents over the permission by the standard.

iii. The fact that high content of heavy metals in the Red River's water while low contents of heavy metals in the mine's water suggests that the arsenic and other heavy metallic pollution in the underground water of the Red River plain is eventually come from the Red River upper course.

iiii. Heavy metals such as As, Cu, Pb, Zn presented in water of the study areas may be linked to the oxidation of sulfides

Due to the limitation of actual data, the tentative conclusions should be further improved.

Acknowledgement

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